PHYSICAL REVIEW VOLUME 132, NUMBER 1 1 OCTOBER 1963

Spin Hamiltonian for Even-Electron Systems Having Even Multiplicity

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(Received 6 May 1963)

The form of spin Hamiltonian necessary to represent the most general zero-field splitting and lowest order magnetic and quadrupole interactions is investigated for systems having an even number of electrons and an even multiplicity. It is shown that, when referred to principal axes, two components of the *g* tensor are necessarily identically zero. Various other peculiar features emerge. In particular, it is shown that in interpretations of electron spin resonance measurements using a spin Hamiltonian for a non-Kramers doublet, considerable misapprehension and error exist in the literature.

I. INTRODUCTION

SINCE the original introduction of the concept of spin Hamiltonian,[1] many investigations have been made of the general form of spin operator adequate to represent splittings of the states concerned. Some of these have asked what spin Hamiltonian is suitable when the splittings are calculated to a certain order in perturbation theory, while some have asked what is adequate to represent matrix elements of given operators within completely arbitrary sets of states.[2–4]

The present paper is concerned with the spin Hamiltonian to be used in describing electron resonance within an even number of states, and especially within a doublet, of an even-electron system. The treatment is entirely general; the only assumption made about the set of states is that no other independent state of the system has the same energy as any of them. It will then appear that some rather curious features of the spin Hamiltonian occur in this situation. These features are consistent with all the available experimental data, as far as this author can discover.

It is well known that it is relatively more difficult to observe resonance in even-electron systems. This is usually ascribed to the fact that there is no necessary degeneracy of the Kramers type and that, therefore, in a system with no symmetry, all states would be expected to be nondegenerate. A nondegenerate state has, of course, no first-order interaction with a magnetic field and, therefore, does not give an electron resonance signal. Furthermore, few pairs of states would be within the small number of wave numbers distant from each other which is necessary in order for the magnetic field of the resonance measurement to mix them. In spite of this, electron resonance has been observed in a number of cases.[2,5] Many of these were doublets and it is with them that we shall be primarily concerned. The others were from triplets or quintets, usually arising from ground states in which there is only spin degeneracy and in which the second-order effect of spin-orbit coupling is insufficient to split the substates excessively. For reasons which will be apparent as we proceed, the peculiar features occurring in the doublets do not appear for triplets or quintets.

For doublets, measurements have usually been interpreted with a spin Hamiltonian,[6]

$$\mathcal{H}(S)=g_z\beta H_zS_z+AS_zI_z+\Delta S_x, \tag{1}$$

with fictitious spin $S=\frac{1}{2}$. The term ΔS_x is the only part of (1) which looks at all odd. Here Δ is a numerical coefficient, having dimensions of energy, and $\Delta\neq 0$ means the two states of the doublet have a zero-field splitting. This is unlike an odd-electron doublet, where the Kramers degeneracy shows that there can be no zero-field splitting and, hence, Δ must be zero. The formulation (1) has not been regarded as the most general possible, but merely one which sums up the observable data in the majority of cases. For example, Bleaney, Llewellyn, Pryce, and Hall[7] have replaced ΔS_x with $\Delta_xS_x+\Delta_yS_y$ in an interpretation of the spectrum of Pr^{3+}. Actually Δ_x and Δ_y were taken to have, not unique values, but distributions of values representing slightly different environments for different praseodymium ions. Also, many authors have added a term $g_\perp\beta(H_xS_x+H_yS_y)$. $g_\perp$ is usually zero, however, and as far as I know has never been observed to have a value significantly different from zero.

The rather startling result we shall demonstrate in this paper is that for any even-electron doublet whatsoever, satisfying the one weak condition mentioned in the second paragraph, $g_\perp=0$. At first sight this may appear obviously absurd. What meaning can the symbol $\perp$ have unless it means perpendicular to some symmetry axis? Furthermore, how can one prove, in general, that $g_x=g_y=0$ without also proving $g_z=0$?

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[1] M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950); A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

[2] B. Bleaney and K. W. H. Stevens, Rept. Progr. Phys. **16**, 108 (1953).

[3] J. S. Griffith, Discussion Faraday Soc. **26**, 178 (1958) (Note misprint: line 4 should read d^3 not d^1); B. Bleaney, Proc. Phys. Soc. (London) **A73**, 939 (1959); G. F. Koster and H. Statz, Phys. Rev. **113**, 445 (1959); H. Statz and G. F. Koster, *ibid.* **115**, 1568 (1959).

[4] J. S. Griffith, Mol. Phys. **3**, 79 (1960).

[5] J. W. Orton, Rept. Progr. Phys. **22**, 204 (1959); C. A. Hutchison and E. Wong, J. Chem. Phys. **29**, 754 (1959); P. A. Forrester and C. F. Hempstead, Phys. Rev. **126**, 923 (1962).

[6] B. Bleaney and H. E. D. Scovil, Phil. Mag. **43**, 999 (1952).

[7] B. Bleaney, P. M. Llewellyn, M. H. L. Pryce, and G. R. Hall, Phil. Mag. **45**, 991 (1954).

The answer to these difficulties turns out to be that the states of the doublet itself define a unique axis (unless $g_x=g_y=g_z=0$) and this axis is a principal axis of the g tensor. When this axis is taken as the z axis, we shall prove that $g_x=g_y=0$.

II. THE SPIN HAMILTONIAN FOR A DOUBLET

The restrictions on the form of spin Hamiltonian arise only from the effects of the Kramers (or time-reversal) operator[8] and the two-dimensionality of the manifold of states. It is well known[9,10] that the eigenstates of a Hamitonian $\mathcal{H}$ for an even-electron system in the absence of a magnetic field may be taken to be real, i.e., that

$$|a\rangle^K=|a\rangle, \quad |b\rangle^K=|b\rangle, \tag{2}$$

where $|a\rangle$ and $|b\rangle$ are a pair of eigenstates and the superscript K represents Kramers's conjugacy operator. The only condition we need add if we are to apply this result to our arbitrary doublet is that there should be no other eigenstates of $\mathcal{H}$ having the same energy as either $|a\rangle$ or $|b\rangle$. This prevents the possibility of, for example, $|a\rangle^K$ being different from and orthogonal to both $|a\rangle$ and $|b\rangle$.

The interaction with an external magnetic field $\mathbf{H}$ is given by the additional term

$$\delta\mathcal{H}=\beta\boldsymbol{\eta}\cdot\mathbf{H}, \tag{3}$$

where

$$\boldsymbol{\eta}=\mathbf{L}+2\mathbf{S}, \quad \boldsymbol{\eta}^K=-\boldsymbol{\eta}. \tag{4}$$

Now consider a component, η_x say, of $\boldsymbol{\eta}$. We have

$$\begin{aligned}\langle a|\eta_x|a\rangle=\langle a|\eta_x|a\rangle^*=\langle a|\eta_x|a\rangle^K=-\langle a|\eta_x|a\rangle,\\ \langle a|\eta_x|b\rangle^*=\langle a|\eta_x|b\rangle^K=-\langle a|\eta_x|b\rangle.\end{aligned} \tag{5}$$

Hence,

$$\langle a|\eta_x|a\rangle=\langle b|\eta_x|b\rangle=0, \quad \langle b|\eta_x|a\rangle=im_x, \tag{6}$$

for some real number m_x. Suppose now we take an orthogonal transformation,

$$\begin{aligned}|a'\rangle&=\cos\theta\,|a\rangle+\sin\theta\,|b\rangle,\\ |b'\rangle&=-\epsilon\sin\theta\,|a\rangle+\epsilon\cos\theta\,|b\rangle,\end{aligned} \tag{7}$$

with $\epsilon=\pm1$. We at once deduce from (6) and (7) that

$$\langle a'|\eta_x|a'\rangle=\langle b'|\eta_x|b'\rangle=0, \quad \langle b'|\eta_x|a'\rangle=\epsilon im_x.$$

In other words, $|m_x|$ is independent of the choice of basis in our two-dimensional mainfold, provided the basis is real.

Now we represent the effects of $\delta\mathcal{H}$ in a spin Hamiltonian with $S=\frac{1}{2}$ by correlating its states with $|a\rangle$ and $|b\rangle$ as follows: Set

$$|\tfrac{1}{2}\rangle\sim\frac{1}{\sqrt{2}}|a\rangle+\frac{i}{\sqrt{2}}|b\rangle, \quad |-\tfrac{1}{2}\rangle\sim\frac{1}{\sqrt{2}}|a\rangle-\frac{i}{\sqrt{2}}|b\rangle; \tag{8}$$

then it follows from (6) that

$$\langle\tfrac{1}{2}|\delta\mathcal{H}|\tfrac{1}{2}\rangle=-\langle-\tfrac{1}{2}|\delta\mathcal{H}|-\tfrac{1}{2}\rangle=\beta\mathbf{m}\cdot\mathbf{H}, \quad \langle\tfrac{1}{2}|\delta\mathcal{H}|-\tfrac{1}{2}\rangle=0,$$

and so $\delta\mathcal{H}$ may be represented by a spin Hamiltonian

$$\mathcal{H}(S)=2\beta\mathbf{m}\cdot\mathbf{H}S_z. \tag{9}$$

If we choose the z axis in real space to lie along the vector $\mathbf{m}$, we then get the simpler expression

$$\mathcal{H}(S)=g_z\beta H_zS_z, \tag{10}$$

where

$$g_z^2=4(m_x^2+m_y^2+m_z^2).$$

We have shown, therefore, that if we refer our spin Hamiltonian to suitable axes that g_x and g_y are identically zero. This is the most interesting result we find and so we pause now to consider various points about it. What are the z axes which are referred to in Eq. (10)? The z axis referred to under g and H is an axis in real space determined directly from the vector $\mathbf{m}$ and indirectly from the actual form of the states $|a\rangle$ and $|b\rangle$. Apart from the possibility of reversing its direction, it is, however, uniquely determined by the space Σ spanned by $|a\rangle$ and $|b\rangle$; in other words, it does not depend on which particular real basis we take for Σ. On the other hand, the z axis for S_z has nothing whatever to do with any axis in real space, and the fact that $g_z\beta H_z$ gets multiplied by S_z rather than some other linear form in the components of $\mathbf{S}$ is a consequence merely of the particular form (8) chosen for our association of the states $|a\rangle$ and $|b\rangle$ with the eigenstates of the fictitious spin component S_z.

The special form (10) depends, as we have just seen, to some extent on particular choices of axes. However, it contains solid observable predictions, namely that the g tensor referred to principal axes has two components identically zero. The literature agrees with this prediction in that $g_\perp$ appears never to have been found significantly different from zero. It disagrees however, in often giving values such as $g_\perp=0.1\pm0.15$ or $g_\perp\approx0$, which imply that $g_\perp$ could be different from zero. We have, therefore, rigorously established that $g=g_z|\cos\theta|$ for a field $\mathbf{H}$ at angle θ to $\mathbf{m}$ and that, in the absence of a zero-field splitting, the intensity of the transition $|\frac{1}{2}\rangle\rightleftharpoons|-\frac{1}{2}\rangle$ is identically zero. Finally, we have found a new general theoretical reason why resonance is rare to observe in polycrystalline even-electron specimens, namely that with $g=g_z|\cos\theta|$ the line shape is such that the majority of the resonance comes from g near zero (or near the zero-field splitting if there is one).

A last point to note at this stage is that the fundamental reason why we get such a difference between these non-Kramers doublets and the more usual

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[8] H. A. Kramers, Akad. Wetenschappen Amsterdam **33**, 959 (1930); E. P. Wigner, Nachr. Ges. Wiss. Göttingen, Math.-Physik. Kl., 546 (1932).

[9] J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge University Press, New York, 1961).

[10] U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press Inc., New York, 1959).

Kramers doublet is the difference of behavior under the Kramers operator. It would be natural to define a fictitious Kramers operator turning one of the fictitious spin states $|\tfrac{1}{2}\rangle$ into the other $|-\tfrac{1}{2}\rangle$. But then we would have

$$(|\tfrac{1}{2}\rangle^K)^K = |-\tfrac{1}{2}\rangle^K = -|\tfrac{1}{2}\rangle,$$

which matches the behavior of the true states under the true Kramers operator for Kramers doublets, but not for non-Kramers doublets. It is this nonmatching which forces the rather unsymmetrical spin Hamiltonian (1) upon us.

We now consider briefly some other terms in $\mathcal{H}(S)$. The same argument as we have just given refers to the nuclear hyperfine interaction, although the vector corresponding to **m** in this case need not lie in the same direction as **m** for the g tensor. Hence, we have the increment

$$\delta\mathcal{H}(S) = (A_{zx}I_x + A_{zy}I_y + A_{zz}I_z)S_z. \qquad (11)$$

Next consider the fine structure. Naturally, if there is a fine structure splitting, we would take the $|a\rangle$ and $|b\rangle$ of Eq. (8) to be eigenstates of $\mathcal{H}$ rather than choose linear combinations such as $|a'\rangle$ and $|b'\rangle$ which would not be. Therefore, we should have

$$\begin{aligned} &\langle a|\mathcal{H}|a\rangle = H_{aa}, \quad \langle b|\mathcal{H}|b\rangle = H_{bb}, \\ &\langle a|\mathcal{H}|b\rangle = \langle b|\mathcal{H}|a\rangle = H_{ab}, \end{aligned} \qquad (12)$$

with $H_{ab}=0$. If we choose the linear combinations the only formal difference is that $H_{ab}\neq 0$. From (8) and (12) we find that the fine-structure part of $\mathcal{H}(S)$ is

$$\delta_1\mathcal{H}(S) = \tfrac{1}{2}(H_{aa}+H_{bb}) + (H_{aa}-H_{bb})S_x + 2H_{ab}S_y. \qquad (13)$$

The first term of (13) only shifts the center of gravity, while the third is zero provided we choose $|a\rangle$ and $|b\rangle$ as eigenstates of $\mathcal{H}$. This, then, justifies both the term ΔS_x in (1) and also the addition of a term $\Delta_y S_y$. However, the term in S_y cannot correspond to anything observable (although $\Delta_x^2+\Delta_y^2$ does) because it can be eliminated by taking $|a\rangle$ and $|b\rangle$ as eigenstates of $\mathcal{H}$. As in our discussion of Eq. (10), similarly here, the suffixes x and y in Eq. (13) have nothing whatever to do with anything in real space. Therefore, it seems to me that it is slightly incorrect to take a distribution for both Δ_x and Δ_y in order to describe a distribution of environments[7,11]; the most general thing one can do along these lines can be expressed adequately by giving a distribution for Δ in Eq. (1).

It is clear now how we should proceed for other quantities which get represented in a spin Hamiltonian. One small new point occurs for the nuclear quadrupole term. Here one has, in the most general case, an operator equivalent of the form

$$\delta_2\mathcal{H}(S) = \sum_{\kappa\lambda} (Q_{\kappa\lambda}{}^0 + Q_{\kappa\lambda}{}^x S_x + Q_{\kappa\lambda}{}^y S_y) I_\kappa I_\lambda, \qquad (14)$$

where the $Q_{\kappa\lambda}{}^\epsilon$ are numbers satisfying $Q_{\lambda\kappa}{}^\epsilon = Q_{\kappa\lambda}{}^\epsilon$ for each ϵ. However, if we take the fine-structure term to have $\Delta_y=0$, we have then defined a precise choice for $|a\rangle$ and $|b\rangle$ and, therefore, cannot, in general, take any of the $Q_{\kappa\lambda}{}^y$ to be zero. Even if $\Delta=0$ we can only eliminate one of the $Q_{\kappa\lambda}{}^y$.

Finally, note that if there is any symmetry, the expressions (11) and especially (14) are often considerably simplified.

III. SPIN HAMILTONIANS FOR ARBITRARY DEGENERACY

The original form of spin Hamiltonian for general fictitious spin S contained only quadratic and bilinear expressions.[1] However, several authors have pointed out that for $S>1\tfrac{1}{2}$, higher order expressions may occur in the fine-structure Hamiltonian[2] and, for $S>1$, in the part concerned with interaction with external or nuclear magnetic field.[3] An essentially complete solution of the problem of determining these operator expressions for general S was given by the present author,[4] but with the assumption that S differed from the true spin by an integer (possibly zero). Because of the Kramers degeneracy, this is necessarily true for odd-electron systems and, therefore, false just for even-electron doublets, quartets, etc. We now derive the general spin Hamiltonian for them, using just the same type of argument as was used previously for the other cases.[4]

Let the even degeneracy be $2S$ and start with $2S$ real functions a, b, c, d, $e\cdots$. Associate these with fictitious spin states by the rules

$$\begin{aligned} |\pm S\rangle &\sim \frac{1}{\sqrt{2}}|a\rangle \pm \frac{i}{\sqrt{2}}|b\rangle, \\ |\pm(S-1)\rangle &\sim \frac{1}{\sqrt{2}}|c\rangle \pm \frac{i}{\sqrt{2}}|d\rangle, \quad \text{etc.}, \end{aligned} \qquad (15)$$

where S, $S-1$, etc., are the M_s values. Then using similar arguments to those of the last section we deduce that for an arbitrary operator ρ satisfying $\rho=\rho^*=\rho^K$ we have

$$\langle m|\rho|m'\rangle = \langle m'|\rho|m\rangle^* = \langle -m'|\rho|-m\rangle, \qquad (16)$$

while for ρ satisfying $\rho=\rho^*=-\rho^K$ we have

$$\langle m|\rho|m'\rangle = \langle m'|\rho|m\rangle^* = -\langle -m'|\rho|-m\rangle. \qquad (17)$$

Previously[4] we used the operator equivalent

$$X = \sum_{c\gamma} (-1)^\gamma Q_\gamma{}^{(c)} S_{-\gamma}{}^{(c)}, \qquad (18)$$

where $S_\gamma{}^{(c)}$ is the irreducible product of degree c of c spin vectors S_μ. The reduced matrix element of each $S_\gamma{}^{(c)}$ was taken to be real. It then followed from $\rho=\rho^*$ that $Q_\gamma{}^{(c)*} = (-1)^\gamma Q_{-\gamma}{}^{(c)}$, and this is true in the present case. The other restrictions on $Q_\gamma{}^{(c)}$, which derive from (16) and (17) by simply expanding the matrix elements

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[11] J. M. Baker and B. Bleaney, Proc. Phys. Soc. (London) **A68**, 1090 (1955); Proc. Roy. Soc. (London) **A245**, 168 (1958).

of $\langle m|X|m'\rangle$ and $\langle -m'|X|-m\rangle$ by the Wigner-Eckart theorem[10] and eliminating the $\bar{V}$ coefficients through their orthonormality properties are now slightly different. For $\rho=\rho^K$, i.e., as in the fine structure matrix, we find $Q_\gamma{}^{(c)}=0$ unless $c+\gamma$ is even. For $\rho=-\rho^K$, i.e., as in the magnetic interactions, we find $Q_\gamma{}^{(c)}=0$ unless $c+\gamma$ is odd.

This completes the general solution. As before, each component of **H** gets multiplied by a separate operator equivalent of the form (18) and satisfying the aforementioned conditions. By choosing axes suitably, the bilinear part of the interaction with **H** can be reduced to $g_z\beta H_zS_z$. Hence, the absence of terms in S_x and S_y is an absolutely general result. This may seem surprising at first sight. However, this surprise is really based upon the view that a general bilinear expression should be the first approximation to the magnetic term in the spin Hamiltonian, which derives in turn from the use of perturbation theory starting from spatially nondegenerate states.[1,2,4] But for such states of even-electron systems the degeneracy is necessarily odd and results deduced for them are irrelevant to the present situation. For example, in the present case, each component of the magnetic field gets multiplied, in a quartet state, by an operator equivalent

$$\begin{aligned}X=aS_z+b(S_xS_z+S_zS_x)+c(S_yS_z+S_zS_y)+dS_z^3\\+e(S_zS_x^2+S_x^2S_z-S_zS_y^2-S_y^2S_z)+f(S_xS_yS_z\\+S_zS_xS_y+S_yS_xS_z+S_zS_yS_x),\quad(19)\end{aligned}$$

and there seems no reason why the energies deriving from aS_z should be larger than those coming from the higher order terms.

Finally, let us note that one rather peculiar feature of the doublet spin Hamiltonian is now much more comprehensible. The components of the spin vector **S** are divided between S_x and S_y in the fine-structure Hamiltonian and S_z in the magnetic Hamiltonian because $c+\gamma$ is even for $S_1{}^1$ and $S_{-1}{}^1$ which are linear combinations of S_x and S_y, but odd for $S_0{}^1=S_z$.

IV. DISCUSSION

We shall now discuss the relationship between the preceding analysis for non-Kramers doublets and the experimental data and their interpretations to be found in the literature. It is the author's belief that the results of the present paper reveal a considerable misapprehension in the past of the nature and significance of the terms occurring in a spin Hamiltonian such as that in Eq. (1). This can be made most clear by considering and summarizing a number of separate points about various terms in the spin Hamiltonian.

First, it has been generally assumed and can be proven[4] that an environmental symmetry implies the corresponding symmetry of the g tensor. The converse implication is not logically true but is at least likely in many circumstances. For the non-Kramers doublet, however, the g tensor is axially symmetric always and so this symmetry implies nothing whatsoever about the nature of the environment—except that it must be sufficiently *unsymmetrical* to have separated out a comparatively isolated doublet of states!

Second, following on from the last point, there is no reason, in general, why the nuclear hyperfine interaction tensor should show symmetry about the same axis as the g tensor. The hyperfine tensor, however, must have the form (11) and, in particular, terms like S_xI_x and S_yI_y cannot occur. In their work on the holmium ion Ho^{3+} which is $4f^{10}$, Baker and Bleaney[11] interpreted the data using a nonzero term $B(S_xI_x+S_yI_y)$ in their spin-Hamiltonian. However, later[11] they partially reinterpreted it without this term and assigned the relevant effects (intensity of $S_z=+\frac{1}{2}$, $I_z=m\rightleftarrows S_z=-\frac{1}{2}$, $I_z=m+1$ hyperfine lines) to interaction with a neighboring state outside the non-Kramers doublet. We have shown their original interpretation must be wrong, although we would have allowed a term $A_{zx}I_xS_z$ or $A_{zy}I_yS_z$ which could give nonzero field-dependent intensity.

Third, for the same reasons, unless one has independent evidence of axial symmetry, there is no reason why the quadrupole tensor should have the form $P[I_z^2-\frac{1}{3}I(I+1)]$ instead of the more general expression (14).

Fourth, the x and y axes in the fine structure Hamiltonian $\Delta_xS_x+\Delta_yS_y$ have nothing to do with spatial axes and only $(\Delta_x^2+\Delta_y^2)^{1/2}$ represents anything observable [see discussion of Eq. (13)].

Fifth, $g_\perp\equiv0$ for doublets (and quartets, sextets, etc.). Therefore, the numerous attempts in the literature to measure this quantity are misplaced.

With reference to all these results note, however, that while they are perfectly general, they apply to finding operators equivalent to certain terms in the true Hamiltonian within a pair of eigenstates of the true Hamiltonian for zero nuclear and external magnetic fields. In case other eigenstates lie near the doublet these will be mixed in by these fields and might produce effects which could be mistaken for those arising from matrix elements of the field within the original pair of eigenstates, as in the holmium ion investigated by Baker and Bleaney[11] and discussed above. This warning, of course, is not peculiar to this situation but always applies when a spin Hamiltonian is used, e.g., for Kramers doublets as well.

Finally, it is well to emphasize that while the observable consequences of our results are real and nontrivial, the special position occupied by the z axis in our spin Hamiltonian is a result of two deliberate choices of axes, one in real space and the other in fictitious spin space.