Correct expression for the generalized spin Hamiltonian for a noncubic paramagnetic center

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It is shown that the phenomenological generalized spin Hamiltonians (GSH) that were written down earlier for noncubic centers implicitly contain inseparable parameter combinations. They are practically unsuitable for the description of EPR, NMR, and ENDOR spectra because of the impossibility of a unique determination of the coupled parameters. It is found that a number of superfluous operators should be eliminated if the correct GSH is to be obtained. A critical analysis of the methods of reducing the GSH is carried out, and it is shown that the maximally reduced spin Hamiltonian (MRSH) can be obtained through the use of a specially chosen unitary transformation. The form of the latter is found from the condition for the invariance of the GSH under point-symmetry operations and time reversal. It is established that the antisymmetric parts $\mathbf{S}^k\mathbf{H}$ ($k = 1,3,5,7$) of the Zeeman interactions can be completely eliminated from the GSH, but that not even one operator of the bilinear-exchange or hyperfine interaction can be reduced. It is shown that all the parameters of the MRSH can be found from experiments carried out in strong magnetic fields.

INTRODUCTION

The methods of constructing generalized spin Hamiltonian (GSH) for the description of EPR, NMR, and ENDOR spectra are well developed.[1–16] The possibility of a unique choice of their characteristics, the convenience of the description, and other advantages of the GSH have been repeatedly verified at high-symmetry centers. But the class of objects investigable with the aid of the methods of microwave spectroscopy is now being extended mainly to include low-symmetry centers in high-symmetry crystals (off-center and Jahn-Teller ions, complexes consisting of pairs of defects, triplets, etc.) or centers in low-symmetry crystals (ferroelectric and ferroelastic crystals, multicomponent compounds). For such centers the number N_0 of GSH parameters allowed by the symmetry exceeds the number N of parameters necessary for the description of the observed resonance line positions,[11–14,17,18] and there arises the problem of the elimination of the superfluous terms in the GSH, i.e., of obtaining the reduced GSH.

Let us, by way of illustration, consider several forms of the expression for the simplest spin Hamiltonian in the $\mathbf{C}_n$-symmetry ($n \geqslant 3$) and spin $S = \frac{1}{2}$ case. The parameters of the Hamiltonian

$$\mathscr{H}_1 = \beta g_\perp (H_x S_x + H_y S_y) + \beta g_\parallel H_z S_z \qquad (1)$$

($\mathbf{H}$ is a constant magnetic field and the z axis is parallel to the $\mathbf{C}_n$ axis) can be uniquely determined from the angular dependences of the spectrum. The phenomenological GSH

$$\mathscr{H}_2 = \beta (g_1^2 + g_7^2)^{1/2} (H_x S_x + H_y S_y) + \beta g_3 H_z S_z \qquad (2)$$

contains an extra parameter, and is clearly unsuitable for the description of experiments, since the problem of the separate determination of g_1 and g_7 amounts here to the solution of one equation with two unknowns. The unsuitability of

$$\mathscr{H}_3 = \beta [g_1 (H_x S_x + H_y S_y) + g_3 H_z S_z + g_7 (H_x S_y - H_y S_x)], \qquad (3)$$

[it is precisely this type of GSH with an antisymmetric part which is allowed by the $\mathbf{C}_n$ ($n \geqslant 3$) symmetry] is not so obvious. But it is easy to verify that the energy levels of $\mathscr{H}_2$ and $\mathscr{H}_3$ are given by one and the same formula:

$$E_{\pm 1/2} = \pm 1/2 \beta [(g_1^2 + g_7^2)(H_x^2 + H_y^2) + g_3^2 H_z^2]^{1/2}, \qquad (4)$$

i.e., the GSH's $\mathscr{H}_2$ and $\mathscr{H}_3$ are equivalent.

Let us call a GSH that does not contain inseparable parameter combinations, i.e., a GSH with the minimum number of operators (the coefficients attached to which will be new independent parameters) a maximally reduced spin Hamiltonian (MRSH). Belonging to the class of MRSH are $\mathscr{H}_1$ and the GSH $\mathscr{H}_2$ with $g_1' = (g_1^2 + g_7^2)^{1/2}$. The Hamiltonian $\mathscr{H}_3$ also becomes a MRSH upon the elimination of $H_x S_x + H_y S_y$ or $H_x S_y - H_y S_x$.

In the case of centers of symmetry lower than the $\mathbf{C}_3$ symmetry, or in the $S > \frac{1}{2}$ case, the number $N_1 = N_0 - N$ of inseparable parameter combinations can be much greater than one. Each of them must be identified and replaced by one parameter, since only the MRSH is the correct GSH, i.e., the GSH that allows a unique description of the spectra.

The problem of obtaining the MRSH is an especially pressing one when a computer had to be used (and, for large N, the determination of all the parameters is possible only with the aid of a computer), since here the external signs of failure in an attempt to find any of the superfluous parameters can sometimes be veiled.

Kneubühl and Bieri[17,18] have suggested that the GSH parameters can be decreased through the rotation of the coordinate system for the electronic (nuclear) spin $\mathbf{S}$, and have found for the groups $\mathbf{C}_n$, $\mathbf{S}_n$, and $\mathbf{C}_{nh}$ ($n \geqslant 3$) the form of the operator effecting this rotation. This approach allows the elimination (through the choice of the Euler angles) of up to three parameters of the $\mathbf{g}$ tensor, i.e., to obtain the MRSH for $S \leqslant 1$, but is is not suitable for the $S \geqslant \frac{3}{2}$ case, in which there occur in the Zeeman part $\mathscr{H}_z$ of the GSH terms of the form $\mathbf{S}^{k_1} \cdot H$ ($k_1 = 3, 5, 7$), which may contain more than three "superfluous" parameters.

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In Refs. 12–14 a unitary transformation of the wave functions that diagonalizes the crystal (**H**-independent) part $\mathscr{H}_C$ of the GSH is employed for the same purpose. In the process the number of GSH parameters is reduced by 4 in the $S=\frac{3}{2}$ case and by 12 in the $S=\frac{5}{2}$ case. But some of the characteristics of the transformation used in these papers turn out to be subdefinite. It is suggested that this circumstance can be used to further reduce the GSH parameters, but it is not clear how many more parameters should be eliminated in order to obtain the MRSH and how this can be done in practice.

The purpose of the present is to: 1) elucidate the procedure for obtaining the MRSH; 2) determine the highest possible number of eliminable GSH parameters; 3) find the specific transformations that take a GSH into the MRSH; 4) construct the MRSH for certain symmetry groups; 5) compare the MRSH with the GSH that have already been used; and 6) demonstrate the possibility of the determination of all the MRSH parameters, using as an example a center with the $\mathbf{C}_1$ symmetry.

1. THE SINGLE PARTICLE GSH AND THE REDUCTION OF ITS PARAMETERS

There are several schemes for obtaining GSH.[1–4,11,15,16] We shall use the irreducible-tensor-operator (ITO) formalism,[4,15,16] in which operator combinations invariant under the transformations of the point-group symmetry (PGS) of interest to us are constructed from integral powers of the components of the effective spin **S** and the magnetic field intensity **H**. Let us denote by $\widetilde{T}_q^{k_1k_2k}$ the irreducible tensor products[16,19]:

$$\widetilde{T}_q^{k_1k_2k}=\{\widetilde{\mathbf{S}}^{k_1}\otimes\widetilde{\mathbf{H}}^{k_2}\}_q^{\,k}=\sum_{q_1}C^{kq}_{k_1q_1k_2q_2}\widetilde{T}_{q_1}^{\,k_1}(S)\widetilde{T}_{q_2}^{\,k_2}(H), \tag{5}$$

where the $C^{kq}_{k_1q_1k_2q_2}$ are the Clebsch-Gordon (Wigner) coefficients; $\widetilde{T}_q^{\,k}=i^kT_q^{\,k}$, $\widetilde{S}_q^{\,k}$, and $\widetilde{H}_q^{\,k}$ are ITO of rank k, constructed from the components of only one axial vector. For $k_2=q_2=0$, we have $\widetilde{T}_q^{k_1,0k}=\widetilde{T}_q^{\,k}(S)$. The phase factor of the single-vector ITO has been chosen such that

$$(\widetilde{T}_q^{\,k})^+=(-1)^{k-q}\widetilde{T}_{-q}^{\,k},\quad \Theta\widetilde{T}_q^{\,k}\Theta^{-1}=(-1)^k(\widetilde{T}_q^{\,k})^+=(-1)^q\widetilde{T}_{-q}^{\,k}, \tag{6}$$

where Θ is the time-reversal operator (other phases are also admissible[16]).

In order to get the ITO (5) and (6) to be as close as possible to Stevens's widely used operators[7,20] O_q^k and Ω_k^q and maintain the succession, let us introduce the following zonal and tesseral tensor operators,[15,21] which are proportional to $\cos q\varphi$ and $\sin q\varphi$ (φ is the azimuthal angle):

$$V_q^{k_1k_2k}=(-i)^k\cdot 2^{-1/2}[\widetilde{T}_{-q}^{k_1k_2k}+(-1)^q\widetilde{T}_q^{k_1k_2k}],\quad q>0\ (\cos),$$
$$V_q^{k_1k_2k}=(-i)^k\widetilde{T}_0^{k_1k_2k},\quad q=0\ (\cos), \tag{7}$$
$$V_q^{k_1k_2k}=(-i)^{k-1}\cdot 2^{-1/2}[\widetilde{T}_{-|q|}^{k_1k_2k}-(-1)^q\widetilde{T}_{|q|}^{k_1k_2k}],\quad q<0\ (\sin).$$

The explicit forms of $V_q^{k_1k_2k}$ and the real coefficients relating V_q^k with O_k^q and Ω_k^q for $k_2=1$, $k_1=1$ and 3 are given in Appendix 1 (for other possible coefficients and their interrelationships, see Rudowicz's review article[21]).

It is easy to verify that

$$\Theta V_q^{k_1k_2k}\Theta^{-1}=(-1)^{k_1+k_2}V_q^{k_1k_2k},\quad (V_q^{k_1k_2k})^+=V_q^{k_1k_2k}. \tag{8}$$

In the most general case the GSH has the form of an expansion in terms of a complete set of ITO:

$$\mathscr{H}=\sum_{k_1k_2kq}v_q^{k_1k_2k}V_q^{k_1k_2k}=\sum_{\varkappa}v_\varkappa V_\varkappa,\quad |k_1-k_2|\leqslant k\leqslant k_1+k_2, \tag{9}$$

$\varkappa$ denotes the set of indices k_1k_2kq; because of the invariance of $\mathscr{H}$ under time reversal, k_1+k_2 should be even, but k can in this case assume both even and odd values. The demonstration, given in Ref. 16, of the admissibility in the GSH of terms with odd k_1+k_2 is unconvincing, since it does not take account of the fact that the configuration-mixing coefficients are not numbers, but matrix elements of the spin-spin and spin-orbit operators, and therefore can change sign under time reversal or space reflections.

In determining the nonzero GSH parameters for a given PGS, we should give consideration to the fact that the operators $\widetilde{T}_q^{k_1k_2k}$ and $\widetilde{T}_q^{\,k}$ transform under rotations of the coordinate system like the spherical harmonics $\widetilde{Y}_{kq}$, but they behave differently under reflections in mirror planes. This is due to the fact that the polar (**E**,**r**) and axial (**H**,**S**,**I**,**L**) vectors possess different transformation properties: under reflections in planes perpendicular to them $\mathbf{r}\to-\mathbf{r}$, but $\mathbf{H}\to\mathbf{H}$, while under reflections in planes passing through them $\mathbf{r}\to\mathbf{r}$, but $\mathbf{H}\to-\mathbf{H}$ (Ref. 22). The tables in Refs. 15 and 23, giving symmetry-adapted tensor operators constructed from the components of a polar vector, cannot be used for axial vectors: Almost all the terms with odd k in the spin Hamiltonians written down with their use[15] for half-integral S will be incorrect. This can be most easily verified by considering the action on $O_1^0=S_z$ or $V_{111}\sim H_xS_y-H_yS_x$ of a vertical plane passing through the z axis. Contrary to what is said in Ref. 15, these terms should not occur in the case of a PGS possessing such a reflection plane.

Let us show that, to obtain the MRSH, it is necessary and sufficient to specially choose the unitary transformation $\mathscr{U}$.

Indeed, the MRSH and the GSH should possess the same eigenvalues, and only unitary transformations will preserve all the matrix elements. The sufficiency can be demonstrated by specifying a procedure for eliminating the inseparable parameter combinations. It is simple. The MRSH should contain the smallest number of operators $V_\varkappa$. Although the unitarity condition imposes limitations on the characteristics of $\mathscr{U}$, some of these characteristics remain arbitrary. It is precisely these ones that must be chosen such that the parameter attached to some operator in $\mathscr{H}'=\mathscr{U}\mathscr{H}\mathscr{U}^{-1}$ vanishes. The rotation of the spin coordinate system[17,18] and the choice of the phase factors of the spin wave functions[1,8] are particular cases of this transformation.

In the unitary transformation $\mathscr{U}=\exp(i\Phi)$ taking the GSH into the MRSH form the Hermitian operator Φ contains only symmetry-allowed operators $V_m^l(\mathbf{S})$ with odd l.

Like any matrix, Φ can be expanded in terms of ITO. Since $\mathscr{U}$ should not depend on **H**, only the operators with $k_2=0$ are retained in the expansion (other wise the coefficients of the operators in $\mathscr{H}'$ will be nonlinear functions of **H**; an example of $\mathscr{U}$ with **H**-dependent matrix elements is the transformation that takes the GSH into the diagonal, and not into the reduced, form). Limitations on the l values follow from the requirement that $\mathscr{H}'$ be invariant under time reversal Θ. Let

$$\Phi=\sum_{lm}\varphi_m{}^l V_m{}^l(\mathbf{S}),\quad l=1,\ldots,2S,\quad m=-l,\ldots,l. \tag{10}$$

It follows from the unitarity condition $\mathcal{U}^+\mathcal{U}=1$ that

$$\Phi^+=\Phi,\quad (\varphi_m{}^l)^*=\varphi_m{}^l. \tag{11}$$

Then

$$\Theta\mathcal{H}'\Theta^{-1}=(\mathcal{H}')^+=\exp(i\Phi)\mathcal{H}\exp(-i\Phi). \tag{12}$$

Since

$$\Theta\exp(i\Phi)\mathcal{H}\exp(-i\Phi)\Theta^{-1}$$
$$=\exp(\Theta i\Phi\Theta^{-1})\Theta\mathcal{H}\Theta^{-1}\exp(-\Theta i\Phi\Theta^{-1}), \tag{13}$$

$\Theta i\Phi\Theta^{-1}=i\Phi=-(i\Phi)^+$, and, consequently, Φ is an odd-Θ operator containing, in accordance with (8), only odd l.

It is now easy to find the number N_u of coefficients $\varphi_m{}^l$ whose arbitrariness can be used to reduce the number of GSH parameters. It is determined by the value of S [the operators $V_m^l(\mathbf{S})$ are nonzero only when $l\leqslant 2S$], and is equal to 3 when $S\leqslant 1$, 3 + 7 when $S\leqslant 2$, 3 + 7 + 11 when $S\leqslant 3$, and 3 + 7 + 11 + 15 when $S=\frac{7}{2}$. Therefore, for the $\mathbf{C}_1$ symmetry the MRSH should contain respectively 3, 10, 21, and 36 parameters less than the GSH.

The system of equations for the determination of the $\varphi_m{}^l$ can be written as:

$$v_u'=\mathrm{Sp}\{V_u{}^+\mathcal{U}\mathcal{H}\mathcal{U}^{-1}\}/\mathrm{Sp}\{V_u{}^+V_u\}=0,\quad u=1,\ldots,N_u, \tag{14}$$

or

$$\mathrm{Sp}\{v_uV_u{}^+V_u+iV_u{}^+[\Phi,\mathcal{H}]+V_u{}^+\Phi\mathcal{H}\Phi+\ldots\}=0,$$
$$u=1,\ldots,N_u, \tag{15}$$

where v_x' is the parameter attached to the operator V_x in $\mathcal{H}'$ and u is an abridged notation for the indices k_1k_2kq labeling those operators which we want to eliminate.

The choice of the latter operators is, generally speaking, arbitrary. It is only necessary that the system of nonlinear equations (14), (15) should possess a solution. For example, in $\mathcal{H}_3$ we can eliminate either $H_xS_x+H_yS_y$ or $H_xS_y-H_yS_x$, but we cannot eliminate H_zS_z, since the equation (14) for g_3' does not contian $\varphi_m{}^l$: $g_3'=g_3$. Actually, there exists a family of equivalent MRSH for each noncubic PGS.

We propose the following principle for operator reduction. The Zeeman part $\mathcal{H}_z$ of the GSH for the $\mathbf{C}_1$ symmetry group and any S contains exactly as many operators $V_q^{k_1k_2k}$ with odd k as the operator (10). Therefore, their elimination will be the only unambiguous procedure for any S. The transition from the GSH to the MRSH in the case of the Hamiltonian represented in the form (9) is effected simply by discarding the terms with odd k.

2. EXAMPLES OF UNITARY TRANSFORMATIONS

2.1 Centers with symmetry C_2, C_{2h}, or C_s and spin $S=\frac{1}{2}$

The GSH contains five parameters:

$$\mathcal{H}_4=\beta\{\tilde{g}_1H_xS_x+g_2H_y\tilde{S}_y+g_3\tilde{H}_zS_z+g_6(H_xS_y+H_yS_x)$$
$$+g_7(H_xS_y-H_yS_x)\}. \tag{16}$$

Using

$$\mathcal{U}_4=\exp(i\varphi_0{}^1V_0{}^1)=\cos(\alpha/2)+2iS_z\sin(\alpha/2)\quad \alpha\equiv\varphi_0{}^1, \tag{17}$$

we obtain $\mathcal{H}_4'=\mathcal{U}_4\mathcal{H}_4\mathcal{U}_4^{-1}$ with the following parameters:

$$\begin{aligned}
&g_1'=g_1\cos\alpha+(g_6+g_7)\sin\alpha,\\
&g_2'=g_2\cos\alpha-(g_6-g_7)\sin\alpha,\quad g_3'=g_3,\\
&g_6'=g_6\cos\alpha-{}^1/_2(g_1-g_2)\sin\alpha,\\
&g_7'=g_7\cos\alpha-{}^1/_2(g_1+g_2)\sin\alpha.
\end{aligned} \tag{18}$$

By equating any of them (except, naturally, g_3') to zero, we can obtain four α values that take $\mathcal{H}_4$ into the MRSH form. For example, for

$$g_6'=0,\quad \mathrm{tg}\,\alpha=2g_6/(g_1-g_2) \tag{19}$$

we have

$$\mathcal{H}_4'=\beta[g_1'H_xS_x+g_2'H_yS_y+g_3'H_zS_z+g_7'(H_xS_y-H_yS_x)], \tag{20}$$

$$g_1'=[g_1(g_1-g_2)+2g_6(g_6+g_7)]/\Gamma,$$
$$g_2'=[g_2(g_1-g_2)-2g_6(g_6-g_7)]/\Gamma, \tag{21}$$
$$g_7'=[g_7(g_1-g_2)-g_6(g_1+g_2)]/\Gamma,\quad \Gamma=[(g_1-g_2)^2+4g_6^2]^{1/2}. \tag{22}$$

After the elimination of $H_xS_y-H_yS_x$, the MRSH $\mathcal{H}_g$ will contain only terms with even k. We can eliminate H_xS_x or H_yS_y by choosing other values of α. Although such MRSH have an unusual form, they are equivalent to (20) and $\mathcal{H}_g$.

Notice that the Hamiltonians (3) and (2) are particular cases of (16), specifically, the cases in which $g_1=g_2$, $g_6=0$.

2.2. Centers with symmetry C_{3v}, D_3, or D_{3d} and spin $S=\frac{3}{2}$

The GSH is given by the sum

$$\mathcal{H}_5=\mathcal{H}_g+\mathcal{H}_u, \tag{23}$$

$$\mathcal{H}_g=v_0{}^2O_0{}^2+3^{-1/2}v_0^{110}\beta[H_xO_1{}^1+H_y\Omega_1{}^1+H_zO_1{}^0]$$
$$+6^{-1/2}v_0^{112}\beta[-H_xO_1{}^1-H_y\Omega_1{}^1$$
$$+2H_zO_1{}^0]+({}^3/_{70})^{1/2}v_0^{312}\beta[H_xO_3{}^1+H_y\Omega_3{}^1+H_zO_3{}^0]$$
$$+280^{-1/2}v_0^{314}\beta[-3(H_xO_3{}^1$$
$$+H_y\Omega_3{}^1)+4H_zO_3{}^0]+{}^1/_4v_3^{314}\beta[3(H_xO_3{}^2-H_y\Omega_3{}^2)+H_zO_3{}^3], \tag{24}$$

$$\mathcal{H}_u=({}^3/_{16})^{1/2}v_{-3}^{313}\beta[-H_xO_3{}^2+H_y\Omega_3{}^2+H_zO_3{}^3]. \tag{25}$$

Here and below the subscript g indicates the terms with even k; the subscript u, the those with odd k. Although the number of superfluous parameters in (23) is not large (it is equal to one!), $\mathcal{H}_u$ cannot be eliminated by any rotations of the spin coordinate system. It can be eliminated by the unitary transformation

$$\mathcal{U}_5=\exp(i\varphi_{-3}{}^3V_{-3}{}^3)$$
$$={}^1/_2(\cos\alpha+1)+{}^2/_3iV_{-3}{}^3\sin\alpha+6^{-1/2}V_0{}^2(\cos\alpha-1), \tag{26}$$

where $\alpha=3\varphi_{-3}{}^3/2$ is determined from the simple, but unwieldy trigonometric equation

$$\mathrm{Sp}\{V_{-3}^{313}\mathcal{U}_5\mathcal{H}_5\mathcal{U}_5{}^{-1}\}=0. \tag{27}$$

3. COMPARISON OF THE GSH AND MRSH FOR NONCUBIC POINT SYMMETRY GROUPS

The Zeeman part $\mathscr{H}_z$ of the GSH contains both even and odd k. The MRSH contains only even k, i.e., coincides with $\mathscr{H}_g$. We found that the GSH for all the noncubic groups contains superfluous parameters (from 1 for the PGS $\mathbf{C}_{6v}$ to 36 for $\mathbf{C}_1$ in the case when $S=\frac{7}{2}$).

Let us compare, for example, the GSH given in Ref. 7 for the PGS $\mathbf{C}_{3v}$ and spin $S=\frac{3}{2}$:

$$\mathscr{H}=b_2^0O_2^0+g_\parallel\beta H_zS_z+g_\perp\beta(H_xS_x+H_yS_y)+g_1\beta H_zO_3^0+g_2\beta H_zO_3^3 +g_3\beta(H_xO_3^1+H_y\Omega_3^1)+g_4\beta(H_xO_3^2-H_y\Omega_3^2) \quad (28)$$

[we have corrected the formula (3.124) by replacing the (incorrect) expression $H_z\Omega_3^3$ by $H_zO_3^3$] with the MRSH, (24), proposed by us. They differ in notation:

$$v_0^{312}=(^{10}/_{21})^{1/2}(3g_1+4g_3),$$

$$v_0^{314}=(^{40}/_{21})^{1/2}(g_1-g_3), \qquad v_3^{314}=g_2+g_4,$$

$$v_{-3}^{313}=3^{-1/2}(3g_2-g_4)$$

and by the expression (25), which should be eliminated from (28). Notice the inconvenience of the $\mathbf{S}^3\cdot\mathbf{H}$-operator combinations used in (28): in contrast to $V_q^{k_1k_2k}$, they are not orthogonal, and are not characterized by definite k values.

After examining the total and partially reduced GSH obtained by different methods and different authors,[1-16,24] we became convinced that all of them contain more parameters than the MRSH, and are therefore unsuitable for the determination of the latter.

There arises the question: Why is it that it was possible in a great number of papers to find the spin-Hamiltonian parameters and describe the experimental data? The point is that, in each of these papers, a significant part of the GSH, e.g., the entire set of terms of the form $\mathbf{S}^{k_1}\cdot\mathbf{H}$ with $k_1\geqslant 3$, is arbitrarily discarded under the assumption that it is small, or for the sake of simplicity, i.e., an incomplete basis is used. This has on occasion[25,26] led to a situation in which the Hamiltonian used contain a smaller number of parameters than the MRSH. But such unjustified reduction of the GSH cannot be recommended generally, since it does not guarantee the reliability of the parameters determined and an accurate description of experiment.

The necessity of the consideration of the $\mathbf{S}^{k_1}\cdot\mathbf{H}$ terms was established long ago.[8,27-30] We found several new cases in which the neglect of these terms led to appreciable discrepancies between the computed and observed positions of the lines. For example, in McPershan's description[31] of the EPR of the $S=2$ state of the Cr^{3+}–Cr^{3+} pair in $CsMgCl_3$ by a simplified Hamiltonian without $\mathbf{S}^3\cdot\mathbf{H}$ operators this discrepancy runs to hundreds of gausses in the three-centimeter microwave range, and is even greater in the eight-millimeter range. Using the MRSH for the PGS $\mathbf{C}_{3v}$ and $S=2$ [to (24) was added $b_4^0O_4^0$] and the program package "Radiospektrosopiya-2" ("Microwave Spectroscopy-2") developed by us, we reprocessed the experimental data reported in Ref. 31. We were able to decrease the rms deviation $\overline{\Delta H^2}$ by a factor of five, determine the new parameters $v_0^{312}=0.008$, $v_0^{314}=-0.008$, $v_3^{314}\leqslant 0.001$, and refine the old: $b_2^0=-222\pm 2$, $b_4^0=313\pm 2$ instead of -218 and 304 (b_k^0, to $10^{-4}\,\mathrm{cm}^{-1}$). The use of the GSH (23) either did not lead to any improvement in the description, or led to the divergence of the $\overline{\Delta H^2}$-minimization process.

Our conclusion: The MRSH is adequate for the description of the line positions.

4. ENERGY LEVELS OF THE SINGLE-PARTICLE GSH FOR $\mathscr{H}_z\gg\mathscr{H}_c$

Let us verify that all the MRSH parameters can be uniquely determined from experiments performed in strong magnetic fields.

In the $\mathscr{H}_z\gg\mathscr{H}_c$ case it is convenient to go over from the crystallographic coordinate system to a system in which the axis $Z\parallel\mathbf{H}$ with the aid of a rotation operator[19] $R(\varphi,\theta,0)$, where φ and θ are the azimuthal and polar angles of $\mathbf{H}$:

$$\mathscr{H}_R=R\mathscr{H}R^{-1}=\sum_{k_1k_2kq}t_q^{k_1k_2k}\sum_{q'}D_{qq'}^{k}(\varphi,\theta,0)\tilde{T}_{q'}^{k_1k_2k}, \quad (29)$$

$$t_q^{k_1k_2k}=2^{-1/2}(-i)^k(-1)^q[v_{|q|}^{k_1k_2k}-iv_{-|q|}^{k_1k_2k}], \quad q>0, \quad (30a)$$

$$t_q^{k_1k_2k}=(-i)^kv_0^{k_1k_2k}, \quad q=0, \quad (30b)$$

$$t_q^{k_1k_2k}=2^{-1/2}(-i)^k[v_{|q|}^{k_1k_2k}+iv_{-|q|}^{k_1k_2k}], \quad q<0. \quad (30c)$$

Here the $D_{qq'}^k$ are the Wigner functions. Retaining only the diagonal matrix elements in $\mathscr{H}_R$, and taking account of the fact that only $\tilde{T}_0^0(\mathbf{H})=1$ and $T_0^1(\mathbf{H})=iH_z$ are nonzero, we obtain

$$\begin{aligned}E_{SM}&=\sum_{k_1k_2kqq'}t_q^{k_1k_2k}D_{qq'}^k(\varphi,\theta,0)\\&\times\sum_{q_1}C_{k_1q_1k_2q_2}^{kq'}\langle SM|\tilde{T}_{q_1}^{k_1}(\mathbf{S})|SM\rangle\tilde{T}_{q_2}^{k_2}(\mathbf{H})\\&=\sum_{kq}D_{q0}^k(\varphi,\theta,0)\\&\times\Big\{\sum_{k_1k_2}t_q^{k_1k_2k}\tilde{T}_0^{k_2}(\mathbf{H})C_{k_10k_20}^{k0}C_{SMk_10}^{SM}\langle S\|i^{k_1}T^{k_1}(\mathbf{S})\|S\rangle(2S+1)^{-1/2}\Big\}.\end{aligned} \quad (31)$$

Since $S_{k_10k_20}^{k0}=0$ for all odd $k+k_1+k_2$ values,[19] in this approximation t_u is not contained in (31) at all (true, only in first order in $\mathscr{H}_u/\mathscr{H}_q$). Because of the orthogonality of the Wigner function, all the expressions of the type enclosed in the curly brackets in (31) can be independently found from the total angular dependences of the resonance frequencies (fields), and since the $t_q^{k_1k_2k}$ enter into these expressions with different $C_{SMk_10}^{SM}T_0^{k_2}(\mathbf{H})$, the contributions from the various k_1 can also be determined separately when the lines with all possible $SM\to SM-1$ are observable.

5. THE MRSH OF CENTERS WITH EXCHANGE OR HYPERFINE INTERACTIONS

The GSH of a pair of spins $\mathbf{S}$ and $\mathbf{I}$ coupled by hyperfine (exchange) interactions can be represented in the form

$$\mathscr{H}=\mathscr{H}_S+\mathscr{H}_I+\mathscr{H}_{SI},$$

where $\mathscr{H}_S$ and $\mathscr{H}_I$ are GSH of the type (9) and

$$\mathscr{H}_{SI}=\sum_{k_1k_2kq}A_q^{k_1k_2k}V_q^{k_1k_2k}(\mathbf{S},\mathbf{I}).$$

The operators $V_q^{k_1k_2k}(\mathbf{S},\mathbf{I})$ can be obtained from (5)

and the expressions given in the Appendix by replacing $\beta\mathbf{H}$ by $\mathbf{I}$. In the cases of 13 PGS the bilinear part of the hyperfine interactions contains antisymmetric components, i.e., the operators $V_q^{111}(\mathbf{S},\mathbf{I})$, and the other $V_q^{k_1k_2k}(\mathbf{S},\mathbf{I})$ with odd k occur in the cases of 23 groups from the classes $\sigma_1-\sigma_4$, $\sigma_6-\sigma_8$ (see Table II. 1 in Ref. 14).

In the $H\neq 0$ case (at least for $S=1=\frac{1}{2}$) none of the hyperfine (exchange) interaction operators of the two-particle GSH can be eliminated with the aid of a unitary transformation.

Since all the possible single-particle operators $V_{q_1}^{k_1}(\mathbf{S})$, $V_{q_2}^{k_2}(\mathbf{I})$ with odd k_1, k_2 are used in the reduction of $\mathscr{H}_S$ and $\mathscr{H}_I$, the reduction of $\mathscr{H}_{SI}$ requires the inclusion in $\mathscr{U}$ of the two-particle operators $V_q^{k_1k_2k}(\mathbf{S},\mathbf{I})$. But because of the invariance of $\mathscr{H}'$ under time reversal, $\mathscr{U}$ cannot contain operators with even values of the sum k_1+k_2. Therefore, we cannot add a single operator to $\mathscr{U}$ in the $S=I=\frac{1}{2}$ case.

For $S\geqslant 1$ we can add operators with $k_1=2$, $k_2=1$ to $\mathscr{U}$. But it is more convenient to use them in the reduction of the antisymmetric part of the $\mathbf{HS}^2\mathbf{I}$ interactions, which occur in the GSH for the $S\geqslant 1$ case. Exchange-coupled complexes consisting of two or more identical centers can possess additional permutation symmetry, which should be taken into account in writing down the GSH and in choosing $\mathscr{U}$. This problem requires further investigation. A number of GSH, reduced with the aid to Kneubühl's method,[17] for exchange-coupled pairs are given in Ref. 32.

6. MRSH IN THE PRESENCE OF AN ELECTRIC FIELD E

For centers in the case of many PGS, the linear electric-field effect is described by the addition to the GSH of the symmetric and antisymmetric g-tensor components that are proportional to the electric field intensity $\mathbf{E}$ (Refs. 11, 14, 33–36). But as shown in Secs. 1 and 2, these tensor elements can be transformed with the aid of a unitary transformation into linear and quadratic—in the field $\mathbf{E}$—corrections to the symmetric components (see, for example, Sec. 2.1). The parameters of the electric field effects will then be overdetermined. Consequently, in the presence of $\mathbf{E}$, the $\mathscr{H}_u$ parameters cannot be independently determined from the line positions, and should be eliminated. The experimental data should be described by a MRSH that differs from the GSH by the fact that only part of the electric-field tensor F_{pqr},

$$\mathscr{H}_E=\sum_{pqr}F_{pqr}E_rH_pS_q,$$

which is symmetric in the indices p and q is retained in the tensor.

7. MAGNETIC RESONANCE LINE INTENSITIES

The probability of spin transitions under the action of a variable magnetic field $\mathbf{H}_\sim(t)$ is given by

$$\langle i|\mathscr{H}_\sim(t)|f\rangle=\langle i'|\mathscr{H}_\sim'(t)|f'\rangle,$$

where $\mathscr{H}_\sim(t)$ can be obtained from $\mathscr{H}_Z$ through the replacement of $\mathbf{H}$ by $\mathbf{H}_\sim(t)$; the primed symbols denote the operators and functions after the unitary transformation. Since the coefficients of the GSH→MRSH transformation found by us do not depend on $\mathbf{H}$, the terms proportional to v_u in $\mathscr{H}'_\sim(t)$ can also be eliminated. Thus, it is also impossible to determine v_u from the line intensities.

The suggestion[17] that the antisymmetric elements of the $\mathbf{g}$ tensor can be determined from the difference between the line intensities measured in right- and left-polarized variable fields is incorrect, since the procedure does not in fact contain a method for the separation of v_g and v_u The error made eby Kneubühl[17] and all those [26,37] who have reproduced his results lies in the fact that no allowance was made in the consideration of a paramagnetic center with $g_1\neq g_2$ for the contributions to the energies and intensities from $g_6(H_yS_y+H_yS_x)$. But in the case of the groups $\mathbf{C}_1$, $\mathbf{C}_i$, $\mathbf{C}_2$, $\mathbf{C}_s$, and $\mathbf{C}_{2h}$, for which $g_1\neq g_2$ and an antisymmetric part $g_7(H_xS_y-H_yS_x)$ exists, there necessarily exists the symmetric off-diagonal part with g_6, i.e., the total number of parameters is not smaller than five. The assertion[17] that three of them can be determined from the line intensities is correct. Only the identification of them with g_1, g_2, and g_7 is incorrect. A rigorous calculation (see Sec. 2) showed that each of the three parameters is an inseparable combination of g_1, g_2, g_6, and g_7.

CONCLUSION

We have shown that a significant fraction of the GSH parameters cannot be determined from either the line positions or the line intensities, but can be eliminated by the requisite unitary transformation. The presence of superfluous parameters is characteristic of not only the GSH. Another method of describing spectra—the perturbation matrix method,[1,11]—has the same shortcoming. For example, for the PGS $\mathbf{C}_3$ and spin $S=3/2$ its matrix contains nine parameters,[11] whereas the MRSH contains only six. Thus, in essence, we have found that a system with a discrete energy spectrum has superfluous (nonphysical) degrees of freedom, and the GSH→MRSH unitary transformation found is a guage transformation. Since the choice (fixing) of the guage is an obligatory step in the solution of physical problems, the transition to the MRSH is necessary and sufficient for the description of the positions and intensities of magnetic resonance lines.

The number of independent characteristics of any noncubic center with arbitrary spin (the number of MRSH parameters) can be obtained by counting up the nonzero $v_q^{k_1k_2k}$ and the possible combinations of specific k_1 and k_2 into a given k. But the construction of the MRSH for the PGS needed by a reader has been reduced by us to the rewriting of the symmetry-adapted operators given in the Appendix. Here in the $H\neq 0$ case both even and odd k can be taken for the exchange and hyperfine interactions, whereas only even k values can be taken for the Zeeman interaction and the crystal field. In principle, other variants of the eliminable parameters can be chosen, but the variant chosen by us is convenient in that it does not depend on the values of S, and, moreover, it simultaneously simplifies $\mathscr{H}$ and $\mathscr{H}_\sim(t)$.

It follows from the analysis carried out that any attempt to extract from the experimental data more parameters than are contained in the MRSH is inadmissible, and will not be successful. In particular, the proposed[38] experiments on the determination of the antisymmetric components of the magnetic-screening tensor from second-order effects are doomed to failure.

Finally, let us note that the hitherto employed procedure for comparing the experimentally determined param-

TABLE I.

k	q						
	0	1	2	3	4	5	6
1	1	1	–	–	–	–	–
2	6	$^1/_2$	2	–	–	–	–
3	10	$^{20}/_3$	$^2/_3$	4	–	–	–
4	280	7	14	1	8	–	–
5	504	$^{168}/_5$	$^6/_5$	$^{144}/_5$	$^8/_5$	16	–
6	3696	44	$^{352}/_5$	$^{88}/_5$	$^{176}/_3$	$^8/_3$	32

eters with the parameters computed from first principles should also be modified: the microtheoretical GSH should be reduced with the aid of a gauge transformation to a MRSH similar in form to the one used in the description of spectra. Only then will the parameters under comparison be adequate.

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APPENDIX

The orthonormalized operators V_q^k and the parameters attached to them are connected with O_k^q, Ω_k^q, B_k^q, and C_k^q (Ref. 7) by the following relations:

$$V_q^k=a_{|q|}^k O_k^q, \quad v_q^k=B_k^q/a_{|q|}^k, \quad q\geqslant 0,$$

$$V_q^k=a_{|q|}^k \Omega_k^q, \quad v_q^k=C_k^q/a_{|q|}^k, \quad q<0.$$

The squares of the coefficients $a_{|q|}^k$ are given in Table I.

The irreducible Hermitian tensor products $V_q^{k_1k_2k}$ (**S**,**H**) can be expressed in terms of $O_{k_1}^{q_1}$ (**S**), $\Omega_{k_1}^{q_1}$ (**S**), and the components of the vector **H** as follows:

$$V_0^{110}=3^{-1/2}\beta[H_xO_1^1+H_y\Omega_1^1+H_zO_1^0],$$

$$V_1^{111}=2^{-1/2}\beta[H_yO_1^0-H_z\Omega_1^1],$$

$$V_0^{111}=2^{-1/2}\beta[H_x\Omega_1^1-H_yO_1^1],$$

$$V_{-1}^{111}=2^{-1/2}\beta[-H_xO_1^0+H_zO_1^1],$$

$$V_2^{112}=2^{-1/2}\beta[H_xO_1^1-H_y\Omega_1^1], \quad V_1^{112}=2^{-1/2}\beta[H_xO_1^0+H_zO_1^1],$$

$$V_0^{112}=6^{-1/2}\beta[-H_xO_1^1-H_y\Omega_1^1+2H_zO_1^0],$$

$$V_{-1}^{112}=2^{-1/2}\beta[H_yO_1^0+H_z\Omega_1^1],$$

$$V_{-2}^{112}=2^{-1/2}\beta[H_x\Omega_1^1+H_yO_1^1],$$

$$V_2^{312}=(280)^{-1/2}\beta[5(H_xO_3^3+H_y\Omega_3^3+2H_zO_3^2)-H_xO_3^1+H_y\Omega_3^1],$$

$$V_1^{312}=(70)^{-1/2}\beta[5(H_xO_3^2+H_y\Omega_3^2)+2H_zO_3^1-H_xO_3^0],$$

$$V_0^{312}=(^3/_{70})^{1/2}\beta[H_xO_3^1+H_y\Omega_3^1+H_zO_3^0],$$

$$V_{-1}^{312}=70^{-1/2}\beta[5(H_x\Omega_3^2-H_yO_3^2)+2H_z\Omega_3^1-H_yO_3^0],$$

$$V_{-2}^{312}=280^{-1/2}\beta[5(H_x\Omega_3^3-H_yO_3^3+2H_z\Omega_3^2)-H_x\Omega_3^1-H_yO_3^1],$$

$$V_3^{313}=(^3/_{16})^{1/2}\beta[H_x\Omega_3^2+H_yO_3^2-H_z\Omega_3^3],$$

$$V_2^{313}=32^{-1/2}\beta[-H_xO_3^3+H_y\Omega_3^3-4H_z\Omega_3^2+H_x\Omega_3^1+H_yO_3^1],$$

$$V_1^{313}=80^{-1/2}\beta[-5(H_x\Omega_3^2+H_yO_3^2)+H_z\Omega_3^1-2H_xO_3^0],$$

$$V_0^{313}=(^3/_{40})^{1/2}\beta[H_x\Omega_3^1-H_yO_3^1],$$

$$V_{-1}^{313}=80^{-1/2}\beta[-5(H_xO_3^2+H_y\Omega_3^2)+H_zO_3^1-2H_xO_3^0],$$

$$V_{-2}^{313}=32^{-1/2}\beta[-H_xO_3^3-H_y\Omega_3^3+4H_zO_3^2-H_xO_3^1+H_y\Omega_3^1],$$

$$V_{-3}^{313}=(^3/_{16})^{1/2}\beta[-H_xO_3^2+H_y\Omega_3^2+H_zO_3^3],$$

$$V_4^{314}=8^{-1/2}\beta[H_xO_3^3-H_y\Omega_3^3],$$

$$V_3^{314}=^1/_4\beta[3(H_xO_3^2-H_y\Omega_3^2)+H_zO_3^3],$$

$$V_2^{314}=224^{-1/2}\beta[-H_xO_3^3-H_y\Omega_3^3+12H_zO_3^2+3(H_xO_3^1-H_y\Omega_3^1)],$$

$$V_1^{314}=112^{-1/2}\beta[3(-H_xO_3^2-H_y\Omega_3^2+H_zO_3^1)+2H_xO_3^0],$$

$$V_0^{314}=280^{-1/2}\beta[-3(H_xO_3^1+H_y\Omega_3^1)+4H_zO_3^0)],$$

$$V_{-1}^{314}=112^{-1/2}\beta[3(-H_x\Omega_3^2+H_yO_3^2+H_z\Omega_3^1)+2H_yO_3^0],$$

$$V_{-2}^{314}=224^{-1/2}\beta[-H_x\Omega_3^3+H_yO_3^3+12H_z\Omega_3^2+3(H_x\Omega_3^1+H_yO_3^1)],$$

$$V_{-3}^{314}=^1/_4\beta[3(H_x\Omega_3^2+H_yO_3^2)+H_z\Omega_3^3],$$

$$V_{-4}^{314}=8^{-1/2}\beta[H_x\Omega_3^3+H_yO_3^3].$$

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