TWO-ION MODEL FOR MONOCLINIC SPIN HAMILTONIAN WITH $S = 1$*

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Spin Hamiltonian formalism with $S = 1$ is mathematically justified for the description of a system of two interacting ions with twofold degenerate ground crystal level. Its interpretation in terms of bilinear spin Hamiltonian with $S_1 = S_2 = 1/2$ is given for monoclinic symmetry of the two-centre crystal field. A large rhombic and monoclinic anisotropy is predicted for the case of perpendicularity between the axis connecting the two ions and the twofold symmetry axis. The effective g-tensor is found to be nonsymmetrical if the two ions are not equivalent.

1. Introduction

We will be concerned with an isolated pair of weakly interacting paramagnetic ions in a crystal field with twofold degenerate ground crystal levels, well separated in energy from the higher levels. For a strict description of the manifold of four ground states of the pair, and admitting all possible interactions, we can use an effective Hamiltonian formalism in the space spanned by the four tensorial products of single ion ground states (see Levy [1] as well as the method presented in the monograph by Vonsovsky *et al.* [2], Chap. VII).

When the single ion ground crystal level possesses full rotational symmetry, *e. g.* if degeneration is due to the spin only, the effective Hamiltonian goes over strictly into the form of bilinear (pair) spin Hamiltonian with $S_1 = S_2 = 1/2$ (Herring [3]). This is the case for Cu^{2+} and Ti^{3+} ions in tetragonal and lower symmetry fields without spin-orbit coupling, which can be treated together with pair interactions as a perturbation.

In the case of ground levels with no full rotational symmetry (orbital degeneracy, strong spin-orbit coupling), the effective Hamiltonian can also be replaced by the bilinear spin Hamiltonian, albeit only if there exists one-to-one unitary mapping of the two

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ground one-ion crystal states onto eigenstates of effective spin operator S_z with $S = 1/2$ preserving the transformational properties of the crystal field symmetry group (see Appendix in [4]). If no such mapping exists, we can use the spin Hamiltonian formalism in the meaning of fictitious spin only (Stevens [5], Levy [6]). This method, however, is too poor in parameters from the group-theoretical point of view, and our further description in terms of bilinear spin Hamiltonian has to be regarded, for such cases, as a simplification.

In a first approximation, if we take into account isotropic exchange interaction only, the manifold of four ground levels of the system splits into a triplet and a singlet, separated by an exchange integral of order $1–10^2\ \mathrm{cm}^{-1}$. Further kinds of interactions split the triplet by amounts such that quantum transitions between the sub-levels are accessible to observation in electron paramagnetic resonance. The sign and magnitude of the exchange integral can be determined from the temperature behaviour of line intensity or from paramagnetic susceptibility measurements.

A number of experimental papers of the EPR spectrum of pairs of Cu^{2+} ions in diamagnetic matrices have recently been reported (see *e. g.* the more theoretically developed Ref. [7]). Their results are expressed in the form of a quadratic spin Hamiltonian with resultant effective spin $S = 1$ for the triplet. Our aim is to justify the application of such a Hamiltonian to the ion-pair system under consideration here, and to interprete it in terms of the bilinear spin Hamiltonian.

Another problem resides in finding the two-ion model for the low symmetry effects in EPR spectrum described by the monoclinic spin Hamiltonian (Kurzyński [4]):

$$\tilde{\mathscr{H}} = DS_\zeta^2 + E(S_\xi^2 - S_\eta^2) + F(S_\xi S_\eta + S_\eta S_\xi) +$$

$$+ \mu_B[g_{\zeta\zeta}H_\zeta S_\zeta + (g_{\xi\xi}H_\xi + g_{\eta\xi}H_\eta)S_\xi + (g_{\xi\eta}H_\xi + g_{\eta\eta}H_\eta)S_\eta] \tag{1}$$

(ζ-axis is directed along the twofold-symmetry axis or is perpendicular to the mirror plane; ξ- and η-axes are taken arbitrarily; the g-tensor need not be symmetrical). In the two-ion system, an additional axis, apart from the crystal field tensor and g-tensor principal axes occurring in the one-centre problem, exists. This axis is the line connecting the ions — its uncoincidence with the other above mentioned axes can lead, as we shall see, to large non-axial terms with E and F. The well-known mechanisms for the one-ion system (Abragam and Pryce [8]) do not provide for the occurrence of such large low symmetry effects in EPR spectrum.

2. Pair spin Hamiltonian

The most general form of spin Hamiltonian for a pair of ions in a two-centred crystal field with monoclinic symmetry and homogeneous external magnetic field $\boldsymbol{H}$ is (Kurzyński [9]):

$$\mathscr{H} = (A + B_0)\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 - 3B_0 S_{1\zeta}S_{2\zeta} + B_1(S_{1\xi}S_{2\xi} - S_{1\eta}S_{2\eta}) +$$

$$+ B_2(S_{1\xi}S_{2\eta} + S_{1\eta}S_{2\xi}) + C_0(S_{1\xi}S_{2\eta} - S_{1\eta}S_{2\xi}) +$$

$$+\mu_B \sum_{i=1,2} [g_{i\zeta\zeta} H_\zeta S_{i\zeta} + (g_{i\xi\xi} H_\xi + g_{i\eta\xi} H_\eta) S_{i\xi} +$$

$$+ (g_{i\xi\eta} H_\xi + g_{i\eta\eta} H_\eta) S_{i\eta}]. \tag{2}$$

Here, A is a parameter of isotropic interaction (exchange integral), B_0, B_1 and B_2 are parameters of symmetrical anisotropic interactions (dipole-dipole and Van Vleck's pseudo-dipolar couplin g)[1], C_0 is a constant of antisymmetrical Dzyaloshinski-Moriya interaction, and g_1, g_2 are g-tensors for the first and second ion, respectively.

The ζ-axis is taken along the principal twofold-symmetry axis of the two-centered crystal field, not necessarily lying in the direction of the interaction connecting the ions. Let us note that the principal axes of the two g-tensors in the $\xi\eta$-plane can in general differ, for this symmetry, one from another as well as from the principal axes of the interaction tensor (occurrence of B_2 term; see Baltes *et al.* [10]). Therefore, the ξ- and η-axes in (2) are taken arbitrarily.

In the interaction coordinate system xyz (z-axis taken along the vector $\boldsymbol{r}_{12}$ connecting the two ions, perpendicular x- and y-axes arbitrary), the interactional part of the Hamiltonian (2) can be written in the usual form:

$$\mathscr{H}_{\text{int}} = J \boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + J_{zz} \left[\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 - 3 \frac{(\boldsymbol{S}_1 \cdot \boldsymbol{r}_{12})(\boldsymbol{S}_2 \cdot \boldsymbol{r}_{12})}{r_{12}^2} \right] +$$

$$+ J_{xx}(S_{1x} S_{2x} - S_{1y} S_{2y}) + \sum_{\alpha \neq \beta} J_{\alpha\beta} S_{1\alpha} S_{2\beta} + \boldsymbol{D} \cdot (\boldsymbol{S}_1 \times \boldsymbol{S}_2), \tag{3}$$

where $J_{\alpha\beta} = J_{\beta\alpha}$ are components of the symmetrical trace-less interaction tensor and $\boldsymbol{D}$ is a pseudovectorial constant of antisymmetrical interaction. The relations between J, $J_{\alpha\beta}$, D_α and A, B_0, B_1, B_2, C_0 depend on the mutual orientation of the two coordinate systems, and will be determined later.

The matrix elements of the Hamiltonian (2) taken within the basis

$$|00\rangle = \frac{1}{\sqrt{2}} \left(\left|\frac{1}{2}\right\rangle_1 \otimes \left|-\frac{1}{2}\right\rangle_2 - \left|-\frac{1}{2}\right\rangle_1 \otimes \left|\frac{1}{2}\right\rangle_2 \right),$$

$$|1-1\rangle = |-\tfrac{1}{2}\rangle_1 \otimes |-\tfrac{1}{2}\rangle_2,$$

$$|10\rangle = \frac{1}{\sqrt{2}} \left(\left|\frac{1}{2}\right\rangle_1 \otimes \left|-\frac{1}{2}\right\rangle_2 + \left|-\frac{1}{2}\right\rangle_1 \otimes \left|\frac{1}{2}\right\rangle_2 \right),$$

$$|11\rangle = |\tfrac{1}{2}\rangle_1 \otimes |\tfrac{1}{2}\rangle_2, \tag{4}$$

where $|\frac{1}{2}\rangle_i$, $|-\frac{1}{2}\rangle_i$ are eigenstates of operators $S_{i\zeta}$ ($i = 1, 2$) and $|SM\rangle$ are eigenstates of the ζ-component of total spin of the system $\boldsymbol{S} = \boldsymbol{S}_1 + \boldsymbol{S}_2$, are given in Table I.

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[1] We have changed the labelling of constants B in [9] namely: B_3 into B_1, B_4 into B_2, and inversely.

TABLE I

Matrix of Hamiltonian (2) within the basis of resultant spin ζ-component eigenstates

	$\|00\rangle$	$\|1{-}1\rangle$	$\|10\rangle$	$\|11\rangle$
$\langle 00\|$	$-\frac{3}{4}A$	$\frac{\mu_B}{2\sqrt{2}}\{[(g_{1\xi\xi}-g_{2\xi\xi})H_\xi+(g_{1\eta\xi}-g_{2\eta\xi})H_\eta]-$ $-i[(g_{1\xi\eta}-g_{2\xi\eta})H_\xi+(g_{1\eta\eta}-g_{2\eta\eta})H_\eta]\}$	$\frac{i}{2}C_0+\frac{\mu_B}{2}(g_{1\zeta\zeta}-g_{2\zeta\zeta})H_\zeta$	$-\frac{\mu_B}{2\sqrt{2}}\{[(g_{2\xi\xi}-g_{2\xi\xi})H_\xi+(g_{1\eta\xi}-g_{2\eta\xi})H_\eta]+$ $+i[(g_{1\xi\eta}-g_{2\xi\eta})H_\xi+(g_{1\eta\eta}-g_{2\eta\eta})H_\eta]\}$
$\langle 1{-}1\|$	c.c.	$\frac{1}{4}A-\frac{1}{2}B_0-\frac{\mu_B}{2}(g_{1\zeta\zeta}+g_{2\zeta\zeta})H_\zeta$	$\frac{\mu_B}{2\sqrt{2}}\{[(g_{1\xi\xi}+g_{2\xi\xi})H_\xi+(g_{1\eta\xi}+g_{2\eta\xi})H_\eta]+$ $+i[(g_{1\xi\eta}+g_{2\xi\eta})H_\xi+(g_{1\eta\eta}+g_{2\eta\eta})H_\eta]\}$	$\frac{1}{2}(B_1+iB_2)$
$\langle 10\|$	c.c.	c.c.	$\frac{1}{4}A+B_0$	$\frac{\mu_B}{2\sqrt{2}}\{[(g_{1\xi\xi}+g_{2\xi\xi})H_\xi+(g_{1\eta\xi}+g_{2\eta\xi})H_\eta]+$ $+i[(g_{1\xi\eta}+g_{2\xi\eta})H_\xi+(g_{1\eta\eta}+g_{2\eta\eta})H_\eta]\}$
$\langle 11\|$	c.c.	c.c.	c.c.	$\frac{1}{4}A-\frac{1}{2}B_0+\frac{\mu_B}{2}(g_{1\zeta\zeta}+g_{2\zeta\zeta})H_\zeta$

3. Case of equivalent ions

If the two-centre point symmetry group contains inversion (geometrical equivalence of the ions) and if simultaneously the two ions are in the same unperturbed one-ion state (physical equivalence), the system possesses permutational symmetry and the value of the total spin S is a good quantum number (see *e. g.* Landau and Lifshitz [11] p. 258). The triplet $S = 1$ is then well separated from the singlet $S = 0$ in the sense that the Hamiltonian matrix elements between them must vanish, leading to:

$$C_0 = 0 \text{ and } g_1 = g_2. \tag{5a}$$

Since $g_1 = g_2$, we can choose the ξ- and η-axes as principal axes of the coinciding g-tensors, putting

$$g_{1\xi\eta} = g_{2\xi\eta} = g_{1\eta\xi} = g_{2\eta\xi} = 0 \tag{5b}$$

in (2).

Under the above conditions, there exists a trivial one-to-one linear mapping

$$|1-1\rangle \leftrightarrow |-\tilde{1}\rangle,\ |10\rangle \leftrightarrow |\tilde{0}\rangle,\ |11\rangle \leftrightarrow |\tilde{1}\rangle, \tag{6}$$

of the well separated (invariant under rotations) subspace of triplet states onto the space spanned by $|-\tilde{1}\rangle$, $|\tilde{0}\rangle$, $|\tilde{1}\rangle$ (corresponding to $|-1\rangle$, $|0\rangle$, $|1\rangle$ respectively in [4]), in which the spin Hamiltonian (1) acts, preserving the scalar product (matrix elements) and symmetry properties of the full orthogonal group, not only those of monoclinic symmetry. Therefore, according to remarks in Appendix of Ref. [4], we can strictly describe the discussed triplet in terms of the "one-ion" Hamiltonian (1). Let us observe that the correspondence (6) is determined in a unique way by the condition (5b).

Comparing the matrix of Hamiltonian (1) given in the g-tensor principal axes system in Table II of Ref. [4] and the matrix of Hamiltonian (2) within the triplet, given in Table I of the present paper, and taking into account that the relations (5) hold for the case of equivalent ions, we have:

$$D = -\tfrac{3}{2}B_0, E = \tfrac{1}{2}B_1, F = \tfrac{1}{2}B_2,$$

$$g_\xi = g_{1\xi\xi} = g_{2\xi\xi}, \quad g_\eta = g_{1\eta\eta} = g_{2\eta\eta}, \quad g_\zeta = g_{1\zeta\zeta} = g_{2\zeta\zeta} \tag{7}$$

(g_ξ, g_η, g_ζ correspond to g_x, g_y, g_z of Ref. [4]).

The only monoclinic group containing a centre of inversion is C_{2h}. Since a system of two identical ions unperturbed by crystal environment possesses symmetry $D_{\infty h}$, two directions of the twofold symmetry axis with regard to the interaction axis are possible:

a) ζ parallel to z

With regard to the arbitrary choice of x- and y-axes, we can assume them to coincide with the principal g-tensor axes ξ and η (see Fig. 1a):

$$S_x = S_\zeta,\ S_y = S_\eta,\ S_z = S_\zeta. \tag{8}$$

Comparing (2 with (3), we obtain:

$$A = J, B_0 = J_{zz},\ B_1 = J_{xx},\ B_2 = J_{xy}. \tag{9}$$

b) ζ perpendicular to z

Chosing the x-axis to coincide with the ζ-axis, we have:

$$S_x = S_\zeta,\ S_y = S_\xi \sin\delta - S_\eta \cos\delta,\ S_z = S_\xi \cos\delta + S_\eta \sin\delta, \tag{10}$$

where δ is the angle between the principal g-tensor ξ-axis and the interaction z-axis (see Fig. 1b). On comparing (2) with (3), we find:

$$\begin{aligned} A &= J - \tfrac{1}{2}(J_{zz}+J_{xx}),\ B_0 = -\tfrac{3}{4}(J_{zz}+J_{xx}), \\ B_1 &= \tfrac{1}{2}(-3J_{zz}+J_{xx})\cos 2\delta + J_{yz}\sin 2\delta, \\ B_2 &= \tfrac{1}{2}(-3J_{zz}+J_{xx})\sin 2\delta - J_{yz}\cos 2\delta. \end{aligned} \tag{11}$$

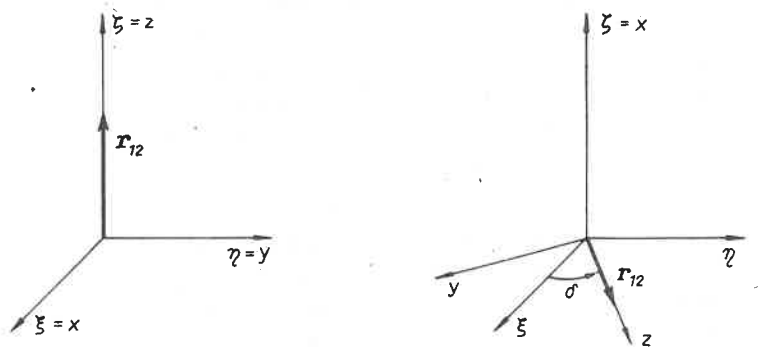

Fig. 1. Diagram showing axes introduced in text (in the case of equivalent ions $\xi\eta\zeta$ denotes the system of g-tensor principal axes). a) the z-axis connecting the two ions coincides with the twofold symmetry ζ-axis; b) the z-axis connecting the two ions is perpendicular to the twofold symmetry ζ-axis

Assuming $J_{zz} > J_{xx}, J_{yz}$ (*i. e.* for pure magnetical dipole-dipole interactions, although quite generally in the presence of exchange interactions this assumption seems to be very probable also) it is seen that in the case b) large unaxial anisotropy can exist. Even putting $J_{zz} = J_{xx}$ and $J_{yz} = 0$, we obtain in this case:

$$D = \tfrac{9}{4} J_{zz},\ E = -\tfrac{1}{2} J_{zz}\cos 2\delta,\ F = -\tfrac{1}{2} J_{zz}\sin 2\delta.$$

The rhombic anisotropy (large E or F term) follows from perpendicularity of the twofold-symmetry axis with respect to that of interaction; the monoclinic anisotropy (large F term) — from nonzero angle between the interaction- and g-tensor-axes.

4. Case of unequivalent ions

In this case, the most general form of the Hamiltonian (2) has to be taken into account. For zero magnetic field, one finds the energy values:

$$\begin{aligned} E_a &= \tfrac{1}{4}A - \tfrac{1}{2}B_0 + \tfrac{1}{2}B, \\ E_b &= \tfrac{1}{4}A - \tfrac{1}{2}B_0 - \tfrac{1}{2}B, \\ E_c &= -\tfrac{1}{4}A + \tfrac{1}{2}B_0 + \tfrac{1}{2}C, \\ E_d &= -\tfrac{1}{4}A + \tfrac{1}{2}B_0 - \tfrac{1}{2}\mathrm{C}, \end{aligned} \tag{12}$$

where

$$B = \sqrt{B_1^2 + B_2^2},\ C = \sqrt{(A+B_0)^2 + C_0^2}, \tag{13}$$

and the corresponding eigenstates of this Hamiltonian:

$$\begin{aligned} |a\rangle &= \frac{1}{\sqrt{2}}|1-1\rangle + \frac{B_1 - iB_2}{\sqrt{2}\,B}|11\rangle, \\ |b\rangle &= -\frac{B_1 + iB_2}{\sqrt{2}\,B}|1-1\rangle + \frac{1}{\sqrt{2}}|11\rangle, \\ |c\rangle &= \cos\gamma|10\rangle + i\sin\gamma|00\rangle, \\ |d\rangle &= \cos\gamma|00\rangle + i\sin\gamma|10\rangle, \end{aligned} \tag{14}$$

where

$$\cos^2\gamma = \frac{A+B_0+C}{2C}. \tag{15}$$

We see that the total spin is no longer a good quantum number, because of the occurrence of the antisymmetrical C_0-term in the Hamiltonian. The influence of this term on the exchange coupled ion pair problem was discussed in some detail be Erdös [12].

From the EPR point of view, we are concerned with the triplet $\{|a\rangle, |b\rangle, |c\rangle\}$ only. Its subspace is not invariant under rotations due to the presence of a $|00\rangle$ state in $|c\rangle$; the only symmetry operations which do not lead out of this subspace are, by assumption, those of the monoclinic symmetry group. The admixture of $|00\rangle$ in $|c\rangle$ is, for usual values $1 < |A| < 10^2\ \mathrm{cm}^{-1}$, $10^{-3} < |C_0| < 10\ \mathrm{cm}^{-1}$ and $10^{-4} < |B_0|, |B_1|, |B_2| < 1\ \mathrm{cm}^{-1}$ (Cherepanov and Nikiforov [13]), of the order of one p. c., such however that the real resultant spin can be treated approximately as an integral of motion. Fig. 2 shows, in schematic diagram, the zero-field splitting for $A > C_0 > B_0, B_1, B_2 > 0$.

The magnetic part of the Hamiltonian (2), as is seen from Table I, leads out of the subspace $[|a\rangle, |b\rangle, |c\rangle]$ of the triplet. Because of proportionality to small $\sin\gamma$, we may neglect its mixed triplet-singlet matrix elements. Such a procedure corresponds to the first order of perturbation calculus for close-lying levels. The matrix elements of

the total Hamiltonian (2) within the states of the triplet $\{|a\rangle, |b\rangle, |c\rangle\}$ (*i. e.* within states of the system unperturbed by an external magnetic field) are:

$$\langle a|\mathscr{H}|a\rangle = \tfrac{1}{2}(A-C)-B_0+\tfrac{1}{2}B,$$

$$\langle b|\mathscr{H}|b\rangle = \tfrac{1}{2}(A-C)-B_0-\tfrac{1}{2}B,$$

$$\langle c|\mathscr{H}|c\rangle = 0,$$

$$\langle a|\mathscr{H}|b\rangle = \frac{\mu_B}{B}(B_1+iB_2)g'_{\zeta\zeta}H_\zeta,$$

$$\langle b|\mathscr{H}|c\rangle = \frac{\mu_B}{2B}\{[(B-B_1)(g'_{\xi\xi}H_\xi+g'_{\eta\xi}H_\eta)-B_2(g'_{\xi\eta}H_\xi+g'_{\eta\eta}H_\eta)]+$$

$$+i[B_2(g'_{\xi\xi}H_\xi+g'_{\eta\xi}H_\eta)-(B+B_1)(g'_{\xi\eta}H_\xi+g'_{\eta\eta}H_\eta)]\},$$

$$\langle c|\mathscr{H}|a\rangle = \frac{\mu_B}{2B}\{[(B+B_1)(g'_{\xi\xi}H_\xi+g'_{\eta\xi}H_\eta)+B_2(g'_{\xi\eta}H_\xi+g'_{\eta\eta}H_\eta)]-$$

$$-i[B_2(g'_{\xi\xi}H_\xi+g'_{\eta\xi}H_\eta)+(B-B_1)(g'_{\xi\eta}H_\xi+g'_{\eta\eta}H_\eta)]\}, \tag{16}$$

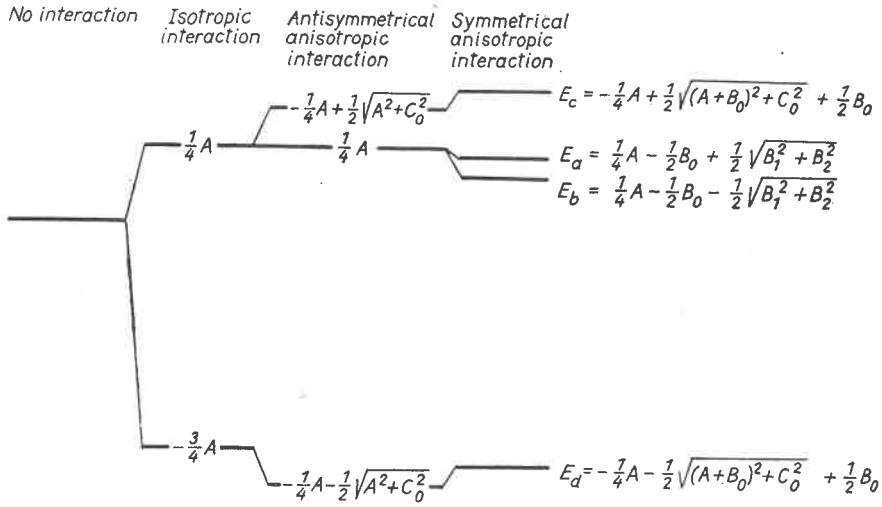

Fig. 2. Diagram of zero-field splitting for a system of two unequivalent ions with $S_1 = S_2 = 1/2$ in a monoclinic two-centre crystal field ($A > C_0 > B_0, B_1, B_2 > 0$)

where:

$$g'_{\zeta\zeta} = \tfrac{1}{2}(g_{1\zeta\zeta}+g_{2\zeta\zeta}),$$

$$g'_{\xi\xi} = \tfrac{1}{2}(g_{1\xi\xi}+g_{2\xi\xi})\cos\gamma-\tfrac{1}{2}(g_{1\xi\eta}-g_{2\xi\eta})\sin\gamma,$$

$$g'_{\eta\eta} = \tfrac{1}{2}(g_{1\eta\eta}+g_{2\eta\eta})\cos\gamma+\tfrac{1}{2}(g_{1\eta\xi}-g_{2\eta\xi})\sin\gamma,$$

$$g'_{\xi\eta} = \tfrac{1}{2}(g_{1\xi\eta}+g_{2\xi\eta})\cos\gamma+\tfrac{1}{2}(g_{1\xi\xi}-g_{2\xi\xi})\sin\gamma,$$

$$g'_{\eta\xi} = \tfrac{1}{2}(g_{1\eta\xi}+g_{2\eta\xi})\cos\gamma-\tfrac{1}{2}(g_{1\eta\eta}-g_{2\eta\eta})\sin\gamma. \qquad (17)$$

Above, we have neglected the additive constant $-\frac{1}{4}A+\frac{1}{2}C+\frac{1}{2}B_0$.

According to the preceding remarks, it is surely not possible to find a one-to-one unitary transformation of the space $[|a\rangle, |b\rangle, |c\rangle]$ onto the space $[|-\tilde{1}\rangle, |\tilde{0}\rangle, |\tilde{1}\rangle]$ of the spin Hamiltonian (1) preserving all rotational properties as in the previous case of equivalent ions. There exists, however, a unitary transformation preserving the transformational properties of the smaller monoclinic symmetry group, and we can always resort to the Hamiltonian (1) as a strict effective Hamiltonian for the description of the discussed triplet (for a definition of an effective Hamiltonian of this kind, see Appendix in Ref. [4]).

Indeed, on neglecting in a first approximation the influence of the crystal field and taking into account isotropic interaction only, the triplet transforms according to the irreducible representation $D^{(1)}$ of the orthogonal group, whereas the singlet transforms according to $D^{(0)}$. The crystal field decomposes $D^{(1)}$ into a direct sum $\Gamma_a \oplus \Gamma_b \oplus \Gamma_c$ of irreducible representations of the monoclinic symmetry group realised in the subspace $[|a\rangle, |b\rangle, |c\rangle]$ and makes $D^{(0)}$ go over into the irreducible representation Γ_d of this group. In our case of triplet-singlet mixing, the representations Γ_d and Γ_c coincide (the admixture of the state $|00\rangle$ in $|c\rangle$ corresponds to this); in the case of equivalent ions, Γ_d differs from the representations connected with the triplet. In both cases, however, the representation $\Gamma_a \oplus \Gamma_b \oplus \Gamma_c$ in the subspace $[|a\rangle, |b\rangle, |c\rangle]$ is equivalent to $D^{(1)}$ in $[|-\tilde{1}\rangle, |\tilde{0}\rangle, |\tilde{1}\rangle]$ which means that the mapping, we are searching for, exists.

We may henceforth attribute an effective spin $S = 1$ to the triplet subject to the distinction that the notion of effective spin does not coincide with that of Stevens' fictitious spin ([5], [6]), the eigenfunctions of which do not possess all the transformational properties of the symmetry group of the system. This conclusion, by the way, does not depend on the type of crystal field symmetry.

The discussed unitary transformation is not unique. One of its possible realizations is the mapping:

$$|a\rangle \leftrightarrow |\tilde{a}\rangle, |b\rangle \leftrightarrow |\tilde{b}\rangle, |c\rangle \leftrightarrow |\tilde{c}\rangle, \qquad (18)$$

where $|\tilde{a}\rangle$, $|\tilde{b}\rangle$ and $|\tilde{c}\rangle$ are eigenfunctions of the interactional part of Hamiltonian (1) (see Ref. [4]; $|\tilde{a}\rangle$, $|\tilde{b}\rangle$, $|\tilde{c}\rangle$ here correspond to $|a\rangle$, $|b\rangle$, $|c\rangle$ there). For the purpose of matrix elements conservation, we compare (16) with the matrix elements of the total Hamiltonian (1) within the basis $\{|\tilde{a}\rangle, |\tilde{b}\rangle, |\tilde{c}\rangle\}$ (see [4], formula (20)):

$$\langle\tilde{a}|\tilde{\mathscr{H}}|\tilde{a}\rangle = D+E_0, \langle\tilde{b}|\tilde{\mathscr{H}}|\tilde{b}\rangle = D-E_0, \langle c|\tilde{\mathscr{H}}|\tilde{c}\rangle = 0,$$

$$\langle\tilde{a}|\tilde{\mathscr{H}}|\tilde{b}\rangle = \frac{\mu_B}{E_0}(E+iF)g_{\zeta\zeta}H_\zeta,$$

$$\langle\tilde{b}|\tilde{\mathscr{H}}|\tilde{c}\rangle = \frac{\mu_B}{2E_0}\{[(E_0-E)(g_{\xi\xi}H_\xi+g_{\eta\xi}H_\eta)-F(g_{\xi\eta}H_\xi+g_{\eta\eta}H_\eta)]+$$

$$+i[F(g_{\xi\xi}H_\xi+g_{\eta\xi}H_\eta)-(E_0+E)(g_{\xi\eta}H_\xi+g_{\eta\eta}H_\eta)]\};$$

$$\langle\tilde{c}|\tilde{\mathscr{H}}|\tilde{c}\rangle = \frac{\mu_B}{2E_0}\{[(E_0+E)(g_{\xi\xi}H_\xi+g_{\eta\xi}H_\eta)+F(g_{\xi\eta}H_\xi+g_{\eta\eta}H_\eta)]-$$

$$-i[F(g_{\xi\xi}H_\xi+g_{\eta\xi}H_\eta)+(E_0-E)(g_{\xi\eta}H_\xi+g_{\eta\eta}H_\eta)]\}; \tag{19}$$

$$E_0^2 = E^2+F^2.$$

We obtain hence the following relations:

$$D = \tfrac{1}{2}(A-C)-B_0, E = \tfrac{1}{2}B_1, F = \tfrac{1}{2}B_2,$$

$$g_{\xi\xi} = g'_{\xi\xi}, \quad g_{\eta\eta} = g'_{\eta\eta}, \quad g_{\zeta\zeta} = g'_{\zeta\zeta},$$

$$g_{\xi\eta} = g'_{\xi\eta}, \quad g_{\eta\xi} = g'_{\eta\xi}. \tag{20}$$

Let us observe that the effective g-tensor is not symmetrical ($g_{\xi\eta} \neq g_{\eta\xi}$ in general). This unsymmetricity, however, is small because of proportionality to $\sin\gamma$ and to differences in g-values, but nevertheless makes it impossible to go over strictly to the system of principal axes of the g-tensor. Our two-ion model thus gives an explanation of the g-tensor asymmetry, admissible by group-theoretical considerations of Baltes *et al.* [10] (the one-ion model of the Hamiltonian (1) due to Abragam and Pryce [8] based on spin-orbit and spin-spin coupling gives no such possibility). Yet another effect consists in a decrease of the corresponding effective g-values by about one p. c. with respect to the one-ion values. Let us note that in the formulas for EPR quantum transitions the exchange integral, although in the second term of square root expansion, has to occur according to the expression for D in (20).

There exist two monoclinic point groups without centre of inversion (the symmetry group of a free pair is $C_{\infty v}$):

a) C_2 — the z-axis connecting the two ions coincides with the twofold symmetry ζ-axis (see Fig. 1 a). We have the same formulas for A, B_0, B_1, B_2 as given by (9) and moreover

$$C_0 = D_z. \tag{21}$$

b) C_s — the z-axis connecting the two ions lies in the mirror plane and therefore is perpendicular to the ζ-axis (see Fig. 1b). We have the same formulas for A, B_0, B_1, B_2 as given by (11) and moreover

$$C_0 = D_x. \tag{22}$$

The same remarks hold with respect to the possibility of large constants E and F.

5. *Note*

As far as we know, monoclinic effects in two-ion systems have not as yet been reported. We attempted to apply the present model to the theoretical explanation of EPR spectra of copper complexes in TGFB: Cu^{2+} (Stankowski [14]), where pairs of Cu^{2+} ions with monoclinic symmetry were to be expected. From the impossibility of describing

those spectra in terms of monoclinic spin Hamiltonian with effective spin $S = 1$ (Kurzyński [4]), it follows in accordance with the results of the present paper that the observed lines do not belong to copper ion pairs, but rather to more highly composite complexes. Other considerations, to be published later (Stankowski, Maćkowiak, Kurzyński [15, 16]), suggest that the lines are due to four-ion complexes.

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