Effective g Tensor of a Pair of Dissimilar Ions in the Strong Isotropic Exchange Limit

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A study of the spin-pair Hamiltonian with regard to the effective g-factor in the strong isotropic exchange limit is presented. The case of two different spins with anisotropic $\mathbf{g}^{(i)}$ and $\mathbf{D}^{(i)}$ tensors is considered. Effective $\mathbf{g}^{\mathrm{s}}$ and $\mathbf{D}^{\mathrm{s}}$ tensors for the various total spin S values are deduced in terms of the corresponding single-ion parameters. The characteristics of the resultant $\mathbf{g}^{\mathrm{s}}$-tensor, in the case of an ion-pair with C_σ symmetry, are treated in detail. The principal values are linear expressions of the single-ion principal values and the principal directions relative to different S values result to be correlated in a characteristic manner. The limits of the present strong exchange treatment are also discussed.

In the last years, an increasing number of authors have studied the E.S.R. spectra of ion pairs[1]. Such studies give in general information about the magnitude and the nature of the magnetic interaction between the ions. Often it is possible to relate the pair data to appropriate single-ion models, and so to obtain informations on the local symmetries and the covalent character of the bonds in the single complex ion[2].

As regards the g factor, Pryce first discussed the pair problem in his well known study on the pentahydrated copper sulphate complex[3]. It results that, in the strong isotropic exchange limit, the spectrum is characterized by an effective $\mathbf{g}$ tensor, mean of the single-ion tensors $\mathbf{g}^{(i)}$, that is

$$g_{\alpha\beta} = \tfrac{1}{2}(g^{(1)}_{\alpha\beta} + g^{(2)}_{\alpha\beta}), \quad \alpha, \beta = x, y, z\,.$$

This expression is not general; it is valid only for equal spins. The case of two different spins has been treated under the simplified assumptions of isotropic $\mathbf{g}^{(i)}$ or with parallel principal axes only[4].

It is interesting, in principle, to study the case of non coincident axes, because significant angular correlations between single-ion and pair tensors could exist. Furthermore, the literature is rather contradictory about the dependence of the effective g on the single-ion g factors. In fact, quadratic forms are usually assumed, though a linear dependence appears more appropriate in the strong exchange limit[5–7].

The clarification of this subject could allow, in a larger number of cases, to deduce single-ion parameters from experimental data on crystals with strongly coupled ions.

In the present paper a study of the spin-pair hamiltonian with regard to the resultant $\mathbf{g}$ tensor, in the strong isotropic exchange limit, is presented. For each value of the total spin, an effective spin hamiltonian, fitting the E.S.R. spectrum, has been deduced. The spectroscopic splitting and fine-structure tensors of the resultant spin have been related to the single-ion parameters of two dissimilar ions. As an example, the tensorial character of g for ion-pairs with C_σ symmetry (the two ions in the plane) has been studied and some implications have been deduced. Finally, the limits in which the present treatment in terms of total spin is applicable, are discussed.

1. Spin-pair Hamiltonian

At first we consider the spin hamiltonian for a pair of different ions, with zero nuclear spins, i. e. in the absence of hyperfine interaction. Limiting the attention to ions in orbital singlet states with spins S_1 and S_2, the pair energy can be written[8, 9]

$$\begin{aligned}\mathbf{H} = J\,\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{Q}\cdot(\mathbf{S}_1\times\mathbf{S}_2) \\ + \beta\,\mathbf{H}\cdot\mathbf{g}^{(1)}\cdot\mathbf{S}_1 + \beta\,\mathbf{H}\cdot\mathbf{g}^{(2)}\cdot\mathbf{S}_2 + \mathbf{S}_1\cdot\mathbf{D}^{(1)}\cdot\mathbf{S}_1 \\ + \mathbf{S}_2\cdot\mathbf{D}^{(2)}\cdot\mathbf{S}_2 + \mathbf{S}_1\cdot\mathbf{\Delta}\cdot\mathbf{S}_2 \end{aligned} \qquad (1)$$

where $\mathbf{D}^{(1)}$, $\mathbf{D}^{(2)}$ and $\mathbf{\Delta}$ are symmetric and traceless tensors. The first term represents the isotropic exchange and is assumed to be the preponderant energy. The second term is the so called skew-symmetric exchange and can be absent under particular conditions of symmetry. The following two terms

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represent the interaction with the external magnetic field. The last three represent the fine structures of the two ions and the anisotropic exchange[10].

The large isotropic exchange couples the spins to give a number of manifolds each characterized by a total spin $S = |S_1 - S_2|,\ |S_1 - S_2| + 1, \ldots, S_1 + S_2$. According to the Landé rule, their energies are

$$E_s = \tfrac{1}{2} J [S(S+1) - S_1(S_1+1) - S_2(S_2+1)]\,. \quad (2)$$

Neclecting terms of order Q^2/J, $D^{(i)2}/J, \ldots$ etc., that is all the matrix elements between different manifolds, a spin hamiltonian for each value of the total spin can be deduced

$$\mathbf{H}^s = \beta\, \mathbf{H} \cdot \mathbf{g}^s \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D}^s \cdot \mathbf{S}\,, \quad (3)$$

where

$$g^s_{\alpha\beta} = A^s(1)\, g^{(1)}_{\alpha\beta} + A^s(2)\, g^{(2)}_{\alpha\beta}\,, \quad (4)$$

$$D^s_{\alpha\beta} = B^s(1,1)\, D^{(1)}_{\alpha\beta} + B^s(2,2)\, D^{(2)}_{\alpha\beta} + B^s(1,2)\, \Delta_{\alpha\beta}\,, \quad (5)$$

with

$$A^s(1) + A^s(2) = 1\,,$$
$$B^s(1,1) + B^s(2,2) + 2\, B^s(1,2) = 1\,,$$

and explicitly

$$A^s(1) = [S(S+1) + S_1(S_1+1) - S_2(S_2+1)]/2\,S(S+1)\,, \quad (6\,\mathrm{a})$$

$$\begin{aligned} B^s(1,1) = \{&3[S(S+1) + S_1(S_1+1) - S_2(S_2+1)]^2 \\ &- 3[S(S+1) + S_1(S_1+1) - S_2(S_2+1)] \\ &- 4\,S(S+1) S_1(S_1+1)\}/ \\ &2\,S(S+1)(2\,S-1)(2\,S+3)\,, \end{aligned} \quad (6\,\mathrm{b})$$

$$\begin{aligned} B^s(1,2) = \{&S^2(S+1)^2 - 3[S_1(S_1+1) \\ &- S_2(S_2+1)]^2 + 2\,S(S+1)[S_1(S_1+1) \\ &+ S_2(S_2+1)]\}/ \\ &2\,S(S+1)(2\,S-1)(2\,S+3)\,. \end{aligned} \quad (6\,\mathrm{c})$$

$A^s(2)$ and $B^s(2,2)$ are obtained in permuting S_1 and S_2 in $A^s(1)$ and $B^s(1,1)$ respectively.

Obviously, Eq. (3) reduces to the only Zeeman part for $S = 1/2$. In the case of $S_1 = S_2$, one obtains the well known Pryce[3] and Judd-Owen[13] expressions.

In the above mentioned limit of strong isotropic exchange the skew-symmetric exchange becomes irrelevant[14, 15], as can be seen from Equations (2) to (5).

2. The g^s Tensor in a C_σ Pair

To study in more detail the tensorial character of the gyromagnetic factor, we refer to the simple case of a pair with C_σ symmetry (the two ions in the plane).

We assume that the $\mathbf{g}^{(1)}$ and $\mathbf{g}^{(2)}$ tensors are symmetric[16] and that the corresponding in-plane principal directions form an angle η. This angle can, in general, be estimated from the structural data of the pair. If $\mathbf{R}_1$ and $\mathbf{R}_2$ represent the rotations (around the z symmetry axis) which connect the pair reference frame x, y, z to the principal directions of the two ions, in Eq. (4), for the i-th ion, we can write

$$\mathbf{g}^{(i)} = \mathbf{R}_i \begin{pmatrix} g_1{}^{(i)} & 0 & 0 \\ 0 & g_2{}^{(i)} & 0 \\ 0 & 0 & g_3{}^{(i)} \end{pmatrix} \mathbf{R}_i{}^{-1}\,, \quad (7)$$

where the $g_n{}^{(i)}$ are the principal values.

It can easily be seen that the principal in-plane directions of the resultant $\mathbf{g}^s$ tensor form angles ϑ_s and φ_s with the corresponding directions of $\mathbf{g}^{(1)}$ and $\mathbf{g}^{(2)}$ respectively, such that

$$\frac{\sin 2\,\vartheta_s}{\sin 2\,\varphi_s} = \frac{A^s(2)}{A^s(1)}\, \frac{g_1{}^{(2)} - g_2{}^{(2)}}{g_1{}^{(1)} - g_2{}^{(1)}}\,, \quad (8)$$

where $\varphi_s = \eta - \vartheta_s$. The principal values result to be

$$\begin{aligned} g_1{}^s = {}& A^s(1)\,(g_1{}^{(1)} \cos^2 \vartheta_s + g_2{}^{(1)} \sin^2 \vartheta_s) \\ &+ A^s(2)\,(g_1{}^{(2)} \cos^2 \varphi_s + g_2{}^{(2)} \sin^2 \varphi_s)\,, \end{aligned} \quad (9\,\mathrm{a})$$

$$\begin{aligned} g_2{}^s = {}& A^s(1)\,(g_1{}^{(1)} \sin^2 \vartheta_s + g_2{}^{(1)} \cos^2 \vartheta_s) \\ &+ A^s(2)\,(g_1{}^{(2)} \sin^2 \varphi_s + g_2{}^{(2)} \cos^2 \varphi_s)\,, \end{aligned} \quad (9\,\mathrm{b})$$

$$g_3{}^s = g_{zz}{}^s = A^s(1)\, g_3{}^{(1)} + A^s(2)\, g_3{}^{(2)}\,. \quad (9\,\mathrm{c})$$

As evident from Eq. (8), there is a $g_n{}^{(i)}$-independent correlation among the principal directions relative to different values of S. Namely

$$\frac{\sin 2\,\vartheta_{s'}}{\sin 2\,\varphi_{s'}} = \frac{A^{s'}(2)\, A^s(1)}{A^{s'}(1)\, A^s(2)}\, \frac{\sin 2\,\vartheta_s}{\sin 2\,\varphi_s}\,. \quad (10)$$

In the case of $S_1 = S_2$, the directions of the resultant $\mathbf{g}^s$ tensor (the same for each S value) depend only on the in-plane $\mathbf{g}^{(i)}$ anisotropies. For different spins, a considerable disalignment among the various $\mathbf{g}^s$ tensors could result. For example, in the hypothetical case of a pair with $S_1 = 1$, $S_2 = 1/2$ and $\eta = \pi/4$, from Eqs. (8) and (10) one obtains

$$\begin{array}{ll} \vartheta_{3/2} \sim -2\,\vartheta_{1/2} \sim 0 & \text{for } k \sim 0\,, \\ \vartheta_{3/2} \sim 13^\circ,\ \vartheta_{1/2} \sim -7^\circ & \text{for } k \sim 1\,, \\ \vartheta_{3/2} \sim 39^\circ,\ \vartheta_{1/2} \sim -34^\circ & \text{for } k \sim 10\,, \\ \vartheta_{3/2} \sim -\vartheta_{1/2} \sim \pi/4 & \text{for } k \sim \infty\,, \end{array}$$

where $k = (g_1{}^{(2)} - g_2{}^{(2)})/(g_1{}^{(1)} - g_2{}^{(1)})$. Obviously, negative ϑ values correspond to directions outside the η angle.

3. Discussion and Conclusions

In the strong isotropic exchange limit, the E.S.R. spectrum of two coupled dissimilar ions tends to be characterized by effective $\mathbf{g}^{\mathrm{s}}$ and $\mathbf{D}^{\mathrm{s}}$ tensors, related to $\mathbf{g}^{(i)}$ and $\mathbf{D}^{(i)}$ single-ion tensors and to $\mathbf{\Delta}$ interaction according to Equations (4) and (5).

In the case of isotropic $g^{(1)}$ and $g^{(2)}$, the weighted mean results:

$$g^{\mathrm{s}} = A^{\mathrm{s}}(1)\, g^{(1)} + A^{\mathrm{s}}(2)\, g^{(2)} \,. \qquad (11)$$

Only if $S_1 = S_2$ (or, as a trivial case, if $g^{(1)} = g^{(2)}$) one has the S-independent formula of Pryce[3].

The effective g^{s} values can be remarkably different from the arithmetical mean of $g^{(1)}$ and $g^{(2)}$. An example is reported by Baker et al.[18]. In tungsto heteropoly complexes, $\mathrm{Co}^{3+}\,(S_1 = 2,\, g^{(1)} \sim 2)$ and $\mathrm{Co}^{2+}\,(S_2 = 3/2,\, g^{(2)} \sim 2.3)$ couple to give a ground magnetic doublet with $g^{1/2} = 1.7$ according to Equation (11). In the low temperature limit, for antiferromagnetic coupling ($S = S_1 - S_2$, with $S_1 > S_2$),

$$g = [\,(S_1 + 1)\, g^{(1)} - S_2\, g^{(2)}]/(S_1 - S_2 + 1)\,,$$

is obtained, and for ferromagnetic coupling ($S = S_1 + S_2$)

$$g = (S_1\, g^{(1)} + S_2\, g^{(2)})/(S_1 + S_2)\,.$$

This last result coincides with the semiclassical expressions of Wangsness[19], obtained from the equations of motion of the magnetization.

As regards the tensorial character of $\mathbf{g}^{\mathrm{s}}$, one can see from Eqs. (9) that, when the spin difference increases, the principal values approach those of the $\mathbf{g}^{(i)}$ relative to the ion with the greater spin. The directions of the principal axes will be closer to those of the ion with the greater spin or with the more anisotropic $\mathbf{g}^{(i)}$, according to Equation (8). Moreover, Eq. (10) could allow significant experimental verification, since it is independent on possible uncertainties on the g values of the single-ions within the pair.

It is interesting to observe, from Eqs. (9), that the principal values of $\mathbf{g}^{\mathrm{s}}$ are linear expressions of the single-ion principal values $g_n{}^{(i)}$. As an example, in the case of similar ions with axial symmetry ($S_1 = S_2$, $g_1{}^{(1)} = g_1{}^{(2)} = g_{\|}$, $g_2{}^{(1)} = g_2{}^{(2)} = g_{\perp}$) they are: $g_1{}^{\mathrm{s}} = g_{\|} \cos^2 \vartheta + g_{\perp} \sin^2 \vartheta$, etc., where $2\,\vartheta$ is the angle between the ions. Hence, there is a significant difference from the single-ion g values in the bisecting directions, i. e.

$$g^{(1)}\,(\vartheta) = g^{(2)}\,(\vartheta) = [g_{\|}{}^2 \cos^2 \vartheta + g_{\perp}{}^2 \sin^2 \vartheta]^{1/2},$$

etc. The last expressions are commonly used[6,7]. However, when the single-ion g anisotropy is small, there is no appreciable numerical difference.

The actual possibility to measure $\mathbf{g}^{\mathrm{s}}$ depends, obviously, on the value of the resultant fine-structure. In fact, when $D^{\mathrm{s}} > h\,\nu$, not all of the spectral components can be observed. Furthermore, for large values of the fine-structure constant, the spectrum can be interpreted in several cases only on the basis of effective spins and effective g values different from the true ones. Such difficulties disappear when the fine structure splittings are comparable or small with respect to the Zeeman energy. In this latter case, we can write

$$\mathbf{H}^{\mathrm{s}} = g^{\mathrm{s}}\, \beta\, H\, S_{z'} + \frac{D^{\mathrm{s}}_{z'z'}}{2}\,[\,3\, S^2_{z'} - S(S+1)\,] + \dots \text{ off-diagonal terms,} \qquad (12)$$

where z' is the Zeeman quantization direction and

$$g^{\mathrm{s}} = \frac{|\,\mathbf{g}^{\mathrm{s}} \cdot \mathbf{H}\,|}{H}\,, \qquad (13)$$

$$D^{\mathrm{s}}_{z'z'} = \frac{\mathbf{H} \cdot \mathbf{g}^{\mathrm{s}} \cdot \mathbf{D}^{\mathrm{s}} \cdot \mathbf{g}^{\mathrm{s}} \cdot \mathbf{H}}{(\mathbf{g}^{\mathrm{s}} \cdot \mathbf{H})^2}\,. \qquad (14)$$

As evident from Eq. (12), if the perturbative hypothesis is valid, g^{s} can be directly deduced from the centre of the spectrum relative to the total spin S value. To neglect the off-diagonal terms means to ignore corrections to the g^{s} value of the order $(D^{\mathrm{s}}/h\,\nu)^2$.

Let us discuss now the consistency of the two assumptions made, that is: isotropic exchange large enough to couple the spins and fine-structure splittings small enough to allow the interpretation of the E.S.R. spectra by means of the total-spin hamiltonians of Equation (3). The condition for the spin coupling, and therefore for the averaging effect on the single-ion $\mathbf{g}^{(i)}$ tensors, is

$$|J| \gg \beta\, |\,(\mathbf{g}^{(1)} - \mathbf{g}^{(2)}) \cdot \mathbf{H}\,| \sim (\Delta g/g)\, h\,\nu\,. \qquad (15)$$

However, when the exchange is very strong, large fine-structure constants may result. In fact, the contributions to the pair fine-structure constants are due to:

1) The local crystal field $D^{(1)}$ and $D^{(2)}$ splittings which, on the other side, could be zero (d^1, d^9 configurations), or very small (d^3, d^5 configurations) or also do not at all contribute [$B^{\mathrm{s}}(i,i) = 0$ for particular values of S_1, S_2 and S, see for example Reference[20]].

2) The dipole-dipole interaction, of order $g^{(1)} g^{(2)} \beta^2/r^3$, which we can assume perturbative compared with the Zeeman interaction, at least as far as the inter-ionic distance is not too small.
3) The pseudodipolar interaction, due to the concomitant presence of spin-orbit coupling and isotropic exchange [21]. Contrary to the preceding ones, this interaction tends to diverge with J.

Considering only atoms in orbital singlet states and with spin-orbit coupling small compared with crystal-field splitting, the condition for the fine structure becomes

$$h\nu \gtrsim D^{(1)}, D^{(2)}, \Delta_{\text{dip-dip}}, \Delta_{\text{ps. dip}} \sim (\Delta g/g)^2 \, |J| \, . \tag{16}$$

Therefore, from Eqs. (15) and (16), the best range for the exchange value is

$$(\Delta g/g) \, h\nu \ll |J| \lesssim (g/\Delta g)^2 \, h\nu \, . \tag{17}$$

Evidently, the smaller the difference between the single-ion Zeeman energies, the larger is this range.

In the particular case of Cu^{2+} complexes, where typically $(\Delta g/g) < 0.1$, it must be, for the two most used wavelenghts

$$\begin{aligned} 0.03\ \text{cm}^{-1} &\ll |J| \lesssim 30\ \text{cm}^{-1} & \lambda &\sim 30\ \text{mm}\,, \\ 0.1\ \text{cm}^{-1} &\ll |J| \lesssim 100\ \text{cm}^{-1} & \lambda &\sim 10\ \text{mm}\,. \end{aligned} \tag{18}$$

Thus it can be understood why, in the well known case of the pentahydrated copper sulphate [22], where the value of exchange is $J \sim 0.15\ \text{cm}^{-1}$, the E.S.R. spectrum consists of only one line at ~ 30 mm, while two lines are resolved at ~ 8.5 mm. On the contrary, in other typical copper compounds, where J is of a few cm^{-1}, like those examined by Abe and Ono [6], no resolution is observed in the range $\lambda \sim 32\ \text{mm} - 5\ \text{mm}$.

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