Effective Hamiltonians for EPR Spectroscopy of Exchange-Coupled Pairs*

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The paper refers to the second-order spin-hamiltonian formalism, recently proposed by the author, describing the EPR properties of an exchange-coupled pair of orbitally not degenerate ions in the limit of strong isotropic exchange (higher-order effects such as biquadratic exchange or exchange striction are considered neglectable). Tables of numerical values for the relevant coefficients involved are given. This allows to write immediately the effective spin operators spanning each total spin multiplet which arises from the coupling between the ions. Explicit formulas for the recurrently encountered cases of pairs where $S_1 = S_2 = 3/2$ or $S_1 = 5/2$ and $S_2 = 1/2$ or $S_1 = 1$ and $S_2 = 1/2$ are deduced. Some salient features of these, concerning the second-order contributions to the zero-field splitting, are discussed in the light of available experimental data. The conclusions drawn seems to encourage a more extensive use of the model.

Recently we have proposed a spin-hamiltonian formalism in order to describe a system of two paramagnetic ions in singlet orbital ground-states and strongly interacting by isotropic exchange [1] (a brief summary is given in the Appendix). It consists of effective spin-hamiltonian operators which span the single multiplets of the total spin arising from the coupling between the ions and therefore appears to be particularly useful in the analysis of the electron paramagnetic resonance (EPR) spectra of coupled system where, due to the energy values involved (strong exchange limit) and to the magnetic dipole selection rules, microwave transitions can only occur between levels belonging to the same total spin multiplet.

This formalism has sensibly larger applicability than previous well known similar models [2–4]. In fact, it assumes contemporaneously arbitrary spin values S_1 and S_2 for the two ions, a general tensorial form for all contributions to the pair energy, and second-order perturbative approximation of the zero-field terms with respect to $J \boldsymbol{S}_1 \cdot \boldsymbol{S}_2$. Owing to the generality, however, the resulting expression is somewhat cumbersome [5]. The second-order corrections, in particular, depend on a lot of coefficients of which general implicit expressions were given. These, moreover, contain terms which in special cases have to be ignored. All that may appear inconvenient for the practical use of experimentalists.

In view of the interest shown, in the present paper numerical values for the coefficients are given in a number of cases of practical interest. Explicit second-order formulas for some recurrent types of exchange-coupled pairs are also written and, when possible, briefly discussed in the light of the available experimental data. The cited coefficients are defined as follows:

$$\alpha = [S(S+1) + S_1(S_1+1) - S_2(S_2+1)]/2S(S+1)\,, \tag{1a}$$

$$\beta = [S(S+1) - S_1(S_1+1) + S_2(S_2+1)]/2S(S+1)\,, \tag{1b}$$

$$\delta^2 = (S-1, S)^2 + (S, S+1)^2\,, \tag{1c}$$

$$\gamma = (S+1)(S, S+1)^2 - S(S-1, S)^2\,, \tag{1d}$$

$$\varepsilon = [S_1(S_1+1) - S_2(S_2+1)] \cdot [(S, S+1)^2/S - (S-1, S)^2/(S+1)]\,, \tag{1e}$$

$$\zeta = (S+2)(S, S+1)^2 - (S-1)(S-1, S)^2\,, \tag{1f}$$

$$\begin{aligned}\eta = {} & [S_1(S_1+1) - S_2(S_2+1)]^2 \\ & \cdot [(S-2)(S-1, S)^2/(S-1)^2(S+1)^2 \\ & - (S+3)(S, S+1)^2/S^2(S+2)^2] \\ & + (2S+5)(S, S+1)^2(S+1, S+2)^2 \\ & - (2S-3)(S-2, S-1)^2(S-1, S)^2\,,\end{aligned} \tag{1g}$$

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$$\lambda = (S-2)(S-1,S)^2 - (S+3)(S,S+1)^2\,, \tag{1h}$$

$$\begin{aligned}\mu = {} & [S_1(S_1+1) - S_2(S_2+1)] \\ & \cdot [(S-2)(S-1,S)^2/(S-1)(S+1) \\ & - (S+3)(S,S+1)^2/S(S+2)]\,, \end{aligned} \tag{1i}$$

$$\begin{aligned}\nu = {} & [S_1(S_1+1) - S_2(S_2+1)]^2 \\ & \cdot [(S,S+1)^2/S^2(S+1)(S+2)^2 \\ & - (S,S-1)^2/(S-1)^2 S(S+1)^2] \\ & + (S-2,S-1)^2(S-1,S)^2/(2S-1) \\ & - (S,S+1)^2/(S+1,S+2)^2/(2S+3)\,, \end{aligned} \tag{1l}$$

$$\xi = (S,S+1)^2/(S+1) - (S-1,S)^2/S\,, \tag{1m}$$

$$\begin{aligned}\varrho = {} & [S_1(S_1+1) - S_2(S_2+1)] \\ & \cdot [(S,S+1)^2/S(S+1)(S+2) - (S-1,S)^2/ \\ & \cdot (S-1)S(S+1)]\,, \end{aligned} \tag{1n}$$

where

$$\begin{aligned}(S-1,S)^2 &= (S,S-1)^2 \\ &= \frac{[S^2-(S_1-S_2)^2][(S_1+S_2+1)^2-S^2]}{4S^2(2S-1)(2S+1)}. \end{aligned} \tag{2}$$

S is the total spin quantum number characteristic of each single multiplet and covers the values $|S_1-S_2|, \ldots, S_1+S_2$.

All terms which, depending on the particular value of S, become undefined (as fractional terms with zero denominator and factors (S', S'') where either S' or S'' exceeds the allowed range of total spin values) have to be considered null.

Numerical values of the coefficients are reported in Tables I and II for a number of cases of practical interest. They are given in form of rational numbers as usual in earlier tables about the same topic [4, 6]. Values in brackets correspond to contributions which become null in the limit cases $S = 1/2$ and $3/2$.

One notes that there are cases in which some coefficients become zero, see for example $(\alpha^2-\delta^2)$ and $(\beta^2-\delta^2)$ in correspondence of $S_1 = S_2 = 3/2$, $S = 2$. This fact has not a particular meaning in itself, but it may represent a fortunate circumstance. Thus, for a coupled pair where $S_1 = S_2 = 3/2$ we can estimate first-order values for the anisotropic interaction (dipolar or pseudopolar in origin) directly from the EPR spectra relative to only the $S = 2$ multiplet [7]. To this fact we can also ascribe that the observed spectral resolution normally is better for $S = 2$ than for $S = 3$ [8, 9].

In the past, second-order formulas and coefficients have been given for the special case of two identical ions interacting by purely isotropic exchange [4] ($S_1 = S_2$, $\boldsymbol{D}_1 = \boldsymbol{D}_2$, $\boldsymbol{Q} = 0$, $\boldsymbol{\Delta} = 0$, in our notation). In that case use was made of a zero-field spin-hamiltonian form in terms of the so-called equivalent operators O_2^0, O_2^2, O_4^0, O_4^2, O_4^4. When transformation to this form is made, from Table I and II coincident expressions are obtained.

As an application of the theory we deduce the second-order spin-hamiltonian operators for three cases of exchange-coupled pairs, one with $S_1 = S_2 = 3/2$, another with $S_1 = 5/2$ and $S_2 = 1/2$, and the last one with $S_1 = 1$ and $S_2 = 1/2$. Representative exponents of these families, for ions in distorted octahedral field, are for example the pairs $\mathrm{Cr}^{3+}-\mathrm{Cr}^{3+}$, $\mathrm{Mn}^{2+}-\mathrm{Cu}^{2+}$ and $\mathrm{Ni}^{2+}-\mathrm{Cu}^{2+}$, the magnetic properties of which have in the last years been considered with increasing interest [4, 7, 10, 11]. In the first case one has four total spin states corresponding to $S = 0, 1, 2, 3$. If we make the assumption of a centrosymmetric pair ($\boldsymbol{g}_1 = \boldsymbol{g}_2 = \boldsymbol{g}$, $\boldsymbol{D}_1 = \boldsymbol{D}_2 = \boldsymbol{D}$ and $\boldsymbol{Q} = 0$) with no hyperfine interaction, the traceless single-multiplet hamiltonians (apart from the trivial case $S = 0$) result as follows

$$\begin{aligned} S = 1\,, \quad \mathscr{H}_S = {} & \mu_B \boldsymbol{H}\cdot\boldsymbol{g}\cdot\boldsymbol{S} + \boldsymbol{S}\cdot\left(-\frac{12}{5}\boldsymbol{D} + \frac{17}{10}\boldsymbol{\Delta}\right)\cdot\boldsymbol{S} \\ & + \frac{1}{J}\left\{\frac{7}{100}\boldsymbol{S}\cdot(2\boldsymbol{D}-\boldsymbol{\Delta})^2\cdot\boldsymbol{S}\right. \\ & - \frac{1}{500}[\boldsymbol{S}\cdot(2\boldsymbol{D}-\boldsymbol{\Delta})\cdot\boldsymbol{S}]^2 \\ & \left. - \frac{23}{500}\operatorname{Tr}(2\boldsymbol{D}-\boldsymbol{\Delta})^2\right\}, \end{aligned} \tag{3}$$

$$\begin{aligned} S = 2\,, \quad \mathscr{H}_S = {} & \mu_B \boldsymbol{H}\cdot\boldsymbol{g}\cdot\boldsymbol{S} + \boldsymbol{S}\cdot\left(\frac{1}{2}\boldsymbol{\Delta}\right)\cdot\boldsymbol{S} \\ & + \frac{1}{J}\left\{-\frac{1}{4}\boldsymbol{S}\cdot(2\boldsymbol{D}-\boldsymbol{\Delta})^2\cdot\boldsymbol{S}\right. \\ & + \frac{1}{12}[\boldsymbol{S}\cdot(2\boldsymbol{D}-\boldsymbol{\Delta})\cdot\boldsymbol{S}]^2 \\ & \left. + \frac{3}{20}\operatorname{Tr}(2\boldsymbol{D}-\boldsymbol{\Delta})^2\right\}, \end{aligned} \tag{4}$$

Table 1. Coefficients for the Zeeman, hyperfine and zero-field splitting contributions in the first-order perturbative approximation.

S_1	S_2	S	α	β	$\alpha^2-\delta^2$	$\beta^2-\delta^2$	$\alpha\beta+\delta^2$
1/2	1/2	0	–	–	–	–	–
		1	1/2	1/2	0	0	1/2
1		1/2	4/3	−1/3	(5/3)	(0)	(−1/3)
		3/2	2/3	1/3	1/3	0	1/3
3/2		1	5/4	−1/4	3/2	0	−1/4
		2	3/4	1/4	1/2	0	1/4
5/2		2	7/6	−1/6	4/3	0	−1/6
		3	5/6	1/6	2/3	0	1/6
7/2		3	9/8	−1/8	5/4	0	−1/8
		4	7/8	1/8	3/4	0	1/8
1	1	0	–	–	–	–	–
		1	1/2	1/2	−1/2	−1/2	1
		2	1/2	1/2	1/6	1/6	1/3
3/2		1/2	5/3	−2/3	(5/2)	(1/6)	(−5/6)
		3/2	11/15	4/15	1/5	−4/15	8/15
		5/2	3/5	2/5	3/10	1/10	3/10
5/2		3/2	7/5	−2/5	28/15	1/15	−7/15
		5/2	31/35	4/35	23/35	−4/35	8/35
		7/2	5/7	2/7	10/21	1/21	5/21
7/2		5/2	9/7	−2/7	45/28	1/28	−9/28
		7/2	59/63	4/63	17/21	−4/63	8/63
		9/2	7/9	2/9	7/12	1/36	7/36
3/2	3/2	0	–	–	–	–	–
		1	1/2	1/2	−6/5	−6/5	17/10
		2	1/2	1/2	0	0	1/2
		3	1/2	1/2	1/5	1/5	3/10
5/2		1	7/4	−3/4	14/5	3/10	−21/20
		2	11/12	1/12	10/21	−5/14	37/84
		3	17/24	7/24	11/30	−1/20	41/120
		4	5/8	3/8	5/14	3/28	15/56
7/2		2	3/2	−1/2	15/7	1/7	−9/14
		3	1	0	5/6	−1/6	1/6
		4	4/5	1/5	39/70	−3/70	17/70
		5	7/10	3/10	7/15	1/15	7/30
5/2	5/2	0	–	–	–	–	–
		1	1/2	1/2	−16/5	−16/5	37/10
		2	1/2	1/2	−10/21	−10/21	41/42
		3	1/2	1/2	−1/45	−1/45	47/90
		4	1/2	1/2	1/7	1/7	5/14
		5	1/2	1/2	2/9	2/9	5/18
7/2		1	9/4	−5/4	9/2	1	−9/4
		2	13/12	−1/12	5/14	−17/21	61/84
		3	19/24	5/24	1/4	−1/3	13/24
		4	27/40	13/40	423/1540	−29/385	1233/3080
		5	37/60	23/60	3/10	1/15	19/60
		6	7/12	5/12	7/22	5/33	35/132
7/2	7/2	0	–	–	–	–	–
		1	1/2	1/2	−6	−6	13/2
		2	1/2	1/2	−8/7	−8/7	23/14
		3	1/2	1/2	−1/3	−1/3	5/6
		4	1/2	1/2	−3/77	−3/77	83/154
		5	1/2	1/2	4/39	4/39	31/78
		6	1/2	1/2	2/11	2/11	7/22
		7	1/2	1/2	3/13	3/13	7/26

Table 2. Coefficients for the second-order corrections to the zero-field splitting term.

S_1	S_2	S	γ	ε	ζ	η	λ	μ	ν	ξ	ϱ
1/2	1/2	0	–	–	–	–	–	–	–	–	–
		1	−1/4	0	0	0	−1/4	0	0	−1/4	0
1		1/2	(1/6)	(5/18)	(5/18)	(−7/18)	(−7/18)	(−7/18)	(2/27)	(2/27)	(2/27)
		3/2	−1/6	−1/18	−1/18,	−1/18	−1/18	−1/18	(−2/27)	(−2/27)	(−2/27)
3/2		1	1/8	3/16	3/16	−1/4	−1/4	−1/4	1/32	1/32	1/32
		2	−1/8	−1/16	−1/16	0	0	0	−1/32	−1/32	−1/32
5/2		2	1/12	1/9	1/9	−5/36	−5/36	−5/36	1/108	1/108	1/108
		3	−1/12	−1/18	−1/18	1/36	1/36	1/36	−1/108	−1/108	−1/108
7/2		3	1/16	5/64	5/64	−3/32	−3/32	−3/32	1/256	1/256	1/256
		4	−1/16	−3/64	−3/64	1/32	1/32	1/32	−1/256	−1/256	−1/256
1	1	0	–	–	–	–	–	–	–	–	–
		1	−1/2	0	1/4	0	−1	0	0	−5/8	0
		2	−1/6	0	−1/12	−1/18	0	0	1/54	−1/24	0
3/2		1/2	(5/12)	(35/36)	(25/36)	(−65/36)	(−35/36)	(−49/36)	(155/432)	(5/27)	(7/27)
		3/2	−4/15	−28/225	16/225	−68/225	−92/225	47/450	(−1216/3375)	(−544/3375)	(−848/3375)
		5/2	−3/20	−3/100	−9/100	−3/100	3/100	1/100	3/2000	−3/125	−1/125
5/2		3/2	7/30	21/50	49/150	−301/450	−21/50	−27/50	(11639/47250)	(14/375)	(6/125)
		5/2	−4/35	−108/1225	16/1225	12/1225	−172/1225	−64/1225	−10434/42875	−1184/42875	−1808/42875
		7/2	−5/42	−5/98	−25/294	5/882	5/98	3/98	−55/18522	−10/1029	−2/343
7/2		5/2	9/56	99/392	81/392	−18/49	−99/392	−121/392	855/43904	9/686	11/686
		7/2	−4/63	−220/3969	16/3969	124/3969	−284/3969	−64/3969	−4288/250047	−2080/250047	−3152/250047
		9/2	−7/72	−35/648	−49/648	7/324	35/648	25/648	−217/93312	−7/1458	−5/1458
3/2	3/2	0	–	–	–	–	–	–	–	–	–
		1	−17/20	0	3/5	7/100	−41/20	0	−1/500	−23/20	0
		2	−1/4	0	0	−1/4	−1/4	0	1/12	−1/12	0
		3	−3/20	0	−1/10	−3/100	1/20	0	1/500	−1/60	0
5/2		1	21/40	21/16	63/80	−273/100	−21/20	−7/4	1437/4000	21/160	7/32
		2	−37/168	−185/1008	145/1008	−74/441	−32/63	−20/63	−104269/296352	−589/6048	−1195/6048
		3	−41/240	−41/576	−103/2880	−451/7200	−143/1440	−1/288	−6017/864000	−881/34560	−127/6912
		4	−15/112	−15/448	−45/448	−15/1568	15/224	5/224	−117/263424	−15/1792	−5/1792
7/2		2	9/28	9/14	3/7	−225/196	−15/28	−45/56	109/1372	1/28	3/56
		3	−1/12	−1/12	1/12	1/36	−1/4	−1/8	−23/324	−1/48	−1/24
		4	−51/420	−51/700	−27/700	17/4900	−31/700	19/1400	−1277/171500	−143/14000	−67/7000
		5	−7/60	−7/150	−7/75	7/900	7/100	7/200	−41/40500	−7/1500	−7/3000
5/2	5/2	0	–	–	–	–	–	–	–	–	–
		1	−37/20	0	8/5	18/25	−101/20	0	−18/875	−53/20	0
		2	−41/84	0	5/21	−2501/1764	−27/28	0	19127/37044	−17/84	0
		3	−47/180	0	1/90	−2303/8100	−17/60	0	7409/364500	−2/45	0
		4	−5/28	0	−1/14	−15/196	−1/28	0	3/1372	−1/70	0
		5	−5/36	0	−1/9	−5/324	1/12	0	5/20412	−1/180	0
7/2		1	9/8	63/16	27/16	−45/4	−9/4	−21/4	1683/1120	9/32	21/32
		2	−61/168	−61/144	457/1008	−305/441	−80/63	−10/9	−435901/296352	−1189/6048	−503/864
		3	−13/48	−91/576	61/576	−91/288	−139/288	−35/288	−1049/34560	−373/6912	−413/6912
		4	−1233/6160	−1233/17600	−2367/123200	−570879/4743200	−9963/61600	−37/8800	−19822113/14609056000	−46953/2464000	−3847/352000
		5	−19/120	−133/3600	−281/3600	−19/450	−1/450	7/450	−37/756000	−859/108000	−287/108000
		6	−35/264	−35/1584	−175/1584	−35/4356	35/396	7/396	−35/1149984	−35/9504	−7/9504
7/2	7/2	0	–	–	–	–	–	–	–	–	–
		1	−13/4	0	3	11/4	−37/4	0	−11/140	−19/4	0
		2	−23/28	0	4/7	−897/196	−55/28	0	7159/4116	−31/84	0
		3	−5/12	0	1/6	−35/36	−3/4	0	1363/17820	−1/12	0
		4	−83/308	0	3/154	−7387/23716	−95/308	0	18721/1826132	−43/1540	0
		5	−31/156	0	−2/39	−713/6084	−5/52	0	10025/4982796	−3/260	0
		6	−7/44	0	−1/11	−21/484	1/44	0	7/15972	−5/924	0
		7	−7/52	0	−3/26	−7/676	5/52	0	7/96668	−1/364	0

$$S=3\,,\quad \mathscr{H}_S=\mu_B\boldsymbol{H}\cdot\boldsymbol{g}\cdot\boldsymbol{S}+\boldsymbol{S}\cdot\left(\frac{2}{5}\boldsymbol{D}+\frac{3}{10}\boldsymbol{\Delta}\right)\cdot\boldsymbol{S}+\frac{1}{J}\left\{-\frac{3}{100}\boldsymbol{S}\cdot(2\boldsymbol{D}-\boldsymbol{\Delta})^2\cdot\boldsymbol{S}+\frac{1}{500}[\boldsymbol{S}\cdot(2\boldsymbol{D}-\boldsymbol{\Delta})\cdot\boldsymbol{S}]^2+\frac{21}{250}\,\mathrm{Tr}\,(2\boldsymbol{D}-\boldsymbol{\Delta})^2\right\}. \tag{5}$$

The application to an actual case requires the diagonalization of the three sub-matrices of dimensions 3×3, 5×5, and 7×7 which correspond to (3)–(5). For simplicity we avoid this process by discussing an already known case. An example has been reported by McPherson et al. [7] who consider pairs $Cr^{3+}-Cr^{3+}$ obtained by doping with trivalent chromium divalent matrices such as $CsMgCl_3$. They fit the angular behaviours of the resonance magnetic fields by phenomenological spin-hamiltonians of the proper complexity, i.e. they assume zero-field spin operators of maximum power two, four, and six to describe spectra corresponding to $S=1$, 2, and 3, respectively. It results that the fourth power component plays an important role, particularly as concerns the $S=2$ spectra. This fact can be well rationalized in terms of second-order contributions from incomplete coupling between the ions. When a generalized axial symmetry along the chromium-chromium direction (z axis) is assumed, (3)–(5) give for the empirical constants (D_Σ, F_Σ) tabulated in [7] the explicit expressions

$$D_1=-\frac{18}{5}D_z+\frac{51}{20}\Delta_z+\frac{27}{500}\,\frac{(2D_z-\Delta_z)^2}{J}\,, \tag{6}$$

$$D_2=\frac{3}{4}\Delta_z-\frac{3}{28}\,\frac{(2D_z-\Delta_z)^2}{J}\,, \tag{7a}$$

$$F_2=\frac{27}{28}\,\frac{(2D_z-\Delta_z)^2}{J}\,, \tag{7b}$$

$$D_3=\frac{3}{5}D_z+\frac{9}{20}\Delta_z-\frac{27}{1750}\,\frac{(2D_z-\Delta_z)^2}{J}\,, \tag{8a}$$

$$F_3=\frac{81}{3500}\,\frac{(2D_z-\Delta_z)^2}{J}\,, \tag{8b}$$

where D_z and Δ_z are the axial values of the tensors $\boldsymbol{D}$ and $\boldsymbol{\Delta}$. As one can see, F_2 and F_3 result in the theoretical ratio 125/3. This (plus or minus a few units) is just the ratio which we systematically observe between the values reported in [7]. The close agreement confirms that (3)–(5) may be considered an adequate description for many purposes. This example suggests to check in general the consistency of values among the fourth power term coefficients as a test of validity for the second-order approach it-self.

Another interesting property of the second-order treatment is that it allows to obtain the coupling constant J directly from resonance magnetic field measurements. This can be immediately seen by inspection of (6)–(8). In a first-order approximation this is possible only on the basis of comparatively less accurate measurements of the variation of EPR spectral intensities with temperature. This fat, recently pointed out by Edgar [4], was one of the reasons to develop our generalized second-order model.

In the second example we have $S_1=5/2$, $S_2=1/2$. Here, as in general in all cases of heteronuclear pairs, one has no reason to neglect a priori skew-symmetric contributions to the exchange energy. Thus, the second-order spin-hamiltonian operators spanning the two possible pair states become

$$\begin{aligned}S=2\,,\quad \mathscr{H}_S=\;&\mu_B\boldsymbol{H}\cdot\left(\frac{7}{6}\boldsymbol{g}_1-\frac{1}{6}\boldsymbol{g}_2\right)\cdot\boldsymbol{S}\\&+\boldsymbol{I}_1\cdot\left(\frac{7}{6}\boldsymbol{A}_1\right)\cdot\boldsymbol{S}+\boldsymbol{I}_2\cdot\left(-\frac{1}{6}\boldsymbol{A}_2\right)\cdot\boldsymbol{S}\\&+\boldsymbol{S}\cdot\left(\frac{4}{3}\boldsymbol{D}_1-\frac{1}{6}\boldsymbol{\Delta}\right)\cdot\boldsymbol{S}\\&+\frac{1}{J}\left\{\frac{1}{12}(\boldsymbol{S}\cdot\boldsymbol{K}\cdot\boldsymbol{S}-2\,\mathrm{Tr}\,\boldsymbol{K})\right.\\&\quad+\frac{1}{9}[(\boldsymbol{Q}\times\boldsymbol{S})\cdot(2\boldsymbol{D}_1-\boldsymbol{\Delta})\cdot\boldsymbol{S}\\&\quad+\boldsymbol{S}\cdot(2\boldsymbol{D}_1-\boldsymbol{\Delta})\cdot(\boldsymbol{Q}\times\boldsymbol{S})]\\&\quad-\frac{5}{36}\boldsymbol{S}\cdot(2\boldsymbol{D}_1-\boldsymbol{\Delta})^2\cdot\boldsymbol{S}\\&\quad+\frac{1}{108}[\boldsymbol{S}\cdot(2\boldsymbol{D}_1-\boldsymbol{\Delta})\cdot\boldsymbol{S}]^2\\&\quad\left.+\frac{43}{180}\,\mathrm{Tr}\,(2\boldsymbol{D}_1-\boldsymbol{\Delta})^2\right\},\end{aligned} \tag{9}$$

$$S=3\,,\quad \mathscr{H}_S=\mu_B\boldsymbol{H}\cdot\left(\frac{5}{6}\boldsymbol{g}_1+\frac{1}{6}\boldsymbol{g}_2\right)\cdot\boldsymbol{S}+\boldsymbol{I}_1\cdot\left(\frac{5}{6}\boldsymbol{A}_1\right)\cdot\boldsymbol{S}+\boldsymbol{I}_2\cdot\left(\frac{1}{6}\boldsymbol{A}_2\right)\cdot\boldsymbol{S}+\boldsymbol{S}\cdot\left(\frac{2}{3}\boldsymbol{D}_1+\frac{1}{6}\boldsymbol{\Delta}\right)\cdot\boldsymbol{S}$$
$$+\frac{1}{J}\left\{-\frac{1}{12}(\boldsymbol{S}\cdot\boldsymbol{K}\cdot\boldsymbol{S}-4\,\mathrm{Tr}\,\boldsymbol{K})-\frac{1}{18}[(\boldsymbol{Q}\times\boldsymbol{S})\cdot(2\boldsymbol{D}_1-\boldsymbol{\Delta})\cdot\boldsymbol{S}+\boldsymbol{S}\cdot(2\boldsymbol{D}_1-\boldsymbol{\Delta})\cdot(\boldsymbol{Q}\times\boldsymbol{S})]\right.$$
$$\left.+\frac{1}{36}\boldsymbol{S}\cdot(2\boldsymbol{D}_1-\boldsymbol{\Delta})^2\cdot\boldsymbol{S}-\frac{1}{108}[\boldsymbol{S}\cdot(2\boldsymbol{D}_1-\boldsymbol{\Delta})\cdot\boldsymbol{S}]^2+\frac{1}{18}\mathrm{Tr}\,(2\boldsymbol{D}_1-\boldsymbol{\Delta})^2\right\}. \tag{10}$$

An example of an EPR spectrum which conforms to (9), especially for what concerns the Zeeman and hyperfine interactions, is shown by the pair $Mn^{2+}-Cu^{2+}$ in Mn doped Cu(pyridine N-oxide)$Cl_2\cdot H_2O$ complex [10, 11]. Unfortunately there is not evidence of measurable second-order effects which might allow a complete check of the theory. This, probably, is due to the large value of the isotropic exchange coupling.

A more favourable case appears to be that of the pair $Mn^{2+}-Cu^{2+}$ in Cu(prp)$_2$en Mn(hfa)$_2$, where (prp)$_2$en is the Schiff base formed by 2-hydroxy-propiophenone and ethylenediamine, and hfa is hexafluoroacetylacetonate. Here, the zero-field splitting shows appreciable discrepancies with respect to a first-order model [12]. In spite of this, the available experimental data are not sufficient to draw definite conclusions. In fact, one has no information about possible fourth power terms in the zero-field splitting operators. We may conjecture only. Thus, we observe that in the cited pyridine N-oxide complex the zero-field splitting interaction for the manganese-copper pair in the $S=2$ state and for the copper-copper host pair in the $S=1$ state are both of a bilinear nature (as said) and characterized by tensors approximately equiaxial with values in the ratio 1/3 [10]. One of the possibilities to account for this is to set $\boldsymbol{D}_1\sim 0$ and $\boldsymbol{Q}\sim 0$, making the assumption that the value of $\boldsymbol{\Delta}$ for the two pairs are comparable. The resulting formulas seem to agree qualitatively with the available data for Cu(prp)$_2$en Mn(hfa)$_2$. In fact, in this approximation the residual second-order corrections should affect the bilinear zero-field contributions relative to the $S=2$ and $S=3$ states by amounts in the theoretical ratio of 5 to 1. This is roughly the observed ratio in the direction of maximum zero-field splitting if one assumes as value of the first-order part ($\frac{1}{6}\Delta_z$) the splitting for $S=2$ measured in the pyridine N-oxide complex. The assumption seems not unreasonable in view, as said, of the probable large value of the coupling constant J for the manganese-copper pair in that compound. Despite the encouraging agreement, we think that this is not the only possible interpretation and that $\boldsymbol{Q}$ and particularly $\boldsymbol{D}_1$ may play an important role. It is possible to conclude, however, that the available experimental data are not incompatible with the proposed model.

As the last application, we limit ourselves to write the spin-hamiltonians spanning the two possible total spin multiplets of a pair with $S_1=1$, $S_2=1/2$:

$$S=1/2\,,\quad \mathscr{H}_S=\mu_B\boldsymbol{H}\cdot\left(\frac{4}{3}\boldsymbol{g}_1-\frac{1}{3}\boldsymbol{g}_2\right)\cdot\boldsymbol{S}+\boldsymbol{I}_1\cdot\left(\frac{4}{3}\boldsymbol{A}_1\right)\cdot\boldsymbol{S}+\boldsymbol{I}_2\cdot\left(-\frac{1}{3}\boldsymbol{A}_2\right)\cdot\boldsymbol{S}, \tag{11}$$

$$S=3/2\,,\quad \mathscr{H}_S=\mu_B\boldsymbol{H}\cdot\left(\frac{2}{3}\boldsymbol{g}_1+\frac{1}{3}\boldsymbol{g}_2\right)\cdot\boldsymbol{S}+\boldsymbol{I}_1\cdot\left(\frac{2}{3}\boldsymbol{A}_1\right)\cdot\boldsymbol{S}+\boldsymbol{I}_2\cdot\left(\frac{1}{3}\boldsymbol{A}_2\right)\cdot\boldsymbol{S}+\boldsymbol{S}\cdot\left(\frac{1}{3}\boldsymbol{D}_1+\frac{1}{3}\boldsymbol{\Delta}\right)\cdot\boldsymbol{S}$$
$$+\frac{1}{J}\left\{-\frac{1}{6}\left(\boldsymbol{S}\cdot\boldsymbol{K}\cdot\boldsymbol{S}-\frac{5}{4}\mathrm{Tr}\,\boldsymbol{K}\right)-\frac{1}{18}[(\boldsymbol{Q}\times\boldsymbol{S})\cdot(2\boldsymbol{D}_1-\boldsymbol{\Delta})\cdot\boldsymbol{S}+\boldsymbol{S}\cdot(2\boldsymbol{D}_1-\boldsymbol{\Delta})\cdot(\boldsymbol{Q}\times\boldsymbol{S})]\right.$$
$$\left.-\frac{1}{18}\left[\boldsymbol{S}\cdot(2\boldsymbol{D}_1-\boldsymbol{\Delta})^2\cdot\boldsymbol{S}-\frac{5}{4}\mathrm{Tr}\,(2\boldsymbol{D}_1-\boldsymbol{\Delta})^2\right]\right\}. \tag{12}$$

A final remark may be made about the adopted form for the zero-field splitting operators. Equations (A2), (3)–(5), (9)–(12) seem to raise the question whether the more advantageous form is the present one in terms of cartesian tensors or the more usual one in terms of equivalent operators. Apart from the fact that in principle it is possible to change from one to the other, we note that the second form is more suitable to investigate qualitatively different contributions to the angular behaviour of levels and resonance fields. The first one, on the contrary, has two advantages. It displays the role of each tensorial term considered as a whole and it can be immediately related to an arbitrary assumed reference frame. This possibility appears to be a favourable point. In fact, it may allow to give general criteria, such as the well known three planes methods [13], for deducing the tensorial constants which appear in the fourth power spin-hamiltonian terms. A work in this sense is in progress.

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Appendix

Second-Order Spin-Hamiltonians for the Single S-Multiplets

We consider ions in singlet orbital ground-states for which, as known, the magnetic properties are essentially of a spin-only nature. The pair energy, then, can be written in the general tensorial form

$$\begin{aligned}\mathscr{H} &= \mu_B \boldsymbol{H}\cdot\boldsymbol{g}_1\cdot\boldsymbol{S}_1 + \boldsymbol{S}_1\cdot\boldsymbol{D}_1\cdot\boldsymbol{S}_1 + \boldsymbol{I}_1\cdot\boldsymbol{A}_1\cdot\boldsymbol{S}_1\\ &\quad + \mu_B \boldsymbol{H}\cdot\boldsymbol{g}_2\cdot\boldsymbol{S}_2 + \boldsymbol{S}_2\cdot\boldsymbol{D}_2\cdot\boldsymbol{S}_2 + \boldsymbol{I}_2\cdot\boldsymbol{A}_2\cdot\boldsymbol{S}_2\\ &\quad + J\boldsymbol{S}_1\cdot\boldsymbol{S}_2 + \boldsymbol{Q}\cdot\boldsymbol{S}_1\times\boldsymbol{S}_2 + \boldsymbol{S}_1\cdot\boldsymbol{\Delta}\cdot\boldsymbol{S}_2\,, \qquad \text{(A.1)}\end{aligned}$$

where $\boldsymbol{D}_1$, $\boldsymbol{D}_2$ and $\boldsymbol{\Delta}$ are traceless. The first six terms represent the local energies and account for the Zeeman, fine and hyperfine interactions of the two ions. The remaining terms represent the interaction between the ions and consist of an isotropic contribution (assumed as the preponderant part) and of two anisotropic contributions (skew-symmetric and symmetric, respectively) to the exchange energy. Biquadratic and higher-order exchange and exchange striction are neglected as minor contributions [14].

For large values of the isotropic exchange the spin $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ couple to give a number of multiplets characterized by total spin values $S = |S_1 - S_2|, \ldots, S_1 + S_2$. In this limit the EPR properties can, as known, be conveniently described in terms of effective spin-hamiltonian operators $\mathscr{H}_S$ which span the levels within each single S-multiplet. These operators are usually derived on the basis of a first-order perturbative treatment with respect to the isotropic exchange energy [2, 3]. In [1] we have proposed a modification of such a single-multiplet formalism in which the possible interactions among different S-multiplets were taken into account with the second-order approximation of the perturbation theory [5]. If we neglect additive constants, which affect the multiplet levels as a whole and therefore do not give observable EPR effects, the result is

$$\begin{aligned}\mathscr{H}_S &= \mu_B \boldsymbol{H}\cdot(\alpha\,\boldsymbol{g}_1 + \beta\,\boldsymbol{g}_2)\cdot\boldsymbol{S} + \boldsymbol{I}_1\cdot(\alpha\boldsymbol{A}_1)\cdot\boldsymbol{S} + \boldsymbol{I}_2\cdot(\beta\boldsymbol{A}_2)\cdot\boldsymbol{S} + \boldsymbol{S}\cdot((\alpha^2-\delta^2)\,\boldsymbol{D}_1 + (\beta^2-\delta^2)\,\boldsymbol{D}_2 + (\alpha\beta+\delta^2)\,\boldsymbol{\Delta})\cdot\boldsymbol{S}\\ &\quad + \frac{1}{J}\Bigg\{\gamma\left[\boldsymbol{S}\cdot\boldsymbol{K}\cdot\boldsymbol{S} - \frac{\operatorname{Tr}\boldsymbol{K}}{3}\,S(S+1)\right] + \varepsilon[(\boldsymbol{Q}\times\boldsymbol{S})\cdot(\boldsymbol{D}_1+\boldsymbol{D}_2-\boldsymbol{\Delta})\cdot\boldsymbol{S} + \boldsymbol{S}\cdot(\boldsymbol{D}_1+\boldsymbol{D}_2-\boldsymbol{\Delta})\cdot(\boldsymbol{Q}\times\boldsymbol{S})]\\ &\qquad + \zeta[(\boldsymbol{Q}\times\boldsymbol{S})\cdot(\boldsymbol{D}_1-\boldsymbol{D}_2)\cdot\boldsymbol{S} + \boldsymbol{S}\cdot(\boldsymbol{D}_1-\boldsymbol{D}_2)\cdot(\boldsymbol{Q}\times\boldsymbol{S})] + \eta\Bigg[\boldsymbol{S}\cdot(\boldsymbol{D}_1+\boldsymbol{D}_2-\boldsymbol{\Delta})^2\cdot\boldsymbol{S}\\ &\qquad - \frac{\operatorname{Tr}(\boldsymbol{D}_1+\boldsymbol{D}_2-\boldsymbol{\Delta})^2}{3}\,S(S+1)\Bigg] + \lambda\left[\boldsymbol{S}\cdot(\boldsymbol{D}_1-\boldsymbol{D}_2)^2\cdot\boldsymbol{S} - \frac{\operatorname{Tr}(\boldsymbol{D}_1-\boldsymbol{D}_2)^2}{3}\,S(S+1)\right]\\ &\qquad + \mu\,[\boldsymbol{S}\cdot((\boldsymbol{D}_1-\boldsymbol{D}_2)(\boldsymbol{D}_1+\boldsymbol{D}_2-\boldsymbol{\Delta}) + (\boldsymbol{D}_1+\boldsymbol{D}_2-\boldsymbol{\Delta})(\boldsymbol{D}_1-\boldsymbol{D}_2))\cdot\boldsymbol{S}\\ &\qquad - \tfrac{2}{3}\operatorname{Tr}((\boldsymbol{D}_1-\boldsymbol{D}_2)(\boldsymbol{D}_1+\boldsymbol{D}_2-\boldsymbol{\Delta}))\cdot S(S+1)]\\ &\qquad + \nu\left[(\boldsymbol{S}\cdot(\boldsymbol{D}_1+\boldsymbol{D}_2-\boldsymbol{\Delta})\cdot\boldsymbol{S})^2 - \frac{\operatorname{Tr}(\boldsymbol{D}_1+\boldsymbol{D}_2-\boldsymbol{\Delta})^2}{30}\cdot S(S+1)(2S-1)(2S+3)\right]\\ &\qquad + \xi\left[(\boldsymbol{S}\cdot(\boldsymbol{D}_1-\boldsymbol{D}_2)\cdot\boldsymbol{S})^2 - \frac{\operatorname{Tr}(\boldsymbol{D}_1-\boldsymbol{D}_2)^2}{30}\cdot S(S+1)(2S-1)(2S+3)\right]\\ &\qquad + \varrho\Bigg[(\boldsymbol{S}\cdot(\boldsymbol{D}_1+\boldsymbol{D}_2-\boldsymbol{\Delta})\cdot\boldsymbol{S})(\boldsymbol{S}\cdot(\boldsymbol{D}_1-\boldsymbol{D}_2)\cdot\boldsymbol{S}) + (\boldsymbol{S}\cdot(\boldsymbol{D}_1-\boldsymbol{D}_2)\cdot\boldsymbol{S})(\boldsymbol{S}\cdot(\boldsymbol{D}_1+\boldsymbol{D}_2-\boldsymbol{\Delta})\cdot\boldsymbol{S})\\ &\qquad - \frac{\operatorname{Tr}((\boldsymbol{D}_1-\boldsymbol{D}_2)(\boldsymbol{D}_1+\boldsymbol{D}_2-\boldsymbol{\Delta}))}{15}\cdot S(S+1)(2S-1)(2S+3)\Bigg]\Bigg\}\,, \qquad \text{(A.2)}\end{aligned}$$

where

$$\boldsymbol{K} = \begin{bmatrix} Q_x^2 & Q_x Q_y & Q_x Q_z \\ Q_x Q_y & Q_y^2 & Q_y Q_z \\ Q_x Q_z & Q_y Q_z & Q_z^2 \end{bmatrix}, \qquad \text{(A.3)}$$

and, for convenience, each second-order term is made traceless singularly. The coefficients are defined in (1).

In the limit $J = \infty$, (A.2) gives the well known first-order expression proposed by Owen [2] for the case $S_1 = S_2$ and extended by Chao [3] to arbitrary spin values. The second-order treatment of the zero-field splitting introduces spin operators of the usual bilinear form, and, characteristically, also fourth power spin operators. It is to be noted, however, that such terms are not equally effective for each value of the total spin. In fact, as mentioned in [1], one verifies the equalities

$$S = 1/2\,, \quad \boldsymbol{S} \cdot \boldsymbol{D}_i \cdot \boldsymbol{S} = 0 \quad (\boldsymbol{D}_i \text{ is an arbitrary tensor supposed symmetric and traceless})\,; \qquad \text{(A.4)}$$

$$S = 1\,, \quad (\boldsymbol{S} \cdot \boldsymbol{D}_i \cdot \boldsymbol{S})(\boldsymbol{S} \cdot \boldsymbol{D}_j \cdot \boldsymbol{S}) + (\boldsymbol{S} \cdot \boldsymbol{D}_j \cdot \boldsymbol{S}) \cdot (\boldsymbol{S} \cdot \boldsymbol{D}_i \cdot \boldsymbol{S}) - \frac{\operatorname{Tr} \boldsymbol{D}_i \boldsymbol{D}_j}{15} \cdot S(S+1)(2S-1)(2S+3) = -\left[\boldsymbol{S} \cdot \boldsymbol{D}' \cdot \boldsymbol{S} - \frac{\operatorname{Tr} \boldsymbol{D}'}{3} S(S+1)\right], \qquad \text{(A.5)}$$

where the matrix elements are

$$D'_{xx} = 2 D_{iyz} D_{jyz} - (D_{iyy} D_{jzz} + D_{izz} D_{jyy})\,,$$

$$D'_{xy} = D_{izz} D_{jxy} + D_{ixy} D_{jzz} - (D_{ixz} D_{jyz} + D_{iyz} D_{jxz})\,, \quad \text{etc.}\,;$$

$$S = 3/2\,, \quad (\boldsymbol{S} \cdot \boldsymbol{D}_i \cdot \boldsymbol{S})(\boldsymbol{S} \cdot \boldsymbol{D}_j \cdot \boldsymbol{S}) + (\boldsymbol{S} \cdot \boldsymbol{D}_j \cdot \boldsymbol{S}) \cdot (\boldsymbol{S} \cdot \boldsymbol{D}_i \cdot \boldsymbol{S}) - \frac{\operatorname{Tr} \boldsymbol{D}_i \boldsymbol{D}_j}{15} \cdot S(S+1)(2S-1)(2S+3) = 0\,. \qquad \text{(A.6)}$$

Equations for terms like $(\boldsymbol{S} \cdot \boldsymbol{D}_i \cdot \boldsymbol{S})^2$ are, as obvious, immediately deduced from these by setting $i = j$.

As a consequence, apart from the trivial case $S = 1/2$, when $S = 1$ or $3/2$ it is possible to reduce our second-order expressions for the zero-field splitting to a more conventional bilinear form. When $S = 3/2$, this reduction is automatic. This is in line with the well known rule that the description of a manifold of spins S needs spin operators of power not greater than $2S$. It follows that only for $S \geqq 2$ specific fourth power spin operators may be necessary.

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