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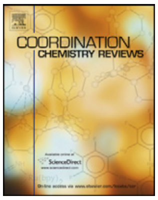

Review

Antisymmetric exchange in polynuclear metal complexes

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ABSTRACT

The irreducible tensor operator approach is utilized as a working tool in the spin Hamiltonian formalism for polynuclear systems. The matrix elements for the dinuclear and trinuclear systems are presented that involve the isotropic exchange, spin-Zeeman term, and the antisymmetric exchange. These basics allow an extensive modeling of the energy levels and magnetic functions (temperature dependence of the magnetic susceptibility and field dependence of the magnetization) for individual Cartesian components and their average for homospin diads and triads. Experimental data on the antisymmetric exchange are reviewed. The tabulations involve data from different sources: the electron paramagnetic resonance, the magnetic susceptibility and magnetization measurements.

1. Introduction

1.1. Motivation

To a first approximation, magnetochemists try to fit their experimental data by assuming that only the isotropic exchange (covered

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Nomenclature

ASE	antisymmetric exchange
$(\vec{A}\cdot\vec{B})$	scalar product of two vectors
$(\vec{A}\times\vec{B})$	vector product of two vectors
$(\vec{A}\otimes\vec{B})$	tensor product of two vectors
B	magnetic induction [T]
$\cosh(x)$	$=(e^{x}+e^{-x})/2$
C_0	$=N_{\mathrm{A}}\mu_0\mu_{\mathrm{B}}^2/k$, reduced Curie constant
$\vec{d}_{AB}(d_x^{AB}, d_y^{AB}, d_z^{AB})$	parameter vector for ASE
$d_{1,q}^{AB}$	spherical transform of the parameter set for ASE, $d_{1,\pm 1}^{AB}=\mp(d_x^{AB}\pm i d_y^{AB})/\sqrt{2}$, $d_{1,0}^{AB}=d_z^{AB}$
$d_a^{AB}=G_a^{AB}$	individual-pair (AB) interaction parameter for ASE in the given direction ($a=x, y, z$)
D_A	axial zero-field splitting parameter (single-ion anisotropy parameter)
D_{AB}	axial asymmetric exchange parameter
E_A	rhombic zero-field splitting parameter (single-ion anisotropy parameter)
E_{AB}	rhombic asymmetric exchange parameter
g_{e}	free-electron g-value
G	many-electron compound parameter for ASE related to the energy gap
$G_z=D_n=A_n$	compound parameter for ASE, normal (out-of-plane) component
(G_x, G_y)	compound parameters for ASE, in-plane components; $\rightarrow(D_l, D_t)=(A_l, A_t)$ –longitudinal and transversal components
$\bar{\bar{g}}_A$	magnetogyric tensor
$\vec{G}_A=(\vec{B}\cdot\bar{\bar{g}}_A)$	magnetogyric parameter vector
HF	high field
ITO	irreducible tensor operator
J_{AB}	isotropic exchange coupling constants,
LF	low field
LT	low temperature
M_{mol}	molar magnetization [A m^2 mol^{-1}]
$M_{\mathrm{mol}}/(N_{\mathrm{A}}\mu_{\mathrm{B}})$	magnetization per particle in units of Bohr magneton [dimensionless]
PT	perturbation theory
$\sinh(x)$	$=(e^{x}-e^{-x})/2$
$\tanh(x)$	$=\sinh(x)/\cosh(x)=(e^{x}-e^{-x})/(e^{x}+e^{-x})$
$T_q^k, T_{k,q}$	spherical tensor of rank k and component q, $-k\le q\le +k$
$\hat{T}_q^k=\{\vec{A}\otimes\vec{B}\}_{k,q}$	compound tensor operator made of the tensor product of the constituent vectors $\vec{A}$ and $\vec{B}$; k – tensor rank, q – component
Z_0	$=\sum_i \exp(-\varepsilon_i^{(0)}/kT)$, zero-field partition function
$Z(B_k)$	$=\sum_i \exp[-\varepsilon_i(B_k)/kT]$, partition function
$\left\langle \alpha j \left\Vert \hat{T}^k \right\Vert \alpha' j' \right\rangle$	reduced matrix element of a tensor operator
$\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix}$	$=\langle j_1 j_2 m_1 m_2 \vert JM\rangle(-1)^{j_1-j_2+M}(2J+1)^{-1/2}$ 3j-symbol for addition of angular momenta; constraints: $m_1+m_2=M$ and $\lvert j_1-j_2\rvert\le J\le j_1+j_2$
$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & J & j_{23} \end{Bmatrix}$	$=(-1)^{j_1+j_2+j_3+J}[(2j_{12}+1)(2j_{23}+1)]^{-1/2}\times\langle j_1 j_2 j_{12} j_3 JM \vert j_1 j_2 j_3 j_{23} JM\rangle$ 6j-symbol for addition of angular momenta; constraints: $(a, b, c)=\begin{cases}(j_1, j_2, j_3)\\(j_1, j_5, j_6)\\(j_4, j_2, j_6)\\(j_4, j_5, j_3)\end{cases}$ in the symbol $\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{Bmatrix}$ have an integral sum, and satisfy the triangular condition $\lvert a-b\rvert\le c\le a+b$
$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & J \end{Bmatrix}$	$=[(2j_{12}+1)(2j_{34}+1)(2j_{13}+1)(2j_{24}+1)]^{-1/2}\times\langle j_1 j_2 j_{12} j_3 j_4 j_{34} J(M) \vert j_1 j_3 j_{13} j_2 j_4 j_{24} J(M)\rangle$ 9j-symbol for addition of angular momenta
(.)	zero matrix element
$(\times)$	non-zero matrix element
$(^*)$	Hermitean-adjoint matrix element
γ_a	$=g_a\mu_{\mathrm{B}}B$, Zeeman factor in the a-th direction
$\kappa=\chi_{\mathrm{mol}}/C_0$	reduced susceptibility [K^{-1}]
λ	$=\pm\xi/2S$, spin–orbit splitting parameter within an atomic term
μ_{eff}	$=\sqrt{(3k/N_{\mathrm{A}}\mu_0)\chi_{\mathrm{mol}}T}=\mu_{\mathrm{B}}\sqrt{3(\chi_{\mathrm{mol}}T/C_0)}$, effective magnetic moment
χ_{mol}	$=\mu_0(\partial M_{\mathrm{mol}}/\partial B)$, molar magnetic susceptibility [m^3 mol^{-1}]
$\chi_{\mathrm{mol}}T/C_0$	product function in units of the reduced Curie constant [dimensionless], recommended presentation
$\chi_{\Vert}$	parallel component of the magnetic susceptibility
$\chi_{\perp}$	perpendicular component of the magnetic susceptibility

by the J_{AB} parameters) operates in dinuclear, trinuclear, or polynuclear spin system. Having the experimental evidence, they continue in improving their models by including the single-ion anisotropy terms (D_A parameters). As a rule, this parameter manifests itself in the zero-field splitting of the spin manifolds owing to which the susceptibility curve (χ *vs* T) deviates from the isotropic-case behavior.

The inclusion of the D_A parameters, however, is far from complete. At the same time other exchange-interaction terms could contribute: the asymmetric exchange (D_{AB} parameters) along with the antisymmetric exchange (d_{AB} parameters) and biquadratic exchange. The uniaxial anisotropy is only a part of the overall effect and in some cases also rhombic anisotropy parameters are relevant (E_A and E_{AB} parameters). Continuing in this list, the monoclinic and triclinic anisotropy parameters could also be in the play though little knowledge about them is available.

The effect of the non-isotropic exchange is obvious: it induces the magnetic anisotropy. The magnetic anisotropy can be obtained by measuring oriented single crystals. The recorded magnetization (susceptibility) components diverge from the isotropic counterparts at lower temperature. With increasing temperature and in extreme magnetic fields the magnetic anisotropy tends to disappear and cannot be detected. However, when low-temperature experiments are done, the magnetic anisotropy can be safely detected also for the powder samples.

The usual hypothesis that the magnetic anisotropy is dominated by the single-ion anisotropy needs a more detailed inspection (theoretical modeling) and experimental verification. In general, such a hypothesis is not fully justified. There are two reasons for complaint. In the strong exchange limit ($\lvert J\rvert\gg 0$), the asymmetric

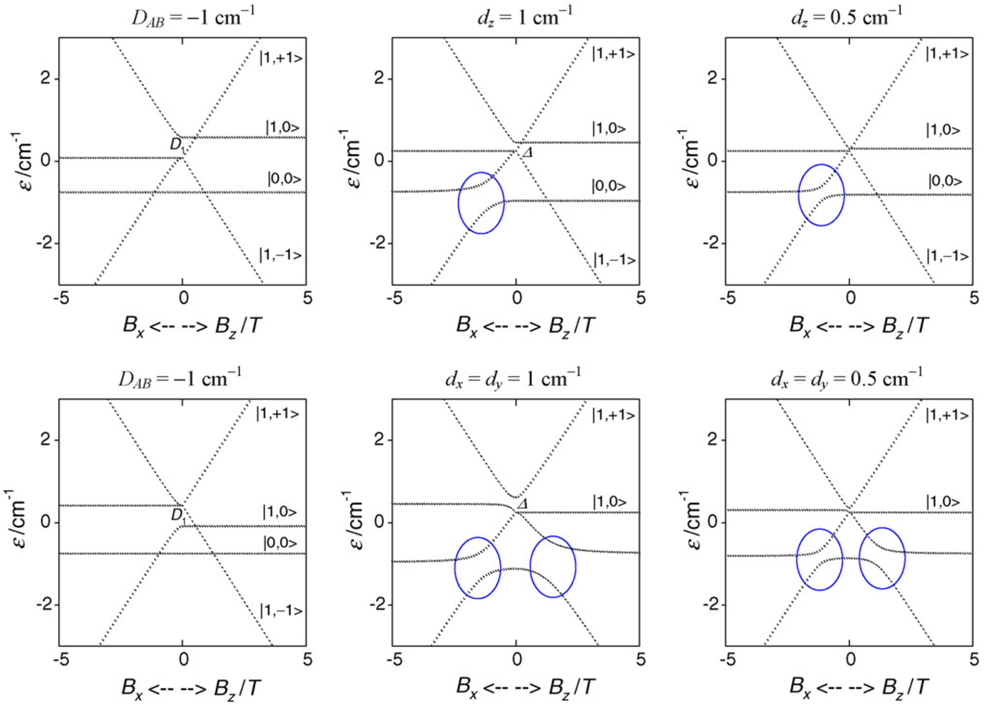

Fig. 1. The energy levels for a $S_A = S_B = 1/2$ diad coupled in an antiferromagnetic manner, $J/hc = -1$ cm^{-1} (weak exchange limit). Left—effect of the asymmetric exchange, right—effect of the antisymmetric exchange. Avoided level crossing is highlighted by a circle.

exchange (D_{AB}) is combined with the single-ion anisotropy parameters (D_A) through combination coefficients of the same order, say

$$D_S = C_A D_A + C_B D_B + C_{AB} D_{AB} \tag{1.1}$$

By ignoring D_{AB}, the "recorded" D_S will lead to incorrect conclusions about the magnitude and sign of D_A. The above addition needs be applied in the tensorial sense which depends upon the particular molecular structure. The D_{AB} (E_{AB}) parameters, in fact, result from the *symmetrized* part of the exchange-coupling tensor. If there is a general anisotropy, the *antisymmetrized* part of the exchange-coupling tensor is also in play and this is nothing else but the antisymmetric exchange. The individual interaction terms entering the spin-Hamiltonian for a diad are termed as follows:

$$\begin{aligned}
\hat{H}_{AB} = \quad & -J_{AB}(\vec{S}_A \cdot \vec{S}_B)\hbar^{-2} \ldots \text{isotropic (bilinear) exchange} \\
& +\mu_B \vec{B} \cdot (\bar{\bar{g}}_A \cdot \vec{S}_A + \bar{\bar{g}}_B \cdot \vec{S}_B)\hbar^{-1} \ldots \text{Zeeman term} \\
& \left.\begin{array}{l} +D_A[\hat{S}_z^A \hat{S}_z^A - (\vec{S}_A \cdot \vec{S}_A)/3]\hbar^{-2} + D_B[\hat{S}_z^B \hat{S}_z^B - (\vec{S}_B \cdot \vec{S}_B)/3]\hbar^{-2} \ldots \text{axial single-ion anisotropy} \\ +E_A(\hat{S}_x^A \hat{S}_x^A - \hat{S}_y^A \hat{S}_y^A)\hbar^{-2} + E_B(\hat{S}_x^B \hat{S}_x^B - \hat{S}_y^B \hat{S}_y^B)\hbar^{-2} \ldots \text{rhombic single-ion anisotropy} \end{array}\right\} \ldots \text{zero-field splitting} \\
& \left.\begin{array}{l} +D_{AB}[\hat{S}_z^A \hat{S}_z^B - (\vec{S}_A \cdot \vec{S}_B)/3]\hbar^{-2} + E_{AB}(\hat{S}_x^A \hat{S}_x^B - \hat{S}_y^A \hat{S}_y^B)\hbar^{-2} \ldots \text{asymmetric exchange} \\ +\vec{d}_{AB} \cdot (\vec{S}_A \times \vec{S}_B)\hbar^{-2} \ldots \text{antisymmetric exchange} \end{array}\right\} \ldots \text{anisotropic exchange} \\
& +\text{biquadratic exchange} + \text{triquadratic exchange} + \text{double exchange} + \ldots
\end{aligned}$$

In order to introduce the reader into the effect of the asymmetric and/or antisymmetric exchange, let us analyze the modeling shown in Fig. 1 for the simplest $S_A = S_B = 1/2$ diad. If only the isotropic exchange coupling is present, the individual spin-multiplets $\left|S, M_S\right\rangle$ are $(2S+1)$-fold degenerate in the absence of the magnetic field; the energy levels develop in the magnetic field uniformly in any direction. The asymmetric exchange causes: (i) a zero-field splitting of the $S = 1$ state by amount of D_1; (ii) a different development of energy levels in different field directions; (iii) a magnetic anisotropy, since the magnetization components (M_z, M_x) and the susceptibility components (χ_z, χ_x) at low temperature visibly differ one from another. The effect of the antisymmetric exchange (ASE) seems analogous in the above three respects. However, the development of energy levels in an applied magnetic field is different and consequently the magnetic anisotropy is quantitatively different with respect to the asymmetric exchange. A characteristic aspect of ASE is an avoided level crossing as seen in Fig. 1. With decreasing ratio d/J the zero-field energy gap Δ tends to disappear and the system behaves like the isotropic case.

There is a principal methodological difference when treating the asymmetric/antisymmetric exchange. For instance, for a dinuclear system $S_A = S_B = 1$, the asymmetric exchange matrix adopts the form

$$\mathbf{H}^{\text{asym}} = \left(\begin{array}{c:ccc:ccccc}
a_0 & \cdot & * & \cdot & * & \cdot & * & \cdot & * \\ \hdashline
\cdot & a_0 & \cdot & a_{-2} & \cdot & * & \cdot & * & \cdot \\
b_0 & \cdot & a_0 & \cdot & * & \cdot & * & \cdot & * \\
\cdot & a_{+2} & \cdot & a_0 & \cdot & * & \cdot & * & \cdot \\ \hdashline
c_{-2} & \cdot & b_{-2} & \cdot & a_0 & \cdot & a_{-2} & \cdot & \cdot \\
\cdot & b_0 & \cdot & b_{-2} & \cdot & a_0 & \cdot & a_{-2} & \cdot \\
c_0 & \cdot & b_0 & \cdot & a_{+2} & \cdot & a_0 & \cdot & a_{-2} \\
\cdot & b_{+2} & \cdot & b_0 & \cdot & a_{+2} & \cdot & a_0 & \cdot \\
c_{+2} & \cdot & b_{+2} & \cdot & \cdot & \cdot & a_{+2} & \cdot & a_0
\end{array}\right) \tag{1.2}$$

(points refer to zero matrix elements and stars to Hermitean adjoint, a_i, b_i and c_i symbols refer to the asymmetric exchange matrix elements) for kets $\left|S, M_S\right\rangle$ ordered in an ascending way. Such a matrix is usually treated in the *strong exchange limit* when only the blocks diagonal in spin ($S' = S$) are considered. On the contrary, the antisymmetric exchange matrix has the following structure (b_i symbols refer to antisymmetric exchange matrix elements)

$$\mathbf{H}^{\mathrm{anti}} = \left(\begin{array}{c|ccc|ccccc} \cdot & * & * & * & \cdot & \cdot & \cdot & \cdot & \cdot \\ \hline \mathrm{b}_- & \cdot & \cdot & \cdot & * & * & * & \cdot & \cdot \\ \mathrm{b}_0 & \cdot & \cdot & \cdot & \cdot & * & * & * & \cdot \\ \mathrm{b}_+ & \cdot & \cdot & \cdot & \cdot & \cdot & * & * & * \\ \hline \cdot & \mathrm{b}_- & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \mathrm{b}_0 & \mathrm{b}_- & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \mathrm{b}_+ & \mathrm{b}_0 & \mathrm{b}_- & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \mathrm{b}_+ & \mathrm{b}_0 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \mathrm{b}_+ & \cdot & \cdot & \cdot & \cdot & \cdot \end{array}\right) \tag{1.3}$$

where the diagonal blocks exactly vanish. Therefore the interaction between off-diagonal blocks ($S' \neq S$) need to be considered which is completely opposite to the case of asymmetric exchange.

The idea about the antisymmetric exchange was pioneered by Dzyaloshinsky and Moriya [1,2]. An important contribution to this field was provided by Belinskii and Tsukerblat. There are sources available where this type of non-isotropic exchange is involved and eventually studied from general point of view [3–8,48b]. What is badly missing is a comprehensive modeling of magnetic functions (susceptibility, χT-product, magnetization) for low-nuclearity spin systems (diads, triads, tetrads) which could help chemists/physicists in the identification of the effect. However, particular studies are already available and they will be briefly reviewed in Chapter 5.

The explosively increasing knowledge about the single-molecule magnets [9,10] relies on the description of the barrier to magnetic tunneling as exclusively provided by the molecular-state D_S (E_S) parameters. Whether the antisymmetric exchange takes part in this business remains an open question so far. No doubt that the antisymmetric exchange itself induces the magnetic anisotropy, and finally it could combine with the asymmetric exchange and the single-ion anisotropy terms.

1.2. The scope of review

Chapter 2 deals with the spin Hamiltonian formalism for polynuclear systems. As a working tool, the irreducible tensor operator (ITO) approach is utilized. For such a reason, the basic algebra with ITOs is presented. The matrix elements for the dinuclear and trinuclear systems are presented that involve the isotropic exchange, spin-Zeeman term, and the antisymmetric exchange. (The asymmetric and biquadratic exchange is not covered by this review. The former has been reviewed in the paper about the zero-field splitting in metal complexes [11].) These basics allow an extensive modeling of the energy levels and magnetic functions (temperature dependence of the magnetic susceptibility and field dependence of the magnetization) for individual Cartesian components and their average (Chapters 3 and 4, Appendix) for homospin diads and triads.

Experimental data on the antisymmetric exchange are reviewed in Chapter 5. The tabulations involve data from different sources: electron paramagnetic resonance, magnetic susceptibility and magnetization measurements.

For the numerical processing of the antisymmetric exchange we selected to work in the basis set of uncoupled spin kets $\left|I\right\rangle = \left|S_A, M_A\right\rangle \left|S_B, M_B\right\rangle \ldots \left|S_N, M_N\right\rangle$ as follows.

- The spin matrices in this basis set are computer-generated and multiplied, to form the operator part that is combined with the corresponding parameter set. The spin-Hamiltonian matrix is then constituted for a reference magnetic field B_k

$$\langle I \left|\hat{H}^S(B_k)\right| J\rangle = \langle I \left|\hat{H}^{iso}\right| J\rangle + \langle I \left|\hat{H}^{anti}\right| J\rangle + \langle I \left|\hat{H}^Z(B_k)\right| J\rangle \tag{1.4}$$

- The magnetic field is aligned either parallel (the z-axis) or perpendicular (x- or y-axis) with respect to the molecular axis A–B. The diagonalization of the spin-Hamiltonian matrix yields a set of eigenvalues for a given magnetic field: $\varepsilon_i(B_k)$. Then the reference magnetic field has been raised by a small increment, $B_{k+1} = B_k + \delta$, in order to obtain three sets of energy levels ($\delta = 10^{-3}$ T).
- The logarithm of the partition function (in the given direction)

$$Z(B_k) = \sum_i \exp\left[-\frac{\varepsilon_i(B_k)}{kT}\right] \tag{1.5}$$

is fitted by a parabola from which the first and the second derivatives are easy to determine. The molar magnetization is then

$$M_{\mathrm{mol}} = N_{\mathrm{A}} kT \left(\frac{\partial \ln Z}{\partial B}\right)_T \tag{1.6}$$

where the derivative refers to the reference field. With the ramping field, the field dependence of the magnetization can be mapped. The averaged magnetization presented below is a simple average

$$M_{\mathrm{av}} = \frac{(M_x + M_y + M_z)}{3} \tag{1.7}$$

The magnetization is given in the units $M_{\mathrm{mol}}/(N_{\mathrm{A}}\mu_{\mathrm{B}})$ which is the magnetization per particle per Bohr magneton. The magnetization and its components are modeled through this review for the temperature $T = 2$ K. This limit is available at plenty laboratories using the commercial SQUID apparatus.

- The molar magnetic susceptibility can be obtained by evaluating the energy levels for three small fields and a subsequent parabolic fit in the a-th direction ($a = x, y, z$)

$$\varepsilon_{i,a}(B) = \varepsilon_{i,a}^{(0)} + \varepsilon_{i,a}^{(1)} B + \varepsilon_{i,a}^{(2)} B^2 \tag{1.8}$$

The van Vleck coefficients obtained are inserted into the van Vleck formula

$$\bar{\chi}_{aa,\mathrm{mol}} = N_{\mathrm{A}}\mu_0 \frac{\sum_i [(\varepsilon_{i,a}^{(1)})^2/kT - 2\varepsilon_{i,a}^{(2)}]\exp(-\varepsilon_{i,a}^{(0)}/kT)}{\sum_i \exp(-\varepsilon_{i,a}^{(0)}/kT)} \tag{1.9}$$

Alternatively, the second derivative of the partition function can be utilized to calculate the differential susceptibility without the limitations of the van Vleck equation as

$$\chi_{aa,\mathrm{mol}} = \mu_0 N_A kT \left(\frac{\partial^2 \ln Z}{\partial B^2}\right)_T \tag{1.10}$$

The most difficult and the most tedious step in this project is the generation of the spin matrices and their eigenvalues. Only in limited cases can they be obtained in an analytic form providing that the magnetization and susceptibility would be expressed through closed formulae. In general, the required matrix elements contain the vector coupling coefficients, i.e. the 3j-symbols, 6j-symbols, and the 9j-symbols. The final formulae for them are presented to the complexity of 3j-symbols and 6j-symbols since their values can be easily computer-generated.

1.3. Notations used

1. SI units are used consistently through the paper; χ_{mol} [SI] = $4\pi \times 10^{-6}$ χ_{mol} [cgs&emu].
2. The energy quantities E (like ε, J, d) are presented in the form of the corresponding wavenumber, i.e. E/hc and given in units of cm^{-1}.
3. The isotropic exchange constants are uniformly thought in the form $-J_{ij}(\vec{S}_i \cdot \vec{S}_j)\hbar^{-2}$. The data from original sources differing from this definition have been rescaled to the above form.
4. The angular momentum operators bring the reduced Planck constant $\hbar$ when operating to a corresponding wavefunction (a ket).
5. The fundamental physical constants (μ_0, N_{A}, $k = k_{\mathrm{B}}$, μ_{B}, $\hbar$) adopt their usual meaning. The reduced Curie constant $C_0 = N_{\mathrm{A}}\mu_0\mu_{\mathrm{B}}^2/k = 4.7141997 \times 10^{-6}\ \mathrm{K\ m^3\ mol^{-1}}$ is met in the paper.
6. The Condon–Shortley phase convention is utilized along with the pseudo-standard phase system for the irreducible tensor operators.
7. The antisymmetric exchange is synonymous to the Dzyaloshinsky–Moriya interaction. The anisotropic exchange is frequently taken as synonymous to the asymmetric exchange. However, the antisymmetric exchange induces magnetic anisotropy as well, so that it is better to distinguish between two contributions to the anisotropic exchange: the asymmetric and antisymmetric exchange, respectively.

2. Methodology

2.1. General spin Hamiltonian

The Hamiltonian that describes the interaction of a set of magnetic centers with the external magnetic field involves the spin Zeeman term, the orbital Zeeman term, the operator of the local spin–orbit coupling, and the operator of the direct spin–spin interaction (spin–spin dipolar term and the spin–spin contact term)

$$\begin{aligned}\hat{H}' &= \hbar^{-1}\mu_B g_e(\vec{B} \cdot \sum_A \vec{S}_A) + \hbar^{-1}\mu_B(\vec{B} \cdot \sum_A \vec{L}_A) + \hbar^{-2}\sum_A \lambda_A(\vec{L}_A \cdot \vec{S}_A) \\ &\quad + \hbar^{-2}\sum_A \sum_{B<A}(\vec{S}_A \cdot \overline{\overline{D_{AB}^{(1)}}} \cdot \vec{S}_B)\end{aligned} \tag{2.1}$$

In terms of the perturbation theory, this Hamiltonian acts as a perturbation that yields the first-order and the second-order corrections to the zero-field and zero-interaction energy [11]. The first-order correction can be rewritten as follows

$$\hat{H}^{(1)} = \langle 0|\hat{H}'|0\rangle = \hbar^{-2}\sum_A \sum_{B<A}(\vec{S}_A \cdot \overline{\overline{D_{AB}^{(1)}}} \cdot \vec{S}_B) + \hbar^{-1}\mu_B g_e(\vec{B} \cdot \sum_A \vec{S}_A) \tag{2.2}$$

assuming the absence of first-order angular momentum in the ground-state wave function $|0\rangle$. The second-order correction contains the matrix elements

$$\langle 0|\hat{H}'|K\rangle = \hbar^{-1}\mu_B\vec{B} \cdot \sum_A \langle 0|\vec{L}_A|K\rangle + \hbar^{-2}\sum_A \lambda_A\vec{S}_A \cdot \langle 0|\vec{L}_A|K\rangle \tag{2.3}$$

based on the assumption of the orthogonality of the state vectors $|K\rangle$. Then

$$\begin{aligned}\hat{H}^{(2)} &= \vec{B} \cdot \left(\sum_A \sum_B \mu_B^2 \overline{\overline{\Lambda}}_{AB}\right) \cdot \vec{B} + \hbar^{-2}\sum_A \sum_B \vec{S}_A \cdot (\lambda_A\lambda_B\overline{\overline{\Lambda}}_{AB}) \cdot \vec{S}_B \\ &\quad + \hbar^{-1}\mu_B\vec{B} \cdot \left(\sum_A \sum_B \overline{\overline{\Lambda}}_{AB}\lambda_B\right) \cdot \vec{S}_B \\ &\quad + \hbar^{-1}\mu_B\vec{B} \cdot \left(\sum_A \sum_B \overline{\overline{\Lambda}}_{AB}\lambda_A\right) \cdot \vec{S}_A\end{aligned} \tag{2.4}$$

where the *lambda tensor* (with the given sign convention) has been introduced

$$\overline{\overline{\Lambda}}_{AB} \equiv -\hbar^{-2}\sum_{K \neq 0} \frac{\langle 0|\vec{L}_A|K\rangle\langle K|\vec{L}_B|0\rangle}{E_K - E_0} \tag{2.5}$$

Finally, the spin Hamiltonian for a polynuclear system becomes

$$\hat{H}^S = (\vec{B} \cdot \overline{\overline{\kappa}} \cdot \vec{B}) + \hbar^{-1}\mu_B(\vec{B} \cdot \sum_A \overline{\overline{g}}_A \cdot \vec{S}_A) + \hbar^{-2}\sum_A \sum_B (\vec{S}_A \cdot \overline{\overline{D}}_{AB} \cdot \vec{S}_B) \tag{2.6}$$

where magnetic parameters (tensors) occur:

(a) the *κ-tensor* (reduced, temperature-independent paramagnetic susceptibility tensor)

$$\overline{\overline{\kappa}} = \left(\sum_A \sum_B \mu_B^2 \overline{\overline{\Lambda}}_{AB}\right) \quad [\text{energy} \times \text{induction}^{-2}] \tag{2.7}$$

(b) the *g-tensors* (magnetogyric ratio tensors) as

$$\overline{\overline{\Delta g}}_A = 2\sum_B \overline{\overline{\Lambda}}_{AB}\lambda_B\ [\text{dimensionless}] \tag{2.8}$$

$$\overline{\overline{g}}_A = g_{\mathrm{e}}\overline{\overline{1}} + \overline{\overline{\Delta g}}_A\ [\text{dimensionless}] \tag{2.9}$$

(c) the *D-tensors* (spin–spin interaction tensors) as

$$\overline{\overline{\Delta D}}_{AB} = \lambda_A\lambda_B\overline{\overline{\Lambda}}_{AB} \quad [\text{energy}] \tag{2.10}$$

$$\overline{\overline{D}}_{AB} = \left[\frac{(1-\delta_{A,B})}{2}\right]\overline{\overline{D_{AB}^{(1)}}} + \overline{\overline{\Delta D}}_{AB}, \quad [\text{energy}] \tag{2.11}$$

The temperature-independent paramagnetic susceptibility tensor is neglected hereafter since it shifts the energy levels uniformly. The magnetic data (the molar magnetic susceptibility) are expected to be already corrected for the TIP correction based upon empirical experience.

The rest of the spin Hamiltonian includes the spin Zeeman term and the spin–spin interaction. The spin–spin interaction consists of two terms:

a) the first-order contribution $\overline{\overline{D_{AB}^{(1)}}}$ involves the direct spin–spin operators (which is usually small),
b) the second-order contribution $\overline{\overline{\Delta D}}_{AB}$, which covers the dominating $\overline{\overline{\Lambda}}_{AB}$ tensor owing to the spin–orbit coupling.

The Hamiltonian that describes the exchange interaction for a pair of spin systems is

$$\hat{H}_{AB}^{ex} = \hbar^{-2}(\vec{S}_A \cdot \overline{\overline{D}}_{AB} \cdot \vec{S}_B) \tag{2.12}$$

where the Cartesian spin–spin interaction tensor $\overline{\overline{D}}_{AB}$, represented by a 3×3 square matrix with elements D_{ab}^{AB}, occurs. This can be decomposed into its symmetric and antisymmetric parts

$$\mathbf{D}_{AB} = J'_{AB}\mathbf{I} + \mathbf{D}_{AB}^{(a)} + \mathbf{D}_{AB}^{(s)} \tag{2.13}$$

where

$$J'_{AB} = \frac{1}{3}Tr(\mathbf{D}_{AB}) = \frac{(D^{AB}_{xx} + D^{AB}_{yy} + D^{AB}_{zz})}{3} \tag{2.14}$$

is one-third of the trace,

$$\bar{\bar{D}}^{(a)}_{AB} = \begin{pmatrix} 0 & (D^{AB}_{xy} - D^{AB}_{yx})/2 & (D^{AB}_{xz} - D^{AB}_{zx})/2 \\ -(D^{AB}_{xy} - D^{AB}_{yx})/2 & 0 & (D^{AB}_{yz} - D^{AB}_{zy})/2 \\ -(D^{AB}_{xz} - D^{AB}_{zx})/2 & -(D^{AB}_{yz} - D^{AB}_{zy})/2 & 0 \end{pmatrix} = \begin{pmatrix} 0 & d^{AB}_{z} & -d^{AB}_{y} \\ -d^{AB}_{z} & 0 & d^{AB}_{x} \\ d^{AB}_{y} & -d^{AB}_{x} & 0 \end{pmatrix} \tag{2.15}$$

is the antisymmetric part that involves three independent components, and

$$\bar{\bar{D}}^{(s)}_{AB} = \begin{pmatrix} D^{AB}_{xx} - J'_{AB} & (D^{AB}_{xy} + D^{AB}_{yx})/2 & (D^{AB}_{xz} + D^{AB}_{zx})/2 \\ (D^{AB}_{xy} + D^{AB}_{yx})/2 & D^{AB}_{yy} - J'_{AB} & (D^{AB}_{yz} + D^{AB}_{zy})/2 \\ (D^{AB}_{xz} + D^{AB}_{zx})/2 & (D^{AB}_{yz} + D^{AB}_{zy})/2 & D^{AB}_{zz} - J'_{AB} \end{pmatrix} \tag{2.16}$$

is the symmetric traceless part with five independent components. Then the spin Hamiltonian can be rewritten using its irreducible components as follows

$$\hat{H}^{ex}_{AB} = \hbar^{-2}[J'_{AB}(\vec{S}_A \cdot \vec{S}_B) + \vec{d}_{AB} \cdot (\vec{S}_A \times \vec{S}_B) + (\vec{S}_A \cdot \bar{\bar{D}}^{(s)}_{AB} \cdot \vec{S}_B)] \tag{2.17}$$

where the first term represents an *isotropic exchange*, the second – an *antisymmetric exchange*, and the last – an *asymmetric exchange*. In the simplest case of the isotropic exchange one has

$$\hat{H}^{iso}_{AB} = J'_{AB}\hbar^{-2}(\vec{S}_A \cdot \vec{S}_B) = -J_{AB}\hbar^{-2}(\vec{S}_A \cdot \vec{S}_B) = -2J''_{AB}\hbar^{-2}(\vec{S}_A \cdot \vec{S}_B) \tag{2.18}$$

(One should be careful in the definition of the constant factor since various numerical and sign conventions occur.) Hereafter $\hat{H}^{iso}_{AB} = -J_{AB}\hbar^{-2}(\vec{S}_A \cdot \vec{S}_B)$ is assumed.

Using the approximations introduced above, and omitting small dipolar contributions, the *z*-component of the ASE parameter vector becomes expressed as follows

$$\begin{aligned} d^{AB}_{z} &= (D^{AB}_{xy} - D^{AB}_{yx})/2 = \lambda_A\lambda_B(\Lambda^{AB}_{xy} - \Lambda^{AB}_{yx})/2 \\ &= -(1/2)\hbar^{-2}\lambda_A\lambda_B \sum_{K \neq 0} \frac{\langle 0 | \hat{L}^A_x | K \rangle \langle K | \hat{L}^B_y | 0 \rangle - \langle 0 | \hat{L}^A_y | K \rangle \langle K | \hat{L}^B_x | 0 \rangle}{E_K - E_0} \end{aligned} \tag{2.19}$$

At the same level of approximation the isotropic exchange coupling constant is

$$\begin{aligned} J_{AB} &= -(D^{AB}_{xx} + D^{AB}_{yy} + D^{AB}_{zz})/3 = -\lambda_A\lambda_B(\Lambda^{AB}_{xx} + \Lambda^{AB}_{yy} + \Lambda^{AB}_{zz}) \\ &= \hbar^{-2}\lambda_A\lambda_B \sum_{K \neq 0} \frac{\langle 0 | \hat{L}^A_x | K \rangle \langle K | \hat{L}^B_x | 0 \rangle + \langle 0 | \hat{L}^A_y | K \rangle \langle K | \hat{L}^B_y | 0 \rangle + \langle 0 | \hat{L}^A_z | K \rangle \langle K | \hat{L}^B_z | 0 \rangle}{E_K - E_0} \end{aligned} \tag{2.20}$$

and the asymmetric exchange parameters adopt the form of

$$D_{AB} = (3/2)D^{AB}_{zz} = (3/2)\lambda_A\lambda_B\Lambda^{AB}_{zz} = -(3/2)\hbar^{-2}\lambda_A\lambda_B \times \sum_{K \neq 0} \frac{\langle 0 | \hat{L}^A_z | K \rangle \langle K | \hat{L}^B_z | 0 \rangle}{E_K - E_0} \tag{2.21}$$

$$E_{AB} = (1/2)(D^{AB}_{xx} - D^{AB}_{yy}) = -(1/2)\hbar^{-2}\lambda_A\lambda_B \times \sum_{K \neq 0} \frac{\langle 0 | \hat{L}^A_x | K \rangle \langle K | \hat{L}^B_x | 0 \rangle - \langle 0 | \hat{L}^A_y | K \rangle \langle K | \hat{L}^B_y | 0 \rangle}{E_K - E_0} \tag{2.22}$$

In its classical paper Moriya [2] considered localized electron orbital states (orthogonal each to the others) and included the spin–orbit coupling as a perturbation

$$\hat{H}' = -J\hbar^{-2}(\vec{S}_1 \cdot \vec{S}_2) + \hbar^{-1}\mu_B g_e \vec{B} \cdot (\vec{S}_1 + \vec{S}_2) + \hbar^{-2}\lambda(\vec{L}_1 \cdot \vec{S}_1) + \hbar^{-2}\lambda(\vec{L}_2 \cdot \vec{S}_2) \tag{2.23}$$

The second-order energy bilinear with respect to the spin–orbit coupling and the exchange interaction is

$$\begin{aligned} E^{(2)} = &\sum^{(1)}_{m \neq n} \frac{\langle n | \lambda\vec{L}_1 \cdot \vec{S}_1 | m \rangle 2J^{n'n}_{mn'}(\vec{S}_1 \cdot \vec{S}_2) + 2J^{n'm}_{nn'}(\vec{S}_1 \cdot \vec{S}_2) \langle m | \lambda\vec{L}_1 \cdot \vec{S}_1 | n \rangle}{\varepsilon_n - \varepsilon_m} \\ &+ \sum^{(2)}_{m' \neq n'} \frac{\langle n' | \lambda\vec{L}_2 \cdot \vec{S}_2 | m' \rangle 2J^{nn'}_{m'n}(\vec{S}_1 \cdot \vec{S}_2) + 2J^{nm'}_{n'n}(\vec{S}_1 \cdot \vec{S}_2) \langle m' | \lambda\vec{L}_2 \cdot \vec{S}_2 | n' \rangle}{\varepsilon_{n'} - \varepsilon_{m'}} \end{aligned} \tag{2.24}$$

where the unperturbed states $|\phi_m\rangle$ are labeled $(n, m, \ldots)$ at the centre 1 and $(n', m' \ldots)$ at the centre 2; $|n\rangle$ and $|n'\rangle$ are ground states. The formula involves the exchange integrals defined as

$$J^{cd}_{ab} = \langle \phi_a(1)\phi_b(2) | r^{-1}_{12} | \phi_c(2)\phi_d(1) \rangle \tag{2.25}$$

Using simple rearrangements

$$E^{(2)} = 2\lambda \sum^{(1)}_{m \neq n} \frac{J^{n'm}_{nn'} \langle n | \vec{L}_1 | m \rangle \cdot [\vec{S}_1, (\vec{S}_1 \cdot \vec{S}_2)]}{\varepsilon_n - \varepsilon_m} + 2\lambda \sum^{(2)}_{m' \neq n'} \frac{J^{m'n}_{nn'} \langle n' | \vec{L}_2 | m' \rangle \cdot [\vec{S}_2, (\vec{S}_1 \cdot \vec{S}_2)]}{\varepsilon_{n'} - \varepsilon_{m'}} \tag{2.26}$$

and the commutator expressions we arrive at the final expression

$$E^{(2)} = 2i\lambda \left[\sum^{(1)}_{m \neq n} \frac{J^{n'm}_{nn'} \langle n | \vec{L}_1 | m \rangle}{\varepsilon_n - \varepsilon_m} - \sum^{(2)}_{m' \neq n'} \frac{J^{m'n}_{nn'} \langle n' | \vec{L}_2 | m' \rangle}{\varepsilon_{n'} - \varepsilon_{m'}} \right] \cdot (\vec{S}_1 \times \vec{S}_2) = \vec{d}_{12} \cdot (\vec{S}_1 \times \vec{S}_2) \tag{2.27}$$

For a single excited state $|e_1\rangle$ and $|e_2\rangle$ at each center one gets an expression [57]

$$\vec{d}_{12} = 2i\lambda \left[(-J^{e1,g2}_{g1,g2}) \frac{\langle e_1 | \vec{L}_1 | g_1 \rangle}{\varepsilon_{e1} - \varepsilon_{g1}} - (-J^{g1,e2}_{g1,g2}) \frac{\langle e_2 | \vec{L}_2 | g_2 \rangle}{\varepsilon_{e2} - \varepsilon_{g2}} \right] \tag{2.28}$$

where $|g_1\rangle$ and $|g_2\rangle$ stand for the ground states. The integral $J^{e1,g2}_{g1,g2} = \langle \phi_{g1}(1)\phi_{g2}(2) | r^{-1}_{12} | \phi_{e1}(2)\phi_{g2}(1) \rangle$ involves the transfer of one electron $g_1 \to g_2$ and the second electron $g_2 \to e_1$. Just this is the basic difference from the asymmetric exchange parameter, for which an analogous procedure gave:

$$D_{12} = \lambda^2(-J_{e1,g2}^{e1,g2}) \left[\frac{\left\langle e_1 \left| \vec{L}_1 \right| g_1 \right\rangle}{\varepsilon_{e1} - \varepsilon_{g1}} \right]^2 + \lambda^2(-J_{g1,e2}^{g1,e2}) \left[\frac{\left\langle e_2 \left| \vec{L}_2 \right| g_2 \right\rangle}{\varepsilon_{e2} - \varepsilon_{g2}} \right]^2 \tag{2.29}$$

The exchange integral can be further replaced by the effective superexchange integral within the Anderson theory of superexchange:

$$J_{nn'}^{m'n} \to 2\frac{b_{nn'}b_{m'n}}{U} \tag{2.30}$$

where U stands for the energy required to transfer an electron from one centre to another, $b_{ab} = \left\langle a \left| \hat{F} \right| b \right\rangle$ is the transfer integral for one-electron states. Within the notation of Anderson theory:

$$J_{12} = 2\frac{|b_{nn'}|^2}{U} \tag{2.31}$$

$$\vec{d}_{12} = \left(\frac{4i}{U}\right)(b_{nn'}\vec{C}_{n'n} - \vec{C}_{nn'}b_{n'n}) \tag{2.32}$$

with

$$\vec{C}_{n'n} = \left(\frac{\lambda}{2}\right) \left[\sum_{m \neq n}^{(1)} \frac{b_{n'm} \left\langle m \left| \vec{L}_1 \right| n \right\rangle}{\varepsilon_n - \varepsilon_m} + \sum_{m' \neq n'}^{(2)} \frac{b_{m'n} \left\langle n' \left| \vec{L}_2 \right| m' \right\rangle}{\varepsilon_{n'} - \varepsilon_{m'}} \right] \tag{2.33}$$

Moriya also presented an estimate for the ASE parameters:

$$d \sim \left(\frac{\Delta g}{g_e}\right) J \tag{2.34}$$

and analogously for the asymmetric exchange parameters

$$D \sim \left(\frac{\Delta g}{g_e}\right)^2 J \tag{2.35}$$

where $\Delta g = g - g_e$ is deviation of the gyromagnetic ratio from the value for a free electron. This is based upon assumptions:

$$C \sim b \cdot \left(\frac{\Delta g}{g_e}\right), \quad J \sim b^2 \tag{2.36}$$

The above estimates subsequently led to numerous mistakes by considering them as "equations" suitable for a reduction of free parameters. The main drawback of such an assumption is that the two-center term d_{12} is constrained through a single-center terms Δg.

2.2. *Irreducible tensors and tensor operators*

The interactions among spins have a directional nature and their description requires working with tensors. However, working with the Cartesian tensors is impractical, and more powerful representation is provided by spherical tensors for which the knowledge about the angular momentum can be effectively utilized [12–20]. The methodology briefly outlined below strictly refers to the irreducible tensor operators (ITO). This approach allows an elegant expression of the matrix elements of the interaction operators (isotropic exchange, Zeeman term, antisymmetric exchange, etc.) by utilizing all the knowledge about the angular momentum.

A free atom spans to the real orthogonal rotation group $\mathbf{R_3}$. Irreducible tensors of the group $\mathbf{R_3}$ are called *spherical tensors*: T_q^k. The superscript (k) refers to the rank of the tensor whereas the subscript (q: $-k \leq q \leq +k$) distinguishes among its components whose number is $(2q+1)$. The components of the *irreducible spherical tensor* transform under a rotation $\hat{R}$ of the coordinate system according to:

$$\hat{R}T_m^k\hat{R}^{-1} = \sum_{n=-k}^{+k} T_n^k(\mathbf{D}_k)_{mn} \tag{2.37}$$

where the *Wigner rotation matrix* $\mathbf{D}_k$ spans the k-th irreducible representation of $\mathbf{R_3}$.

The *tensor product* of two irreducible tensors (tensor operators) of rank l and k is defined as a set of $(2l+1)(2k+1)$ quantities:

$$\hat{T}^k \otimes \hat{T}^l = \{\hat{T}_m^k\hat{T}_n^l\} \tag{2.38}$$

This set of operators is in general reducible but a proper linear combination of them can be taken irreducible. It can be used in constructing an *irreducible tensor product* of order K with $(2K+1)$ elements indexed as $-K \leq M \leq K$ by using Clebsch–Gordan coefficients, or $3j$-symbols:

$$\begin{aligned}\{\hat{T}^k \otimes \hat{T}^l\}_M^K &= \sum_n \sum_m < k, l, n, m|K, M > \hat{T}_n^k\hat{T}_m^l \\ &= \sum_n \sum_m (2K+1)^{1/2}(-1)^{l-k-K} \begin{pmatrix} k & l & K \\ n & m & -M \end{pmatrix} \hat{T}_n^k\hat{T}_m^l\end{aligned} \tag{2.39}$$

with the constraint $|k-l| \leq K \leq (k+l)$. The compound irreducible tensor operator can be constituted from elementary vectors according to the formulae listed in Supplementary material (Table S1).

The *Wigner–Eckart theorem* states that the matrix element of a tensor operator can be expressed through a more fundamental quantity—the *reduced matrix element* (which is free of projections of angular momenta) and a coupling coefficient:

$$\begin{aligned}\left\langle \alpha jm \left| \hat{T}_M^K \right| \alpha' j' m' \right\rangle &= (\text{reduced matrix element}) \\ &\quad \times (\text{coupling coefficient})\end{aligned} \tag{2.40}$$

The form used hereafter matches that of Racah [16], Judd [17], Wybourne [18], which was accepted also by Slater [19], i.e. in terms of the $3j$-symbols:

$$\left\langle \alpha jm \left| \hat{T}_M^K \right| \alpha' j' m' \right\rangle = \left\langle \alpha j \left\| \hat{T}^K \right\| \alpha' j' \right\rangle (-1)^{j-m} \begin{pmatrix} j & K & j' \\ -m & M & m' \end{pmatrix} \tag{2.41}$$

(Tabulated values of the reduced matrix elements can differ when taken from different sources owing to different conventions.) Some elementary reduced matrix elements are presented in Supplementary materials (Table S2) [20]. The conjugate of a reduced matrix element is $\left\langle \alpha j \left\| \hat{T}^K \right\| \alpha' j' \right\rangle^* = (-1)^{j'-j} \left\langle \alpha' j' \left\| (\hat{T}^K)^\dagger \right\| \alpha j \right\rangle$.

Having the reduced matrix element determined one can easily evaluate all the matrix elements of a tensor operator. Of frequent interest are matrix elements for a tensor product of two irreducible tensor operators giving rise to:

$$\begin{aligned}&\left\langle j_1 j_2 J_{12} M_{12} \right| \{\hat{T}^k \otimes \hat{T}^l\}_M^K \left| j_1' j_2' J_{12}' M_{12}' \right\rangle \\ &= \left\langle j_1 j_2 J_{12} \left\| \{\hat{T}^k \otimes \hat{T}^l\}^K \right\| j_1' j_2' J_{12}' \right\rangle (-1)^{J_{12}-M_{12}} \begin{pmatrix} J_{12} & K & J_{12}' \\ -M_{12} & M & M_{12}' \end{pmatrix}\end{aligned} \tag{2.42}$$

The reduced matrix element (free of projections of angular momenta) can be evaluated according to the *decoupling formula*:

$$\begin{aligned}&\left\langle j_1 j_2 J_{12} \left\| \{\hat{T}^k \otimes \hat{T}^l\}^K \right\| j_1' j_2' J_{12}' \right\rangle \\ &= \left\langle j_1 \left\| \hat{T}^k \right\| j_1' \right\rangle \left\langle j_2 \left\| \hat{T}^l \right\| j_2' \right\rangle \left[(2J_{12}+1)(2J_{12}'+1)(2K+1)\right]^{1/2} \\ &\quad \times \begin{Bmatrix} j_1 & j_1' & k \\ j_2 & j_2' & l \\ J_{12} & J_{12}' & K \end{Bmatrix}\end{aligned} \tag{2.43}$$

(Owing to the symmetry properties of the $9j$-symbol another ordering of its indices may be equivalent.) This formula, in fact, represents a decoupling of the angular momenta because on the left side we have coupled angular momenta (J_{12}, J'_{12}, K) whereas on the right side only reduced matrix elements among uncoupled angular momenta (j_1, k, j'_1) and (j_2, l, j'_2) are present. The main advantage of this formula is that for the evaluation of matrix elements we do not need an explicit form of the coupled wave functions. Moreover, this formula can be simplified or extended to some important cases (Supplementary material, Table S3). The coupling coefficients on the right side can be easily evaluated by the standard techniques. It is assumed hereafter that the first irreducible tensor operator, $\hat{T}_k(j_1)$, acts on the vector space $\left|j_1 m_1\right\rangle$ and the second one, $\hat{T}_l(j_2)$, on the $\left|j_2 m_2\right\rangle$.

We met three types of the vector coupling (recoupling) coefficients: the 3*j*-, 6*j*-, and 9*j*-symbols. For evaluation of the 3*j*- and 6*j*-symbols closed Racah formulae are available [6,7–12,20]. They can be readily generated also by the Mathematica package [21]. The 9*j*-symbols can be expressed with the help of the 6*j*-symbols.

The scalar product that involves the Cartesian tensor (hereafter the *scalar sum*) can be rewritten into an equivalent form:

$$s = \vec{A} \cdot \overline{\overline{P}} \cdot \vec{B} = t(\vec{A} \cdot \vec{B}) + \vec{p} \cdot (\vec{A} \times \vec{B}) + \vec{A} \cdot \overline{\overline{P^{(s)}}} \cdot \vec{B} \tag{2.44}$$

The products involved are:

(a) the scalar (dot) product:

$$(\vec{A} \cdot \vec{B}) = A_x B_x + A_y B_y + A_z B_z \tag{2.45}$$

(b) the vector (cross) product giving rise to an *axial vector*:

$$(\vec{A} \times \vec{B}) = \left\{ A_y B_z - B_y A_z ; A_z B_x - B_z A_x ; A_x B_y - B_x A_y \right\} = -(\vec{B} \times \vec{A}) \tag{2.46}$$

(The axial vector is conserved upon inversion of coordinates as opposite to the true, polar vector.) Using the tensor (Kronecker) product of two vectors:

$$\overline{\overline{O}} = \vec{A} \otimes \vec{B} = \begin{pmatrix} A_x B_x & A_x B_y & A_x B_z \\ A_y B_x & A_y B_y & A_y B_z \\ A_z B_x & A_z B_y & A_z B_z \end{pmatrix} \tag{2.47}$$

the scalar sum becomes expressed as follows:

$$\begin{aligned} s &= A_x P_{xx} B_x + A_x P_{xy} B_y + A_x P_{xz} B_z + A_y P_{yx} B_x + A_y P_{yy} B_y + A_y P_{yz} B_z + A_z P_{zx} B_x + A_z P_{zy} B_y + A_z P_{zz} B_z \\ &= P_{xx} O_{xx} + P_{xy} O_{xy} + P_{xz} O_{xz} + P_{yx} O_{yx} + P_{yy} O_{yy} + P_{yz} O_{yz} + P_{zx} O_{zx} + P_{zy} O_{zy} + P_{zz} O_{zz} \\ &= \sum_a^{x,y,z} \sum_b^{x,y,z} P_{ab} O_{ab} = (P^{(2)} \cdot O^{(2)}) \end{aligned} \tag{2.48}$$

In this content the *scalar product* of two tensors $(P^{(2)} \cdot O^{(2)})$ is defined as a contraction over all indices (the superscript means the tensor rank).

2.3. Uncoupled basis set

We are seeking a set of eigenvalues of the spin Hamiltonian that represent the energy levels. These are invariant with respect to an arbitrary unitary transformation applied to the basis set of spin kets.

The spin Hamiltonian operates either to a set of the uncoupled spin kets $\left|S_A, M_{SA}, S_B, M_{SB}, \ldots\right\rangle$ or to a set of coupled spin kets $\left|S_A, S_B, S_{AB}, S_C, S_{ABC}, \ldots S, M_S\right\rangle$. Their number (and consequently the number of the magnetic energy levels) $K = \prod_A^N (2S_A + 1)$ varies from a few ($K = 2^2 = 4$ for two centers with $S_A = S_B = 1/2$) to several millions ($K = 6^8 = 1{,}679{,}616$ for eight centers with $S_A = 5/2$).

The spin kets abstract from any orbital contribution: they do not recognize whether the electrons were on s-, p-, or d-orbitals. This is a strong approximation. They do not recognize the spatial symmetry either, so that in a homo-binuclear system they abstract from the Σ_g and Σ_u states and also from Σ or Π states. For instance, in a binuclear Cu(II) complex the number of molecular states obtained with two sets of d-orbitals ($d = 5 + 5$) is

$$K = \begin{pmatrix} \text{spinorbitals} \\ \text{electrons} \end{pmatrix} = \begin{pmatrix} 2 \cdot d \\ n \end{pmatrix} = \begin{pmatrix} 20 \\ 18 \end{pmatrix} = 190 \tag{2.49}$$

but there are only four spin-kets (one for $S = 0$ and three for $S = 1$). The situation becomes more dramatic when considering a binuclear $S_1 = S_2 = 5/2$ system, like a Mn(II) dimer. Now the number of molecular states is

$$K = \begin{pmatrix} 20 \\ 10 \end{pmatrix} = 184756 \tag{2.50}$$

The number of the states of a given spin S can be evaluated with the help of the Weyl's formula

$$K_S = \frac{2S+1}{d+1} \begin{pmatrix} d+1 \\ n/2 - S \end{pmatrix} \begin{pmatrix} d+1 \\ n/2 + S + 1 \end{pmatrix} \tag{2.51}$$

where the number of atomic orbitals is $d = 10$ and the number of electrons $n = 10$. The spin Hamiltonian formalism deals only with a single state of each spin what brings totally 36 states. The simplification is tremendous.

As the first strategy, all matrix elements can be evaluated in the basis set of uncoupled spin functions. The basis set is a tensor product expansion of the local spin states:

$$\left|I\right\rangle = \left|S_A, M_A\right\rangle \left|S_B, M_B\right\rangle \ldots \left|S_N, M_N\right\rangle \tag{2.52}$$

and its dimension is $K = (2S_A + 1)^N$. The spin Hamiltonian matrix is

$$\mathbf{H}^{\mathrm{S}} = \mathbf{H}^{\mathrm{iso}} + \mathbf{H}^{\mathrm{Z}} + \mathbf{H}^{\mathrm{anti}} + (\mathbf{H}^{\mathrm{asym}} + \mathbf{H}^{\mathrm{bq}} + \ldots) \tag{2.53}$$

where the individual terms correspond to the isotropic exchange, Zeeman interaction, antisymmetric exchange, asymmetric exchange, biquadratic exchange, and eventual other types of interactions.

The eigenvalues of the spin Hamiltonian are found by solving the secular equation. In fact the variation method is used. This approach is quite general, irrespective of the strong or weak exchange limit and the magnitude of the magnetic field. It has, however, a disadvantage: the matrices may adopt large dimension and they cannot be split into blocks of the reduced dimension unless symmetry considerations are applied.

In parallel to the Cartesian representation of the magnetic tensors their spherical transform bears some advantages since in that case the Wigner–Eckart theorem can be directly applied. The spherical transforms are reviewed in Supplementary material (Table S4).

The expressions for the matrix elements of the exchange interaction operators in the uncoupled basis set are collected in Table 1. Hereafter, the local and pair-interaction vectors, tensors and matrices have the centre as a subscript; in their components the centre is a superscript, e.g. $\bar{\bar{g}}_A$ and $g_{xx}^A = g_x^A$.

We have seen that the matrix elements of the exchange-interaction terms in the local basis set can be expressed in a closed form. All of them can be generated by using the *spin matrices*. These matrices refer either to Cartesian frames, shift-operator form, or the spherical-tensor form and they can be used in constructing all other spin matrices relevant to the exchange (Supplementary material,

Table 1

Matrix elements of the exchange interaction in the local basis set of the uncoupled kets[a].

Operator $\hat{O}$	$\left\langle ...S_A, M'_A, ...S_B, M'_B, ... \middle| \hat{O} \middle| ...S_A, M_A, ...S_B, M_B, ... \right\rangle$
1. Isotropic exchange $\hat{H}_{AB}^{iso} = -J_{AB}\hbar^{-2}(\vec{S}_A \cdot \vec{S}_B)$	$-J_{AB}\{\delta_{M'_A,M_A}\delta_{M'_B,M_B}M_A M_B + \delta_{M'_A,M_A+1}\delta_{M'_B,M_B-1}(1/2)\sqrt{(S_A+M_A+1)(S_A-M_A)}\sqrt{(S_B-M_B+1)(S_B+M_B)}$ $+\delta_{M'_A,M_A-1}\delta_{M'_B,M_B+1}(1/2)\sqrt{(S_A-M_A+1)(S_A+M_A)}\sqrt{(S_B+M_B+1)(S_B-M_B)}\}$
2. Zeeman interaction $\hat{H}_A^Z = \mu_B\hbar^{-1}(\vec{B}\cdot\bar{\bar{g}}_A\cdot\vec{S}_A)$ (diagonal g-tensor)	$\mu_B\{B_z g_z^A \delta_{M'_A,M_A}M_A + (1/2)(B_x g_x^A + iB_y g_y^A)\delta_{M'_A,M_A-1}\sqrt{(S_A-M_A+1)(S_A+M_A)} + (1/2)(B_x g_x^A - iB_y g_y^A)\delta_{M'_A,M_A+1}\sqrt{(S_A+M_A+1)(S_A-M_A)}\}$
3. Antisymmetric exchange $\hat{H}_{AB}^{anti} = \vec{d}_{AB}\cdot(\vec{S}_A\times\vec{S}_B)\hbar^{-2}$	$-i(1/2)\{(d_x^{AB} + id_y^{AB})[\delta_{M'_A,M_A}\delta_{M'_B,M_B-1}M_A\sqrt{(S_B-M_B+1)(S_B+M_B)} - \delta_{M'_A,M_A-1}\delta_{M'_B,M_B}\sqrt{(S_A-M_A+1)(S_A+M_A)}M_B]$ $+d_z^{AB}[\delta_{M'_A,M_A+1}\delta_{M'_B,M_B-1}\sqrt{(S_A+M_A+1)(S_A-M_A)}\sqrt{(S_B-M_B+1)(S_B+M_B)} - \delta_{M'_A,M_A-1}\delta_{M'_B,M_B+1}\sqrt{(S_A-M_A+1)(S_A+M_A)}\sqrt{(S_B+M_B+1)(S_B-M_B)}]$ $-(d_x^{AB} - id_y^{AB})[\delta_{M'_A,M_A+1}\delta_{M'_B,M_B}\sqrt{(S_A+M_A+1)(S_A-M_A)}M_B - \delta_{M'_A,M_A}\delta_{M'_B,M_B+1}M_A\sqrt{(S_B+M_B+1)(S_B-M_B)}]\}$

[a] Asymmetric exchange and biquadratic exchange were omitted as they do not span the scope of this review.

Table S5). The only algebra involves a multiplication of these matrices. As these matrices really are sparse, special (fast) algorithms for their multiplication can be applied.

2.4. Coupled basis set

The coupling represents a unitary transformation among basis-set kets. For more than two constituents several coupling paths exist. Although the matrix elements of the spin Hamiltonian will depend upon the coupling path (upon the intermediate quantum numbers), the final energy levels remain invariant.

The basis set of the uncoupled microstates $\left\{\left|..., S_A, M_A, ...\right\rangle\right\}$ and the molecular states $\left\{\left|S, M\right\rangle\right\}$ are interrelated through an orthogonal transformation:

$$\left\{\left|S, M\right\rangle\right\} = \mathbf{U}\left\{\left|...S_A, M_A...\right\rangle\right\} \tag{2.54}$$

where $\mathbf{U}$ is an orthogonal matrix

$$\mathbf{U}\mathbf{U}^{\mathrm{T}} = \mathbf{I} \tag{2.55}$$

Such a matrix can be generated via an iterative procedure during which the next-generation coupling coefficients are created from the previous-generation coefficients and a new set of the Clebsch–Gordan coefficients.

Having the coupling matrix determined, all the interaction matrices can be transformed from the local basis set into the molecular-state basis, hence

$$\mathbf{H}_{\mathrm{mol}}^{\mathrm{iso}} = \mathbf{U}\mathbf{H}_{\mathrm{loc}}^{\mathrm{iso}}\mathbf{U}^{\mathrm{T}}, \quad \text{[block-diagonal form]} \tag{2.56}$$

$$\mathbf{H}_{\mathrm{mol}}^{\mathrm{Z}} = \mathbf{U}\mathbf{H}_{\mathrm{loc}}^{\mathrm{Z}}\mathbf{U}^{\mathrm{T}} \tag{2.57}$$

$$\mathbf{H}_{\mathrm{mol}}^{\mathrm{anti}} = \mathbf{U}\mathbf{H}_{\mathrm{loc}}^{\mathrm{anti}}\mathbf{U}^{\mathrm{T}} \tag{2.58}$$

Such a transformation may have some advantages. The isotropic exchange matrix in the molecular-state basis adopts a block-diagonal form: only the matrix elements corresponding to the same spin are non-zero:

$$(H_{\mathrm{mol}}^{\mathrm{iso}})_{S',M',S,M} = \left\langle S', M' \middle| \hat{H}^{\mathrm{iso}} \middle| S, M \right\rangle \delta_{S,S'} \tag{2.59}$$

For example, for the $S_A = S_B = S_C = 1/2$ spin system the structure of the isotropic exchange matrix is

$$\mathbf{H}_{\mathrm{mol}}^{\mathrm{iso}} = \left(\begin{array}{c|c:c} S=3/2 & 0 & 0 \\ \hline 0 & S=1/2 & \times \\ \hdashline 0 & \times & S=1/2 \end{array}\right) \tag{2.60}$$

(elements denoted as × are non-zero). Such a blocking meets computational advantages when dealing with a large number of basis-set functions.

The z-component of the Zeeman matrix appears only at the diagonal of the local matrix $\mathbf{H}_{\mathrm{loc}}^{\mathrm{Z}}$. However, after the transformation into the molecular-state basis the off-diagonal elements become non-zero. For small magnetic fields the Zeeman term can be treated as a perturbation and then the second-order perturbation theory can be applied in order to determine the magnetic energy levels:

$$\varepsilon_i(S, M; B) = \varepsilon_{0i}(S, M) + \sum_{j \neq i} \frac{H_{ij}^Z H_{ji}^Z}{\varepsilon_{0i} - \varepsilon_{0j}} \tag{2.61}$$

where the summation (j) runs over a row of the interaction matrix. There is no need for the diagonalization of the high-dimensional matrices and an identification of the van Vleck coefficients is an easy task.

For high-dimensional matrices the time required for the transformation of the interaction matrices from the local into the molecular-state basis set may increase considerably and the procedure loses its advantages. Either the direct diagonalization of the spin Hamiltonian in the local basis set or the irreducible tensor method could be faster.

Three aspects need be clarified as far as the coupling of spins is concerned:

(1) the addition of spins giving rise to a “spin tree”;
(2) the assignment of the tensor ranks for the operators involved;
(3) the evaluation of the matrix elements of the type $\left\langle \text{bra}|\text{operator}|\text{ket}\right\rangle$.

We will consider a consecutive coupling of spins hereafter, i.e., the spin S_2 is added to S_1 yielding $S_{12} \equiv \tilde{S}_2$, then S_3 is added to giving $S_{123} \equiv \tilde{S}_3$, etc. (Notice, alternative ways of coupling are possible.)

The calculation of the intermediate spin quantum numbers is an easy task since there is the following recipe:

$$\left|S_1 - S_2\right| \le \tilde{S}_2 \le S_1 + S_2 \tag{2.62}$$

$$\left|\tilde{S}_2 - S_3\right| \le \tilde{S}_3 \le \tilde{S}_2 + S_3 \tag{2.63}$$

etc. Then the *spin tree* has the form as exemplified by the following case:

Added spin S_n	$S_1 = 1$	$S_2 = 1$	$S_3 = 1$
Intermediate spins $\tilde{S}_n$	1	0	1
	.	1	0
	.	2	1
	.	.	2
	.	.	1
	.	.	2
	.	.	3

It may be of a great advantage to have defined the coupling history vector. During the generation of the spin tree it is not time consuming to do attachments to each final spin the complete set of the intermediate spins.

The complete matrix element $\left\langle \ldots\tilde{S}'_n M' \left| \hat{T}_{k,q} \right| \ldots\tilde{S}_n M\right\rangle$, that involves the projections (M) –Eckart theorem as follows:

$$\begin{aligned}
&\left\langle S_1, S_2, \tilde{S}'_2, \ldots, S_{n-1}, \tilde{S}'_{n-1}, S_n, \tilde{S}'_n, M' \left| \hat{T}_{k,q} \right| S_1, S_2, \tilde{S}_2, \ldots, S_{n-1}, \tilde{S}_{n-1}, S_n, \tilde{S}_n, M \right\rangle \\
&\quad = (-1)^{\tilde{S}'_n - M'} \begin{pmatrix} \tilde{S}'_n & k & \tilde{S}_n \\ -M' & q & M \end{pmatrix} \\
&\quad \times \left\langle S_1, S_2, \tilde{S}'_2, \ldots, S_{n-1}, \tilde{S}'_{n-1}, S_n, \tilde{S}'_n \left\| \hat{T}_k \right\| S_1, S_2, \tilde{S}_2, \ldots, S_{n-1}, \tilde{S}_{n-1}, S_n, \tilde{S}_n \right\rangle
\end{aligned} \tag{2.64}$$

where q is the component of the spherical tensor of rank k occurring in the 3j-symbol. The reduced matrix element $\left\langle \ldots\tilde{S}'_n \left\| \hat{T}_k \right\| \ldots\tilde{S}_n \right\rangle$ no longer depends upon either the components of the bras and kets or the operator (M', q, and M).

The *decoupling formula* is based on the recoupling of the spins when a new spin $\left|S_n\right\rangle$ is added to the previous-generation set $\left|S_1, \ldots, \tilde{S}_{n-1}\right\rangle$ to yield the new-generation set $\left|S_1, \ldots, \tilde{S}_{n-1}, \tilde{S}_n\right\rangle$, i.e.

$$\begin{aligned}
&\left\langle \ldots, \tilde{S}'_{n-1}, \tilde{S}'_n \left\| \hat{T}_{K_n} \right\| \ldots, \tilde{S}_{n-1}, \tilde{S}_n \right\rangle = \left\langle \ldots, \tilde{S}'_{n-1} \left\| \hat{T}_{K_{n-1}} \right\| \ldots, \tilde{S}_{n-1} \right\rangle \\
&\quad \times \left\langle S_n \left\| \hat{T}_{k_n}(\vec{S}_n) \right\| S_n \right\rangle \cdot \left[(2\tilde{S}'_n + 1)(2\tilde{S}_n + 1)(2K_n + 1)\right]^{1/2} \\
&\quad \times \begin{Bmatrix} \tilde{S}'_{n-1} & \tilde{S}_{n-1} & K_{n-1} \\ S'_n & S_n & k_n \\ \tilde{S}'_n & \tilde{S}_n & K_n \end{Bmatrix}
\end{aligned} \tag{2.65}$$

Thus the new-generation reduced matrix element equals to the previous-generation one, times the reduced matrix element for the added spin, times the normalization constant, times the 9j-symbol. The first column in the 9j-symbol contains the quantum numbers of the bra-vector, the second column those of the ket-vector and the third column the tensor ranks of the operator concerned. The reduced matrix element $\left\langle S_n \left\| \hat{T}_{k_n}(\vec{S}_n) \right\| S_n \right\rangle$ for the added spin S_n, depending upon the tensor rank k_n, is calculated via Table S2.

At the beginning of the coupling one has $\left|S_n\right\rangle = \left|S_1\right\rangle$ and the reduced matrix elements are evolved as follows:

bra	ket	reduced matrix element
$\left\langle S_1 \right\|$	$\left\| S_1 \right\rangle$	$\left\langle S_1 \left\| \hat{T}_{k_1} \right\| S_1 \right\rangle$
$\left\langle \tilde{S}'_2 \right\|$	$\left\| \tilde{S}_2 \right\rangle$	$\left\langle S_1, S_2, \tilde{S}'_2 \left\| \hat{T}_{k_2} \right\| S_1, S_2, \tilde{S}_2 \right\rangle$
$\left\langle \tilde{S}'_3 \right\|$	$\left\| \tilde{S}_3 \right\rangle$	$\left\langle S_1, S_2, \tilde{S}'_2, S_3, \tilde{S}'_3 \left\| \hat{T}_{k_3} \right\| S_1, S_2, \tilde{S}_2, S_3, \tilde{S}_3 \right\rangle$

etc. Therefore it is natural to calculate the nth generation matrix element with the help of the $(n-1)$th generation matrix.

The above mentioned ranks of tensor operators need be attached individually for the bilinear spin–spin interaction pairs, components of the Zeeman term and eventually the terms of the asymmetric or antisymmetric exchange.

For the spin–spin interaction pairs one has a simple evolution of the type:

Pair	k_n (centre)					K_n (resulting spin)				
$\hat{T}_k(\vec{S}_i \otimes \vec{S}_j)$	k_1	k_2	k_3	k_4	...	(K_1)	K_2	K_3	K_4	...
$\vec{S}_1 \otimes \vec{S}_2$	1	1	0	0		1	0	0	0	
$\vec{S}_1 \otimes \vec{S}_3$	1	0	1	0		1	1	0	0	
$\vec{S}_2 \otimes \vec{S}_3$	0	1	1	0		0	1	0	0	
$\vec{S}_1 \otimes \vec{S}_4$	1	0	0	1		1	1	1	0	
$\vec{S}_2 \otimes \vec{S}_4$	0	1	0	1		0	1	1	0	
$\vec{S}_3 \otimes \vec{S}_4$	0	0	1	1		0	0	1	0	
etc.					...					...

The lower-case ranks k_n for individual centres are attached in accordance with the pairs in the interaction: $k_i = k_j = 1$ for the interaction $\hat{T}_k(\vec{S}_i \otimes \vec{S}_j)$; the remaining k_n=0 for centres $n \neq i, j$. The result of the interaction (for an isotropic exchange) is a scalar product for which $K_n = 0$. (For antisymmetric exchange the result of the interaction has $K_n = 1$ whereas for the asymmetric exchange $K_n = 2$ belongs to the resulting interaction.)

For the Zeeman term even simpler attachment holds true, i.e.

Pair	k_n (centre)					K_n (resulting spin)				
$\hat{T}_k(\vec{S}_i)$	k_1	k_2	k_3	k_4	...	(K_1)	K_2	K_3	K_4	...
$\vec{S}_1$	1	0	0	0		1	1	1	1	
$\vec{S}_2$	0	1	0	0		0	1	1	1	
$\vec{S}_3$	0	0	1	0		0	0	1	1	
$\vec{S}_4$	0	0	0	1		0	0	0	1	
etc.					...					...

The detailed calculation of the isotropic exchange and Zeeman interaction can be found in Supplementary material.

2.5. Antisymmetric exchange in coupled basis set

a) *Operator expressions*. The antisymmetric exchange operator for a diad (AB) = (12) adopts the form of:

$$\hat{H}^{anti} = \hbar^{-2}[\vec{d}_{AB} \cdot (\vec{S}_A \times \vec{S}_B)] = \hbar^{-2}(\vec{d}_{AB} \cdot \vec{A}_{AB}) \tag{2.66}$$

where $\vec{d}_{AB}(d_x^{AB}, d_y^{AB}, d_z^{AB})$ is the parameter vector and $\vec{A}_{AB}$ the operator part. Remember that the components of the parameter vector are interrelated to the antisymmetric part $\overset{=}{D}{}_{AB}^{(a)}$ of the

Table 2
Matrix elements of the antisymmetric exchange for a general diad[a].

General expression for the type $t=(S';S)$ $H^{anti}_{IJ}(t)_q=(-1)^q(-1)^{S'-M'}\begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix}(-i\sqrt{2})d^{AB}_{1,-q}R^{AB}_{t=(S';S)}\hbar^{-2}$	Parameter set $d^{AB}_{1,\pm 1}=\mp(d^{AB}_x \pm id^{AB}_y)/\sqrt{2}$, $d^{AB}_{1,0}=d^{AB}_z$
Angular part	Radial part
a-type: for $S'=S$, $M'=M, M\pm 1$	
$H(a_-)=\left\langle S(M-1)\left\vert \hat{H}^{anti}\right\vert SM\right\rangle=(-i\sqrt{2})(-1)^{S-(M-1)+1}\begin{pmatrix} S & 1 & S \\ -(M-1) & -1 & M \end{pmatrix}$	$\times 0$
$H(a_0)=\left\langle SM\left\vert \hat{H}^{anti}\right\vert SM\right\rangle=(-i\sqrt{2})(-1)^{S-M}\begin{pmatrix} S & 1 & S \\ -M & 0 & M \end{pmatrix}$	$\times 0$
$H(a_+)=\left\langle S(M+1)\left\vert \hat{H}^{anti}\right\vert SM\right\rangle=(-i\sqrt{2})(-1)^{S-(M+1)+1}\begin{pmatrix} S & 1 & S \\ -(M+1) & +1 & M \end{pmatrix}$	$\times 0$
b-type: for $S'=S-1$, $M'=M, M\pm 1$	
$H(b_-)=\left\langle (S-1)(M-1)\left\vert \hat{H}^{anti}\right\vert SM\right\rangle=(-i\sqrt{2})(-1)^{(S-1)-(M-1)+1}\begin{pmatrix} (S-1) & 1 & S \\ -(M-1) & -1 & M \end{pmatrix}$	$\times d^{AB}_{1,+1}R^{AB}_{S-1;S}\hbar^{-2}$
$H(b_0)=\left\langle (S-1)M\left\vert \hat{H}^{anti}\right\vert SM\right\rangle=(-i\sqrt{2})(-1)^{(S-1)-M}\begin{pmatrix} (S-1) & 1 & S \\ -M & 0 & M \end{pmatrix}$	$\times d^{AB}_{1,0}R^{AB}_{S-1;S}\hbar^{-2}$
$H(b_+)=\left\langle (S-1)(M+1)\left\vert \hat{H}^{anti}\right\vert SM\right\rangle=(-i\sqrt{2})(-1)^{(S-1)-(M+1)+1}\begin{pmatrix} (S-1) & 1 & S \\ -(M+1) & +1 & M \end{pmatrix}$	$\times d^{AB}_{1,-1}R^{AB}_{S-1;S}\hbar^{-2}$
RME, $R^{AB}_{S-1;S}=\left[S(S_A+S_B+S+1)(S_A+S_B-S+1)(S_A-S_B+S)(-S_A+S_B+S)/8\right]^{1/2}\hbar^2$	

[a] The first column is exactly the same as for the Zeeman interaction; only μ_B has been replaced by $(-i\sqrt{2})$. This column should be multiplied by the second one.

exchange coupling tensor as follows

$$\bar{\bar{D}}^{(a)}_{AB}=\begin{pmatrix} 0 & d^{AB}_z & -d^{AB}_y \\ -d^{AB}_z & 0 & d^{AB}_x \\ d^{AB}_y & -d^{AB}_x & 0 \end{pmatrix} \tag{2.67}$$

The scalar product of two vectors can be written in terms of the spherical components as follows:

$$\vec{d}_{AB}\cdot\vec{A}_{AB}=\sum_{q=-1}^{+1}(-1)^q d^{AB}_{1,-q}\hat{A}^{AB}_{1,q}=-d^{AB}_{1,+1}\hat{A}^{AB}_{1,-1}+d^{AB}_{1,0}\hat{A}^{AB}_{1,0}-d^{AB}_{1,-1}\hat{A}^{AB}_{1,+1} \tag{2.68}$$

with the spherical transforms of the parameter set:

$$d^{AB}_{1,\pm 1}=\mp(d^{AB}_x\pm id^{AB}_y)/\sqrt{2},\ d^{AB}_{1,0}=d^{AB}_z \tag{2.69}$$

The members of the cross product can be expressed through the first-rank tensor product:

$$\hat{A}^{AB}_{1,q}=(\vec{S}_A\times\vec{S}_B)_{1,q}=(-i\sqrt{2})\{\hat{T}_{1,q}(\vec{S}_A\otimes\vec{S}_B)\} \tag{2.70}$$

b) *Reduction*. Application of the Wigner–Eckart theorem for the spherical ($q=0,\pm 1$) components yields:

$$\langle\ldots S'M'\left\vert\hat{A}^{AB}_{1,q}\right\vert\ldots SM\rangle=(-i\sqrt{2})(-1)^{S'-M'}\times\begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix}\langle\ldots S'\left\Vert\hat{T}_1(\vec{S}_A\otimes\vec{S}_B)\right\Vert\ldots S\rangle \tag{2.71}$$

Then the matrix elements of the antisymmetric exchange adopt the form of:

$$H^{\text{anti}}_{S'M';SM}=\sum_{q=-1}^{+1}(-1)^q(-1)^{S'-M'}\times\begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix}(-i\sqrt{2})d^{AB}_{1,-q}R^{AB}_{S';S}\hbar^{-2} \tag{2.72}$$

Owing to the restriction for the non-zero $3j$-symbols, namely $M'=M+q$, only one of the three q-terms can contribute. The expressions for the required $3j$-symbols are identical to those entering the Zeeman term.

Table 3
Compact form of the matrix elements of the antisymmetric exchange for a general diad.

Type $H^{anti}_{S',M',S,M}(t)$	Expression
$H^{anti}_{S+1,M-1,S,M}(b_-)$	$=(-id_x+d_y)\frac{1}{4}\left[\frac{(S-M+1)(S-M+2)}{(2S+1)(2S+3)}\right]^{1/2}\times[(S_A+S_B+S+2)(S_A+S_B-S)(S_A-S_B+S+1)(-S_A+S_B+S+1)]^{1/2}$
$H^{anti}_{S+1,M,S,M}(b_0)$	$=-id_z\frac{1}{2}\left[\frac{(S-M+1)(S+M+1)}{(2S+1)(2S+3)}\right]^{1/2}\times[(S_A+S_B+S+2)(S_A+S_B-S)(S_A-S_B+S+1)(-S_A+S_B+S+1)]^{1/2}$
$H^{anti}_{S+1,M+1,S,M}(b_+)$	$=(id_x+d_y)\frac{1}{4}\left[\frac{(S+M+1)(S+M+2)}{(2S+1)(2S+3)}\right]^{1/2}\times[(S_A+S_B+S+2)(S_A+S_B-S)(S_A-S_B+S+1)(-S_A+S_B+S+1)]^{1/2}$
RME, $R^{(12)}_{S+1;S}$	$=\left[(S+1)(S_A+S_B+S+2)(S_A+S_B-S)(S_A-S_B+S+1)(-S_A+S_B+S+1)/8\right]^{1/2}$

Table 4
Symmetry rules for the antisymmetric exchange.

Moriya symmetry rules [2] for a pair AB aligned to the z-axis:
(i) when there is an n-fold axis ($n \geq 2$) along AB (z), $\vec{d}$ is parallel to AB, $d_z \neq 0$;
(ii) when a mirror plane (xy) perpendicular to AB bisects A–B, $\vec{d}$ is parallel to the mirror plane (perpendicular to A–B); $d_x \neq 0$, $d_y \neq 0$;
(iii) when there is a mirror plane (xz) including A and B, $\vec{d}$ is perpendicular to the mirror plane; $d_y \neq 0$;
(iv) when a twofold rotation axis (y) perpendicular to AB passes through the midpoint of AB, $\vec{d}$ is perpendicular to the twofold axis; $d_x \neq 0$, $d_z \neq 0$;
(v) when a centre of inversion is located at the midpoint of A–B, $\vec{d} = 0$.

c) *Decoupling*. The reduced matrix element is decoupled and the 9j-symbol expressed through the 6j-symbol:

$$\begin{aligned} R^{AB}_{S';S} &= \langle S_A S_B S' \| \hat{T}_1(\vec{S}_A \otimes \vec{S}_B) \| S_A S_B S \rangle = \left\langle S_A \left| \hat{T}_1(\vec{S}_A) \right| S_A \right\rangle \\ &\times \left\langle S_B \left| \hat{T}_1(\vec{S}_B) \right| S_B \right\rangle [(2S+1)(2S'+1)(2\cdot 1+1)]^{1/2} \\ &\times \frac{S(S+1) - S'(S'+1)}{2[1\cdot 2\cdot 3\cdot S_A(S_A+1)(2S_A+1)]^{1/2}} (-1)^{S'+S_B+1+S_A} \\ &\times \begin{Bmatrix} S & S' & 1 \\ S_B & S_B & S_A \end{Bmatrix} \end{aligned} \qquad (2.73)$$

For $S' = S$ this vanishes; consequently the a-type reduced matrix elements are exactly equal to the zero. The only non-zero case results from the triangular conditions for the 6j-symbol and the reduced matrix element of the b-type survives. The final formulae are collected in Tables 2 and 3.

The antisymmetric exchange has a vector nature and thus it vanishes exactly when the molecule (crystal) contains an inversion centre. Therefore it is not realistic accounting for it in the homospin diads with inversion centre (unless the centers possess a very different coordination sphere). However, for the heterospin diads (heterometallic dinuclear complexes) it appears as a natural contribution that accounts for the inequivalence of the magnetic centers. Some other symmetry considerations are embraced in the *Moriya symmetry rules* (Table 4).

The antisymmetric exchange operator appropriate to a trinuclear system adopts the form of:

$$\begin{aligned} \hat{H}^{anti} &= \hbar^{-2}[\vec{d}_{12}\cdot(\vec{S}_1 \times \vec{S}_2) + \vec{d}_{13}\cdot(\vec{S}_1 \times \vec{S}_3) + \vec{d}_{23}\cdot(\vec{S}_2 \times \vec{S}_3)] \\ &= \hbar^{-2}\sum_{A}^{3}\sum_{A<B}^{3}\vec{d}_{AB}\cdot(\vec{S}_A \times \vec{S}_B) = \hbar^{-2}\sum_{A}^{3}\sum_{A<B}^{3}(\vec{d}_{AB}\cdot\vec{A}_{AB}) \end{aligned} \qquad (2.74)$$

Using the above methodology the matrix elements of the antisymmetric exchange become reduced as:

$$\begin{aligned} H^{\text{anti}}_{S'_{12}S'M';S_{12}SM} &= \sum_{A}^{3}\sum_{B<A}^{3}\sum_{q=-1}^{+1}(-1)^{q}(-1)^{S'-M'} \\ &\times \begin{pmatrix} S' & 1 & S \\ -M' & q & M \end{pmatrix} (-i\sqrt{2}) d^{AB}_{1,-q} R^{AB}_{S'_{12}S';S_{12}S} \hbar^{-2} \end{aligned} \qquad (2.75)$$

Owing to the restriction for the non-zero 3j-symbols, namely $M' = M + q$, only one of the three q-terms can contribute. The expressions for the required 3j-symbols are identical to those entering the Zeeman term. The reduced matrix elements:

$$R^{AB}_{S'_{12}S';S_{12}S} = \left\langle S_1 S_2 S'_{12} S_3 S' \left\| \hat{T}_1(\vec{S}_A \otimes \vec{S}_B) \right\| S_1 S_2 S_{12} S_3 S \right\rangle \qquad (2.76)$$

are evaluated according to the general decoupling formula. A simplification is obtained when the 9j-symbols are further manipulated by utilizing special formulae resulting only in the 6j-symbols (Supplementary material, Table S14).

The triangular restriction for the 6j-symbol implies that $S' = S, S \pm 1$ and $S'_{12} = S_{12}, S_{12} \pm 1$ should be fulfilled. A further restriction follows from the expansion of the 9j-symbols containing three ones. Consequently the reduced matrix elements can fill only the places according to the recipe

Total spin	Intermediate spin	Reduced matrix elements	
$S' = S$	$S'_{12} = S_{12}$	0	b
	$S'_{12} = S_{12} - 1$	b	0
$S' = S - 1$	$S'_{12} = S_{12}$	c	d
	$S'_{12} = S_{12} - 1$	d	c

It can be concluded that the matrix elements of the antisymmetric matrix closely follow those for the Zeeman operator. The complete formulae for the matrix elements are listed in Supplementary material (Tables S15, S16).

3. Modeling of dinuclear spin systems

For the $S_A = S_B = 1/2$ system the structure of the antisymmetric exchange matrix is

$$\mathbf{H}^{\text{anti}} = \left(\begin{array}{c|ccc} 0 & (1/\sqrt{8})E^{*} & (-1/2)C^{*} & (1/\sqrt{8})D^{*} \\ \hline (1/\sqrt{8})E & 0 & 0 & 0 \\ (-1/2)C & 0 & 0 & 0 \\ (1/\sqrt{8})D & 0 & 0 & 0 \end{array}\right) \qquad (3.1)$$

with parameters $C \equiv id_z$, $D \equiv +id_x + d_y$, $E \equiv -id_x + d_y$. This bears some analogy with the Zeeman interaction matrix:

$$\mathbf{H}^{Z} = \mu_{B}\left(\begin{array}{c|ccc} 0 & (1/\sqrt{8})e^{*} & (1/2)c & (1/\sqrt{8})d^{*} \\ \hline (1/\sqrt{8})e & -a & (1/\sqrt{2})b^{*} & 0 \\ (1/2)c & (1/\sqrt{2})b & 0 & (1/\sqrt{2})b^{*} \\ (1/\sqrt{8})d & 0 & (1/\sqrt{2})b & a \end{array}\right) \qquad (3.2)$$

where the following parameters occur: $\bar{\bar{g}}' = \bar{\bar{g}}_A - \bar{\bar{g}}_B \neq 0$, $a = g_z B_z$, $b = g_x B_x - i g_y B_y$, $c = g'_z B_z$, $d = -g'_x B_x + i g'_y B_y$, and $e = g'_x B_x + i g'_y B_y$. The complete interaction matrix becomes expressed as:

$$\mathbf{H} = \left(\begin{array}{c|ccc} 0 & * & * & * \\ \hline (1/\sqrt{8})(E+\mu_B e) & -J-\mu_B a & * & 0 \\ (1/2)(-C+\mu_B c) & (1/\sqrt{2})\mu_B b & -J & * \\ (1/\sqrt{8})(D+\mu_B d) & 0 & (1/\sqrt{2})\mu_B b & -J+\mu_B a \end{array}\right) \qquad (3.3)$$

where the stars denote Hermitian adjoint.

In the zero magnetic field, the exact eigenvalues of the ASE matrix are

$$-J,\ -J,\ \frac{[-J-(d_x^2+d_y^2+d_z^2+J^2)^{1/2}]}{2},\ \frac{[-J+(d_x^2+d_y^2+d_z^2+J^2)^{1/2}]}{2} \qquad (3.4)$$

and this justifies that the ASE manifests itself as a kind of the zero-field splitting. The ASE components cause an opening of the zero-field energy gap Δ for the triplet state. While two components stay doubly degenerate, the third component (that defines the energy gap) increases with increasing $|d/J|$.

Approximate energy levels can be obtained under the assumption:

$$J^2 \gg d^2 = d_x^2 + d_y^2 + d_z^2 \qquad (3.5)$$

by expanding the square root as follows:

$$[-J-(d_x^2+d_y^2+d_z^2+J^2)^{1/2}]/2 = -J[1+\sqrt{1+\left(\frac{d^2}{J^2}\right)}]/2 \doteq -\frac{J-d^2}{4J} \qquad (3.6)$$

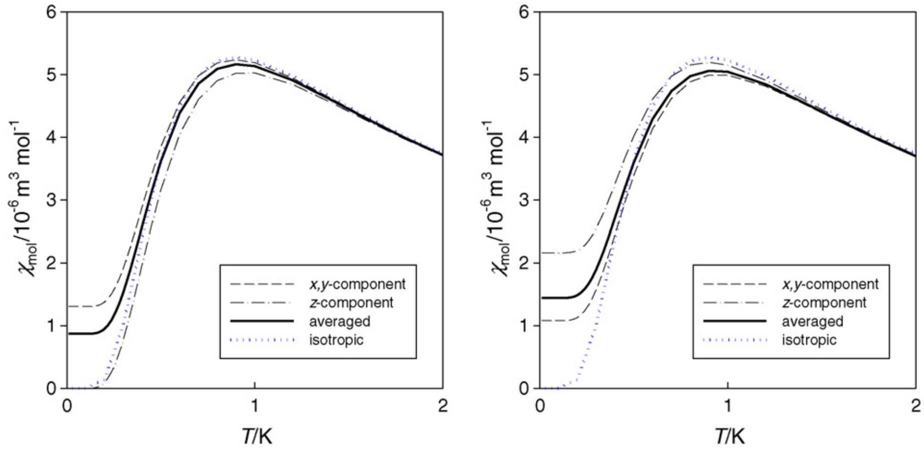

Fig. 2. Susceptibility components for $S_A = S_B = 1/2$ system with $J/hc = -1\,{\rm cm}^{-1}$ and ASE components: left—parallel ASE component $d_z/hc = 0.5\,{\rm cm}^{-1}$; right—perpendicular ASE components $d_x/hc = d_y/hc = 0.5\,{\rm cm}^{-1}$.

$$\frac{[-J + (d_x^2 + d_y^2 + d_z^2 + J^2)^{1/2}]}{2} = -J\left[\frac{1-\sqrt{1+(d^2/J^2)}}{2}\right] \doteq +\frac{d^2}{4J} \qquad (3.7)$$

and this rationalizes why the energy gap raises quadratically with d irrespective of the particular components $\{d_x, d_y, d_z\}$.

A modeling for antiferromagnetic exchange ($J < 0$) and non-zero parallel component d_z yields the averaged magnetic susceptibility which to a low–temperature limit is weakly positive; the z-susceptibility turns to the zero (Fig. 2). This reflects that the d_z component mixes only the non-magnetic states $|0,0\rangle$ and $|1,0\rangle$

$$\mathbf{H}(z) = \left(\begin{array}{c:ccc} 0 & 0 & * & 0 \\ \hdashline 0 & -J - \mu_{\rm B} g_z B_z & 0 & 0 \\ (1/2)(-{\rm i}d_z + \mu_{\rm B} g'_z B_z) & 0 & -J & 0 \\ 0 & 0 & 0 & -J + \mu_{\rm B} g_z B_z \end{array}\right) \qquad (3.8)$$

owing to which the z-component of the susceptibility is zero at $T \to 0$.

The $\{x, y\}$-components of the susceptibility reflect the mixing of $|0,0\rangle$, $|1,0\rangle$ and $|1,\pm1\rangle$ states due to the combined effect of the Zeeman and ASE terms

$$\mathbf{H}(x,y) = \left(\begin{array}{c:ccc} 0 & * & * & * \\ \hdashline (1/\sqrt{8})\mu_{\rm B}(g'_x B_x + {\rm i}g'_y B_y) & -J & * & 0 \\ (1/2)(-{\rm i}d_z) & (1/\sqrt{2})\mu_{\rm B}(g_x B_x - {\rm i}g_y B_y) & -J & * \\ (1/\sqrt{8})\mu_{\rm B}(-g'_x B_x + {\rm i}g'_y B_y) & 0 & (1/\sqrt{2})\mu_{\rm B}(g_x B_x - {\rm i}g_y B_y) & -J \end{array}\right) \qquad (3.9)$$

owing to which they are finite at $T \to 0$. Consequently the averaged susceptibility is non-zero in the limit of $T \to 0$.

For perpendicular ASE $\{d_x, d_y\}$ the interaction matrix for the magnetic field in the z-direction reads

$$\mathbf{H}(z) = \left(\begin{array}{c:ccc} 0 & * & * & * \\ \hdashline (1/\sqrt{8})(-{\rm i}d_x + d_y) & -J - \mu_{\rm B} g_z B_z & 0 & 0 \\ (1/2)(\mu_{\rm B} g'_z B_z) & 0 & -J & 0 \\ (1/\sqrt{8})(+{\rm i}d_x + d_y) & 0 & 0 & -J + \mu_{\rm B} g_z B_z \end{array}\right) \qquad (3.10)$$

and owing to the mixing of $|0,0\rangle$, $|1,0\rangle$ and $|1,\pm1\rangle$ states the ground state is magnetic and the z-susceptibility is non-zero in the limit of $T \to 0$. Consequently, the averaged susceptibility on temperature lowering approaches a non-zero limit.

As a second example, for the $S_A = S_B = 1$ system the structure of the antisymmetric exchange matrix is given by (1.3). This matrix again resembles the structure of the Zeeman matrix except the a-type elements (diagonal in S) which vanish exactly. The angular part is identical to that met for the Zeeman interaction. The radial part involves the reduced matrix elements and the parameter set

$$H_q^{\rm radial} = d_{1,q}^{AB}\left(\begin{array}{c:c:c} 0 & * & * \\ \hdashline R_{1;0}^{AB} & 0 & * \\ \hdashline 0 & R_{2;1}^{AB} & 0 \end{array}\right) = d_{1,q}^{AB}\left(\begin{array}{c:c:c} 0 & * & * \\ \hdashline 1 & 0 & * \\ \hdashline 0 & \sqrt{5} & 0 \end{array}\right) \qquad (3.11)$$

so that for the parameter vector $\vec{d}(d_x, d_y, d_z)$ with its spherical transforms, $d_{1,0} = d_z$ and $d_{1,\pm1} = \mp(d_x \pm id_y)/\sqrt{2}$, we get

$$\mathbf{H}^{\rm anti} = (-{\rm i}\sqrt{2})\left(\begin{array}{c:ccc:ccccc} 0 & * & * & * & . & . & . & . & . \\ \hdashline (-1/\sqrt{3})d_{1,+1} & . & . & . & * & * & * & . & . \\ (+1/\sqrt{3})d_{1,0} & . & . & . & . & * & * & * & . \\ (-1/\sqrt{3})d_{1,-1} & . & . & . & . & . & * & * & * \\ \hdashline . & -d_{1,+1} & . & . & . & . & . & . & . \\ . & (+1/\sqrt{2})d_{1,0} & (-1/\sqrt{2})d_{1,+1} & . & . & . & . & . & . \\ . & (-1/\sqrt{6})d_{1,-1} & (+\sqrt{2/3})d_{1,0} & (-1/\sqrt{6})d_{1,+1} & . & . & . & . & . \\ . & . & (-1/\sqrt{2})d_{1,-1} & (+1/\sqrt{2})d_{1,0} & . & . & . & . & . \\ . & . & . & -d_{1,-1} & . & . & . & . & . \end{array}\right) \qquad (3.12)$$

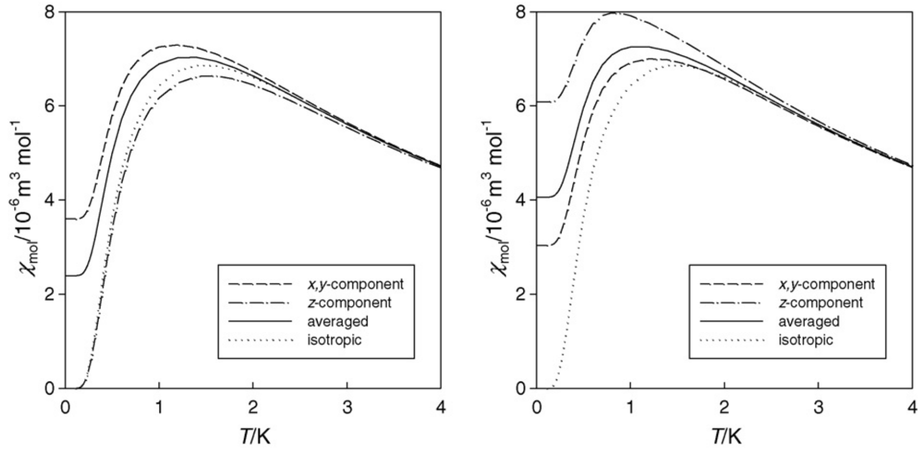

Fig. 3. Susceptibility components for $S_A = S_B = 1$ system with $J/hc = -1\ \text{cm}^{-1}$ and ASE components: left—parallel ASE component $d_z/hc = 0.5\ \text{cm}^{-1}$; right—perpendicular ASE components $d_x/hc = d_y/hc = 0.5\ \text{cm}^{-1}$.

Using substitutions $a \equiv id_z$, $b \equiv +id_x + d_y$, $c \equiv -id_x + d_y = b^*$ we finally obtain

$$\mathbf{H}^{\text{anti}} = \left(\begin{array}{c|ccc|ccccc} 0 & * & * & * & 0 & 0 & 0 & 0 & 0 \\ \hline (1/\sqrt{3})c & 0 & 0 & 0 & * & * & * & 0 & 0 \\ (-\sqrt{2/3})a & 0 & 0 & 0 & 0 & * & * & * & 0 \\ (1/\sqrt{3})b & 0 & 0 & 0 & 0 & 0 & * & * & * \\ \hline 0 & c & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -a & (1/\sqrt{2})c & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & (1/\sqrt{6})b & (-2/\sqrt{3})a & (1/\sqrt{6})c & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & (1/\sqrt{2})b & -a & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & b & 0 & 0 & 0 & 0 & 0 \end{array}\right) \quad (3.13)$$

A modeling in Fig. 3 shows that the averaged susceptibility on temperature lowering converges to a non-zero limit.

For $S_A = 1/2, S_B = 1$ and $a \equiv id_z$, $b \equiv +id_x + d_y$, $c \equiv -id_x + d_y = b^*$ we get the interaction matrix in the form

$$\mathbf{H}^{\text{anti}} = \left(\begin{array}{cc|cccc} 0 & 0 & * & * & * & 0 \\ 0 & 0 & 0 & * & * & * \\ \hline (\sqrt{3/8})c & 0 & 0 & 0 & 0 & 0 \\ (-1/\sqrt{2})a & (1/\sqrt{8})c & 0 & 0 & 0 & 0 \\ (1/\sqrt{8})b & (-1/\sqrt{2})a & 0 & 0 & 0 & 0 \\ 0 & (\sqrt{3/8})b & 0 & 0 & 0 & 0 \end{array}\right) \quad (3.14)$$

A modeling shows (Fig. 4) that in this case the ASE brings only a small anisotropy that is quantitatively irrelevant.

For the general case of $s = S_A = S_B$, the antisymmetric exchange matrix has the following structure

$$\mathbf{H}^{\text{anti}} = \left(\begin{array}{c|ccc|c} . & * & * & * & . \\ \hline b_- & . & . & . & \cdots \\ b_0 & . & . & . & \cdots \\ b_+ & . & . & . & \cdots \\ \hline . & \cdots & \cdots & \cdots & \cdots \end{array}\right), \text{ for kets } \left[\begin{array}{c} |0,0\rangle \\ \hline |1,-1\rangle \\ |1,0\rangle \\ |1,+1\rangle \\ \hline \cdots \end{array}\right] \quad (3.15)$$

In the strong exchange limit ($J \ll 0$) we can restrict ourselves only to the ground singlet and the first excited triplet. Then

$$R^{AB}_{S+1;S}\Big|_{S=0}\hbar^{-2} = \left[\frac{s(s+1)}{2}\right]^{1/2} \quad (3.16)$$

giving rise to

$$\mathbf{H}^{\text{anti}} = (-i\sqrt{2})\left(\begin{array}{c|ccc} 0 & * & * & * \\ \hline -(1/\sqrt{3})d_{1,+1} & 0 & 0 & 0 \\ +(1/\sqrt{3})d_{1,0} & 0 & 0 & 0 \\ -(1/\sqrt{3})d_{1,-1} & 0 & 0 & 0 \end{array}\right)\left[s(s+1)/2\right]^{1/2} \quad (3.17)$$

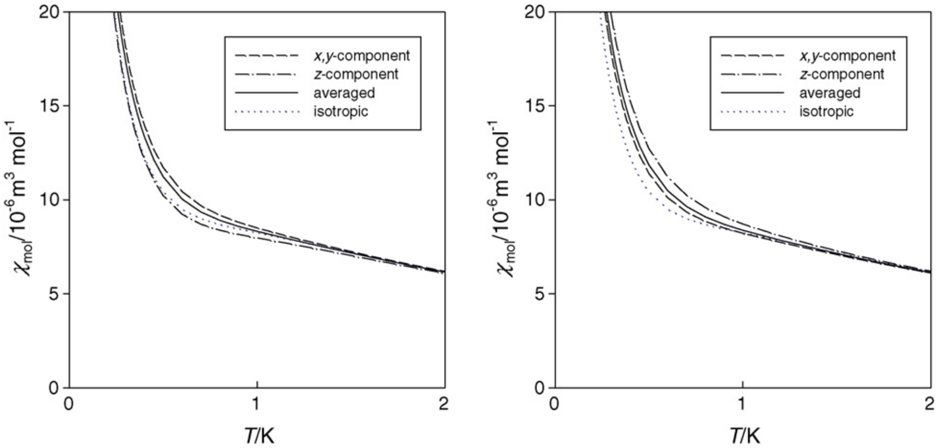

Fig. 4. Susceptibility components for $S_A = 1/2$ and $S_B = 1$ system with $J/hc = -1\ \text{cm}^{-1}$ and ASE components: left—parallel ASE component $d_z/hc = 0.5\ \text{cm}^{-1}$; right—perpendicular ASE components $d_x/hc = d_y/hc = 0.5\ \text{cm}^{-1}$.

so that the zero-field exchange matrix is

$$\mathbf{H}^{\text{iso}}+\mathbf{H}^{\text{anti}}=\left(\begin{array}{c|ccc} 0 & * & * & * \\ \hdashline -\mathrm{i}[(d_x-\mathrm{i}d_y)/\sqrt{2}][s(s+1)/3]^{1/2} & -J & 0 & 0 \\ -\mathrm{i}d_z\,[s(s+1)/3]^{1/2} & 0 & -J & 0 \\ +\mathrm{i}[(d_x-\mathrm{i}d_y)/\sqrt{2}][s(s+1)/3]^{1/2} & 0 & 0 & -J \end{array}\right) \tag{3.18}$$

with the factors for the individual spins between $s = 1/2$ and $5/2$

$$\left[s(s+1)/3\right]^{1/2}=\begin{cases} 1/2 \\ \sqrt{2/3} \\ \sqrt{5}/2 \\ \sqrt{2} \\ \sqrt{35/3}/2 \end{cases} \tag{3.19}$$

In the zero magnetic field, the exact eigenvalues of the ASE matrix are

$$-J,\ -J,\ \frac{\{-J-[4d^2s(s+1)/3+J^2]^{1/2}\}}{2},\ \frac{\{-J+[4d^2s(s+1)/3+J^2]^{1/2}\}}{2} \tag{3.20}$$

Approximate energy levels can be obtained under the assumption $J^2 \gg d^2 = d_x^2 + d_y^2 + d_z^2$, by expanding the square root as follows

$$\frac{[-J-\sqrt{4d^2s(s+1)/3+J^2}]}{2} \doteq -J-\frac{[d^2s(s+1)/3]}{J} \tag{3.21}$$

$$\frac{[-J+\sqrt{4d^2s(s+1)/3+J^2}]}{2} \doteq \frac{+[d^2s(s+1)/3]}{J} \tag{3.22}$$

The results of extensive modeling are given in Tables A1–A5. The effect of the antisymmetric exchange is investigated for the reduced parameter $kT/|J|$ and a different ratio of the magnetic parameters $|d_z/J|$, and $|d_x/J| = |d_y/J|$. For two signs of the isotropic coupling constant we arrive at four panels for which the zero-field magnetic susceptibility and the lowest energy levels are mapped. In order to get an appropriate scale of energy levels, they were plotted in units of $|J|/\Delta S$, where $\Delta S = (1/2)[S_{\max}(S_{\max}+1) - S_{\min}(S_{\min}+1)]$ stands for the band width; this provides that the zero-field energy levels normalized in such a way vary between 0 and 1.

It is noted that the primary effect of the antisymmetric exchange is an opening of the energy gap for the spin multiplets with $S \geq 1$, so that the ASE refers to a kind of the zero-field splitting. The opening of the energy gap Δ is well seen for higher ratio $|d/J| \sim 0.4$. The effect of the ASE for the averaged magnetic susceptibility at low temperature (LT) is different for the cases of the antiferromagnetic/ferromagnetic exchange:

1. For the antiferromagnetic exchange the LT-susceptibility is always higher relative to the isotropic exchange because the magnetoactive states $\left|S, M_S\right\rangle$ are admixed to the ground state $\left|0, 0\right\rangle$.
2. With the ferromagnetic exchange the energy level diagram is inverted and the LT-susceptibility is always lower relative to the isotropic exchange; this reflects an admixture of the magnetically less productive states to the ground state $\left|S, S\right\rangle$. The suppression of the susceptibility causes that instead of an LT plateau the χT product function drops down.
3. All these effects progressively increase with increasing ratio $|d/J|$.

Each spin diad was investigated in a strong-negative ($J/hc = -50\,\text{cm}^{-1}$) and strong-positive ($J/hc = +50\,\text{cm}^{-1}$) limit for two sets of parameters: parallel component $d_z/hc = 20\,\text{cm}^{-1}$, and/or perpendicular component $d_x/hc = d_y/hc = 20\,\text{cm}^{-1}$, using $g_{\text{iso}} = 2.0$. The energy levels, zero-field magnetic susceptibility and its components, product function χT and its components, as well as the isothermal magnetization ($T = 2.0\,\text{K}$) and its components are presented in Tables A6–A10. The principal observations are discussed below. It need be mentioned that in the weak exchange limit ($|J/hc| \sim 1\,\text{cm}^{-1}$) the energy levels "interact" expressively and are heavily influenced by the Zeeman terms; there are manifold avoided level crossings when $|d/J| \gg 0$.

3.1.1. *Observations for $S_A = S_B = 1/2$ (Table A6)*

a) For the antiferromagnetic exchange coupling, $J < 0$, and $d_z \neq 0$:
   - the d_z component of the ASE mixes the non-magnetic states $\left|0, 0\right\rangle$ and $\left|1, 0\right\rangle$ states owing to which the z-component of the susceptibility is zero at $T \to 0$;
   - with non-zero d_z, the perpendicular Zeeman term $\{B_x, B_y\}$ mixes all $\left|0, 0\right\rangle$, $\left|1, 0\right\rangle$ and $\left|1, \pm 1\right\rangle$ spin-states owing to which the $\{\chi_x, \chi_y\}$-components approach a non-zero limit on $T \to 0$;
   - averaged magnetic susceptibility to a low-temperature limit is weakly positive;
   - on temperature lowering, all components of the product function χT approach zero;
   - the parallel d_z-component of ASE (aligned along the A–B linkage) produces slight, almost invisible anisotropy of χT; the admixture of the excited triplet state to the ground singlet causes, that as $T \to 0$ the averaged χT is *above* the isotropic curve;
   - the magnetization anisotropy is oddly detectable for the given set of parameters; the averaged magnetization is higher that that for the isotropic exchange.

b) For the antiferromagnetic exchange coupling, $J < 0$, and $d_x = d_y \neq 0$:
   - with non-zero $\{d_x, d_y\}$, the ground state is no longer diamagnetic since the ASE admixes triplet components $\left|1, \pm 1\right\rangle$ to the diamagnetic state $\left|0, 0\right\rangle$ also in the B_z-direction;
   - on $T \to 0$ all susceptibility components approach a non-zero limit;
   - there is almost invisible anisotropy of the product function χT; however on $T \to 0$ the averaged χT value is *above* the isotropic curve;
   - the magnetization anisotropy is resolved at 2 K and the averaged magnetization lies above the isotropic-exchange curve.
   - In summary, the effect of ASE for most applications could be ignored for an antiferromagnetically coupled pair, except in the LT region.

c) For the ferromagnetic exchange coupling, $J > 0$, and $d_z \neq 0$:
   - the parallel d_z-component of ASE produces visible anisotropy of the susceptibility and the product function;
   - the z-component of χ passes through a maximum and then turns to the zero as $T \to 0$;
   - on temperature lowering the averaged χT starts to depart from the isotropic-exchange curve, it passes through a maximum and then drops down;
   - the z-component of χT is *below* the averaged χT and the $\{x, y\}$-component lies above it;
   - the magnetization anisotropy can be resolved at 2 K for the given set of parameters; however for a weaker isotropic exchange ($J/hc = +10\,\text{cm}^{-1}$) and the same ratio $|d/J| = 0.4$ the magnetization components are not resolved.

d) For the ferromagnetic exchange coupling, $J > 0$, and $d_x = d_y \neq 0$:
   - the z-component of the susceptibility is greater than the x-component; both approach a constant limit on $T \to 0$;
   - the z-component of the χT product function is *above* the averaged χT while the $\{x, y\}$-components are below it;
   - the magnetization anisotropy can be resolved at 2 K for the given set of parameters.

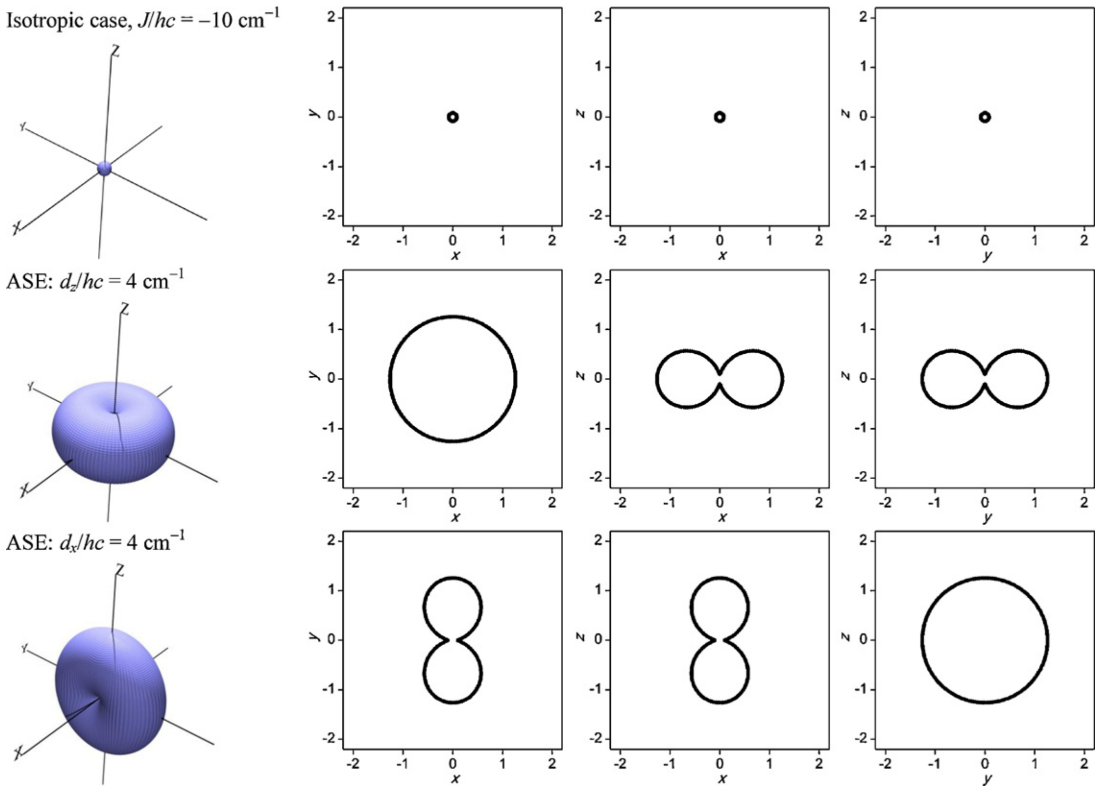

Fig. 5. Magnetization for $s = 5/2$ diad in various field directions ($T = 2.0$ K, $B = 6$ T); effect of the single ASE component. Appearance of the easy plane (*xy* or *yz*) perpendicular to the ASE component (d_z or d_x); equivalent to the retention of the magnetization in the direction of the ASE component (hard axis).

In summary, the effect of ASE cannot be ignored for ferromagnetically coupled pair (however, the existence of the centre of inversion excludes its presence).

3.1.2. Observations for $S_A = S_B \geq 1$ (Tables A7–A10)

The observations are qualitatively analogous to those found for the $S_i = 1/2$ diads. This is due to the fact that for the antiferromagnetic coupling the ground state is $S = 0$ followed by the $S = 1$, etc. However, the quantitative aspects are much more enhanced: the magnetic anisotropy is better resolved for the components of the susceptibility, components of the product function, as well as for the components of the magnetization. The enhancement of the anisotropy rises progressively with the increasing spin.

The development of the magnetization in an arbitrary field direction is visualized *via* three-dimensional diagrams (and their two-dimensional cuts) in Figs. 5–7. It can be concluded that the magnetization exhibits retention ("a hole") just in the direction of the ASE components. Thus the hard axis of magnetization coincides with the ASE vector $\vec{d} = (d_x, d_y, d_z)$ in dinuclear spin systems.

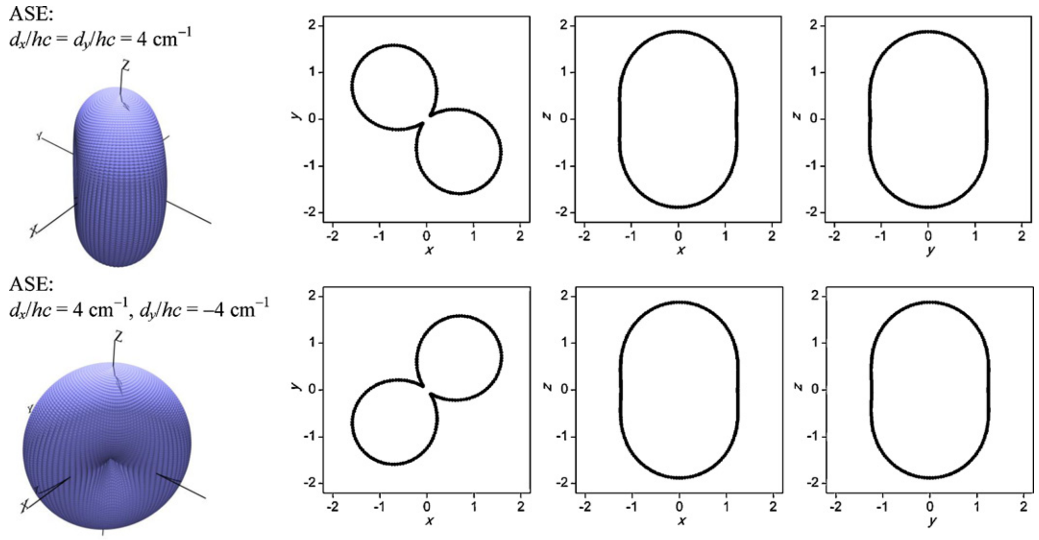

Fig. 6. Magnetization for $s = 5/2$ diad in various field directions ($T = 2.0$ K, $B = 6$ T); effect of the perpendicular ASE components. Retention of the magnetization in the direction of the ASE components ($\{x,y\}$ or $\{x,-y\}$). Easy axis—*z*.

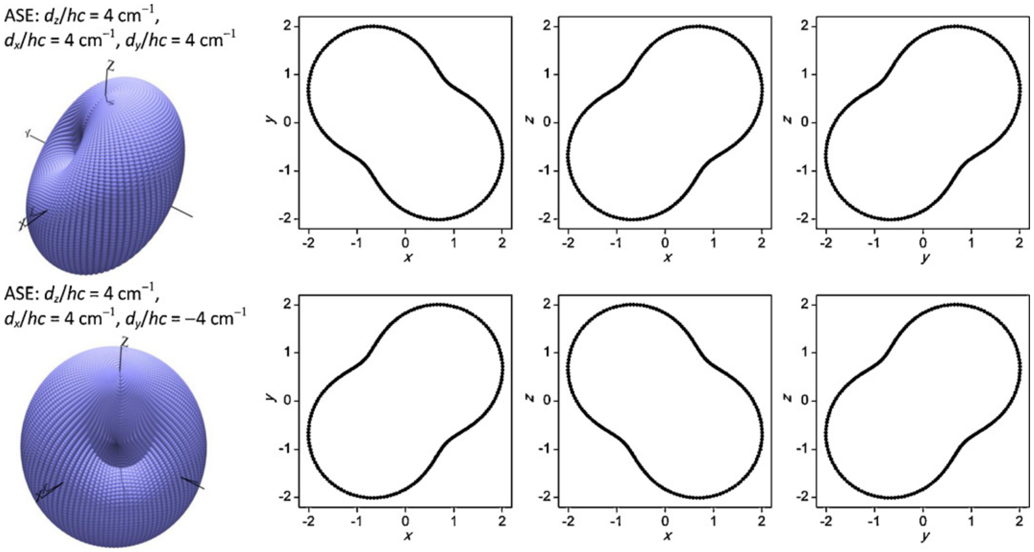

Fig. 7. Magnetization for $s = 5/2$ diad in various field directions ($T = 2.0$ K, $B = 6$ T); effect of three ASE components. Retention of the magnetization in the direction of the ASE components ($\{x,y,z\}$ or $\{x,-y,z\}$).

4. Modeling of trinuclear spin systems

As an example, for the $S_1 = S_2 = S_3 = 1/2$ triad the structure of the antisymmetric exchange matrix is

$$\mathbf{H}^{\mathrm{anti}} = \left(\begin{array}{cccc|cc:cc} 0 & . & . & . & * & . & * & . \\ . & 0 & . & . & * & * & * & * \\ . & . & 0 & . & * & * & * & * \\ . & . & . & 0 & . & * & . & * \\ \hline \mathrm{c}_+ & \mathrm{c}_0 & \mathrm{c}_- & . & 0 & . & * & * \\ . & \mathrm{c}_+ & \mathrm{c}_0 & \mathrm{c}_- & . & 0 & * & * \\ \hdashline \mathrm{d}_+ & \mathrm{d}_0 & \mathrm{d}_- & . & \mathrm{b}_0 & \mathrm{b}_- & 0 & . \\ . & \mathrm{d}_+ & \mathrm{d}_0 & \mathrm{d}_- & \mathrm{b}_+ & \mathrm{b}_0 & . & 0 \end{array}\right) \text{ for kets } \left[\begin{array}{lll} S_{12} = 1 & S = 3/2 & M = -3/2 \\ & & M = -1/2 \\ & & M = +1/2 \\ & & M = +3/2 \\ \hline S_{12} = 1 & S = 1/2 & M = -1/2 \\ & & M = +1/2 \\ \hdashline S_{12} = 0 & S = 1/2 & M = -1/2 \\ & & M = +1/2 \end{array}\right] \tag{4.1}$$

The letters indicate the type of the reduced matrix element (common within a block); the subscripts ($q = 0, \pm 1$) indicate different angular parts (different 3j – symbols) owing to the application of the Wigner–Eckart theorem. The angular part of the interaction matrix is identical to those met for the Zeeman interaction. The reduced matrix elements evaluated for each pair

$$R^{AB} = \left(\begin{array}{c|c:c} R^{AB}_{S_{12},S;S_{12},S} & * & * \\ \hline R^{AB}_{S_{12},S-1;S_{12},S} & R^{AB}_{S_{12},S-1;S_{12},S-1} & * \\ \hdashline R^{AB}_{S_{12}-1,S-1;S_{12},S} & R^{AB}_{S_{12}-1,S-1;S_{12},S-1} & R^{AB}_{S_{12}-1,S-1;S_{12}-1,S-1} \end{array}\right) \tag{4.2}$$

gave the radial part of the interaction matrix

$$\mathbf{H}_q^{\mathrm{radial}} = (-\mathrm{i}\sqrt{2})\left[d_{1,q}^{(12)} \left(\begin{array}{c|c:c} 0 & * & * \\ \hline 0 & 0 & * \\ \hdashline 1/\sqrt{2} & 1/2 & 0 \end{array}\right) + d_{1,q}^{(13)} \left(\begin{array}{c|c:c} 0 & * & * \\ \hline \sqrt{3/8} & 0 & * \\ \hdashline 1/\sqrt{8} & -1/2 & 0 \end{array}\right) + d_{1,q}^{(23)} \left(\begin{array}{c|c:c} 0 & * & * \\ \hline \sqrt{3/8} & 0 & * \\ \hdashline -1/\sqrt{8} & 1/2 & 0 \end{array}\right)\right] \tag{4.3}$$

which finally yields

$$\mathbf{H}^{\mathrm{anti}} = (-\mathrm{i}\sqrt{2})\left(\begin{array}{cccc|cc:cc} 0 & . & . & . & * & . & * & . \\ . & 0 & . & . & * & * & * & * \\ . & . & 0 & . & * & * & * & * \\ . & . & . & 0 & . & * & . & * \\ \hline (-1/2)c_{-1} & (-1/\sqrt{6})c_0 & (-1/2\sqrt{3})c_{+1} & . & 0 & . & * & * \\ . & (-1/2\sqrt{3})c_{-1} & (-1/\sqrt{6})c_0 & (-1/2)c_{+1} & . & 0 & * & * \\ \hdashline (-1/2)d_{-1} & (-1/\sqrt{6})d_0 & (-1/2\sqrt{3})d_{+1} & . & (-1/\sqrt{6})b_0 & (-1/\sqrt{3})b_{+1} & 0 & . \\ . & (-1/2\sqrt{3})d_{-1} & (-1/\sqrt{6})d_0 & (-1/2)d_{+1} & (+1/\sqrt{3})b_{-1} & (1/\sqrt{6})b_0 & . & 0 \end{array}\right) \tag{4.4}$$

with parameters of pair-interactions

$$b_q = (1/2)d_{1,q}^{(12)} + (-1/2)d_{1,q}^{(13)} + (1/2)d_{1,q}^{(23)} \tag{4.5}$$

$$c_q = (0)d_{1,q}^{(12)} + (\sqrt{3/8})d_{1,q}^{(13)} + (\sqrt{3/8})d_{1,q}^{(23)} \tag{4.6}$$

$$d_q = (1/\sqrt{2})d_{1,q}^{(12)} + (1/\sqrt{8})d_{1,q}^{(13)} + (-1/\sqrt{8})d_{1,q}^{(23)} \tag{4.7}$$

In the general case the matrix elements of ASE contain 3 × 3 = 9 (spherical, shift-operator, or Cartesian) parameters $d_{1,q}^{AB}$. Some of

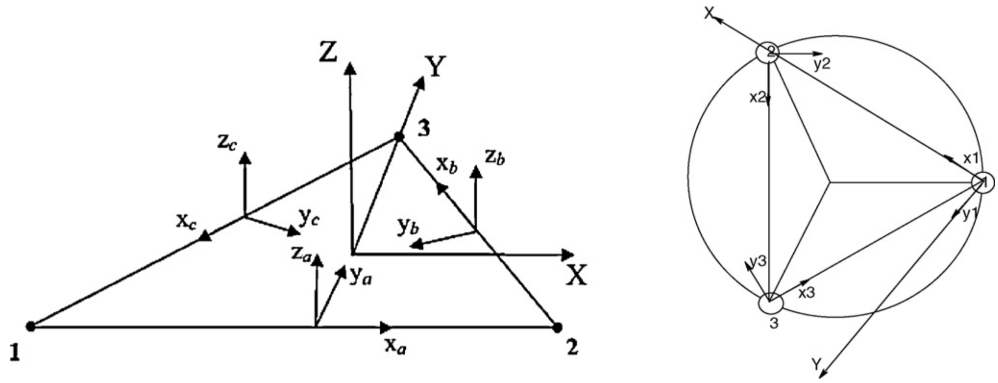

Fig. 8. Interrelations between the local and the global {*X*, *Y*, *Z*} coordinate systems.

them, however, are mutually dependent owing to the spatial symmetry of the system under study.

The first note refers to the property of the vector product: $\vec{d}_{31} \cdot (\vec{S}_3 \times \vec{S}_1) = -\vec{d}_{31} \cdot (\vec{S}_1 \times \vec{S}_3)$. When the permutational symmetry, natural for the *equilateral* triangle A$_3$, is applied to the Hamiltonian

$$\hat{H}^{\text{anti}} = \hbar^{-2}[\vec{d}_{12} \cdot (\vec{S}_1 \times \vec{S}_2) + \vec{d}_{23} \cdot (\vec{S}_2 \times \vec{S}_3) + \vec{d}_{31} \cdot (\vec{S}_3 \times \vec{S}_1)] \quad (4.8)$$

then the parameter vectors fulfill

$$\vec{d}_{12} = \vec{d}_{23} = \vec{d}_{31} = \vec{d} \equiv \{d_x, d_y, d_z\} \quad (4.9)$$

Otherwise, when the Hamiltonian is written in an ascending pair-indices ($\vec{d}_{AB} = -\vec{d}_{BA}$)

$$\hat{H}^{\text{anti}} = \hbar^{-2}[\vec{d}_{12} \cdot (\vec{S}_1 \times \vec{S}_2) + \vec{d}_{23} \cdot (\vec{S}_2 \times \vec{S}_3) + \vec{d}_{13} \cdot (\vec{S}_1 \times \vec{S}_3)] \quad (4.10)$$

then

$$\vec{d}_{12} = \vec{d}_{23} = -\vec{d}_{13} \quad (4.11)$$

Overlooking this property led to severe errors existing in literature.

We are seeking for the transformation of three local coordinate systems (*x*-aligned along the pairs *a* = 12, 23, and 31) and the global (molecule-frame) system {*X*, *Y*, *Z*}. The trigonometric relationships result from Fig. 8.

There are two possibilities: (1) to use molecule-frame parameter set and then to rotate properly the operator part; (2) to use the molecule-frame operator part and to rotate the parameter set. The molecule-frame parameter set consists of three components {A_l, A_t, A_n}; the A_l and A_t are the in-plane components that are averaged as $A_i = (A_l^2 + A_t^2)^{1/2}$; the $A_n = A_z$ is the component normal to the plane (out-of plane). The transformation formulae refer to the rotations along local *z*-axes

$$\begin{pmatrix} d_x^{(a)} \\ d_y^{(a)} \\ d_z^{(a)} \end{pmatrix} = \begin{pmatrix} \cos\varphi_a & +\sin\varphi_a & 0 \\ -\sin\varphi_a & \cos\varphi_a & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} A_l \\ A_t \\ A_n \end{pmatrix}, \quad \begin{pmatrix} A_l \\ A_t \\ A_n \end{pmatrix} = \begin{pmatrix} \cos\varphi_a & -\sin\varphi_a & 0 \\ +\sin\varphi_a & \cos\varphi_a & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} d_x^{(a)} \\ d_y^{(a)} \\ d_z^{(a)} \end{pmatrix} \quad (4.12)$$

The rotation angle φ_a refers to the position of the local frames: $\varphi_{12} = 0, \varphi_{23} = 240$, and $\varphi_{31} = 120^\circ$ (see Fig. 7). With the above settings:

$$d_x^{(12)} = A_l; \quad d_y^{(12)} = A_t \quad (4.13)$$

$$d_x^{(23)} = (-1/2)A_l + (-\sqrt{3}/2)A_t; \quad d_y^{(23)} = (\sqrt{3}/2)A_l + (-1/2)A_t \quad (4.14)$$

$$d_x^{(31)} = (-1/2)A_l + (\sqrt{3}/2)A_t; d_y^{(31)} = (-\sqrt{3}/2)A_l + (-1/2)A_t \quad (4.15)$$

(For deviations from the equilateral triangle, different angles φ_a can be attached.) The Cartesian parameter set is transformed to the spherical set by the way

$$d_{1,\pm1}^{(12)} = (\mp1/\sqrt{2})(d_x^{(12)} \pm i d_y^{(12)}) = (\mp1/\sqrt{2})(A_l \pm iA_t) \quad (4.16)$$

$$\begin{aligned} d_{1,\pm1}^{(23)} &= (\mp1/\sqrt{2})(d_x^{(23)} \pm i d_y^{(23)}) \\ &= (\mp1/2\sqrt{2})[(-A_l - \sqrt{3}A_t) \pm i(\sqrt{3}A_l - A_t)] \end{aligned} \quad (4.17)$$

$$\begin{aligned} d_{1,\pm1}^{(31)} &= (\mp1/\sqrt{2})(d_x^{(31)} \pm i d_y^{(31)}) \\ &= (\mp1/2\sqrt{2})[(-A_l + \sqrt{3}A_t) \pm i(-\sqrt{3}A_l - A_t)] \end{aligned} \quad (4.18)$$

whereas the *q* = 0 component is trivial

$$d_{1,0}^{AB} = d_z^{AB} = A_n \quad (4.19)$$

By using $d_{1,q}^{(13)} = -d_{1,q}^{(31)}$, the radial factors occurring in the antisymmetric exchange matrix are calculated as follows

$$b_{\pm1} = (1/2)(d_{1,\pm1}^{(12)} + d_{1,\pm1}^{(31)} + d_{1,\pm1}^{(23)}) = 0 \quad (4.20)$$

$$\begin{aligned} c_{\pm1} &= (\sqrt{3/8})(-d_{1,\pm1}^{(31)} + d_{1,\pm1}^{(23)}) = (-3/4)i(A_l \pm iA_t) \\ &= (\pm3\sqrt{2}/4)iA_{\pm1} \end{aligned} \quad (4.21)$$

$$\begin{aligned} d_{\pm1} &= (1/\sqrt{8})(2d_{1,\pm1}^{(12)} - d_{1,\pm1}^{(31)} - d_{1,\pm1}^{(23)}) = (\mp3/4)(A_l \pm iA_t) \\ &= (3\sqrt{2}/4)A_{\pm1} \end{aligned} \quad (4.22)$$

$$b_0 = (3/2)A_n, \quad c_0 = d_0 = 0 \quad (4.23)$$

where we used a spherical transform of the molecular parameter set

$$A_{\pm1} = \mp(A_l \pm iA_t)/\sqrt{2} \quad (4.24)$$

Finally, the full matrix of the antisymmetric exchange for the *equilateral* triangle A$_3$ becomes

$$\mathbf{H}^{\mathrm{anti}} = \left(\begin{array}{cccc|cc|cc} 0 & . & . & . & * & . & * & . \\ . & 0 & . & . & 0 & * & 0 & * \\ . & . & 0 & . & * & 0 & * & 0 \\ . & . & . & 0 & . & * & . & * \\ \hline (-3/4)A_+ & 0 & (\sqrt{3}/4)A_- & . & 0 & . & * & 0 \\ . & (-\sqrt{3}/4)A_+ & 0 & (3/4)A_- & . & 0 & 0 & * \\ \hline (3/4)\mathrm{i}A_+ & 0 & (\sqrt{3}/4)\mathrm{i}A_- & . & (-\sqrt{3}/2)\mathrm{i}A_n & 0 & 0 & . \\ . & (\sqrt{3}/4)\mathrm{i}A_+ & 0 & (3/4)\mathrm{i}A_- & 0 & (\sqrt{3}/2)\mathrm{i}A_n & . & 0 \end{array}\right) \text{ for } \left[\begin{array}{ccc} S_{12}=1 & S=3/2 & M=-3/2 \\ & & M=-1/2 \\ & & M=+1/2 \\ & & M=+3/2 \\ \hline S_{12}=1 & S=1/2 & M=-1/2 \\ & & M=+1/2 \\ \hline S_{12}=0 & S=1/2 & M=-1/2 \\ & & M=+1/2 \end{array}\right] \tag{4.25}$$

On adding the isotropic exchange, with the matrix elements $\left\langle S_{3/2}\left|H^{iso}\right|S_{3/2}\right\rangle = -(3/4)J$ and $\left\langle S_{1/2}\left|H^{iso}\right|S_{1/2}\right\rangle = +(3/4)J$, we get the set of eigenvalues (each doubly degenerate)

$$\varepsilon_{1,2} = (\sqrt{3}/4)\{-A_n - [A_\perp^2 + (A_n - \sqrt{3}J)^2]^{1/2}\} \tag{4.26}$$

$$\varepsilon_{5,6} = (\sqrt{3}/4)\{-A_n + [A_\perp^2 + (A_n - \sqrt{3}J)^2]^{1/2}\} \tag{4.27}$$

$$\varepsilon_{3,4} = (\sqrt{3}/4)\{+A_n - [3A_\perp^2 + (A_n + \sqrt{3}J)^2]^{1/2}\} \tag{4.28}$$

$$\varepsilon_{7,8} = (\sqrt{3}/4)\{+A_n + [3A_\perp^2 + (A_n + \sqrt{3}J)^2]^{1/2}\} \tag{4.29}$$

for $A_\perp$ equal to either A_l ($A_t = 0$) or A_t ($A_l = 0$).

In the strong exchange limit, when $|J| \gg d$, the spin is a "good quantum number", and then $\varepsilon(S_{12}, S)$ labeling is possible; by expanding square roots into a series, the approximate formulae for energy levels result

$$\varepsilon(1, 3/2) = -(3/4)J + A_i^2/(8J) \tag{4.30}$$

$$\varepsilon(1, 3/2) = -(3/4)J + 3A_i^2/(8J) \tag{4.31}$$

$$\left.\begin{array}{l} \varepsilon(1, 1/2) \\ \varepsilon(0, 1/2) \end{array}\right\} \to \left\{\begin{array}{l} \varepsilon(a, 1/2) = +(3/4)J - (\sqrt{3}/2)A_n + A_i^2/(8J) \\ \varepsilon(b, 1/2) = +(3/4)J + (\sqrt{3}/2)A_n + 3A_i^2/(8J) \end{array}\right. \tag{4.32}$$

It can be seen that the A_n component acts as a first-order correction that removes the accidental degeneracy of the spin doublets $\varepsilon(0, 1/2)$ and $\varepsilon(1, 1/2)$ belonging to the ^{2}E state. On the contrary, the in-plane component A_i acts as a second-order correction to all energy levels.

In the actual implementation the trial molecule-frame parameter set $\{A_l, A_t, A_n\}$ is decomposed into three local sets $\vec{d}_a = \{d_x^a, d_y^a, d_z^a\}$. These can be applied directly in conjunction with the Cartesian form of the ASE operator. More convenient is to proceed with the shift-operator form of the ASE operator requiring the shift-operator parameter sets $\vec{d}_a = \{d_+^a = (d_x^a + id_y^a), d_-^a = (d_x^a - id_y^a), d_z^a\}$. The third possibility is to handle with the spherical-operator form of the ASE and the spherical transforms of the parameter set $\vec{d}_a = \{d_{1,+1}^a = -d_+^a/\sqrt{2}, d_{1,-1}^a = d_-^a/\sqrt{2}, d_{1,0}^a = d_z^a\}$.

There is a fourth possibility to work in the basis set of uncoupled kets. With the kets $\left|M_A M_B M_C\right\rangle$ ordered in the standard ascending way

$$\left|M_A M_B M_C\right\rangle = (1/2)\begin{bmatrix} - & - & - \\ - & - & + \\ - & + & - \\ - & + & + \\ + & - & - \\ + & - & + \\ + & + & - \\ + & + & + \end{bmatrix} \tag{4.33}$$

the ASE-matrix is

$$\mathbf{H}_a^{\mathrm{anti}} = i(d_-^a \mathbf{A}_+^a + d_+^a \mathbf{A}_-^a + d_z^a \mathbf{A}_z^a) \tag{4.34}$$

with the shift-operator form (that absorb all numerical constants)

$$\mathbf{A}_+^{(12)} = \frac{1}{4}\begin{pmatrix} . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . \\ -1 & . & . & . & . & . & . & . \\ . & -1 & . & . & . & . & . & . \\ 1 & . & . & . & . & . & . & . \\ . & 1 & . & . & . & . & . & . \\ . & . & -1 & . & 1 & . & . & . \\ . & . & . & -1 & . & 1 & . & . \end{pmatrix},$$

$$\mathbf{A}_+^{(23)} = \frac{1}{4}\begin{pmatrix} . & . & . & . & . & . & . & . \\ -1 & . & . & . & . & . & . & . \\ 1 & . & . & . & . & . & . & . \\ . & -1 & 1 & . & . & . & . & . \\ . & . & . & . & . & . & . & . \\ . & . & . & . & -1 & . & . & . \\ . & . & . & . & 1 & . & . & . \\ . & . & . & . & . & -1 & 1 & . \end{pmatrix}, \tag{4.35}$$

$$\mathbf{A}_+^{(31)} = \frac{1}{4}\begin{pmatrix} . & . & . & . & . & . & . & . \\ 1 & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . \\ . & . & 1 & . & . & . & . & . \\ -1 & . & . & . & . & . & . & . \\ . & 1 & . & . & -1 & . & . & . \\ . & . & -1 & . & . & . & . & . \\ . & . & . & 1 & . & . & -1 & . \end{pmatrix}$$

and the shift-down matrices which are hermitean-adjoint $\mathbf{A}_-^a = (\mathbf{A}_+^a)^\dagger$.

There are the *Moriya symmetry rules* [2] that deduce zero- or non-zero components of the parameter set $\{A_l, A_t, A_n\}$; these are collected in Table 5 for important point-groups. Which case is appropriate is determined by the overall (but idealized) symmetry of the molecule containing the triangulo-unit. Some consequences of the antisymmetric exchange for trinuclear systems are discussed elsewhere [22].

The results of extensive modeling in reduced coordinates are given in Tables A11–A15. Each spin triad is calculated in a strong-negative ($J/hc = -50\,\mathrm{cm}^{-1}$) and strong-positive ($J/hc = +50\,\mathrm{cm}^{-1}$) limit for two set of ASE parameters: out-of-

Table 5
Symmetry rules for the antisymmetric exchange in triads.

Definition of the molecule-frame parameters $\{A_n, A_l, A_t\}$ for the triad:
  Symmetry $\mathbf{D_{3h}}$ $\{C_3, 3C_2, S_3, \sigma_h, 3\sigma_v\}$: $d_{12,z} = d_{23,z} = d_{31,z} = A_n \neq 0$
  Symmetry $\mathbf{D_3}$ $\{C_3, 3C_2\}$: $A_n \neq 0$; $A_l \neq 0$
  Symmetry $\mathbf{C_{3v}}$ $\{C_3, 3\sigma_v\}$: $A_n \neq 0$; $A_t \neq 0$
  Symmetry $\mathbf{C_3}$ $\{C_3\}$: $A_n \neq 0$; $A_l \neq 0$; $A_t \neq 0$
Parallel (normal) component $A_\parallel \equiv A_n$
Perpendicular (in-plane) component $A_\perp \equiv (A_l^2 + A_t^2)^{1/2} = A_i$

plane component $A_n/hc = 20\,\text{cm}^{-1}$, and/or in-plane component $A_t/hc = A_l/hc = 20\,\text{cm}^{-1}$. The strong exchange limit secures that the spin multiplets are well separated each from the others and the Zeeman term does not mix them. The behavior of the magnetic functions is different for the half-integral ($n/2$) and integral (n) spins:

1. for the half-integral spins and antiferromagnetic exchange the ground state is always a Kramers doublet $\left|a, S = 1/2, M = \pm 1/2\right\rangle$ that results from splitting of orbitally degenerate doublet ^{2}E covered by $\left|S_{12} = 0, S = 1/2, M = \pm 1/2\right\rangle$ and $\left|S_{12} = 1, S = 1/2, M = \pm 1/2\right\rangle$ spin kets; the first excited state is the second Kramers doublet $\left|b, S = 1/2, M = \pm 1/2\right\rangle$;
2. for the integral spins and the antiferromagnetic exchange the ground state refers to a singlet, $S = 0$;
3. for the ferromagnetic exchange the ground state is always the maximum spin state, $S_{\max} = 3n/2$ and $S_{\max} = 3n$, respectively.

4.1.1. *Observations for $S_1 = S_2 = S_3 = n/2$ (Tables A16, A18 and A20)*

(a) For the antiferromagnetic exchange coupling, $J < 0$, and $A_n \neq 0$:
- the A_n component of the ASE mixes the magnetic states $\left|S_{12} = 0, S = 1/2, M = \pm 1/2\right\rangle$ and $\left|S_{12} = 1, S = 1/2, M = \pm 1/2\right\rangle$ owing to which the z-component of the susceptibility is *non-zero* at $T \to 0$ and closely maps the case of the isotropic-only exchange;
- at the same time the perpendicular $\{x,y\}$-components of the susceptibility approach small, but non-zero limit as $T \to 0$;
- the averaged magnetic susceptibility to an LT limit lies below the curve of the isotropic-only exchange;
- on temperature lowering, only the $\{x,y\}$-components of the product function χT approach zero, while the z-component adopts a constant value;
- consequently the averaged product function χT collapses to the-zero value as $T \to 0$ unlike the curve for the isotropic-only exchange that converges to $\chi T/C_0 = 1$;
- the z-component of the magnetization per particle rises to a step of $M_1 = 1{,}0\,\mu_{\text{B}}$ (easy axis), whereas the $\{x,y\}$-components are much lower;
- the magnetization anisotropy is detectable for the given set of parameters.

In can be concluded that for the *triangulo*-[$n/2$,$n/2$,$n/2$] spin system the magnetic anisotropy is just opposite to that found for the [$n/2$,$n/2$] diad when $J < 0$, and $A_n \neq 0$.

(b) For the antiferromagnetic exchange coupling, $J < 0$, and $A_i \neq 0$:
- with non-zero A_i the splitting of the ^{2}E manifolds is less effective as this is the second-order effect; the behavior of the susceptibility components is qualitatively analogous to the previous case; however, on $T \to 0$ the $\{x,y\}$-components of the susceptibility converge to much higher non-zero limit;
- the anisotropy of the product function χT increases progressively with the genuine spins;
- the magnetization anisotropy is detectable for the given set of parameters even for $s = 1/2$ but this grows rapidly for higher genuine spins $s = 3/2$ and $5/2$.

In can be concluded that for the *triangulo*-[$n/2$,$n/2$,$n/2$] spin system the magnetic anisotropy matches that found for the [$n/2$,$n/2$] diad when $J < 0$, and $A_i \neq 0$.

(c) For the ferromagnetic exchange coupling, $J > 0$, and $A_n \neq 0$:
- the high-spin ground state is well isolated from the excited ones and it is not influenced by A_n; therefore the system copies the isotropic-only exchange and stays isotropic. The magnetization per particle saturates according to the Brillouin function until $M_1 = 6(n/2)\mu_{\text{B}}$.

(d) For the ferromagnetic exchange coupling, $J > 0$, and $A_i \neq 0$:
- the z-component of the susceptibility is greater than that for the isotropic-only exchange while the $\{x,y\}$-component converges to a small finite value on $T \to 0$;
- the z-component of the χT product function is *above* the averaged χT while the $\{x, y\}$-components turn to zero;
- the averaged product function χT lies below the curve for the isotropic-only exchange; it passes through a maximum and then drops to a non-zero limit at $T \to 0$;
- the z-component of the magnetization saturates more rapidly than the Brillouin curve (easy axis) whereas the $\{x,y\}$-components are retarded;
- the magnetization anisotropy is very large for the given set of parameters.

In summary, the effect of ASE cannot be ignored for ferromagnetically coupled triad. The magnetic anisotropy grows progressively with the values of the genuine spins.

4.1.2. *Observations for $S_1 = S_2 = S_3 = n$ (Tables A17 and A19)*

- The behavior of the magnetic functions for $J < 0$ copies that found for antiferromagnetically coupled [n,n] diads.
- On the contrary, for $J > 0$ the behavior of magnetic functions is analogous to that found for ferromagnetically coupled *triangulo*-[$n/2$,$n/2$,$n/2$] systems.
- The above observations are comprehensively presented in Table 6.

The development of the magnetization in an arbitrary field direction is visualized *via* three-dimensional diagrams (and their two-dimensional cuts) in Figs. 9–12. In the present case of *triangulo*-[5/2,5/2,5/2] system and the antiferromagnetic exchange the z-component of the magnetization refers to the easy axis irrespective whether the normal component (A_n) or the in-plane components (A_t, A_l) of the ASE are active. However, the quantitative consequences are different.

The magnetization in moderate fields exhibits an *easy axis* in the direction of the ASE z-component. With the ramping field the easy axis alters to the easy plane at the field B_{iso} and in the very high field the system again becomes isotropic (Fig. 12).

5. Experimental data

The literature information about the antisymmetric exchange parameters is listed in Table 7. However, a variety of symbols for them is utilized (d_a^{AB}, D_a, G, G_a, G_a^{AB}, A_n, A_l, A_t, D_n, D_l, D_t) in original sources with different meaning that causes a direct comparison rather difficult. The individual-pair (AB) interaction parameters in the given direction ($a = x, y, z$) can be identified as $d_a^{AB} = G_a^{AB}$. The compound parameters appropriate to a *triangulo*-triad are $D_n = A_n$ and $(D_l, D_t) = (A_l, A_t)$; n – normal, l – longitudinal, t – transversal component. In the effective interaction Hamiltonian restricted to the basis of two Kramers doublets 2D$^{(1/2)}$, the parameter $G = (G_x^2 + G_y^2 + G_z^2)^{1/2}$ with the components $G_a = \alpha \sum_{A \neq B}^{cyclic} G_\alpha^{AB}$ refers to a many-electron compound parameter related to the zero-field energy gap ($\Delta = 2G$). For *triangulo*-triads, when $G_x = G_y = 0$ is fulfilled, the following relationships hold true: $G_z^{AB} = G_z^{(12)} = G_z^{(23)} = G_z^{(31)}$, and $G \leftarrow G_z = 3\alpha G_z^{AB}$; $G_z^{AB} = d_z^{AB}$.

Prior to discuss the individual achievements, let us remember that the isotropic exchange Hamiltonian appropriate to a *triangulo*-triad

$$\hat{H}^s = -J\hbar^{-2}[(\vec{S}_1 \cdot \vec{S}_2) + (\vec{S}_2 \cdot \vec{S}_3) + (\vec{S}_3 \cdot \vec{S}_1)] \tag{5.1}$$

with $J < 0$ brings the degenerate Kramers doublet as a ground state ^{2}E for half-integral genuine spins $s = 1/2$, 3/2, and 5/2. The orbital

Table 6
Comparison of magnetic anisotropy for dinuclear and trinuclear spin systems with ASE[a].

Property	$[n/2,n/2]$ and $[n,n]$	*triangulo*-$[n,n,n]$	*triangulo*-$[n/2,n/2,n/2]$
Based upon Tables	A6–A10	A17, A19	A16, A18, A20
(a) $J<0$	$d_z \neq 0$	$A_n \neq 0$	$A_n \neq 0$
Ground state	$S=0$	$S=0$	$S=1/2$
First excited state	$S=1$, split by d_z	Components of $S=1$	$S=1/2$
$\chi_z(T\to 0)$	0, close to *iso*	0, close to *iso*	Close to *iso* (Curie law)
$\chi_{x,y}(T\to 0)$	Finite, small	Finite, small	Small, but non-zero
$\chi_{\mathrm{av}}(T\to 0)$	Finite, above *iso* (0)	Finite, above *iso* (0)	Below iso
$M_z(B=3\,\mathrm{T})$	Close to 0, close to *iso*	Close to 0, close to *iso*	Higher, close to *iso* [easy axis]
$M_{x,y}(B=3\,\mathrm{T})$	Small [easy plane]	Small [easy plane]	Small
$\Delta M(B=3\,\mathrm{T})$	Small	Small	Visible
(b) $J<0$	$d_x=d_y\neq 0$	$A_i \neq 0$	$A_i \neq 0$
Ground state	$S=0$	$S=0$	$S=1/2$
First excited state	$S=1$, split by d_x	Components of $S=1$	$S=1/2$
$\chi_z(T\to 0)$	Finite, higher	Finite, higher	Above *iso*
$\chi_{x,y}(T\to 0)$	Finite, lower	Finite, lower	Finite, small
$\chi_{\mathrm{av}}(T\to 0)$	Finite, above *iso* (0)	Finite, above *iso* (0)	Below *iso*
$M_z(B=3\,\mathrm{T})$	Small, higher [easy axis]	Small, higher [easy axis]	Higher [easy axis]
$M_{x,y}(B=3\,\mathrm{T})$	Small, lower	Small, lower	Smaller
$\Delta M(B=3\,\mathrm{T})$	Small	Small	Large
(c) $J>0$	$d_z \neq 0$	$A_n \neq 0$	$A_n \neq 0$
Ground state	$S_{\max}=2n$, split by d_z	$S_{\max}=3n$, untouched by A_n	$S_{\max}=3n/2$, untouched by A_n
$\chi_z(T\to 0)$	0	Coincides with *iso*	Coincides with *iso*
$\chi_{x,y}(T\to 0)$	Finite, below *iso*	Coincides with *iso*	Coincides with *iso*
$\chi_{\mathrm{av}}(T\to 0)$	Finite, below *iso*	Infinite	Coincides with *iso*
$M_z(B=3\,\mathrm{T})$	High, lower	Coincides with *iso*, saturates rapidly	Coincides with *iso*, saturates rapidly
$M_{x,y}(B=3\,\mathrm{T})$	High, saturates rapidly like *iso* [easy plane]	Coincides with *iso*, saturates rapidly	Coincides with *iso*, saturates rapidly
$\Delta M(B=3\,\mathrm{T})$	Very large	Invisible, isotropic	Invisible, isotropic
(d) $J>0$	$d_x=d_y\neq 0$	$A_i \neq 0$	$A_i \neq 0$
Ground state	$S_{\max}=2n$, plit by d_x	$S_{\max}=3n$, split by A_i	$S=3n/2$, split by A_i
$\chi_z(T\to 0)$	Finite, higher	Above *iso*	Above *iso*
$\chi_{x,y}(T\to 0)$	Finite, lower	Finite, small	Finite, small
$\chi_{\mathrm{av}}(T\to 0)$	Finite, below *iso*	Below *iso*	Below *iso*
$M_z(B=3\,\mathrm{T})$	High, higher, below *iso* [easy axis]	Saturates more rapidly than *iso* [easy axis]	Saturates more rapidly than *iso* [easy axis]
$M_{x,y}(B=3\,\mathrm{T})$	High, lower	Below *iso*	Below *iso*
$\Delta M(B=3\,\mathrm{T})$	Visible/large	Very large	Very large

[a] Magnetic parameters: $J/hc=\pm 50\,\mathrm{cm}^{-1}$, $d_i/hc=20\,\mathrm{cm}^{-1}$, $A_i/hc=20\,\mathrm{cm}^{-1}$; *iso*—curve for isotropic-only exchange.

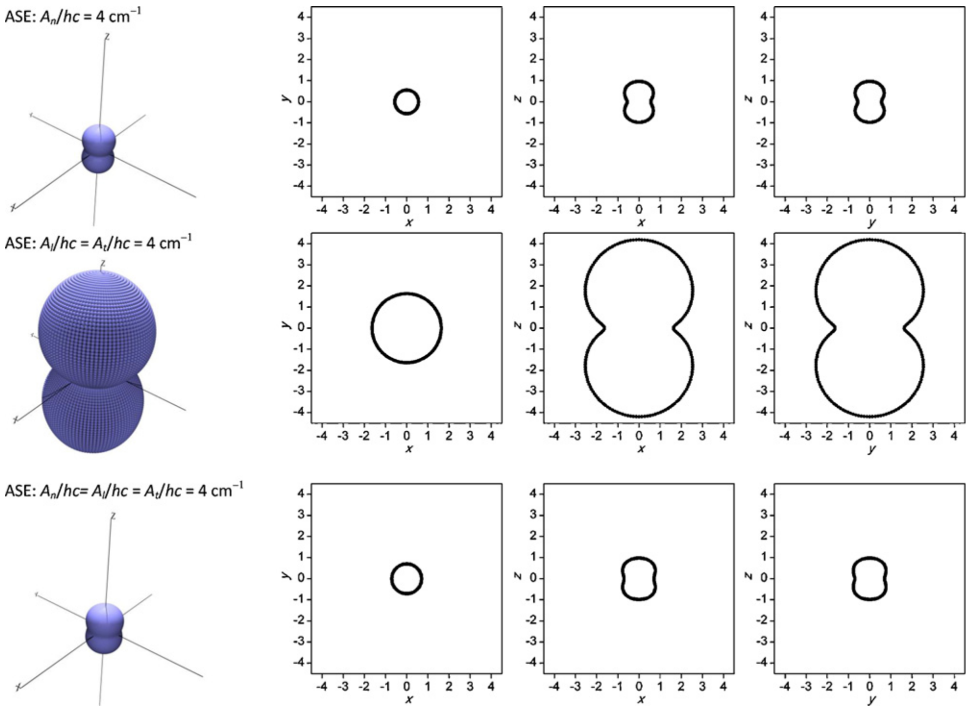

Fig. 9. Magnetization for $s=5/2$ triad in various field directions, $J/hc=-10\,\mathrm{cm}^{-1}$, $T=2.0\,\mathrm{K}$, $B=6\,\mathrm{T}$. Effect of the components of the ASE parameter vector.

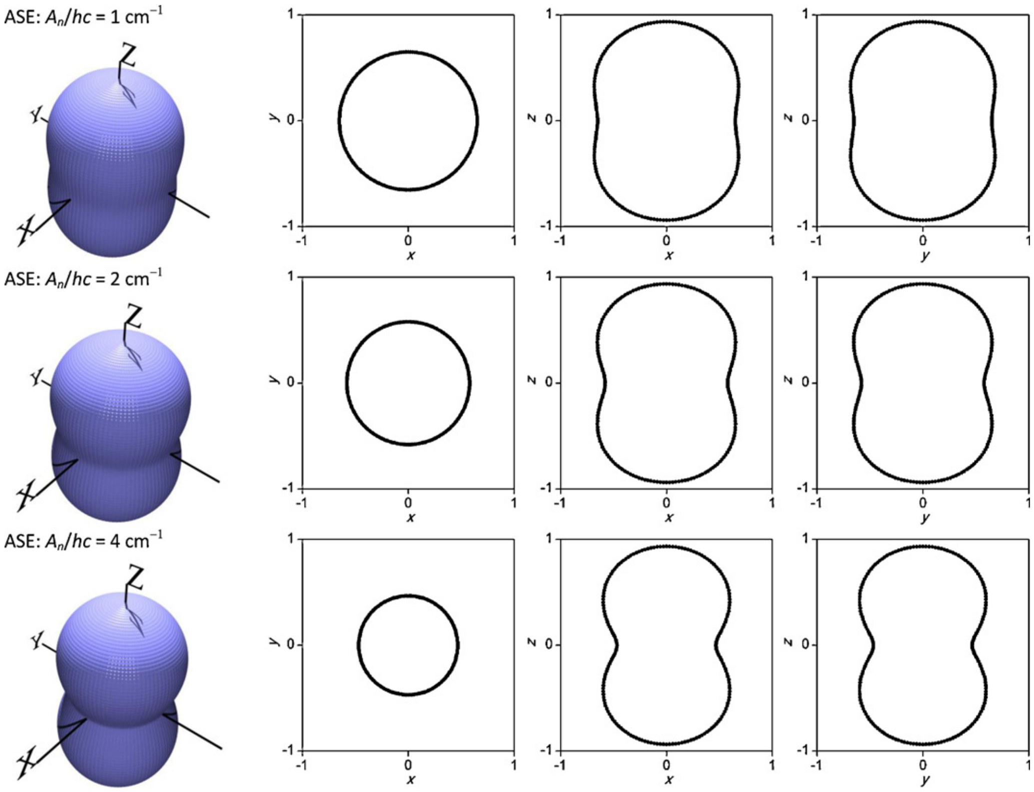

Fig. 10. Magnetization for $s = 5/2$ triad in various field directions, $J/hc = -10\,\mathrm{cm}^{-1}$, $T = 2.0$ K. Effect of the normal component of the ASE.

degeneracy is removed by introducing a distortion from equilateral AAA system to isosceles ABA one, and two nomenclatures can be met as follows:

$$\hat{H}^s = \hbar^{-2}[-J_1(\vec{S}_1\cdot\vec{S}_2) - J_1(\vec{S}_1\cdot\vec{S}_3) - J_2\hbar^{-2}(\vec{S}_2\cdot\vec{S}_3)] \tag{5.2}$$

$$\hat{H}^s = -J_0\hbar^{-2}[(\vec{S}_1\cdot\vec{S}_2) + (\vec{S}_2\cdot\vec{S}_3) + (\vec{S}_3\cdot\vec{S}_1)] - J_1\hbar^{-2}(\vec{S}_3\cdot\vec{S}_1) \tag{5.3}$$

(often a factor -2 occurs in front of the coupling constant in literature sources; $-J_1 = -2J_1'$). In the first nomenclature the zero-field

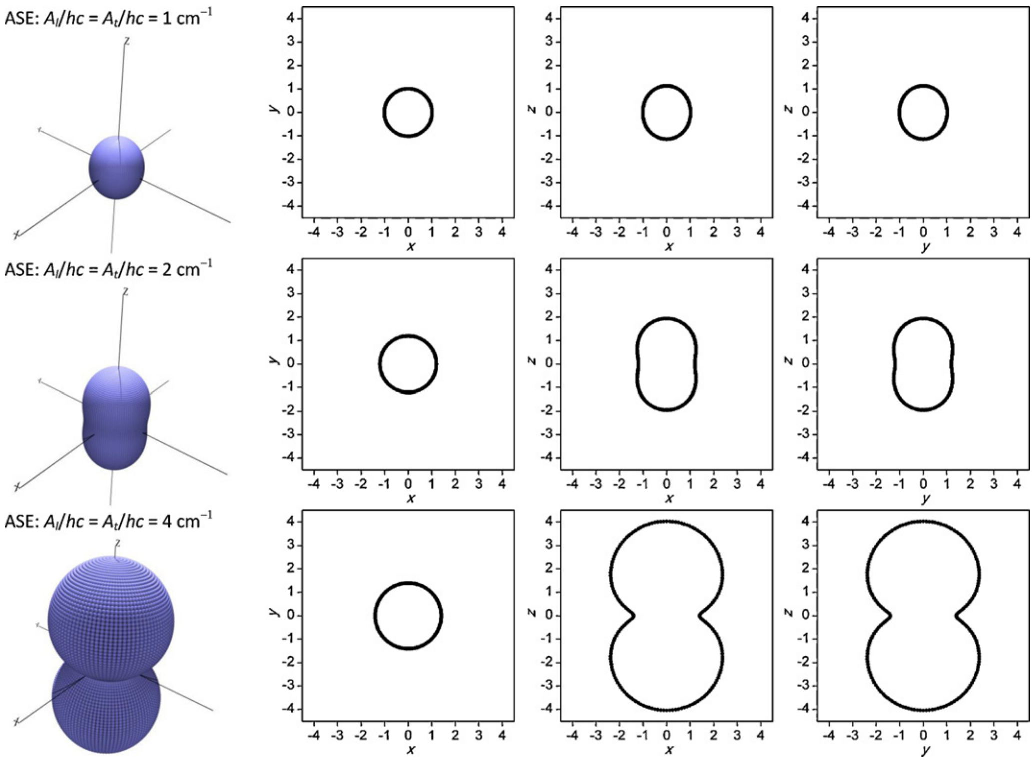

Fig. 11. Magnetization for $s = 5/2$ triad in various field directions, $J/hc = -10\,\mathrm{cm}^{-1}$, $T = 2.0$ K. Effect of the in-plane ASE parameters.

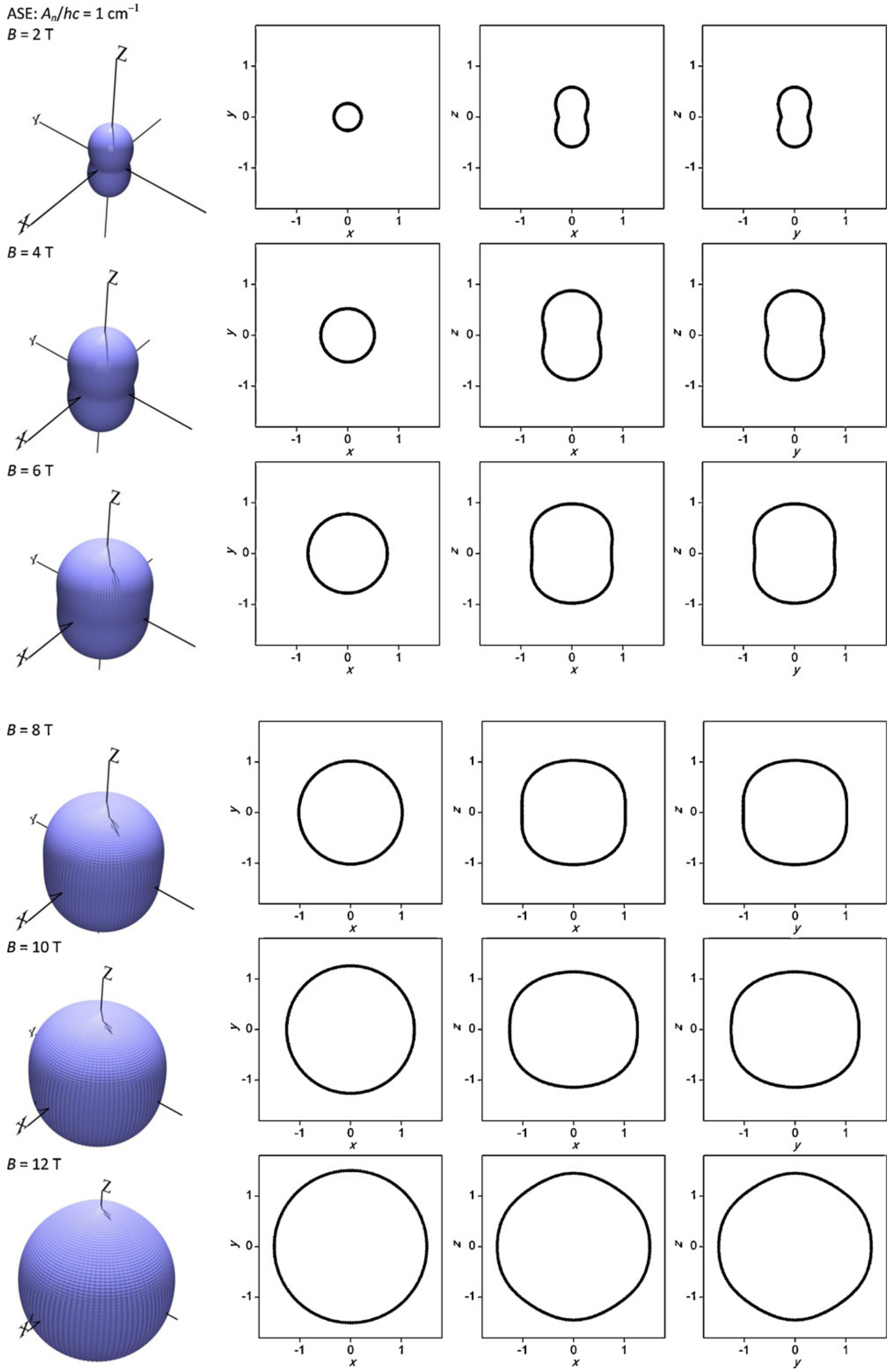

Fig. 12. Magnetization for $s = 5/2$ triad in various field directions, $J/hc = -10\,\mathrm{cm}^{-1}$, $T = 2.0$ K. Effect of the magnetic field strength: switch of the easy axis to the easy plane with the field strength above 8 T.

energy levels become

$$\varepsilon(S', S) = -(J_1/2)[S(S+1) - \sum_{A=1}^{3} s_A(s_A+1)] \\ -[(J_1 - J_2)/2][S'(S'+1) - \sum_{A=2}^{3} s_A(s_A+1)] \tag{5.4}$$

where the intermediate spin is $S' = S_2 + S_3$. With any kind of the isotropic exchange, the system stays magnetically isotropic so that the magnetization and susceptibility develop in all directions uniformly.

The net effect of the antisymmetric exchange in the zero field is analogous: a splitting of the ^{2}E state into two Kramers doublets (Fig. 13). However, the resulting states no longer can be attributed to a definite intermediate spin as an effect of their mixing. In addition, the excited quartet $^4A_2$ is also split. At the same time magnetic anisotropy appears and this is the most important consequence of the antisymmetric exchange.

Table 7
Experimental data on antisymmetric exchange for molecular (0D) compounds.

Compound[a]	Method[b]	$(J/hc)/\mathrm{cm}^{-1}$ [c]	g	$(d/hc)/\mathrm{cm}^{-1}$ [d]	Ref.	Notation
$[\mathrm{Cu}^{\mathrm{II}}_3]$ complexes						
$[\mathrm{Cu_3(OH)(pyridine\text{-}2\text{-}aldoxime)_3](SO_4)\cdot 10.5H_2O}$	X	$J_{iso}=-300$	$g_{iso}=2.1$	$G=12$	Tsu [25]	$G^2 = 3(G_x^2+G_y^2+G_z^2)$
$[\mathrm{Cu_3(OH)(aaat)_3(H_2O)_3](NO_3)_2\cdot H_2O}$	X	$J_1=-191.0$ $J_2=-156.4$	$g_{xy}=2.00$ $g_z=2.09$	$G=27.8$ $(d_z=96.3)$	Fer [26]	$G=\sqrt{3}G_z/6$
$\{[\mathrm{Cu_3(OH)(aat)_3(SO_4)]\cdot 6H_2O}\}_n$	X	$J_1=-175.4$ $J_2=-153.2$	$g_{xy}=2.10$ $g_z=2.10$	$G=31.0$ $(d_z=107.4)$	Fer [26]	$G=\sqrt{3}G_z/6$
$[\mathrm{Cu_3(DBED)_3(OH)_3](ClO_4)_3}$	ESR, MCD	$\delta=17.5$	$g_{eff}=2.32$	$G=36.0$	Yoo [27,28]	$G=G_z$ $\delta=J_{12}-J_{23}$
	X	$J_{av}=-210$ $J_{inter}=+1.1$	$g_{iso}=2.06$	$G=35$	Mir [29]	
$[\mathrm{Cu_3Cl(Mes\text{-}Hpz)_2(Mes\text{-}pz)_3(OMe)]Cl}$	X	$J_{av}=-194$ $\delta=48$	$[g_{xy}=2.20]$ $g_z=2.12$	$G=33$	Liu [30]	$G=\sqrt{3}G_z/6$ $J_{av}=(2J+J')/3$ $\delta=2\lvert J-J'\rvert$
	ESR		$g_{xy}=2.21$ $g_z=1.47$			
$[\mathrm{Cu_3Br(Mes\text{-}Hpz)_2(Mes\text{-}pz)_3(OMe)]Br}$	X	$J_{av}=-210$ $\delta=126$	$[g_{xy}=2.20]$ $g_z=2.20$	$G=47$	Liu [30]	$G=\sqrt{3}G_z/6$
	ESR		$g_{xy}=2.19$ $g_z=1.52$			
$[\mathrm{Cu_3(L^1)_3(Im)_3](ClO_4)_3}$	X	$J=-75$			Cha [54]	
	ESR		$g=2.101$ $g=2.087$	$G_{eff}=5.5$	Pad [55]	
$[\mathrm{Cu_3(L^2)(\mu_3\text{-}O)](ClO_4)_4\cdot 2H_2O}$	X	$J=+109$ $zj'=-0.72$	$g=1.88$		Suh [56]	
	ESR, C		$g_{xy}=2.021$ $g_z=2.064$	$G_{12}=42.3$	Yoo [57]	$\sqrt{3}G_{12}=73.3$
$[\mathrm{Cu_3(PhPyCNO)_3(OCH_3)(Cl)(ClO_4)}]$	X, M	$J=-800$ $\delta=30$	$g=1.99$ $g=[2.00]$	$d_z=15$	Afr [58]	
	ESR		$g_z=2.08$ $g_{xy}=1.83$			
$[\mathrm{Cu_3(PhPyCNO)_3(\mu_3\text{-}OH)(2,4,5\text{-}T)_2}]$	X, M	$J=-440$ $\delta=40$	$g=2.10$ $g=[2.10]$	$d_z=20$	Afr [59]	
	ESR		$g_z=2.12$ $g_{xy}=1.80$			
$\mathrm{Na_9[Cu_3Na_3(H_2O)_9(\alpha\text{-}AsW_9O_{33})_2]\cdot 26H_2O}$	X	$J=-2.72$	$g=2.208$		Kor [60]	
	M, ESR	$J_{12}^{x,y}=3.13$ $J_{12}^{z}=3.17$ $J_{23,31}^{x,y}=2.80$ $J_{23,31}^{z}=2.82$	$g_{xy}=2.25$ $g_z=2.06$	$d_x=d_y=d_z=0.368$	Cho [61] reanalyzed by [62]	
$\mathrm{Na_9[Cu_3Na_3(H_2O)_9(\alpha\text{-}SbW_9O_{33})_2]\cdot 26H_2O}$	X	$J=-2.08$	$g=2.223$		Sto [63]	
	ESR	$J_{12}^{x,y}=3.12$ $J_{12}^{z}=3.16$ $J_{23,31}^{x,y}=2.12$ $J_{23,31}^{z}=2.75$	$g_{11}^{xx,yy}=2.24$ $g_{22}^{xx,yy}=2.11$ $g_{33}^{xx,yy}=2.40$ $g_{11,22,33}^{zz}=2.07$	$d_x=d_y=d_z=0.359$	Cho [64]	
$[\mathrm{Cr}^{\mathrm{III}}_3]$ complexes						
$[\mathrm{Cr_3O(C_2H_5COO)_6(H_2O)_3]NO_3\cdot 2H_2O}$	X	$J_0=-18.3$	$[g_z=2]$ $[g_{xy}=1.96]$		Nis [31]	
	ESR		$g_z=2.0$ $g_{xy}=1.89$	$d_z^{AB}=0.21$	Nis [31]	$D_z = d_z^{12}+d_z^{23}+d_z^{31}$
	X	$J_0=-18.8$ $J_1=-2.7$	$g_{iso}=1.98$		Hon [32]	$J_0=J_{12}=J_{23}=J_{31}$ $J_1=J_{31}$
	ESR-SC, $T=4.2$ K	$J_0=-18.8$ $J_1=-2.7$	$g_{iso}=1.98$ $(g_z=1.98)$ $(g_{xy}=1.89)$	$d_z^{AB}=0.24$	Hon [32]	$D_z=(4/\sqrt{3})(d_z^{12}+d_z^{23}+d_z^{31})$ $\lvert\vec{D}\rvert=4\sqrt{3}\lvert d_z^{AB}\rvert$
	M, $B=35$ T, $T=0.64$, 4.2 K				Hon [33]	Data compatible with above ESR parameters
$[\mathrm{Cr_3O(CH_3COO)_6(H_2O)_3]Cl\cdot 6H_2O}$	X				Hon [32]	
	A1 site	$J_0=-22.2$ $J_1=+1.0$	$g_{iso}=1.98$			$J_0=J_{12}=J_{23}=J_{31}$ $J_1=J_{31}$
	A2 site	$J_0=-19.6$ $J_1=-3.0$	$g_{iso}=1.98$			
	ESR-SC, $T=4.2$ K				Hon [32]	

Table 7 (*Continued*)

Compound[a]	Method[b]	$(J/hc)/\mathrm{cm}^{-1}$ [c]	g	$(d/hc)/\mathrm{cm}^{-1}$ [d]	Ref.	Notation
	A1 site	$J_0 = -22.2$ $J_1 = +1.0$	$g_{iso} = 1.98$ $(g_z = 1.98)$ $(g_{xy} = 1.93)$	$d_z^{AB} = 0.06$		
	A2 site	$J_0 = -19.6$ $J_1 = -3.0$	$g_{iso} = 1.98$ $(g_z = 1.98)$ $(g_{xy} = 1.84)$	$d_z^{AB} = 0.34$		
	M, $B = 45$ T, $T = 0.62$, 1.3, 4.2 K				Hon [33]	Data compatible with above ESR parameters
$[Cr_3O\{O_2C(OH)Ph_2\}_6(H_2O)_3]$ $NO_3{\cdot}2H_2O{\cdot}3Me_2CO$	X				Psy [34]	
	a-set	$J_1 = -21.2$ $J_2 = -19.8$	$g = 1.87$			$J_1(\times 2), J_2(\times 1)$
	b-set	$J_1 = -20.2$ $J_2 = -21.8$	$g = 1.87$			
	ESR, $T = 4.2$ K		$g_{xy} = 1.90$ $g_z = 1.98$	$d = 0.1$	Psy [34]	$d = 4\sqrt{3}d_z^{AB}$
$[Cr_3O(PhCOO)_6(H_2O)_3]NO_3{\cdot}1.9MeCN$ $\cdot 0.5H_2O$	X				Psy [34]	
	a-set	$J_1 = -23.4$ $J_2 = -19.2$	$g = 1.82$			$J_1(\times 2), J_2(\times 1)$
	b-set	$J_1 = -20.4$ $J_2 = -25.8$	$g = 1.82$			
	ESR, $T = 4.2$ K		$g_{xy} = 1.53$ $g_z = 1.82$	$d = 1.1$	Psy [34]	$d = 4\sqrt{3}d_z^{AB}$
$[Cr_3O(PhCOO)_6(H_2O)_3]NO_3{\cdot}4H_2O{\cdot}2CH_3OH$	X	$J = -20.2$	$g = 1.97$		Fig [35]	
	ESR	$\delta = 2.5$	$[g = 2]$	$G_z = 0.25$	Fig [35]	$G = 4\sqrt{3}G_z$ $\delta = 2\lvert J_0 - J_1\rvert$
$[Cr_3O(O_2CPh)_6(MeOH)_3](NO_3){\cdot}2MeOH$	X	$J = -18.6$	$g = 1.98$		Vla [65]	
	ESR	$\delta = 2.0$	$[g = 1.98]$	$d_z = 0.17$		
$[Cr_3O(RCOO)_6(H_2O)_3]^+$	ESR, X (Q)-band		g_{iso}	δ/Δ	Tsu [25c]	$2\Delta = 2(G^2 + \delta^2)^{1/2}$
$R = CH_3$			1.80 (1.972)	0.932 (0.994)		
$R = ClCH_2$			1.91	0.947		
$R = Cl_3C$			1.92 (1.97)	0.955 (0.992)		
$R = H$			1.93	0.962		
$R = 4\text{-}Cl\text{-}Ph$			1.95	0.977		
$[Cr_2FeO(RCOO)_6(H_2O)_3]A{\cdot}S$	ESR		g_{iso}	δ/Δ	Kuy [25d]	$2\Delta = 2(G^2 + \delta^2)^{1/2}$
$R = CH_3$; $A = NO_3^-$; $S = CH_3COOH$			1.93	0.56		
$R = ClCH_2$; $A = NO_3^-$; $S = 3H_2O$			1.93	0.56		
$R = C_2H_6$; $A = NO_3^-$			1.94	0.56		
$R = CH_3$; $A = PtCl_5^-$; $S = 12H_2O$			1.96	0.58		
$R = C_6H_5$; $A = NO_3^-$			1.94	0.56		
$R = C_4H_9$; $A = NO_3^-$; $S = H_2O$			1.92	0.55		
$R = C_5H_{11}$; $A = NO_3^-$; $S = 2H_2O$			1.92	0.55		
$R = CCl_3$; $A = CCl_3COO^-$; $S = 4H_2O$			1.93	0.56		
$[CrFe_2O(RCOO)_6(H_2O)_3]A{\cdot}S$	ESR				Kuy [25d]	$2\Delta = 2(G^2 + \delta^2)^{1/2}$
$R = CH_3$; $A = NO_3^-$; $S = CH_3COOH$			1.95	0.53		
$R = ClCH_2$; $A = NO_3^-$; $S = 3H_2O$			1.94	0.53		
$R = C_2H_6$; $A = NO_3^-$			1.93	0.52		
$R = CH_3$; $A = PtCl_5^-$; $S = 12H_2O$			1.96	0.54		
$R = C_6H_5$; $A = NO_3^-$			1.95	0.53		
$R = C_4H_9$; $A = NO_3^-$; $S = H_2O$			1.92	0.51		
$R = C_5H_{11}$; $A = NO_3^-$; $S = H_2O$			1.92	0.51		
$R = CCl_3$; $A = CCl_3COO^-$			1.98	0.55		
$[Co_3^{II}]$ complexes						
$[Co(depa)Cl]_3$	X	$J = -5.7$	$g_{xy} = 1.96$ $g_z = 2.7$	$G = 2.8$	Ber [36]	$G = 2\sqrt{3}d_z^{AB}$
$[V_3^{IV}V_3^{IV}]$ complexes						
$(NH_4)_{21}[\{VO(H_2O)\}_6$ $\{Mo(H_2O)_2(OH)Mo\}_3$ $\{Mo_{15}(MoNO)_2O_{58}$ $(H_2O)_2\}_3].65H_2O$	X, $B = 1$ T	$J = -195$ $J' = -2.6$	1.97	$G = 5$	Gat [37]	$G = 3d_z^{AB}$ J' – between triangles
$(NH_2Me_2)_{18}(NH_4)_6$ $[\{VO(H_2O)\}_6$ $\{Mo(H_2O)_2(O)Mo\}_3$ $\{Mo_{15}(MoNO)_2$ $O_{58}(H_2O)_2\}_3].14H_2O$	X, $B = 1$ T	$J = -158$ $J' = -3.3$	1.85	$G = 9$	Gat [37]	$G = 3d_z^{AB}$ J' – between triangles
$[V_3^{IV}]$ complexes						

Table 7 (*Continued*)

Compound[a]	Method[b]	$(J/hc)/\mathrm{cm}^{-1}$ [c]	g	$(d/hc)/\mathrm{cm}^{-1}$ [d]	Ref.	Notation
$K_6[V_{15}As_6O_{42}(H_2O)]\cdot 8H_2O$	ESR	$J = -1.69$	1.96	$\Delta = 0.14$	Tsu [38]	$\Delta = \sqrt{3}d_z^{AB}$
	M, $B = 5$ T; $T = 0.1$ - 4.2 K	$J = -1.71$	$g_{iso} = 1.94$	$D_\perp = 0.238$ $D_n = 0.054$	Tar [23] Tsu [72]	
	ESR	$J = -0.85$		$d_x = d_z = 0.02$ $d_y = 0$	Kaj [66]	
	Modeling				Rae [67] Tsu [68] Mach [69,70]	
$K_6[V_{15}As_6O_{42}]\cdot 9D_2O$	INS	$J = -1.70$		$2\Delta = 0.28$	Cha [71]	
$[Fe_2^{III}]$ complexes						
$Me_4N[Fe_2(HXTA)(O_2CMe)_2]$	MS, X	$J = -20$	$[g = 2]$	$d = 2.2$	Kau [39]	
MMOH	MS, X	$J = -15$	$[g = 2]$	$d = 1.5$	Kau [39]	
$\{2Fe\text{-}2S\}^{1+}$ core in reduced Tt Rieske protein	ESR	$J = -43$	$g = 2.14, 1.94, 1.81$	$d = 8$	Oli [40]	
$\{(NH_4)_2[Fe_2O(ox)_2Cl_2]\cdot 2H_2O\}_n$	MS	$J = -46.4$	$g = 2.0$	$G_x = G_y = 3.6$	Arm[73]	
$[Fe_3^{III}]$ complexes						
$\{3Fe\text{-}4S\}^+$ core of ferredoxin II	MS, ESR	$J_{ij} = -300$ to -310	$[g_z = 2]$ $g_{xy} = 1.97$	$d = 0.4$	San [41]	$d = d_z^{12} = d_z^{23} = d_z^{31}$ $g_\perp = g_0\left(1 - \frac{243d^2}{2\delta^2}\right)$ $\delta \approx 3(J_{23} - J_{13})$
$[Fe_3O(O_2CEt)_6(H_2O)_3]Cl\cdot 5H_2O$	ESR $T = 4.2$ K	$J = -60$	$g_z = 2.020$ $g_{xy} = 2.000$	$d = 1.4$	Rak [42]	
$\{Fe_3O\}^{7+}$ core in $[Fe_6Na_2O_2(O_2CPh)_{10}(pic)_4(EtOH)_4(H_2O)_2](ClO_4)_2\cdot 2EtOH$	X, ESR, MS				Bou [43] San [44]	$J_1(\times 2), J_2(\times 1)$
	a-set	$J_1 = -54.8$ $J_2 = -41.8$	$g_{iso} = 2.0$ $g_{xy} = 1.70$ $g_z = 2.00$	$d \approx 2 - 4$		$\Delta^2 = \sigma^2 + 243d^2$
	b-set	$J_1 = -45.4$ $J_2 = -63.2$				
$(NH_4)[Fe_3(OH)(H_2L)_3(HL)_3]$	X, M, ESR	$J_1 = -38.4$ $J_2 = -64.6$	$[g = 2]$	ineffective	Rap [45]	$J_1(\times 2), J_2(\times 1)$
$(Et_3NH)_4\ [Fe_3O(NO_2\text{-}pz)_6Cl_3]Cl_2$	X, M, ESR				Pin [46]	
	a-set	$J_1 = -80.1$ $J_2 = -72.4$	$g_{iso} = 2.00$	$d_z = 5.09$		$J_1(\times 2), J_2(\times 1)$
	b-set	$J_1 = -70.6$ $J_2 = -80.8$	$g_{xy} = 1.53$ $g_z = 1.1$	$d_z = 9.87$		
Other complexes						
$[Ni_3(pmdien)_3(\mu\text{-ttc})](ClO_4)_3$		$J = 1.67$	$g_z = 2.099$ $g_x = 1.265$	$d_z = 4.95$	Kop [47]	
$[M_n]$ complexes						
$[Cu_4OCl_6(OPPh_3)_4]$	X	$J^+/d = -0.4$	$\gamma^2 = 0.46$	$d = 62.5$	Lin [48]	
$[Ni_4(ROH)_4L_4]$	X		$D = 6.5$ $E = 2.27$	$G_{xy} = 5$ $G_z = -6$	Kir [51]	$J_A(\times 2), J_B(\times 4)$
	M	$J_A = -2.4$ $J_B = +14.0$	$D = 6$ $E = 2.89$	$G_{xy} = 4.8$ $G_z = -10$		
	INS	$J_A = -2.4$ $J_B = +14.0$	$D = 7.8$	$G_{xy} = 4.9$ $G_z = -7$		
$[PPN][Cu_6(\mu_3\text{-}O)_2(\mu\text{-}4\text{-}Br\text{-}pz)_6(\mu\text{-}3,5\text{-}Ph_2\text{–}4\text{-}Br\text{-}pz)_3]$	X, M	$J_{23} = -722$ $J_{13} = -667$ $J_{12} = -637$ $J_{14} = -26$	$g = 1.95$	$d_z = 30$	Zue [53]	
$[NaFe_6(OCH_3)_{12}(C_{17}H_{15}O_4)_6]\ ClO_4$	M, $T = 0.04$ K, $B = 28$ T	$J = 21.8$		$\lvert d_i - d_{i+1}\rvert = 0.0136$ J	Cin [74]	Fe_6-ring
					Has [75]	

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[a] Abbreviations for ligands: Haaat = 3-acetylamino-5-amino-1,2,4-triazole; Haat = 3-acetylamino-1,2,4-triazole; HXTA = N,N′-(2-hydroxy-5-methyl-1,3-xylylene)bis(N-carboxymethylglycine); MMOH = dinuclear iron cluster of the oxidized hydroxylase component of methane monooxygenase; Hdepa = 2,2′-(bis-4-ethylpyridyl)amine, Mes-Hpz = 3{5}-(2,4,6-trimethylphenyl)pyrazole; DBED = N,N′-di-*tert*-butylethylenediamine; H_3L = orotic acid, L^1 = 1,4,7.trimethyl- 1,4,7-triazacyclononane, Im = imidazolide, L^2 = dodecaaza macrotetracycle, 2,4,5-T = 2,4,5-trichlorophenoxyacetate.

[b] Methods: X – magnetic susceptibility, M – magnetization, ESR – electron spin resonance, SC – single crystal, MS – Mössbauer spectroscopy, MCD – magnetic circular dichroism, C – calculations, INS – inelastic neutron scattering.

[c] The J-constants eventually rescaled to the form $\hat{H}_{AB}^{iso} = -J_{AB}(\vec{S}_A \cdot \vec{S}_B)$; $J_{av} = (2J_1 + J_2)/3$; δ and δ' are the small changes in the isotropic exchange due to symmetry lowering. Fixed parameters are given in brackets.

[d] The sign of the antisymmetric exchange parameter is uncertain: d means $|d|$. (E/k) [K] = $1.4388(E/hc)$ [cm^{-1}].

The best studied case is consideration of the z-component of the parameter vector (A_n) for genuine spins $s = 1/2$ that is appropriate to $[\mathrm{V}_3^{\mathrm{IV}}]$ or $[\mathrm{Cu}_3^{\mathrm{II}}X]$ cores. In this case the interaction matrix is

$$\mathbf{H}_z^{\mathrm{anti}} = \left(\begin{array}{cccc|cc:cc} 0 & . & . & . & 0 & . & 0 & . \\ . & 0 & . & . & 0 & 0 & 0 & 0 \\ . & . & 0 & . & 0 & 0 & 0 & 0 \\ . & . & . & 0 & . & 0 & . & 0 \\ \hline 0 & 0 & 0 & . & 0 & . & * & * \\ . & 0 & 0 & 0 & . & 0 & * & * \\ \hdashline 0 & 0 & 0 & . & (+\sqrt{3}/2)\mathrm{i}A_n & 0 & 0 & . \\ . & 0 & 0 & 0 & 0 & (-\sqrt{3}/2)\mathrm{i}A_n & . & 0 \end{array}\right) \text{for} \left[\begin{array}{lll} S_{12}=1 & S=3/2 & M=-3/2 \\ & & M=-1/2 \\ & & M=+1/2 \\ & & M=+3/2 \\ \hline S_{12}=1 & S=1/2 & M=-1/2 \\ & & M=+1/2 \\ \hdashline S_{12}=0 & S=1/2 & M=-1/2 \\ & & M=+1/2 \end{array}\right] \tag{5.5}$$

In the uncoupled basis set ordered in the standard ascending way there is

$$(\mathbf{H}_{12}^{\mathrm{anti}} + \mathbf{H}_{23}^{\mathrm{anti}} + \mathbf{H}_{31}^{\mathrm{anti}})_z = i(A_n/2) \begin{pmatrix} . & . & . & . & . & . & . & . \\ . & . & * & . & * & . & . & . \\ . & +1 & . & . & * & . & . & . \\ . & . & . & . & . & * & * & . \\ . & -1 & +1 & . & . & . & . & . \\ . & . & . & +1 & . & . & * & . \\ . & . & . & -1 & . & +1 & . & . \\ . & . & . & . & . & . & . & . \end{pmatrix} \tag{5.6}$$

These two matrices are equivalent representation of the antisymmetric exchange as they are related by the unitary transformation (the coupling). They possess an identical set of eigenvalues: $\{-(\sqrt{3}/2)A_n\}$-twice, $\{+(\sqrt{3}/2)A_n\}$-twice, and $\{0\}$-four-times. On adding the isotropic exchange, the zero-field energy levels $\varepsilon(S_{12}, S)$ become

$$\left.\begin{array}{l} \varepsilon(1, 1/2) \\ \varepsilon(0, 1/2) \end{array}\right\} = \left\{\begin{array}{l} +(3/4)J - (\sqrt{3}/2)A_n \\ +(3/4)J + (\sqrt{3}/2)A_n \end{array}\right. \tag{5.7}$$

(due to the "interaction" the doublets cannot be assigned to a definite intermediate spin S_{12}). This means that the degeneracy of $\left|1, 1/2\right\rangle$ and $\left|0, 1/2\right\rangle$ states is removed just by the antisymmetric exchange. (The asymmetric exchange is incapable of such a kind of zero-field splitting because there is no interaction element between $\left|1, 1/2\right\rangle$ and $\left|0, 1/2\right\rangle$ kets.)

For the kets $\left|S_{12}, S, M\right\rangle$ ordered differently, the ASE matrix has been derived in the form [23]

$$\mathbf{H}^{\mathrm{anti}} = \left(\begin{array}{cc:cc|cccc} . & . & * & . & * & . & * & . \\ . & . & . & * & . & * & . & * \\ \hdashline (\sqrt{3}/2)\mathrm{i}A_n & . & . & . & * & . & * & . \\ . & (-\sqrt{3}/2)\mathrm{i}A_n & . & . & . & * & . & * \\ \hline (3/4)\mathrm{i}A_- & . & (3/4)A_- & . & . & . & . & . \\ . & (\sqrt{3}/4)\mathrm{i}A_- & . & (\sqrt{3}/4)A_- & . & . & . & . \\ (\sqrt{3}/4)\mathrm{i}A_+. & . & (-\sqrt{3}/4)A_+ & . & . & . & . & . \\ . & (3/4)\mathrm{i}A_+ & . & (-3/4)A_+ & . & . & . & . \end{array}\right) \text{for} \left[\begin{array}{lll} S_{12}=0 & S=1/2 & M=+1/2 \\ & & M=-1/2 \\ \hdashline S_{12}=1 & S=1/2 & M=+1/2 \\ & & M=-1/2 \\ \hline S_{12}=1 & S=3/2 & M=+3/2 \\ & & M=+1/2 \\ & & M=-1/2 \\ & & M=-3/2 \end{array}\right] \tag{5.8}$$

This matrix differs from the above derivation by a phase factor that is irrelevant to the eigenvalues. The corresponding isotropic exchange + Zeeman matrix (in the approximation of the strong exchange limit) is

$$\mathbf{H}^{\mathrm{iso+Z}} = \left(\begin{array}{cc:cc|cccc} -3j/2+\gamma_z/2 & * & . & . & . & . & . & . \\ -\gamma_+/\sqrt{2} & -3j/2-\gamma_z/2 & . & . & . & . & . & . \\ \hdashline . & . & -3j/2+\gamma_z/2 & * & . & . & . & . \\ . & . & -\gamma_+/\sqrt{2} & -3j/2-\gamma_z/2 & . & . & . & . \\ \hline . & . & . & . & 3j/2+3\gamma_z/2 & * & . & . \\ . & . & . & . & (-\sqrt{3}/2)\gamma_+ & 3j/2+\gamma_z/2 & * & . \\ . & . & . & . & . & -\sqrt{2}\gamma_+ & 3j/2-\gamma_z/2 & * \\ . & . & . & . & . & . & (-\sqrt{3}/2)\gamma_+ & 3j/2-3\gamma_z/2 \end{array}\right) \tag{5.9}$$

where the Zeeman factors are $\gamma_\pm \equiv \mp g_\perp \mu_{\mathrm{B}}(B_x \pm iB_y)/\sqrt{2}$, $\gamma_z \equiv g_\parallel \mu_{\mathrm{B}} B_z$, and the isotropic exchange constant has altered sign $2j \equiv -J$. With the magnetic field applied *parallel* to the three-fold rotation axis ($B_\perp C_3$), after introducing the Zeeman factor $\gamma \equiv g_\perp \mu_B B_\perp$, we get the exact eigenvalues

$$\begin{aligned} \varepsilon_{1,3}^{\perp} &= (-3/2)j - (1/2)\sqrt{3A_n^2 + \gamma^2} \\ &= (-3/2)j - (\sqrt{3}/2)A_n\sqrt{1 + (\gamma/3A_n)^2} \end{aligned} \tag{5.10}$$

$$\begin{aligned} \varepsilon_{2,4}^{\perp} &= (-3/2)j + (1/2)\sqrt{3A_n^2 + \gamma^2} \\ &= (-3/2)j + (\sqrt{3}/2)A_n\sqrt{1 + (\gamma/3A_n)^2} \end{aligned} \tag{5.11}$$

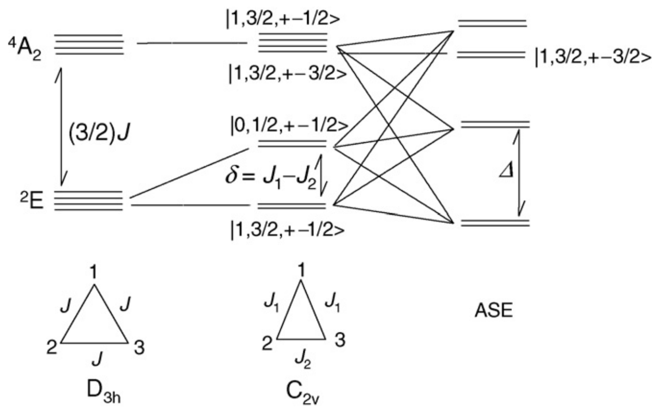

Fig. 13. Splitting of the zero-field energy levels by the isotropic and antisymmetric exchange for $s = 1/2$ *triangulo*-triads.

$$\varepsilon_{5,6}^{\perp} = (3/2)j \mp (1/2)\gamma \quad (5.12)$$

$$\varepsilon_{7,8}^{\perp} = (3/2)j \mp (3/2)\gamma \quad (5.13)$$

The zero-field energy levels are split into two Kramers doublets separated by the gap $\Delta = \sqrt{3}A_n$. At low fields (LF), when $\gamma \equiv g_{\perp}\mu_B B_{\perp} < \Delta$, the Zeeman energy levels stay doubly degenerate but they show a quadratic dependence upon the field

$$\varepsilon_{1,3}^{\perp}(LF) = -(3/2)j - (\sqrt{3}/2)A_n - \gamma^2/(4\sqrt{3}A_n) \quad (5.14)$$

$$\varepsilon_{2,4}^{\perp}(LF) = -(3/2)j - (\sqrt{3}/2)A_n + \gamma^2/(4\sqrt{3}A_n) \quad (5.15)$$

The dependence upon the high field (HF) approaches a linear dependence since then

$$\varepsilon_{1,3}^{\perp}(HF) = -(3/2)j - \gamma/2 - 3A_n^2/\gamma \quad (5.16)$$

$$\varepsilon_{2,4}^{\perp}(HF) = -(3/2)j + \gamma/2 + 3A_n^2/\gamma \quad (5.17)$$

There is not an avoided crossing of energy levels owing to the perpendicular component of the ASE (Fig. 14). However, with the in-plane components ($A_i \neq 0$ or $A_l \neq 0$) the ASE acts as a first-order perturbation that causes an avoided crossing of the ground ($S = 1/2$) and excited ($S = 3/2$) states.

The molar magnetization is as a thermal average of the microscopic magnetic moment

$$M_{\text{mol}} = N_{\text{A}}[\sum_i -(\partial\varepsilon_i/\partial B)\exp(-\varepsilon_i/kT)]/[\sum_i \exp(-\varepsilon_i/kT)] \quad (5.18)$$

Only the low-lying levels contribute to the magnetization at low temperature. Using the shifted energy levels for two Kramers doublets:

$$\varepsilon_{1,3}^{\perp} = -(3A_n^2 + \gamma^2)^{1/2}/2 \quad (5.19)$$

$$\varepsilon_{2,4}^{\perp} = +(3A_n^2 + \gamma^2)^{1/2}/2 \quad (5.20)$$

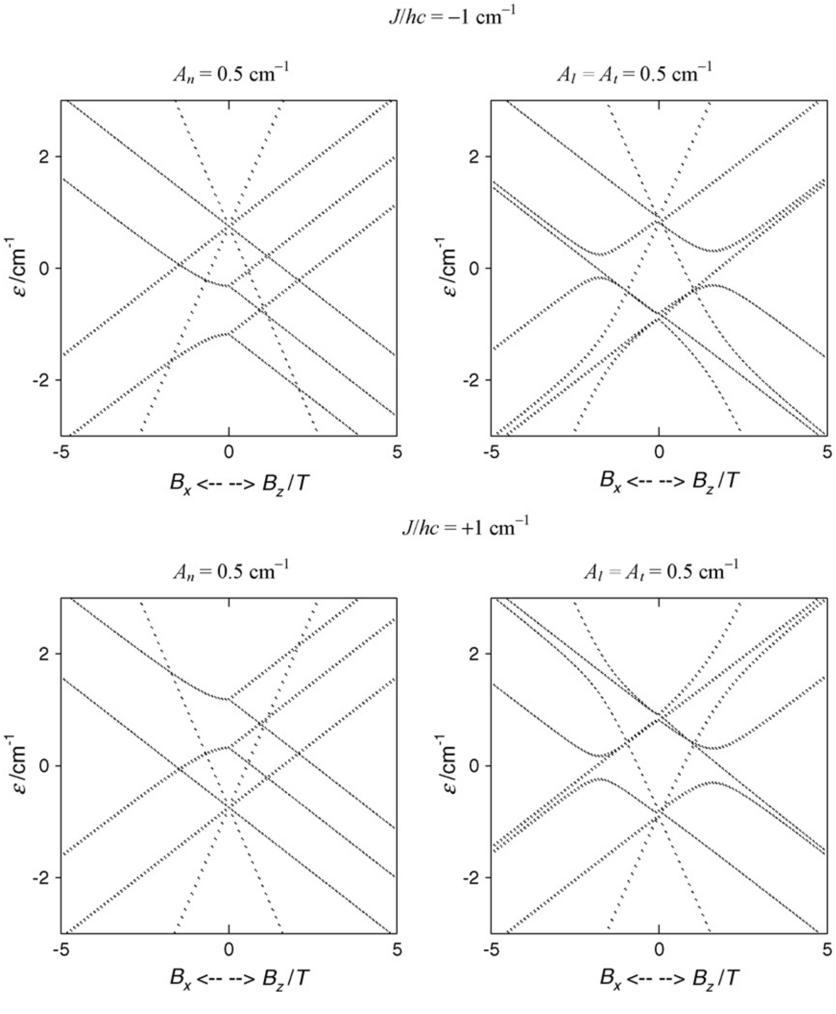

Fig. 14. Development of energy levels for *triangulo*-[1/2,1/2,1/2] spin system in the magnetic field taken in the weak exchange limit. Net effect of the normal component (left) and of the in-plane component (right) of the antisymmetric exchange.

Table 8
Proportionality constant α for the ASE in *triangulo*-triads[a].

$s=S_1=S_2=S_3$	S'_{12}	S_{12}	α_s[b]	Energy gap[c]
1/2	1	0	$\sqrt{3}/6$	$\Delta = 2G = 2G_z = \sqrt{3}G_z^{AB} = \sqrt{3}d_z^{AB}$
3/2	2	1	$2\sqrt{3}/3$	$\Delta = 4\sqrt{3}G_z^{AB}$
5/2	3	2	$3\sqrt{3}/2$	$\Delta = 9\sqrt{3}G_z^{AB}$

[a] For heteronuclear triads consult [3,24]. S_{12} is the smaller of the two values of intermediate spin.

[b] Many-electron parameter $G_a = \alpha \sum_{A \neq B}^{\text{cyclic}} G_\alpha^{AB} = \alpha[G_a^{(12)} + G_a^{(23)} + G_a^{(31)}]$ for $a=x$, y, z; $G^2 = G_x^2 + G_y^2 + G_z^2$. For *triangulo*-triads $G_x = G_y = 0$, $G_z^{AB} = G_z^{(12)} = G_z^{(23)} = G_z^{(31)}$, and $G \leftarrow G_z = 3\alpha G_z^{AB} = 3\alpha d_z^{AB}$.

[c] Zero-field splitting of two Kramers doublets.

whose derivatives with respect to the magnetic field are ($\gamma' \equiv g_\perp \mu_B$)

$$\varepsilon'^{\perp}_{1,3} = -\gamma'\gamma(3A_n^2 + \gamma^2)^{-1/2}/2 \tag{5.21}$$

$$\varepsilon'^{\perp}_{2,4} = +\gamma'\gamma(3A_n^2 + \gamma^2)^{-1/2}/2 \tag{5.22}$$

with $\gamma' = \mu_B g_\perp$, the magnetization results in the form of:

$$M_{\text{mol}}^{\perp} = N_A \frac{\gamma'\gamma}{2(3A_n^2 + \gamma^2)^{1/2}} \times \frac{\exp[+(3A_n^2 + \gamma^2)^{1/2}/2kT] - \exp[-(3A_n^2 + \gamma^2)^{1/2}/2kT]}{\exp[+(3A_n^2 + \gamma^2)^{1/2}/2kT] + \exp[-(3A_n^2 + \gamma^2)^{1/2}/2kT]} \tag{5.23}$$

In the low-field and low-temperature limit the exponential-containing term collapses to 1:

$$\frac{\exp(+a/T) - \exp(-a/T)}{\exp(+a/T) + \exp(-a/T)} = \tanh(a/T) \xrightarrow{T \to 0} 1 \tag{5.24}$$

(using $a \equiv (3A_n^2 + \gamma^2)^{1/2}/2k$) and then we get the simple formula:

$$M_{\text{mol}}^{\perp}(LF) = N_A \mu_B g_\perp \frac{\gamma}{2(3A_n^2 + \gamma^2)^{1/2}} \tag{5.25}$$

for $\gamma \equiv g_\perp \mu_B B_\perp$. Notice, the zero-field energy gap is related to the factor $\Delta = \sqrt{3}A_n = 2G = G'$ where new parameters (G or G'), met later, occur. Remember also the notation used: $d_{1,0}^{AB} = d_z^{AB} = A_n$. The perpendicular component of the susceptibility *per triad* is then:

$$\chi_{\text{mol}}^{\perp}(LF) \doteq \mu_0 M_\perp / B = \{N_A \mu_0 \mu_B^2 g_\perp^2 / [2(3A_n^2 + \gamma^2)^{1/2}]\} \tanh[(3A_n^2 + \gamma^2)^{1/2}/2kT] \tag{5.26}$$

which matches the earlier derivations with $3A_n^2 = 4G^2 = G'^2$ [3] (Note: the susceptibility formula was originally presented per metal ion, differing thus by a factor of 1/3.) In the low-temperature limit it becomes:

$$\chi_{\text{mol}}^{\perp}(LF, LT) \to N_A \mu_0 \mu_B^2 g_\perp^2 / (2\sqrt{3}A_n) \tag{5.27}$$

(In paper [37], the energy gap between two Kramers doublets is claimed to be $\Delta = 3\sqrt{3}G_{AB}$, with $G = 3G_{AB} = 3d_z^{AB}$, and in the formula for $\chi_\perp$ a factor of (1/2) is missing.)

When three lowest levels $\left|S_{12}, S, M\right\rangle$ are involved, namely $\left|0, 1/2, -1/2\right\rangle$, $\left|1, 1/2, -1/2\right\rangle$, and $\left|1, 3/2, -3/2\right\rangle$, the energy levels in this restricted basis are [23]:

$$\varepsilon_1^{\perp} = -(3/2)j - \gamma/2 \tag{5.28}$$

$$\varepsilon_7^{\perp} = -\gamma + (1/8)[18A_\perp^2 + 16(\gamma - 3j)^2]^{1/2} \tag{5.29}$$

$$\varepsilon_3^{\perp} = -\gamma - (1/8)[18A_\perp^2 + 16(\gamma - 3j)^2]^{1/2} \tag{5.30}$$

Since

$$\varepsilon'^{\perp}_3 = -\gamma'\{1 + 2(\gamma - 3j)[18A_\perp^2 + 16(\gamma - 3j)^2]^{-1/2}\} \tag{5.31}$$

the perpendicular component of the magnetization in the high-field (and low temperature) becomes:

$$M_{\text{mol}}^{\perp}(HF) = N_A g \mu_B \left\{1 + 2(\gamma - 3j)[18A_\perp^2 + 16(\gamma - 3j)^2]^{-1/2}\right\} \tag{5.32}$$

Tsukerblat et al. [3,24] derived that the ASE operator for a triad, restricted to the basis of two Kramers doublets $2D^{(1/2)}$, can be represented in a universal form:

$$\hat{H}^{\text{anti}} = \sum_{A \neq B}^{\text{cyclic}} \vec{G}_{AB} \cdot (\vec{S}_A \times \vec{S}_B) \to G_x(\boldsymbol{\sigma}_y \otimes \boldsymbol{\sigma}_x) + G_y(\boldsymbol{\sigma}_y \otimes \boldsymbol{\sigma}_y) + G_z(\boldsymbol{\sigma}_y \otimes \boldsymbol{\sigma}_z) \tag{5.33}$$

where ($\boldsymbol{\sigma}_x$, $\boldsymbol{\sigma}_y$, $\boldsymbol{\sigma}_z$) are Pauli matrices. The constants (G_x, G_y, G_z) are regarded as many-electron antisymmetric exchange parameters obeying the addition:

$$G_a = \alpha \sum_{A \neq B}^{\text{cyclic}} G_\alpha^{AB} \tag{5.34}$$

($a = x, y, z$) while the proportionality constant is defined as follows:

$$\alpha = 6^{-1/2}(-1)^{S_1+S_2+S_3+1/2}(S'_{12} + S_{12} + 1) \times [S_1(S_1+1)(2S_1+1)(2S_{12}+1)(2S'_{12}+1)]^{1/2} \times \begin{Bmatrix} S'_{12} & S_1 & S_2 \\ S_1 & S_{12} & 1 \end{Bmatrix} \begin{Bmatrix} S'_{12} & 1/2 & S_3 \\ 1/2 & S_{12} & 1 \end{Bmatrix} \tag{5.35}$$

with S_{12} being the smaller of the two values of intermediate spin (Table 8). In writing the 4 × 4 interaction matrix the members of the basis set are ordered as follows:

$$\left|S_{12}, S, M\right\rangle = \begin{pmatrix} \left|S_{12}, 1/2, +1/2\right\rangle \\ \left|S_{12}, 1/2, -1/2\right\rangle \\ \left|S_{12}+1, 1/2, +1/2\right\rangle \\ \left|S_{12}+1, 1/2, -1/2\right\rangle \end{pmatrix} \tag{5.36}$$

In order to study the single-crystal ESR spectra a more general form of the Zeeman term is appropriate in which the anisotropy of the Zeeman interaction is taken into account:

$$\hat{H}^Z = \hbar^{-1} \mu_B g(\vec{B} \cdot \vec{S}) = \gamma \hat{S}_z \cos\vartheta \tag{5.37}$$

where ϑ is the angle between the direction of the magnetic field and the trigonal (z) axis of the *triangulo*-triad and $\gamma \equiv g\mu_B B$. This leads to the magnetic energy levels [3]:

$$\varepsilon_{1,2}^{\pm} = \pm[G^2 \pm G\gamma\cos\vartheta + (\gamma/2)^2]^{1/2} \tag{5.38}$$

revealing a zero-field energy gap of $\Delta = 2G = 2G_z = \sqrt{3}G_z^{AB} = \sqrt{3}d_z^{AB}$. We need be careful since in this case:

$$G^2 = G_x^2 + G_y^2 + G_z^2, G_a = (\sqrt{3}/6)[G_a^{(12)} + G_a^{(23)} + G_a^{(31)}], G \leftarrow G_z = (\sqrt{3}/2)G_z^{AB} \tag{5.39}$$

Using an altered definition [25]:

$$G'^2 = 3(G'^2_x + G'^2_y + G'^2_z), G'_a = G_a^{(12)} + G_a^{(23)} + G_a^{(31)}, G' \leftarrow \sqrt{3}G'_z \tag{5.40}$$

one arrives at the energy levels:

$$\varepsilon_{1,2}^{\pm} = \pm(1/2)[G'^2 \pm 2G'\gamma\cos\vartheta + \gamma^2]^{1/2} \tag{5.41}$$

and the zero-field energy gap of $\Delta = |G'|$.

With $\vartheta = 0$ the energy levels depend linearly upon the field:

$$\varepsilon_{||}^{\pm} = \pm[G^2 \pm G\gamma + (\gamma/2)^2]^{1/2} = \pm|G \pm \gamma/2| \tag{5.42}$$

and after substitution into the van Vleck formula we get the parallel susceptibility component in the form of the Curie law:

$$\chi_{\text{mol}}^{||}(LF) = (N_{\text{A}}\mu_0\mu_{\text{B}}^2/k)g_{||}^2/(4T) = C_0 g_{||}^2/4T \tag{5.43}$$

With $\vartheta = \pi/2$ and in small fields the expansion of the square root yields the energy levels:

$$\begin{aligned}\varepsilon_{\perp}^{\pm} &= \pm[G^2 + (\gamma/2)^2]^{1/2} \\ &= \pm G[1 + (\gamma/2G)^2]^{1/2} \doteq \pm\,[G + \gamma^2/(8G)]\end{aligned} \tag{5.44}$$

and then, by applying the van Vleck formula, the perpendicular susceptibility component results in the form

$$\chi_{\text{mol}}^{\perp}(LF) = N_{\text{A}}\mu_0\mu_{\text{B}}^2 \frac{g_{\perp}^2}{4G} \frac{\exp(+G/kT) - \exp(-G/kT)}{\exp(+G/kT) + \exp(-G/kT)} \tag{5.45}$$

which no longer resembles a Curie paramagnet. Remember that

$$\frac{\exp(+G/kT) - \exp(-G/kT)}{\exp(+G/kT) + \exp(-G/kT)} = \tanh(G/kT) \xrightarrow{T \to 0} 1 \tag{5.46}$$

so that the low-temperature perpendicular susceptibility component approaches a constant limit

$$\chi_{\text{mol}}^{\perp}(LF, LT) \to N_{\text{A}}\mu_0\mu_{\text{B}}^2 g_{\perp}^2/(4G) = C_0 g_{\perp}^2/(4G/k) \tag{5.47}$$

The theory of the antisymmetric exchange in the exchanged coupled equilateral and distorted metal trimers of the type *triangulo*-[M_3^{III}O] (M = Cu, Cr, Fe) and *triangulo*-[$\text{M}_2^{\text{III}}\text{M}'^{\text{III}}$O] (M = Fe, M′ = Cr and vice versa) have been developed by Tsukerblat and co-workers and applied mostly in the explanation of the EPR and Mössbauer spectroscopy and also in the magnetism and the heat capacity experiments [24–25d,95–100].

The $s = 3/2$ triads, referring to *triangulo*-[Cr_3^{III}O] complexes, have been studied in detail by HONDA [32]. With antiferromagnetic coupling, the lowest energy levels refer to $|S_{12}, S, M\rangle$ spin states of which $|1, 1/2, \pm 1/2\rangle$ and $|2, 1/2, \pm 1/2\rangle$ are the lowest Kramers doublets. Restricting to them, the matrix elements of the spin Hamiltonian:

$$\begin{aligned}\hat{H}^s = {} & -J_0\hbar^{-2}[(\vec{S}_1 \cdot \vec{S}_2) + (\vec{S}_2 \cdot \vec{S}_3) + (\vec{S}_3 \cdot \vec{S}_1)] - J_1\hbar^{-2}(\vec{S}_3 \cdot \vec{S}_1) \\ & + \hbar^{-2}[\vec{d}_{12} \cdot (\vec{S}_1 \times \vec{S}_2) + \vec{d}_{23} \cdot (\vec{S}_2 \times \vec{S}_3) + \vec{d}_{31} \cdot (\vec{S}_3 \times \vec{S}_1)] \\ & + \hbar^{-1}\mu_B B(\sin\vartheta\cos\varphi g_x\hat{S}_x + \sin\vartheta\sin\varphi g_y\hat{S}_y + \cos\vartheta g_z\hat{S}_z)\end{aligned} \tag{5.48}$$

are

$$H_{ij} = \left(\begin{array}{cc|cc} \delta/2+\gamma_z & * & * & * \\ \gamma_+/2 & \delta/2-\gamma_z & * & * \\ \hline \mathrm{i}D_z/2 & \mathrm{i}D_-/2 & -\delta/2+\gamma_z & * \\ \mathrm{i}D_+/2 & -\mathrm{i}D_z/2 & \gamma_+/2 & -\delta/2-\gamma_z \end{array}\right) \text{ for } \begin{bmatrix} |2,1/2,+1/2\rangle \\ |2,1/2,-1/2\rangle \\ |1,1/2,+1/2\rangle \\ |1,1/2,-1/2\rangle \end{bmatrix} \tag{5.49}$$

where $\delta = -4J_1' = -2J_1$ refers to the zero-field energy gap in the isotropic exchange limit, the Zeeman components are $\gamma_a = g_a\mu_{\text{B}}B_a$ ($a = x, y, z$), $\gamma_{\pm} = \gamma_x \pm i\gamma_y$, and the antisymmetric exchange components are, for the moment, labeled as $D_a = (4/\sqrt{3})[d_a^{(12)} + d_a^{(23)} + d_a^{(31)}]$ and $D_{\pm} = D_x \pm iD_y$; the relationship with the above conventions is $D_a = 2G_a = G_a'$. The diagonalization of the interaction matrix yields the exact energy levels in the form:

$$\varepsilon_{1-4} = \pm\left[\Delta^2 + \gamma^2 \pm 2\sqrt{\delta^2\gamma^2 + (\vec{\gamma} \cdot \vec{D})^2}\right]^{1/2} \Big/ 2 \tag{5.50}$$

where $\vec{D} = (D_x, D_y, D_z)$, $\vec{\gamma} = (\gamma_x, \gamma_y, \gamma_z)$, and $\Delta = (\delta^2 + \vec{D}^2)^{1/2}$. Angular dependence of the resonance fields B_i^{r} for seven ESR transitions can be derived with the help of the substitutions:

$$g = |\vec{\gamma}|/(\mu_B B) = (g_x^2 \sin^2\vartheta\cos^2\varphi + g_y^2 \sin^2\vartheta\sin^2\varphi + g_z^2\cos^2\vartheta)^{1/2} \tag{5.51}$$

$$d = (\vec{\gamma} \cdot \vec{D})/|\vec{\gamma}| = (D_x g_x \sin\vartheta\cos\varphi + D_y g_y \sin\vartheta\sin\varphi + D_z g_z\cos\vartheta)/g \tag{5.52}$$

and for the microwave energy $\varepsilon_0 = h\nu$ they are

$$g\mu_B B_{1,2,5,6}^{\text{r}} = \varepsilon_0\left|\frac{\Delta^2 - \varepsilon_0^2}{\delta^2 + d^2 - \varepsilon_0^2}\right| \tag{5.53}$$

$$g\mu_B B_{3,4}^{\text{r}} = \mp\sqrt{\varepsilon_0^2 + d^2 - \vec{D}^2} + \sqrt{\delta^2 + d^2} \tag{5.54}$$

$$g\mu_B B_7^{\text{r}} = \sqrt{\varepsilon_0^2 + d^2 - \vec{D}^2} - \sqrt{\delta^2 + d^2} \tag{5.55}$$

The effective *g*-factors for the low-field transitions are

$$g_{\text{eff}} = g\left[1 - \frac{\vec{D}^2 - d^2}{\Delta^2 - \varepsilon_0^2}\right]^{1/2} \tag{5.56}$$

For the axially symmetric system, when $D_x = D_y = 0$ is assumed, some simplifications become evident:

$$|\vec{\gamma}| = \mu_B B(g_{xy}^2\sin^2\vartheta + g_z^2\cos^2\vartheta)^{1/2} \tag{5.57}$$

$$(\vec{\gamma} \cdot \vec{D}) = 4\sqrt{3}D_z(\mu_{\text{B}} B g_z \cos\vartheta) \tag{5.58}$$

$$|\vec{D}| = 4\sqrt{3}|D_z| \tag{5.59}$$

These formulae have been used in a detailed analysis of the single-crystal ESR spectra [32] and accepted also by followers [35]. In the forthcoming publication [33] the matrix elements of the ASE for the full 64 × 64 matrix are reported and applied in interpreting the high-field magnetization data. The antisymmetric exchange matrix has been previously used by Nishimura [31] in the form:

$$H_{IJ}^{\text{anti}} = (2/\sqrt{3})\left(\begin{array}{cc|cc} \cdot & \cdot & * & * \\ \cdot & \cdot & * & * \\ \hline -\mathrm{i}D_z & -\mathrm{i}D_x - D_y & \cdot & \cdot \\ -\mathrm{i}D_x + D_y & \mathrm{i}D_z & \cdot & \cdot \end{array}\right) \text{ for } \begin{bmatrix} |1,1/2,+1/2\rangle \\ |1,1/2,-1/2\rangle \\ |2,1/2,+1/2\rangle \\ |2,1/2,-1/2\rangle \end{bmatrix} \tag{5.60}$$

where the parameters in use were $D_a = d_a^{(12)} + d_a^{(23)} + d_a^{(31)}$.

The $s = 3/2$ triad, referring to a *triangulo*-[Co_3^{II}] complex (formed of units with $^4\text{A}_2$ tetrahedral sites), has been studied by BERRY [36] in the restricted basis of 4 kets. With the definitions of $G = G_z = (2/\sqrt{3})(d_z^{(12)} + d_z^{(23)} + d_z^{(31)}) = 2\sqrt{3}d_z^{AB}$ and $\gamma_i = g_i\mu_{\text{B}}B$, the lowest magnetic energy levels are

$$\begin{aligned}\varepsilon_{1,2}^{+} = {} & +[(2G \pm \gamma_{||}\cos\vartheta)^2 + (\gamma_{\perp}\sin\vartheta)^2]^{1/2}/2 \xrightarrow{\text{LF}} +G \pm (\gamma_{||}/2)\cos\vartheta \\ & + \gamma_{\perp}^2\sin\vartheta^2/(8G)\end{aligned} \tag{5.61}$$

$$\begin{aligned}\varepsilon_{1,2}^{-} = {} & -[(2G \pm \gamma_{||}\cos\vartheta)^2 + (\gamma_{\perp}\sin\vartheta)^2]^{1/2}/2 \xrightarrow{\text{LF}} -G \mp (\gamma_{||}/2)\cos\vartheta \\ & - \gamma_{\perp}^2\sin\vartheta^2/(8G)\end{aligned} \tag{5.62}$$

separated by an energy gap of $\Delta = 2G$ at $B = 0$; ϑ is the angle between the field and the C_3 axis of the triangle. For the *z*- and *x*-orientation the energy levels are

$$\varepsilon_{1,2}^{+}(z) = +G \pm (\gamma_{||}/2) \tag{5.63}$$

$$\varepsilon^-_{1,2}(z) = -G \mp (\gamma_{||}/2) \tag{5.64}$$

$$\varepsilon^+_{1,2}(x) = +(4G^2 + \gamma_\perp^2)^{1/2}/2 \xrightarrow{\mathrm{LF}} +G + \gamma_\perp^2/(8G) \tag{5.65}$$

$$\varepsilon^-_{1,2}(x) = -(4G^2 + \gamma_\perp{}^2)^{1/2}/2 \xrightarrow{\mathrm{LF}} -G - \gamma_\perp^2/(8G) \tag{5.66}$$

Under the assumption that the rest of the energy spectrum follows the isotropic pattern, with the substitutions of

$$\Gamma \equiv \exp(G/kT), A \equiv \exp(j/kT) = \exp(J/2kT) \tag{5.67}$$

the zero-field partition function is

$$\begin{aligned} Z_0 &= \sum_S N_S \cdot (2S+1)\exp(-\varepsilon_S^{(0)}/kT) = 2 \cdot (\Gamma^{-1} + \Gamma)A^0 + 4 \cdot 4A^3 \\ &\quad + 3 \cdot 6A^8 + 2 \cdot 8A^{15} + 1 \cdot 10A^{24} \\ &= 2[2\cosh(\Gamma) + 8A^3 + 9A^8 + 8A^{15} + 5A^{24}] \end{aligned} \tag{5.68}$$

where the occurrence factor for individual spin states is $N_S = 2$, 4, 3, 2, and 1 for $S = 1/2$ through $S = 9/2$ lying at 0, $-3j$, $-8j$, $-15j$ and $-24j$; ($2j = J$). Then the susceptibility components in the low-field limit (when the van Vleck formula is operative) become expressed as:

$$\begin{aligned} \breve{\chi}_{||} &= C_0(g_{||}^2/4T)[2\cosh(\Gamma) + 40A^3 + 105A^8 \\ &\quad + 168A^{15} + 165A^{24}]2/Z_0 \end{aligned} \tag{5.69}$$

$$\begin{aligned} \breve{\chi}_{\perp} &= C_0(g_{\perp}^2/4T)[(kT/G)2\sinh(\Gamma) + 40A^3 + 105A^8 \\ &\quad + 168A^{15} + 165A^{24}]2/Z_0 \end{aligned} \tag{5.70}$$

where the special symbol points to the approximations involved: strong exchange limit and low field. At low temperature the isotropic remainder of the partition function vanishes ($A \to 0$ for negative J), and one gets:

$$\breve{\chi}_{||}(LT) = C_0 g_{||}^2/4T \tag{5.71}$$

$$\breve{\chi}_{\perp}(LT) = [C_0 g_\perp^2/(4G/k)]\tanh(G/kT) \xrightarrow{T\to 0} C_0 g_\perp^2/(4G/k) \tag{5.72}$$

The last formula differs from the Curie law. The magnetization components at arbitrary field are reported in [36].

The above procedure in deriving the susceptibility formulae can be applied also for other relevant cases. For the $s = 1/2$ triads, with the help of the α-coefficient from Table 8 we get $G = G_z = (\sqrt{3}/6)(d_z^{(12)} + d_z^{(23)} + d_z^{(31)}) = (\sqrt{3}/2)d_z^{AB}$. The zero-field partition function is

$$Z_0 = 2 \cdot (\Gamma^{-1} + \Gamma)A^0 + 1 \cdot 4A^3 = 2[2\ \cosh(\Gamma) + 2A^3]$$

with the occurrence factors for individual spin states $N_S = 2$ and 1 for $S = 1/2$ (lying at 0) and $S = 3/2$ (at $-3j$), respectively; $2j = J$. Then

$$\breve{\chi}_{||} = C_0(g_{||}^2/4T)[2\ \cosh(\Gamma) + 20A^3]2/Z_0 \tag{5.73}$$

$$\breve{\chi}_{\perp} = C_0(g_{\perp}^2/4T)[(kT/G)2\ \sinh(\Gamma) + 20A^3]2/Z_0 \tag{5.74}$$

where in treating the numerators we utilized:

$$\sum_{M_S=-S}^{+S} M_S^2 = S(S+1)(2S+1)/3 \tag{5.75}$$

Neglecting the A-term, we arrive at the low-temperature limit that matches the above-presented derivations for $s = 1/2$ and $s = 3/2$ triads.

In general, the zero-field partition function can be written in the form

$$Z_0 = 2 \cdot (\Gamma^{-1} + \Gamma)A^0 + \sum_{S \neq 1/2} N_S \cdot (2S+1)A^{S(S+1)-3/4} \tag{5.76}$$

where we shifted the energy levels of the two $S = 1/2$ states to zero. (The occurrence factors of individual spin states N_S can be calculated on the reduction chain of the groups $\mathbf{SU_{(2s+1)}} \to \mathbf{Sp_{(2s+1)}} \to \mathbf{R_3}$, by summing up how many times the spin S in the full-rotation group $\mathbf{R_3}$ occurs in the irreducible representations $[\lambda]$ of the unitary group $\mathbf{SU_{(2s+1)}}$.) For $s = 5/2$ the N_S values for $S = 1/2$ through 15/2 are: 2, 4, 6, 5, 4, 3, 2, 1. The susceptibility components are written in the form:

$$\breve{\chi}_{||} = C_0(g_{||}^2/4T)[2\ \cosh(\Gamma) + 4R]2/Z_0 \tag{5.77}$$

$$\breve{\chi}_{\perp} = C_0(g_{\perp}^2/4T)[(kT/G)2\ \sinh(\Gamma) + 4R]2/Z_0 \tag{5.78}$$

where the remainder is

$$R = \sum_{S \neq 1/2} N_S \cdot (2S+1)[S(S+1)/3]A^{S(S+1)-3/4} \tag{5.79}$$

Remember that the many-electron parameter $G = G_z = \alpha_s(d_z^{(12)} + d_z^{(23)} + d_z^{(31)}) = 3\alpha_s d_z^{AB}$ depends upon the genuine spins s. The closed formulae for magnetic functions of triangulo-systems with the antisymmetric exchange are comprehensively listed in Table 9.

A modeling of the magnetization components for some triangulo systems is presented in Fig. 15.

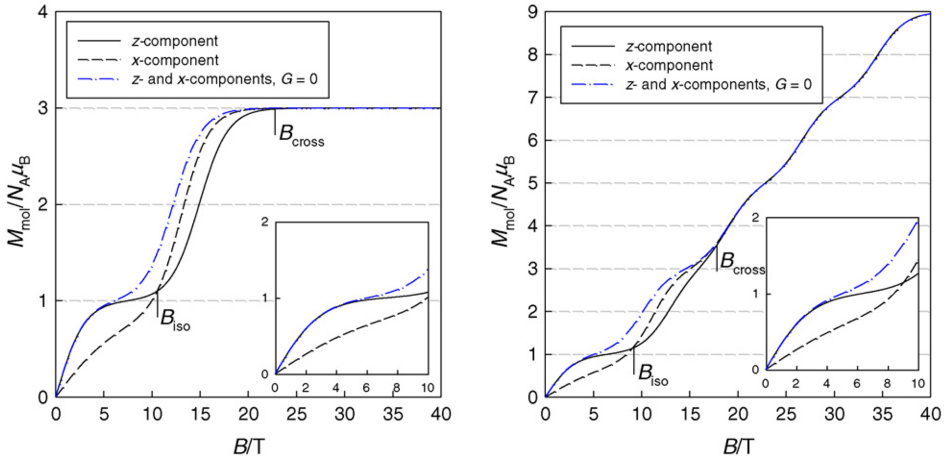

Fig. 15. Modeling of the magnetization components for *triangulo*-[$s = 1/2$] and *triangulo*-[$s = 3/2$] systems with closed formulae in the strong exchange limit; $J/k = -10$ K, $G/k = 5$ K, $T = 2$ K.

Table 9
Closed formulae for the molar magnetization and molar susceptibility upon antisymmetric exchange[a].

Case 1a: *triangulo*-[$s = 1/2$] according to Tsukerblat [3,23, 24]; – many-electron coupling constant $G = G_z = (\sqrt{3}/6)(d_z^{(12)} + d_z^{(23)} + d_z^{(31)}) = (\sqrt{3}/2)d_z^{AB}$; $4G^2 = 3A_n^2$; – restriction to two interacting Kramers doublets ($S = 1/2$) with exact perpendicular eigenvalues		
Perpendicular eigenvalues	Derivatives	Substitutions
$\varepsilon^{\perp}_{(S=1/2)} = -(4G^2 + \gamma^2)^{1/2}/2$ $\varepsilon^{\perp}_{(S=1/2)} = +(4G^2 + \gamma^2)^{1/2}/2$	$\varepsilon'^{\perp}_{(S=1/2)} = -\gamma'\gamma(4G^2 + \gamma^2)^{-1/2}/2$ $\varepsilon'^{\perp}_{(S=1/2)} = +\gamma'\gamma(4G^2 + \gamma^2)^{-1/2}/2$	$\gamma \equiv g_\perp \mu_B B_\perp$, $\gamma' \equiv g_\perp \mu_B$; zero-field energy gap $\Delta = 2G$
Magnetization $M_\perp = N_A \frac{\gamma'\gamma}{2(4G^2+\gamma^2)^{1/2}} \frac{\exp[+(4G^2+\gamma^2)^{1/2}/2kT] - \exp[-(4G^2+\gamma^2)^{1/2}/2kT]}{\exp[+(4G^2+\gamma^2)^{1/2}/2kT] + \exp[-(4G^2+\gamma^2)^{1/2}/2kT]} =$ $N_A \frac{\gamma'\gamma}{2(4G^2+\gamma^2)^{1/2}} \tanh[(4G^2 + \gamma^2)^{1/2}/2kT]$ Approximate susceptibility (low-field, linear magnetic behavior) $\chi_\perp(\mathrm{LF}) \doteq \mu_0 M_\perp / B_\perp = \{N_A \mu_0 \mu_B^2 g_\perp^2 / [2(4G^2 + \gamma^2)^{1/2}]\} \tanh[(4G^2 + \gamma^2)^{1/2}/2kT]$ Low-field and low-temperature limit $M_\perp(\mathrm{LF, LT}) \xrightarrow{T=0} N_A \frac{\gamma'\gamma}{2(4G^2+\gamma^2)^{1/2}} = N_A \mu_B^2 g_\perp^2 \frac{B_\perp}{2(4G^2+\mu_B^2 g_\perp^2 B_\perp^2)^{1/2}}$ $\chi_\perp(\mathrm{LF, LT}) \xrightarrow{T=0} N_A \mu_0 \mu_B^2 g_\perp^2/(4G) = C_0 g_\perp^2/(4G/k)$		
Case 1b: restriction to two interacting Kramers doublets ($S = 1/2$) with approximate perpendicular eigenvalues		
Approximate eigenvalues	van Vleck coefficients	Substitution
$\varepsilon^{\perp}_{(S=1/2)} = -G - \gamma^2/8G$ $\varepsilon^{\perp}_{(S=1/2)} = +G + \gamma^2/8G$	$\varepsilon^{(0),\perp}_{(S=1/2)} = -G$, $\varepsilon^{(2),\perp}_{(S=1/2)} = -(g_\perp \mu_B)^2/8G$ $\varepsilon^{(0),\perp}_{(S=1/2)} = +G$, $\varepsilon^{(2),\perp}_{(S=1/2)} = +(g_\perp \mu_B)^2/8G$	$\gamma \equiv g_\perp \mu_B B_\perp$,
Application of van Vleck formula (low field) $\chi_\perp(\mathrm{LF}) = N_A \mu_0 \mu_B^2 \frac{g_\perp^2}{4G} \frac{\exp(+G/kT) - \exp(-G/kT)}{\exp(+G/kT) + \exp(-G/kT)} = C_0 \frac{g_\perp^2}{4(G/k)} \tanh(G/kT)$ $\chi_\perp(\mathrm{LF,LT}) \to N_A \mu_0 \mu_B^2 g_\perp^2/(4G) = C_0 g_\perp^2/(4G/k)$		
Case 1c: restriction to two interacting Kramers doublets ($S = 1/2$) with exact parallel eigenvalues		
Parallel eigenvalues (exact)	van Vleck coefficients	Substitution
$\varepsilon^{\parallel}_{(S=1/2)} = -G \pm \gamma_\parallel/2$ $\varepsilon^{\parallel}_{(S=1/2)} = +G \pm \gamma_\parallel/2$	$\varepsilon^{(0),\parallel}_{(S=1/2)} = -G$, $\varepsilon^{(1),\parallel}_{(S=1/2)} = \pm(1/2) g_\parallel \mu_B$ $\varepsilon^{(0),\parallel}_{(S=1/2)} = +G$, $\varepsilon^{(1),\parallel}_{(S=1/2)} = \pm(1/2) g_\parallel \mu_B$	$\gamma_\parallel \equiv g_\parallel \mu_B B_\parallel$
Application of van Vleck formula (low field) $\chi^{\parallel}_{\mathrm{mol}}(LF) = (N_A \mu_0 \mu_B^2/k) g_\parallel^2/(4T) = C_0 g_\parallel^2/4T$ (Curie law)		
Case 1d: Involvement of excited quartet ($S = 3/2$) to *triangulo*-[$s = 1/2$] with $2j = J$; – many-electron coupling constant $G = G_z = (\sqrt{3}/6)(d_z^{(12)} + d_z^{(23)} + d_z^{(31)}) = (\sqrt{3}/2)d_z^{AB}$; – approximate perpendicular eigenvalues and exact parallel eigenvalues		
Parallel eigenvalues	van Vleck coefficients	Substitution
$\varepsilon^{\parallel}_{(S=1/2)} = -G \pm (1/2)\gamma_\parallel$ $\varepsilon^{\parallel}_{(S=1/2)} = +G \pm (1/2)\gamma_\parallel$ $\varepsilon^{\parallel}_{(S=3/2)} = -3j \pm (1/2)\gamma_\parallel$ $\varepsilon^{\parallel}_{(S=3/2)} = -3j \pm (3/2)\gamma_\parallel$	$\varepsilon^{(0),\perp}_{(S=1/2)} = -G$, $\varepsilon^{(1),\parallel}_{(S=1/2)} = \pm(1/2) g_\parallel \mu_B$ $\varepsilon^{(0),\perp}_{(S=1/2)} = +G$, $\varepsilon^{(1),\parallel}_{(S=1/2)} = \pm(1/2) g_\parallel \mu_B$ $\varepsilon^{(0),\perp}_{(S=3/2)} = -3j$, $\varepsilon^{(1),\parallel}_{(S=3/2)} = \pm(1/2) g_\parallel \mu_B$ $\varepsilon^{(0),\perp}_{(S=3/2)} = -3j$, $\varepsilon^{(1),\parallel}_{(S=3/2)} = \pm(3/2) g_\parallel \mu_B$	$\gamma_\parallel \equiv g_\parallel \mu_B B_\parallel$
Perpendicular eigenvalues $\varepsilon^{\perp}_{(S=1/2)} = -(4G^2 + \gamma^2)^{1/2}/2$ $\varepsilon^{\perp}_{(S=1/2)} = +(4G^2 + \gamma^2)^{1/2}/2$ $\varepsilon^{\perp}_{(S=3/2)} = -3j \pm (1/2)\gamma$ $\varepsilon^{\perp}_{(S=3/2)} = -3j \pm (3/2)\gamma$		Substitutions $\gamma \equiv g_\perp \mu_B B_\perp$, $\Gamma \equiv \exp(G/kT)$, $A \equiv \exp(j/kT) = \exp(J/2kT)$
Approximate perpendicular eigenvalues $\varepsilon^{\perp}_{(S=1/2)} = -G - \gamma^2/8G$ $\varepsilon^{\perp}_{(S=1/2)} = +G + \gamma^2/8G$ $\varepsilon^{\perp}_{(S=3/2)} = -3j \pm (1/2)\gamma$ $\varepsilon^{\perp}_{(S=3/2)} = -3j \pm (3/2)\gamma$	van Vleck coefficients $\varepsilon^{(0),\perp}_{(S=1/2)} = -G$, $\varepsilon^{(2),\perp}_{(S=1/2)} = -(g_\perp \mu_B)^2/8G$ $\varepsilon^{(0),\perp}_{(S=1/2)} = +G$, $\varepsilon^{(2),\perp}_{(S=1/2)} = +(g_\perp \mu_B)^2/8G$ $\varepsilon^{(0),\perp}_{(S=3/2)} = -3j$, $\varepsilon^{(1),\perp}_{(S=3/2)} = \pm(1/2) g_\perp \mu_B$ $\varepsilon^{(0),\perp}_{(S=3/2)} = -3j$, $\varepsilon^{(1),\perp}_{(S=3/2)} = \pm(3/2) g_\perp \mu_B$	Substitution $\gamma \equiv g_\perp \mu_B B_\perp$
Parallel magnetization $M_\parallel = N_A \frac{\mu_B g_\parallel}{2} \frac{\mathrm{Num}}{\mathrm{Den}}$ $\mathrm{Num} = A^0(\Gamma + \Gamma^{-1})(Z - Z^{-1}) + A^3[(Z - Z^{-1}) + 3(Z^3 - Z^{-3})]$ $\mathrm{Den} = A^0(\Gamma + \Gamma^{-1})(Z + Z^{-1}) + A^3[(Z + Z^{-1}) + (Z^3 + Z^{-3})]$		Substitutions $Z = \exp(\mu_B B g_\parallel/2kT)$, $\Gamma \equiv \exp(G/kT)$, $A \equiv \exp(j/kT) = \exp(J/2kT)$
Perpendicular magnetization $M_\perp = N_A \frac{\mu_B g_\perp}{2} \frac{\mathrm{Num}}{\mathrm{Den}}$		Substitutions $X = \exp(\mu_B B g_\perp/2kT)$, $S = [4G^2 + (g_\perp \mu_B B)^2]^{1/2}$, $\Sigma \equiv \exp(S/2kT)$

Table 9 (*Continued*)

Case 1d: Involvement of excited quartet ($S=3/2$) to *triangulo*-[$s=1/2$] with $2j=J$; – many-electron coupling constant $G=G_z=(\sqrt{3}/6)(d_z^{(12)}+d_z^{(23)}+d_z^{(31)})=(\sqrt{3}/2)d_z^{AB}$; – approximate perpendicular eigenvalues and exact parallel eigenvalues		
Parallel eigenvalues	van Vleck coefficients	Substitution
$\mathrm{Num}=A^0(\mu_B g_\perp B)2(\Sigma-\Sigma^{-1})(S^{-1})+A^3[(X-X^{-1})+3(X^3-X^{-3})]$ $\mathrm{Den}=A^0 2(\Sigma+\Sigma^{-1})+A^3[(X+X^{-1})+(X^3+X^{-3})]$ Approximate susceptibility (strong exchange limit, van Vleck formula, low field) $\chi_\parallel(\mathrm{LF})=C_0(g_\parallel^2/4T)[2\cosh(\Gamma)+20A^3]2/Z_0$ $\chi_\perp(\mathrm{LF})=C_0(g_\perp^2/4T)[(kT/G)2\sinh(\Gamma)+20A^3]2/Z_0$ $Z_0=2[2\cosh(\Gamma)+2A^3]$ Low-temperature limit ($A\to 0$ for $j<0$ and $T\to 0$) $\chi_\parallel(\mathrm{LF,LT})=C_0 g_\parallel^2/4T$ (Curie law) $\chi_\perp(\mathrm{LF,LT})=[C_0 g_\perp^2/(4G/k)]\tanh(G/kT)\xrightarrow{T=0}C_0 g_\perp^2/(4G/k)$		
Case 2: *triangulo*-[$s=3/2$] according to Berry [36] with $2j\equiv +J$; – spin occurrence factors $N_S=2, 4, 3, 2$, and 1 for $S=1/2$ through $S=9/2$ lying at 0, $-3j$, $-8j$, $-15j$ and $-24j$; $D^{(S_1=3/2)}\times D^{(S_2=3/2)}\times D^{(S_3=3/2)}=2D^{(S=1/2)}+4D^{(S=3/2)}+3D^{(S=5/2)}+2D^{(S=7/2)}+D^{(S=9/2)}$; - many-electron coupling constant $G=G_z=(2/\sqrt{3})(d_z^{(12)}+d_z^{(23)}+d_z^{(31)})=2\sqrt{3}d_z^{AB}$		
Perpendicular eigenvalues	Derivatives	Substitutions
$\varepsilon^\perp_{(S=1/2)}=-(4G^2+\gamma_\perp{}^2)^{1/2}/2$ $\varepsilon^\perp_{(S=1/2)}=+(4G^2+\gamma_\perp^2)^{1/2}/2$ $\varepsilon^\perp_{(S=3/2)}=-3j+M_S\gamma_\perp$ $\varepsilon^\perp_{(S=5/2)}=-8j+M_S\gamma_\perp$ $\varepsilon^\perp_{(S=7/2)}=-15j+M_S\gamma_\perp$ $\varepsilon^\perp_{(S=9/2)}=-24j+M_S\gamma_\perp$	$\varepsilon'^\perp_{(S=1/2)}=-\gamma'_\perp\gamma_\perp(4G^2+\gamma_\perp^2)^{-1/2}/2$ $\varepsilon'^\perp_{(S=1/2)}=+\gamma'_\perp\gamma_\perp(4G^2+\gamma_\perp^2)^{-1/2}/2$ $\varepsilon'^\perp_{(S=3/2)}=M_S g_\perp\mu_B$ $\varepsilon'^\perp_{(S=5/2)}=M_S g_\perp\mu_B$ $\varepsilon'^\perp_{(S=7/2)}=M_S g_\perp\mu_B$ $\varepsilon'^\perp_{(S=9/2)}=M_S g_\perp\mu_B$	$\gamma_\perp\equiv g_\perp\mu_B B_\perp$, $\gamma'_\perp\equiv g_\perp\mu_B$; $\Gamma\equiv\exp(G/kT)$, $A\equiv\exp(j/kT)=\exp(J/2kT)$
Approximate eigenvalues $\varepsilon^\perp_{(S=1/2)}=-G-\gamma_\perp^2/(8G)$ $\varepsilon^\perp_{(S=1/2)}=+G+\gamma_\perp^2/(8G)$ $\varepsilon^\perp_{(S=3/2)}=-3j+M_S\gamma_\perp$ $\varepsilon^\perp_{(S=5/2)}=-8j+M_S\gamma_\perp$ $\varepsilon^\perp_{(S=7/2)}=-15j+M_S\gamma_\perp$ $\varepsilon^\perp_{(S=9/2)}=-24j+M_S\gamma_\perp$	van Vleck coefficients $\varepsilon^{(0),\perp}_{(S=1/2)}=-G$, $\varepsilon^{(2),\perp}_{(S=1/2)}=-(g_\perp\mu_B)^2/8G$ $\varepsilon^{(0),\perp}_{(S=1/2)}=+G$, $\varepsilon^{(2),\perp}_{(S=1/2)}=+(g_\perp\mu_B)^2/8G$ $\varepsilon^{(0),\perp}_{(S=3/2)}=-3j$, $\varepsilon^{(1),\perp}_{(S=3/2)}=M_S g_\perp\mu_B$ $\varepsilon^{(0),\perp}_{(S=5/2)}=-8j$, $\varepsilon^{(1),\perp}_{(S=5/2)}=M_S g_\perp\mu_B$ $\varepsilon^{(0),\perp}_{(S=7/2)}=-15j$, $\varepsilon^{(1),\perp}_{(S=7/2)}=M_S g_\perp\mu_B$ $\varepsilon^{(0),\perp}_{(S=9/2)}=-24j$, $\varepsilon^{(1),\perp}_{(S=9/2)}=M_S g_\perp\mu_B$	
Parallel eigenvalues $\varepsilon^\parallel_{(S=1/2)}=-G\pm(1/2)\gamma_\parallel$ $\varepsilon^\parallel_{(S=1/2)}=+G\pm(1/2)\gamma_\parallel$ $\varepsilon^\parallel_{(S=3/2)}=-3j+M_S\gamma_\parallel$ $\varepsilon^\parallel_{(S=5/2)}=-8j+M_S\gamma_\parallel$ $\varepsilon^\parallel_{(S=7/2)}=-15j+M_S\gamma_\parallel$ $\varepsilon^\parallel_{(S=9/2)}=-24j+M_S\gamma_\parallel$	van Vleck coefficients $\varepsilon^{(0),\parallel}_{(S=1/2)}=-G$, $\varepsilon^{(1),\parallel}_{(S=1/2)}=\pm(1/2)g_\parallel\mu_B$ $\varepsilon^{(0),\parallel}_{(S=1/2)}=+G$, $\varepsilon^{(1),\parallel}_{(S=1/2)}=\pm(1/2)g_\parallel\mu_B$ $\varepsilon^{(0),\parallel}_{(S=3/2)}=-3j$, $\varepsilon^{(1),\parallel}_{(S=3/2)}=M_S g_\parallel\mu_B$ $\varepsilon^{(0),\parallel}_{(S=3/2)}=-8j$, $\varepsilon^{(1),\parallel}_{(S=5/2)}=M_S g_\parallel\mu_B$ $\varepsilon^{(0),\parallel}_{(S=3/2)}=-15j$, $\varepsilon^{(1),\parallel}_{(S=7/2)}=M_S g_\parallel\mu_B$ $\varepsilon^{(0),\parallel}_{(S=3/2)}=-24j$, $\varepsilon^{(1),\parallel}_{(S=9/2)}=M_S g_\parallel\mu_B$	
Approximations: strong exchange limit, van Vleck formula (low field) $\chi_\parallel(\mathrm{LF})=C_0(g_\parallel^2/4T)[2\cosh(\Gamma)+40A^3+105A^8+168A^{15}+165A^{24}]2/Z_0$ $\chi_\perp(\mathrm{LF})=C_0(g_\perp^2/4T)[(kT/G)2\sinh(\Gamma)+40A^3+105A^8+168A^{15}+165A^{24}]2/Z_0$ $Z_0=2[2\cosh(\Gamma)+8A^3+9A^8+8A^{15}+5A^{24}]$ Low-temperature limit ($A\to 0$ for $j<0$ and $T\to 0$) $\chi_\parallel(\mathrm{LF,LT})=C_0 g_\parallel^2/4T$ $\chi_\perp(\mathrm{LF,LT})=[C_0 g_\perp^2/(4G/k)]\tanh(G/kT)\xrightarrow{T\to 0}C_0 g_\perp^2/(4G/k)$		
Parallel magnetization $M_\parallel=N_A\dfrac{\mu_B g_\parallel}{2}\dfrac{\mathrm{Num}}{\mathrm{Den}}$ $\mathrm{Num}=A^0(\Gamma+\Gamma^{-1})(Z-Z^{-1})$ $+4\cdot A^3[(Z-Z^{-1})+3(Z^3-Z^{-3})]$ $+3\cdot A^8[(Z-Z^{-1})+3(Z^3-Z^{-3})+5(Z^5-Z^{-5})]$ $+2\cdot A^{15}[(Z-Z^{-1})+3(Z^3-Z^{-3})+5(Z^5-Z^{-5})+7(Z^7-Z^{-7})]$ $+1\cdot A^{24}[(Z-Z^{-1})+3(Z^3-Z^{-3})+5(Z^5-Z^{-5})+7(Z^7-Z^{-7})+9(Z^9-Z^{-9})]$ $\mathrm{Den}=A^0(\Gamma+\Gamma^{-1})(Z+Z^{-1})$ $+4\cdot A^3[(Z+Z^{-1})+(Z^3+Z^{-3})]$ $+3\cdot A^8[(Z+Z^{-1})+(Z^3+Z^{-3})+(Z^5+Z^{-5})]$ $+2\cdot A^{15}[(Z+Z^{-1})+(Z^3+Z^{-3})+(Z^5+Z^{-5})+(Z^7+Z^{-7})]$ $+1\cdot A^{24}[(Z+Z^{-1})+(Z^3+Z^{-3})+(Z^5+Z^{-5})+(Z^7+Z^{-7})+(Z^9+Z^{-9})]$		$A\equiv\exp(j/kT)=\exp(J/2kT)$ $Z=\exp(\mu_B Bg_\parallel/2kT)$ $\Gamma\equiv\exp(G/kT)$

Table 9 (*Continued*)

Case 2: *triangulo*-$[s=3/2]$ according to Berry [36] with $2j \equiv +J$; – spin occurrence factors $N_S = 2, 4, 3, 2$, and 1 for $S=1/2$ through $S=9/2$ lying at 0, $-3j$, $-8j$, $-15j$ and $-24j$; $D^{(S_1=3/2)} \times D^{(S_2=3/2)} \times D^{(S_3=3/2)} = 2D^{(S=1/2)} + 4D^{(S=3/2)} + 3D^{(S=5/2)} + 2D^{(S=7/2)} + D^{(S=9/2)}$; - many-electron coupling constant $G = G_z = (2/\sqrt{3})(d_z^{(12)} + d_z^{(23)} + d_z^{(31)}) = 2\sqrt{3}d_z^{AB}$		
Perpendicular eigenvalues	Derivatives	Substitutions
Perpendicular magnetization $M_\perp = N_A \frac{\mu_B g_\perp}{2} \frac{\text{Num}}{\text{Den}}$ $\text{Num} = A^0(\mu_B g_\perp B)2(\Sigma - \Sigma^{-1})(S^{-1})$ $+4 \cdot A^3[(X - X^{-1}) + 3(X^3 - X^{-3})]$ $+3 \cdot A^8[(X - X^{-1}) + 3(X^3 - X^{-3}) + 5(X^5 - X^{-5})]$ $+2 \cdot A^{15}[(X - X^{-1}) + 3(X^3 - X^{-3}) + 5(X^5 - X^{-5}) + 7(X^7 - X^{-7})]$ $+1 \cdot A^{24}[(X - X^{-1}) + 3(X^3 - X^{-3}) + 5(X^5 - X^{-5}) + 7(X^7 - X^{-7}) + 9(X^9 - X^{-9})]$ $\text{Den} = A^0 2(\Sigma + \Sigma^{-1})$ $+4 \cdot A^3[(X + X^{-1}) + (X^3 + X^{-3})]$ $+3 \cdot A^8[(X + X^{-1}) + (X^3 + X^{-3}) + (X^5 + X^{-5})]$ $+2 \cdot A^{15}[(X + X^{-1}) + (X^3 + X^{-3}) + (X^5 + X^{-5}) + (X^7 + X^{-7})]$ $+1 \cdot A^{24}[(X + X^{-1}) + (X^3 + X^{-3}) + (X^5 + X^{-5}) + (X^7 + X^{-7}) + (X^9 + X^{-9})]$ In the limit of very strong-negative exchange ($A=0$) $M_\perp \xrightarrow{A=0} N_A \frac{\mu_B g_\perp}{2} \frac{(\mu_B g_\perp B)S^{-1}(\Sigma - \Sigma^{-1})}{(\Sigma + \Sigma^{-1})}$ which matches the case of $s=1/2$ for $\gamma = \mu_B g_\perp B$ $M_\perp = N_A \frac{\gamma' \gamma}{2(4G^2+\gamma^2)^{1/2}} \frac{\exp[+(4G^2+\gamma^2)^{1/2}/2kT] - \exp[-(4G^2+\gamma^2)^{1/2}/2kT]}{\exp[+(4G^2+\gamma^2)^{1/2}/2kT] + \exp[-(4G^2+\gamma^2)^{1/2}/2kT]}$		$A \equiv \exp(j/kT) = \exp(J/2kT)$ $X = \exp(\mu_B B g_\perp/2kT)$ $S = [4G^2 + (g_\perp \mu_B B)^2]^{1/2}$ $\Sigma \equiv \exp(S/2kT)$
Case 3: *triangulo*-$[s=n/2]$ for $n = 1, 3, 5, 7$ with $2j \equiv +J$; – N_S – occurrence of spin states for $S=1/2$ through $S=3n/2$ lying at 0, $-3j$, $-8j$, .., $-[S(S+1)-3/4]j$; – many-electron coupling constant $G = G_z = \alpha_s(d_z^{(12)} + d_z^{(23)} + d_z^{(31)}) = 3\alpha_s d_z^{AB}$		
Approximate eigenvalues	van Vleck coefficients	Substitutions
Lowest $\varepsilon^\perp_{(S=1/2)} = -G - \gamma_\perp^2/(8G)$ $\varepsilon^\perp_{(S=1/2)} = +G + \gamma_\perp^2/(8G)$ Remaining $\varepsilon^\perp_S = -[S(S+1)-3/4]j + M_S\gamma_\perp$ Approximations: strong exchange limit, van Vleck formula (low field) $\chi_\parallel(\text{LF}) = C_0(g_\parallel^2/4T)[2\cosh(\Gamma) + 4R]2/Z_0$ $\chi_\perp(\text{LF}) = C_0(g_\perp^2/4T)[(kT/G)2\sinh(\Gamma) + 4R]2/Z_0$ $R = \sum_{S \neq 1/2}^{\text{rest}} N_S \cdot \sum_{M_S=-S}^{+S} M_S^2 \cdot A^{S(S+1)-3/4} = \sum_{S \neq 1/2}^{\text{rest}} N_S[S(S+1)(2S+1)/3]A^{S(S+1)-3/4}$ $Z_0 = 2 \cdot (\Gamma^{-1} + \Gamma)A^0 + \sum_{S \neq 1/2} N_S \cdot (2S+1)A^{S(S+1)-3/4}$ Low-temperature limit ($A \to 0$ for $j<0$ and $T \to 0$) $\chi_\parallel(\text{LF, LT}) = C_0 g_\parallel^2/4T$ $\chi_\perp(\text{LF, LT}) = [C_0 g_\perp^2/(4G/k)]\tanh(G/kT) \xrightarrow{T\to 0} C_0 g_\perp^2/(4G/k)$	$\varepsilon^{(0),\perp}_{(S=1/2)} = -G$, $\varepsilon^{(2),\perp}_{(S=1/2)} = -(g_\perp\mu_B)^2/8G$ $\varepsilon^{(0),\perp}_{(S=1/2)} = +G$, $\varepsilon^{(2),\perp}_{(S=1/2)} = +(g_\perp\mu_B)^2/8G$ $\varepsilon^{(0),\perp}_S = -[S(S+1)-3/4]j$, $\varepsilon^{(1),\perp}_S = M_S g_\perp \mu_B$	$\Gamma \equiv \exp(G/kT)$, $A \equiv \exp(j/kT) = \exp(J/2kT)$

[a] Reduced Curie constant $C_0 = N_A \mu_0 \mu_B^2/k$.

Rakitin et al. [42] utilized quite general form of the Hamiltonian:

$$\begin{aligned}\hat{H}^s &= J_0\hbar^{-2}[(\vec{S}_1 \cdot \vec{S}_2) + (\vec{S}_2 \cdot \vec{S}_3) + (\vec{S}_3 \cdot \vec{S}_1)] + \delta'\hbar^{-2}(\vec{S}_2 \cdot \vec{S}_3) \\ &\quad + \delta''\hbar^{-2}(\vec{S}_1 \cdot \vec{S}_2) + \hbar^{-2}\vec{G} \cdot [(\vec{S}_1 \times \vec{S}_2) + (\vec{S}_2 \times \vec{S}_3) + (\vec{S}_3 \times \vec{S}_1)] \\ &\quad + \hbar^{-1}\mu_B B(\sin\vartheta\cos\varphi g_x \hat{S}_x + \sin\vartheta\sin\varphi g_y \hat{S}_y + \cos\vartheta g_z \hat{S}_z) \end{aligned} \tag{5.80}$$

(note the sign convention for the isotropic exchange terms), and for the basis set of 4 kets spanning the ^{2}E representation they get its matrix elements in the form:

$$H_{ij} = \left(\begin{array}{cc:cc} -\delta'/2+\delta''/4+\gamma_z/2 & * & * & * \\ \gamma_+/2 & -\delta'/2+\delta''/4-\gamma_z/2 & * & * \\ \hdashline (\sqrt{3}/4)\delta''-\mathrm{i}D_z/2 & -D_+/2 & +\delta'/2-\delta''/4+\gamma_z/2 & * \\ D_-/2 & (\sqrt{3}/4)\delta''-\mathrm{i}D_z/2 & \gamma_+/2 & +\delta'/2-\delta''/4-\gamma_z/2 \end{array}\right) \tag{5.81}$$

The kets were ordered as follows:

$$\left|S_{12}, S, M_S\right\rangle = \begin{bmatrix} \left|L, 1/2, +1/2\right\rangle \\ \left|L, 1/2, -1/2\right\rangle \\ \left|H, 1/2, +1/2\right\rangle \\ \left|H, 1/2, -1/2\right\rangle \end{bmatrix} \tag{5.82}$$

where L and H means the lower and higher intermediate spin, respectively. The field-dependent terms are $\gamma_x = g_x\mu_B B \sin\vartheta\cos\varphi$, $\gamma_y = g_y\mu_B B\sin\vartheta\sin\varphi$, $\gamma_z = g_z\mu_B B\cos\vartheta$ and $\gamma_\pm = \gamma_x \pm i\gamma_y$. The field-independent parameters are $D_\pm = D_y \pm iD_x$ (different notation with respect to the shift-operator); $\vec{D} = \alpha_s\vec{G}$ where $\alpha_s = \sqrt{3}$,

$\alpha_s = 4\sqrt{3}$, and $\alpha_s = 9\sqrt{3}$ for genuine spin $s = 1/2$, 3/2, and 5/2, respectively. The authors argued that in systems having the same symmetry, the components of the spin ^2E trimer ground state belong to the same representation irrespective of the half-integer spin value. Thus the matrix elements of the Hamiltonian with various half-integer spins coincide to recalibration of the parameters. This leads to the eigenvalues:

$$\varepsilon_{1-4} = \pm\left[\Delta^2 + \gamma^2 \pm 2\sqrt{\delta^2\gamma^2 + (\vec{\gamma}\cdot\vec{D})^2}\right]^{1/2} \Big/ 2 \qquad (5.83)$$

where $\Delta^2 = \delta^2 + \vec{D}^2$ and $\delta^2 = (\delta' - \delta''/2)^2 + (3/4)(\delta'')^2$. In addition to the modeling of the ESR transitions, an analysis of ESR data for a *triangulo*-[Fe_3] complex has been reported.

The fitting of magnetic data (the temperature dependence of the magnetic susceptibility, the field dependence of the magnetization) for systems having a lot of states can be done in a fully numerical manner. For instance, the *triangulo*-[Fe_3] possesses a basis of 256 magnetic states. The matrix elements of the isotropic exchange (1), Zeeman interaction (2), and the antisymmetric exchange (3) (complex-Hermitean) can be generated with the help of the apparatus reviewed in Chapters 2 through 4. The easiest way is to construct the matrices of the individual spin centers in the basis set of uncoupled spins, say $S_{IJ}^{(Ca)} = \left\langle \ldots S_A M_{SA} \ldots \left| \hat{S}_{Ca} \right| \ldots S_B M_{SB} \ldots \right\rangle$, where a stays for the component (spherical, Cartesian, or shift-operator). Proper matrix products generate the representation of the operators involved as evident from Table S5 (Supplementary material). The eigenvalues returned from the diagonalization routine enters the partition function (in the given field direction), from which the magnetization and susceptibility components are obtained as the first and the second derivatives with respect to the magnetic field. The procedure like this has been successfully applied in fitting the magnetic data for a *triangulo*-$(Et_3NH)_4[Fe_3O(NO_2\text{-pz})_6Cl_3]Cl_2$ complex [46].

In a similar manner a non-Kramers system of *triangulo*-$[Ni_3(pmdien)_3(\mu\text{-ttc})](ClO_4)_3$ has been treated [47].

The involvement of the antisymmetric exchange in tetranuclear systems was pioneered by Lines et al. [48] and by Kuyavskaya et al. [48b]. The conclusions about the presence of the antisymmetric exchange have been revisited by another group on the basis of ESR data [49]. A careful theoretical analysis of the antisymmetric exchange in tetranuclear systems of various symmetry (T_d, D_{4h}, S_4, C_{4v}, C_{4h} and D_{2d}) appeared recently [50]. A fitting of susceptibility, magnetization, and inelastic neutron scattering data for a *tetrahedro*-[Ni_4] system has been reported in [51]. A discussion about the antisymmetric exchange in {Cu_6} and {Mn_6} hexagons embedded in D_{3d}-symmetric polyoxotungstates is presented in [52]. A direct fitting of magnetic data for a *prismo*-[Cu_6] complex is reported in [53].

Some modeling of the magnetic behavior need be mentioned, at least for a remarkable cluster $[Mo_{72}Fe_{30}O_{252}(Mo_2O_7(H_2O))_2\text{–}(Mo_2O_8H_2(H_2O))(CH_3COO)_{12}(H_2O)_{91}]\cdot 150H_2O$ [75].

There is extensive literature about the antisymmetric exchange in extended systems (1D chains, 2D-networks, 3D-networks) as exemplified by the following references: $(NH_3CH_2CH_2COOH)_2CuCl_4$ and $(NH_3CH_2CH_2COOH)_2CuBr_4$ [76–78], $KMnF_3$ [79], $KCuF_3$ [80,81], Sr-doped ferrites $Ba_{0.6}Sr_{2.4}Zn_2Fe_{24}O_{41}$ and $Ba_{0.4}Sr_{1.6}Zn_2Fe_{12}O_{22}$ [82], $CuGeO_3$ [83], $(NH_3(CH_2)_4NH_3)CuCl_4$ [84,85], $Ni(C_2H_8N_2)_2NO_2(ClO_4)$ [86], $Cu_2(C_5H_{12}N_2)_2Cl_4$ [87], $SrCu_2(BO_3)_2$ [88], $[CoNi(pmtz)_4]$ [89].

There exist a number of articles devoted to theoretical studies of the antisymmetric exchange, with impact mostly to ESR spectroscopy [90–115]. The EasySpin software package can be conveniently used to simulate and analyze ESR spectra including the antisymmetric exchange [116].

6. Conclusion

There are two principal difficulties with the antisymmetric exchange: (i) it is difficult to understand and to accept that it is important; (ii) it is difficult to handle.

The antisymmetric exchange brings a kind of the magnetic anisotropy. This means that the components of the magnetization develop in the magnetic field differently; however at very high field they converge to the same saturation limit. The components of the magnetic susceptibility also develop differently with temperature and if the temperature is high enough, they tend to average. The principal features of the antisymmetric exchange, however, are different from those brought by the asymmetric exchange (combined with the single-ion anisotropy). The most evident consequences of the antisymmetric exchange can be seen in electron spin resonance spectra.

In finite molecular systems the matrix elements of the antisymmetric exchange, along with the isotropic exchange and the spin Zeeman term can be generated by several alterative algorithms: by analytical formulae in the basis set of uncoupled or coupled spins, or by multiplication of matrices of the individual spin centers in the basis set of uncoupled spins.

In contrast to the cases of the isotropic exchange and the asymmetric exchange, the analytical formulae for the magnetization and/or susceptibility are rarely available and one is left with a fully numerical approach. A direct fitting of the magnetic data (magnetization and magnetic susceptibility) for small clusters (Fe_3, Cu_6, ...) is a realistic task at present and it becomes a routine approach.

There is an increasing volume of information revealing that antisymmetric exchange has an impact on the existence of single molecule magnets [117]. For this reason this phenomenon is no longer an exotic task, left to the specialists, and it penetrates to the topical centre of interest of how to assembly and tune the properties of single molecule magnets.

Acknowledgements

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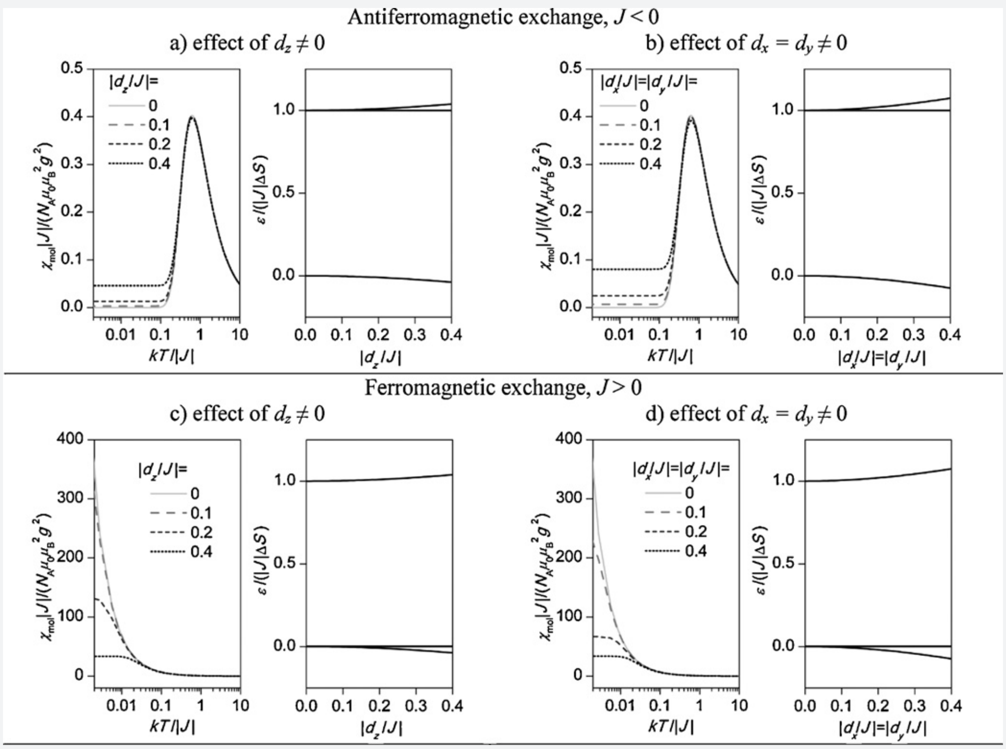
Appendix A.

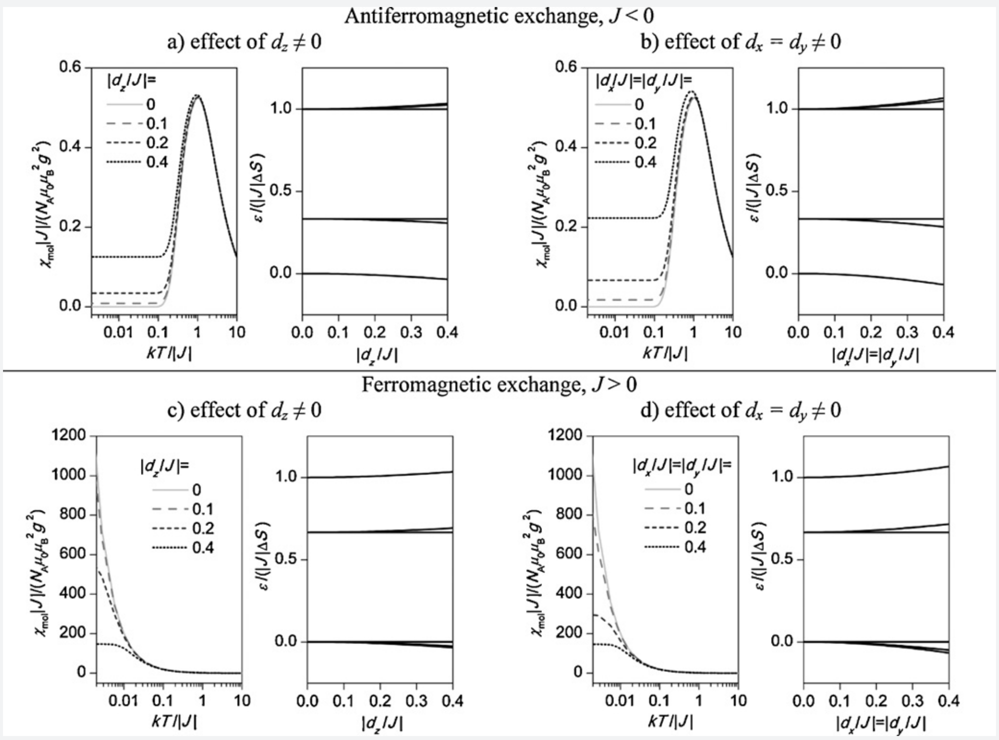
Tables A1–A20.

Table A1
Antisymmetric exchange in dinuclear spin-systems [$S_A = S_B = 1/2$].



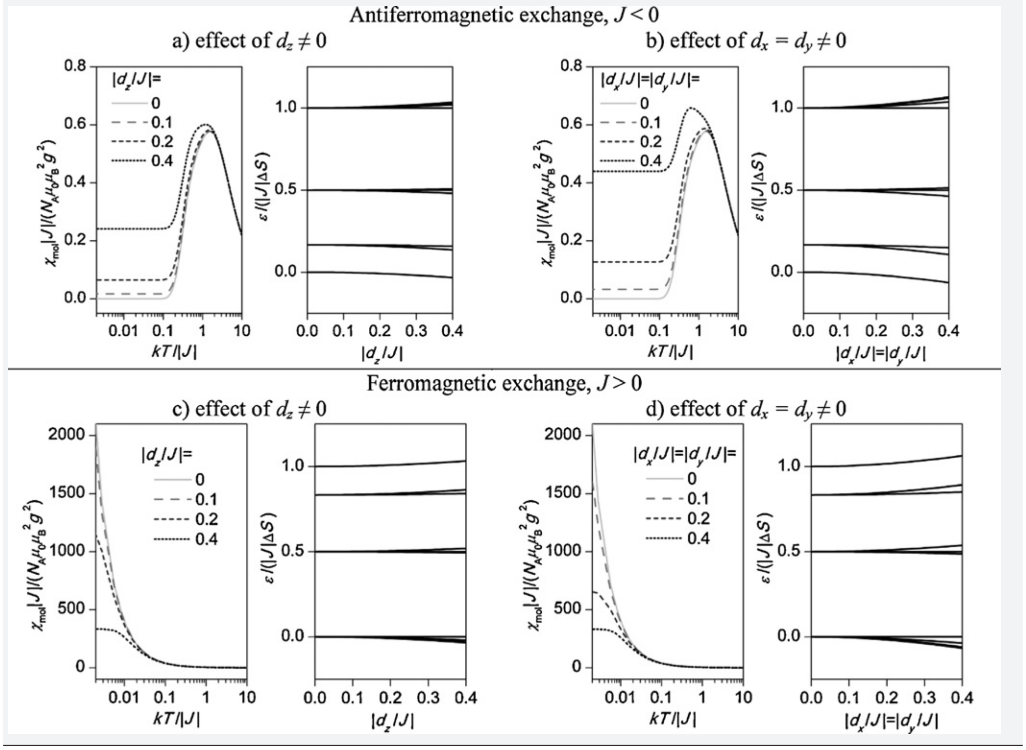
Left – reduced, zero-field magnetic susceptibility for different ratios of $|d_i/J|$.
Right – zero-field splitting of energy levels due to antisymmetric exchange.
$\Delta S = \left(1/2\right)[S_{\max}(S_{\max}+1) - S_{\min}(S_{\min}+1)] = 1$.

Table A2
Antisymmetric exchange in dinuclear spin-systems [$S_A = S_B = 1$].



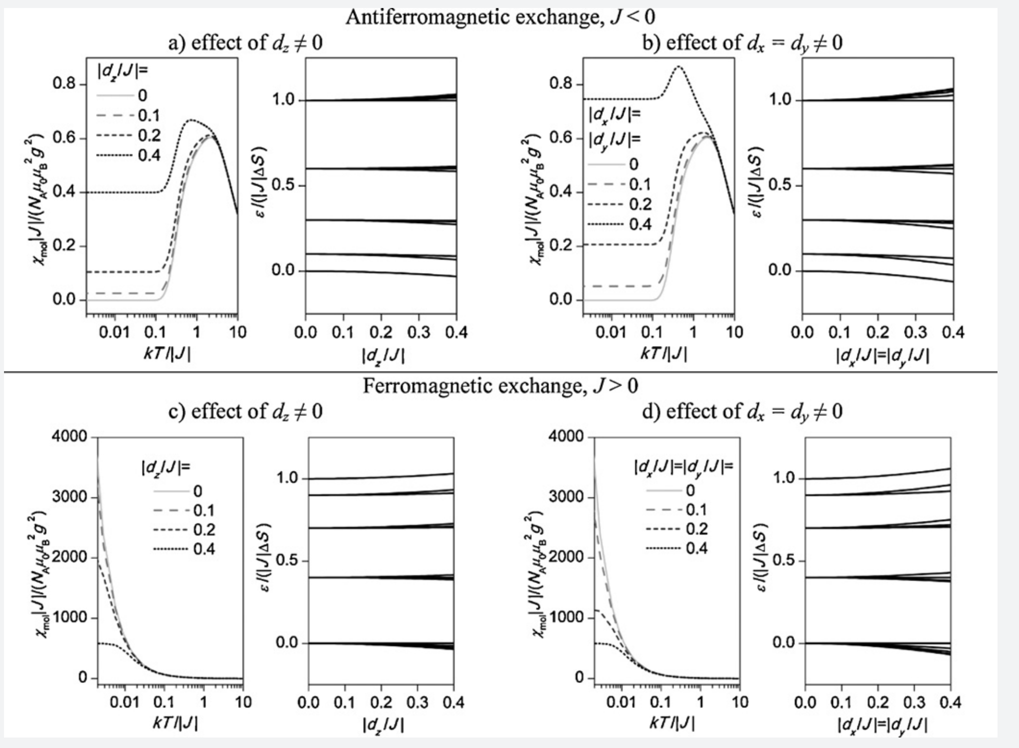
Left – reduced, zero-field magnetic susceptibility for different ratios of $|d_i/J|$.
Right – zero-field splitting of energy levels due to antisymmetric exchange.
$\Delta S = (1/2)[S_{\max}(S_{\max}+1) - S_{\min}(S_{\min}+1)] = 3$.

Table A3
Antisymmetric exchange in dinuclear spin-systems [$S_A = S_B = 3/2$].



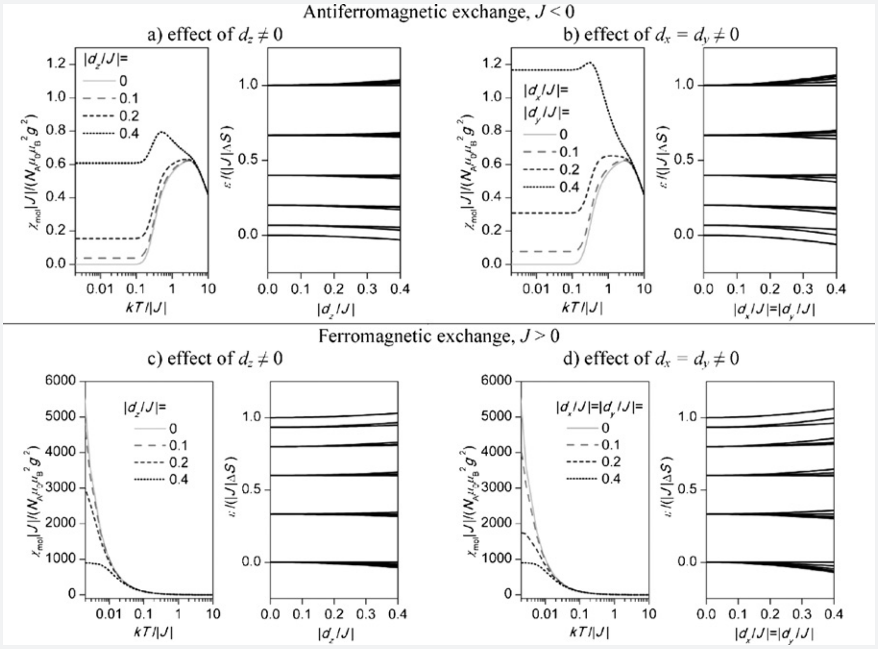
Left – reduced, zero-field magnetic susceptibility for different ratios of $|d_i/J|$.
Right – zero-field splitting of energy levels due to antisymmetric exchange.
$\Delta S = (1/2)\,[S_{\max}(S_{\max}+1) - S_{\min}(S_{\min}+1)] = 6$.

Table A4
Antisymmetric exchange in dinuclear spin-systems [$S_A = S_B = 2$].



Left – reduced, zero-field magnetic susceptibility for different ratios of $|d_i/J|$.
Right – zero-field splitting of energy levels due to antisymmetric exchange.
$\Delta S = \left(1/2\right)\,[S_{\max}(S_{\max}+1) - S_{\min}(S_{\min}+1)] = 10$.

Table A5
Antisymmetric exchange in dinuclear spin-systems [$S_A = S_B = 5/2$].

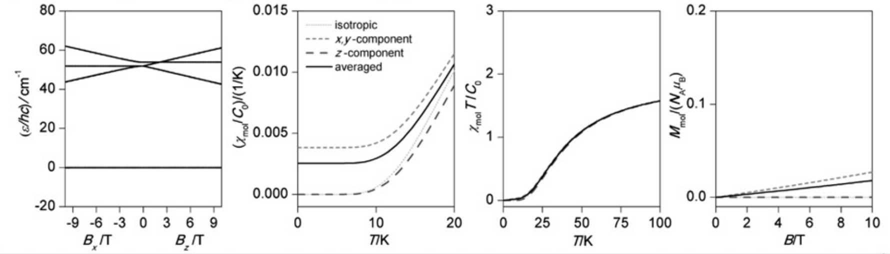


Left – reduced, zero-field magnetic susceptibility for different ratios of $|d_i/J|$.
Right – zero-field splitting of energy levels due to antisymmetric exchange.
$\Delta S = \left(1/2\right)[S_{\max}(S_{\max}+1) - S_{\min}(S_{\min}+1)] = 15$.

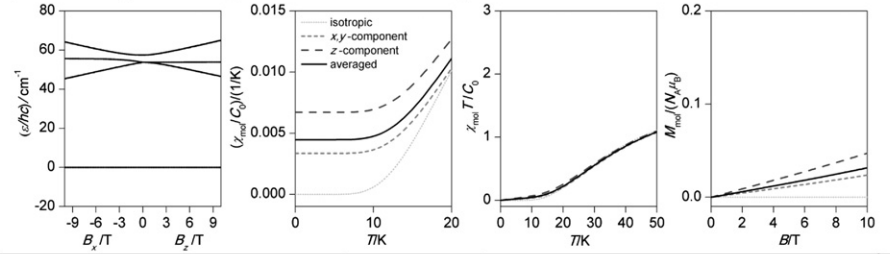
Table A6

Magnetic functions for dinuclear spin-systems [$S_A = S_B = 1/2$] in presence of antisymmetric exchange.

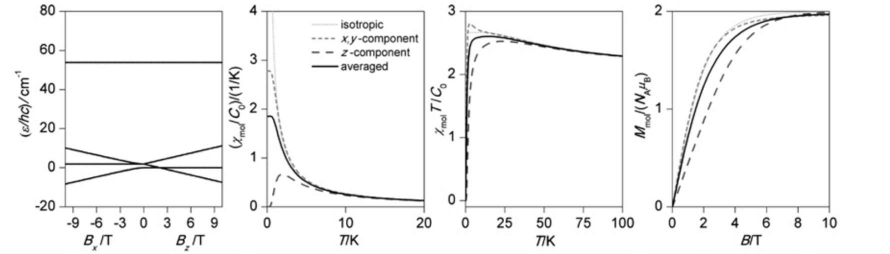
a) antiferromagnetic exchange $J/hc = -50\ \mathrm{cm}^{-1}$, $d_z/hc = 20\ \mathrm{cm}^{-1}$



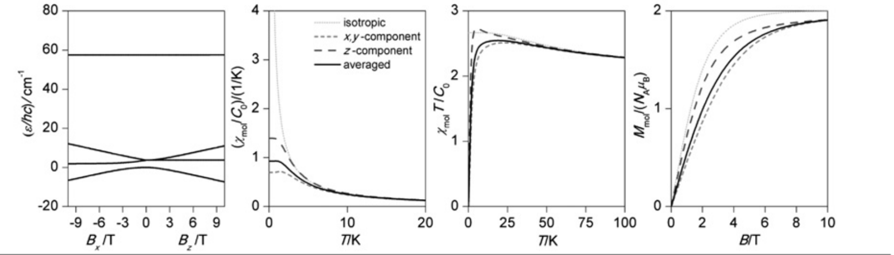
b) antiferromagnetic exchange $J/hc = -50\ \mathrm{cm}^{-1}$, $d_x/hc = d_y/hc = 20\ \mathrm{cm}^{-1}$



c) ferromagnetic exchange $J/hc = +50\ \mathrm{cm}^{-1}$, $d_z/hc = 20\ \mathrm{cm}^{-1}$



d) ferromagnetic exchange $J/hc = +50\ \mathrm{cm}^{-1}$, $d_x/hc = d_y/hc = 20\ \mathrm{cm}^{-1}$

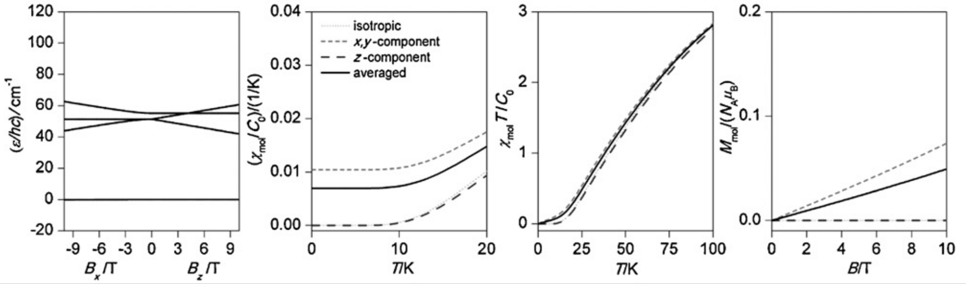


Energy levels, product function, isothermal magnetization ($T = 2.0\ \mathrm{K}$) and zero-field magnetic susceptibility.

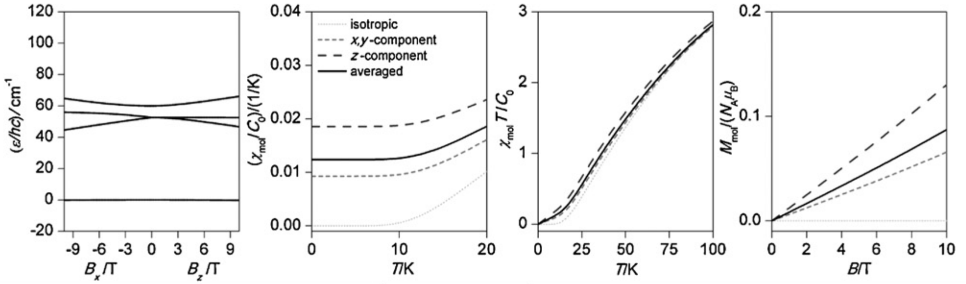
Table A7

Magnetic functions for dinuclear spin-systems [$S_A = S_B = 1$] in presence of antisymmetric exchange.

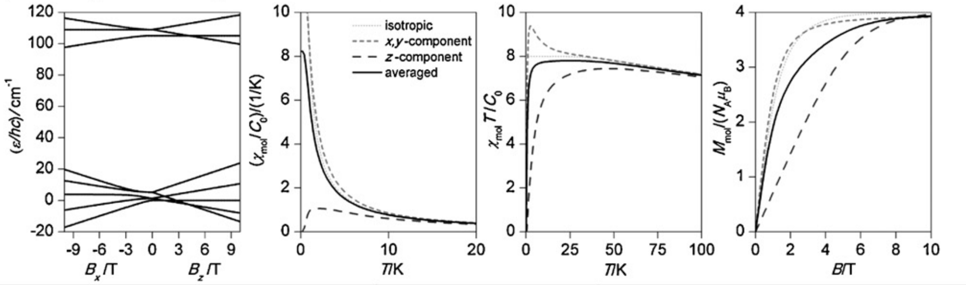
a) antiferromagnetic exchange $J/hc = -50\ \mathrm{cm}^{-1}$, $d_z/hc = 20\ \mathrm{cm}^{-1}$



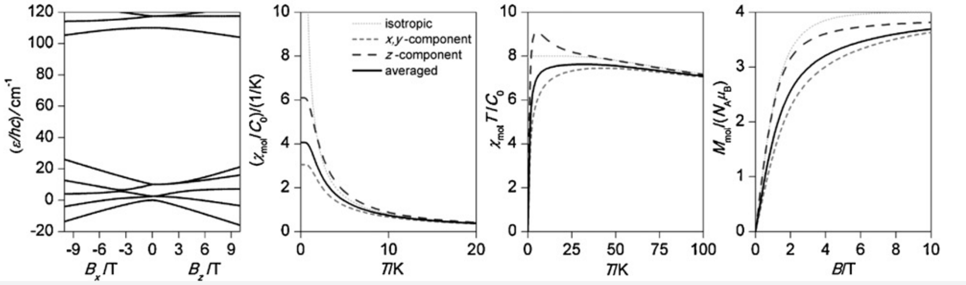
b) antiferromagnetic exchange $J/hc = -50\ \mathrm{cm}^{-1}$, $d_x/hc = d_y/hc = 20\ \mathrm{cm}^{-1}$



c) ferromagnetic exchange $J/hc = +50\ \mathrm{cm}^{-1}$, $d_z/hc = 20\ \mathrm{cm}^{-1}$



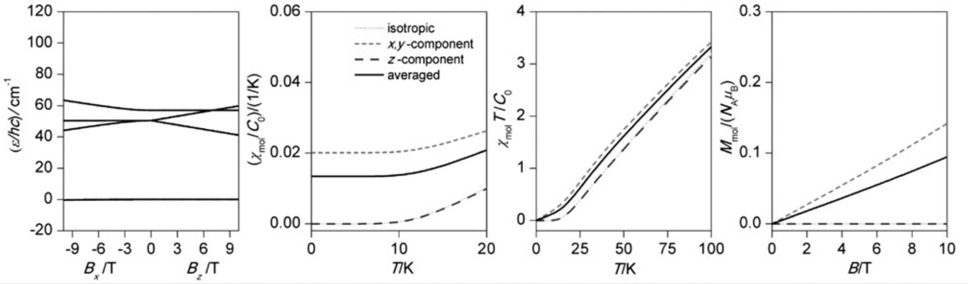
d) ferromagnetic exchange $J/hc = +50\ \mathrm{cm}^{-1}$, $d_x/hc = d_y/hc = 20\ \mathrm{cm}^{-1}$



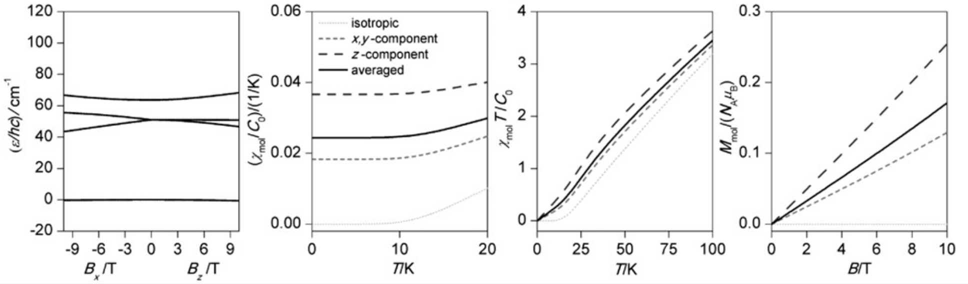
Energy levels, product function, isothermal magnetization ($T = 2.0$ K) and zero-field magnetic susceptibility.

Table A8
Magnetic functions for dinuclear spin-systems [$S_A = S_B = 3/2$] in presence of antisymmetric exchange.

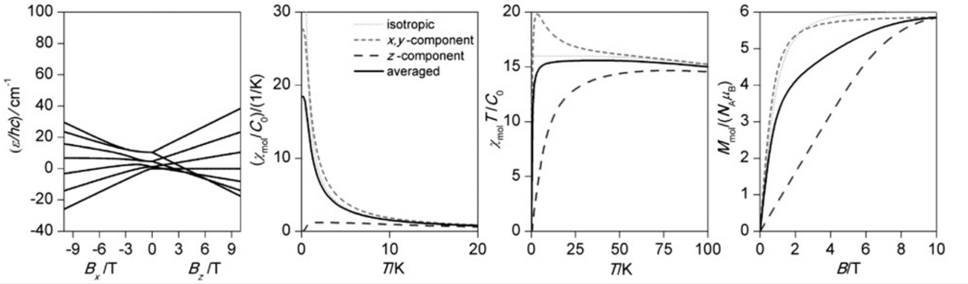
a) antiferromagnetic exchange $J/hc = -50$ cm^{-1}, $d_z/hc = 20$ cm^{-1}



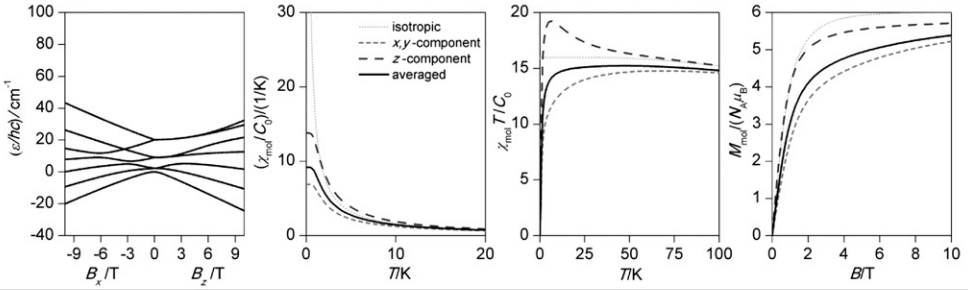
b) antiferromagnetic exchange $J/hc = -50$ cm^{-1}, $d_x/hc = d_y/hc = 20$ cm^{-1}



c) ferromagnetic exchange $J/hc = +50$ cm^{-1}, $d_z/hc = 20$ cm^{-1}



d) ferromagnetic exchange $J/hc = +50$ cm^{-1}, $d_x/hc = d_y/hc = 20$ cm^{-1}

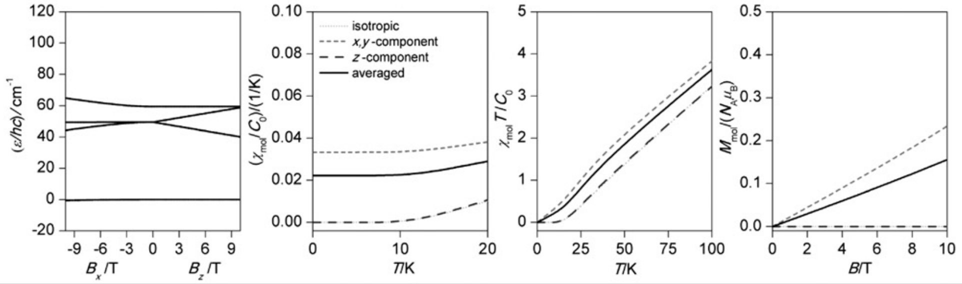


Energy levels, product function, isothermal magnetization ($T = 2.0$ K) and zero-field magnetic susceptibility.

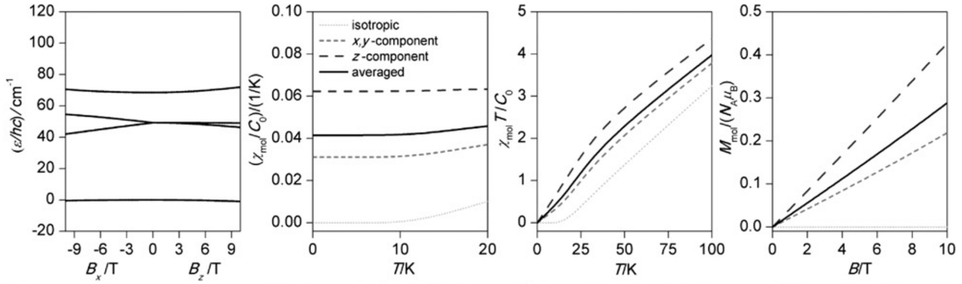
Table A9

Magnetic functions for dinuclear spin-systems [$S_A = S_B = 2$] in presence of antisymmetric exchange.

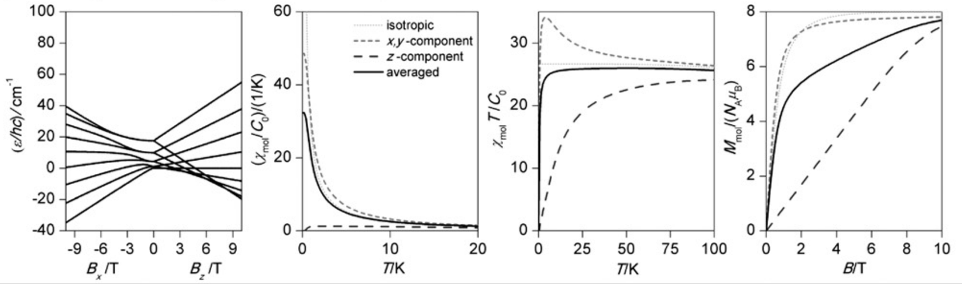
a) antiferromagnetic exchange $J/hc = -50$ cm^{-1}, $d_z/hc = 20$ cm^{-1}



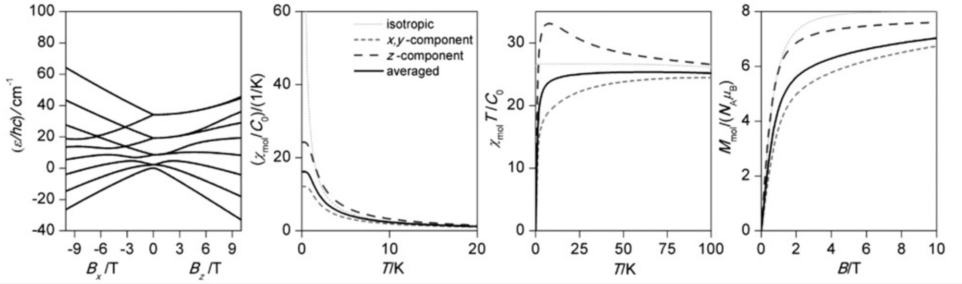
b) antiferromagnetic exchange $J/hc = -50$ cm^{-1}, $d_x/hc = d_y/hc = 20$ cm^{-1}



c) ferromagnetic exchange $J/hc = +50$ cm^{-1}, $d_z/hc = 20$ cm^{-1}



d) ferromagnetic exchange $J/hc = +50$ cm^{-1}, $d_x/hc = d_y/hc = 20$ cm^{-1}

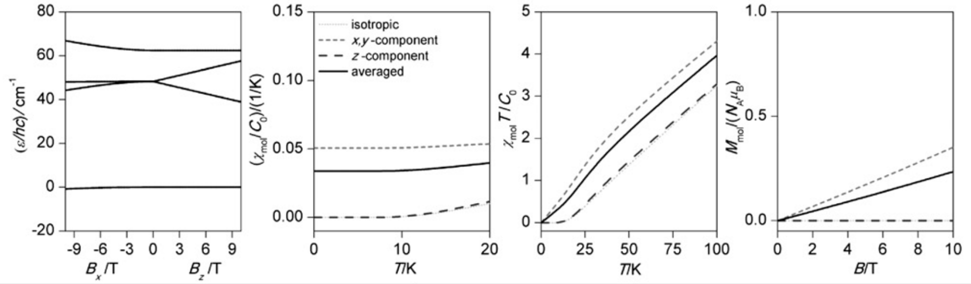


Energy levels, product function, isothermal magnetization ($T = 2.0$ K) and zero-field magnetic susceptibility.

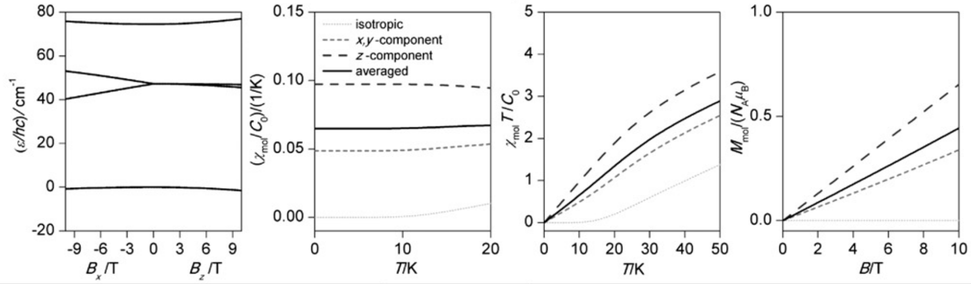
Table A10

Magnetic functions for dinuclear spin-systems [$S_A = S_B = 5/2$] in presence of antisymmetric exchange.

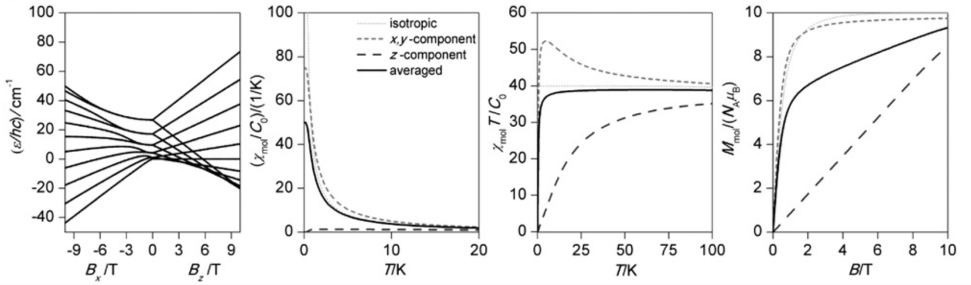
a) antiferromagnetic exchange $J/hc = -50$ cm^{-1}, $d_z/hc = 20$ cm^{-1}



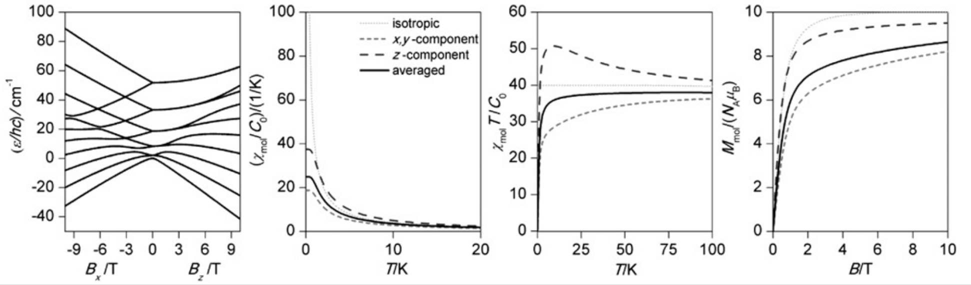
b) antiferromagnetic exchange $J/hc = -50$ cm^{-1}, $d_x/hc = d_y/hc = 20$ cm^{-1}



c) ferromagnetic exchange $J/hc = +50$ cm^{-1}, $d_z/hc = 20$ cm^{-1}

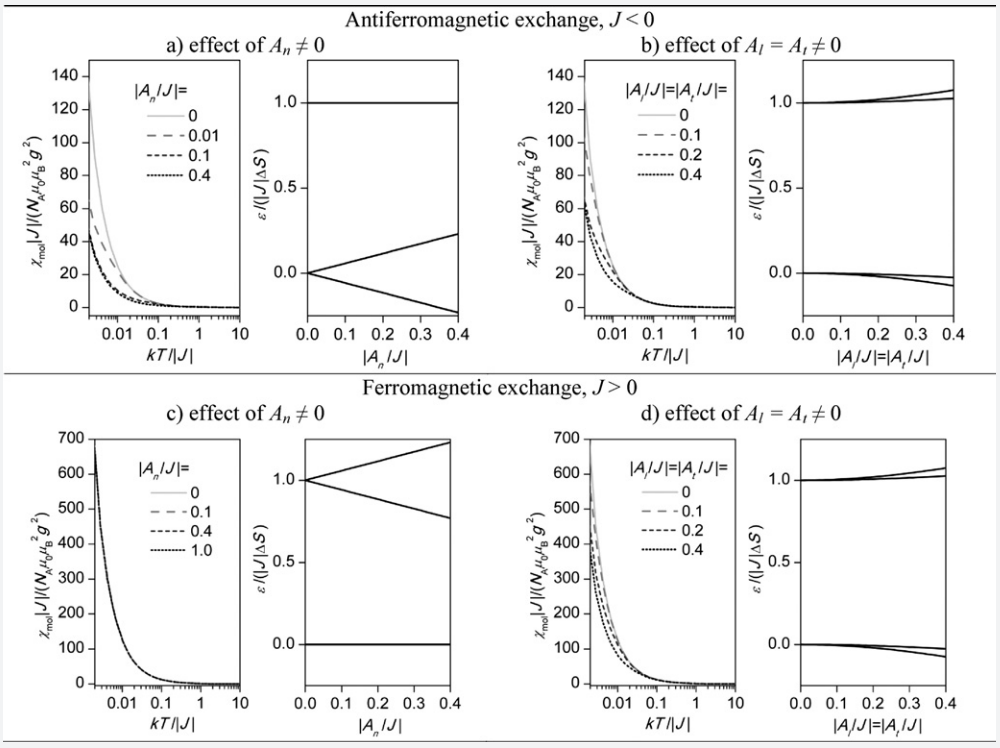


d) ferromagnetic exchange $J/hc = +50$ cm^{-1}, $d_x/hc = d_y/hc = 20$ cm^{-1}



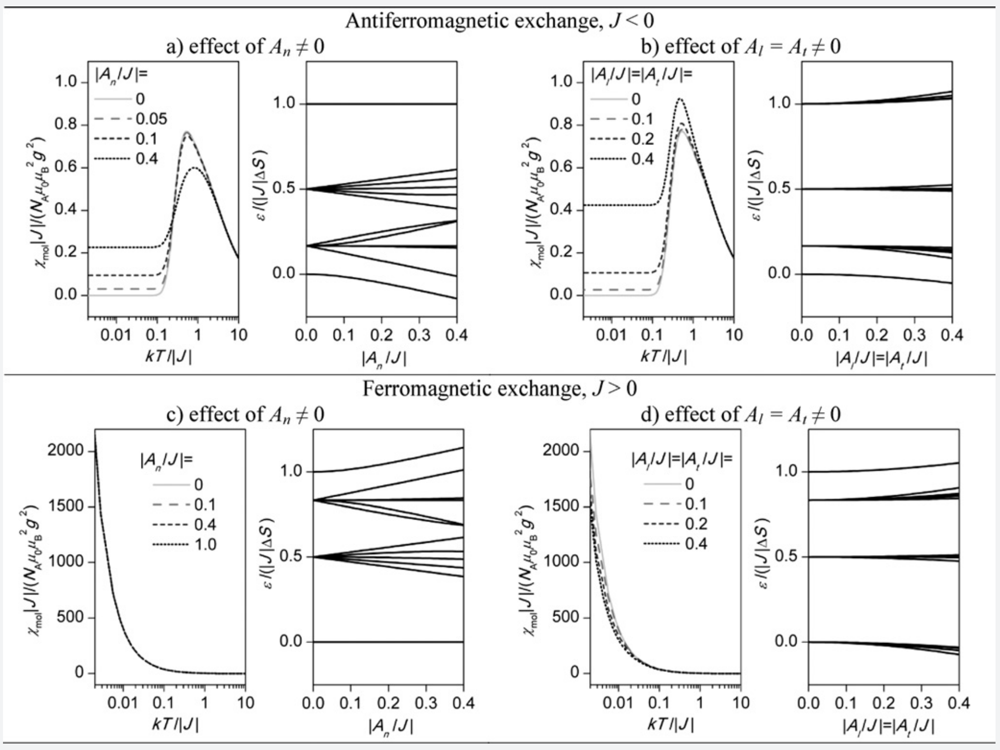
Energy levels, product function, isothermal magnetization ($T = 2.0$ K) and zero-field magnetic susceptibility.

Table A11
Antisymmetric exchange in *triangulo*-[$S_A = S_B = S_C = 1/2$] spin-systems.



Left – reduced, zero-field magnetic susceptibility for different ratios of $|A_i/J|$.
Right – zero-field splitting of energy levels due to antisymmetric exchange.
$\Delta S = \left(1/2\right) [S_{\max}(S_{\max}+1) - S_{\min}(S_{\min}+1)] = 3/2$.

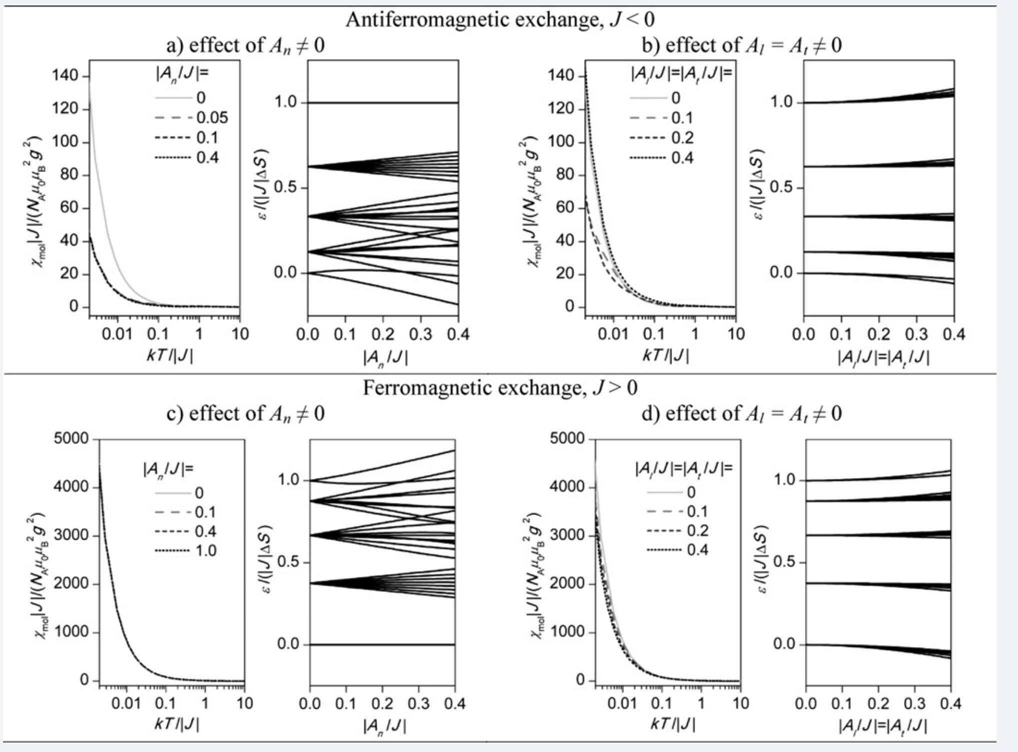
Table A12
Antisymmetric exchange in *triangulo*-[$S_A = S_B = S_C = 1$] spin-systems.



Left – reduced, zero-field magnetic susceptibility for different ratios of $|A_i/J|$.
Right – zero-field splitting of energy levels due to antisymmetric exchange.
$\Delta S = \left(1/2\right) [S_{\max}(S_{\max}+1) - S_{\min}(S_{\min}+1)] = 6$.

Table A13

Antisymmetric exchange in *triangulo*-[$S_A = S_B = S_C = 3/2$] spin-systems.



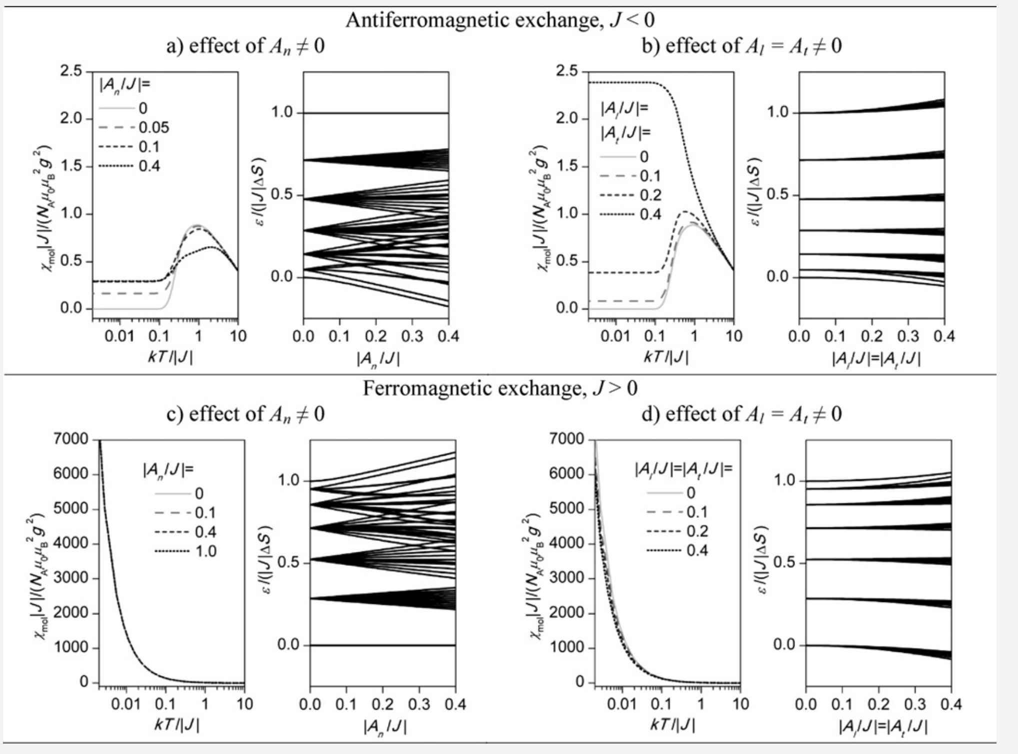
Left – reduced, zero-field magnetic susceptibility for different ratios of $|A_i/J|$.

Right – zero-field splitting of energy levels due to antisymmetric exchange.

$\Delta S = \left(1/2\right)[S_{\max}(S_{\max}+1) - S_{\min}(S_{\min}+1)] = 12.$

Table A14

Antisymmetric exchange in *triangulo*-[$S_A = S_B = S_C = 2$] spin-systems.

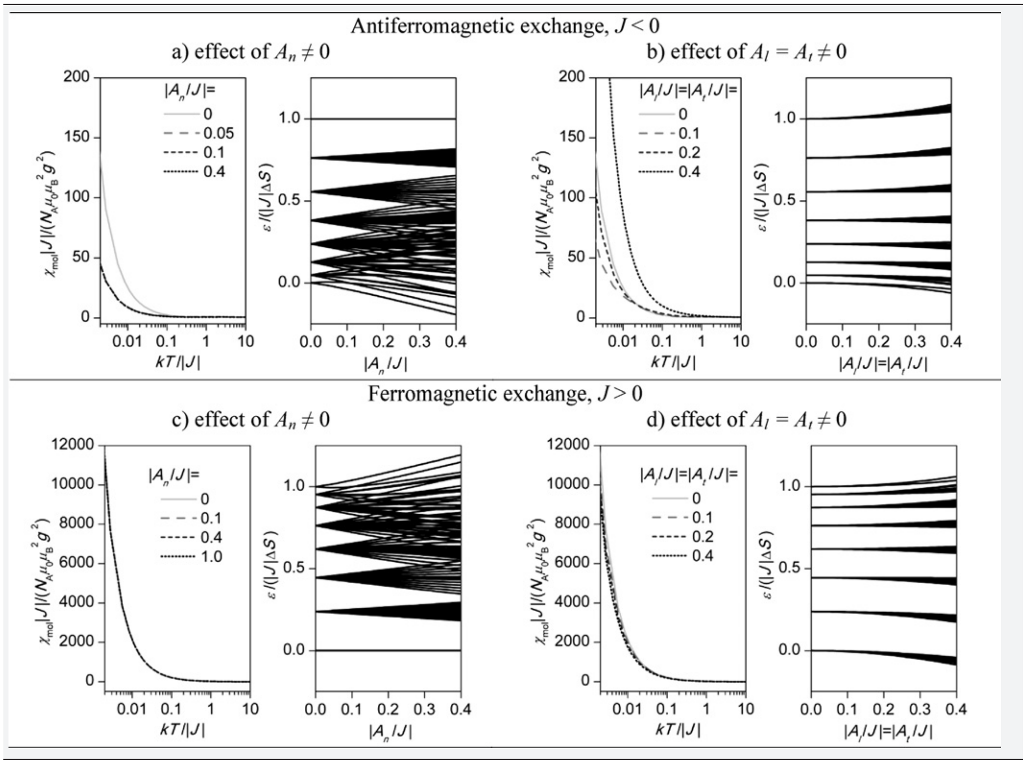


Left – reduced, zero-field magnetic susceptibility for different ratios of $|A_i/J|$.

Right – zero-field splitting of energy levels due to antisymmetric exchange.

$\Delta S = \left(1/2\right)[S_{\max}(S_{\max}+1) - S_{\min}(S_{\min}+1)] = 21.$

Table A15
Antisymmetric exchange in *triangulo*-[$S_A = S_B = S_C = 5/2$] spin-systems.

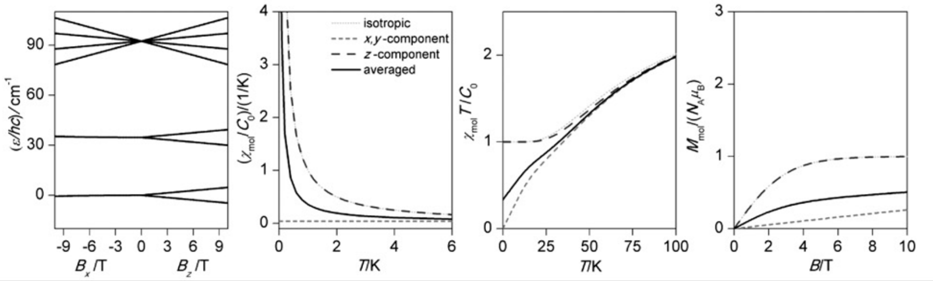


Left – reduced, zero-field magnetic susceptibility for different ratios of $|A_i/J|$.
Right – zero-field splitting of energy levels due to antisymmetric exchange.
$\Delta S = \left(1/2\right)[S_{\max}(S_{\max}+1) - S_{\min}(S_{\min}+1)] = 63/2 = 63/2$.

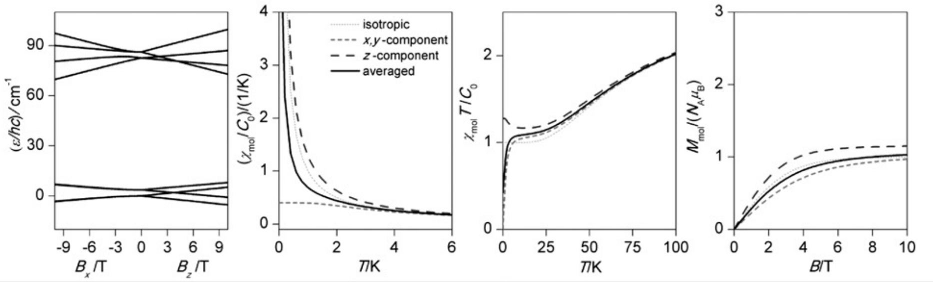
Table A16

Magnetic functions for *triangulo*-[$S_A = S_B = S_C = 1/2$] spin-systems in presence of antisymmetric exchange.

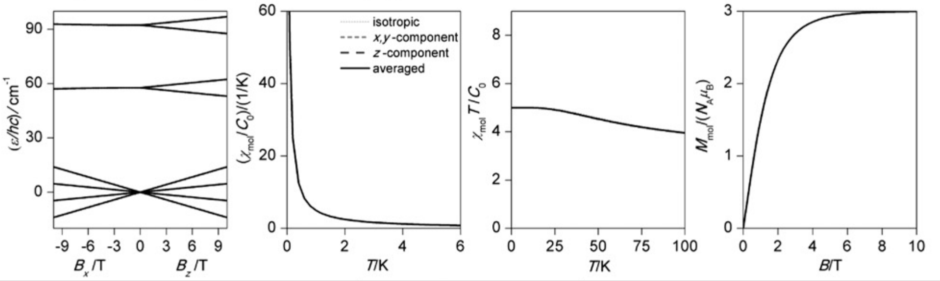
a) antiferromagnetic exchange $J/hc = -50\ \mathrm{cm}^{-1}$, $A_n/hc = 20\ \mathrm{cm}^{-1}$



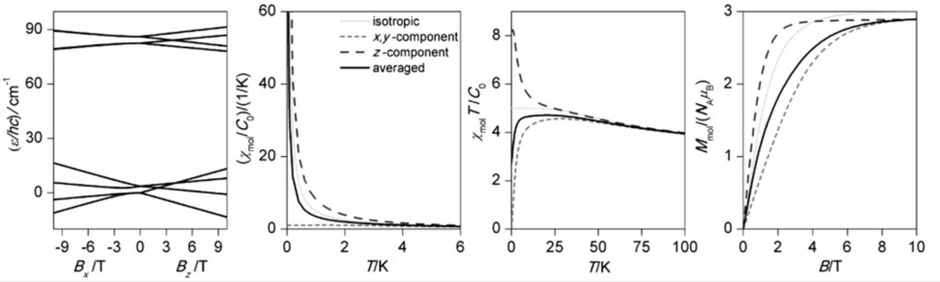
b) antiferromagnetic exchange $J/hc = -50\ \mathrm{cm}^{-1}$, $A_l/hc = A_t/hc = 20\ \mathrm{cm}^{-1}$



c) ferromagnetic exchange $J/hc = +50\ \mathrm{cm}^{-1}$, $A_n/hc = 20\ \mathrm{cm}^{-1}$



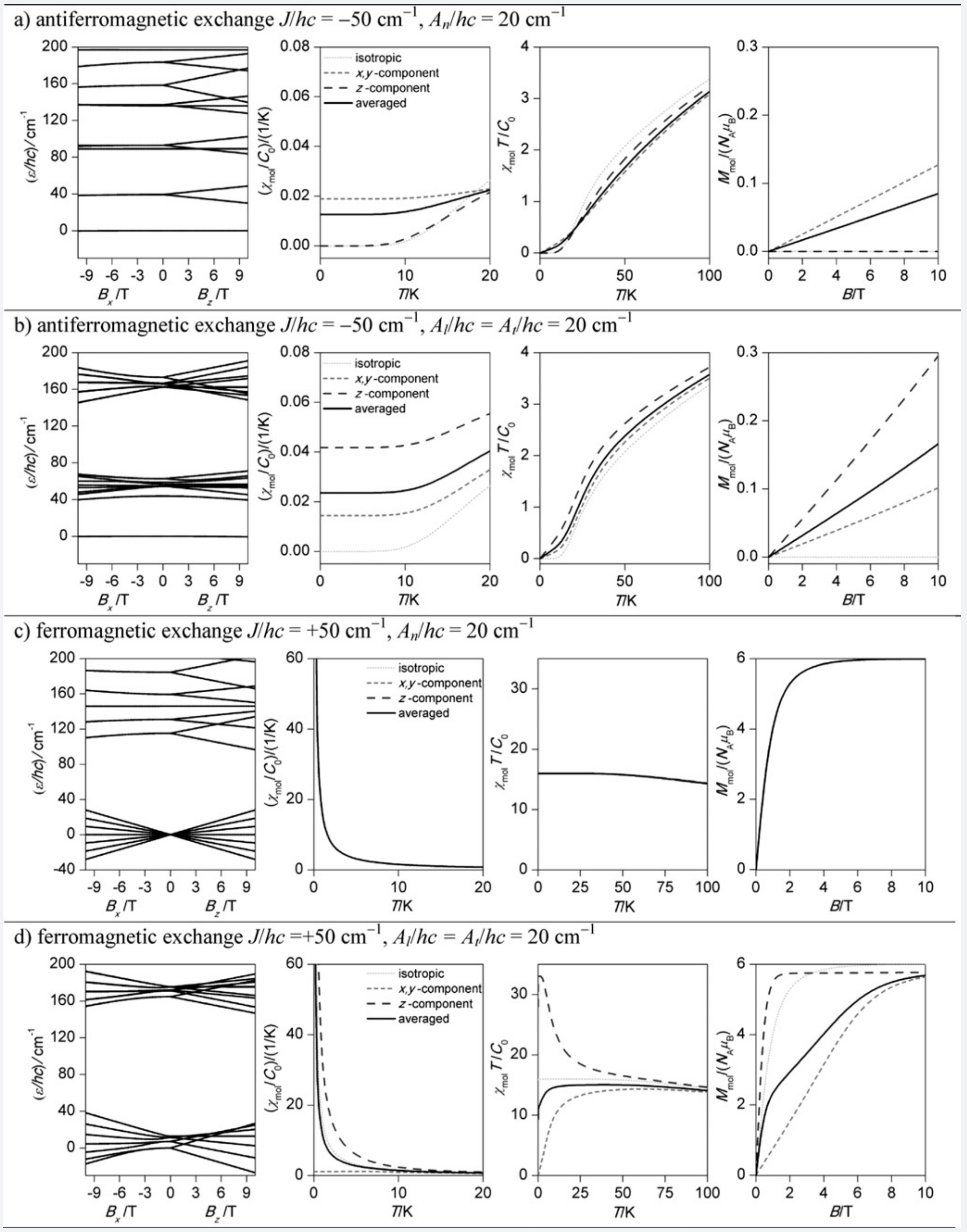
d) ferromagnetic exchange $J/hc = +50\ \mathrm{cm}^{-1}$, $A_l/hc = A_t/hc = 20\ \mathrm{cm}^{-1}$



Energy levels, product function, isothermal magnetization ($T = 2.0$ K) and zero-field magnetic susceptibility.

Table A17

Magnetic functions for *triangulo*-[$S_A = S_B = S_C = 1$] spin-systems in presence of antisymmetric exchange.



a) antiferromagnetic exchange $J/hc = -50\ \mathrm{cm}^{-1}$, $A_n/hc = 20\ \mathrm{cm}^{-1}$

b) antiferromagnetic exchange $J/hc = -50\ \mathrm{cm}^{-1}$, $A_l/hc = A_t/hc = 20\ \mathrm{cm}^{-1}$

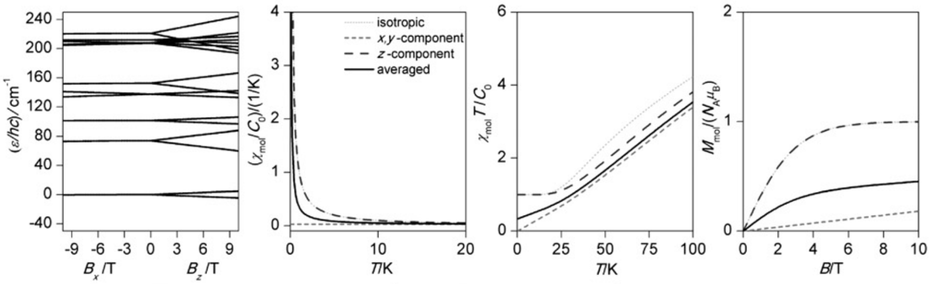
c) ferromagnetic exchange $J/hc = +50\ \mathrm{cm}^{-1}$, $A_n/hc = 20\ \mathrm{cm}^{-1}$

d) ferromagnetic exchange $J/hc = +50\ \mathrm{cm}^{-1}$, $A_l/hc = A_t/hc = 20\ \mathrm{cm}^{-1}$

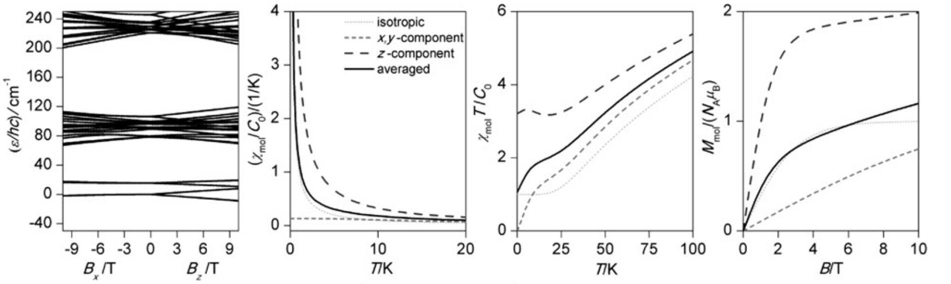
Energy levels, product function, isothermal magnetization ($T = 2.0$ K) and zero-field magnetic susceptibility.

Table A18
Magnetic functions for *triangulo*-[$S_A = S_B = S_C = 3/2$] spin-systems in presence of antisymmetric exchange.

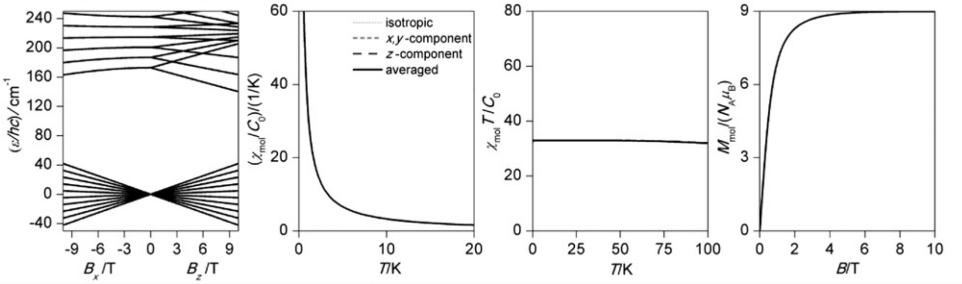
a) antiferromagnetic exchange $J/hc = -50$ cm^{-1}, $A_n/hc = 20$ cm^{-1}



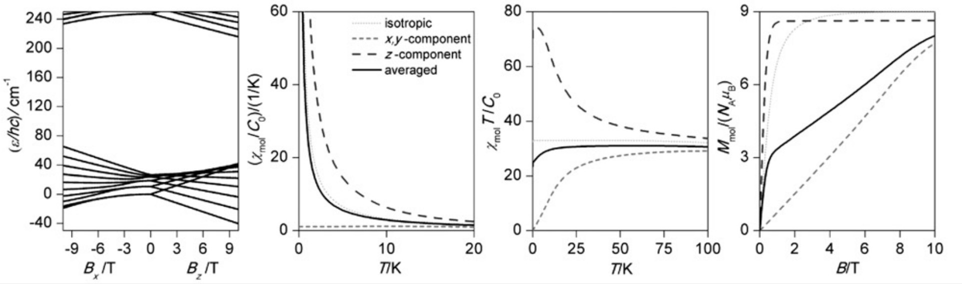
b) antiferromagnetic exchange $J/hc = -50$ cm^{-1}, $A_l/hc = A_t/hc = 20$ cm^{-1}



c) ferromagnetic exchange $J/hc = +50$ cm^{-1}, $A_n/hc = 20$ cm^{-1}



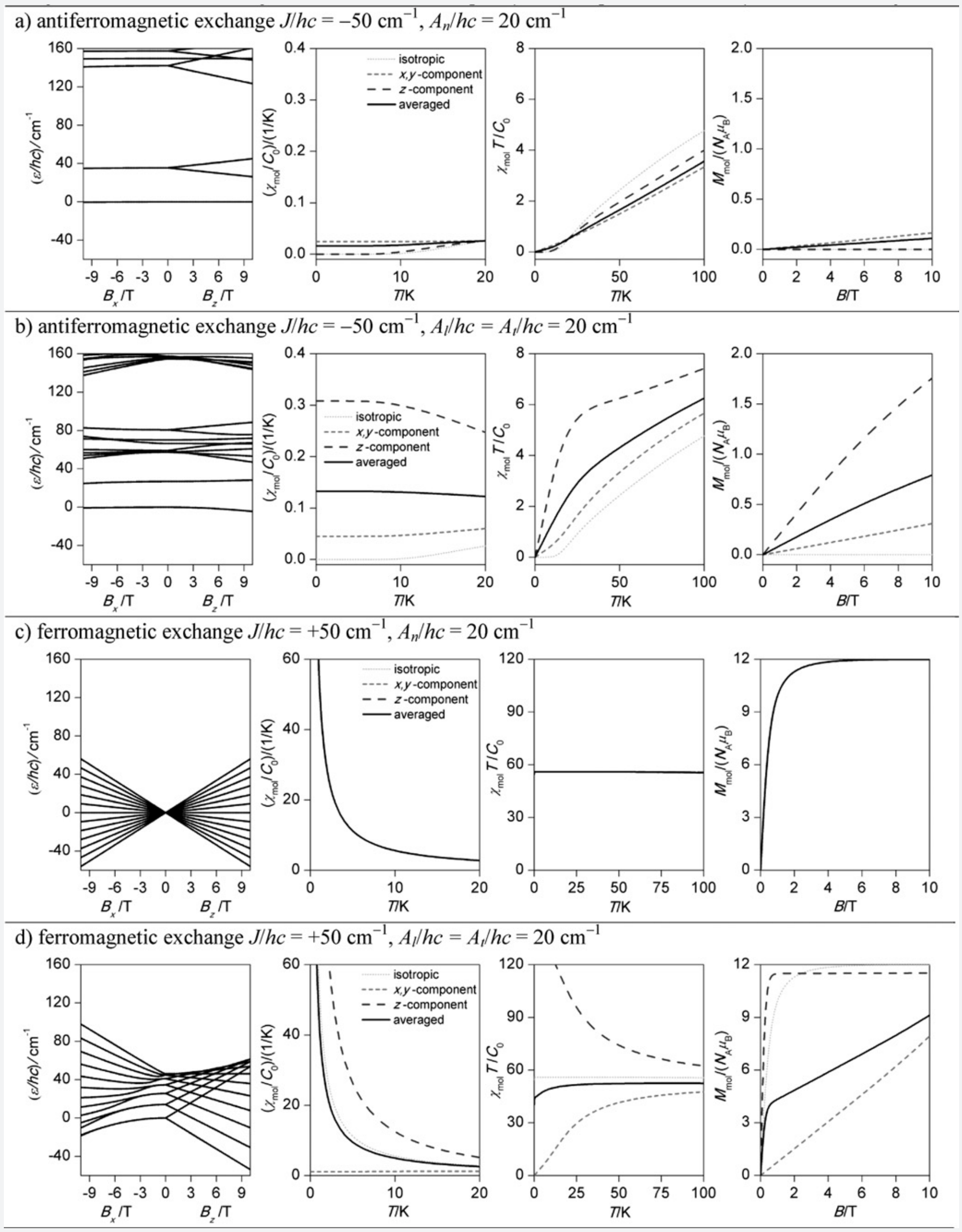
d) ferromagnetic exchange $J/hc = +50$ cm^{-1}, $A_l/hc = A_t/hc = 20$ cm^{-1}



Energy levels, product function, isothermal magnetization ($T = 2.0$ K) and zero-field magnetic susceptibility.

Table A19

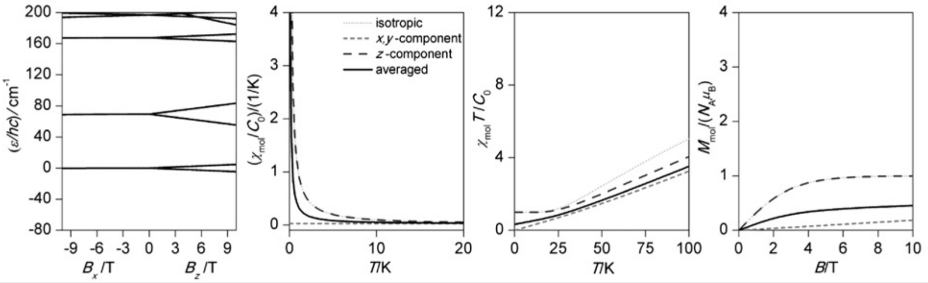
Magnetic functions for *triangulo*-[$S_A = S_B = S_C = 2$] spin-systems in presence of antisymmetric exchange.



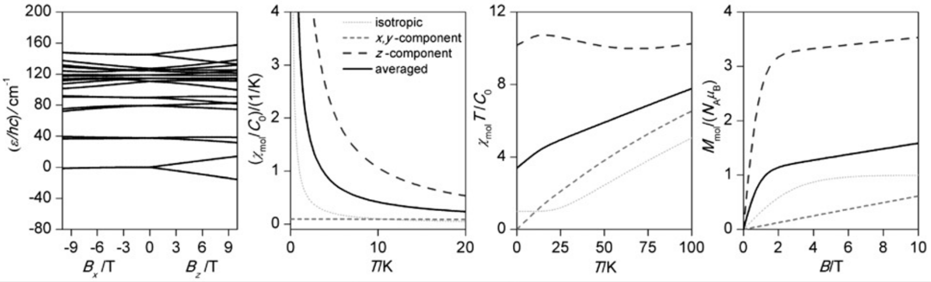
Energy levels, product function, isothermal magnetization ($T = 2.0$ K) and zero-field magnetic susceptibility.

Table A20
Magnetic functions for *triangulo*-[$S_A = S_B = S_C = 1/2$] spin-systems in presence of antisymmetric exchange.

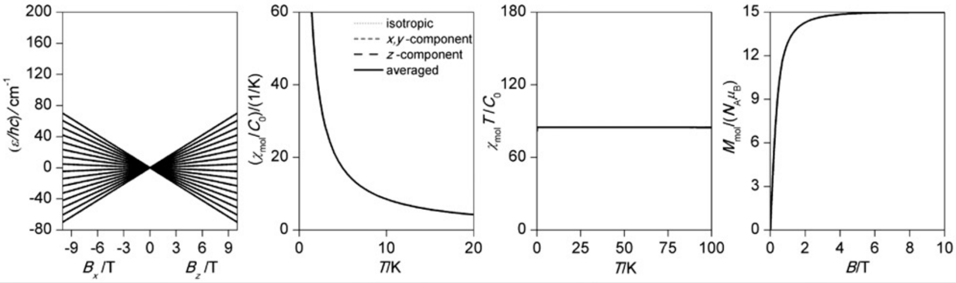
a) antiferromagnetic exchange $J/hc = -50\ \mathrm{cm}^{-1}$, $A_n/hc = 20\ \mathrm{cm}^{-1}$



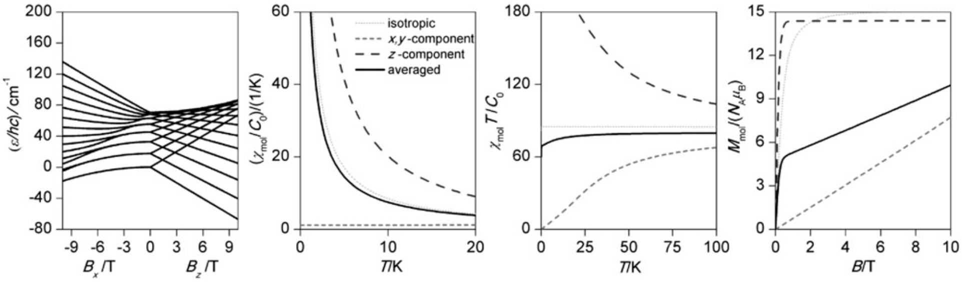
b) antiferromagnetic exchange $J/hc = -50\ \mathrm{cm}^{-1}$, $A_l/hc = A_t/hc = 20\ \mathrm{cm}^{-1}$



c) ferromagnetic exchange $J/hc = +50\ \mathrm{cm}^{-1}$, $A_n/hc = 20\ \mathrm{cm}^{-1}$



d) ferromagnetic exchange $J/hc = +50\ \mathrm{cm}^{-1}$, $A_l/hc = A_t/hc = 20\ \mathrm{cm}^{-1}$



Energy levels, product function, isothermal magnetization ($T = 2.0$ K) and zero-field magnetic susceptibility.

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ccr.2010.06.012.

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