UTILIZATION OF THE SPIN SYMMETRY IN FITTING THE MAGNETIC DATA FOR LARGE EXCHANGE CLUSTERS

ROMAN BOČA

Department of Chemistry, University of SS. Cyril and Methodius, SK-917 01 Trnava, Slovak Republic (roman.boca@stuba.sk)

Abstract: The Heisenberg Hamiltonian appropriate to exchange clusters commutes with the square of the total spin ant its third component. Therefore in studying the exchange coupled clusters of medium/high nuclearity the spin quantum number S can be utilized in factoring of large interaction matrices (dimension of which is 10^4 - 10^5). Then the blocks of much lower size can be diagonalized using the desktop computers. To this end, the eigenvalues form the partition function $Z(T,B)$ from which all thermodynamic properties, including the magnetization $M(B,T_0)$ and the magnetic susceptibility $\chi(T,B_0)$, can be reconstructed. The matrix elements of the interaction operators in the coupled basis set of spin kets have been generated with the help of the irreducible tensor operators for a loop for $S = S_{min}$ until $S = S_{max}$. In addition to the modelling of energy levels for different topologies, a fitting of magnetic data is exemplified by a number of examples like $[Fe_6]$ and $[Mn_3Cr_4]$ systems.

Key words: spin symmetry, exchange clusters, Fe(III) complexes, magnetic data

1. Introduction

Synthesis, structural and spectral characterization of polynuclear homo- or heteronuclear complexes represents one of the most rapidly developing areas of the Coordination Chemistry. Of various properties the magnetic behavior represents a centre of interest since new architecture of complexes led to discovery of new magnetic phenomena that possess a great potential for technical exploitation. Reports on the medium-sized metal complexes build of 4 to 8 (or even more) metal centers are rather numerous. The magnetic data of them (the temperature dependence of the magnetic susceptibility and eventually the field dependence of the magnetization) used to be reported for them. However, a complete understanding of those data requires a fixing of magnetic parameters (at least the exchange coupling constants J_{AB}, and the magnetogyric-ratio g_A) by an appropriate fitting procedure.

The principal problem associated with a computational approach lies in the size of the interaction matrices. The Heisenberg Hamiltonian appropriate to the exchange coupled system reads

$$\hat{H}^{\mathrm{ex}} = -\sum_{A<B}^{N} J_{AB}(\mathbf{S}_A \cdot \mathbf{S}_B) \tag{1}$$

and it generates an interaction matrix $H_{LK} = \left\langle L \middle| \hat{H}^{\mathrm{ex}} \middle| K \right\rangle$ in the basis set of spin kets. The size of such a matrix grows rapidly with the number of constituent spins, i.e.

$$M = \prod_{A=1}^{N} (2S_A + 1) \rightarrow (2S_A + 1)^N \tag{2}$$

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For instance, in the hexanuclear $[Fe^{III}_6]$ complex one has to consider $M = 6^6 = 46656$ spin kets leading to the same number of magnetic energy levels.

2. Results and discussion

The Heisenberg exchange Hamiltonian commutes with the total spin of the system

$$\left[\hat{H}^{\mathrm{ex}}, \hat{S}^2\right] = 0\,, \quad \left[\hat{H}^{\mathrm{ex}}, \hat{S}_z\right] = 0 \tag{3}$$

Therefore a set of eigenstates common for $\{\hat{H}^{\mathrm{ex}}, \hat{S}^2, \hat{S}_z\}$ operators exists; this means that the states spanning different total spin are orthogonal

$$H_{LK} = \left\langle L:...S'M' \middle| \hat{H}^{\mathrm{ex}} \middle| K:...SM \right\rangle = \delta_{S'S}\delta_{M'M}(2S+1)^{-1/2} \left\langle L:...S \middle\| \hat{H}^{\mathrm{ex}} \middle\| K:...S \right\rangle \tag{4}$$

It allows a factoring of the interaction matrix into blocks of a much lower size

$$\mathbf{H}^{\mathrm{ex}} \rightarrow \begin{pmatrix} \boxed{S = S_{\min}} & 0 & ... & 0 & 0 \\ 0 & \boxed{S = S_{\min}+1} & ... & 0 & 0 \\ ... & ... & ... & ... & ... \\ 0 & 0 & ... & \boxed{S = S_{\max}-1} & 0 \\ 0 & 0 & ... & 0 & \boxed{S = S_{\max}} \end{pmatrix} \tag{5}$$

which can be treated (diagonalized) independently. Table 1 illustrates the effect of the S-blocking for systems with the genuine spins $S_A = 5/2$, e.g. for the $[Fe^{III}_N]$ clusters.

The matrix elements of the interaction operators in the coupled basis set of spin kets $|K\rangle = |(S_1, S_2, ...S_N), (S_{12}, S_{1...3}, ..., S_{1...N}), S\rangle$ have been generated with the help of the irreducible tensor operators (BOČA, 1999) for a loop for $S = S_{\min}$ until $S = S_{\max}$. The intermediate spins (IS) are abbreviated as $S_{1...N} = \tilde{S}_N$ and the full set of IS is $(\tilde{S}_N)$. The general form of such matrix elements utilizes a consecutive decoupling of spins until the elementary spin operators with the help of the 9*j*-symbols (recoupling coefficients of the angular momenta) according to the formula

$$\begin{aligned} &\left\langle S_1 S_2 ... S_N (\tilde{S}') S' \middle\| \hat{H}^{\mathrm{ex}} \middle\| S_1 S_2 ... S_N (\tilde{S}) S \right\rangle \\ &= \sum_{k_1 k_2 ... k_N} \left\langle S_N \middle\| \hat{T}_{k_N}(\vec{S}_N) \middle\| S_N \right\rangle \times \sum_{\tilde{k}_2 \tilde{k}_3 ... \tilde{k}_{N-1}} G[k_1 k_2(\tilde{k}_2) k_3(\tilde{k}_3) ... k_{N-1}(\tilde{k}_{N-1}) k_N] \\ &\times \prod_{i=1}^{N-1} [(2\tilde{S}'_{i+1}+1)(2\tilde{S}_{i+1}+1)(2\tilde{k}_{i+1}+1)]^{1/2} \begin{Bmatrix} \tilde{S}'_i & \tilde{S}_i & \tilde{k}_i \\ S_{i+1} & S_{i+1} & k_{i+1} \\ \tilde{S}'_{i+1} & \tilde{S}_{i+1} & \tilde{k}_{i+1} \end{Bmatrix} \left\langle S_i \middle\| \hat{T}_{k_i}(\vec{S}_i) \middle\| S_i \right\rangle \end{aligned} \tag{6}$$

The only non-zero proportionality factor accounting for the relationship between the scalar and tensor product of spin operators is

$$G[k_1 k_2(\tilde{k}_2) k_3(\tilde{k}_3)...k_{N-1}(\tilde{k}_{N-1}) k_N] = \sqrt{3} J_{ij} \quad (7)$$

where the tensor ranks are $k_i = k_j = 1$ for $i \neq j$, $k_f = 0$ for $f \neq i, j$, and $k = \tilde{k}_N = 0$. The matrix elements of the elementary spin operators are

$$\left\langle S_f \left\| \hat{T}_{k_f=0}(\vec{S}_f) \right\| S_f \right\rangle = (2s_f + 1)^{1/2}, \left\langle S_f \left\| \hat{T}_{k_f=1}(\vec{S}_f) \right\| S_f \right\rangle = [s_f(s_f+1)(2s_f+1)]^{1/2} \quad (8)$$

with $(s_f) = S_1 S_2 ... S_N$.

Table 1. Effect of the S-blocking for A_N systems with the genuine spins S_A =5/2.

A_N system	Magnetic states, all M	Zero-field states	Numerousity $n(S)$ from the lowest spin, S_{min} = 0 or 1/2, to the highest spin $S_{max} = NS_A$
A_3	216	27	2, 4, 6, 5, 4, 3, 2, 1
A_4	1296	146	6, 15, 21, 24, 24, 21, 15, 10, 6, 3, 1
A_5	7776	780	45, 84, 111, 120, 115, 100, 79, 56, 35, 20, 10, 4, 1
A_6	46656	4332	111, 315, 475, 575, 609, 581, 505, 405, 300, 204, 126, 70, 35, 15, 5, 1
A_7	279936	24017	1050, 1974, 2666, 3060, 3150, 2975, 2604, 2121, 1610, 1140, 750, 455, 252, 126, 56, 21, 6, 1
A_8	1679616	135954	2666, 7700, 11900, 14875, 16429, 16576, 15520, 13600, 11200, 8680, 6328, 4333, 2779, 1660, 916, 462, 210, 84, 28, 7, 1
A_9	10077696	767394	26775, 50904, 70146, 83000, 88900, 88200, 82005, 71904, 59661, 46920, 34980, 24696, 16478, 10360, 6111, 3360, 1707, 792, 330, 120, 36, 8, 1

The calculated zero-field energy levels for a variety of topologies are presented in Table 2. It can be seen that the energy spectrum drastically depends upon the connectivity of centers (octahedron, trigonal prism, ring, chain, a star).

The main computational problem arises when the magnetic field is applied: the matrix elements of the Zeeman term in the basis set of the coupled kets are off-diagonal in the total spin number. There is one exception: when all *g*-factors are equal, then the off-diagonal matrix elements of the Zeeman operator vanish exactly. This is really a fortunate case, since then the Zeeman contributions can be simply added to the roots of the zero-field Hamiltonian

$$\varepsilon(S, B) = \varepsilon_0(S) + \mu_B g_{iso} B M_S \quad (9)$$

Then the magnetic functions can be exactly expressed with the help of the true partition function

$$M_{mol} = N_A \frac{1}{Z} T_1, \quad \tilde{\chi}_{mol} = \frac{N_A \mu_0}{kT} \frac{1}{Z^2} (T_2 Z - T_1^2) \quad (10)$$

The terms entering the magnetisation and the differential magnetic susceptibility are

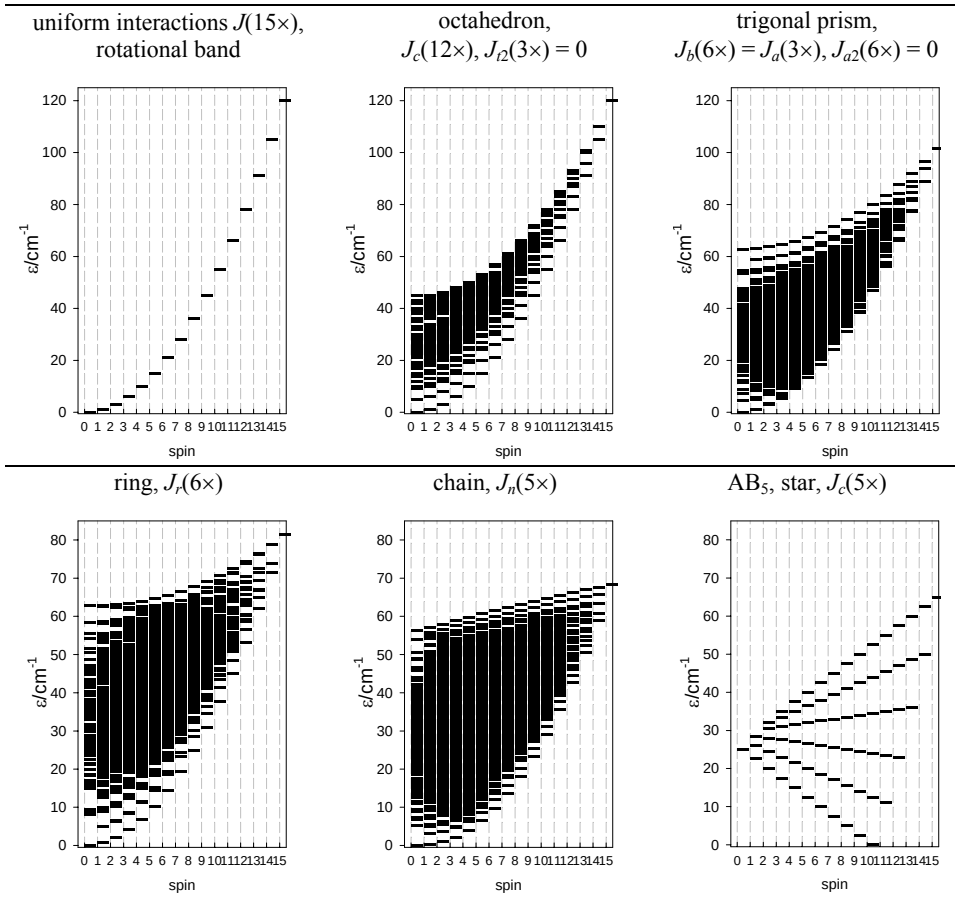
$$Z = \sum_i \exp(-\varepsilon_i / kT) = \sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} \exp[(n_S J - \mu_B g B M_S)/kT] \quad (11)$$

$$T_1 = \sum_i \left(-\frac{\partial \varepsilon_i}{\partial B}\right) \exp(-\varepsilon_i / kT) = \mu_B g \sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} M_S \exp[(n_S J - \mu_B g B M_S)/kT] \quad (12)$$

$$T_2 = \sum_i \left(\frac{\partial \varepsilon_i}{\partial B}\right)^2 \exp(-\varepsilon_i / kT) = (\mu_B g)^2 \sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} M_S^2 \exp[(n_S J - \mu_B g B M_S)/kT] \quad (13)$$

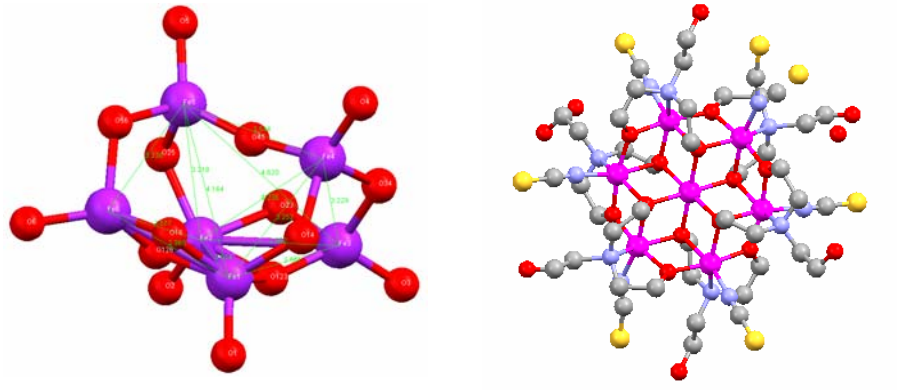
with $n_S = S(S+1)/2$.

Table 2. Modelling of the zero-field energy levels for hexanuclear spin systems, $S_A = 5/2$, $J/hc = -1$ cm^{-1}.



The approach described above has been applied to a number of large-spin clusters (BOČA, 2009). The first example refers to a hexanuclear Fe(III) complex (Fig. 1a) possessing a low symmetry (KUSSEROW *et al.,* 2013). The structure of the cluster

implies that at least three different coupling constants need be considered. The experimental magnetic data are displayed in Fig. 2 along with the calculated ones as they resulted from the fitting procedure. The results show three strong coupling paths of an antiferromagnetic nature ($S = 0$ ground state).



a b

Fig 1. Structure of the polynuclear complexes under study.

The second example refers to a heteronuclear $[Mn^{II}_3Cr^{III}_4]$ complex (Fig. 1b) for which the size of the problem is $M = 6^3 4^4 = 55296$. The zero field states $M_{zf} = 5737$ are factored according to the total spin between $S = 1/2$ and 27/2 as follows: 326, 661, 852, 915, 862, 726, 550, 375, 228, 122, 56, 21, 6, and 1 (i.e. 326 doublets, 661 quartets, etc). For the complex $[Mn_3Cr_4(NCS)_6(Htea)_6]$ the magnetic data are displayed in Fig. 3. With the optimized set of magnetic parameters the ground state of the complex is $S = 15/2$ (fifteen unpaired electrons). This rationalizes why the magnetization per particle taken at $T = 2.0$ K saturates to the value of $M_{mol}/N_A = 15\ \mu_B$ (SEMENAKA *et al.*, 2010).

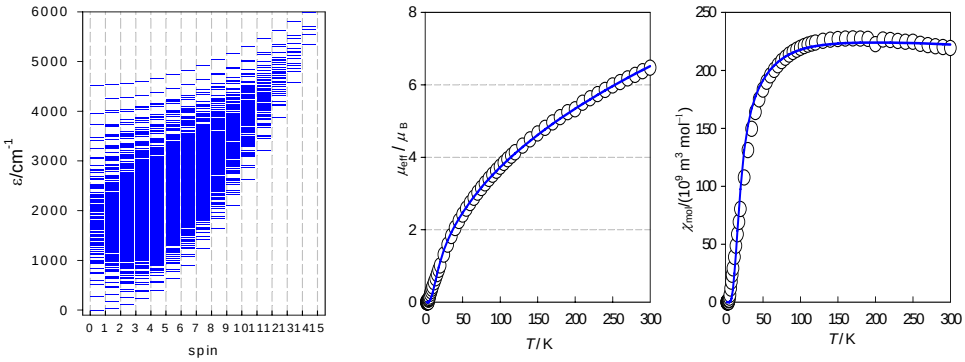


Fig. 2. The zero-field energy spectrum, and the magnetic functions for the complex $[Fe^{III}_6O_3(O^tBu)_5(O^iPr)_7]$; solid line – calculated with $J_1/hc = -28.7$, $J_2/hc = -110.6$, $J_3/hc = -49.3$ cm^{-1}, $g_{eff} = 2.163$; $R(\chi) = 0.0046$.

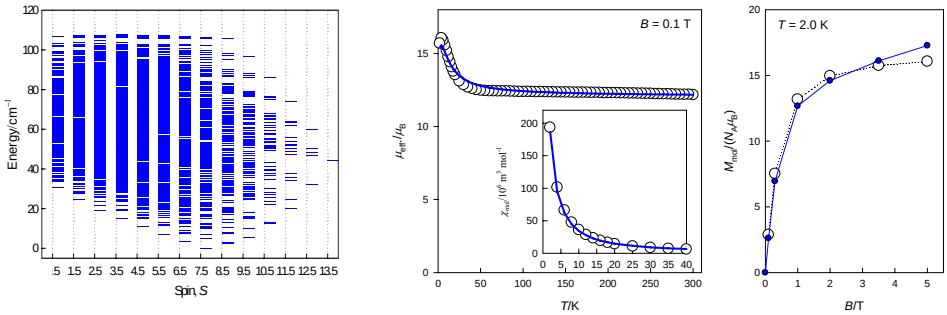


Fig. 3. The zero-field energy spectrum, and the magnetic functions for the complex $[Mn^{II}_3Cr^{III}_4(NCS)_6(Htea)_6]$; solid line – calculated with $J_{Mn\text{-}Cr}/hc$ = +0.43 cm^{-1}, $J_{Cr\text{-}Cr}/hc$ = -4.75 cm^{-1}, $J_{Mn\text{-}Mn}/hc$ = +1.78 cm^{-1}, g_{eff} = 1.878; $R(\chi)$ = 0.045, $R(M)$ = 0.049.

3. Conclusions

It has been demonstrated that the fitting of magnetic data (susceptibility and magnetization) for the medium-sized metal complexes and clusters can be effectively done by utilizing the spin symmetry. This leads to the factoring of the large-dimensional interaction matrix of the order of $10^5 – 10^6$ to the eigenvalue problems of much lower dimensions (10^2 - 10^3) that can be performed even at desk computers.

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