
Software News and Updates

MAGPACK¹ A Package to Calculate the Energy Levels, Bulk Magnetic Properties, and Inelastic Neutron Scattering Spectra of High Nuclearity Spin Clusters

Received 7 September 2000; accepted 21 December 2000

Introduction

Magnetic molecular clusters, i.e., molecular assemblies formed by a finite number of exchange-coupled magnetic moments, are currently receiving much attention in several active areas of research as molecular chemistry, magnetism, and biochemistry. A reason for this interest lies in the possibility to use simple molecular clusters as magnets of nanometer size exhibiting unusual magnetic properties as superparamagnetic like behavior or quantum tunneling of magnetization.^{2–4} Organic molecules of increasing sizes and large number of unpaired electrons are being explored as a means of obtaining building blocks for molecule-based magnets.⁵ Magnetic clusters of metal ions are also relevant in biochemistry.⁶

This area between molecule and bulk will require new theoretical concepts and techniques for investigation of their peculiar properties. Still, the theoretical treatment required to understand the magnetic and spectroscopic properties of this wide variety of compounds is a challenging problem in molecular magnetism.⁷ For a long time, this problem has been mostly restricted to treat comparatively simple clusters comprising a reduced number of exchange-coupled centers and special spin topologies, for which solutions can be obtained either analytically or numerically. However, on increasing the spin nuclearity of the cluster, the problem rapidly becomes unapproachable because the lack of translational symmetry in the clusters. An additional complication is the spin anisotropy of the cluster. Until now only the isotropic-exchange case has been treated, so as to take full advantage of

the spin symmetry of the cluster.⁸ In this article we present a very powerful and efficient computational approach to solve the exchange problem in high nuclearity spin clusters with all kind of exchange interactions (isotropic and anisotropic), including the single-ion anisotropic effects. The clusters are formed by an arbitrary number of exchange-coupled centers that combine different spin values and arbitrary topology. This approach is based on the use of the irreducible tensor operators (ITO) technique.^{7,9–12} It allows evaluation of both eigenvalues and eigenvectors of the system, and then, calculation of the magnetic susceptibility, magnetization, or heat capacity, and also the inelastic neutron scattering spectra.

In the following sections we will present both the theory and the four different implemented FORTRAN programs that integrate a package called MAGPACK. In the last section some examples are presented in order to show the possibilities of the programs.

Theoretical Background

The development of the generalized spin Hamiltonian and the way to express this Hamiltonian in terms of ITO's has been worked out in ref. 13. We present here a brief survey of these results.

The system consists of N magnetic sites with local spins S_i ($i = 1, \dots, N$). These spins are coupled in a successive way, $|S_1 S_2(\tilde{S}_2) S_3(\tilde{S}_3) \dots S_{N-1}(\tilde{S}_{N-1}) SM\rangle = |(\tilde{S})SM\rangle$.¹³ The generalized spin-Hamiltonian operating in the spin space of this

system can be expressed as:

$$\begin{aligned} \hat{H}_S = & \sum_{k_1 k_2 \dots k_N} \sum_{\tilde{k}_2 \tilde{k}_3 \dots \tilde{k}_{N-1}} \\ & \times \sum_{kq} C_q^{(k)} (k_1 k_2 (\tilde{k}_2) \dots k_{N-1} (\tilde{k}_{N-1}) k_N) \\ & \times \hat{T}_q^{(k)} (k_1 k_2 (\tilde{k}_2) \dots k_{N-1} (\tilde{k}_{N-1}) k_N) \end{aligned} \quad (1)$$

where $\hat{T}_q^{(k)} (k_1 k_2 (\tilde{k}_2) \dots k_{N-1} (\tilde{k}_{N-1}) k_N)$ represents the q th component of the complex ITO of the rank k composed from the ITO $\hat{S}_{q1}^{(k_1)}(i)$ acting in the spin space of the individual spins. $C_q^{(k)}$ are the numerical parameters defined later for each kind of exchange Hamiltonian. Finally, k_i represents the rank of the ITOs acting in the individual spin spaces, and \tilde{k}_i the rank of the ITOs acting in the successive spin-coupled systems.

It is possible to express all kind of contributions to the spin Hamiltonian expressed in terms of the conventional spin operators, in function of this generalized Hamiltonian expressed in terms of ITOs. We present here as example the HDVV (\hat{H}_O), eq. (2), biquadratic (\hat{H}_{BQ}), eq. (3), anisotropic (\hat{H}_{AN}), eq. (4), and zero-field splitting (\hat{H}_{ZFS}), eq. (5), interactions.

$$\hat{H}_O = -2 \sum_{if} J_{if} \hat{S}_i \hat{S}_f = 2\sqrt{3} \sum_{if} J_{if} \hat{T}^{(0)}(11|if) \quad (2)$$

$$\begin{aligned} \hat{H}_{BQ} = & - \sum_{if} J_{if} (\hat{S}_i \hat{S}_f)^2 \\ = & - \sum_{if} J_{if} \left[\sqrt{5} \hat{T}^{(0)}(22|if) + \frac{\sqrt{3}}{2} \hat{T}^{(0)}(11|if) \right] \end{aligned} \quad (3)$$

$$\begin{aligned} \hat{H}_{AN} = & -2 \sum_{if} \sum_{\alpha=x,y,z} J_{if}^{\alpha} \hat{S}_i^{\alpha} \hat{S}_f^{\alpha} \\ = & -2J_{if}^x \hat{S}_i^x \hat{S}_f^x - 2J_{if}^y \hat{S}_i^y \hat{S}_f^y - 2J_{if}^z \hat{S}_i^z \hat{S}_f^z \\ = & \frac{2}{\sqrt{3}} \sum_{if} [(J_{if}^x + J_{if}^y + J_{if}^z) \hat{T}^{(0)}(11|if)] \\ & + \sum_{if} \left[(J_{if}^y - J_{if}^x) [\hat{T}_2^{(2)}(22|if) + \hat{T}_{-2}^{(2)}(11|if)] \right. \\ & \left. + \frac{2}{\sqrt{6}} (J_{if}^x + J_{if}^y - 2J_{if}^z) \hat{T}_0^{(2)}(11|if) \right] \end{aligned} \quad (4)$$

$$\begin{aligned} \hat{H}_{ZFS} = & \sum_i D_i (S_i^z)^2 \\ = & \sum_i D_i \left[\frac{-1}{\sqrt{3}} \hat{T}^{(0)}(00|i) + \sqrt{\frac{2}{3}} \hat{T}_0^{(2)}(2|i) \right] \end{aligned} \quad (5)$$

where $\hat{T}_q^{(k)}(k_i k_f | if)$ and $\hat{T}_q^{(k)}(k_i | i)$ are a simple notation of the complex ITO that contains all the information necessary to be evaluated.

The evaluation of the energy matrix elements can be made applying the Wigner–Eckart theorem and the successive decoupling procedure of the individual ITOs. This procedure gives the following result:

$$\begin{aligned} & \langle (\tilde{S}') S' M' | \hat{T}_q^{(k)} (k_1 k_2 (\tilde{k}_2) \dots k_{N-1} (\tilde{k}_{N-1}) k_N) | (\tilde{S}) S M \rangle \\ & = (-1)^{2k} (2S+1)^{-1/2} C_{SMkq}^{S'M'} \langle S_N \| \hat{S}^{(k_N)} \| S'_N \rangle \\ & \times \prod_{i=1}^{N-1} \sqrt{(2\tilde{k}_{i+1}+1)(2\tilde{S}_{i+1}+1)(2\tilde{S}'_{i+1}+1)} \\ & \times \langle S_i \| \hat{S}^{(k_i)} \| S'_i \rangle \left\{ \begin{matrix} \tilde{k}_i & k_{i+1} & \tilde{k}_{i+1} \\ \tilde{S}'_i & S'_{i+1} & \tilde{S}'_{i+1} \\ \tilde{S}_i & S_{i+1} & \tilde{S}_{i+1} \end{matrix} \right\} \end{aligned} \quad (6)$$

The energy matrix element is expressed only in terms of Clebsch–Gordan coefficients, 9- j symbols, and reduced matrices of the individual spins that are tabulated. With this procedure one can evaluate the energy matrix and, therefore, the eigenvalues and eigenvectors of the system. In some cases we need to introduce the interaction between the spin system and the external magnetic field (Zeeman effect). This interaction can also be expressed in terms of ITOs:

$$\begin{aligned} \hat{H}_{ZEE} = & \sum_i g_i^z \hat{S}_i^z H^z + g_i^{xy} (\hat{S}_i^x H^x + \hat{S}_i^y H^y) \\ = & \sum_i [g_i^z \hat{T}^0(0|i) \\ & + g_i^{xy} / \sqrt{2} (\hat{T}_{-1}^{(1)}(1|i) + \hat{T}_1^{(1)}(1|i)) H^{xy}] \end{aligned} \quad (7)$$

Once we have the eigenvalues of the system at different magnetic fields or temperatures, one can evaluate the partition function Z and the different thermodynamic properties of the system, as magnetization, magnetic susceptibility, and magnetic specific heat:

$$M = NkT \frac{\partial \ln Z}{\partial H} \quad (8)$$

$$\chi = \left(\frac{\partial M}{\partial H} \right)_{H \rightarrow 0} \quad (9)$$

$$C_p = \frac{\partial}{\partial T} \left(RT^2 \frac{\partial \ln Z}{\partial T} \right) \quad (10)$$

Organization of the Package

The MAGPACK package is based on the theory presented in the previous section. This package generates the spin functions of the system and then calculates the energy matrix and diagonalizes it to

TABLE I.
Different Programs Included in the Package and Its Peculiarities.

	Kind of System		Kind of Calculation	
	Isotropic	Anisotropic	Thermodynamic Properties	INS
ISOMAG1.F	yes	no	no	yes
ISOMAG2.F	yes	no	yes	no
ANIMAG1.F	no	yes	no	yes
ANIMAG2.F	no	yes	yes	no

get the eigenvalues and eigenvectors. In a final step these data are used to evaluate the derived thermodynamic and spectroscopic properties.

Due to the large amount of memory used to evaluate each physical property and the great number of parameters involved in the calculation, the package contains four independent programs (ISOMAG1.F, ISOMAG2.F, ANIMAG1.F, and ANIMAG2.F). Each of these programs has been adapted to a specific type of spin clusters and kind of property (thermodynamical or spectroscopic) to optimize the memory and time requirements. This subdivision facilitates program maintenance and development.

Two of the programs are adapted to calculate isotropic systems and the other two calculate the anisotropic ones (this difference is denoted by the prefixes ISO and ANI, respectively). The suffixes 1 and 2 denote the properties to evaluate. Suffix 1 is associated to the programs that perform an INS spectrum evaluation and suffix 2 to those evaluating the thermodynamical properties. The set of programs is summarized in Table I, and the general organization of the package is shown in Figure 1.

Organization of Code and Data Flow

Each program has a similar structure of subroutines. Only a few of these subroutines have a global character (i.e., share data with others), whereas the rest are self-container modular subroutines or functions called by the global ones. In general, global subroutines perform a general task. Examples include setting up of the parameters, evaluation of the energy matrix, evaluation of the different properties, etc. On the contrary, modular subroutines accomplish a particular task as for example the evaluation of mathematical functions.

The parameters involved in the spin system (nuclearity, topology, exchange parameters, etc.) and the evaluation of the properties are transferred to the program through two FORTRAN INCLUDE

files (see Table II). After execution, the program generates different output files containing all the information concerning the initialization, evaluation, and simulation processes.

MAGPACK is entirely written in standard portable FORTRAN77. Figure 2 shows, in a very schematic way, the essential flow chart of all the programs. Here, the main program first calls the WAR subroutine, second ENE, which alternatively calls SUS, MAG, and INS.

The fundamental task of WAR is to read the INCLUDE files and to verify their information and to initialize a large common block area containing the data needed to run a calculation. This subroutine creates one of the output files (EIG.RES) containing in a schematic way all the information concern-

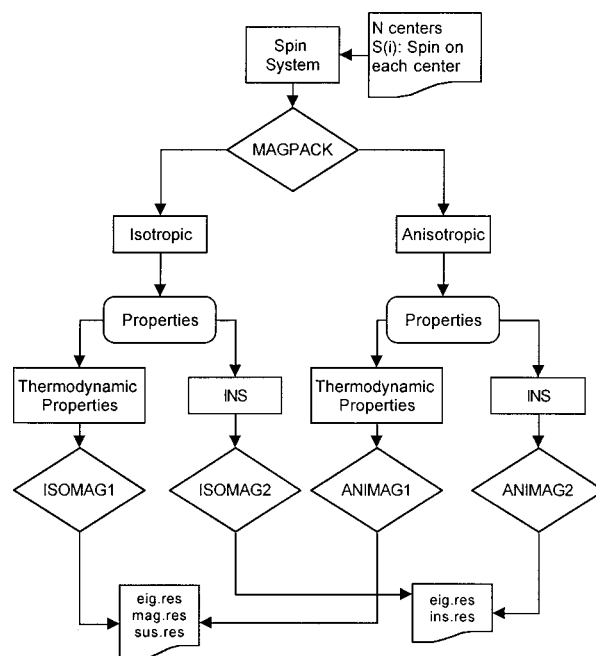


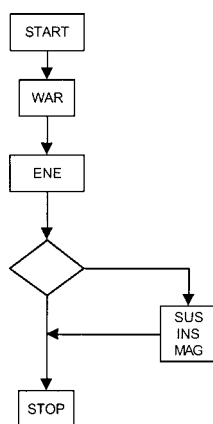
FIGURE 1. General organization of the MAGPACK package showing the different programs.

TABLE II.
Associated INCLUDE Files.

ISOMAG1.F	ISOMAG2.F
PARISO11	PARISO21
PARISO12	PARISO22
ANIMAG1.F	ANIMAG2.F
PARANI11	PARANI21
PARANI12	PARANI22

ing the system definition, the errors, and warnings generated at the different steps of the initialization process.

After the initialization process, the program enters in ENE, the core of the program, where the first task is to generate the starting spin functions by invoking the common block generated at WAR. Second, the energy matrix elements are evaluated by a successive addition of the different interaction contributions. Each different contribution is associated to an independent subroutine: ISO is for the isotropic exchange interactions (bilinear and biquadratic), ANI is for the anisotropic exchange interactions, and ANL is for the single ion anisotropy. Each of these subroutines use the general expression, eq. (6), to evaluate the energy matrix elements. To evaluate the mathematical functions involved in this expression (Clebsch–Gordan coefficients, $6 - j$ and $9 - j$ symbols, etc.), different EXTERNAL FUNCTIONS have been defined. Finally, to obtain the eigenvalues, the energy matrix is diagonalized by a standard subroutine DSPEV of the LAPACK Mathematical Library.¹⁴

**FIGURE 2.** Schematic flow chart of the MAGPACK programs. Only the most significant subroutines are shown.**TABLE III.**
Associated Output Files.

ISOMAG1.F	ISOMAG2.F
eig.res	eig.res
ins_spc.res	sus.res
ins_qdq.res	mag.res
ANIMAG1.F	ANIMAG2.F
eig.res	eig.res
ins_spc.res	sus.res
ins_qdq.res	mag.res

To evaluate the properties of the spin cluster, the different subroutines associated to these properties are called from ENE. These subroutines are SUS, MAG, and INS. They calculate magnetic susceptibility and heat capacity, magnetization, and inelastic neutron scattering, respectively. For the anisotropic systems, the magnetic field perturbs the zero field levels, and this perturbation depends on the relative orientation of the external magnetic field with respect to the magnetic axis of the system. Therefore, to calculate the magnetization and the susceptibility one needs a new evaluation of the energy matrix that includes the additional interaction of the system with the external field. This new contribution is evaluated in the subroutine ZEE. To obtain a proper evaluation of these properties for powder samples, MAG and SUS subroutines assure a correct integration of the properties over the different orientations of the external magnetic field.

MAGPACK returns from SUS, MAG, and INS different output files containing the evaluated properties in a column text type format that allows an easy plot for graphic package. In Table III we summarize the associated output files.

Each one of the programs mentioned in the previous section has two main include files associated with them (see Table II). In these files we define not only the kind of system we want to analyze but also the working area that fits its necessities. One defines the nature of the system (number of centers, spin value on each center, the values of the different kinds of interactions involved, ...), as well as the properties to be evaluated. After the compilation of the code, one builds an executable that is well adapted to the dimension of the problem.

Concerning the output files, several of them can be obtained, depending on which kind of calculation is performed. The file eig.res will be always written. It shows different messages of warnings and errors that allow to check that one has defined in a coherent way the system and also to follow

the different steps in the calculation. Other useful information, as the basis function set and the list of eigenvalues and eigenvectors, is also written. Depending on the case, four output files can be also created: *sus.res*, *mag.res*, *ins_spc.res*, and *ins_qdp.res*, corresponding to the magnetic susceptibility, magnetization, or INS calculation, respectively. In Table III we summarize the associated output files.

Applications of the Program

In this section we will show with some examples the possibilities of the program. This powerful approach can be applied to the study of high-nuclearity systems with isotropic and anisotropic interactions. As an example of an isotropic system we consider the problem of a Heisenberg chain containing alternating spins 1/2 and 2. In this case, the behavior of the infinite chain can be obtained by extrapolation of the exact results performed on chains of increasing size. Thus, the calculations have been performed on closed chains of up to five pairs 1/2–2 with two alternating antiferromagnetic exchange interactions J and J' . This kind of system is relevant to analyze the properties of some Mn-porphyrine chains.¹⁵ Down to very low temperatures the differences between curves calculated for four and five spin pairs are negligible, so in a wide range of temperatures (down to $kT/|J| = 1$) the calculation on the five spin pairs closely reproduces the infinite chain behavior.

Figures 3 and 4 show the product χT and the specific heat for this system at different ratios of J'/J . When $J' = 0$ the behavior corresponds to that of

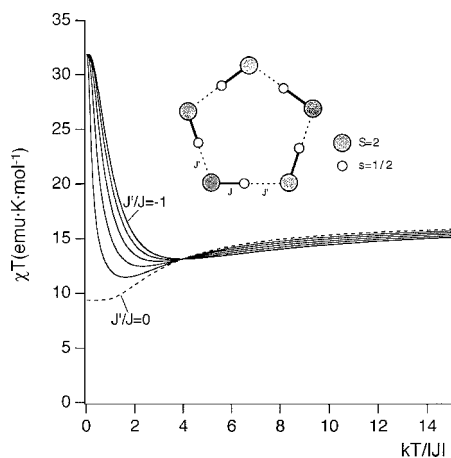


FIGURE 3. The product χT for the isotropic chain at different values of the ratio J'/J .

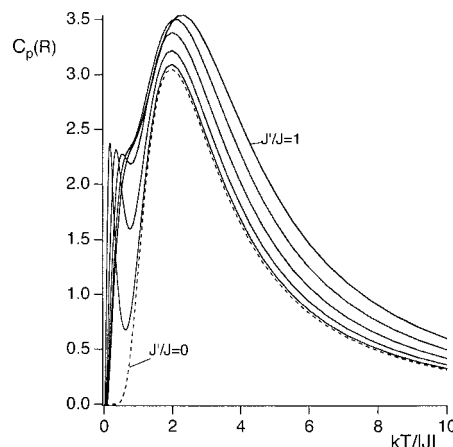


FIGURE 4. Magnetic specific heat for the ferrimagnetic isotropic chain $[1/2, 2]$ at different values of the ratio J'/J .

an antiferromagnetic dimer of spins 1/2 and 2; the product χT decreases when decreasing the temperature, and reaches a plateau at low temperature corresponding to the $3/2$ ground spin state. When J' is different from zero, a ferrimagnetic chain behavior is observed, which is characterized by a minimum in χT followed by a divergence at lower temperatures corresponding to an infinite spin ground state in the chain (and to a $S = 15/2$ in the ring of five pairs).

The specific heat presents a single maximum when J' is zero, corresponding to an antiferromagnetic dimer, but when J' is different from zero, a new maximum associated to this new interactions appears. This new maximum shifts in temperature when J' increases, and finally both maxima join together when the ratio J'/J is close to 1.

As an anisotropic system we propose a tetrameric cluster of Ni(II) with a rhombic symmetry leading to two different ferromagnetic Heisenberg exchange interactions, namely the interaction through the edge of the rhomb J , and the interaction through the short diagonal J' . Each Ni center has a single ion zero-field splitting, D . This system is relevant to interpret the properties of $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{-10}$ compound that contains a rhomb-like Ni_4 central cluster.¹⁶ In the case of anisotropic systems, the magnetic susceptibility of a powder is given as an average between the susceptibility calculated with the magnetic field perpendicular to the principal magnetic axis and with the field parallel $\chi = (\chi_{\parallel} + 2\chi_{\perp})/3$. The output file gives the two contribution and the average (performed in the subroutine SUS). In Figure 5 we show these for the case of $g_{\perp} = 2$ and $g_{\parallel} = 2.3$. In this case, the three curves present a maximum in χT corresponding to a ferromag-

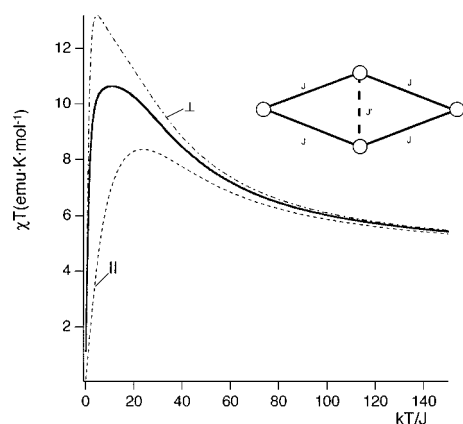


FIGURE 5. The product χT for the Ni cluster. $J'/J = 0.5$; $D/J = 0.5$.

netic interaction between the centers followed by a decrease at low temperatures, due to the zero-field splitting contribution. In Figure 6 we show the curve for the heat capacity of this system. The curve presents a round maximum around 25 K and a sharp maximum at ca. 0.5 K.

Another possibility of the program is to calculate the magnetization. In the case of anisotropic systems with axial anisotropy, this physical property depends on the orientation of the magnetic field with respect to the Z axis. The program evaluates this property averaging the magnetization curves calculated at different angles in the XZ plane (performed in subroutine MAG). Figure 7 shows the magnetization curves of the tetrameric Ni(II) ferromagnetic system at 0.2 K and angles from 0 to 90 respect the Z axis. When the magnetic field is paral-

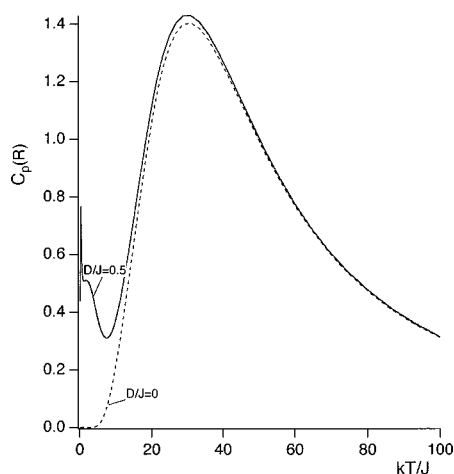


FIGURE 6. The specific heat for the ferromagnetic Ni cluster without single ion anisotropy (dashed line) and with single ion anisotropy (full line). $J'/J = 0.5$, $D/J = 0.5$.

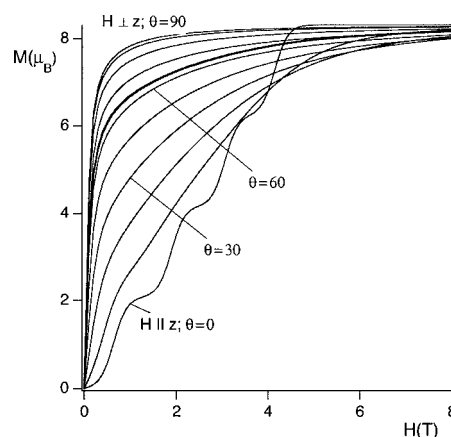


FIGURE 7. The magnetization for the Ni cluster, $J'/J = 0.5$, $D/J = 0.5$. Bold line corresponds to the averaged behavior of the powder.

lel to the Z axis we observe at low temperature that the magnetization shows different steps. That corresponds to the change of the M quantum number of the ground state when H is increasing.

The other kind of property that the program can reproduce is the INS spectra of magnetic clusters, i.e., the energies and intensities of the magnetic excitations and their dependencies with the scattering vector Q and the temperature. This possibility has been exploited in refs. 16 and 17 to model the properties of tetrameric clusters Ni4 and Co4 encapsulated by the polyoxometalates $[\text{M}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{-10}$.

Finally, the other property of interest is the electronic paramagnetic resonance spectroscopy of these clusters. So far the available programs allow simulation of the spectra of a single ion consisting of a spin multiplet splitted under the effect of a magnetic anisotropy. However, the general case of a spin cluster has not been approached. The developed approach can be easily adapted to treat this problem. We hope to provide this kind of program in the near future.

Acknowledgments

Financial support of the MEC (grant PB96-0862-C02-02) and the Generalitat Valenciana (grant GVDOC00-01-02) are acknowledged. B.S.T. thanks the University of Valencia for a visiting professor grant and Generalitat of Valencia for the financial support.

References

1. The package is available from the authors upon request by e-mail: juan.j.borras@uv.es; juan.m.clemente@uv.es.
2. Gatteschi, A.; Caneschi, L. P.; Sessoli, R. *Science* 1994, 265, 105.
3. Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* 1993, 365, 141.
4. Ceesman, M. R.; Oganessian, V. S.; Sessoli, R.; Gatteschi, D.; Thomson, A. J. *Chem Commun* 1997, 1667.
5. Fujita, I.; Yeki, Y.; Takui, T.; Kinoshita, T.; Itoh, K.; Miko, F.; Sawaki, Y.; Iwamura, H.; Izuoka, A.; Sugawara, T. *J Am Chem Soc* 1990, 112, 4074.
6. Blondin, G.; Girerd, J. J. *Chem Rev* 1989, 90, 1359.
7. Clemente, J. M.; Pali, A. V.; Tsukerblat, B. S.; Georges, R. *Molecular Magnetism: From Molecular Assemblies to the Devices*; NATO ASI E321; Kluwer Academic Publishers: Dordrecht, 1996.
8. Gatteschi, D.; Pardi, L. *Gazz Chim It* 1993, 123, 231.
9. Tsukerblat, B. S.; Belinskii, M. I. *Magnetochemistry and Spectroscopy of Exchange Clusters*; Shtiintsa: Kishinev, 1983.
10. Tsukerblat, B. S.; Belinskii, M. I.; Fainzilberg, V. E. *Magnetochemistry and Spectroscopy of Transition Metal Exchange Cluster*; Horwood Academic Pub.: Amsterdam, 1987, vol. 9.
11. Varsalovich, D. A.; Moskalev, A. N.; Khersonskii, V. K. *Quantum Theory of Angular Momentum*; World Scientific: Singapor, 1988.
12. Silver, B. L. *Irreducible Tensor Methods; An Introduction for Chemists*; Academic Press: London, 1988.
13. Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerblat, B. S. *Inorg Chem* 1999, 38, 6081.
14. Anderson, E.; Bai, Z.; Bischof, C.; Blackford, S.; Demmel, J.; Dongarra, J.; Croz, J. D.; Greenbaum, A.; Hammarling, S.; McKenney, A.; Sorensen, D., Eds. *LAPACK User's Guide*; Society for Industrial and Applied Mathematics: 1999, 3rd ed.
15. Miller, J. S.; Calabrese, J. C.; McLean, R. S.; Epstein, A. J. *Adv Mater* 1992, 4, 498.
16. Clemente-Juan, J. M.; Andres, H.; Borrás-Almenar, J. J.; Coronado, E.; Güdel, H. U.; Aebersold, M.; Kearly, G.; Büttner, H.; Zolliker, M. *J Am Chem Soc* 1999, 121, 10021.
17. Andres, H.; Clemente-Juan, J. M.; Aebersold, M.; Güdel, H. U.; Coronado, E.; Büttner, H.; Kearly, G.; Melero, J.; Burriel, R. *J Am Chem Soc* 1999, 121, 10028.

J. J. BORRÁS-ALMENAR, J. M. CLEMENTE-JUAN
E. CORONADO, B. S. TSUKERBLAT*
Departamento de Química Inorgánica
Universidad de Valencia, C.Dr. Moliner 50
46100 Burjassot, Spain

*On leave from the Quantum Chemistry Department, Institute of Chemistry, Academy of Sciences of Moldova, MD-2028, Kishinev, Moldova.