# Symmetry and energy spectrum of high-nuclearity spin clusters

O. Waldmann

*Physikalisches Institut III, Universität Erlangen–Nürnberg, D-91058 Erlangen, Germany*

(Received 9 June 1999)

A general and efficient procedure is presented, which allows us to reduce the computational efforts for the calculation of the energy levels of high-nuclearity spin clusters. The method consists of block factorizing the Hamiltonian matrix using the invariance of the spin Hamiltonian with regard to interchanges of spin sites. It can be applied to any arbitrary spin Hamiltonian. In order to demonstrate the flexibility in handling different spin Hamiltonian terms and symmetry groups, its application to several model clusters is discussed.

## I. INTRODUCTION

In recent years, the magnetic properties of large clusters of interacting magnetic centers have become the focus of an intensive research activity since their dimensions and sizes are intermediate between that of simple paramagnets and that of bulk materials.[1,2] Molecular clusters of metal ions are of particular interest as they exhibit no dispersion of size and shape of the cluster and the number of interacting spin centers[1,3] Moreover, the magnetic intercluster interactions frequently are vanishingly small, so that each cluster constitutes an isolated magnetic domain.[3,4] These so-called high-nuclearity spin clusters (HNSC) were found to be of interest in several fields of research. For example, clusters with high-spin ground states were found to represent superparamagnets.[5–7] In several clusters macroscopic quantum effects like quantum tunneling of the magnetization were observed.[2,3,8–11] A $Mn_{12}$ cluster compound was even found to form a molecular magnetically bistable nanomagnet,[12] with an accordingly large technological impact. HNSC are also found among biological systems, like, e.g., ferritin.[2,10,13,14]

However, a detailed interpretation of the magnetic properties of HNSC is hampered by the difficulties of the calculation of the thermally accessible energy levels. Almost generally, the energy spectrum is described by an effective spin Hamiltonian. Its simplest form including interactions among spin centers, effects of ligand fields, and Zeeman splitting is

$$H = -\sum_{i<j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j + \sum_i \mathbf{S}_i \cdot \mathbf{D}_i \cdot \mathbf{S}_i + \mu_B \sum_i \mathbf{S}_i \cdot \mathbf{g}_i \cdot \mathbf{B}, \quad (1)$$

i.e., $H$ is restricted to bilinear terms and an isotropic coupling. $i$ and $j$ runs over all spin centers, $\mathbf{D}_i$ and $\mathbf{g}_i$ denote Cartesian tensors with $\mathbf{D}_i$ being traceless.

Since the dimension of the Hamiltonian matrix grows enormously with increasing number of spin centers and spin quantum numbers, an exact diagonalization of the Hamiltonian matrix quickly exceeds the capabilities of any computer. It is obvious that then one should take advantage of symmetries in order to block factorize the Hamiltonian matrix and thereby to reduce the dimension of the matrices to be diagonalized. As has been pointed out by Gatteschi and

Pardi,[15] there are two basic symmetries that might be considered, the total spin symmetry and the point group symmetry of the cluster.

*Total spin symmetry*. Total spin symmetry may be applied to the Hamiltonian Eq. (1) if $\mathbf{D}_i = 0$ and $\mathbf{g}_i = \mathbf{g}$ for all $i$. Thus

$$H = -\sum_{i<j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j + \mu_B \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B}, \quad (2)$$

with $\mathbf{S} = \Sigma \mathbf{S}_i$ the total spin. The calculation of the energy levels is conveniently performed in two steps. First, one calculates the spectrum for the exchange term alone, which will be denoted as $H_J$. Since $[\mathbf{S}_i \cdot \mathbf{S}_j, \mathbf{S}] = 0$ for arbitrary $i,j$, $H_J$ commutes with both $\mathbf{S}^2$ and $S_z$. The eigenfunctions may thus be written as $|SM\alpha\rangle$ and the energies as $E_J(S,\alpha)$, which are independent of $M$. $\alpha$ denotes additional quantum numbers necessary for an unambiguous classification of the levels. Using irreducible tensor operator techniques, Gatteschi and Pardi[15] developed a general procedure employing total spin symmetry for the calculation of the spectrum of $H_J$ for any possible values of $J_{ij}$ and arrangement of coupling pathways. It thus represents a very powerful tool for the determination of $E_J(S,\alpha)$ for a great deal of different clusters. Knowing the $E_J(S,\alpha)$, it is a straightforward task to calculate the spectrum of $H$ of Eq. (2) for arbitrary values of magnetic field, and thereby to calculate the magnetization. Taking the quantization axis $\xi$ to be in the direction of $\mathbf{g} \cdot \mathbf{B}$, the Zeeman term of Eq. (2) can be written as $\mu_B g_{eff} S_\xi B$, where $g_{eff}$ depends on the direction of $\mathbf{B}$ with respect to the principal axes of $\mathbf{g}$.[16] For the energies it thus follows

$$E(S,M,\alpha) = E_J(S,\alpha) + \mu_B g_{eff} M B. \quad (3)$$

The magnetic susceptibility is then calculated directly using the well-known formula of Van-Vleck.[17,18] However, it seems to have not been noted before that also the magnetic moment $m(T,B)$ can be expressed in a closed form, which will be given here for convenience:

$$m = \mu_B g_{eff} \frac{\sum_{S,\alpha} e^{-\beta E_J(S,\alpha)} \sinh\left(\frac{2S+1}{2}x\right) S B_S(Sx)}{\sum_{S,\alpha} e^{-\beta E_J(S,\alpha)} \sinh\left(\frac{2S+1}{2}x\right)}, \quad (4)$$

where $x = \beta \mu_B g_{eff} B$, $\beta = 1/(k_B T)$, and $B_S(y)$ denotes the Brillouin function.[18]

*Point group symmetry.* Since the symmetry operations of the point group of the cluster produce interchanges of the spin sites, the point group symmetry is reflected in the spin Hamiltonian by an invariance among permutations of the spin centers. These permutational properties were already noted by Griffith,[19] who actually used them for a classification of the spin states of a trinuclear cluster by the irreducible representations of the rotation group in spin domain and the point group. The general group-theoretical procedure has been given by Tsukerblatt *et al.*[20] In applying this classification scheme, Delfs *et al.*[6] arrived at a computation of the energy spectrum of the octanuclear high-spin Fe(III) cluster complex $[(tacn)_6 Fe_8 O_2 (OH)_{12}]^{8+}$. Thereby they took advantage from the fact, that the eight spin centers of the $Fe_8$ cluster with approximate $D_2$ symmetry can be split into two subsets of four spin centers with again $D_2$ symmetry for each subset. Both spin and point group symmetry had to be used since with spin symmetry alone the dimension of the largest matrix was only reduced from 1 679 616 to 16 576, what is still intractable. Applying both symmetries, the maximal dimension could be reduced to 4,170. The same approach allowed Taft *et al.*[21] to calculate the susceptibility curve for a cyclic ring of eight $S = 5/2$ spin centers.

However, the permutational properties were actually already exploited as early as 1964 by Bonner and Fisher,[22] without denoting them so. They calculated the energy spectra of linear rings of $S = 1/2$ spins with an anisotropic coupling. By classifying the states by $S_z$ and a wave number $k$ related to the translational invariance of the ring, they were able to treat rings with up to 11 spin sites. This technique is discussed in more detail in Carboni and Richards.[23] Along this line, Kouzoudis[24] recently was able to calculate exact analytical expressions for the energy levels and the partition function of the Heisenberg ring of 5, 6, and 7 $S = 1/2$ spin sites. In a very recent work, Bärwinkel *et al.* developed a recursive method for applying both translational invariance and total spin symmetry to Heisenberg rings.[25] This allowed them to obtain analytical expressions also for the $N = 5$, $S = 1$, and $N = 8$, $S = 1/2$ rings.

In contrast to the situation for total spin symmetry no efficient and general procedure has been developed so far in order to deal with point group symmetry. Furthermore, all systems treated till now represent cases where both symmetries, total spin symmetry, and point group symmetry may be exploited, i.e., only isotropic spin Hamiltonians of the form of Eq. (2) were considered.

The denotation of the permutational properties by the term point group symmetry is not entirely satisfying since the point group refers to operations in space, while permutations of the spin centers are meant. Actually, in some sense the permutational properties can be regarded as an artificial symmetry of the spin Hamiltonian, which of course is related to, but not identical with the point group symmetry of the cluster. This will become clearer in the following. Therefore, the notation ''spin permutational symmetry'' is preferred by the author in order to emphasize this distinction.

The aim of this work is to present a general approach for block factorizing the Hamiltonian matrix using spin permutational symmetry, which actually is applicable to any arbi-
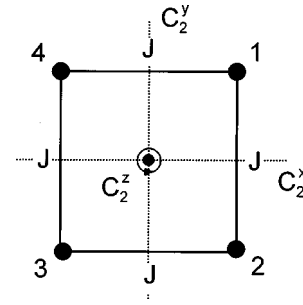


FIG. 1. Coupling graph of the tetranuclear square planar cluster discussed in the text. The symmetry elements of $D_2$ are also depicted.

trary spin Hamiltonian. As will be shown, it leads to a very simple and intuitive, but still effective scheme. The paper is organized as follows. In the next paragraph the required group theoretical techniques are presented. In paragraph III spin permutational symmetry is discussed for a square planar tetranuclear cluster in the weak exchange limit. Then a hexanuclear ring of six $S = 5/2$ spins additionally exhibiting total spin symmetry is considered. These two examples were chosen since they can be solved without resorting to spin permutational symmetry. This allows us to check the validity of the methods by comparing the results of calculations performed with using and without using spin permutational symmetry. Furthermore, these examples are of experimental relevance since the corresponding molecular cluster complexes were synthesized recently. The discussion will partly refer to the experimental results. In the following paragraph various further aspects will be considered. The paper is finished with a conclusion.

## II. BASICS

The general procedure of taking advantage of a symmetry[26] consists of first finding operations $R$, which leave the Hamiltonian invariant. The operations $R$ form the symmetry group of the Hamiltonian. Then with each $R$ one associates an operator $O(R)$, which acts on wave functions denoted by $|n\rangle$. Since $R$ leaves the Hamiltonian invariant, $[H, O] = 0$ and the Hamiltonian matrix can be block factorized using the symmetry adapted basis functions $|\Gamma^{(j)} n\rangle$ instead of $|n\rangle$, where $|\Gamma^{(j)} n\rangle$ transforms according to the irreducible representation $\Gamma^{(j)}$ of the symmetry group. The states $|\Gamma^{(j)} n\rangle$ can be constructed using the basis function generating machine[26]

$$|\Gamma_\lambda^{(j)} n\rangle = \frac{l_j}{h} \sum_R \Gamma^{(j)}(R)_{\lambda\lambda}^* O(R)|n\rangle, \qquad (5)$$

where $h$ is the order of the symmetry group and $l_j$ the dimension of $\Gamma^{(j)}$.

In the case of the spin permutational symmetry the operations $R$ refer to those permutations of spin centers, which leave the spin Hamiltonian invariant. It is useful to draw the coupling pathways among the spin centers as a graph like that in Fig. 1 for a square planar tetranuclear cluster, since it reflects the possible invariant permutations. Such a graph will be denoted as the coupling graph. E.g., the permutation

R(3412) representing the renumbering $1\rightarrow3,2\rightarrow4,3\rightarrow1,4\rightarrow2$ of the spin centers can be regarded as a 180° rotation of the coupling graph of Fig. 1.

As basis functions $|n\rangle$, one may choose the product wave functions $|S_1M_1\rangle|S_2M_2\rangle|S_3M_3\rangle\cdots|S_NM_N\rangle$, with $N$ the number of spin centers. These wave functions will be abbreviated by $|M_1M_2M_3\cdots M_N\rangle$ or even shorter by $|\{M_i\}\rangle$. Another possibility are the spin wave functions $|SM\beta\rangle$, where $\beta$ denotes the intermediate spin quantum numbers arising from the chosen coupling scheme. For instance, $\beta = S_1S_2S_{12}S_3S_4S_{34}$ for the scheme $\mathbf{S}_{12}=\mathbf{S}_1+\mathbf{S}_2$, $\mathbf{S}_{34}=\mathbf{S}_3 +\mathbf{S}_4$, and $\mathbf{S}=\mathbf{S}_{12}+\mathbf{S}_{34}$. Whether the functions $|\{M_i\}\rangle$ or the $|SM\beta\rangle$ are most appropriate depends on the particular cluster complex under consideration. This point will be clarified in the following.

As final problem, one has to calculate the effects of the operators $O(R)$ on the basis functions, i.e., of $O(R)|\{M_i\}\rangle$ or $O(R)|SM\beta\rangle$, respectively. This will be done in the next two paragraphs.

## III. SPIN CLUSTERS IN THE WEAK EXCHANGE LIMIT

As first example a square planar tetranuclear cluster is considered, the spin Hamiltonian of which is at first assumed to be of the form

$$H=-J(\mathbf{S}_1\cdot\mathbf{S}_2+\mathbf{S}_2\cdot\mathbf{S}_3+\mathbf{S}_3\cdot\mathbf{S}_4+\mathbf{S}_4\cdot\mathbf{S}_1)+\sum_{i=1}^{4} H_i^{center}. \tag{6}$$

$H_i^{center}$ denotes the spin Hamiltonian for the $i$th spin center and consists of the Zeeman term and eventually of terms describing the zero-field-splitting (ZFS) due to ligand field interactions, etc.

As basis functions the product wave functions $|M_1M_2M_3M_4\rangle$ are chosen. The only molecular cluster complexes forming strict square planar systems, the Me-[2×2] grid molecules with Me denoting a twofold positively charged metal ion, exhibit exchange splittings much weaker than the ZFS.[4,27,28] In this so-called weak exchange limit the product wave functions are most appropriate.

The effect of the operator $O(R)$ is actually determined easily since it leads to nothing else than a permutation of the quantum numbers. E.g., the operator $O(3412)$ associated with the group element $R(3412)$ results in $O(3412)|M_1M_2M_3M_4\rangle=|M_3M_4M_1M_2\rangle$.

Now one is left with the specification of the symmetry group, and in general several groups are possible. If the square planar cluster is considered as a linear chain with periodic boundaries, then the appropriate symmetry group is the translation group similar to the situation in crystals. However, several of the irreducible representations are complex. Numerically this is unfavorable since it requires the implementation of a complex arithmetic. Therefore this group will not be considered here. The full symmetry group of a square is $D_4$. Nevertheless, for simplicity we will consider a subgroup of $D_4$, i.e., $D_2$. The symmetry elements are depicted in Fig. 1. Table I gives the operators $O(R)$ associated with each group element $R$.

TABLE I. Operators $O(R)$ associated with the group elements of $D_2$ for the square planar tetranuclear cluster and the cyclic hexanuclear cluster.

| Cluster | $E$ | $C_2^z$ | $C_2^y$ | $C_2^x$ |
|---|---|---|---|---|
| Tetran. | $O(1234)$ | $O(3412)$ | $O(4321)$ | $O(2143)$ |
| Hexan. | $O(123456)$ | $O(456123)$ | $O(321654)$ | $O(654321)$ |

In the case of the Co-[2×2] grid molecules the spin of each center is $S=3/2$.[28] The Hamiltonian matrix is thus of dimension 256. The reduction of the reducible representation $\Gamma(H)$ yields

$$\Gamma(H)=76\cdot A_1\oplus60\cdot A_2\oplus60\cdot B_1\oplus60\cdot B_2 \tag{7}$$

and the basis functions $|\Gamma^{(j)}\{M_i\}\rangle$ are easily constructed with Table I and Eq. (5). E.g., for $\Gamma^{(j)}=A_2$ one obtains

$$|A_2\{M_i\}\rangle=\frac{1}{4}[1\cdot O(1234)+1\cdot O(3412)-1\cdot O(4321)$$
$$-1\cdot O(2143)]|\{M_i\}\rangle. \tag{8}$$

So far, it has been assumed implicitly that in Eq. (6) a ZFS term is absent and that all the tensors $\mathbf{g}_i$ are isotropic and identical to each other. However, the presented method is not limited to this case. One may include ZFS, anisotropic $\mathbf{g}_i$ tensors, anisotropic, or biquadratic exchange terms, and so on. One only needs to figure out which permutations leave the Hamiltonian invariant. The occurrence of these terms can be depicted in the coupling graph such that it still reflects the symmetry of the spin Hamiltonian with respect to permutations. E.g., different isotropic $g$ factors may be indicated by different sizes of the points in Fig. 1.

Here the difference between the actual point group symmetry of the cluster and the spin permutational symmetry becomes obvious. The notation of the above group with $D_2$ is somewhat arbitrary, since one can regard $O(2143)$ as a rotation as well as a reflection. In the latter case one would have denoted the spin permutational group as $C_{2v}$. Furthermore, it is easy to find examples where the point group symmetry has higher/lower symmetry than the spin permutational symmetry. For example, the point group of the Me-[2×2] grid molecules is close to $D_2$, whereas the coupling graph exhibits $D_4$ symmetry.

The above procedure has been used extensively to interpret the magnetization data of the Co-[2×2] and Ni-[2×2] grid molecules.[4,29] In particular, isotropic, uniaxial anisotropic, and biquadratic exchange, uniaxial ZFS, and $g$-factor anisotropy were considered demonstrating the flexibility of the method. The Hamiltonian matrix of Co-[2×2] has a dimension of only 256 and is diagonalized very rapidly, but a fitting of powder magnetization curves requires quite a lot (about 100 000) of diagonalizations and is thus rather time consuming. Assuming that the computation time increases cubically with the dimension of the matrices, one expects a reduction of the computation time by a factor of 15. In practice we observed a factor of about 20, i.e., the computation time was reduced from 6 hours to 20 min on a fast workstation. The full $D_4$ symmetry led to a further reduction of the computation time by a factor of about 2.
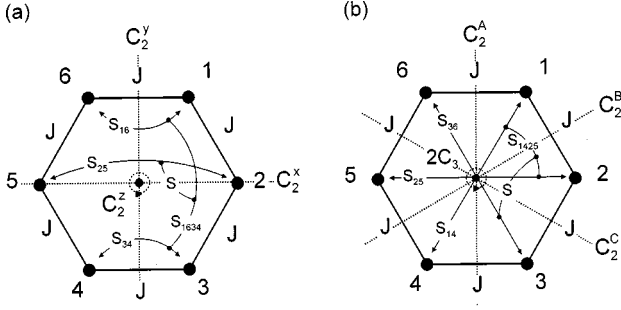
(a)

(b)



FIG. 2. Coupling graph of the hexanuclear ring discussed in the text for (a) $D_2$ and (b) $D_3$ symmetry. The symmetry elements are depicted by dotted lines, the coupling scheme by the thin lines.

## IV. SPIN CLUSTERS IN THE STRONG EXCHANGE LIMIT

### A. Hexanuclear cluster with isotropic coupling

As next example, a regular ring of six identical spin centers will be considered. The new aspect of the following treatment is that both total spin symmetry and permutational symmetry will be applied. Therefore, the correct basis functions are spin wave functions where total spin symmetry is already exploited. The spin Hamiltonian is

$$H = -J\left(\sum_{i=1}^{5} \mathbf{S}_i \cdot \mathbf{S}_{i+1} + \mathbf{S}_6 \cdot \mathbf{S}_1\right) + \mu_B g \mathbf{S} \cdot \mathbf{B}, \quad (9)$$

a special case of Eq. (2). Due to reasons which will become clear below, first $D_2$ will be used as symmetry group. The coupling graph is depicted in Fig. 2(a). The operators $O(R)$ associated with the group elements are given in Table I.

Since $\mathbf{S}$ commutes with $O(R)$ the states of $H$ can be classified simultaneously by the irreducible representations of the spin rotation group, i.e., by $S$ and $M$, and those of the spin permutational symmetry group, $\Gamma^{(j)}$. These states are denoted by $|\Gamma^{(j)}SM\alpha\rangle$, where $\alpha$ again represents additional quantum numbers. Starting from the spin wave functions $|SM\beta\rangle$ as basis functions with $\beta$ denoting the intermediate spin quantum numbers arising from the chosen coupling scheme, one has to construct a set of basis functions $|\Gamma^{(j)}SM\beta\rangle$, analogously to Eq. (8). As coupling scheme, the special choice $\mathbf{S}_{16} = \mathbf{S}_1 + \mathbf{S}_6$, $\mathbf{S}_{34} = \mathbf{S}_3 + \mathbf{S}_4$, $\mathbf{S}_{1634} = \mathbf{S}_{16} + \mathbf{S}_{34}$, $\mathbf{S}_{25} = \mathbf{S}_2 + \mathbf{S}_5$, and $\mathbf{S} = \mathbf{S}_{1634} + \mathbf{S}_{25}$ is made, so that $\beta = S_1 S_6 S_{16} S_3 S_4 S_{34} S_{1634} S_2 S_5 S_{25}$. The coupling scheme is depicted graphically in Fig. 2(a).

The effect of the operators $O(R)$ on the states $|SM\beta\rangle$ is calculated exemplarily for the operator $O(456123)$. The state $|SM\beta\rangle$ is first decomposed into the product wave functions $|S_1 M_1 S_2 M_2 \ldots S_6 M_6\rangle$ according to the coupling scheme:

$$|SMS_1 S_6 S_{16} S_3 S_4 S_{34} S_{1634} S_2 S_5 S_{25}\rangle$$

$$= \sum_{\Sigma M_i = M} \langle 1,6,16\rangle\langle 3,4,34\rangle\langle 16,34,1634\rangle\langle 2,5,25\rangle$$

$$\times \langle 1634,25,S\rangle |S_1 M_1 S_2 M_2 S_3 M_3 S_4 M_4 S_5 M_5 S_6 M_6\rangle, \quad (10)$$

where the shorthand notation $\langle i,j,k\rangle = \langle S_i M_i S_j M_j | S_i S_j S_k M_k\rangle$ for the Clebsch-Gordon coeffi-

cients is introduced. Application of the operator $O(456123)$ to Eq. (10) and a subsequent change of indices in the sum according to $4\rightarrow1$, $5\rightarrow2$, $6\rightarrow3$, etc., (i.e., according to $R^{-1}$) yields

$$O(456123)|SMS_1 S_6 S_{16} S_3 S_4 S_{34} S_{1634} S_2 S_5 S_{25}\rangle$$

$$= \sum_{\Sigma M_i = M} \langle 4,3,34\rangle\langle 6,1,16\rangle\langle 34,16,1634\rangle\langle 5,2,25\rangle$$

$$\times \langle 1634,25,S\rangle |S_1 M_1 S_2 M_2 S_3 M_3 S_4 M_4 S_5 M_5 S_6 M_6\rangle. \quad (11)$$

Equation (11) can be brought back into the form of Eq. (10) by using the property $\langle j,i,k\rangle = (-1)^{S_i + S_j - S_k}\langle i,j,k\rangle$ of the Clebsch-Gordon coefficients with the final result

$$O(456123)|SMS_1 S_6 S_{16} S_3 S_4 S_{34} S_{1634} S_2 S_5 S_{25}\rangle$$

$$= (-1)^{S_3 + S_4 - S_{34} + S_1 + S_6 - S_{16} + S_{16} + S_{34} - S_{1634} + S_2 + S_5 - S_{25}}$$

$$\times |SMS_4 S_3 S_{34} S_6 S_1 S_{16} S_{1634} S_5 S_2 S_{25}\rangle. \quad (12)$$

Since the effect of the operators $O(R)$ is known now, the new basis functions $|\Gamma^{(j)}SM\beta\rangle$ can be set up with Eq. (5) and Table I.

The simple result that each state $O(R)|SM\beta\rangle$ is expressed by only one basis function $|SM\beta'\rangle$ is the consequence of the particular choice of the symmetry group and the coupling scheme. In some sense, the symmetry group and the coupling scheme are compatible. I.e., if one applies for example the permutation $R(213)$ to the coupling scheme $\mathbf{S}_{12} = \mathbf{S}_1 + \mathbf{S}_2$, $\mathbf{S} = \mathbf{S}_{12} + \mathbf{S}_3$ one obtains $\mathbf{S}_{12} = \mathbf{S}_2 + \mathbf{S}_1$, $\mathbf{S} = \mathbf{S}_{12} + \mathbf{S}_3$ being identical to the former coupling scheme. One may thus say that the group elements leave the coupling scheme invariant. This is also reflected by the symmetry of the coupling graph extended by the graphical representation of the coupling scheme, see Fig. 2(a).

If one wants to take advantage of the full symmetry group of a regular hexagon, i.e., of $D_6$, a further aspect needs to be considered since the operators $O(R)$ do not longer leave the coupling scheme invariant. This will be discussed in the following for $D_3$. The extension of the results to $D_6$ is straightforward.

The coupling scheme $\mathbf{S}_{14} = \mathbf{S}_1 + \mathbf{S}_4$, $\mathbf{S}_{25} = \mathbf{S}_2 + \mathbf{S}_5$, $\mathbf{S}_{36} = \mathbf{S}_3 + \mathbf{S}_6$, $\mathbf{S}_{1425} = \mathbf{S}_{14} + \mathbf{S}_{25}$, and $\mathbf{S} = \mathbf{S}_{1425} + \mathbf{S}_{36}$ is chosen, with $\beta = S_1 S_4 S_{14} S_2 S_5 S_{25} S_{1425} S_3 S_6 S_{36}$. The coupling graph including the coupling scheme is depicted in Fig. 2(b). The fact that the operators $O(R)$ do not leave the coupling scheme invariant can be inferred from Fig. 2(b), taking into account that the coupling scheme must not be "rotated." However, in order to infer the coupling scheme of the state $O(R)|SM\beta\rangle$ from the coupling graph, one has to apply the permutation $R^{-1}$ on the coupling graph since such a change of indices was necessary to obtain Eq. (11). E.g., for $O(345612)$, a counter clockwise 180°-rotation of the hexagon, the resulting state is coupled according to $\mathbf{S}_{2536} = \mathbf{S}_{25} + \mathbf{S}_{36}$, and $\mathbf{S} = \mathbf{S}_{2536} + \mathbf{S}_{14}$. The resulting state can then be reexpressed by the basis functions $|SM\beta\rangle$ using Wigner-6j symbols.[15] Going through the calculation similarly to Eq. (10)–(12), one obtains

TABLE II. Parts of the classification scheme for the hexanuclear cluster with $S=5/2$ for all spin centers in the $D_2$ and the $D_3$ group.

| | $D_2$ | | | | $D_3$ | | | |
|---|---|---|---|---|---|---|---|---|
| $S$ | $A_1$ | $A_2$ | $B_1$ | $B_2$ | $A_1$ | $A_2$ | $E$ | Tot. deg. |
| 0 | 15 | 27 | 27 | 42 | 22 | 19 | 35 | 111 |
| 1 | 93 | 78 | 78 | 66 | 54 | 51 | 105 | 315 |
| 2 | 108 | 117 | 117 | 133 | 81 | 74 | 160 | 475 |
| 3 | 158 | 142 | 142 | 133 | 101 | 94 | 190 | 575 |
| 4 | 144 | 150 | 150 | 165 | 106 | 97 | 203 | 609 |
| 5 | 158 | 143 | 143 | 137 | 100 | 91 | 195 | 581 |
| 6 | 121 | 124 | 124 | 136 | 90 | 81 | 167 | 505 |
| ⋮ | | | | | | | | |
| 15 | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 1 |

$$O(345612)|SMS_1S_4S_{14}S_2S_5S_{25}S_{1425}S_3S_6S_{36}\rangle$$

$$=(-1)^{S_1+S_4-S_{14}+S_2+S_5-S_{25}}\sum_{S'_{1425}}\sqrt{2S_{1425}+1}$$

$$\times\sqrt{2S'_{1425}+1}\begin{Bmatrix}S_{25} & S_{14} & S_{1425}\\ S_{36} & S & S'_{1425}\end{Bmatrix}$$

$$\times(-1)^{S_{25}+S_{14}+S_{36}+S+S_{36}+S_{2536}-S}$$

$$\times|SMS_3S_6S_{36}S_4S_1S_{14}S'_{1425}S_5S_2S_{25}\rangle, \qquad (13)$$

with similar results for the other operators. The classification scheme for a regular ring of six $S=5/2$ spin centers is given in Table II for $D_2$ and $D_3$.

The above discussion shows that in general the result of the application of an operator $O(R)$ to the state $|SM\beta\rangle$ can be expressed by one single spin wave function, which, however, is coupled according to a different coupling scheme than $|SM\beta\rangle$ if the operator $O(R)$ does not leave the coupling scheme invariant. In that case, the resulting spin wave function can be expanded into spin functions $|SM\beta'\rangle$ using the Wigner-6j symbols. Obviously, this approach allows us to deal with the spin permutational symmetry of any isotropic spin Hamiltonian.

### B. Strong exchange limit

For an interpretation of the experimental results of real molecular cluster complexes a ZFS term due to ligand-field or dipole-dipole interactions has to be retained in the spin Hamiltonian for most cases, i.e., one has to resort to the spin Hamiltonian of Eq. (1). However, there exist a great deal of cluster complexes for which total spin symmetry is almost fulfilled. Then, in the so-called strong exchange limit, the isotropic spin Hamiltonian of Eq. (2) is a reasonable first approximation and the energy splittings due to the ZFS term (and the Zeeman term) can be calculated by first-order perturbation theory.

In particular, this is actually the situation encountered in the molecular $Fe_6$ ferric wheels consisting of six Fe(III) ions forming a regular hexagon. Their low-lying energy spectrum and magnetic anisotropy was investigated recently in detail and could be successfully interpreted by the spin Hamiltonian of Eq. (1) in the strong exchange limit.[30–32] The interpretation required an evaluation of the matrix elements $\langle SM\alpha|T_k^q|S'M'\alpha'\rangle$, where $|SM\alpha\rangle$ denotes the zero-order wave functions and $T_k^q$ the $k$th component of an irreducible tensor operator of rank $q$. The calculation of the matrix elements was found to be rather involved, but just tractable for the $Fe_6$ ferric wheels.[32]

However, since the ZFS term is left invariant by the permutations $R$, spin permutational symmetry here also allows us to reduce the computational efforts. For the $Fe_6$ ferric wheels the $S=1$ zero-order state $|1M\alpha\rangle$, e.g., is a linear combination of 315 spin wave functions $|1M\beta\rangle$ (see Table II). Thus a total of $315\times315=99225$ terms need to be calculated in order to evaluate the matrix element $\langle 1M\alpha|T_k^q|1M'\alpha\rangle$. The number of terms can be reduced significantly by using spin permutational symmetry. For instance, by applying $D_2$ symmetry only a total of $93^2+78^2+78^2+66^2=25173$ terms arise (see Table I), corresponding to a reduction by a factor of 4. Since spin permutational symmetry additionally reduces the time for the computation of the zero-order basis functions, a significant overall time saving is achieved.

### V. ADDITIONAL ASPECTS

Now all information has been provided, which is required to deal with the spin permutational symmetry of any arbitrary spin Hamiltonian. However, in this paragraph some additional aspects will be elaborated.

Let us consider a regular ring of eight $S=3/2$ spin centers with isotropic coupling. The appropriate spin Hamiltonian needs not to be written down explicitly because it is similar to Eq. (9). In Table III parts of the classification schemes

TABLE III. Parts of the classification scheme for the octanuclear cluster with $S=3/2$ for all spin centers in the $D_1$, $D_2$, $D_4$, and $D_8$ group.

| | $D_1$ | $D_2$ | | | | $D_4$ | | | | | $D_8$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $S$ | $A$ | $A_1$ | $A_2$ | $B_1$ | $B_2$ | $A_1$ | $A_2$ | $B_1$ | $B_2$ | $E$ | $A_1$ | $A_2$ | $B_1$ | $B_2$ | $E_1$ | $E_2$ | $E_3$ |
| 0 | 364 | 124 | 80 | 80 | 80 | 74 | 30 | 50 | 50 | 80 | 37 | 15 | 15 | 37 | 50 | 40 | 40 |
| 1 | 1,000 | 220 | 260 | 260 | 260 | 100 | 140 | 120 | 120 | 260 | 52 | 68 | 72 | 48 | 120 | 130 | 130 |
| 2 | 1,400 | 380 | 340 | 340 | 340 | 200 | 160 | 180 | 180 | 340 | 102 | 78 | 82 | 98 | 180 | 170 | 170 |
| 3 | 1,505 | 353 | 384 | 384 | 384 | 168 | 199 | 185 | 185 | 384 | 87 | 96 | 103 | 81 | 185 | 192 | 192 |
| 4 | 1,351 | 361 | 330 | 330 | 330 | 189 | 158 | 172 | 172 | 330 | 98 | 76 | 82 | 91 | 172 | 165 | 165 |
| 5 | 1,044 | 246 | 266 | 266 | 266 | 118 | 138 | 128 | 128 | 266 | 62 | 66 | 72 | 56 | 128 | 133 | 133 |
| ⋮ | | | | | | | | | | | | | | | | | |

TABLE IV. Typical computation times required for an octanuclear ring with $S=3/2$ for all spin centers. The calculations were performed on a 233 MHz Pentium II PC. The times for setting up the matrices, for the calculation of the energy values, and for the complete run are given. The values in the brackets refer to calculations where both energy values and eigenvectors were computed.

| Symmetry group | Matrices | Energies (energ.&eigenvec.) | Total |
|---|---|---|---|
| $D_1$ | 402 s | 558 s (61439 s) | 963 s (63690 s) |
| $D_2$ | 385 s | 27 s (2701 s) | 416 s (3254 s) |
| $D_4$ | 502 s | 11 s (969 s) | 523 s (1549 s) |
| $D_8$ | 499 s | 7 s (249 s) | 526 s (795 s) |

applying $D_1$, $D_2$, $D_4$, and $D_8$ are shown. Table IV presents the computation times typically required on a fast PC for the calculation of the representation matrices and the energy values. It is seen that the time for the energy values is reduced drastically, as expected, while the time consumption for setting up the representation matrices remains almost constant. For the higher symmetries than $D_1$ almost all of the computation time is actually wasted for setting up the representation matrices and not for the calculation of the energy values. Therefore, the great advantage of applying spin permutational symmetry to the calculation of the spectra of isotropic spin Hamiltonians lies in a saving of memory and less in a reduction of computation time.

The considerable time required for setting up the matrices is due to the fact that for the calculation of the matrix elements $\langle \Gamma SM\beta | H | \Gamma SM\beta' \rangle$ the wave functions $|\Gamma SM\beta\rangle$ have to be expanded into spin functions $|SM\beta\rangle$ [see Eq. (5)] and that for the calculation of $\langle SM\beta | H | SM\beta' \rangle$ many Wigner-6j symbols need to be evaluated. Actually, the times presented in Table IV were only achieved after having implemented the following idea. Using the rearrangement theorem, the great orthogonality relation, and the unitarity of the irreducible representations,[26] one can simplify the calculation of the matrix elements $\langle \Gamma_\lambda^{(j)} n | H | \Gamma_\lambda^{(j)} n' \rangle$ to

$$\langle \Gamma_\lambda^{(j)} n | H | \Gamma_\lambda^{(j)} n' \rangle = \left(\frac{l_j}{h}\right)^2 \sum_{R,R'} \Gamma_{\lambda\lambda}^{(j)}(R)\Gamma_{\lambda\lambda}^{(j)}(R')$$

$$\times \langle n | O(R) H O(R') | n' \rangle$$

$$= \frac{l_j}{h} \sum_R \Gamma_{\lambda\lambda}^{(j)}(R) \langle n | H O(R) | n' \rangle. \quad (14)$$

Here $n$ abbreviates additional quantum numbers. Equation (14) demonstrates that the double sum can be reduced to a single sum over all group elements with a corresponding drastic reduction of computation time.

However, in order to calculate, e.g., the ZFS in the strong exchange limit or the inelastic neutron-scattering cross-section one needs not only the energy values, but also the eigenvectors. Typical times for the calculation of both the energy values and the eigenvectors are given in brackets in Table IV. Since the calculation of the eigenvectors requires much more time than the energy values, the computation time for setting up the representation matrices is of minor

importance. Actually, Table IV demonstrates that here spin permutational symmetry is quite effective in saving computation time.

Contrary to the situation for the spin wave functions, the calculation of the matrix elements of $H$ using the product wave functions $|\{M_i\}\rangle$ costs very little time compared to the diagonalization. Thus, for dealing with clusters where total spin symmetry cannot be applied, e.g., for systems in the weak exchange limit, it is more convenient to use the $|\{M_i\}\rangle$ as has been done in paragraph III for the tetranuclear cluster.

The above discussion shows that in the cases where the time for setting up the matrices is only a fraction of the overall computation time, spin permutational symmetry provides its full power. It leads not only to a saving of memory but also to an efficient reduction of computation time.

So far, situations were encountered where the isotropic spin Hamiltonian Eq. (2) was not diagonal in the intermediate spin quantum numbers being abbreviated by $\beta$. However, in cases where the spin Hamiltonian commutes with all intermediate spin quantum numbers the calculation of the energy values is quite easy since then Kambe's vector coupling method can be applied.[33] But even if $H$ does not commute with all intermediate spin quantum numbers, one can take advantage of this further symmetry. If the same octanuclear ring as above is considered with an additional spin center situated at the center of the octagon, the exchange term of the spin Hamiltonian is of the form

$$H_J = -J\left(\sum_{i=1}^{7} \mathbf{S}_i \cdot \mathbf{S}_{i+1} + \mathbf{S}_8 \cdot \mathbf{S}_1\right) - J' \mathbf{S}_9 \cdot \left(\sum_{i=1}^{8} \mathbf{S}_i\right). \quad (15)$$

It is obvious that $H_J$ and thereby $H$ commutes with both $\mathbf{S}_9$ and $\mathbf{S}_{1-8} = \Sigma_{i=1}^{8} \mathbf{S}_i$. Thus $H_J$ can be written as

$$H_J = -J\left(\sum_{i=1}^{7} \mathbf{S}_i \cdot \mathbf{S}_{i+1} + \mathbf{S}_8 \cdot \mathbf{S}_1\right) - \frac{J'}{2}(\mathbf{S}^2 - \mathbf{S}_9^2 - \mathbf{S}_{1-8}^2), \quad (16)$$

and the energy levels can be calculated from the energy values $E_8(S_{1-8},\alpha)$ of the octanuclear ring according to

$$E(S,S_9,S_{1-8},\alpha) = E_8(S_{1-8},\alpha) - \frac{J'}{2}[S(S+1) - S_9(S_9+1)$$

$$- S_{1-8}(S_{1-8}+1)]. \quad (17)$$

For the calculation of the $E_8(S_{1-8},\alpha)$ spin permutational symmetry can of course be exploited as above.

Finally, the efficiency of spin permutational symmetry in block factorizing the Hamiltonian matrix shall be estimated. It is obvious that the sum over the dimensions of all blocks gives the total number $N$ of states, whereby taking into account that a block corresponding to a $l_j$-dimensional representation $\Gamma^{(j)}$ has to be counted $l_j$-times. I.e., $N=\Sigma_j l_j X_j$, where $X_j$ is the dimension of the block corresponding to $\Gamma^{(j)}$. An inspection of Eq. (7) and Tables II and III suggests that the dimension of the blocks can be roughly approximated by $X_j = l_j X$, i.e., the dimension of the blocks corresponding to a one-dimensional representation is roughly $X$, that for a two-dimensional representation is roughly $2X$, and so on. Since $\Sigma_j l_j^2 = h$, $X$ can be calculated as

$$X = \frac{N}{h}. \tag{18}$$

Equation (18) provides a simple estimation of the block dimensions with an accuracy of about 50%.

## VI. CONCLUSION

In summary, a general and efficient procedure has been presented that allows us to block factorize the matrix representation of any spin Hamiltonian based on its invariance with respect to permutations of the spin sites. This symmetry, named spin permutational symmetry, is related to the point group symmetry of the cluster since it arises going from the real electrostatic Hamiltonian to the effective spin Hamiltonian, but has been demonstrated to be of different physical significance. The flexibility of the method in handling various different spin Hamiltonian terms and permutational symmetries was demonstrated for several cluster models. So was it possible to take advantage of the full symmetry of an octanuclear ring cluster, i.e., of $D_8$. It has been shown that the method actually can be applied to any arbitrary spin Hamiltonian. It is believed that the presented techniques will be useful for the interpretation of the physical properties of a great variety of different high-nuclearity spin clusters.

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