Néel probability and spin correlations in some nonmagnetic and nondegenerate states of hexanuclear antiferromagnetic ring Fe₆:
Application of algebraic combinatorics to finite Heisenberg spin systems

Wojciech Florek and Sylwia Bucikiewicz
A. Mickiewicz University, Institute of Physics, ul. Umultowska 85, 61–614 Poznań, Poland
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The spin correlations $\omega^r$, $r = 1, 2, 3$, and the probability $p_N$ of finding a system in the Néel state for the antiferromagnetic ring Fe₆[III] (the so-called ‘small ferric wheel’) are calculated. States with magnetization $M = 0$, total spin $0 \leq S \leq 15$ and labeled by two (out of four) one-dimensional irreducible representations (irreps) of the point symmetry group $D_8$ are taken into account. This choice follows from importance of these irreps in analyzing low-lying states in each $S$-multiplet. Taking into account the Clebsch–Gordan coefficients for coupling total spins of sublattices ($S_A = S_B = S = 15/2$) the global Néel probability $p_N$ can be determined. Dependencies of these quantities on state energy (per bond and in the units of exchange integral $J$) and the total spin $S$ are analyzed. Providing we have determined $p_S(S)$ etc. for other antiferromagnetic rings (Fe₁₀, for instance) we could try to approximate results for the largest synthesized ferric wheel Fe₁₆. Since thermodynamic properties of Fe₆ have been investigated recently, in the present considerations they are not discussed, but only used to verify obtained values of eigenenergies. Numerical results are calculated with high precision using two main tools: (i) thorough analysis of symmetry properties including methods of algebraic combinatorics and (ii) multiple precision arithmetic library GMP. The system considered yields more than 45 thousands basic states (the so-called Ising configurations), but application of the method proposed reduces this problem to 20-dimensional eigenproblem for the ground state ($S = 0$). The largest eigenproblem has to be solved for $S = 4$; its dimension is 60. These two facts (high precision and small resultant eigenproblems) confirm efficiency and usefulness of such an approach, so it is briefly discussed here.

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I. INTRODUCTION

Magnetic hysteresis with a pure molecular origin first time was observed in the mixed-valence Mn complex $\text{[Mn}_{12}\text{O}_{12}\text{(CH}_3\text{COO})_{16}\text{(H}_2\text{O})_4]\text{2CH}_3\text{COOH\cdot4H}_2\text{O}$ (commonly referred to as Mn$_{12}$acetate), synthesized and investigated by Lis in 1980. Due to this discovery mesoscopic magnetic systems, comprising transition-metal ions, have attracted a great deal of attention. Many large molecular aggregates have been fabricated and investigated both experimentally and theoretically (including numerical simulations). This includes Mn molecules like Mn$_{12}$, a ferromagnetic copper ring, mixed Mn-Cr compounds like [Cr$_{11}$$(\text{CNMn}_{11}\text{L})_6](\text{ClO})_4$ and some nickel complexes [1] and many polynuclear iron clusters known as Fe$_n$ with $n$ varying from two through 20 [2]. Some interesting features have been also observed in a single crystal made of nanometric molecules (so-called V$_{15}$) and in a single cobalt nanocluster [3].

Such systems of mesoscopic dimensions containing transition-metal ions and oxygen are attracting increasing interest for several reasons, including the possibility of observing quantum phenomena on a macroscopic scale. It may lead to better understanding of the mechanism associated with the transition from simple paramagnetic to bulk magnetism (also low-dimensional in magnetic chains). On the other hand, clusters comprising transition elements exist in several metalloenzymes and metalloproteins as ferritin storing Fe in mammals. Moreover, nanostructures are part of the development of high density magnetic recording media and quantum computing.

Molecular magnets show both antiferro- and ferromagnetic behavior, though in many cases single spins are coupled antiferromagnetically. Incomplete compensation of this coupling may lead to the large spin ground state of a cluster, e.g. $S = 10$ in Fe$_8$ and Mn$_{12}$, what is related to a strong easy-axis term (Ising-type anisotropy). There are also purely ferromagnetic molecules as dodecanuclear nickel complex (Ni$_{12}$) with the ground state characterized by $S = 12$ [4]. The other class of nanomagnets comprises molecules where the cancellation is complete and the ground state has $S = 0$. The most profound example is provided by a series of antiferromagnetic Fe(III) rings Fe$_6$, Fe$_{10}$, Fe$_{12}$, and Fe$_{18}$. Recently a new octanuclear cluster Fe$_8$ has been synthesized and investigated [5]. A deviation from coplanarity in the case of Fe$_{10}$ ring, about 9.8 Å in diameter, is less than 0.01 Å so these rings can be considered as two-dimensional structures of very high symmetry: at least idealized or approximate point-group symmetry isomorphic to the dihedral group $D_n$ ($S_4$ or $D_{5d}$, for example).

Due to the presence of organic ligands wrapping the clusters, the inter-cluster interactions are vanishingly small (or can be reduced) by dissolving the clusters in the appropriate solvent [6]. Each magnetic object has perfectly defined size and new techniques of molecular chemistry provide ensembles of iso-oriented nanomagnets.


Properties of such systems can be very well simulated using contemporary computers within the framework of finite spin models. However, direct calculations of eigenenergies and eigenstates, even using the Lanczos exact diagonalization technique, are subjected to the so-called “combinatorial explosion”. For example, in the case of the largest “ferric wheel” Fe$_{18}$ one has to deal with more than 10$^{14}$ basic states. This is especially important in the case of antiferromagnetic systems when the ground state lies in the subspace of states with the total magnetization $M = 0$ and determination of some low-lying states only is a formidable task. This can be done a bit more manageable exploiting symmetry properties of a given Hamiltonian $\mathcal{H}$ (including the time-reversal symmetry) and good quantum numbers, i.e., eigenvalues of operators commuting with $\mathcal{H}$. In the latter case we consider the total magnetization $M$ (the eigenvalue of $S^z = \sum_{j=1}^{n} s_j^z$) and the total spin $S$ (the eigenvalues of the squared total spin $S^2 = (\sum_{j=1}^{n} s_j^z)^2$) are $S(S+1)$, of course. While model Hamiltonians commute with $S^z$ as a rule, the additional anisotropy terms break commutation with $S^2$. However, if the isotropic Heisenberg interactions

$$\mathcal{H}_H = J \sum_{\langle j,k \rangle} s_j \cdot s_k$$  \hspace{1cm} (1)$$

(the sum is taken over the nearest-neighbor pairs) are dominant, then the effect of magnetic anisotropy and Zeeman interaction can be considered separately for each $S$-multiplet. Therefore, in this article we restrict ourselves to Hamiltonians commuting with $S^2$. It should be stressed that this includes interactions with different ranges (e.g., next-nearest-neighbors) and forms (e.g., bi-quadratic terms $(s_j \cdot s_k)^2$).

As regards symmetry properties, the simplest task is to take into account the time-reversal symmetry. It is enough to consider states with $M \geq 0$ since the others (with $M < 0$) are determined in a straightforward way. The largest eigenproblem dimension is reached considering the subspace $L_0$ comprising states with $M = 0$ (the are more than 5.5 · 10$^{12}$ such basic states for $s = \frac{5}{2}$ and $n = 18$). The point-group symmetry $G$ enters the problem considered via the Schur Lemma: eigenspaces of operators commuting with all representation operators $P(g)$, $g \in G$, are labeled by the irreducible representations (irreps) of $G$. However, numbers $n(\Gamma)$ in the decomposition

$$P = \bigoplus_{\Gamma} n(\Gamma) \Gamma$$  \hspace{1cm} (2)$$

are very large, even if $P$ is restricted to $L_0$. Let $L^r_\Gamma$, $1 \leq r \leq n(\Gamma)$, be copies of the eigenspace of an irrep $\Gamma$ spanned over vectors $\{(\gamma) \mid 1 \leq \gamma \leq \dim L^r_\Gamma\}$. Solving an eigenproblem for any operator of symmetry $G$ we have to construct an $n(\Gamma) \times n(\Gamma)$ matrix for an arbitrarily chosen, but fixed, vector index $\gamma$. To do it in an efficient way, the single, meaningless, repetition index $r$ has to be replaced by a series of indices with well-determined mathematical notion. In the case considered the representation $P$ is in fact a permutation representation, so the methods of algebraic combinatorics give an efficient way to deal with this problem. Such approach to finite spin systems has been discussed recently in a series of papers. In this work we aim to present and discuss results obtained for the “small ferric wheel” Fe$_6$. The reason of such a choice is threefold: (i) this molecule has been well investigated, so we can verify our results; (ii) the number of states are relatively small ($6^6 = 46656$ and dim $L_0 = 4332$), then many characteristics can be obtained without tedious calculations; (iii) all numerical algorithms and procedures can be tested before going to larger problems.

The paper is organized as follows. In Sec. II a short account of the iron antiferromagnetic rings is presented. Combinatorial classification of finite spin system states is briefly discussed in Sec. III. Section IV contains eigenproblem solutions for Fe$_6$ cluster. Eigenstates obtained are analyzed in Sec. V (e.g., static spin correlations are calculated). Some concluding remarks are made in Sec. VI. Due to reasons given in Sec. IV states corresponding to two one-dimensional irreps are considered only. Hence, the energy spectrum is not determined and the thermodynamic quantities are not calculated.

## II. ANTIFERROMAGNETIC FERRIC WHEELS

There are several mesoscopic clusters comprising iron ions bridged by o xo-groups with different magnetic properties. Some of them have the ground state with high total spin $S$, e.g., Fe$_{12}^{III}$OCH$_3_6$(dpm)$_6$ with $S = 5$, Fe$_{12}^{III}$(tacn)O$_2$(OH)$_{12}$Br$_3$ with $S = 10$ and ferromagnetic Fe$_3^I$ with $S = 8$. On the other hand, in some systems antiferromagnetic coupling results in complete cancellation of local spins leading to nonmagnetic ($S = 0$) ground state; all such molecules contain iron(III) ions arranged in cycles or dimers as in [Fe(OMe)(dbm)$_2$]$_2$. In the first case we have three types of Fe$_6$ rings, a medium ferric wheel [Cs$\subset$Fe$_8$N(CH$_2$CH$_2$O)$_3$]Cl$_2$, the Fe$_{10}$(OCH$_3$)$_2$0(C$_6$H$_2$O$_2$Cl)$_{10}$ ring, and the largest ferric wheel Fe$_{18}$. There is also a ring-shaped molecule Fe$_{12}$ with a net spin $S = 0$ in the ground state, but it does not exhibit full cyclic symmetry. The number of basic states is given as $6^n$, $n = 2, 6, 8, 10, 12, 18$, so we deal with eigenproblems of dimensions 36, 46656, 1679616, 60666176, 2176782336, and 1015596668416, respectively. The dimensions of $L_0$, the subspace containing states with $M = 0$ are as follows: 6, 4332, 135954, 4395456, 144840476, and 5542414273884; the approximate ratios $6^n$/dim $L_0$ are 6.00, 10.77, 12.35, 13.76, 15.03, and 18.32, respectively, so dim $L_0$ increases a bit slower than $6^n$.

In this work the small ferric wheel is considered; the following three molecules of this type are known and investigated.
The first cluster has crystallographically imposed $S_6$ point-group symmetry, whereas in the other cases this symmetry is approximate. Therefore, the results obtained here are mostly relevant to the first one.

III. CLASSIFICATION OF STATES BY MEANS OF ALGEBRAIC COMBINATORICS

The method proposed can be roughly divided into four steps: combinatorial, linear, magnetic, and numerical. The last one consists in efficient implementation of proposed algorithms, working-out methods of storing of configuration etc. These problems have been recently presented elsewhere and reused lately in many articles, for example by Waldmann in Ref. Therefore, below we concentrate on the first step since combinatorial methods (especially methods of algebraic combinatorics) are not so popular. More detailed discussion on this topic, from the mathematical point of view, can be found in a monograph by Kerber.

To begin with, we have to introduce the notion of a (finite) group action and define two structures: an orbit and a stabilizer. We say that a group $G$ acts on a set $X$ if for each $g \in G$ and $x \in X$ a product $gx \in X$ is uniquely determined and for all $g, g' \in G$, $x \in X$

$$(gg')x = g(g'x)$$

and $e_Gx = x$,

where $e_G$ denotes the unit element in $G$. If both $G$ and $X$ are finite we call the action finite. An orbit $G(x) \subset X$ of an element $x \in X$ is a set containing all $x' \in X$ which can be obtained from $x$, i.e.,

$$G(x) = \{gx \mid g \in G \}.$$

Since an orbit is an equivalence class then it can be represented by any of its elements. For each $x \in X$ its stabilizer

$$G_x = \{g \mid gx = x \} \subseteq G$$

contains elements of $G$ leaving $x$ invariant. It can be shown that orders $|G(x)|$ and $|G_x|$ of an orbit and its stabilizer, respectively, are related by the following formula

$$|G| = |G(x)||G_x|.$$

Moreover stabilizers of all elements in a given orbit $G(x)$ are conjugated to each other (as subgroups of $G$): a class of conjugated subgroups determines a type of an orbit.

For any set $Y$ the action of $G$ on $X$ can be raised to an action of $G$ on functions $f: X \to Y$ as follows

$$\forall x \in X \quad (gf)(x) = f(g^{-1}x).$$

In the case of finite systems the so-called Ising configurations (basic states) can be considered as mappings $\mu: X \to Y$, where $X = \{1, 2, \ldots, n\}$ is a set of node labels and $Y = \{-s, -s + 1, \ldots, s\}$ is a set of $z$-projections for the spin number $s$. Basic states $|m_1, m_2, \ldots, m_n\rangle$, $m_j \in Y$ for $1 \leq j \leq n$, are in a one-to-one correspondence with functions $\mu$ providing that for all $x \in X$ the equality $\mu(j) = m_j$ holds. The largest (discrete) group acting on $X$ is the symmetric group $\Sigma_n$ comprising all $n!$ permutations $\sigma$ of the $n$-element set $X$. According with Eq. 8 one obtains

$$(\sigma \mu)(j) = \mu(\sigma^{-1}j) \quad (\forall 1 \leq j \leq n)$$

or, writing it for basic states $|m_1, m_2, \ldots, m_n\rangle$,

$$\sigma|m_1, m_2, \ldots, m_n\rangle = |m_{\sigma^{-1}1}, m_{\sigma^{-1}2}, \ldots, m_{\sigma^{-1}n}\rangle.$$

Let us consider, for example, a system of $n = 4$ spins $s = \frac{1}{2}$. One of the Ising configurations is a state $|\psi\rangle = |\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\rangle$. Acting with all $4! = 24$ permutations on this state one obtains only six different states (i.e. $|G(|\psi\rangle)| = 6$), since a stabilizer $G_\psi$ is given as

$$G_\psi = \{1, (12), (34), (12)(34)\},$$

where $(jk)$ denotes a transposition of nodes $j, k$ and 1 is the unit element (identity) in $\Sigma_n$. To obtain all elements of the orbit $G(|\psi\rangle)$ it is enough to act with representatives of left cosets $\Sigma_n/G_\psi$, for example with permutations $(1, 13), (1, 14), (2, 13), (2, 14), (3, 14), (2, 14)$. If $\sigma$ is a transposition then $\sigma^{-1} = \sigma$, so

$$G(|\psi\rangle) = \{ |\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, \frac{3}{2}, \frac{1}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, \frac{1}{2}, \frac{3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, \frac{1}{2}, \frac{1}{2}, \frac{3}{2}\rangle \}.$$

Note, that this orbit is determined in unambiguous way by a nonordered partition $[0, 0, 2, 2]$ of $n = 4$ into $2(3/2) + 1 = 4$ non-negative parts. Each entry $k_l, l = 0, 1, \ldots, 2s$, of $[k] = [k_0, k_1, \ldots, k_{2s}]$ denotes a number of projections $m_j, j = 1, 2, \ldots, n$, equal to $l - s$. Since $[k]$ is a partition of $n$, then

$$\sum_{l=1}^{2s+1} k_l = n \quad \text{and} \quad k_l \geq 0.$$

An orbit containing states with $k_l$ projections $l - s$ is denoted hereafter as $O[k]$ and is represented, for example, by a configuration

$$|−s, −s, \ldots, −s, −s + 1, \ldots, −s + 1, \ldots, s, \ldots, s\rangle.$$

Moreover stabilizers of all elements in a given orbit $G(x)$ are conjugated to each other (as subgroups of $G$): a class of conjugated subgroups determines a type of an orbit.

$$M = \sum_{l=0}^{2s} (l - s) k_l = \sum_{l=0}^{2s} l k_l - ns.$$

Therefore, the results obtained here are mostly relevant to the first one.
In the example presented one obtains $M = -\frac{1}{2} 0 - \frac{1}{2} 0 + \frac{1}{2} \cdot 2 + \frac{1}{2} \cdot 2 = 4$. The same magnetization $M = 4$ is obtained for states from the four-element orbit $O[0,1,0,3]$ represented by a state $| -\frac{1}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \rangle$. Some group-theoretical properties of orbits $O[k]$ depend on their type, i.e. on a class of conjugated subgroups of $\Sigma_n$ a stabilizer of states in $O[k]$ belongs to. Such classes are represented by the so-called Young subgroups $\Sigma_{\sigma} \subset \Sigma_n$, where $|\sigma|$ is an ordered partition $[\kappa_0, \kappa_1, \ldots, \kappa_z]$, $z \leq 2s + 1$, of $n$ into no more than $2s + 1$ nonzero parts $\kappa_0 \geq \kappa_1 \geq \ldots \geq \kappa_z \geq 0$. The Young subgroup $\Sigma_{\sigma}$ is a direct product of symmetric groups $\Sigma_{\kappa_l}$, $l = 0, 1, \ldots, z$. Each group $\Sigma_{\kappa_l}$ contains permutations of a $\kappa_l$-element set $\{K_l + 1, K_l + 2, \ldots, K + \kappa_l\}$, where $K_l = \sum_{i=0}^{l-1} \kappa_i$. The nonordered partition $[0,0,2,2]$ is of a type represented by the ordered partition $[2,2]$ with a number of nonzero parts equal to $z + 1 = 2$. Therefore, a class of conjugated orbit representatives is obtained by the Young subgroup $\Sigma_2 \times \Sigma_2$, where the first group $\Sigma_2$ contains permutations of the set $\{1, 2\}$ ($K_0 = 0$) and the second factor $\Sigma_2$ — of the set $\{3, 4\}$ ($K_1 = 2$). Other orbits of the same type are represented by states $[a, b, a, b]$, where $a, b = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$ and $a \neq b$. A relation between nonordered partitions $k$ of type $[2,2]$ and states representing orbits $O[k]$ is presented below; the magnetization $M$ for states in a given orbit is also calculated:

| Nonordered partition | Orbit representative | $M$ |
|----------------------|----------------------|-----|
| $[2,2,0,0]$          | $-3/2,-3/2,-1/2,-1/2$ | $-4$ |
| $[2,0,2,0]$          | $-3/2,-3/2,+1/2,+1/2$ | $-2$ |
| $[2,0,0,2]$          | $-3/2,-3/2,+3/2,+3/2$ | $0$ |
| $[0,2,2,0]$          | $-1/2,-1/2,+1/2,+1/2$ | $0$ |
| $[0,2,0,2]$          | $-1/2,-1/2,+3/2,+3/2$ | $2$ |
| $[0,0,2,2]$          | $+1/2,+1/2,+3/2,+3/2$ | $4$ |

In the actual physical problems a symmetry group $G$ is, or at least can be embedded as, a subgroup of $\Sigma_n$. In a general case a restriction $\Sigma_n \downarrow G$ yields a decomposition of an orbit $O[k]$ into orbits of $G$. This decomposition depends on a type $|\sigma|$ of a nonordered partition, not on $|k|$ itself. In the example presented each six-element orbit of type $[2,2]$ (determined by the action of $\Sigma_4$) is decomposed into two orbits of $D_4 \subset \Sigma_4$. The first is represented by the states $[a, a, b, b]$ and contains four states, since its stabilizer (in $D_4$) contains only the identity $E$ and the two-fold rotation $U_2$, which, as an element of $\Sigma_4$, is a permutation $12(34)$ since the stabilizer is two-element subgroup of the eight-element group $D_4$, then the orbit $2/2 = 4$ elements: $[a, a, b, b], [a, b, b, a], [b, b, a, a], [b, a, a, b]$. The other two elements, $[a, b, a, b]$ and $[b, a, b, a]$, form a two-element orbit with the stabilizer $D_4^2 = \{E, C_2, U_0, U_2\}$. All six orbits presented above have the same decompositions into orbits of $D_4$. More detailed discussion of combinatoric properties of the system of four spin $s = \frac{3}{2}$ is presented in the Appendix.

Therefore, we have determined a few starting steps of our procedure: (i) generate ordered partitions $|\sigma|$ of $n$ into no more than $2s + 1$ nonzero parts; (ii) find a decomposition of an orbit $O[|\sigma|]$ into orbits of the Hamiltonian symmetry group $G$; (iii) for a chosen $-ns \leq M \leq ns$ determine all nonordered partitions $|k|$ satisfying the condition (\[\square\]); (iv) decompositions of orbits $O[k]$ into orbits of $G$ are analogous to those determined in Step (ii) (see Note). Therefore, we have determined a few starting steps of our procedure: (i) generate ordered partitions $|\sigma|$ of $n$ into no more than $2s + 1$ nonzero parts; (ii) find a decomposition of an orbit $O[|\sigma|]$ into orbits of the Hamiltonian symmetry group $G$; (iii) for a chosen $-ns \leq M \leq ns$ determine all nonordered partitions $|k|$ satisfying the condition (\[\square\]); (iv) decompositions of orbits $O[k]$ into orbits of $G$ are analogous to those determined in Step (ii) (see Note).
The formula obtained contains products of two factors: a matrix element \( \langle Uv \mid Uv \rangle \) and a group-theoretical parameter of a model under discussion. Determination of the first one is a numerical problem, so it is not discussed here. More details can be found in other papers of authors.\(^{29}\) The second factor depends only on the symmetry group \( G \) and can be determined once for all models with a given symmetry group. Moreover, it is possible to determine such factors in an analytical form for a family of groups, for example it has been done recently for the dihedral groups \( D_n \) describing symmetry of molecular rings.\(^{11}\)

The “magnetic” step of the procedure proposed can be applied to models with dominating Heisenberg term \( J \). At first we take into account the magnetization \( M \) restricting all considerations to subspaces \( L_M \). We determine matrices of the operator \( S^2 \) for all irreps \( \Gamma \) and solve eigenproblems \( S^2 | \psi \rangle = S(S + 1) | \psi \rangle \) for \( 0 \leq S \leq n_s \). In fact, since each \( S \)-multiplet contains a state with \( M = 0 \) (if \( n_s \) is integer), then states \( |SM \rangle \) can be obtained from states \( |S0 \rangle \) acting with the total step operators \( S^\pm = \sum_{j=1}^{n_s} s_j^\pm \). If we are interested in the ground state of a bipartite antiferromagnet only, then we can limit calculations to the case \( S = 0 \) and the one-dimensional irrep. In most cases this is the unit representation \( \Gamma_0 \) (\( A_1 \) in the case of dihedral groups). However, if \( s \) is half-integer and \( n \) is not divisible by four, then the ground state is labeled by the representation usually denoted as \( \Gamma_1 \) (\( B_1 \) for dihedral groups). This follows from the Marshall criterion.\(^{10,11}\) Ising configurations related by the action of any pair of operators \( s_j^+ s_k^- \) have coefficients with opposite signs in the decomposition of the ground state into the basic states. In the case considered the ground state has to contain the Néel configuration \( |N_1 \rangle = |s, -s, \ldots, -s \rangle \). According with the Marshall rule the other Néel state, \( |N_2 \rangle = |-s, s, \ldots, s \rangle \), should enter the ground state with the same (opposite) sign if \( n_s \) is even (odd). Hence, the ground state has to contain the state \( |Néel \rangle = (|N_1 \rangle \pm |N_2 \rangle)/\sqrt{2} \) which behaves as the basis vector of \( \Gamma_0 \) (\( \Gamma_1 \), respectively).

### IV. EIGENPROBLEMS AND THEIR SOLUTIONS FOR THE SMALL FERRIC WHEEL

The dimension of the subspace \( L_0 \) in the case of six spins \( s = \frac{3}{2} \) is equal to 4332. Since \( \dim L_1 = 4221 \) then there are 111 (\( 4332 - 4221 \)) states with \( S = 0 \).\(^{12,12}\) At first we determine such non-ordered partitions \( |k \rangle = |k_0, k_1, \ldots, k_5 \rangle \) of \( N = 6 \) into \( 2s + 1 = 6 \) parts that

\[
\sum_{l=0}^{5} k_l(l - \frac{3}{2}) = 0 \iff \sum_{l=0}^{5} k_l l = 15.
\]

There are 11 ordered partitions of \( N = 6 \) but only seven of them lead to non-ordered partitions satisfying the condition presented above. An algorithm discussed in Ref.\(^{11}7\) generates them in the following order:

- \([1, 1, 1, 1, 1, 1]\)
- \([2, 2, 1, 1, 1, 1]\)
- \([3, 1, 1, 1, 1, 1]\)
- \([3, 2, 1, 1, 1, 1]\)
- \([4, 1, 1, 1, 1, 1]\)
- \([3, 3, 1, 1, 1, 1]\)
- \([5, 1, 1, 1, 1, 1]\)

These are all 385 orbits leading to the total magnetization \( M = 0 \).\(^{11}4\)

| \( U \) | \([1, 1, 1, 1, 1, 1]\) | \([2, 2, 1, 1, 1, 1]\) | \([3, 1, 1, 1, 1, 1]\) | \([3, 2, 1, 1, 1, 1]\) | \([4, 1, 1, 1, 1, 1]\) | \([3, 3, 1, 1, 1, 1]\) | \([5, 1, 1, 1, 1, 1]\) |
|---|---|---|---|---|---|---|---|
| \( C_1 \) | 60 | 14 | 10 | 4 | 2 | 1 | 0 |
| \( D_0^1 \) | 0 | 2 | 0 | 2 | 1 | 1 | 1 |
| \( D_0^2 \) | 0 | 0 | 0 | 0 | 0 | 1 | 0 |

The Hamiltonian point-symmetry group is \( G = S_6 \simeq D_6 \).\(^{13}\) There are 10 classes of conjugated subgroups for this group, but only seven of them can play a role of an orbit stabilizer.\(^{13}\) In the case considered, i.e. for the partitions presented above, only three subgroups appear in the decompositions of orbits of \( \Sigma_0 \): \( C_1 \), \( D_0^1 \), and \( D_0^2 \). These decompositions are presented in Table\(^{11}1\). For example, each of six 120-element orbit of type \([3, 1, 1, 1, 1]\) decomposes into ten 12-element orbits with the trivial stabilizer \( C_1 \). Taking into account numbers of orbits of \( \Sigma_0 \) one obtains: 339 orbits with a stabilizer \( C_1 \), 43 orbits with a stabilizer \( D_0^1 \), and 3 orbits with a stabilizer \( D_0^2 \). These are all 385 orbits leading to the total magnetization \( M = 0 \).
In the next step we take into account decompositions of transitive representations $R^{D_6;U}$ (i.e. the permutation representation restricted to an orbit of type $U$) into irreps $\Gamma$ of $D_6$. The three stabilizers mentioned above give the following decompositions:

$$\begin{align*}
R^{D_6;C_1} &= A_1 \oplus A_2 \oplus B_1 \oplus B_2 \oplus 2E_1 \oplus 2E_2; \\
R^{D_6;D_1} &= A_1 \oplus B_1 \oplus E_1 \oplus E_2; \\
R^{D_6;D_3} &= A_1 \oplus B_1. 
\end{align*}$$

This completes combinatorial and group-theoretical classifications of states with $M = 0$. In a similar way one can classify states with $M = 1$, what enables us to determine irreducible representations related to $S = 0$. The numbers $n(\Gamma)$ of subspaces with a given symmetry $\Gamma$ for $M = 0, 1$ and $S = 0$ are collected in Table II.

Using the formulas discussed in Sec. III, and presented in the previous papers, matrices of the Hamiltonian $H$ and the squared total spin $S^2$ can be constructed. Of course, one can construct matrices for each $\Gamma = A_1, A_2, B_1, B_2, E_1, E_2$. However, considering the ground state it is enough to consider $\Gamma = B_1$: the ground state is a linear combination of 385 Ising states with $M = 0$ transforming as $|B_1b_1\rangle$. We take into account also $\Gamma = A_1$ since, starting from a theorem proved by Lieb and Mattis, it can be shown that these representations alternate with the lowest energy for $S = 0, 1, 2, \ldots, 15$ ($A_1$ for odd $B_1$ for even $S$, respectively). The eigenstates determined for all $S$ and $\Gamma = A_1, B_1$ are used to transform the Hamiltonian matrix to a block (quasi-diagonal) form. For example, to find the ground state and its energy we have to solve 20-dimensional eigenproblem (cf. Table II).

A short note on numerical solutions are in place here. In the case of $S^2$ operator and one-dimensional irreps eigenproblems can be solved exactly. It has been achieved using the integer functions included in the GMP package. The square roots yielded by the action of $s^z$ operators and following from the formulas for matrix elements can be easily removed by the appropriate substitution. In this way each eigenproblem for $S^2$ can be written as a system of homogeneous linear equations with integer coefficients. Therefore, the solution(s) can be expressed by elements of the smallest number field containing integers, so—in a general case—by rational numbers also easily maintained with the use of the GMP package. The Hamiltonian matrix, with entries calculated with the GMP-functions, is transformed to a block-form using the float functions from this package.

The default precision is set to 256 bits. At this moment a procedure for solving eigenproblems using the float GMP-functions has not been finished, so the eigenvalues and eigenvectors are determined using the standard procedures on 64-bit IRIX computers. The largest, 60-dimensional, eigenproblem has been reached for $S = 4$ and $\Gamma = B_1$. Obtained vectors are verified checking their scalar products (including norms) and their eigenvalues for $S^2$ and $H$ matrices.

In this way we have obtained 770 states expressed as linear combinations of the Ising configurations. Since states with $S > 0$ represent in fact multiplets then eigenvalues of 8436 states have been determined (4291 $A_1$ and 4145 $B_1$ states). The ground state energy is equal to $E_0 = -43.934717$, for other values of the total spin $S$ the lowest energies are in good agreement with Lande’s rule $\Delta S = (E_0(S) - E_0)/J = S(S + 1)/3$, which approximates the energy gaps. The largest relative deviation (3.75%) is reached for $S = 1$ when Lande’s rule gives $\Delta_1 = \frac{2}{3}$, whereas the value obtained is equal to 0.69169. The other gaps ($S = 2, 3, \ldots, 15$) are 2.0744, 4.1469, 6.9070, 10.3517, 14.4772, 19.2792, 24.7534, 30.8952, 37.7002, 45.1633, 53.2789, 62.0396, 71.4347, 81.4347 and 93471, respectively. Obtained vectors are verified checking their scalar products (including norms) and their eigenvalues for $S^2$ and $H$ matrices.

V. SPIN CORRELATIONS AND THE CLASSICAL ORDERING

The thermodynamic quantities have been already determined for the Fe$_6$ cluster and the results have been compared with the experimental data. Therefore, in this paper we focus our attention on the eigenstates properties: the spin correlations $\omega^z_{r,s} = \langle \sum_{j=1}^r s^z_j s^z_{j+r} \rangle / N$ for $r = 1, 2, 3$ and the probability $p_N$ of finding the system in the Néel state. The latter one is, of course, equal to $a^2_{N1} = a^2_{N2}$, i.e. to the square of the coefficient of $|N1\rangle$ or $|N2\rangle$ in a state under consideration. It has to be stressed that $a_{N1}$ is nonzero if $S$ is even (odd) and $\Gamma = A_1$ ($B_1$, respectively). The value of $p_N$ can be used to compare quantum states determined with the classical ordering of
antiferromagnets.

\section*{A. Spin correlations}

In the case \(S = 0\), due to isotropy in spin-space, the \(z\)-correlations of the nearest neighbors, \(\omega_1^z\), should be one third of energy (per spin) in a given state. This has been confirmed by the calculations presented elsewhere. For other states with \(M = 0\) (\(\Gamma = A_1, B_1, 0 \leq S \leq 15\)) we have plotted \(\omega^z\) versus energy per spin \(E = E/6J\).

Typical drawings are presented in Fig. 1 for \(S = 4\) and \(\Gamma = B_1\). In all cases \(\omega_1^z\) is almost linear function of \(E\) (with a positive slope) and only a few values for high energies are larger than zero. On the other hand, \(\omega_2^z\) decreases with growing \(E\), but only some low-lying states show positive (ferromagnetic) \(\omega_2^z\) with negative \(\omega_1^z\) and \(\omega_3^z\), the feature characteristic for the ground state of an antiferromagnetic system. However, it might happen that for \(\omega_2^z < 0\) spin correlations of the next-nearest neighbors are positive for other quantization axes. It could be checked considering terms \(\sum s_j \cdot s_{j+2}\), what has not been done in our calculations. We tried to fit some simple functions to \(\omega_2^z(E)\), but the results obtained occurred rather ambiguous. It seems that an exponential function \(\omega_2^z(E) + 1.132 = \exp(-1.224 - 0.432E)\) fits better than the power law \(\omega_2^z(E) + 3.191 = 6.850 \cdot (E - \varepsilon_0)^{-0.532}\) (\(S = 4, \Gamma = B_1\)). The correlations with the third neighbors \(\omega_3^z(E)\) show positive maximum for all \(S < 14, \Gamma = A_1\) and \(S < 13, \Gamma = B_1\). It is interesting that single states, obtained for pairs \((S, \Gamma) = (13, B_1), (14, B_1), (15, A_1)\), have \(\omega_3^z\) negative: \(-0.1833, -0.6327, -0.2155\), respectively; there are no states for pairs \((14, A_1)\) and \((15, B_1)\).

The correlation \(\omega_1^z\) has been analyzed in two aspects. At first, assuming linear dependence \(\omega_1^z(E) = a(S)E + b(S)\) for each \(S\), we have plotted coefficients \(a(S)\) and \(b(S)\) versus \(S\) (see Fig. 2). Results of linear regressions are denoted by the crosses ‘+’ are obtained for pairs \((S, \Gamma)\) containing the ground state of an \(S\)-multiplet, i.e. \(S\) even, \(\Gamma = B_1\) and \(S\) odd, \(\Gamma = A_1\); the diamonds ‘○’ denote results for the other pairs. Since \(a(S)\) behaves differently in those cases, then the linear functions \(a_0(S)\) (the first case, dashed line) and \(a_1(S)\) (the other case, dotted line) have been considered separately. The points for \(S = 0\) in both cases and for \(S = 1\) in the first case have been omitted due to highly irregular behavior (see also below and Fig. 3). As the results we have obtained

\[
a_0(S) = 0.0221S + 0.291, \quad a_1(S) = 0.0424S + 0.245.
\]

It has to be stressed that \(a_0(S)\) deviates from a line for high \(S\) and, maybe, a parabolic fit should be applied in this region. The intercept \(b(S)\) does not show such irregularities so all results are fitted to one (second order) function. The best-fit line is given as

\[
b(S) = -0.0197S^2 + 0.0591S - 0.0518.
\]

Let \(\omega_0(S)\) denote \(\omega_1^z\) in the state with the lowest energy for each \(S\)-multiplet. The plot in Fig. 3 shows this

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Correlations vs energy per spin for \(S = 4, \Gamma = B_1\).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{(a) A slope \(a(S)\) and (b) an intercept \(b(S)\) as a function of the total spin \(S\); ‘○’ and ‘+’ results of linear regression \(\omega_1^z(E) = a(S)E + b(S)\); lines give (a) linear regressions of \(a_0(S)\) (dashed line), \(a_1(S)\) (dotted line) and (b) a parabolic fit to \(b(S)\) (see text for details).}
\end{figure}
function fitted by a relation analogous to Lande’s rule

$$\omega_0(S) = \frac{1}{12} S(S+1) + \frac{1}{2} \xi_0.$$  

(6)

Substituting Lande’s rule $\Delta_S = S(S+1)/3$ one obtains

$$\omega_0(S) = \frac{1}{4}(\mathcal{E}_0(S) + \mathcal{E}_0) .$$  

(7)

Lande’s rule for correlations is broken for $S = 0, 1$. In the first case Eq. (6) yields $\omega_0(S) = \frac{1}{4} \xi_0$, whereas the exact value is $\mathcal{E}_0/3$. The latter case, $S = 1$, shows deviation in the other direction: calculated value of $\omega_0(1)$ is $-4.172$, whereas from Eq. (6) one obtains $-3.632$, so the real value is about 15% larger in magnitude. Similar results have been obtained for six spins $\frac{1}{2}$ and $\frac{3}{2}$.

\[ \text{B. Néel probability} \]

It is interesting to compare the results obtained with correlations in the Néel state. In this case $z$-correlations (per bond) are equal to $\pm 0.25$ since the Néel state exhibits the long-range order. The ground state determined here has alternating, but decreasing in magnitude, correlations. However, the total nearest neighbors correlation, equal to the ground state energy $3\omega_0(0)$, is larger than in the Néel state, since in the Néel state $x$- and $y$-correlations are equal to zero. The orbit containing the both Néel states gives one state with symmetry $\Gamma = B_1$, namely $|\text{Néel} \rangle$. The absolute value of the coefficient of this state in the ground state is $a_N = 0.3284$, so the probability is equal $p_N = 0.1078$. The probability of a single Néel state is $p_{N1} = p_{N2} = \frac{1}{2} p_N = 0.0539$. Such small number does not explain so strong nearest neighbor correlation in the ground state. However, one has to take into account that the Néel state, $|N1 \rangle$ or $|N2 \rangle$, represents only one possibility of such spin arrangement that each of sublattices (of a bipartite antiferromagnet) has the maximum total spin $S_{\text{max}}$ (in the other words—each sublattice is ordered ferromagnetically), but magnetizations have opposite directions. For a given spin number, $S_{\text{max}}$ in the case considered, there are $2S_{\text{max}} + 1$ possible spin projections, so there are $2S_{\text{max}} + 1$ different Néel states, each of them corresponds to different choice of quantization axis and its orientation. In the case considered $S_{\text{max}} = 3 \times \frac{5}{2} = \frac{15}{2}$, there then are 16 Néel states. Two of these states are given by $|N1 \rangle$ and $|N2 \rangle$, whereas the others can be obtained as linear combinations of states with $S = M = 0$. Hence, the global probability is $p_N^* = 16 p_{N1} = 0.8624$. To have a bit deeper insight we have analyzed the Néel probability $p_N$ for other $S$-multiplets. As it has been mentioned earlier only states with $S$ even, $\Gamma = B_1$ and $\Gamma = A_1$ for $S$ odd are taken into account. The lowest lying state (with energy $\mathcal{E}_0(S)$) has always the maximum $p_N$, much higher than in the other states. A rough estimate shows exponential decreasing. For example, in the case $S = 4$, $\Gamma = B_1$ the best-fit line is given as $p_N(\mathcal{E}) = \exp(-2.176 \mathcal{E} - 14.700)$ (see also Fig. 4). Fitting a function $\exp(\alpha(S) \mathcal{E} + \beta(S))$ to $p_N$ in each $S$-multiplet we have obtained series $\alpha(S)$, $\beta(S)$ which can be approximated by exponential functions $\alpha(S) = -\exp(0.463 S - 4.781) - 2.122$ and $\beta(S) = \exp(0.463 S - 3.061) - 14.643$, respectively (see Fig. 4). Points for $S = 0, 1$ have not been taken into account due to their irregular behavior.

All above considerations concern the Néel probability $p_N$. However, as it has been mentioned discussing the ground state, the Néel states $|N1 \rangle$ and $|N2 \rangle$ are only two of $ns + 1$ possible states $|S_A, m; S_B, -m \rangle$ with $S_A = S_B = \frac{1}{2} ns$ and $|m| \leq \frac{1}{2} ns$, where $S_A$ ($S_B$) denotes the total spin in one sublattice of a bipartite antiferromagnet. Coupling of sublattice spins leads to $(ns + 1)^2$ states with the total spin $0 \leq S \leq ns$. In each $S$-multiplet there is one state $|S, 0 \rangle$ with the magnetization equal to zero. This state is a linear combination of $ns + 1$ states $|S_A, m; S_B, -m \rangle$, namely

$$|S, 0 \rangle = \sum_{m = -ns/2}^{ns/2} \left[ \frac{1}{2} ns \frac{1}{2} ns \begin{array}{ccc} S & 0 \\ m & -m & 0 \end{array} \left| \frac{1}{2} ns, m; \frac{1}{2} ns, -m \right. \right],$$

where the expression in brackets is the Clebsch–Gordan coefficient (CGC) for coupling spin representations $D_+^S$. 

\[ \text{FIG. 3: Correlations in the state with the lowest energy in each S-multiplet vs the total spin S (diamonds). The dotted line: Lande’s rule for correlations given by Eq. (6)}. \]

\[ \text{FIG. 4: The Néel probability p_N versus energy E for states with S = 4, \Gamma = B_1}. \]
In the case $S = 0$ the appropriate CGC’s are equal to

$\alpha_{S} = (1)^{S} \frac{n!}{(n + 1)!} \beta_{S}$,

so all states $|\frac{1}{2}n, m; \frac{1}{2}n, -m\rangle$ have the same probability and, therefore, the global Néel probability $p_{N}^{S} = (n + 1)p_{N}$. Note the Néel states $|N1\rangle$ and $|N2\rangle$ correspond to $m = \pm \frac{1}{2}n$, respectively. Hence, these states enter $|0, 0\rangle$ with opposite signs for odd $n$s, according with the Marshall rule.

In this paper we consider states with total magnetization equal to zero and the Néel states correspond to sublattice states with $S A = S B = |m| = ns/2$. So, we are interested in the CGC’s for these values; they can be derived from a general formula \(a\) and one obtains

$$\alpha_{N1(2)} = \begin{pmatrix} \frac{1}{2} n \quad \frac{1}{2} n \quad S \\ \pm \frac{1}{2} n \quad \mp \frac{1}{2} n \quad 0 \end{pmatrix} \frac{1}{\sqrt{(n - S)}!} \left(\frac{S}{n + 1}\right)! (n - S)! \left(\frac{S}{n + S + 1}\right)! .$$

For example, the maximum total spin $S = ns$ yields equal coefficients for the both Néel states

$$\alpha_{N1} = \alpha_{N2} = \frac{(n - S)!}{\sqrt{(2ns)!}} .$$

this ordering is slightly ‘broken’ or, in the other words, the ground state of quantum antiferromagnetic rings are ordered to some extent only. In our case it is reflected by the value $p_{N} = 0.86258$. However, this number has to be compared with $p_{N, \text{dis}}^{S}$ in a completely disordered state. One of possible definitions of such a state, appropriate in our considerations, is to combine all vectors with $M = 0$ and $\Gamma = B_{1}$. There are 385 such vectors, so $\alpha_{N} = 385 \beta_{N} = 0.051$; then $p_{N, \text{dis}}^{S} \approx 0.235$. The value obtained is almost four times smaller than that in the ground state. Of course, this ratio should decrease for larger rings, since—as it is well known—as long-ordered exists in linear antiferromagnets. On the other hand, however, small antiferromagnetic nanoclusters should exhibit a well-ordered ground state.

VI. FINAL REMARKS

The small ferric wheel Fe$_{3}$ has been recently investigated by many authors, so we have decided to analyze some less discussed properties—spin correlations and probability of finding the state in the Néel state. In both cases we obtain results suggesting quite well-ordered ground state with highly correlated spins. For example, $\omega_{1} = -2.441$, $\omega_{2} = 1.959$, and $\omega_{5} = -1.952$. It should be stressed that $z$-correlations reach maximum magnitude in states with $S = 1$ (cf. Fig. 3); the values are $-4.172, 3.907, \text{and} -3.897$, respectively. However, these states are not isotropic, so $x$- and $y$-correlations are much smaller, whereas total spin correlations $\omega_{r} = 3\omega_{z}^{2}$ for $S = 0$. As regards the Néel probability, deviation

| $S$ | $10^{3} \cdot p_{N1} [%]$ | $\alpha_{N1} [%]$ | $p_{N} [%]$ |
|-----|-----------------|-----------------|-------------|
| 0   | 340.126         | 16              | 86.258      |
| 1   | 1430.567        | 272/45          | 86.470      |
| 2   | 18634.880       | 816/175         | 86.892      |
| 3   | 17979.305       | 15504/3185      | 87.520      |
| 4   | 13999.674       | 5168/819        | 88.340      |
| 5   | 9062.557        | 15504/1573      | 89.324      |
| 6   | 4928.709        | 1504/845        | 90.432      |
| 7   | 2254.612        | 118864/2925     | 91.621      |
| 8   | 863.2259        | 6902/65         | 92.857      |
| 9   | 273.7878        | 31280/91        | 94.111      |
| 10  | 70.76512        | 594320/441      | 95.368      |
| 11  | 14.54000        | 46512/7         | 96.613      |
| 12  | 2.286329        | 1069776/25      | 97.834      |
| 13  | 0.2584271       | 3440756/9       | 98.979      |
| 14  | 0.0186955       | 5348880         | 100.000     |
| 15  | 0.000864467     | 155117520       | 100.000     |
from the classical ordering in the ground state can be observed. On the other hand, \( p_N^* = 1 \) in the cases \( S = 14, 15 \) shows that these multiplets behave classically. It has to be stressed that states with \( M = 0 \) are considered only. Hence, we obtain energies for all states in a given \( S \)-multiplet (for \( \Gamma = A_1, B_1 \)). However, correlations calculated are related to states \(|S, 0\rangle\) — they cannot be used for states with \( M \neq 0 \). For example, in the case of the unique multiplet \( S = 15 \) we have \( \omega_\pi^* = 6.25, r = 1, 2, 3, \) for \( M = \pm 15 \), whereas for \( M = 0 \) we have \( \omega_\pi^* = -0.2155, r = 1, 2, 3 \). Plotting \( p_N^* \) versus the total spin \( S \) one can observe almost linear dependence for high \( S \) (omitting point \( S = 15 \)). A better approximation has been obtained for a function \( p_N^*(S) = \exp(-0.31S + 2.84\sqrt{S} - 8.25) + 0.86 \) (cf. Eq. 5) and Fig. 6). Having determined such relations (see also Figs. 2, 3, 5) for ferric dimers \( \text{Fe}_2 \) and the ferric wheel \( \text{Fe}_{10} \) we would try to approximate results for \( \text{Fe}_{18} \). The ring \( \text{Fe}_8 \) recently studied by Waldmann et al. might lead to inconsistent results, since the ground state corresponds to \( \Gamma = A_1 \) (see Ref. 22 and the end of Sec. 11). Note that there is lack of \( \text{Fe}_{14} \), but nevertheless it seems interesting to investigate such a molecule. There are about \( 8 \times 10^{16} \) basic states, but ‘only’ about \( 5 \times 10^9 \) of them have \( M = 0 \); the total spin \( S = 0 \) leads to \( 56,267,133 \) states (there are not basis states, however). Taking into account symmetry properties will decrease these numbers significantly.

The methods proposed by Bonner and Fisher almost forty years ago have been mainly used to estimate properties of magnetic materials in the thermodynamic limit. On the other hand, magnetic nanoclusters have given rise to more detailed investigations of small spin systems comprising ions with high spin number \( s \). The numeric complexity is similar: there are \( 60,466,176 \) basic states in the case of ten spin \( s = \frac{5}{2} \) what is comparable with that number for 26 spins \( s = \frac{7}{2} \). However, our aims are a bit different in these cases. Trying to determine properties in the thermodynamic limit we observe their dependencies on number of spins \( n \), whereas investigating nanomagnets we rather try to determine a ‘best-fit’ model of a given molecule. Therefore, in the first case the considerations are mainly limited to one, sometimes simplified, model, while fitting to experimental data we may need to investigate some different and rather complicated models.

Amongst many magnetic molecules those containing \( \text{Fe}^{3+} \) ions seem to be very interesting, since they can be used as models of such metalloprotein as ferritin. A fact that this molecule contains as many as 4500 \( \text{Fe} \) ions does not depreciate validity of results obtained for molecules comprising several magnetic ions. Experimental data show that noncompensate spin in ferritin is about 50 and it originates from surface randomness. Moreover, these data suggest that ferritin exhibits quantum tunneling similar to that observed in \( \text{Mn}_{12} \) molecules.

Since recently some papers using a similar approach have been published we would like to stress differences and advantages of the method applied in this paper. At first, we go much deeper into structure of the permutation representations introducing additional indices (ordered and nonordered partitions) for basic states. This also leads to some simplifications in the procedure generating operator matrices. A general formula for matrix elements significantly reduces a number of cases to be considered. Note that this formula needs introduction of double cosets, a structure not mentioned in the earlier papers. Moreover, many results for the dihedral groups can be presented in easy-to-use analytical form.

We do not need to use any projection procedure to derive irreducible basis, because it is determined for transitive representations of the dihedral groups in a general form. Using any package for multiple precision arithmetic, like GMP we are able to find exact eigenvectors of \( S^2 \) operator in the case of one-dimensional irreps (and also for two-dimensional irreps in some simple cases, e.g. for \( \text{D}_6 \) or \( \text{D}_8 \), when \( \cos(2\pi/n) \) can be expressed by square roots of integers). This allows determination of spin correlations and Néel probabilities with high accuracy.

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**APPENDIX A: AN EXAMPLE**

To illustrate the method for generating operator matrices the case of four spin \( s = \frac{3}{2} \) is presented below. The solutions of eigenproblems of \( S^2 \) and \( \mathcal{H} \) as well as discussion of the spin correlations and Néel probability are left out, since at the actual stage of the project they are performed by means of (more or less) standard numeric
methods (the only change is application of procedures from the GMP library).

Assuming the isotropic Heisenberg Hamiltonian both $S$ and $M$ are good quantum numbers. There are $4^4 = 256$ Ising configurations and the maximum total spin number is $S = 6$; hence, the possible magnetizations are $M = 0, \pm 1, \ldots, \pm 6$. The dimensions of subspaces $L_M$ containing states with a given $M$ are as follows:

$$
\begin{array}{c|cccccccc}
M & \pm 6 & \pm 5 & \pm 4 & \pm 3 & \pm 2 & \pm 1 & 0 \\
\text{dim } L_M & 1 & 4 & 10 & 20 & 31 & 40 & 44 \\
\end{array}
$$

It allows determination of numbers $n(S)$ of $S$-multiplets for each $S$ as $n(S) = \text{dim } L_{M=S} - \text{dim } L_{M=S+1}$ for $S < 6$ and $n(S = 6) = 12$, hence one obtains:

$$
\begin{array}{c|cccccccc}
S & 6 & 5 & 4 & 3 & 2 & 1 & 0 \\
n(S) & 1 & 3 & 6 & 10 & 11 & 9 & 4 \\
\end{array}
$$

Of course we have $\sum_{S=0}^{S=6}(2S + 1)n(S) = 256$ and $\sum_{S=0}^{S=6}n(S) = 44 = \text{dim } L_{M=0}$ since each $S$-multiplet contains the state $|SM = 0\rangle$. To investigate nonmagnetic states with $M = 0$ one has to decompose the 44-dimensional space $L_0$ into seven subspaces labeled by $S$ and with dimensions given in the table presented above.

To begin with we start from considering ordered partitions of $n = 4$ into no more than four parts. There are five such partitions, namely

$$[4], [3, 1], [2, 2], [2, 1, 1], [1, 1, 1, 1].$$

Each of this partition represents a class of nonordered partitions of $n = 4$ into four non-negative parts $k_0, k_1, k_2$, and $k_3$. There are 35 such partitions collected in Table IV. From this table one can learn that there are five nonordered partitions with $\sum_{i=0}^{i=3} k_i = 6$, i.e., the magnetization $M = 0$ (see Eq. (4)). These five partition come in three types: $[3, 1], [2, 2]$, and $[1, 1, 1, 1]$. Therefore, to investigate states with $M = 0$ one has to consider only these three ordered partitions. The number of configurations of type $[k]$ is determined by the polynomial coefficient $n!/(k_0!k_1!k_2!k_3!)$ and is the same for all nonordered partitions of a given type $[k]$. In the case considered, i.e. for $[k] = [3, 1], [2, 2]$, and $[1, 1, 1, 1]$ these numbers are 4, 6, and 24, respectively, then there are four states corresponding to $[k] = [0, 3, 0, 1], [1, 0, 3, 0]$, six states for $[k] = [2, 0, 0, 2], [0, 2, 2, 0]$, and 24 states for $[k] = [1, 1, 1, 1]$; 44 states in total. For example, the partition $[1, 0, 3, 0]$ labels a four-element set of states:

$$\{|-\frac{\sqrt{2}}{2}, \frac{\sqrt{2}}{2}, \frac{\sqrt{2}}{2}, \frac{\sqrt{2}}{2}\}, \{\frac{\sqrt{2}}{2}, -\frac{\sqrt{2}}{2}, \frac{\sqrt{2}}{2}, \frac{\sqrt{2}}{2}\}, \{\frac{\sqrt{2}}{2}, \frac{\sqrt{2}}{2}, -\frac{\sqrt{2}}{2}, -\frac{\sqrt{2}}{2}\}, \{\frac{\sqrt{2}}{2}, \frac{\sqrt{2}}{2}, \frac{\sqrt{2}}{2}, -\frac{\sqrt{2}}{2}\}$$

since relations $k_0 = 1, k_2 = 3$, and $k_3 = k_3 = 0$ means that there are one spin projection $+\frac{1}{2}$ and three projections $\frac{1}{2}$. On the other hand, the unique orbit labeled by $[k] = [1, 1, 1, 1]$ contains $4! = 24$ states with all projections different: $\{-\frac{\sqrt{2}}{2}, -\frac{\sqrt{2}}{2}, \frac{\sqrt{2}}{2}, -\frac{\sqrt{2}}{2}\}, \{-\frac{\sqrt{2}}{2}, -\frac{\sqrt{2}}{2}, -\frac{\sqrt{2}}{2}, \frac{\sqrt{2}}{2}\}$ etc.

The decomposition of an orbit $O[k]$ (of the symmetric group $\Sigma_4$) into orbits of a Hamiltonian symmetry group $G$ (isomorphic to the dihedral group $D_4$ in the case considered) depends on its type, i.e. on the ordered partition $[k]$. Before presenting these decompositions a brief outlook of the group $D_4$ is necessary. This group is generated by the four-fold rotation $C_4$ and the two-fold rotation $U_0$ with the generating relations

$$C_4^4 = E, \quad U_0^2 = E, \quad (C_4U_0)^2 = U_0^2 = E,$$

where $E$ denotes the unit element in $D_4$. The labeling scheme of group elements and numbering of nodes (spins) is presented in Fig. 8. There are five classes of conjugated elements: $\{E\}, \{C_2\}, \{C_4, C_4^{-1}\}, \{U_0, U_2\}, \{U_1, U_3\}$ and, hence, five irreducible representations: $A_1, A_2, B_1, B_2, E_3$, with characters presented in Table IV. The dihedral group $D_4$ has ten subgroups collected in eight classes of conjugated subgroups (in this very simple case only two classes contain two subgroups). However, three subgroups are excluded from a set of possible configuration

| $[k]$ | $[k]$ | $M$ | orbit representative |
|-------|-------|-----|---------------------|
| $[4]$ | $[4]$ | $-6$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[0, 4, 0, 0]$ | $-2$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[0, 0, 4, 0]$ | $2$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[0, 0, 0, 4]$ | $6$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[3, 1]$ | $[3, 1]$ | $-5$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[3, 0, 1, 0]$ | $-4$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[3, 0, 0, 1]$ | $-3$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[1, 3, 0, 0]$ | $-3$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[0, 3, 1, 0]$ | $0$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[0, 1, 3, 0]$ | $1$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[0, 0, 1, 3]$ | $3$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[0, 1, 0, 3]$ | $3$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[0, 0, 0, 3]$ | $5$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[2, 2]$ | $[2, 2]$ | $-4$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[2, 0, 2, 0]$ | $-2$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[2, 0, 0, 2]$ | $0$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[0, 2, 2, 0]$ | $0$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[0, 2, 0, 2]$ | $2$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[0, 0, 2, 2]$ | $4$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[2, 1, 1]$ | $[2, 1, 1]$ | $-3$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[2, 1, 0, 1]$ | $-2$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[2, 0, 1, 1]$ | $0$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[1, 2, 1, 0]$ | $-2$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[1, 2, 0, 1]$ | $0$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[1, 1, 2, 0]$ | $1$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[1, 1, 0, 2]$ | $1$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[1, 0, 1, 2]$ | $2$ | $-3/2, -3/2, -3/2, -3/2$ |
| $[0, 1, 1, 2]$ | $3$ | $-3/2, -3/2, -3/2, -3/2$ |
is also an orbit of the dihedral group \( D_4 \) by states. As representatives of these eight-element orbits one can choose states labeled by the nonordered partition \([3, 1]\) or \([2, 2]\); its stabilizer is \( D_2^3 \) so it belongs to the orbit represented by \( \nu = [\frac{1}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}] \) and as a representative \( g_2 \) of the left coset \( g_2D_2^3 \in D_4/D_2^3 \) one can choose the four-fold rotation \( C_4 \), since \( \mu = C_4 \nu \).

The partition \([k]\) may be used to simplify determination of matrix elements of \( S^2 \) or \( \mathcal{H} \). Assuming that only bilinear terms are present one can notice that states labeled by \([2, 0, 0, 2]\) can be transformed into states labeled by \([1, 1, 1, 1]\) only. States of all types comprise two projections \( \frac{3}{2} \) and two projections \(-\frac{3}{2}\). Therefore, the only nontrivial action of a bilinear term \( s_j^+ s_k^- \) is possible when \( s_j^+ \) acts on the projection \(-\frac{3}{2}\) and \( s_k^- \) acts on \( \frac{3}{2} \). It results in the state containing all four different projections, i.e. of the type \([1, 1, 1, 1]\). Similar discussion of all other partitions leads to the following graph:

\[
\begin{array}{c}
[0, 3, 0, 1] \\
[0, 2, 2, 0] \\
[1, 1, 1, 1] \\
[2, 0, 0, 2] \\
[1, 0, 3, 0]
\end{array}
\]

The lines join partitions, which are related by the action of bilinear terms \( s_j^+ s_k^- \); encircled partitions denote loops in this graph, i.e. for each state labeled by these partitions exist such a term \( s_j^+ s_k^- \) that a state labeled by the same partition is obtained after its action. For example, \( s_1^+ s_2^- |\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{1}{2} \rangle = 4|\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2}, -\frac{1}{2} \rangle \).

The obtained orbits have four different stabilizers: \( C_1 \), \( D^0_1 \), \( D^1_1 \), and \( D^2_1 \). Note that there are three orbits of the first type and two orbits of each of the other types. To introduce the linear structure one has to decompose (transitive) permutation representation \( R^{D_4}D_4 \) into (linear) irreducible ones. For these four groups these decompositions are as follows:

\[
\begin{align*}
R^{D_4}D_1 & = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \oplus 2E_1 , \\
R^{D_4}D_0 & = A_1 \oplus B_1 \oplus E_1 , \\
R^{D_4}D_1 & = A_1 \oplus B_2 \oplus E_1 , \\
R^{D_4}D_0 & = A_1 \oplus B_1 .
\end{align*}
\]

Therefore, the 44-dimensional space \( L_0 \) can be decomposed into nine subspaces labeled by \( \Gamma = A_1 \), three by \( \Gamma = A_2 \), seven by \( \Gamma = B_1 \), five by \( \Gamma = B_2 \), and ten by \( \Gamma = E_1 \). Analogous considerations for 40-dimensional space \( L_{M=1} \) give us numbers 7, 3, 7, 3, and 10, respectively. It means that amongst four \((44 - 40)\) multiplets with \( S = 0 \) two \((9 - 7)\) are labeled by \( A_1 \), and the other two \((5 - 3)\) by \( B_2 \). In the case of antiferromagnetic interactions the ground state has the symmetry \( A_1 \), so it belongs to the first pair.
