

Exact ground state properties of the classical Heisenberg model for giant magnetic molecules

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We find the exact ground state energy and magnetic moment for an arbitrary magnetic field H of the classical Heisenberg model of spins on the vertices of an icosidodecahedron. This model provides an accurate description of the magnetic properties of the giant paramagnetic molecule $\{\text{Mo}_{72}\text{Fe}_{30}\}$ in which 30 Fe^{3+} ions are coupled via antiferromagnetic exchange. The strong frustration of the magnetic interaction in the molecule is relaxed when the angle between nearest-neighbor spins is 120° . We predict that the magnetic moment is linear with H until saturating at a critical field H_c , and this is consistent with the results of a recent experiment at 0.46 K. We derive our results using a graph-theoretical construction and a special property, three-colorability, of the icosidodecahedron. We also consider spins on the vertices of an octahedron, icosahedron, and dodecahedron.

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The subject of molecular magnets has greatly advanced in recent years¹⁻⁴ and has led to the synthesis of bulk samples of large paramagnetic molecules with very weak intermolecular but strong intramolecular magnetic interactions. The neutral Keplerate species,⁴ abbreviated as $\{\text{Mo}_{72}\text{Fe}_{30}\}$, in the substance with molecular formula $[\text{Mo}_{72}\text{Fe}_{30}\text{O}_{252}(\text{Mo}_2\text{O}_7(\text{H}_2\text{O}))_2(\text{Mo}_2\text{O}_8\text{H}_2(\text{H}_2\text{O}))(\text{CH}_3\text{COO})_{12}(\text{H}_2\text{O})_{91}] \cdot 150 \text{H}_2\text{O} = \{\text{Mo}_{72}\text{Fe}_{30}\} \cdot 150 \text{H}_2\text{O}$, is by far the largest paramagnetic molecule synthesized to date. It is especially interesting due to the fact that 30 paramagnetic Fe^{3+} ions (spins $S=5/2$) are embedded within a molecule on the vertices of a regular Archimedean polytope, an icosidodecahedron⁵ (see Fig. 1). A crucial role is played by O-Mo-O bridges mediating antiferromagnetic coupling between nearest-neighbor Fe ions within a given molecule. For $\{\text{Mo}_{72}\text{Fe}_{30}\}$ we may thus focus on the magnetic behavior of a system of 30 interacting spins on the complex geometry of the icosidodecahedron. Because of the geometry of the spin sites and the antiferromagnetic exchange, magnetic frustration and competing ordered states are expected to occur. The analysis of the high-temperature ($T > 20$ K) susceptibility, which behaves according to a Curie-Weiss law, yields an exchange constant $J/k_B \approx 1.57$ K between nearest-neighbor spins.⁶ One generally expects quantum effects to be of importance for temperatures $T \leq 0.25S(S+1)J/k_B \approx 3.4$ K. Surprisingly, as is shown in Ref. 6, very good agreement between experimental data for the spin susceptibility with classical numerical simulations exists for $T > 0.1$ K. For these reasons it is extremely interesting to have insight into the nature of the ground state as well as the magnetic response of the classical Heisenberg system.

In this paper we find the exact ground state energy and magnetization for arbitrary magnetic field of the classical Heisenberg model of spins on an icosidodecahedron as a model for $\{\text{Mo}_{72}\text{Fe}_{30}\}$. The frustration of the magnetic interactions in the molecule is relaxed when the relative angle between nearest-neighbor spins is 120° . Using a graph-theoretical construction, we show that no global frustration is left after these bonds are formed. A special property, *three-colorability*, of the polytope is shown to be a necessary con-

dition for this behavior. Similar graph-theoretical techniques are used to determine the behavior in an external magnetic field and to analyze three additional polytopes, the octahedron, icosahedron, and dodecahedron.

We start from the classical Heisenberg model with spins located at the vertices of an icosidodecahedron within an external magnetic field \mathbf{H} :

$$\mathcal{H} = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - g \mu_B \sum_i \mathbf{H} \cdot \mathbf{S}_i. \quad (1)$$

The exchange constant J is chosen to be positive so as to describe antiferromagnetic coupling. Here the \mathbf{S}_i 's denote classical vectors of length⁷ $\sqrt{S(S+1)}$. The summation $\langle ij \rangle$ is over all distinct nearest-neighbor pairs on the molecule, g is the spectroscopic splitting factor, and μ_B denotes the Bohr magneton. In Fig. 2 we show a planar projection of the polytope; i.e., all edges and vertices correspond to the ones shown in Fig. 1. In what follows we will first derive an exact expression for the (classical) ground state energy E_0 of Eq.

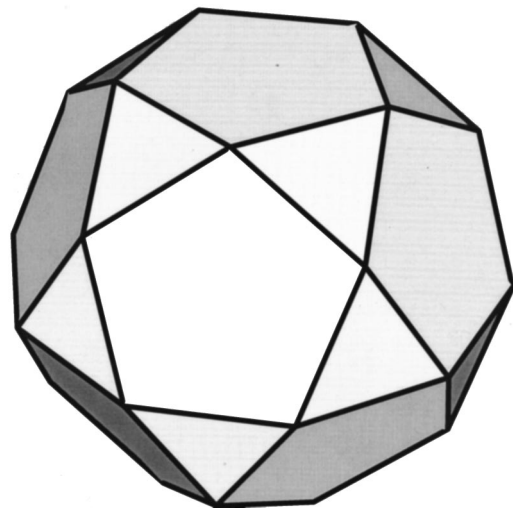


FIG. 1. The 30 Fe^{3+} ions of the $\{\text{Mo}_{72}\text{Fe}_{30}\}$ molecule are located on the vertices of an icosidodecahedron.

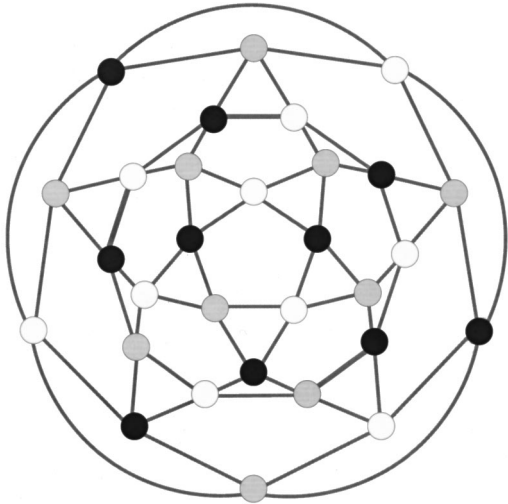


FIG. 2. Planar projection of the icosidodecahedron. All edges and vertices are identical to those shown in Fig. 1. The graph is three-colorable; i.e., one can decorate the graph with three colors such that no neighboring vertices have the same color. Physically, the three colors correspond to the three different directions of spins with a relative angle 120° .

(1) for $\mathbf{H}=0$, using a graph-theoretical construction. Next, we generalize the result to the case of a finite magnetic field so as to find $E_0(H)$ and $M(H)$, the field-dependent magnetic moment for $T=0$ K.

Our derivation of the exact ground state energy E_0 of Eq. (1) without magnetic field proceeds in three steps. First, we determine a lower bound for E_0 , which is based on the physical picture that the frustrated magnetic interaction is dominated by the arrangement of spins on the triangular faces of the icosidodecahedron. Second, we find an upper bound for E_0 by explicitly constructing a specific spin configuration and determining its energy. Third, we determine E_0 upon observing that both bounds, upper and lower, are in fact identical.

In order to obtain a good lower bound for the ground state energy, we use the fact that each bond between nearest-neighbor spins belongs to exactly one of the 20 triangles and that each spin belongs to exactly two triangles. Thus we can split the summation over all bonds according to

$$J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j = \frac{J}{2} \sum_{t=1}^{20} [\mathbf{s}_t^2 - 3S(S+1)] \geq 20E_\Delta, \quad (2)$$

where t denotes the index of the triangle with total spin $\mathbf{s}_t = \mathbf{S}_i + \mathbf{S}_j + \mathbf{S}_k$, and i, j , and k are the three sites that form triangle t . All bonds are taken into account by this procedure. Here $E_\Delta = -\frac{3}{2}JS(S+1)$ is the ground state energy of the classical Heisenberg model of spins on a single triangle. To obtain Eq. (2) we used the well-known result $\mathbf{S}_i \cdot \mathbf{S}_j = S(S+1)\cos(2\pi/3)$ for a classical triangle with antiferromagnetic exchange, where the relative angles between the three spins are all 120° , implying that the three spin vectors are coplanar. Note that $\mathbf{s}_t^2 = 0$ in this case. This leads to

$$E_0 \geq -30JS(S+1). \quad (3)$$

In the next step we calculate the energy \tilde{E} of a specific realizable spin configuration. This energy is necessarily an upper bound for the ground state energy, i.e.,

$$E_0 \leq \tilde{E}. \quad (4)$$

If we are able to find a configuration with energy $\tilde{E} = 20E_\Delta$, we can combine Eqs. (3) and (4) and have an exact expression for the ground state energy. Thus our procedure is successful if we can find a configuration with an energy which is 20 times the energy of the triangle ground state. In order to find out whether such a configuration exists, one may use the following recipe. Start with one given triangle on the icosidodecahedron and fix the spins to have relative angles of 120° . Fix all neighboring spins to have relative angles of 120° to those of the starting triangle. Continue this procedure trying to make an assignment for all 30 spins such that “on the other side” of the polytope nearest-neighbor spins meet the 120° requirement. If now all spin vectors are configured to have a relative angle of 120° between nearest neighbors, we will have found a configuration with energy $20E_\Delta$. Of course, for such a large molecule this recipe is very complex and cumbersome.

An elegant solution to this problem can be found by using a graph-theoretical approach. Here we interpret the projection of the molecule on the plane as a graph with vertices corresponding to Fe ions of the molecule (Fig. 2). Instead of analyzing relative spin directions on the molecule, we assign to each vertex of this graph one of three different colors. If we can color the graph in a manner that there are no neighboring vertices with the same color, the graph is called *three-colorable*.⁸ As explicitly shown in Fig. 2, the graph of the icosidodecahedron is indeed three-colorable. It is now easy to recognize that a three-colorable graph can be decorated by a spin configuration with all spins on all triangles having a relative angle of 120° between nearest neighbors and all spins are coplanar. Each of the three colors corresponds to one of the allowed spin vectors. Thus, due to the special property, three-colorability, of the icosidodecahedron, we have found a trial configuration with energy $\tilde{E} = 20E_\Delta$, which must be an upper bound for E_0 . Combining this result with Eq. (3), we arrive at the final result

$$E_0 = 20E_\Delta = -30JS(S+1). \quad (5)$$

We have thus found an exact expression for the ground state energy of the classical Heisenberg model of the icosidodecahedron.

We have been unable to rigorously exclude the possibility of noncoplanar ordering which is degenerate with the planar configuration described. However, numerical simulations⁶ performed on the classical Heisenberg model for temperatures $T < J/k_B$ support the fact that there are only configurations in which all spins are coplanar. Assuming this, we find from a straightforward case analysis that all possible allowable coplanar configurations can be generated from that shown in Fig. 2 by using an arbitrary automorphism of a graph of the icosidodecahedron and an arbitrary permutation of the three colors.

Our method can also be applied to other polytopes. In the case of the octahedron, which is also decomposable into triangles and the vertices admit a proper three-coloring, we find that all spins are coplanar with relative angle 120° between nearest neighbors. On the other hand, one cannot provide a proper three-coloring for an icosahedron. In this case four colors are necessary, implying that the angle between nearest-neighbor spins is different from 120° and that the spins are not coplanar. Both conclusions are confirmed in numerical simulations which give⁶ a relative angle of 116.6° for nearest-neighbor spin vectors. Finally, the dodecahedron is a polytope which is three-colorable; however, it is not decomposable in terms of triangles, but only in terms of pentagons. For this system numerical simulations show⁶ that there is a relative angle of 138.2° between nearest-neighbor spin vectors. We thus expect a considerably different magnetic response at low temperatures for spins on an icosahedron or dodecahedron.

The argumentation of the previous paragraphs, including our graph coloring construction, can straightforwardly be generalized to the case of a finite magnetic field. Similar to Eq. (2), we rewrite the Hamiltonian as a sum over terms from different triangles:

$$\mathcal{H} = \sum_{i=1}^{20} \left[\frac{J}{2} [\mathbf{s}_i^2 - 3S(S+1)] - \frac{g\mu_B}{2} \mathbf{H} \cdot \mathbf{s}_i \right]. \quad (6)$$

The factor of $\frac{1}{2}$ in front of the magnetic field term takes into account that each spin is shared by two neighboring triangles. A lower bound for the ground state energy is again given by that of a single triangle in a field $H/2$ times the number of triangles, i.e.,

$$E_0(H) \geq 20E_\Delta(H/2). \quad (7)$$

Because of the three-colorability of the polytope, a configuration that corresponds to the ground state energy of a single triangle in half the field can be utilized for all triangles to yield a realizable configuration of the 30 spins of the icosidodecahedron. This globally compatible configuration also has energy $20E_\Delta(H/2)$, and it serves as an upper bound to $E_0(H)$. Thus the ground state energy is

$$E_0(H) = 20E_\Delta(H/2). \quad (8)$$

The energy of the Heisenberg model with magnetic field on a triangle was determined in Sec. II B 2 of Ref. 9. Using those results and Eq. (8), we obtain

$$E_0(H) = -20 \left(\frac{3}{2} JS(S+1) [1 + 3(H/\tilde{H}_c)^2] \right), \quad (9)$$

for $H < \tilde{H}_c$, where $\tilde{H}_c = 6J\sqrt{S(S+1)}/(g\mu_B)$, and

$$E_0(H) = -120JS(S+1) [1 + 3(H - \tilde{H}_c)/(2\tilde{H}_c)], \quad (10)$$

for $H > \tilde{H}_c$. These results demonstrate that the magnetic properties of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ are due to the strong magnetic correlations on its triangles.

Using our explicit formulas for $E_0(H)$, we immediately arrive at expressions for experimentally relevant quantities,

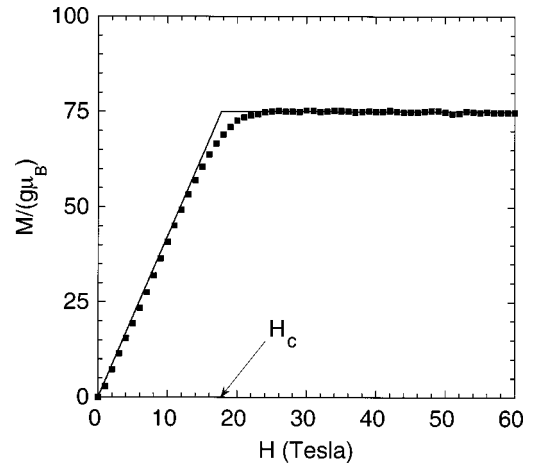


FIG. 3. Magnetic field dependence of the magnetic moment of the classical Heisenberg model for spins on an icosidodecahedron in the low-temperature limit (solid lines). Below the critical field $H_c = 17.7$ T, M is strictly linear in H , whereas it is saturated for larger fields. Experimental data (Ref. 6) for a sample of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ at 0.46 K as obtained using a pulsed field technique are given by the solid squares. Use of the pulsed field leads to an estimated effective temperature of approximately 4 K. To keep the figure legible, we have chosen to display only a very small fraction of the measured data set.

the ground state magnetic moment $M(H) = -\partial E_0(H)/\partial H$ and the ground state susceptibility $\chi = \partial M/\partial H$. The behavior for the ground state moment is shown by the solid lines in Fig. 3. Note the linear behavior up to the critical field \tilde{H}_c . For larger fields the moment is saturated and independent of H . At this point we remark that the moment of the saturated state is $30g\mu_B\sqrt{S(S+1)}$. However, this value is larger than the maximally allowed moment $M_{\max} = 30g\mu_B S$ of a quantum-mechanical system, an effect which is, of course, beyond our classical treatment. To adapt it to a description of $\{\text{Mo}_{72}\text{Fe}_{30}\}$, we suggest that the linear dependence of M on H should be used until M_{\max} is reached at the critical field

$$H_c = \frac{S}{\sqrt{S(S+1)}} \tilde{H}_c = \frac{6JS}{g\mu_B}; \quad (11)$$

for larger fields, M remains saturated at this value. Due to the rather small value of J , the physically relevant critical field H_c is experimentally accessible. Using the values of all the relevant parameters, including⁶ $g = 1.974$, Eq. (11) yields $H_c = 17.7$ T. These predictions are consistent with the results of recent⁶ measurements (shown as solid squares in Fig. 3) at 0.46 K on $\{\text{Mo}_{72}\text{Fe}_{30}\}$. In particular, the observed value of H_c is consistent with our predicted value.

Using Eq. (9), we note that for $H < H_c$, the exact value for the classical ground state susceptibility per molecule is given by

$$\chi = 5(g\mu_B)^2/J. \quad (12)$$

This translates into a value of $\chi = 4.67$ emu/mol. This value coincides with both the low-temperature value of the suscep-

tibility determined by classical numerical simulations⁶ and, remarkably, with susceptibility measurements performed⁶ at $H=0.5$ T down to 0.12 K.

Summarizing, using a graph-theoretical approach, we have determined the classical ground state energy of the Heisenberg model of an icosidodecahedron, the structure of $\{\text{Mo}_{72}\text{Fe}_{30}\}$, the largest magnetic molecule synthesized to date. Using two special properties of the icosidodecahedron graph (being decomposable into triangles and its proper three-colorability), we were able to show that in the ground state the relative angle between nearest-neighbor spin vectors is 120° . This surprising result has immediate consequences for the magnetic field dependence of the magnetic moment and the susceptibility. We found that the limiting ($T \rightarrow 0$ K) magnetic moment is strictly linear with H until a critical field $H_c \approx 17.7$ T and is saturated (all spins parallel) for $H > H_c$. Recent measurements⁶ of M versus H , performed at 0.46 K, are consistent with these predictions, including our value for H_c . Using the same line of argument, analogous results can be derived for the octahedron. We have predicted that the icosahedron and dodecahedron will have a different magnetic response at low temperatures.

Our strategy for determining the ground state energy was to derive an upper as well as lower bound for E_0 , which are

identical, where the upper bound was determined from an explicit construction. This is similar to the strategy used by Moessner and Chalker¹⁰ who also determined the classical ground state of the pyrochlore lattice, consisting of tetrahedra that share sites, where frustration plays an essential role for the determination of the ground state configuration as well.¹¹

The paramagnetic molecule $\{\text{Mo}_{72}\text{Fe}_{30}\}$ is truly exceptional since the present *classical* treatment, limited to 0 K, provides a result for the dependence of the magnetic moment on magnetic field that is consistent with measurements at 0.46 K. The success of the classical treatment is explained by a study of an approximate quantum model^{12,13} of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ showing that quantum deviations from the classical results should be manifested only below 50 mK.

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