Two-dimensional molecular magnets with weak topological invariant magnetic moments: mathematical prediction of targets for chemical synthesis

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An open problem in applied mathematics is to predict interesting molecules that are realistic targets for chemical synthesis. In this paper, we use a spin Hamiltonian-type model to predict molecular magnets (MMs) with magnetic moments that are intrinsically robust under random shape deformations to the molecule. Using the concept of convergence in probability, we show that for MMs in which all spin centres lie in-plane and all spin centre interactions are ferromagnetic, the total spin of the molecule is a ‘weak topological invariant’ when the number of spin centres is sufficiently large. By weak topological invariant, we mean that the total spin of the molecule depends only upon the arrangement of spin centres in the molecule, and is unlikely to change under shape deformations to the molecule. Our calculations show that only between 20 and 50 spin centres are necessary for the total spin of these MMs to be a weak topological invariant. The robustness effect is particularly enhanced for two-dimensional ferromagnetic MMs that possess a small number of spin rings in the structure.
1. Introduction

Compared with physics or even biology, the application of non-elementary mathematics to problems in chemistry remains relatively unexplored. The purpose of this paper is to show how analytical concepts such as convergence in probability and rates of convergence can be used to predict interesting new molecules that are reasonable targets for chemical synthesis. As a convenient example, we consider a class of molecules called molecular magnets (MMs). MMs are large molecules containing 4–100 electron spin centres (typically the d electrons of transition metal ions) coupled in such a way that the molecule has a large total electron spin and an appreciable magnetic moment [1–4]. MMs possess unique magnetic properties that span both classical and quantum domains, making them of great fundamental interest, and the elaborate structures of large MMs make them challenging targets for synthetic chemistry [5].

Figure 1 shows the structure of the prototypic example of an MM, Mn$_{12}$ (acetate) [formally Mn$_{12}$O$_{12}$(O$_2$CCH$_3$)$_{16}$(H$_2$O)$_4$]. Mn$_{12}$ (acetate) consists of four Mn$^{4+}$ ions and eight Mn$^{3+}$ ions connected together through Mn–O–Mn or Mn–O–O–Mn bridges. The coupling between the electrons of the Mn ions via the Mn–O–Mn and Mn–O–O–Mn bridges gives the Mn$_{12}$ (acetate) molecule a total electron spin of 10 [2,6]. The structure of MMs is often described in terms of the arrangement of spin centres in the molecule. In the case of Mn$_{12}$ (acetate), the four Mn$^{4+}$ ions are arranged in a tetrahedral ‘core’, with the eight Mn$^{3+}$ ions arranged in a ring around the periphery of the tetrahedron. Many other types of MMs with a wide range of spin centre arrangements have also been characterized in the literature. A small sample includes the tetrahedral, cubic and planar Mn$_4$ and lanthanide-4 complexes [7–10], the cage-like Fe$_{15}$ and Fe$_{36}$ complexes [11,12], the Fe$_{10}$ ring [13], the dual-tetrahedral Fe$_7$ complex [14] and the large torus-shaped Mn$_{84}$ complex [15,16].

A key problem that is currently facing the MM community is how to bind MMs to conducting surfaces or thin films in such a way that the magnetic properties of the molecule remain intact. Adsorption of MMs to surfaces is necessary for technological applications of MMs and also to study their magnetization properties in scanning tunnelling microscopy experiments [17,18]. However, the equilibrium gas-phase shape of an MM is not expected to be maintained upon adsorption owing to various uncontrollable factors, such as the orientation of the molecule upon collision with the surface, the small-scale roughness of the surface and the thermal motions of the atoms of the surface. Experimental and quantum chemical studies have shown that the magnetic polarization of Mn$_{12}$ (acetate) is reduced when adsorbed to metallic surfaces owing to oxidation of the Mn ions and structural deformations of the molecule [19–21]. The magnetic properties of a different Mn$_{12}$ complex were also reported to be affected when the molecule was adsorbed on a gold surface with a self-assembled monolayer [22]. Other studies have further shown that significant structural deformations and changes in the spin centre–spin centre coupling strengths occur when Cr$_7$Ni and Mn$_6$ MMs are adsorbed on gold surfaces [23–25]. On the other hand, some experiments have achieved surface-adsorbed MMs with intact magnetic properties. For example, it has been demonstrated that by a careful choice of deposition method and substrate surface, the magnetic properties of Mn$_{12}$ (acetate) could be preserved upon adsorption to a surface [26,27]. Moreover, it was recently reported that the magnetic properties of certain Fe$_4$ and Fe$_2$Cr complexes are relatively robust upon adsorption to a gold surface [28–30]. While these experimental advancements are promising, it is still desirable to identify other MMs with magnetic properties that are intrinsically stable to shape deformations to the molecule.

Let us consider the task of using a mathematical model to predict structures for MMs with robust magnetic properties under shape deformations. In order to achieve this, we need a model that is sufficiently idealized yet still realistic enough to capture key molecular properties of interest. MMs are a rare class of molecules for which such models—spin Hamiltonians—are available. In its simplest form, the spin Hamiltonian can be written as

$$\hat{H} = - \sum_{ij} J_{ij} \hat{s}_i \cdot \hat{s}_j, \quad (1.1)$$
where the sum runs over all pairs of interacting spin centres (e.g. Mn ions) in the molecule, $J_{ij}$ measures the coupling strength (exchange energy) between spin centres $i$ and $j$, and $\hat{s}_i$ is the spin operator for spin centre $i$. Despite their simplicity, spin Hamiltonian models provide a qualitatively correct description of the magnetic properties of MMs [31,32], and with certain additional terms, are even capable of describing some exotic magnetic phenomena such as quantum tunnelling of the magnetization in the Mn$_{12}$(acetate) molecule [33]. In spin Hamiltonian models, much of the detailed physics of the MM is condensed into the coupling constants $J_{ij}$. This prevents spin Hamiltonian models from describing certain phenomena such as the origin of the spin centre–spin centre coupling in an MM (e.g. the superexchange mechanism through the oxygen atoms [34,35]) or how the coupling strengths are affected by the molecular structure of the MM (e.g. the organic groups attached to the O atoms in Mn$_{12}$-type molecules [36,37]). Spin Hamiltonian models are therefore potentially useful if we are strictly interested in predicting MMs with interesting magnetic properties, such as robustness of the total spin under molecular shape deformations.

In this paper, we use a modification of the spin Hamiltonian model to show that for a certain class of MMs, the total spin behaves like a weak topological invariant when the number of electron spin centres in the molecule is sufficiently large and the molecule is in the ground state of the total spin. By ‘weak topological invariant’, we mean a physical property that only depends upon the arrangement of spin centres in the equilibrium molecule and is unlikely to change when the equilibrium shape of the molecule undergoes a small, random deformation, provided that the deformations do not alter the chemical structure of the molecule. Such random deformations might arise from the thermal motion of the adsorbent surface or from adsorption onto a particularly rough region of the surface. The prefix ‘weak’ indicates that there may exist deformations that do cause large changes to the total spin but have a low probability of occurring. While our definition of weak topological invariant is more restrictive than the usual definition of topological invariant, it is still a sufficient criterion for identifying robust molecules. The class of MMs that are considered are where all spin centre interactions in the molecule are ferromagnetic, all distances between interacting spins centres are equal, and all spins centres

![Figure 1. Structure of the Mn$_{12}$(acetate) molecule. The large atoms are Mn ions, and the Mn ions are connected together by oxygen atoms and acetate ligands. The radii of the Mn atoms have been enlarged from their usual ionic radii for clarity. (Online version in colour.)](image)
lie in a two-dimensional plane (two-dimensional ferromagnetic MMs, 2DFMMs). While these are significant idealizations compared to realistic MMs, our model can be extended to include antiferromagnetic interactions and varying distances between interacting spin centres. However, it turns out that for 2DFMMs, the weak topological invariant property appears quite naturally from the model. We will see that when the molecule contains a relatively small number of 'spin rings' (i.e. interacting spin centres arranged in a ring shape), only between 20 and 50 spins are necessary for the total spin to behave like a weak topological invariant. While such large two-dimensional MMs do not appear to have been reported in the chemistry literature, they are within the size range of most three-dimensional MMs that have been reported (between about 4 and 100 spins). In particular, we find that ferromagnetic MMs composed of only one spin ring and around 20 spins have total spins that are particularly robust to shape deformations. Smaller rings composed of 8–10 metal ions are well known in the MM literature [13,38], and therefore the 'large' spin rings that we predict here may be reasonable targets for chemical synthesis. As will be seen, our definition of weak topological invariant is closely related to the mathematical concept of convergence in probability of a random variable, and the task of predicting two-dimensional MMs with weak topological invariant total spins is related to the important problem of bounding rates of convergence in probability. This work might therefore be regarded as a kind of 'mathematical chemistry', i.e. the prediction of interesting molecules using non-elementary mathematical concepts.

2. Model

We first develop the model for the general case where the spins of the MM are not restricted to a two-dimensional plane. The equilibrium structure of the MM is represented as a collection of points (‘vertices’) in a three-dimensional Euclidean space $\mathbb{R}^3$, with each vertex representing the location of an electron spin centre in the MM (e.g. Mn ions). Edges are drawn between vertices that correspond to interacting spin centres (e.g. Mn–O–Mn bridges). Only nearest-neighbour interactions are considered. Vertex $i$ lies at point $r_i$ and the length of the edge between vertex $i$ and vertex $j$ is $r_{ij}$. We assume constant edge lengths, i.e. that $r_{ij} = r = 1$ (in appropriate units) for all interacting spin centres. The strength of the interaction between spin centre $i$ and spin centre $j$ is described by associating a function $J_{ij} = J(r_{ij})$ with the edge $(i,j)$. $J_{ij}$ describes the exchange interaction between the electrons at spin centres $i$ and $j$. Because all edges have a constant length, the functions $J_{ij}$ are independent of $i$ and $j$, and are equal to $J(r)$. We assume that all interactions between spin centres are ferromagnetic, i.e. that $J(r) > 0$. Shape deformations to the molecule are modelled by adding random vectors $X_1, X_2, \ldots$ to the corresponding position vectors $r_1, r_2, \ldots$. The components of $X_1, X_2, \ldots$ are independent Gaussian random variables with mean 0 and variance $\sigma^2$. Following the deformation, the interaction strength between spin centres $i$ and $j$ changes by an amount $\Delta J_{ij} = J(r + \Delta r_{ij}) - J(r)$, where $\Delta r_{ij}$ is the change in the distance between vertices $i$ and $j$ following the deformation. The deformations are assumed to be first order in $\Delta r_{ij}$. A simplified sketch of the model is shown in figure 2. A deformation roughly resembles the procedure used in Monte Carlo simulations of the compressible Ising model [39].

The effect of the deformation on the energy of the ground total spin state $|S^2, M_s\rangle_g$ of the MM can be analysed with the spin Hamiltonian $\hat{H}$. Before the deformation, $\hat{H} = -\sum_{(i,j)\in E} J_{ij} \hat{s}_i \cdot \hat{s}_j$, where $E$ is the collection of edges in the molecule. Under the ferromagnetic coupling assumption, the energy of $|S^2, M_s\rangle_g$ is $-n_e J$, where $n_e$ is the number of edges in the molecule and $J = J(r)$. The deformation adds a perturbation $\hat{H}' = -\sum_{(i,j)\in E} \Delta J_{ij} \hat{s}_i \cdot \hat{s}_j$ to $\hat{H}$. The perturbation to the energy of $|S^2, M_s\rangle_g$ is therefore $-\sum_{(i,j)\in E} \Delta J_{ij}$. Now, consider the random variable $R = \sum_{(i,j)\in E} \Delta J_{ij}/(n_e)$. To first order, $R$ can be written as

$$R = \frac{c}{n_e} \sum_{(i,j)\in E} \Delta r_{ij},$$

where $c = dJ(r + \Delta r)/d\Delta r|_{\Delta r=0}$. $c$ measures the variation in the spin centre–spin centre coupling strength about the equilibrium separation. $R$ measures the size of the perturbation to the energy.
Figure 2. Sketch of the model for an Mn$_{12}$-like MM undergoing a random shape deformation. Only some of the interaction constants $J_{ij}$ and random vectors $X_i$ are shown for clarity. The sketch shows a more general case where the distance between neighbouring spin centres is allowed to vary.

of $|S^2, M_s\rangle_g$ relative to the unperturbed energy of $|S^2, M_s\rangle_g$ under the random deformation. If $R$ is close to zero, then the change in the energy of $|S^2, M_s\rangle_g$ is also small under the deformation. This means that if the molecule is initially in state $|S^2, M_s\rangle_g$, then it will not make a transition out of $|S^2, M_s\rangle_g$ to another total spin state under the deformation. In other words, if $R$ is sufficiently small for a deformation, then the direction and magnitude of the total spin of a ground state MM will not change under the deformation.

We say that the total spin of a particular MM is a *weak topological invariant* if

$$P(|R|<\epsilon) > 1 - \epsilon,$$

for some small $\epsilon > 0$, where $P$ is the probability measure (from the probability space on which $R$ is defined). In order to determine whether a particular structure for an MM has a robust total spin, we therefore need to compute the distribution of $R$ and verify whether equation (2.2) is satisfied. In appendix A, it is shown that $R$ is a normal random variable with mean zero and variance,

$$\text{var}(R) = 2\sigma^2 \left( \frac{c}{J} \right)^2 Q,$$

where

$$Q = \frac{1}{n_e} + \frac{1}{n_e^2} \sum_{\phi \in A} \cos \phi.$$

Here, $A$ is the set of internal angles of the molecule (angles between adjacent edges). $Q$ is always positive because $\text{var}(R) \geq 0$ by definition. Because $R$ is a normal random variable, values of $P(|R|<\epsilon)$ that are close to 1 will be achieved for MMs that have small $\text{var}(R)$. Equation (2.3) therefore shows that the total spin of an MM will be stable to shape deformations if the factors $|c/J|$ and $Q$ are small. $|c/J|$ measures the degree to which the spin–spin interaction strength within the MM changes under an arbitrary deformation. There do not appear to be any experimental data or quantum chemical calculations that can be used to estimate a realistic value of $|c/J|$. We therefore set $|c/J|=2$, which is reasonable, because for small shape deformations, the variation of $J$ about $r$ will be approximately quadratic. The factor $Q$ is related to the geometric structure of the MM. Equation (2.3) therefore allows us to explore how the geometry of an MM is related to the stability of the total spin through equation (2.4). For MMs containing more than several spins, this task is unsuitable for quantum chemical calculations with current computing power.

Let us consider the Platonic solids (the tetrahedron, octahedron, cube, dodecahedron and icosahedron) as an example calculation. The Platonic solids resemble many of the spin centre arrangements that appear in real MMs. For example, the tetrahedral and cube spin arrangement appears in some Mn$_4$ and Ln$_4$ complexes [8–10], and the octahedral spin arrangement appears in...
the Mn$_6$Br$_4$(Me$_2$dbm)$_6$ ion [40]. We can compute $P(|R| < \epsilon)$ using the formula

$$P(|R| < \epsilon) = P(R < \epsilon) - P(R < -\epsilon).$$  \hfill (2.5)

Using $\epsilon = 0.05$, $\sigma_x = 0.15$ (i.e. deformations that shift the spin centres a distance of 15% of the edge lengths on average) and the formula for $\text{var}(R)$ and $Q$ above, we find that $P(|R| < \epsilon) = 0.16$ for the tetrahedron ($n_e = 6$), $P(|R| < \epsilon) = 0.31$ for the cube ($n_e = 12$), $P(|R| < \epsilon) = 0.23$ for the octahedron ($n_e = 12$), $P(|R| < \epsilon) = 0.70$ for the dodecahedron ($n_e = 30$), and $P(|R| < \epsilon) = 0.48$ for the icosahedron ($n_e = 30$). We would therefore expect the total spin of a ferromagnetic MM with a tetrahedral arrangement of spins to be much more sensitive to shape deformations to the molecule than the total spin of an MM with a dodecahedral arrangement of spins. However, in none of these cases is $P(|R| < 0.05) > 0.95$, and therefore none of these molecules has a weak topological invariant total spin.

Before proceeding, let us establish the connection between the definition of a weak topological invariant and the mathematical concept of convergence in probability. Suppose we have an infinite sequence of MMs labelled by $1, 2, \ldots$, such that for all $\epsilon > 0$, $P(|R_k| < \epsilon) \to 1$ as $k \to \infty$. By definition, this means that the sequence of random variables $R_1, R_2, \ldots$ converges to zero in probability. Now, convergence in probability of the sequence $R_1, R_2, \ldots$ can be described by the Ky Fan metric [41],

$$d(R_k, 0) = \inf\{\delta > 0 : P(|R_k| < \delta) > 1 - \delta\},$$  \hfill (2.6)

which shows that for any fixed $\epsilon > 0$, there exists an integer $n_0$ such that for all $k > n_0$, $P(|R_k| < \epsilon) > 1 - \epsilon$. Hence, all MMs with labels greater than $n_0$ have weak topological invariant total spins. Moreover, if the rate of convergence in probability of the sequence $R_1, R_2, \ldots$ is known, then the integer $n_0$ can be evaluated, and MMs with weak topological invariant total spins can be identified. We will make use of this connection further in §3.

3. Two-dimensional ferromagnetic molecular magnets

The connection between weak topological invariance and convergence in probability suggests that a better strategy for searching for MMs with weak topological invariant total spins is to set up a sequence of MMs such that $R \to 0$ in probability. We therefore consider the special case of 2DFMMs. Let $P_k$ denote a polygon with $k$ spin centres and constant edge lengths. $P_{k_1}|P_{k_2}$ indicates that the polygons $P_{k_1}$ and $P_{k_2}$ share an edge, and $(P_{k_1}|P_{k_2})P_{k_3}$ indicates that polygon $P_{k_3}$ shares an edge with any one of the edges of the structure $P_{k_1}|P_{k_2}$. An arbitrary 2DFMM can be constructed in the following way. Choose $N$ polygons $P_{k_1}, P_{k_2}, \ldots, P_{k_N}$ and create the structure $P_{k_1}|P_{k_2}$. Then create the structure $(P_{k_1}|P_{k_2})P_{k_3}$, and then the structure $((P_{k_1}|P_{k_2})P_{k_3})P_{k_4}$, and so on. The resulting structure has the form (figure 3)

$$T = (((P_{k_1}|P_{k_2})\ldots)|P_{k_{N-1}})|P_{k_N}).$$  \hfill (3.1)

The polygons $P_{k_1}, P_{k_2}, \ldots, P_{k_N}$ of $T$ are required to all lie within the same plane, and the internal angles of each polygon are fixed at $\pi - 2\pi/k$, where $k$ is the number of spins in the polygon. Note that the atoms of the ligands connecting the spin centres are not restricted to lie within the two-dimensional plane of the spin centres. We further require that a vertex in $T$ can only belong to two polygons at most. This means that for any three polygons $P_i$, $P_j$ and $P_l$ in a 2DFMM structure, such that $P_i|P_j|P_l$, $P_i$ and $P_l$ are separated by at least one edge. This assumption is reasonable because for 2DFMMs that do not satisfy this condition, the ligands may be very close together or overlapping in space. Several examples of real MMs that have nearly planar geometries have been reported in the literature, including an Fe$_4$ complex [42], an Fe$_8$ complex [43] and an Fe$_{19}$ complex [44].
(a) Convergence in probability of sequences of two-dimensional ferromagnetic molecular magnets

We can create a sequence of 2DFMMs as follows. First, note that an arbitrary 2DFMM can be classified according to \((n_v, n_e, N)\), where \(n_v\) is the number of vertices, \(n_e\) is the number of edges, and \(N\) is the number of polygons. Applying Euler's formula to a 2DFMM gives the result \(n_v = n_e + N - 1\), which shows that the value of \(n_e\) is known if both \(n_v\) and \(N\) are specified. We can therefore use the two numbers \((n_v, N)\) to divide the 2DFMMs into classes. Now, fix a value of \(N\) (say, \(N_0\)) and for each class of 2DFMMs with \(N\) fixed at \(N_0\), choose the 2DFMM that has the largest value of \(Q\) in equation (2.4). For any fixed \(N\), we can therefore construct an infinite sequence of 2DFMMs such that the number of vertices \(n_v\) increases along the sequence. Our next goal is to show that for such a sequence, \(R \to 0\) in probability as \(n_v \to \infty\). In the following, a subscript \((n_v, N)\) on a quantity means that the quantity pertains a 2DFMM from the class \((n_v, N)\).

For a given class \((n_v, N)\), let us first identify a 2DFMM that has the largest value of \(Q_{(n_v, N)}\). Because \(n_e\) is fixed for a 2DFMM in the class \((n_v, N)\), it is sufficient to consider the quantity

\[
\Phi_{(n_v, N)} = \sum_{\phi \in A} \cos \phi
\]

from equation (2.4). We propose that a structure of the type shown on the right-hand side of figure 3 (the ‘maximal structure’) has the largest value of \(\Phi_{(n_v, N)}\) of all 2DFMMs in the class \((n_v, N)\). Let the notation \(P_{k_1} c P_{k_2} \ldots P_{k_c}\) indicate that the polygon \(P_{k_1}\) shares edges with \(c\) polygons of the form \(P_{k_j}\), and let \(P_{k_1}^c = P_{k_1}\) \(P_{k_2}\) \(P_{k_3}\) \(\ldots\) \(P_{k_c}\), where the polygon \(P_{k_1}\) appears \(c\) times in the structure \(P_{k_1} P_{k_1}^c \ldots P_{k_c}\).

The maximal structure for the class \((n_v, N)\) can be written as

\[
T^*_{(n_v, N)} = \begin{cases} 
  P_{n_v - 2(N - 1)(N - 1)} P_{4v - 2(N - 1)} & \text{if } (N - 1) - A_{(n_v, N)} \leq 0, \\
  (A_{(n_v, N)} - 1) P_4 P_{n_v - 2(N - 1)} | P_4^{N - A_{(n_v, N)}}, & \text{if } (N - 1) - A_{(n_v, N)} > 0,
\end{cases}
\]

where \(A_{(n_v, N)} = (n_v - 2(N - 1))/2\) if \(n_v - 2(N - 1)\) is even and \(A_{(n_v, N)} = (n_v - 2(N - 1) - 1)/2\) if \(n_v - 2(N - 1)\) is odd. \(A_{(n_v, N)}\) is the maximum number of polygons that can share an edge with the polygon \(P_{n_v - 2(N - 1)}\). The factor \(\Phi^*_{(n_v, N)}\) for the maximal structure works out to be

\[
\Phi^*_{(n_v, N)} = (n_v - 2(N - 1)) \cos \frac{2\pi}{n_v - 2(N - 1)} - 2(N - 1) \sin \frac{2\pi}{n_v - 2(N - 1)},
\]

if \((N - 1) - A_{(n_v, N)} \leq 0\) and

\[
\Phi^*_{(n_v, N)} = (n_v - 2(N - 1)) \cos \frac{2\pi}{n_v - 2(N - 1)} - 2A_{(n_v, N)}
\]

\[
\times \sin \frac{2\pi}{n_v - 2(N - 1)} - 2(N - A_{(n_v, N)} - 1),
\]

if \((N - 1) - A_{(n_v, N)} > 0\).
if \((N - 1) - A_{n_v,N} N > 0\). Our proposition that \(\Phi^*_n \geq \Phi_{(n_v,N)}\) for any 2DFMM in the class \((n_v,N)\) was confirmed via Monte Carlo simulations. In these simulations, we generated \(10^5\) independent 2DFMMs with \(N\) polygons, where \(N\) was uniformly sampled between 2 and 100 and \(k_1, \ldots, k_N\) were uniformly sampled between 4 and 10. We also performed simulations of \(10^3\) independent 2DFMMs with \(k_2, k_4, \ldots\) sampled between 4 and 5 and \(k_3, k_5\) sampled between 6 and 10 to explore the effect of combinations of small and large neighbouring polygons. In every simulation, it was found that \(\Phi_{(n_v,N)}\) was always equal to or less than \(\Phi^*_n\) for the maximal structure \(T^*_n\). For any 2DFMM from the class \((n_v,N)\), we can therefore estimate \(Q_{(n_v,N)}\) with the inequality

\[
Q_{(n_v,N)} \leq Q^*_n = \frac{1}{n_v + N - 1} + \frac{\Phi_{(n_v,N)}}{(n_v + N - 1)^2}.
\]  

(3.6)

Moreover, we can estimate the probability \(P(|R_{(n_v,N)}| < \epsilon)\) for any 2DFMM from the class \((n_v,N)\) with the inequality

\[
P(|R_{(n_v,N)}| < \epsilon) \geq P(Z_{(n_v,N)} < \epsilon) - P(Z_{(n_v,N)} < -\epsilon),
\]  

(3.7)

where \(Z_{(n_v,N)}\) is a Gaussian random variable with mean 0 and variance \(\text{var}(R) = 2\sigma_x^2 \epsilon / f R^2 Q^*_n\). The bounds in equations (3.6) and (3.7) are the tightest bounds to \(Q_{(n_v,N)}\) and \(P(|R_{(n_v,N)}| < \epsilon)\) that can be constructed for an arbitrary 2DFMM from the class \((n_v,N)\). Proving equations (3.6) and (3.7) rigorously is very difficult, so we do not attempt it here.

Let us now fix a value of \(N\) and consider the sequence of 2DFMMs with increasing \(n_v\) that was constructed previously. The previous paragraph shows that this is actually a sequence of maximal structures. The right-hand side of equation (3.6) shows that \(Q^*_n \to 0\) as \(n_v \to \infty\) for any fixed \(N\). Now, let us consider any infinite sequence of 2DFMMs (not necessarily maximal structures) such that the number of vertices \(n_v\) is increasing to infinity and \(N\) is fixed. The upper bound in equation (3.6) then shows that \(Q_{(n_v,N)} \to 0\) as \(n_v \to \infty\). Equation (2.3) and the Markov inequality then shows that for this sequence, \(P(|R_{(n_v,N)}| < \epsilon)\) also converges to 1 for all \(\epsilon > 0\), and hence that \(R_{(n_v,N)} \to 0\) in probability (note that this is not a trivial consequence of the law of large numbers because the random variables in the numerator of equation (2.1) are not independent). The definition in equation (2.2) then shows that the total spin of any sufficiently large 2DFMM is a weak topological invariant.

(b) Predictions of two-dimensional ferromagnetic molecular magnets with weak topological invariant total spins

The above construction shows that for any arbitrary 2DFMM with \(n_v\) spin centres and \(N\) polygons, \(P(|R| < \epsilon)\) is bounded below according to equation (3.7). We can use this to estimate the number of spin centres that a 2DFMM must have for the total spin to be a weak topological invariant. A plot of \(P(Z_{(n_v,N)} < \epsilon) - P(Z_{(n_v,N)} < -\epsilon)\) is shown in figure 4 using \(\sigma_x = 0.15\) and \(\epsilon = 0.05\) for various \(n_v\) and \(N\). When \(P(Z_{(n_v,N)} < \epsilon) - P(Z_{(n_v,N)} < -\epsilon)\) exceeds the value 0.95, then the total spin of any 2DFMM with \(n_v\) spin centres and \(N\) polygons can be regarded as a weak topological invariant. It can be seen that for \(N\) between 1 and 5, only between 20 and 50 spins are needed for the total spin of a 2DFMM to be a weak topological invariant, whereas for \(N\) between 6 and 10, around 60–80 spins are needed for the total spin to be a weak topological invariant. This calculation therefore shows that the stability of the total spin of a 2DFMM is enhanced when the number of rings in the molecule is small. Some examples of 2DFMMs with weak topological invariant total spins are shown in figure 5. 2DFMMs such as these containing around 20–50 spins are much smaller than the largest MMs that have been reported in the literature (such as the \(Mn_{184}\) torus [15,16]), and therefore 2DFMMs of this size built from a small number of spin rings (between 1 and 5) may be reasonable targets for synthetic chemistry. A particularly stable total spin can be achieved when the molecule contains only one spin ring. Smaller molecules of this
Figure 4. Plots of $P(Z_{(n,N)} < \epsilon) - P(Z_{(n,N)} < -\epsilon)$ for $\epsilon = 0.05$. Starting from the left, the curves correspond to $N = 1$ (one spin ring) up to $N = 10$ (10 spin rings) in order. The curves are tight lower bounds to $P(|R_{(n,N)}| < \epsilon)$ for any arbitrary 2DMM with $n_v$ spin centres and $N$ spin rings. The regions where $P(Z_{(n,N)} < \epsilon) - P(Z_{(n,N)} < -\epsilon) > 0.95$ are where the total spin is a weak topological invariant.

Figure 5. Examples of 2DSFMMs with weak topological invariant total spins for $\epsilon = 0.05$. (a) $n_v = 18$, $N = 1$. (b) $n_v = 30$, $N = 2$. (c) $n_v = 42$, $N = 4$.

type consisting of 8–10 metal ions have been widely studied in the literature [13,38]. Slightly larger spin rings consisting of 20 ions therefore appear to be very reasonable targets for the synthesis of MMs with weakly topological invariant total spins.

4. Discussion and final remarks

By using a modification of the spin Hamiltonian model, we studied how the energy of the ground total spin state of an MM varies under small, random shape deformations to the molecule. While we have focused on the idealized case of ferromagnetic MMs, our model can also be applied to other cases by allowing for the coupling constants and distances between pairs of spins to vary. However, the advantage of studying the ferromagnetic case is that it straightforwardly leads to MMs with highly stable magnetic moments. By employing mathematical concepts such as
convergence in probability and convergence bounds, we showed that for 2DFMMs containing a sufficiently large number of spins (between 20 and 50) and a small number of spin rings (between 1 and 5), the energy of the ground total spin state is extremely insensitive to shape deformations. These molecules are therefore very unlikely to make transitions out of the ground spin state under a deformation, and the magnitude and direction of the total spin will remain unchanged. In this sense, we can regard the total spin of such MMs as a ‘weak topological invariant’, i.e. a quantity that only depends upon the arrangement of the spin centres in the molecule and not upon shape deformations to the molecule. The prefix ‘weak’ means that there may exist deformations that cause a large change in the total spin of the molecule, but which have a low probability of occurring. The result holds for ‘small’ shape deformations. While there is no clear upper bound on the size of the deformations, computer simulations of our model for a variety of MMs show that equations (2.1) and (2.2) hold up to about $\sigma_x = 0.2$, i.e. deformations that shift the spin centres a distance of about 20% of the spin centre–spin centre distance (result not shown). For the case of the Mn$_{12}$(Ac) molecule, the average distance between neighbouring Mn ions is about 3.20 Å. For 2DFMMs with edge lengths around 3.20 Å, our conclusions should therefore hold for deformations that shift the spin centres up to a distance of about 0.60 Å on average. The ionic radii of Mn$^{3+}$ and Mn$^{4+}$ are around 0.58 Å and 0.53 Å, respectively [45], which are comparable to the distance 0.60 Å. Thus, by ‘small’ deformations, we mean deformations that shift the spin centres about one ionic radius away from their equilibrium position.

While two-dimensional MMs containing 20–50 spin centres do not appear to have been reported in the literature, these sizes are well within the size range of the three-dimensional MMs that have been reported, and therefore might be good targets for chemical synthesis. The requirement that all spin–spin couplings be ferromagnetic poses an interesting challenge for synthetic chemists because in a majority of the molecules synthesized to date, the magnetic properties arise from a competition between both ferromagnetic and antiferromagnetic couplings. Moreover, it is known in MMs with anisotropy that the strength of the anisotropy scales roughly inversely with the number of spins [46]. It might therefore turn out that large 2DFMMs with weak topological invariant magnetic moments lack some of the interesting physics that is seen in smaller MMs such as Mn$_{12}$. Nonetheless, these 2DFMMs may be attractive targets for applications that strictly require molecular-sized components with highly robust magnetic moments.

While our model and calculations appear reasonable, there does not appear to be any reasonable experimental data or quantum chemical calculation that we can compare our results to. While it is standard to perform density functional theory calculations on small MMs, these calculations are very time consuming and are not practical for the present problem, which requires the calculations to be repeated many times for many different deformations to the molecule. Moreover, these calculations are limited to MMs containing less than a dozen metal ions, whereas our claims hold for larger MMs. However, as long as one is content working with the spin Hamiltonian (which is widely regarded qualitatively accurate for MMs [1,2]) and small displacements, then the conclusions from our work are scientifically meaningful. An important issue that needs to be addressed is how the ratio $|c/J|$ in equations (2.1) and (2.3) varies as the spin centre–spin centre distance varies about its equilibrium distance. We interpreted our calculations by assuming that $J$ varies quadratically about $r$, which is expected if the variation is sufficiently small. However, it may be that $J$ varies in a much more complicated manner within the deformation range in which the model applies. For example, it is known that $J$ also depends on the Mn–O–Mn angles in various MMs [47] and the entire structure of the ligand connecting the two spins [37]. In a future study, we will extract the functional form of $J$ from detailed first-principle calculations and also consider applying similar mathematical approaches to the design of molecules with other highly functional properties.

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Appendix A

The distribution of \( R \) in equation (2.1) can be computed as follows. Let \( r'_{ij} \) be the distance between spin centres \( i \) and \( j \) after the spin centres are shifted by the random vectors. We have \( r'_{ij} = |(r_i + X_i) - (r_j + X_j)| \). Expanding \( r'_{ij} \) into its Taylor series, and retaining only the terms that are linear in the components of \( X_i \) and \( X_j \) gives

\[
\Delta r_{ij} = \frac{1}{r_{ij}}((r_i^x - r_j^x)X_i + (r_i^y - r_j^y)Y_i + (r_i^z - r_j^z)Z_i + (r_i^x - r_j^x)X_j + (r_i^y - r_j^y)Y_j + (r_i^z - r_j^z)Z_j),
\]

(A 1)

where \( \Delta r_{ij} = r'_{ij} - r_{ij} \). The components of \( \Delta r_{ij} \) are adjacent in the molecule. Suppose that \( j \) is the set of internal angles in the molecule (angles between adjacent edges). Substituting equation (A 1) into equation (2.1) shows that \( R \) is a normal random variable with mean zero. The variance can be computed using the formula

\[
\text{var}(R) = \frac{(e/j)^2}{n_c^2} \left( \sum_{(i,j) \in E} \text{var}(\Delta r_{ij}) + 2 \sum_{(i,j),(k,l) \in E^2,(i,j) \neq (k,l)} \text{cov}(\Delta r_{ij}, \Delta r_{kl}) \right),
\]

(A 2)

where \( E \) is the edge set of the molecule under consideration and \( n_c \) is the number of edges in the molecule. Choose an arbitrary edge from the molecule \( (i,j) \). Using equation (A 1), we find that

\[
\text{var}(\Delta r_{ij}) = 2\sigma_x^2((r_i^x - r_j^x) + (r_i^y - r_j^y) + (r_i^z - r_j^z)).
\]

(A 3)

The term in the brackets is simply \( r_{ij}^2 = 1 \), and so the first sum in equation (A 2) is

\[
\sum_{(i,j) \in E} \text{var}(\Delta r_{ij}) = 2n_c\sigma_x^2.
\]

(A 4)

Choose an arbitrary pair of edges \( (i,j) \) and \( (k,l) \) from \( E^2 \). Because \( \Delta r_{ij} \) and \( \Delta r_{kl} \) both have mean zero, the covariance of \( \Delta r_{ij} \) and \( \Delta r_{kl} \) is equal to \( E(\Delta r_{ij} \Delta r_{kl}) \). According to equation (A 1), if one of \( k \) or \( l \) is not equal to either \( i \) or \( j \), then \( \Delta r_{ij} \) and \( \Delta r_{kl} \) are independent random variables and \( E(\Delta r_{ij} \Delta r_{kl}) = 0 \). We therefore only need to consider the case where the edges \( (i,j) \) and \( (k,l) \) are adjacent in the molecule. Suppose that \( j = l \). Using equation (A 1) and the fact that \( E((X_i - X_j)(X_k - X_j)) = -\sigma_x^2 \) (and similarly for the \( y \) and \( z \) components), we find that

\[
E(\Delta r_{ij} \Delta r_{kl}) = -\sigma_x^2((r_i^x - r_j^x)(r_k^x - r_j^x) + (r_i^y - r_j^y)(r_k^y - r_j^y) + (r_i^z - r_j^z)(r_k^z - r_j^z)).
\]

(A 5)

The term in the brackets is equal to \( (r_i - r_j) \cdot (r_j - r_k) = \cos(\pi - \phi) \), where \( \phi \) is the angle \( i,j,k \). The second sum in equation (A 2) therefore works out to be

\[
\sum_{(i,j),(k,l) \in E^2,(i,j) \neq (k,l)} \text{cov}(\Delta r_{ij}, \Delta r_{kl}) = \sigma_x^2 \sum_{\phi \in \Lambda} \cos \phi,
\]

(A 6)

where \( \Lambda \) is the set of internal angles in the molecule (angles between adjacent edges). Substituting equations (A 6) and (A 4) into (A 2) gives equation (2.3) of the main paper.

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