Toroidal magnetic molecules stripped to their basics

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Molecular magnetic toroidal moments are molecule-based structures of quantum spins that are expected to boost magnetic storage technology and quantum computing. We study selected fictitious but typical examples of single-molecule toroidal magnet behavior, discuss the essence of the concept, and clarify inappropriate or even wrong assignments of physical properties. We provide an outlook that discusses necessary ingredients to the concept of toroidicity.

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I. INTRODUCTION

Magnetic molecules constitute a fascinating class of magnetic materials, see, e.g., Refs. [1-5], for which in particular two properties give rise to hope for technological applications. The first property is the appearance of slow relaxation of the magnetization [6–11], which would allow us to use a single molecule as a bit of magnetic storage. The main obstacle in the context of this paper is the appearance of temperatureindependent quantum tunneling of the magnetization due to a tunneling gap (avoided level crossing) that opens up for non-Kramers systems, for instance, for noncollinear arrangements of easy anisotropy axes [12,13].

The second property is slow decoherence, which would allow us to use a single molecule as a bit in quantum computing schemes [14–25]. Here, recent efforts focus on clock transitions, i.e., transitions where at least the first derivative of the transition energy with respect to an external magnetic field is zero. Such transitions are more robust against fluctuations of the field than others and should thus exhibit longer coherence times.

Molecular toroidal magnetic states [13,26–41] are often advertised as a means to improve the properties for the use as both units of single-molecule magnetic storage and quantum q bits. The basic quantum states to be manipulated in such schemes are left and right circular (chiral) orientations of the toroidal (ground) states. One of the reasons for the assumed improved properties is that toroidal arrangements of spins appear less susceptible to fluctuating magnetic fields, at least in a mean-field picture, which should shield them from magnetic disturbances by other spins, compare discussion in Ref. [42] for the related chirality in spin triangles. This might indeed be the case but the usability of toroidal states and structures depends on finer details of the spin Hamiltonian as well as on the precise coupling to disturbing sources [43–45].

In the following, we demonstrate that quantum spin Hamiltonians that consist of isotropic Heisenberg interaction terms as well as of toroidal arrangements of single-ion easy-axis anisotropy terms may have toroidal low-lying states but these states do not offer any new insight compared to systems with simple noncollinear single-ion easy-axis anisotropy terms. The reason is that the toroidal arrangement of single-ion easy axes can be transformed into nontoroidal arrangements without altering the Hamiltonian and its spectrum. This insight also explains that the S-shape of magnetization curves, often taken as hallmark of toroidal systems, is not a feature that can be used to unquestionably identify toroidal spin systems.

Non-Kramers toroidal spin systems, i.e., systems with integer total spin, practically unavoidably possess a tunneling gap between their lowest states at B = 0. One therefore must expect non-negligible quantum tunneling as decades of investigations of single-molecule magnets have taught us. We present tunneling gaps for dimeric and trimeric systems. For Kramers systems (odd number of half-integer spins), which show no gap, transition rates between toroidal ground states induced by small (fluctuating) fields may impact their stability, see Ref. [13] for a recent discussion.

If toroidal states should provide concepts and prospects beyond what we already know from single-molecule magnets we have to ask which terms in a Hamiltonian would foster a new behavior that is indeed intimately connected to the concept of toroidal moments. Again in line with Ref. [13], we think that dipolar interactions as well as Dzyaloshinskii-Moriya interactions or anisotropic exchange in general are a prerequisite for a magnetization dynamics where toroidicity plays a role.

The paper is organized as follows. In Sec. II we discuss spin Hamiltonians with toroidal arrangements of easy-axis single-ion anisotropies together with their properties. In Sec. III we discuss necessary prerequisites for the use of toroidal moments in magnetic molecules. A summary is provided in Sec. IV.

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FIG. 1. The toroidal moment of a single spin is arbitrary due to the arbitrariness of the point of reference (X). In (a) the toroidal moment is nonzero, in (b) it is zero. The red arrow depicts a classical spin, the brown bar symbolizes the easy-axis single-ion anisotropy (for later use).

II. SPIN SYSTEMS WITH NONCOLLINEAR SINGLE-ION ANISOTROPIES

A typical Hamiltonian employed for magnetic molecules made of d elements (and used as approximation for f elements) consists of a Heisenberg exchange term, a term collecting the single-ion anisotropies, and a Zeeman term, i.e.,

$$\begin{array}{l}
H_{\sim} = -2 \sum_{i < j} J_{ij} \vec{s}_i \cdot \vec{s}_j + \sum_i \vec{s}_i \cdot \mathbf{D}_i \cdot \vec{s}_i \\
+ \mu_B \vec{B} \cdot \sum_i g_i \vec{s}_i.
\end{array}$$
(1)

Here operators are marked by a tilde, and J_{ij} denotes the exchange parameters between spins at sites *i* and *j*. A negative J_{ij} corresponds to an antiferromagnetic interaction, a positive one to a ferromagnetic interaction. For the sake of simplicity it is assumed that the spectroscopic splitting is given by numbers g_i .

 \mathbf{D}_i denotes the single-ion anisotropy tensor of the spin at site *i*, which, in its eigensystem \vec{e}_i^1 , \vec{e}_i^2 , \vec{e}_i^3 , can be decomposed as

$$\mathbf{D}_i = D_i \vec{e}_i^3 \otimes \vec{e}_i^3 + E_i \big\{ \vec{e}_i^1 \otimes \vec{e}_i^1 - \vec{e}_i^2 \otimes \vec{e}_i^2 \big\}.$$
(2)

In the following we will assume that the E_i are zero and all $D_i < 0$, i.e., the anisotropy is locally of pure easy axis type.¹

Such a Hamiltonian is often employed when approximately modeling, e.g., dysprosium-containing magnetic molecules where the Dy moments experience very strong easy axes [13,28,46]. This corresponds to large negative D_i .

A toroidal moment of a set of spins is defined as

$$\vec{\tau} = \sum_{i} \vec{r}_i \times \vec{s}_i, \tag{3}$$

where the \vec{r}_i are classical position vectors of the respective spin sites with respect to a chosen point of reference. The definition reminds one of the respective formula for the angular momentum, and it shares with that definition the property that the quantity contains some arbitrariness due to the arbitrariness of the point of reference, see Fig. 1 for the simple example of a single spin.



FIG. 2. The nonzero toroidal moment of the ground state of an antiferromagnetically coupled classical dimer defined with respect to the center between both spins (a) can be transformed to zero (b) by a common rotation of both easy axes (brown bars) by 90° about a common axis.

A. Symmetry properties, toroidal moments, and energy spectrum

Hamiltonian (1) possesses an interesting symmetry in view of the concept of toroidal moments. If one rotates all easy axes as well as the field vector by the same angle about a common axis, the energy spectrum remains the same, and so does the magnetization as function of temperature T and magnitude of the field B. The reason is that the Heisenberg term is isotropic and does not know anything about the absolute orientation of the anisotropy tensors in space. Only the relative orientations of the anisotropy tensors with respect to each other matter.

This is a very important and far-reaching property since it allows us to transform a toroidal moment to a value between a minimum and a maximum by a global rotation without changing the energy spectrum and the magnetization. In many, in particular symmetric, cases the toroidal moment can thus be eventually transformed to zero.

The following graphical representations show such transformations for classical spin systems for simplicity but symmetries and transformations extend to the respective quantum versions. The applied field is not shown; one should keep in mind that it has to be transformed alongside.

Figure 2(a) shows the simple case of a toroidal moment of the ground state of an antiferromagnetically coupled classical dimer defined with respect to the center between both spins. This moment can be transformed to zero, compare Fig. 2(b), by a common rotation of both easy axes by 90° about a common axis.

The same is true for other arrangements as, for instance, shown in Fig. 3 for a triangular configuration that can be transformed to zero toroidal moment without changing the energy spectrum and the magnetization. Squares, hexagons, etc. behave in the same way.

Therefore we can state that if a spin Hamiltonian contains only Heisenberg interactions and single-ion anisotropy, the concept of toroidicity is virtually meaningless insofar as it does not offer any new insight into the magnetic properties of the spin system. The energy spectrum as well as thermal expectation values of magnetization, susceptibility, or heat capacity remain unchanged under the discussed transformation, i.e., are not correlated at all with the expectation value of the toroidal moment.

 $^{{}^{1}\}mathbf{D}_{i}$ should not be confused with a similar symbol denoting the Dzyaloshinskii-Moriya vector. The latter is a vector and connects two spins.



FIG. 3. The nonzero toroidal moment of the ground state of an antiferromagnetically coupled classical spin triangle defined with respect to the center of the triangle (a) can be transformed to zero (b) by a common rotation of the easy axes (brown bars) by 90° about a common axis.

We demonstrate these statements on the simple example of a spin dimer. The arrangement is similar to that of the hexagonal ring in Ref. [28] where the easy anisotropy axes are tilted with respect to a plane that is perpendicular to the field along z direction, compare Fig. 4.

We evaluate the toroidal moment as well as the magnetization, which both point along z direction, at T = 0 for a small magnetic field. This problem, by the way, can be solved analytically [47]. For $\phi = 0$, which corresponds to the situation shown in Fig. 4, the ground state $|\psi_0\rangle$ has got a nonvanishing toroidal moment $\tau_0 = \langle \psi_0 | \tau^z | \psi_0 \rangle$. With increasing ϕ the toroidal moment decreases steadily until it vanishes at $\phi = 90^{\circ}$, see Fig. 5(a). The magnetization of the ground state, $M_0 = -g\mu_B \langle \psi_0 | S^z | \psi_0 \rangle$, does not change at all and neither does the whole energy spectrum (only ground-state energy E_0 shown). This means that both the magnetization along z direction as well as the powder-averaged magnetization remain the same for all angles ϕ as it must be since the Hamiltonian is not at all altered by the symmetry transformation. The result is shown in Fig. 5(b), where the magnetization curves for $\phi = 0^{\circ}$ and $\phi = 90^{\circ}$ are displayed along the field.



FIG. 4. (a) Top view of an antiferromagnetically coupled classical dimer with slightly tilted easy axes (brown bars). The tilt angle is seen in the side view (b). ϕ denotes the angle by which the anisotropy axes are collectively rotated about the field axis.



FIG. 5. (a) Ground-state magnetization, toroidal moment, and energy for a magnetic field of B = 0.1 T as a function of $\phi = 0...90^{\circ}$ (appropriately scaled). Without loss of generality we choose typical parameters J = -0.5 K, $D_i = -2$ K, and $g_i = 2.0$. The anisotropy axes are tilted by 10° with respect to the plane perpendicular to the field axis, compare Fig. 4(b). (b) Magnetization along *z* and powder average as function of field strength *B* for T = 2 K for the two extreme cases with $\phi = 0$ and $\phi = 90^{\circ}$.

B. Shape of magnetization curves

Sometimes, it is argued that a shape of the low-temperature low-field magnetization curve, which resembles the letter **S**, is a signature of a toroidal moment, see Ref. [46] for an example. The same authors weaken their statement in Ref. [41]. As one may deduce from the previous discussion, **S**-shaped magnetization curves cannot be taken as signature of toroidal moments. In particular, cases where the toroidal moment can be transformed to zero without altering the magnetization curve demonstrate unquestionably that such a simple relation cannot exist.

Figure 6 nicely demonstrates that the magnetization may assume an S-shape, here shown for the triangle introduced in Fig. 3. The curves show the magnetization for three spins s = 5/2 for a strong easy-axis anisotropy D = -10 K as function of increasing antiferromagnetic coupling, $J = 0, -0.1, -0.2, \dots -2.0$ K from left to right. B_x points along one of the easy axes. This figure does not change if the easy axes are oriented in toroidal fashion, Fig. 3(a) or are collectively rotated and point along radial directions, Fig. 3(b).



FIG. 6. Magnetization of the triangular spin arrangement (Fig. 3): s = 5/2, D = -10 K, curves for increasing antiferromagnetic coupling, $J = 0, -0.1, -0.2, \dots - 2.0$ K from left to right. B_x points along one of the easy axes.

In general, the situation is much more involved. It seems that one needs a certain strength of exchange interaction compared to the easy-axis anisotropy in order to obtain S-shape magnetization curves. We provide two examples along this line: an hourglasslike spin system that might stand for Dy_6Cr and similar compounds [41,46] and a hexagonal ring. For simplicity, the easy axes are aligned in toroidal fashion in a plane, see Fig. 7. When looking at these structures one should keep in mind that the magnetization as well as other magnetic properties do not change, when all anisotropy tensors are rotated by a common angle of 90° about the field axis. The toroidal moment could collapse to zero under such a transformation.

Figure 8 shows several magnetization curves along x or z direction for various parameter sets for an hourglass molecule and a hexagonal ring. Depending on parameters and field direction the curves might resemble an S-shape or not, compare Ref. [41] for similar experimental curves. The same also holds for the powder average, which again would not change if all anisotropy axes in Fig. 7 would be rotated by 90° about the z-axis to point radially outwards.

Sometimes the S-shape is taken as signature of a nonmagnetic ground state, but this statement is too weak because a nonmagnetic ground state dominates the low-field



FIG. 7. Structures of an hourglass molecule (left-hand side) and a hexagonal ring (right-hand side). Yellow sticks represent the easy axes; the red and blue connections represent J_1 and J_2 in the hourglass, whereas the blue connections represent J for the ring.



FIG. 8. Magnetization curves for various parameter sets as function of applied field along x or z direction for (top) an hourglass molecule and (bottom) a hexagonal ring. z denotes the direction perpendicular to the triangular or hexagonal planes whereas x is in plane.

magnetization only if it is separated by a non-negligible energy gap from magnetic states. Thus an S-shaped magnetization curve signals that the low-energy spectrum is populated with nonmagnetic states whereas magnetic states appear only above some energy gap.

C. Tunneling gap

The key problem of toroidal arrangements of easy axes (including the antiferromagnetic dimer discussed above) is the tunneling gap at the avoided level crossing of the two lowest-energy eigenstates at B = 0. This practically unavoidable property of many spin Hamiltonians, in particular in case of noncollinear easy axes, not only leads to a quantum tunneling of the magnetization [48,49], but also of the toroidal moment. In view of the symmetry discussed above, the tunneling rates are just the same and thus a major obstacle against bistability and thus technological use.

We provide tunneling gaps Δ for antiferromagnetic dimers as well as trimers with J = -0.5 K and D as well as s in Tables I and II, respectively. A slight prospect is provided by the observation that the tunneling gap shrinks with increasing easy axes anisotropy D_i of the participating spins as well as with increasing spin quantum number [50], the latter being a good argument to use dysprosium in such compounds. We conjecture that the major reason for this behavior is that with increasing spin quantum number as well as with increasing D the contribution of the single-ion anisotropy to the total energy

TABLE I. Tunneling gaps Δ for antiferromagnetic dimers with J = -0.5 K and D as well as s as given in the table. All quantities are provided in kelvin. For real materials the accuracy of the gap is of course not better than for J and D.

 D	-1.0	-2.0	-4.0	-8.0
s = 1	0.561553	0.372281	0.216990	0.116844
s = 3/2	0.227998	0.087343	0.027536	0.007767
s = 2	0.072088	0.015878	0.002738	0.000407
s = 5/2	0.019653	0.002519	0.000239	0.000019

increases. Since single-ion anisotropy is a one-body operator this increases the anisotropy relative to the Heisenberg interaction and therefore decreases the entanglement between the spins, which is due to the Heisenberg interaction, in the zero-field split ground states. This way the system approaches the limit of independent, i.e., noninteracting spins, for which there is no avoided level crossing.

But even with a very small tunneling gap or for Kramers systems (in total odd number of spin 1/2), where $\Delta = 0$, the ground state might be very susceptible to small transverse fields since the anisotropy axes are not collinear and ground states are thus superpositions of basis states with various magnetic quantum numbers, compare investigations in, e.g., Refs. [13,49,51–53].

III. INTERACTIONS THAT FOSTER TOROIDAL MOMENTS

Under which circumstances is the concept of toroidal moments useful? We are convinced that one needs terms in the Hamiltonian that break the symmetry of the discussed collective rotations. There are (at least) two options: The exchange interactions are also anisotropic, due to contributions of, e.g., antisymmetric Dzyaloshinskii-Moriya interaction, dipolar interaction, as well as anisotropic symmetric exchange, or the magnetic field depends on the space coordinates and has got cyclic character, for instance.

The following Hamiltonian contains both options:

$$\begin{array}{l}
H_{\sim} = -2 \sum_{i < j} \vec{s}_i \cdot \mathbf{J}_{ij} \cdot \vec{s}_j + \sum_i \vec{s}_i \cdot \mathbf{D}_i \cdot \vec{s}_i \\
+ \mu_B \sum_i g_i \vec{B}(\vec{r}_i) \cdot \vec{s}_i.
\end{array} \tag{4}$$

Here \mathbf{J}_{ij} is the 3 × 3 matrix of the anisotropic exchange between spins at sites *i* and *j*.

TABLE II. Tunneling gaps Δ for antiferromagnetic trimers with J = -0.5 K and D as well as s as given in the table. All quantities are provided in kelvin. For real materials the accuracy of the gap is of course not better than for J and D.

 D	-1.0	-2.0	-4.0	-8.0
s = 1	0.415911	0.161685	0.047158	0.013061
s = 3/2 $s = 2$	0.011954	0.001137	0.000074	0.000004
s = 5/2	0	0	0	0



FIG. 9. Magnetization along the field direction of a spin ring with single spins s = 2 and a toroidal arrangement of easy axes as shown in Fig. 7. (a) Comparison of magnetization curves for a ring with ferromagnetic nearest-neighbor coupling of J = 0.5 without (red) and with dipolar interactions (blue). (b) Comparison of magnetization curves for a ring with dipolar interactions with (blue) and without ferromagnetic nearest-neighbor coupling of J = 0.5 (green). The field is applied in the *xy* plane defined by the toroidal anisotropy axes along one of these axes.

Anisotropic exchange comprises all kinds of anisotropic interactions, among them symmetric anisotropic exchange, e.g., with 4d or 5d elements [54] or Kitaev interactions [55–58] as well as antisymmetric anisotropic exchange of Dzyaloshinskii-Moriya type [59–61] and generalizations thereof, e.g., topological-chiral magnetic interactions [62–64]. The strength of such interactions does of course depend on the symmetry of the chemical structure of the considered molecules (including ligands, etc.). However, many 4d or 5d ions that show anisotropic exchange are effective doublets (effective spins s = 1/2), and therefore do not possess single-ion anisotropy. The simplest anisotropic interaction is the dipolar interaction, which acts between all kinds of magnetic moments and in addition to all other terms in the Hamiltonian.

One should, however, keep in mind that the thermal stability of toroidal effects is limited by the strength of the respective anisotropic interaction at work. For instance, if the contribution of the dipolar interaction to the Hamiltonian amounts to 1 K, then one cannot expect it to stabilize toroidal states for temperatures above this scale, and such a system will be similar to that without dipolar interactions for higher temperatures. We demonstrate this behavior with the follow-



FIG. 10. Artistic view of a toroidal dimer whose toroidal quantum states can be driven by the field of the tunneling current of the scanning probe microscope. Unfortunately, the estimated field of about 10^{-6} T for realistic tunnel currents at the sites of the spins is too weak for practical use.

ing example of a toroidal hexagonal ring, see right-hand side of Fig. 7.

Figure 9 compares three scenarios. Figure 9(a) compares the magnetization curves for a ring with a ferromagnetic nearest-neighbor coupling of J = 0.5 without (red) and with dipolar interactions (blue). The dipolar interaction was taken to be realistic for a six-membered ring such as in Refs. [30,37] (R = 3.74 Å); it acts pairwise between all spins of the ring. One notices that the dipolar interaction indeed stabilizes the toroidal arrangement of the ground state since the field at which the magnetization jumps at low temperatures is shifted to higher values. One also notices that this effect is weakened by higher temperatures; in particular at T = 2 K it is almost gone. It should be added here that the dipolar interaction does not necessarily stabilize a toroidal moment; it may also counteract.

Figure 9(b) investigates how the dipolar interaction alone would perform compared to a combined action of ferromagnetic and dipolar interaction. The result is depicted by the green curves in Fig. 9(b). They show that at least for the discussed example the magnetization is not stabilized against the magnetic field, which leads us to conclude that a combined action of isotropic and anisotropic exchange is preferential. Finally we would like to speculate about toroidal magnetic fields that would match toroidal states perfectly in the same way a homogeneous field matches a collinear arrangement of ferromagnetically aligned spins. A perfectly suited magnetic field to pick up or initialize a toroidal moment would be the field of a straight wire as for instance realized by the tunneling current in a scanning tunneling microscope, see artistic view in Fig. 10. Unfortunately, such a tunneling current generates a much too weak field of only about 10^{-6} Tesla for today's STMs [65]. One could, however, employ a magnetic tip that would initialize or pick up a toroidal moment by being placed above one of the magnetic ions as was demonstrated in Ref. [66].

IV. DISCUSSION AND CONCLUSIONS

There are three lessons to be learned from our investigation.

(i) Even if a magnetic molecule possesses easy anisotropy axes that are arranged in a toroidal fashion its properties will not be related to possible toroidal moments if the Hamiltonian consists dominantly of Heisenberg exchange and single-ion anisotropy. The toroidal moment is a coincidence and does not influence the spectrum and thermal properties.

(ii) Toroidal moments might play a role if additional anisotropic exchange enters the Hamiltonian [13]. Then a symmetry transform as discussed above is not possible, and the toroidal moment might be stabilized by the anisotropic exchange. In such a case one can hope to employ toroidal moments for quantum devices.

(iii) In physics one can usually estimate simple figures of merit by looking at scales. Here, the thermal stability of the toroidal moment is given by the magnitude of the anisotropic interactions. If these terms sum up to less than a kelvin, then the concept of a toroidal moment is useful below a kelvin and useless above a kelvin. Thus, we need to search for materials where both the single-ion anisotropy as well as the anisotropic exchange are large.

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