Highlights

**Toroidal Moment in a Family of Spin-Frustrated Heterometallic Triangular Nanomagnets Without Spin-Orbit Coupling: Applications in a Molecular Spintronics Device**

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- Toroidal states can arise in spin rings in the limit of zero spin-orbit coupling.
- Degenerate ground quartet carries a non-zero toroidal moment in each state.
- Possible to generate toroidal moments in ground doublets.
- Can reverse the polarization of a spin current.
- Can control the populations of the toroidal states in a spintronics device.
Toroidal Moment in a Family of Spin-Frustrated Heterometallic Triangular Nanomagnets Without Spin-Orbit Coupling: Applications in a Molecular Spintronics Device

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ABSTRACT

We theoretically investigate a family of spin-frustrated triangular molecular nanomagnets with arbitrary on-site spin, featuring one heterometallic ion, in the limit of zero spin-orbit coupling. Analytical evaluation of the Heisenberg exchange states and spectrum shows that the ground state can either be the first example of a toroidal quartet, or feature two weakly split toroidal doublets, depending on the exchange parameters. The nonequilibrium spin dynamics of these toroidal states is modelled within a three-terminal molecular spintronics device, showing that gate and bias voltages can be used to tune the nonequilibrium population of these toroidal states, thus to monitor the ensuing toroidal magnetization of the device.

1. Introduction

The increasing demands of data storage and processing, as well as fundamental interest, have been driving research into the behavior of magnetic complexes [1, 2, 3]. The many diverse phenomena displayed by magnetic complexes, such as single-molecule magnetism [4, 5, 6], spin crossover [7] and toroidal moments [8, 9], are now seen as key areas of interest. In particular, the elusive property of toroidal moments has generated much interest recently, due to its applications in quantum computation [10], molecular spintronics devices [11], and magnetoelectric coupling for multiferroics [12, 13].

Toroidal states are vortex states that occur due to the head-to-tail arrangement of spins. The toroidal moment can be understood as the antisymmetric part of the magnetic quadrupole moment, which is odd under both time reversal and space reversal transformations [13, 14]. Molecular toroidal moments were first predicted [15] and observed [16, 17] in 2008, when quantum states with large nonzero toroidal moments were identified in a strongly anisotropic molecular ring, namely the Dy₃ triangle [18] with anisotropy axes tangential to the ring.

Toroidal moments interact with the curl component of a magnetic field, thus do not interact with homogeneous magnetic fields [13, 14]. This, combined with the fact that a quadrupole moment interacts over a shorter range than a dipole moment, means that toroidal states can lead to a much denser packing of quantum states than a qubit traditionally implemented with spin dipoles [15].

This concept has sparked a great interest in exploring toroidal moments, both in terms of theory [16, 19] and experiment [20, 17, 21], with interest in Dy rings moving past the three-membered systems to four-, five- and six-membered systems [22, 23, 24, 25, 26], and also into heterometallic rings [27, 28, 29, 30, 31, 32]. Although most of the early interest in this area was in highly anisotropic rings with strong spin-orbit coupling and low site exchange [8], molecules with weak spin-orbit coupling have also been investigated, such as Cu₃ and V₁₅ [13, 10, 33, 34, 35, 36, 39].

It is possible to split the populations of different toroidal states by applying a curling magnetic field [13, 14], but there is currently no known method for producing inhomogeneous magnetic fields on the molecular scale. We therefore consider using electric and spin currents to analyze these systems [11, 37, 38, 39], as there have been recent advances in the development of devices that can measure and manipulate spin states [40, 41, 42, 43, 44, 45].

While most studies so far demonstrate the possible existence of two distinct ground toroidal states [13, 16, 39], we demonstrate here that an “isosceles” spin triangle can produce four distinct, nonmagnetic toroidal states within...
Figure 1: Schematic of the spin triangle of interest. Regardless of the overall geometry, the site spins as well as their couplings have a lateral plane of symmetry, so we describe the triangle as “isosceles”. That is, the spins at sites one and two are equal, while the exchange interaction between sites one and three is equal to that between sites two and three.

a frustrated ground quartet. Additionally, particular isosceles systems can produce toroidal states in spin-frustrated doublets. In each case, we present analytical expressions for the toroidal moment quantum numbers. While several heterometallic spin triangles have been synthesized and characterized in literature [53, 54, 55], our results present specific ranges of spin exchange for which such systems would show these interesting properties, thus presenting a new avenue for future synthetic efforts.

We also analyze and optimize the performance of the isosceles spin triangle in a previously proposed spintronics device [11, 39], and explain how spin-transfer torque leads to a difference in the populations of the clockwise and counterclockwise toroidal states. Because our study explores the zero spin-orbit coupling regime, the spintronics device of interest has now been predicted to produce net toroidal magnetizations on triangles with strong [11], weak [39], or zero spin-orbit coupling.

2. Toroidal moment in a spin triangle with a $S_3 = \frac{1}{2}$ heteroatom

The isosceles spin triangle is depicted in Fig. 1. Sites one and two have spins $S_1 = S_2 \equiv S$, while site three has spin $S_3 = \frac{1}{2}$. The exchange interaction between sites one and two is $J_{ex}$, and the other two exchange interactions are $\lambda_{ex}$. The Hamiltonian for such a system can be written using a Heisenberg spin-model as:

$$\hat{H}_{ex} = -J_{ex}(\hat{S}_1 \cdot \hat{S}_2) - \lambda_{ex}(\hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_1) = \frac{-J_{ex}}{2}(\hat{S}_{12}^2 - \hat{S}_1^2 - \hat{S}_2^2) - \frac{\lambda_{ex}}{2}(\hat{S}_T^2 - \hat{S}_3^2 + \hat{S}_{12}^2),$$

where $\hat{S}_{12} = \hat{S}_1 + \hat{S}_2$ and $\hat{S}_T = \hat{S}_1 + \hat{S}_2 + \hat{S}_3$. The operators $\hat{S}_1^2$, $\hat{S}_2^2$ and $\hat{S}_3^2$ always give constants which can be set as zero energy. As a result, the energies are:

$$E(S_{12}, S_T) = \frac{-\lambda_{ex}}{2}S_T(S_T + 1) - \frac{J_{ex} - \lambda_{ex}}{2}S_{12}(S_{12} + 1).$$

We are interested in particular in a spin frustrated configuration, i.e. an antiferromagnetic ring with $J_{ex} < 0$ and $\lambda_{ex} < 0$, giving ground states with the lowest possible values of $S_{12}$ and $S_T$. For the first few values of $S_{12}$, the energies are:

- $S_{12} = 0, S_T = \frac{1}{2} \Rightarrow E(0, \frac{1}{2}) = -\frac{3\lambda_{ex}}{8}$
- $S_{12} = 1, S_T = \frac{1}{2} \Rightarrow E(1, \frac{1}{2}) = -\frac{3\lambda_{ex}}{8} \pm |J_{ex} - \lambda_{ex}|$
- $S_{12} = 1, S_T = \frac{3}{2} \Rightarrow E(1, \frac{3}{2}) = -\frac{15\lambda_{ex}}{8} \pm |J_{ex} - \lambda_{ex}|$
- $S_{12} = 2, S_T = \frac{1}{2} \Rightarrow E(2, \frac{1}{2}) = -\frac{15\lambda_{ex}}{8} \pm |J_{ex} - \lambda_{ex}|$
- $S_{12} = 2, S_T = \frac{3}{2} \Rightarrow E(2, \frac{3}{2}) = -\frac{15\lambda_{ex}}{8} \pm 3|J_{ex} - \lambda_{ex}|$
- $S_{12} = 2, S_T = \frac{5}{2} \Rightarrow E(2, \frac{5}{2}) = -\frac{35\lambda_{ex}}{8} \pm 3|J_{ex} - \lambda_{ex}|$
and so on, where the ‘+’ sign occurs for $|J_{ex}| > |\lambda_{ex}|$, and the ‘−’ sign occurs for $|J_{ex}| < |\lambda_{ex}|$.

When $|J_{ex}| > |\lambda_{ex}|$, the $S_{T_2} = 0, S_{T} = \frac{1}{2}$ doublet is the lowest energy. We call this doublet $|A, M_{T}\rangle$, where $M_{T} = \pm \frac{1}{2}$ is the projection of $S_{T}$ along the z-axis, perpendicular to the plane of the triangle. Whereas when $|\lambda_{ex}| < |J_{ex}| < |\lambda_{ex}|$, we get $S_{T_2} = 1, S_{T} = \frac{1}{2}$ as the lowest energy doublet, which we call $|B, M_{T}\rangle$. For the case $|J_{ex}| = |\lambda_{ex}|$, the A and B doublets are equal in energy, so the ground manifold is a frustrated quartet.

Using standard angular-momentum coupling theory, expressions for $|A, M_{T}\rangle$ and $|B, M_{T}\rangle$ in terms of the individual site spins can be readily found:

$$\sqrt{2S+1}|A, \pm \frac{1}{2}\rangle = \sum_{m=-S}^{S} (-1)^{S-m} |S, m\rangle_1 \otimes |S, -m\rangle_2 \otimes |\frac{1}{2}, \pm \frac{1}{2}\rangle_3,$$  \hspace{1cm} (3)

$$\sqrt{S(S+1)}|B, \pm \frac{1}{2}\rangle = \pm \sum_{m=a}^{b} (-1)^{S-m} S(S+1) - m(m+1)|S, m\rangle_1 \otimes |S, -m \pm 1\rangle_2 \otimes |\frac{1}{2}, \pm \frac{1}{2}\rangle_3,$$

$$- \sum_{m=-S}^{S} (-1)^{S-m} m|S, m\rangle_1 \otimes |S, -m\rangle_2 \otimes |\frac{1}{2}, \pm \frac{1}{2}\rangle_3,$$  \hspace{1cm} (4)

\((a, b) = \begin{cases} \ (-S+1, S), \text{ for } |B, +\frac{1}{2}\rangle \\ \ (-S, S - 1), \text{ for } |B, -\frac{1}{2}\rangle. \end{cases}\)

Next, following up from our recent investigation of toroidal moments in a frustrated spin triangle with $S_1 = S_2 = S_3 = 1/2$ [39], we want to probe the existence of a toroidal ground state having zero magnetic moment in this generalised spin triangle. The toroidal moment operator reads:

$$\hat{\tau} = g \mu_B \sum_{p=1}^{3} (\hat{r}_p \times \hat{S}_p),$$  \hspace{1cm} (5)

where $\hat{r}_p$ is the position vector of site $p$. Although toroidal states exist for general triangular geometries, we present the equilateral case as an illustrative example. For $|\hat{r}_p\rangle = R, \alpha_p = \frac{2\pi(p-1)}{3}$ and $\hat{S}_p^z = \hat{S}_{px} \pm \hat{S}_{py}$, the z-component of the toroidal moment operator becomes:

$$\hat{\tau}_z = - \frac{ig \mu_B R}{2} \sum_{p=1}^{3} (e^{-ia_p} \hat{S}_{p+} - e^{ia_p} \hat{S}_{p-}).$$  \hspace{1cm} (6)

For the case $|J_{ex}| = |\lambda_{ex}|$, the matrix representation of the toroidal moment operator $\mathbb{T}_z$ over the four-fold ground manifold defined by the A and B doublets Eq. (3) can be readily evaluated as:

$$\frac{2\mathbb{T}_z}{g \mu_B R} = \begin{bmatrix} 0 & e^{(+i\frac{\pi}{6})} & 0 & -\frac{2}{\sqrt{3}} e^{(-i\frac{\pi}{3}) \sqrt{S(S+1)}} \\ e^{(-i\frac{\pi}{6})} & 0 & -\frac{2}{\sqrt{3}} e^{(+i\frac{\pi}{3}) \sqrt{S(S+1)}} & 0 \\ 0 & -\frac{2}{\sqrt{3}} e^{(-i\frac{\pi}{3}) \sqrt{S(S+1)}} & 0 & -e^{(+i\frac{\pi}{6})} \\ -\frac{2}{\sqrt{3}} e^{(+i\frac{\pi}{3}) \sqrt{S(S+1)}} & 0 & -e^{(-i\frac{\pi}{6})} & 0 \end{bmatrix},$$  \hspace{1cm} (7)

with eigenvectors (grouped in two toroidal doublets $\omega = 1, 2$, see Fig. 2 for a graphical representation):

$$2|\tau_{\omega \pm}\rangle = \pm e^{i\frac{2\pi}{3}} |A, +\frac{1}{2}\rangle - (-1)^{\omega} |A, -\frac{1}{2}\rangle \pm (-1)^{\omega} e^{i\frac{2\pi}{3}} |B, +\frac{1}{2}\rangle + |B, -\frac{1}{2}\rangle,$$
Figure 2: Local spin expectation values \(\langle S_p \rangle\) in the toroidal states, shown for \(S = 2, S_3 = \frac{1}{2}\). In \(|\tau_{1\pm}\rangle\) and \(|\tau_{2\pm}\rangle\), the spin expectation values at sites one and two have magnitudes \(|\langle S_1 \rangle\rangle = |\langle S_2 \rangle\rangle = \frac{S+1}{6}\), and angles with the horizontal of \(\cos^{-1}\left(\frac{1}{2}\right)\) and \(\cos^{-1}\left(\frac{S+1}{6}\right)\), while \(|\langle S_3 \rangle\rangle = 0\) along the horizontal. In \(|\tau_{A\pm}\rangle\), \(|\langle S_1 \rangle\rangle = |\langle S_2 \rangle\rangle = \frac{1}{2}\), and angles with the horizontal of \(\cos^{-1}\left(\frac{1}{2}\right)\) and \(\cos^{-1}\left(\frac{S+1}{6}\right)\), while \(|\langle S_3 \rangle\rangle = 0\).

while the associated eigenvalues are the elusive toroidal moments we find for the two degenerate ground doublets:

\[
\tau_{\alpha\pm} = \pm \left(\sqrt{\frac{S(S+1)}{3}} - \frac{(-1)^\alpha}{2}\right) g\mu_B R. 
\]

(8)

Note that for \(S = 1/2\), we recover the case of a triangle with equal on-site spins \(S = 1/2\) [39], where only two states of the degenerate quartet carry a non-zero toroidal moment \(\tau = \pm g\mu_B R\), see Eq. (8).

However, for \(S > 1/2\) and \(J_{ex} = \lambda_{ex}\), from Eq. (8) we can see that the ground quartet now consists of four distinct toroidal states carrying a non-zero toroidal moment: \(|\tau_{1\pm}\rangle\), \(|\tau_{1\pm}\rangle\), \(|\tau_{2\pm}\rangle\) and \(|\tau_{2\pm}\rangle\). We also consider the cases \(|\lambda_{ex}\rangle < |J_{ex}\rangle \text{ and } |\lambda_{ex}\rangle < |J_{ex}\rangle \text{ by finding the eigenstates of the toroidal moment operator within the subspaces} \{|A, +\frac{1}{2}\rangle, |A, -\frac{1}{2}\rangle\} \text{ and } \{|B, +\frac{1}{2}\rangle, |B, -\frac{1}{2}\rangle\}| \text{ first and second } 2 \times 2 \text{ blocks of } \mathbb{T}_2, \text{ respectively, see Eq. (7)}. \text{ We label these toroidal states as } |S_{A\pm}\rangle \text{ and } |S_{B\pm}\rangle, \text{ and depict their local spin expectation values in Fig. 2.}

\[
\sqrt{2}|S_{A\pm}\rangle = \pm e^{i\pi \frac{\tau_{A\pm}}{2}} |A, +\frac{1}{2}\rangle + |A, -\frac{1}{2}\rangle, \quad \tau_{A\pm} = \pm \frac{1}{2} g\mu_B R, 
\]

(9)

\[
\sqrt{2}|S_{B\pm}\rangle = \pm e^{i\pi \frac{\tau_{B\pm}}{2}} |B, +\frac{1}{2}\rangle + |B, -\frac{1}{2}\rangle, \quad \tau_{B\pm} = \pm \frac{1}{2} g\mu_B R. 
\]

(10)

3. Toroidal moment for arbitrary values of the heterometallic spin \(S_3\)

We now generalize our model for a generic spin \(S_3\). Using the energies in Eq. (2), we look for values of \(S_3\) which lead to frustrated ground states, which may then give rise to toroidal states. For integer \(n\) in the antiferromagnetic isosceles spin triangle with \(S_1 = S_2 = S\):
If \( S_3 = n \), the ground state will have \( S_{12} = n' \leq n \) and integer \( S_T = n - n' \), so will not be frustrated.

If \( S_3 = n + \frac{1}{2}, 2S \geq n \) and \( |\lambda_{ex}| < |J_{ex}| \), the ground state will have \( S_{12} = n \) and \( S_T = S_3 - S_{12} = \frac{1}{2} \), so will be a doublet (termed \( A' \)).

If \( S_3 = n + \frac{1}{2}, 2S \geq n + 1 \) and \( |\lambda_{ex}| < |J_{ex}| \), the ground state will have \( S_{12} = n + 1 \) and \( S_T = S_{12} - S_3 = \frac{1}{2} \), so will be a doublet (termed \( B' \)).

We therefore focus on the case \( S_3 = n + \frac{1}{2} \) with frustrated ground states \(|A', M_T\rangle\) and \(|B', M_T\rangle\). Such systems have been synthesized for example: Gd\(^{III}\)\(_2\)Mn\(^{IV}\) [53], Fe\(^{III}\)\(_2\)Gd\(^{III}\) [54, 55] and Mn\(^{III}\)\(_2\)Gd\(^{III}\) [54] for various values of \( \lambda_{ex} \) and \( J_{ex} \). We present \(|A', +\frac{1}{2}\rangle\) and \(|B', +\frac{1}{2}\rangle\) here, written in a direct product basis with \( m, l - m \) and \( \frac{1}{2} - l \) as the z-components of the spins at sites one, two and three, respectively:

\[
\langle \Gamma, +\frac{1}{2} \rangle = \sum_{l=0}^{a_1} \left( \sum_{m=-S+l}^{S} |S, m\rangle_1 \otimes |S, l-m\rangle_2 C_{12}^+(a_1, l, m, S) \right) \otimes |n + \frac{1}{2}, +\frac{1}{2} - l\rangle_3 C_3\Gamma(n, l) \\
+ \sum_{l=-a_1}^{-l} \left( \sum_{m=-S}^{S+l} |S, m\rangle_1 \otimes |S, l-m\rangle_2 C_{12}^-(a_1, l, m, S) \right) \otimes |n + \frac{1}{2}, +\frac{1}{2} - l\rangle_3 C_3\Gamma(n, l),
\]

\[
C_{12}^\pm(n, l, m, S) = \sqrt{\frac{(2n+1)(2S-n)!(a_5+l)!(a_6-l)!(n-l)!}{(2S+n+1)!(a_5)!}} \sum_{q=a_3}^{a_4} (-1)^{a_5-a_6+q} \binom{a_6}{q} \binom{a_5}{n-q} \binom{n}{q-l}, \quad l = a_1 - a_2 + 1,
\]

\[
(a_5, a_6) = (S-m, S+m), \quad \sqrt{(n+1)(2a_1+1)} \text{C}_3\Gamma(n, l) = (-1)^{a_1-l} \sqrt{n-a_2+1},
\]

\[
(a_1, a_2) = \begin{cases} (n, l), & \text{if } \Gamma = A' \\ (n+1, -l), & \text{if } \Gamma = B' \end{cases}, \quad (a_3, a_4) = \begin{cases} (l, n), & \text{for } C_{12}^+(n, l, m, S) \\ (0, n+l), & \text{for } C_{12}^-(n, l, m, S) \end{cases}.
\]

Using the symmetry and normalization properties of the Clebsch-Gordan coefficients between sites one and two:

\[
\sum_{m=-S+l}^{S} \langle S, m + \frac{l}{2}, S, -m + \frac{l}{2} | n, l \rangle^2 = 1,
\]

\[
\langle S, m_1, S, m_2 | n, l \rangle^2 = \langle S, m_2, S, m_1 | n, l \rangle^2 = \langle S, -m_1, S, -m_2 | n, -l \rangle^2.
\]

together with the following identity:

\[
\sum_{m=-S+n}^{S} \binom{m-n/2}{m-n/2}^2 \frac{(S-m+n)!(S+m)!}{(S+n-m)!(S-m)!} = \frac{(2S+n+2)!}{4(2n+1)(2n+3)(\frac{2n}{n})!},
\]

we evaluate the relevant reduced matrix elements \( \langle \Gamma | \hat{T}^1(\hat{S}_p) | \Gamma \rangle \) on the basis \( |\Gamma, M_T\rangle = \{|A', +\frac{1}{2}\rangle, |A', -\frac{1}{2}\rangle, |B', +\frac{1}{2}\rangle, |B', -\frac{1}{2}\rangle\} \) for \( S_3 = n + \frac{1}{2} \) as:

- \( \langle A'| \hat{T}^1(\hat{S}_1) | A' \rangle = -n / \sqrt{6} \)
- \( \langle A'| \hat{T}^1(\hat{S}_2) | A' \rangle = -n / \sqrt{6} \)
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- $\langle A' | \hat{T}^1(\hat{S}_3) | A' \rangle = (3 + 2n)/\sqrt{6}$
- $\langle A' | \hat{T}^1(\hat{S}_1) | B' \rangle = -2\sqrt{(S - \frac{n}{2})(S + 1 + \frac{n}{2})/6}$
- $\langle A' | \hat{T}^1(\hat{S}_2) | B' \rangle = +2\sqrt{(S - \frac{n}{2})(S + 1 + \frac{n}{2})/6}$
- $\langle A' | \hat{T}^1(\hat{S}_3) | B' \rangle = 0$
- $\langle B' | \hat{T}^1(\hat{S}_1) | B' \rangle = (2 + n)/\sqrt{6}$
- $\langle B' | \hat{T}^1(\hat{S}_2) | B' \rangle = (2 + n)/\sqrt{6}$
- $\langle B' | \hat{T}^1(\hat{S}_3) | B' \rangle = (-1 - 2n)/\sqrt{6}$

Using these results, we can represent the toroidal moment operator in various ground manifolds. For example, for an equilateral triangle with $S_3 = n + \frac{1}{2}$, setting $\lambda_{\text{ex}} = J_{\text{ex}}$ and representing $\hat{\tau}_z$ on the basis $\{|A', +\frac{1}{2}\}, |A', -\frac{1}{2}\}$, $|B', +\frac{1}{2}\}, |B', -\frac{1}{2}\}$ gives the following eigenvalues:

$$\tau_{A'} = \frac{n + 1}{2} \pm \frac{(S - \frac{n}{2})(S + 1 + \frac{n}{2})}{3} \mu_B R.$$  \hspace{1cm} (18)

$$\tau_{B'} = \frac{n + 1}{2} \pm \frac{(S - \frac{n}{2})(S + 1 + \frac{n}{2})}{3} \mu_B R.$$  \hspace{1cm} (19)

Alternatively, setting $|\lambda_{\text{ex}}| < |J_{\text{ex}}|$ and representing $\hat{\tau}_z$ on $\{|A', +\frac{1}{2}\}, |A', -\frac{1}{2}\}$, or setting $|\lambda_{\text{ex}}| < |J_{\text{ex}}|$ and representing $\hat{\tau}_z$ on $\{|B', +\frac{1}{2}\}, |B', -\frac{1}{2}\}$, gives the following eigenvalues:

Thus, the strengths of the exchange couplings determine whether there are two or four distinct toroidal states in the frustrated ground manifolds, regardless of the choices for $S$ and $S_3$.

4. Use in a Spintronics Device

With these toroidal states in mind, we now explore how this family of triangular molecules would behave in the tunneling spintronics device proposed in earlier works [11, 39]. The device consists of a spin-polarized source lead and an unpolarized drain lead, whose Fermi levels are offset by an external bias potential, see Fig. 3. An external gate potential is also applied, to induce resonance between the ground states of the triangle in its redox-neutral and redox-polarized forms. These two biases promote electrons to pass from the source lead, onto the triangle and then onto the drain lead. That is, we apply a sequential tunneling model under the Coulomb Blockade regime (doubly-reduced states are considered energetically inaccessible). The Hamiltonian describing these tunneling processes is [46, 47]:

$$\hat{H}_T = \sum_{p=1}^3 \sum_k \sum_{L} \sum_{\gamma} \beta_{pL} (\hat{a}^\dagger_{pL} \hat{c}_{kL\gamma} + \hat{c}^\dagger_{kL\gamma} \hat{a}_{pL}).$$  \hspace{1cm} (20)

where $\hat{a}^\dagger_{pL}$ creates an electron on site $p$ with spin $\gamma = \uparrow$ or $\downarrow$; $\hat{c}^\dagger_{kL\gamma}$ creates an electron with wavenumber $k$ on lead $L = S$ or $D$ (source or drain) with spin $\gamma$; $k$ varies within the first Brillouin zone of a lead’s electronic band structure; and $\beta_{pL}$ is the tunneling amplitude between site $p$ and lead $L$.

We set up the master equation for the nonequilibrium populations of the triangle’s redox-neutral and singly-reduced states in the usual manner, by applying the Born-Markov approximation and considering coherences between different states of the triangle as negligible [48]:

$$\frac{dP_j}{dt} = \sum_{i \neq j} P_i W_{i \rightarrow j} - P_j \sum_{i \neq j} W_{j \rightarrow i},$$  \hspace{1cm} (21)

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where $W_{i \rightarrow j}$ is the transition rate from state $|i\rangle$ to state $|j\rangle$. To find the transition rates, we apply the Fermi golden rule and integrate over all wavenumbers in each lead’s first Brillouin zone, treating the tunneling amplitudes $\beta_{pL}$ and densities of spin states $\rho_{pL}$ as being essentially constant [49, 50]:

$$W^{L_L}_{r_i \rightarrow r_j} = \frac{2\pi \rho_{pL}}{\hbar} \left| \langle r_j | \sum_{p=1}^{3} \beta_{pL} \hat{a}_{p}^\dagger | r_i \rangle \right|^2 F_L (\Delta E),$$

(22)

where $W^{L_L}_{r_i \rightarrow r_j}$ is the charging rate from neutral state $|r_i\rangle$ to reduced state $|r_j\rangle$, with the extra electron coming from lead $L$ and having spin $\gamma$; $\Delta E = E(r_j) - E(r_i)$ is the energy difference between the two states; and $F_L(\Delta E) = [1 + \exp(\frac{\Delta E - \mu_p}{k_B T})]^{-1}$, with $\mu_S = +eV_B$ and $\mu_D = -eV_B$ being the Fermi levels of the source and drain leads. A discharging rate such as $W^{L_L}_{r_j \rightarrow r_i}$ is defined similarly, but is weighted by $[1 - F_L(\Delta E)]$ rather than $F_L(\Delta E)$.

Before proceeding further, we must establish how the triangle would interact with an extra electron which is passing through. We consider exchange coupling between the extra electron’s spin and the local spin where the electron temporarily resides, and delocalization of the extra electron across all three sites [51, 52]:

$$\hat{H}_{\text{Hund}} = -\sum_{p=1}^{3} \sum_{\gamma, \delta} J_{H p} \left( \hat{a}_{p \gamma}^\dagger \hat{a}_{p \delta} \sigma_{\gamma \delta} \cdot \hat{S}_p \right),$$

(23)

$$\hat{H}_{\text{hop}} = \sum_{p=1}^{3} \sum_{\gamma} t_{p, p+1} \left( \hat{a}_{p+1, \gamma}^\dagger \hat{a}_{p, \gamma} + \hat{a}_{p, \gamma}^\dagger \hat{a}_{p+1, \gamma} \right).$$

(24)

The subscripts $\gamma$ and $\delta$ indicate the rows and columns of the entries in the Pauli matrices $\sigma_x$, $\sigma_y$, and $\sigma_z$ to be used in the dot product with $\hat{S}_p$. The isosceles nature of the triangle is used to reduce the number of parameters in the above Hamiltonians, such that $J_{H11} = J_{H22} \equiv J_{H12}$ and $t_{12} = t_{23} \equiv t_3$.

We apply first-order degenerate perturbation theory to solve $\hat{H}_{\text{Hund}}$ and $\hat{H}_{\text{hop}}$ simultaneously within the ground manifolds of $\hat{H}_{\text{ex}}$. That is, we choose $|J_{ex}|, |\lambda_{ex}| \gg J_{H12}, J_{H3}, t_{12}, t_3, \beta_{pL}, eV_B, k_B T$ and inspect each ground manifold separately: $|J_{ex}| > |\lambda_{ex}|, |J_{ex}| = |\lambda_{ex}|, |\lambda_{ex}| < |J_{ex}| < |\lambda_{ex}|$. We then solve Eq. (21) under the steady-state approximation to obtain the nonequilibrium populations of states. For the case of $|J_{ex}| = |\lambda_{ex}|$, see Fig. 4.

Based on a numerical analysis of the transition rates in Eq. (22), we have concluded that the mechanism behind the population splitting for a forward bias voltage is as follows: The rate at which an electron moves from the source lead to the triangle is faster when the initial exchange coupling between the electron and the triangle is favorable. For example,
consider the scenario where $|J_{ex}| = |\lambda_{ex}|$ and the Hund exchange coupling to an extra electron is ferromagnetic. In states $|\tau_{1-}\rangle$ and $|\tau_{2-}\rangle$, the local spin which is nearest to the source lead is almost parallel to the source’s polarization direction, see Fig. 3. With this alignment, there will be an efficient transfer in population from $|\tau_{1-}\rangle$ and $|\tau_{2-}\rangle$ (redox-neutral) to $|\tau_{1}\rangle$ and $|\tau_{2}\rangle$ (singly-reduced) as the electron moves onto the triangle. Meanwhile, the drain lead is unpolarized, so the rate at which an electron moves from the triangle to the drain is less dependent on the triangle’s spin state, so any of $|\tau_{1\pm}\rangle$ or $|\tau_{2\pm}\rangle$ may be regenerated. The overall effect is a transfer of population from $|\tau_{1-}\rangle$ and $|\tau_{2-}\rangle$ to $|\tau_{1+}\rangle$ and $|\tau_{2+}\rangle$, thus a net toroidal magnetization is produced, see Fig. 4.

Conversely, for a reverse bias voltage, the triangle may be in any redox-neutral state $|\tau_{1\pm}\rangle$ or $|\tau_{2\pm}\rangle$ when an electron tunnels from the unpolarized drain lead onto the triangle to produce a singly-reduced state $|\tau_{1}\rangle$ or $|\tau_{2}\rangle$. However, the electron must be spin-up when it tunnels onto the polarized source lead. Thus, in the case of ferromagnetic Hund coupling, the triangle is more likely to be reset into a clockwise state ($|\tau_{1+}\rangle$ or $|\tau_{2+}\rangle$) than a counterclockwise state ($|\tau_{1-}\rangle$ or $|\tau_{2-}\rangle$) when the electron departs. (For antiferromagnetic Hund coupling or a down-polarized source lead, the preference for clockwise or counterclockwise is simply reversed.)

Since the selectivity in transition rates for clockwise or counterclockwise states depends on the orientations of the local spins, when the triangle is rotated within its plane, the strength of the population splitting varies dramatically, see Fig. 5. For example, if the local spin which is nearest to the source is oriented roughly perpendicular to the source’s spin-polarization direction, the initial Hund coupling will be relatively unaffected by the choice of a clockwise state over a counterclockwise state, so the corresponding charging rates will become equal, and there will be no population splitting. Alternatively, if that local spin is aligned along the polarization direction, there will be a significant difference in the charging rates, and the mechanism described above takes place.

To further understand this mechanism, we studied the dependence of the population splitting on the strengths of the Hund couplings, and found the splitting to be larger when $|J_{H12}S| > |J_{H3}S_3|$, see Fig. 6. In this case, the ground singly-reduced states are $|\tau_{1}\rangle$ and $|\tau_{2}\rangle$, in which the extra electron predominantly resides on either of the two sites with spin $S$, whereas when $|J_{H12}S| < |J_{H3}S_3|$, the extra electron predominantly resides only on the site with spin $S_3$. To produce the spin-transfer torque needed to induce a net toroidal magnetization on the triangle, the extra electron’s spin must be rotated as it moves across the triangle, which is best achieved via Hund coupling to two differently oriented spins, so the case of $|J_{H12}S| > |J_{H3}S_3|$ is more effective.

Of course, if this spintronics device is to be used for high-density data storage applications, we require a method to measure the net toroidal magnetization as being clockwise or counterclockwise. This would be virtually impossible to do via direct magnetic probing of the triangular nanomagnet, as non-dipolar toroidal states do not interact with homogeneous magnetic fields [13, 14]. Rather, we propose to look for evidence of the toroidal magnetization by measuring the spin currents passing through the device.

With the populations of states known, we simply multiply by the relevant transition rates to evaluate the spin
The geometry shown in Fig. 3, using SV Rao, JM Ashtree and A Soncini: Figure 6: Nonequilibrium population splitting regime for producing a strong toroidal magnetization is the geometry shown in Fig. 3 (i.e., \( S \) varies in accordance with the mechanism for population splitting described above, see Fig. 7. For example, with the similar to the extent of population splitting. For example, the strength of spin-switching increases for larger \( J_{H12} S \), and the angular dependence of the spin currents resembles the angular dependence of the population splitting, see Figs. 5 and 8.

\[
I^\uparrow_S - I^\downarrow_S = e \sum_{i,j} \left( \left( W^{S \uparrow}_{i \to j} - W^{S \downarrow}_{i \to j} \right) P_{\tau_i} - \left( W^{S \downarrow}_{j \to i} - W^{S \uparrow}_{j \to i} \right) P_{\tau_j} \right), \tag{25}
\]

\[
I^\uparrow_D - I^\downarrow_D = -e \sum_{i,j} \left( \left( W^{D \uparrow}_{i \to j} - W^{D \downarrow}_{i \to j} \right) P_{\tau_i} - \left( W^{D \downarrow}_{j \to i} - W^{D \uparrow}_{j \to i} \right) P_{\tau_j} \right). \tag{26}
\]

We find that the polarization of the spin current passing through the device is partially reversed, to an extent which varies in accordance with the mechanism for population splitting described above, see Fig. 7. For example, with the geometry shown in Fig. 3 (i.e. \( \theta = 0 \)), there is a strong selectivity in the charging rates from the spin-polarized source lead, but only minor selectivity in the discharging rates to the unpolarized drain lead, thus the forward spin-up and spin-down drain currents mostly cancel each other out. By contrast, for a reverse bias voltage and ferromagnetic Hund coupling, spin-down electrons from the drain prefer to tunnel onto clockwise states, while spin-up electrons from the drain prefer to tunnel onto counterclockwise states. The excess population in the clockwise states for a reverse bias means that more spin-down electrons will flow (backwards) through the drain than spin-up electrons. (Note: The redox-neutral clockwise states are selectively regenerated upon discharging spin-up electrons to the source lead.)

Because both phenomena are caused by spin-transfer torque, the extent of this spin-switching effect follows a pattern similar to the extent of population splitting. For example, the strength of spin-switching increases for larger \( J_{H12} S \), and the angular dependence of the spin currents resembles the angular dependence of the population splitting, see Figs. 5 and 8.
Figure 7: Spin currents vs. bias voltage, using the geometry shown in Fig. 3 (i.e. $\theta = 0$), $S = \frac{7}{2}$, $S_3 = \frac{1}{2}$ and $|J_{ex}| = |\lambda_{ex}| \gg J_{H12} S > J_{H3} S_3$, $t_{12}$, $t_3$, $\beta_{pl}$, $eV_B$, $k_B T$, with $\rho_{S1} = 1$ cm, $\rho_{S1} = 0$ cm, $\rho_{D1} = \rho_{D1} = 0.5$ cm, $\beta_{1D} = \beta_{2x} = 0.1$ cm$^{-1}$, other $\beta_{pL} = 0$ cm$^{-1}$. For a negative bias, more than half of the tunneling electrons’ spins are reversed by the triangle’s toroidal spin texture.

Figure 8: Spin currents vs. in-plane angle of rotation $\theta$ relative to the geometry shown in Fig. 3, using $S = \frac{7}{2}$, $S_3 = \frac{1}{2}$ and $|J_{ex}| = |\lambda_{ex}| \gg J_{H12} S > J_{H3} S_3$, $t_{12}$, $t_3$, $\beta_{pl}$, $eV_B$, $k_B T$, with $\rho_{S1} = 1$ cm, $\rho_{S1} = 0$ cm, $\rho_{D1} = \rho_{D1} = 0.5$ cm. The tunneling amplitudes $\beta_{pL}$ are the same as in Fig. 5, but with proportionality constants of 0.2 cm$^{-1}$.

Figure 9: Nonequilibrium population splitting in the $A$ and $B$ doublets vs. bias voltage, using $\theta = \pi$ and $J_{H12} > J_{H3}$, $t_{12}$, $t_3$, $\beta_{pl}$, $eV_B$, $k_B T$.

Similar behavior also occurs when $|J_{ex}| > |\lambda_{ex}|$ (i.e. in the $|r_{A\pm}\rangle$ doublet) and when $|\lambda_{ex}| < |J_{ex}| < |\lambda_{ex}|$ (i.e. in the $|r_{B\pm}\rangle$ doublet), but the extents of population splitting and spin switching are smaller than for $|J_{ex}| = |\lambda_{ex}|$, as the ground states in those regimes have smaller toroidal moments, see Figs. 9 and 10. Another key difference is that none of the spin textures of the redox-neutral or singly-reduced states arising from the $A$ or $B$ doublets depend on the value of $S$, so the behavior of the spintronics device in those regimes is also independent of $S$. 
Figure 10: Spin currents vs. bias voltage for the A and B doublets, using $J_{H12} > J_{H3}$, $I_{12}$, $I_3$, $\beta_{pL}$, $eV_B$, $k_BT$, with $\rho_{S1} = 1 \text{ cm}$, $\rho_{S2} = 0 \text{ cm}$, $\rho_{D1} = \rho_{D2} = 0.5 \text{ cm}$, $\beta_{1D} = \beta_{2S} = 0.1 \text{ cm}^{-1}$, other $\beta_{pL} = 0 \text{ cm}^{-1}$.

5. Conclusion

Both from the perspective of fundamental interest and practical applicability, toroidal states are an exciting field of study. By predicting the existence of toroidal ground states in isosceles spin triangles, we have extended the number of candidate molecules without spin-orbit coupling well beyond the equilateral spin $\frac{1}{2}$ case.

When the exchange interactions between each of the spins are equal, four distinct toroidal states can be produced from the frustrated ground manifold. In the case where not all the couplings are equal, there are still toroidal moments in the ground doublets. In each scenario, we obtain analytical expressions for the toroidal moments for any values of the spins, provided $S_1 = S_2$.

This family of molecules may also be used in a tunneling spintronics device to reverse the polarization of an injected spin current and simultaneously produce a net toroidal magnetization on the triangle — a property which has exciting possibilities for high-density data storage.

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