Theory of high-symmetry tetramer single molecule magnets

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We present a microscopic theory of single molecule magnets. From our exact single-ion spin matrix elements for four arbitrary spins, we study the single-ion anisotropy of equal spins exhibiting \( T_d, D_{2d}, \) or \( C_{4v} \) molecular group symmetry. Each group generates site-dependent single-ion anisotropy.

For weak anisotropy, accurate Hartree expressions for the magnetization, specific heat, electron paramagnetic resonance (EPR) absorption and inelastic neutron scattering cross-section are given. For \( D_{2d} \), azimuthal single-ion anisotropy leads to the observed Ni4 EPR splittings.

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Single molecule magnets (SMM’s) have been a topic of great interest for more than a decade,\cite{1} because of their potential uses in quantum computing and/or magnetic storage.\cite{2} which are possible due to magnetic quantum tunneling (MQT) and entangled states. In fits to a wealth of data, the Hamiltonian within an SMM was assumed to be the Heisenberg exchange interaction plus weaker global (total, or giant) spin anisotropy interactions, with a fixed overall global spin quantum number \( s \).\cite{3} MQT and entanglement were studied in this simple model.

The simplest SMM’s are dimers.\cite{3, 4} Surprisingly, two antiferromagnetic dimers, an Fe\(_2\) and a Ni\(_2\), appear to have substantial single-ion anisotropy without any appreciable global anisotropy.\cite{4, 5, 6} Although the most common SMM’s have ferromagnetic (FM) intramolecular interactions and contain \( n \geq 8 \) magnetic ions,\cite{7} a number of intermediate-sized FM SMM’s with \( n = 4 \) and rather simple molecular structures were recently studied. Co\(_4\) and Cr\(_4\) have \( s = 6 \) ground states with spin 3/2 ions on the corners of tetrahedrons.\cite{8, 9} A number of high symmetry \( s = 4 \) ground state Ni\(_4\) structures with spin 1 ions were reported.\cite{10, 11, 12} Inelastic neutron scattering (INS) experiments provided strong evidence for single-ion anisotropy in Co\(_4\) and a Ni\(_4\).\cite{10} Fits to electron paramagnetic resonance (EPR) Ni\(_4\) data assuming a fixed \( s \) were also problematic.\cite{12, 13}

Yet there is no microscopic model of FM SMM’s in which the MQT and entanglement issues crucial for quantum computing can be understood. To analyze the differences between single-ion and global anisotropy in FM systems, we found exact expressions for the single-ion spin matrix elements of four general spins, and compared global and single-ion anisotropies in the Hartree approximation for the magnetization, specific heat, EPR and INS transitions for equal-spin SMM tetramers with molecular group \( T_d, D_{2d}, \) and \( C_{4v} \) symmetries. Surprisingly, we also found that each molecular group symmetry generates site-dependent single-ion anisotropy, and that azimuthal \( D_{2d} \) single-ion anisotropy has a continuous symmetry, observed as splittings in the Ni\(_4\) EPR resonances.\cite{14}

We assume four equal spins \( s_1 \) sit on opposite corners of an orthorhombic prism with sides \((a, a, c)\) or on a square, with the geometric center at the origin, as in Fig. 1. For molecular (site point) groups \( g = T_d, D_{2d}, \) and \( C_{4v} \) with \( \sum_{n=1}^{4} r_n = 0 \), the relative spin positions are

\[ r_n = -\frac{a}{2}[\gamma_1^+ \hat{x} + (-1)^n \hat{y}] + \frac{c}{2} \gamma_n^+ \hat{z}, \]

\[ \gamma_n^+ = e_n^+(-1)^{n/2} + e_n^{-}(-1)^{(n+1)/2}, \]

where \( e_n^\pm = [1 \pm (-1)^n]/2 \).\cite{14} In tetrahedrons with \( g = T_d \), \( c/a = 1 \), approximately as in Co\(_4\) and Cr\(_4\),\cite{8, 9} In squares with \( g = C_{4v} \), \( c = 0 \), as in one Mn\(_4\) SMM and Nd\(_4\) (with equal total angular momentum \( j = 9/2 \)).\cite{12, 15, 16} In prisms with \( g = D_{2d} \), \( c/a > 1 \), approximately as in Ni\(_4\), a Fe\(_4\) and a Cu\(_4\),\cite{12} or \( c/a < 1 \). \( \hat{x}, \hat{y}, \hat{z} \) are the molecular (or global) axes of each tetramer SMM.

The local (or single-ion) azimuthal vectors satisfying all \( g = C_{4v} \) symmetries are \( \hat{x}^g_n = (\gamma_1^+ \hat{x} + \gamma_n^+ \hat{y})/\sqrt{2} \), as in the right panel of Fig. 1, and the common local axial vector is \( \hat{z}^g_n = \hat{z} \). For \( g = T_d, D_{2d} \), we take the group symmetry-satisfying local axial vectors to be \( \hat{z}^g_n = r_n/a_0 \), as in the left panel of Fig. 1, where \( a_0 = \sqrt{2a^2 + c^2} \), and we set \( \tau = c/a_0 \) and \( a = a_0 \sqrt{(1 - \tau^2)/2} \). We define the local azimuthal vectors from \( (\hat{z}^g_n)^T = (\tau, \bar{\tau}, \overline{\tau}) \),

\[ \hat{x}_1^g = \frac{1}{2} \left( \frac{-(1 + \overline{\tau}) \cos \mu + (1 - \tau) \sin \mu}{(1 - \tau) \cos \mu - (1 + \tau) \sin \mu} \right), \]

\[ \hat{y}_1^g = \hat{z}_1^g \times \hat{x}_1^g \]. For \( \mu = 0 \), \( \hat{x}_1^g \cdot \hat{z}_1^g = 0 \). A rotation by the arbitrary angle \( \mu \) about \( \hat{z}_1^g \) leads to Eq. 3. The

![Fig. 1: D_{2d} (left) and C_{4v} (right) ion sites (filled). Circle: origin. Arrows: local axial (left), azimuthal (right) vectors.](image-url)
other local azimuthal vectors are obtained by π rotations of \( \hat{x}_n, \hat{y}_n, \hat{z}_n \) about \( \hat{x}, \hat{y}, \hat{z} \). They automatically satisfy all of the mirror planes of \( D_{2d} \). Although \( \mu \) is a degree of freedom in \( D_{2d} \), no \( \mu \) choice satisfies the remaining group operations (rotations by ±2π/3 about the cube diagonals) of \( T_d \). Hence, \( T_d \) only has local axial vectors.

In the local coordinates of groups \( g = T_d, D_{2d}, C_{4v}, \) the most general quadratic single-ion Hamiltonian is

\[
\mathcal{H}_{\text{si}}^\mu = -\sum_n \left( J_n(S_n \cdot \hat{z}_n)^2 + J_e[(S_n \cdot \hat{x}_n)^2 - (S_n \cdot \hat{y}_n)^2] \right),
\]

which for these equal-spin, high symmetry systems has site-independent \( J_n, J_e \). \( \mathcal{H}_{\text{si}}^\mu \) is invariant under all allowed \( g \) symmetries. Unequal spin values or ligands or local structural distortions from the ideal molecular group symmetry, as commonly occur in real systems, break these \( g \) symmetries, and also lead to Dyzalooshinshii-Moriya (DM) interactions, which vanish for precise molecular groups \( T_d, D_{2d}, \) or \( C_{4v} \). Such lower symmetry cases will be discussed elsewhere.\[20\]

To make contact with experiment, we rewrite \( \mathcal{H}_{\text{si}}^\mu \) in the molecular \( (\hat{x}, \hat{y}, \hat{z}) \) representation,

\[
\hat{J}_{\text{si}}^\mu = \sum_{\alpha\beta} J_{n,\alpha\beta}^\mu(S_{n,x}^\alpha S_{n,y}^\beta + J_{n,xy}^\mu(S_{n,x}^\alpha S_{n,y}^\beta),
\]

where \( \alpha, \beta = x, y, z \), and the remaining non-vanishing couplings are \( J_{n,xy}^\mu = J_{n} = J_{n}/2, J_{n,xy}^\mu = J_{n}(-1)^{n}/2, J_{n,xy}^\mu = J_{n}(1-\tau^2)sin(2\mu) \), \( J_{n,xy}^\mu = J_{n}(\tau^2 + \tau^2) + 3J_{n} \tau sin(2\mu) \), \( J_{n,zy}^\mu = J_{n}(\tau^2 - \tau^2)sin(2\mu) \), and we subtracted an irrelevant constant. To preserve the \( g \) symmetries of \( \mathcal{H}_{\text{si}}^\mu \), \( \mathcal{H}_{\text{si}}^\mu \) contains the site-dependent interactions \( J_{n,\alpha\beta}^\mu(\mu) \). The continuous (rotational) symmetry of the local azimuthal vectors in \( D_{2d} \) leads to anisotropy energy strengths in \( \mathcal{H}_{\text{si}}^\mu \) that are periodic functions of \( \mu \), as in one-dimensional optical phonon bands.

We assume a molecular Hamiltonian of \( \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{si}}^\mu + \mathcal{H}_p \), where the Heisenberg and Zeeman interactions are

\[
\mathcal{H}_0 = -JS^2/2 - \gamma B \cdot S - \delta J^\rho (S_{13}^2 + S_{24}^2)/2,
\]

where \( \delta J^\rho = 0,J^\rho - J \), and \( -\delta J \) for \( g = T_d, D_{2d}, \) and \( C_{4v} \), respectively. \( S_{13} = S_1 + S_3, S_{24} = S_2 + S_4, S = S_{13} + S_{24}, \gamma = g_B \mu_B \) is the gyromagnetic ratio (assumed isotropic, with \( g \approx 2 \)), and \( B = B(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \) is the magnetic induction at an arbitrary direction \((\theta, \phi)\) relative to the molecular coordinates. The time correlation functions of the classical analog of this \( C_{4v} \) \( \mathcal{H}_0 \) model were published.\[10\]

The phenomenological global anisotropy interactions usually studied in SMM’s are

\[
\mathcal{H}_p = -J_b S_x^2 - J_d(S_x^2 - S_y^2),
\]

containing axial and azimuthal contributions, respectively.\[\Box\] They are generally defined relative to the global spin principal axes, which for equal spin, high symmetry systems are the molecular axis vectors.

To take proper account of \( B \) in \( \mathcal{H}_0 \), we construct our SMM eigenstates in the induction representation by \((\hat{x}, \hat{y}, \hat{z}) = (\hat{x}, \hat{y}, \hat{z}) \cdot \hat{M} \) so that \( B = \hat{B} \cdot \hat{M} \), where

\[
\hat{M} = \begin{pmatrix}
\cos \theta \cos \phi & \cos \theta \sin \phi & -\sin \theta \\
-\sin \phi & \cos \phi & 0 \\
\sin \theta \cos \phi & \sin \theta \sin \phi & \cos \theta
\end{pmatrix}.
\]

A subsequent arbitrary rotation about \( \hat{z} \) does not affect the eigenstates.\[\Box\] We then set \( \hbar = 1 \) and write

\[
S^2 |\psi_{s,m}^{13,24}\rangle = s(s + 1) |\psi_{s,m}^{13,24}\rangle,
\]

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\]

\[
S^2 |\psi_{s,m}^{13,24}\rangle = s_{13}(s_{13} + 1)|\psi_{s,m}^{13,24}\rangle,
\]

\[
S^2 |\psi_{s,m}^{13,24}\rangle = m_{13} |\psi_{s,m}^{13,24}\rangle,
\]

\[
S^2 |\psi_{s,m}^{13,24}\rangle = A_{2m}^{s} |\psi_{s,m}^{13,24}\rangle,
\]

\[
A_{2m}^{s} = \sqrt{(s - m)(s + m + 1)},
\]

where \( S_{13} = \pm i \delta S_{24} \) with \( \delta = \pm \). For brevity, we denote \( \nu = \{s, m, s_{13}, s_{24}, \{s_n\}\} \), and write \( |\nu\rangle = |\psi_{s,m}^{13,24}\rangle \). From Eqs.\[11\] to \[14\], \( \langle \nu | \mathcal{H}_0 | \nu \rangle = E_{\nu,0} \delta_{\nu',\nu} \), where

\[
E_{\nu,0} = -JS(s + 1)/2 - \gamma B m
\]

\[
-\delta J^\rho (s_{13}(s_{13} + 1) + s_{24}(s_{24} + 1))/2.
\]

We then transform \( \mathcal{H}_{\text{si}}^\mu \) and \( \mathcal{H}_p \) to the induction representation, and make a standard perturbation expansion for small anisotropy energies \( |J_1| \) \((J_0, J_b, J_d, J_e)\) relative to \( |J| \) and \( \gamma B \). The matrix elements of \( \mathcal{H}_p \) are then obtained from Eqs.\[11\] and \[15\]. However, the matrix elements of \( \mathcal{H}_{\text{si}}^\mu \) contain more interesting physics.

By using symbolic manipulation software for the Clebsch-Gordan algebra, we find the single-ion spin matrix elements with general \( \{s_n\} = \{s_1, s_2, s_3, s_4\} \) to be

\[
\langle \nu' | S_n, z | \nu \rangle = \delta_{m',m} \left( m \delta_{s',s} \Gamma^{(s_n)}_{s_{13}, s_{24}, s_{24}}^{s_{13}, s_{24}, s_{24}} + \delta_{s',s} + C_{m}^{s_{13}, s_{24}, s_{24}} \Gamma^{(s_n)}_{s_{13}, s_{24}, s_{24}}^{s_{13}, s_{24}, s_{24}} \right).
\]

\[
\langle \nu' | S_n, x | \nu \rangle = \delta_{m',m} \left( m \delta_{s',s} \Gamma^{(s_n)}_{s_{13}, s_{24}, s_{24}}^{s_{13}, s_{24}, s_{24}} - \delta_{s',s} + D_{s}^{s_{13}, s_{24}, s_{24}} \Gamma^{(s_n)}_{s_{13}, s_{24}, s_{24}}^{s_{13}, s_{24}, s_{24}} \right).
\]
\[ C^m = \sqrt{s^2 - m^2}, \]
\[ D^m = \delta \sqrt{(s - \delta m)(s - \delta m - 1)}, \]
\[ \Gamma^{(s_n), s, m}_{\delta, s, n} = \delta_{\delta, s, n} \frac{m}{2} \]
\[ \Delta^{(s_n), s, m}_{\delta, s, n} = \delta_{\delta, s, n} \frac{m}{2} \]
\[ \alpha^{s, n}_{\delta, s, n} (s_{13}, s'_{13}) = \frac{1}{4} \left( 1 + \xi_{s, s_{13}, s_{24}} \right) \delta s_{13}^{s_{13}} - \gamma_{n} \]
\[ \beta^{s, n}_{\delta, s, n} (s_{13}, s'_{13}) = \frac{(-1)^{n}}{4} \eta_{n} \delta s_{13}^{s_{13}} - \gamma_{n} \]
\[ \frac{F^{s_{13}, s_{24}}_{\delta, s, n}}{A^{s_{13}, s_{24}}_{\delta, s, n}} = \frac{\delta_{\delta, s, n}}{4s(s + 1)}, \]
\[ \frac{G^{s_{13}, s_{24}}_{\delta, s, n}}{A^{s_{13}, s_{24}}_{\delta, s, n}} = \frac{\delta_{\delta, s, n}}{4s(s + 1)}, \]
\[ \frac{\eta_{z, x, y}}{A^{y} \rightarrow A^{y} \rightarrow} = \frac{2}{\sqrt{2} (4z^2 - 1)}, \]
\[ \xi_{z, x, y} = \frac{x(z + 1) - y(z + 1)}{z(z + 1)}, \]

where \( \gamma_{n} \) is given by Eq. (2). The prefactors \( m, \Gamma^m, \)
\( C^m, \Delta^m, \beta^m, \alpha^m, \) and \( D^m \) are consequences of the
Wigner-Eckart theorem for a vector operator.\[14\] The challenge was to obtain the coefficients \( \Gamma^{(s_n), s, n}_{\delta, s, n}, \)
\( \Delta^{(s_n), s, m}_{\delta, s, n}, \) and \( \alpha^{s, n}_{\delta, s, n} (s_{13}, s'_{13}) \). Their hierarchical structure based upon
the unequal-spin dimer suggests that analogous coefficients with \( n > 4 \) may be obtainable.\[4\]

At arbitrary \((\theta, \phi)\), the first order corrections \( E_{\nu,1} \)
\( = \langle \nu | H + H^0_{\text{st}} | \nu \rangle \) to the eigenstate energies are
\[ E_{\nu,1} = \frac{\beta_{\nu, \theta}^{\theta} (\mu)}{2} \]
polarized oscillatory fields normal to $B$ is

$$\mathbb{V}g^{(1)}_{\sigma} = \frac{\gamma^2}{Z_0^2} \text{Tr}^g B_{\nu}^g e^{-\beta g} \left[ M_{\nu,\nu'} \right]^2 \times \delta(\epsilon' - \epsilon + \omega) - \delta(\epsilon' - \epsilon + \omega),$$

where $M_{\nu,\nu'} = A_{\nu}^{\text{spin}} \delta_{\nu,\nu'} + \delta_{\nu,\nu'} \delta_{\nu',\nu}$, and $B_{\nu}^g = \sum_{\nu'} J_{\nu,\nu,\nu'} \mathcal{D}_{\nu}^g (\epsilon') d_{\nu'}$. The resonant inductions for $g = D_{2d}$, the weak center of each $B_{\nu}^g$, Eq. (37), are equally surrounded by two strong resonances split by $\Delta B_{\nu}^g = 2|J_{\nu,\nu,\nu'}|$, where $\omega_{\nu} = \sqrt{x_{\nu}^2 + y_{\nu}^2}$, $y_{\nu} = \sum_{\nu'} J_{\nu,\nu,\nu'} [3m^2 - s(s + 1)] \sin^2 \theta \cos(2\phi)$, and $x_{\nu} = \sum_{\nu'} J_{\nu,\nu,\nu'} [2m + \omega_s s(s + 1)] \sin^2 \theta + m^2 (3 \cos^2 \theta - 1)$. For $\theta = 0$, $\Delta B_{\nu}^g = 6\alpha^2 [(2m + \sigma) \alpha |\nu,\nu|]$, nicely fitting $s = 4 (\sigma \alpha = 1/7)$ data on three Ni$_4$ compounds. For $c/a \approx 1.1$, $|J_{\nu,\nu,\nu'}| \approx 0.07K$, and 0.91K.11 More $B_{\nu}^g (\theta, \phi)$ data are urged.

The Hartree INS cross-section $S_{\nu}^g(B,q,\omega)$ is

$$S_{\nu}^g = \text{Tr}^g \sum_{\nu'} e^{-\beta \epsilon_{\nu'}} \sum_{\alpha,\beta} \left( \delta_{\alpha,\beta} - \hat{q}_h \hat{q}_\beta \right) \sum_{n,n'=1}^4 \times e^{i q \cdot (r_n - r_{n'})} \langle \nu| S_{\nu,n,\alpha} \nu' \rangle \langle \nu'| S_{\nu,n,\beta} \nu \rangle,$$

where $\hat{\alpha}, \hat{\beta} = \hat{x}, \hat{y}, \hat{z}$, $\hat{q}_\beta = \sin \theta_{h,q} \cos \phi_{h,q}$, $\hat{q}_\beta = \sin \theta_{h,q} \sin \phi_{h,q}$, and $\hat{q}_\beta = \cos \theta_{h,q} \phi_{h,q}$, and $\hat{q}_\beta$ describe the relative orientations of $B$ and $q$.4 The $r_n$ and $\langle \nu'| S_{\nu,n,\alpha} \nu \rangle$ are given by Eqs. (11), (13), and (14) respectively, and the scalar $q \cdot (r_n - r_{n'})$ is invariant under the rotation, Eq. (11). As for the dimer,21 additional EPR and INS transitions with amplitudes higher order in the $\{J_{\nu,\nu,\nu'}\}$ are obtained in the extended Hartree approximation, but will be presented elsewhere for brevity.21

We presented a microscopic theory of high-symmetry single molecule magnets. From our exact single-ion spin matrix elements for four general spins, we studied the most general quadratic single-ion interactions in equal-spin tetramers with molecular group symmetry $T_d$, $D_{2d}$, or $C_{4v}$. Each group introduces site-dependent single-ion interactions, and azimuthal anisotropy with $D_{2d}$ symmetry has a continuous symmetry observed as splittings in Ni$_4$ EPR resonances, providing a direct measure of the microscopic interaction. We used the Hartree approximation to provide explicit expressions for the magnetization, specific heat, EPR absorption, and INS cross-section, valid at low temperatures and sufficiently large magnetic fields. Our procedure is extendable to systems with lower symmetry, higher-order single-ion interactions, and possibly to systems with $n > 4$ spins.

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