Behind the Giant Spin Approximation: the view from EPR

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- Introduction to giant spin approximation – why use it?
  - Mn_{12} SMM as an example.
- A model system: a tetranuclear nickel complex
  - Evaluation of giant spin Hamiltonian parameters
    - Excellent application of high-field EPR
  - Evaluation of single-ion zero-field splitting tensors
  - Origin of fourth- and higher-order zfs interactions
  - Assessment of the giant spin approximation

- Some consequences

- Summary and conclusions

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Why use a giant spin approximation?

\[ \text{Mn}_{12} \]

- \( S = 2, \) (5 × 5) matrix
- \( S = \frac{3}{2}, \) (4 × 4) matrix

\[ 5^8 \times 4^4 = 10^8 \text{ states!} \]
Why use a giant spin approximation?

- Full Hilbert space for Mn$_{12}$ is about $10^8 \times 10^8$
- Even after major approximation: Hilbert space is $10^4 \times 10^4$
- Multiple exchange coupling parameters ($J^s$); anisotropy (LS-coupling); different oxidation and different symmetry sites.
Why use a giant spin approximation?

\[ J_s \gg k_B T \]

- Hilbert space is 21 × 21
- Quite successful describing low-T magnetic properties
- \( J^s \) irrelevant (apparently)!!
- Ignores \((10^8 - 21)\) higher-lying states

\[ S = 10, \text{ plus anisotropy} \]

\[ \varepsilon = Dm^2 \]

 EMPLOYED EXTENSIVELY IN FIELD OF SINGLE-MOLECULE MAGNETS
Requirements for a single-molecule magnet

1. Well defined giant spin ground state
   - Clusters of transition metal oxides: Mn, Fe, Ni, Co, etc..
   - Ferro-, Ferri-, or frustrated magnetic interactions
   - Giant spin approximation

\[ \hat{H}_{zfs} = D \hat{S}_z^2 \quad (D < 0) \]

2. Large uniaxial (negative) magnetoanisotropy

\[ \varepsilon = Dm^2 \]

Energy levels:
- \[ E_{-10} \] to \[ E_{10} \]
- "up" and "down" states
Requirements for a single-molecule magnet

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   - Ferro-, Ferri-, or frustrated magnetic interactions
   - Giant spin approximation

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Other considerations....

3. Symmetry
   - Fast quantum dynamics

   \[ \hat{\mathcal{H}}_{zfs} = D \hat{S}_z^2 + \hat{\mathcal{H}}_T \]  \( \text{e.g.} \quad \hat{\mathcal{H}}_T = E \left( S_x^2 - S_y^2 \right) \)

4. What if symmetry is high?

   Try: \( \hat{\mathcal{H}}_T = \frac{1}{2} B_4^4 \left( S_x^4 + S_y^4 \right) \) then higher order terms

   How do \( D, E, B_4^4 \) etc.. relate to real physics (LS coupling)?
Let's simplify matters: a Ni$_4$ cube

\[ \hat{H} = D\hat{S}_z^2 + B_4^0\hat{O}_4^0 + B_4^4\hat{O}_4^4 + g\mu_B B \cdot \hat{S} \]

No solvent in the structure!

hmpH = \includegraphics[width=0.2\textwidth]{hmp.png}

tBuEtOH = \includegraphics[width=0.2\textwidth]{tBuEtOH.png}

[\textbf{Ni(hmp)(dmb)Cl]}_4

\textit{S}_4\text{ symmetry}

Can make the Zn analog
Let's simplify matters: a Ni$_4$ cube

\[ \hat{H} = D\hat{S}_z^2 + B_4^0\hat{O}_4^0 + B_4^4\hat{O}_4^4 + g\mu_B B \cdot \hat{S} \]

\[ \hat{S}_z^4 \quad \hat{S}_x^4 + \hat{S}_y^4 \]

- $S = 1$ Ni ions form cube (3x3 matrix)
- Ni ions couple ferromagnetically to give $S = 4$
- Full Hilbert space: $3^4 \times 3^4 = 81 \times 81$
- High symmetry ($S_4$): ~ single $J$ parameter

No solvent in the structure!
Fast quantum tunneling in spite of its high symmetry!
Single-crystal easy-axis spectra for $\text{[Ni(hmp)(dmb)Cl]}_4$

- Typical for a SMM with negative magnetocrystalline anisotropy
- Note the splittings and additional peaks at high-$T$
- Note also the uneven spacing of the peaks
Single-crystal easy-axis spectra for [Ni(hmp)(dmb)Cl]$_4$

- Typical for a SMM with negative magnetocrystalline anisotropy
- Note the splittings and additional peaks at high-T
- Note also the uneven spacing of the peaks
Frequency dependence of the easy axis spectra

- Enables determination of diagonal giant spin zfs parameters

Note uneven spacing

- $D_L = -0.600 \text{ cm}^{-1}$
- $D_U = -0.577 \text{ cm}^{-1}$
- $B_4^0 = -0.00012 \text{ cm}^{-1}$
- $g_{//} = 2.30$
Fit to hard axis data for $[\text{Ni(hmp)(dmb)Cl}_4]_4$

101 GHz, hard plane rotation

- Four-fold line shifts due to a quartic transverse interaction in $\mathcal{H}_T$
- $B_4^4$ is the only free parameter in the fit

Kirman et al., JAP 97, 10M501 (2005)

\[
\frac{1}{2} B_4^4 \left( \hat{S}_+^4 + \hat{S}_-^4 \right)
\]

- $B_4^4 = 4 \times 10^{-4} \text{ cm}^{-1}$
- Very effective at mixing $M_s = \pm 4$ ground states.
- 2nd order perturbation.
- 12 MHz tunnel splitting!
Evaluation of the Ni\textsuperscript{II} single-ion spin Hamiltonian

\[ [\text{Ni}_{0.02}\text{Zn}_{0.98}(\text{hmp})(\text{dmb})\text{Cl}]_4 \]

\[ S = 1 \]

\begin{align*}
\hat{H}_i &= d\hat{S}_{iz}^2 + e(\hat{S}_{ix}^2 - \hat{S}_{iy}^2) + g\mu_B\mathbf{B}\cdot\hat{\mathbf{s}}_i
\end{align*}

No 4\textsuperscript{th} order operators!!
Frequency-dependence

- Single-ion tensors are not collinear $\Rightarrow$ multiple EPR fine structures

$B//c$

$T = 2.5 \text{ K}$

$D_i = -5.30(5) \text{ cm}^{-1}$
$E_i = \pm 1.20(2) \text{ cm}^{-1}$
$g_z = 2.30(5)$

tilt = $15^\circ$

$\mathbf{Mag}$netic field (tesla)

Initialize $d$ and $e$ parameters from Frequency dep.

$d = -5.30(5) \text{ cm}^{-1}$
$e = \pm 1.20(1) \text{ cm}^{-1}$
$g_{//} = 2.30(5)$
tilt = $15^\circ$
Angle-dependence to find orientation of ZFS interaction


3 planes of rotation. One single fit to all of the data.
Four-spin, single $J$ model (vs giant spin model)

\[
\hat{H} = \sum_i \sum_{j \neq i} J_{ij} \hat{s}_i \cdot \hat{s}_j + \sum_i \left[ d \hat{s}_{zi}^2 + e \left( \hat{s}_{xi}^2 - \hat{s}_{yi}^2 \right) + g \mu_B \vec{B} \cdot \hat{s}_i \right]
\]

- $81 \times 81$ matrix
- Reasonably well isolated $S = 4$ state

$S \sim 2$, etc..

\[ d = -4.72 \text{ cm}^{-1} \]
\[ e = \pm 1.19 \text{ cm}^{-1} \]
\[ J = -5.9 \text{ cm}^{-1} \]
\[ \text{Tilt} = 15^\circ \]

Energy (cm$^{-1}$) vs Magnetic field (tesla)
Four-spin vs. giant spin model

$\mathbf{d, e, J}$ + orientations of tensors

No 4\textsuperscript{th} order

- Simple projection onto $S = 4$ state gives only 2\textsuperscript{nd} order (quadratic) zfs parameters, i.e. $D$ and $E$.
- Symmetry guarantees $E = 0$ - no tunneling!!

$D \hat{S}_z^2$ produces quadratic $m_s$ dependence of eigenvalues and a linear $m_s$ dependence of the zero-field splittings.

Therefore, higher order effects required to explain $B_4^0$ (uneven EPR peak spacing)

$D = 0.5 \text{ cm}^{-1}$

$B_4^0 \text{ (cm}^{-1})$
- 0.0007
- 0.0003
- 0.00
- -0.0003
- -0.0007

* Andrea Cornia’s talk earlier today (also v. important, but not the main focus of this talk)
\( J \) and the \( B_{4^0} \) Parameter

\[
\hat{H} = \sum_{i=1}^{4} \sum_{j>i} J \mathbf{S}_i \cdot \mathbf{S}_j + \text{dipolar} + \sum_{i=1}^{4} \left[ d \hat{\mathbf{O}}_0^2(i) + e \hat{\mathbf{O}}_2^2(i) + g \mu_B \mathbf{B} \cdot \mathbf{S}_i \right] \\
\text{(isotropic exchange)} + (\text{anisotropic LS coupling})
\]

** Exact matrix diagonalization **

- Isotropic perturbation admixes \( S = 3, 2, \text{etc..} \) to the \( S = 4 \) state
- Causes interactions between spin multiplets
- Renormalizes zfs
- Corrections to zfs order \( (D \hat{S}_z^2)^n \)
- Hence, 4th, 6th order, etc..
Same with $J$ and the $B_4^4$ Parameter

- Again, mixing to higher lying states reproduces the four-fold behavior ($B_4^4$)
- Higher order effects scale as $J^{-1}$

$2.7$ to $3$ cm$^{-1}$
Full comparison of the two models

Fit to $S = 3$ EPR peak intensities

\[ \text{Fit Parameters (cm}^{-1}) \]

- $D_4 = -0.600$
- $D_3 = -0.300$
- $D_2 = -0.300$
- $D_1 = D_0 = 0$
- $g = 2.25$

\[ J = -6.5 \text{ cm}^{-1} \]

Fit to Kambe model + anisotropy (GSA)

**Experimental**

- $d = -5.30 \text{ cm}^{-1}$
- $e = \pm 1.20(1) \text{ cm}^{-1}$
- $J = -6.5 \text{ cm}^{-1}$
- Tilt = 15°

**From $\chi_M T$ data**

- $J = -7 \text{ cm}^{-1}$ (four spin)
- $J = -10.5 \text{ cm}^{-1}$ (Kambe)

**Results of this study:**

Fit of Ni$_4$ data to the four spin model

\[ d = -4.72 \text{ cm}^{-1} \]

\[ e = \pm 1.19(1) \text{ cm}^{-1} \]

\[ J = -5.9 \text{ cm}^{-1} \]

Tilt = 15°
Some possible consequences
Be careful making predictions at vastly different energy scales

\[ \hat{H} = \sum_i \sum_{j \neq i} J_{ij} \hat{S}_i \cdot \hat{S}_j + \sum_i \left[ d \hat{S}_{zi}^2 + \frac{e}{2} \left( \hat{S}_{+,i}^2 + \hat{S}_{-,i}^2 \right) + g \mu_B \hat{B} \cdot \hat{S}_i \right] \]

\[ B \parallel \hat{z} \]

Giant spin: \[ \hat{H} = \left( \frac{D'}{S^2} \right) \hat{S}_z^2 + \left( \frac{B'}{S^4} \right) \hat{S}_z^4 + \left( \frac{C'}{S^4} \right) \hat{O}_4^4 \]

• Both of these models explain the HF EPR data extremely well, but........

Angle dependence of tunnel splitting

\[ J = -200 \text{ GHz} \]

Close to best fit

Field orientation relative to hard axis (in plane)

Giant spin model
\[ B = -18 \text{ GHz} \]
\[ B_0' = -0.0036 \text{ GHz} \]
\[ B_4' = 0.012 \text{ GHZ} \]
Conclusions

• Fourth (and higher) order terms are routinely found in fits to giant spin model for SMMs
  – In many cases, they are the main source of MQT
• Fast magnetization tunneling in Ni$_4$ due to $B_4^4$ of $S = 4$ ground state.
• $B_4^0$ and $B_4^4$ arise from mixing of components of different spin states.
• We begin to see the inner workings of the giant spin Hamiltonian
• These conclusions likely generalize to all SMMs