Electron-Nanomagnet Interactions: A DFT Many-Body Approach for Quantum-Device Simulation

Mark R. Pederson

HAPPY BIRTHDAY EUGENE!

Thanks for your many contributions to Science, MM and human rights.

• OUTLINE
  • How do we study spin-dependent transport across a molecular magnet?
  • Electrons disrupt exchange coupling and anisotropies?
  • Other environmental effects (dislocations, pressure, water, leads etc) do as well.
  • DFT+NRLMOL: Magnetic Anisotropy and Exchange Coupling
  • A DFT-based many-electron approach.

Collaborators:

• S, Khanna (VCU)
• J. Kortus (TU Freiberg)
• S. Hellberg (NRL)
• T. Baruah (UTEP)
• K. Park (Vtech)
• S. Richardson (Howard)
• N. Bernstein (NRL)
• J. Ribas (Barcelona)
• C. Canali (Kalmer)

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TOOL: NRLMOL
All-Electron Density Functional Based Code.
Molecular Magnets: A new field for DFT Investigations

**Questions for Theory**

- What determines the magnetic reorientation barrier?
- What mediates the dynamics in resonant tunneling of magnetization?
- How can such simplicity arise from the so much complexity?
- What relative energy scales allow for molecular magnetism?

[Diagram of Mn₁₂O₁₂(RCOO)₁₆(H₂O)₄ with indications of Majority Spin Electrons and Minority Spin Electrons]

What other conditions are necessary?
Ingredients of Calculation:

Geometry Optimization
Electronic Structure
Exchange Interactions
Spin-Orbit Coupling

Heisenberg Hamiltonian
Single Spin Anisotropy Hamiltonian

Retrospective & Rational Approach
Amenable to systems where there are no low-energy one or two-electron excitations.
Density of States for Passivated Mn$_{12}$O$_{12}$ Magnet

- DOS are similar at energies below minority spin HOMO.
- Ten extra electrons between majority and minority HOMO states. Net Moment = 20
- Some O(2p)-Mn(3d) covalent bonding.
- Half Metallic Ferrimagnet?

Minority Gap: 2.03 eV
Majority Gap: 0.43 eV
Spin Manifolds in Mn$_{12}$-Acetate

Park, Pederson and Hellberg PRB 69 014416 (2004)

<table>
<thead>
<tr>
<th>$Sz$</th>
<th>Energy (eV)</th>
<th>MAE (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.000</td>
<td>54.21</td>
</tr>
<tr>
<td>9-b</td>
<td>0.062</td>
<td>54.56</td>
</tr>
<tr>
<td>9-c</td>
<td>0.145</td>
<td>54.98</td>
</tr>
<tr>
<td>8</td>
<td>0.138</td>
<td>55.09</td>
</tr>
<tr>
<td>6-c</td>
<td>0.038</td>
<td>55.03</td>
</tr>
<tr>
<td>6-b</td>
<td>0.080</td>
<td>55.35</td>
</tr>
<tr>
<td>5-a</td>
<td>0.134</td>
<td>55.52</td>
</tr>
<tr>
<td>5-b</td>
<td>0.092</td>
<td>54.92</td>
</tr>
<tr>
<td>13</td>
<td>0.151</td>
<td>53.70</td>
</tr>
</tbody>
</table>

Spin Gap is in Excellent Agreement with Experiment

(Petukhov, Hill, Chakov, Christou, Aboud cond-mat0403435)
Multiplets Split Due to Interionic Exchange Coupling (K Park & MRP)

Each Spin Multiplets Splits due to LS Coupling
(Pederson and Khanna, PRB 1999)

(2S+1)-fold degeneracy

S=9

S=9

S=9

S=10

33 K

7 K

41 K

Good Agreement with Experiment in Many cases.

Multiplets Split Due to Interionic Exchange Coupling (K Park & MRP)
Other Contributions to Magnetic Anisotropy: Beyond Mean Field

\[ |\Psi \rangle = C_0 |\Phi_0 \rangle + C_1 |\Phi_1 \rangle + C_2 |\Phi_2 \rangle + C_3 |\Phi_3 \rangle + \ldots \]

\[
(\Psi| V_{L.S} |\Psi \rangle = \sum_v C_v^* C_v <\Phi_v | V_{L.S} | \Phi_v > + \sum_{v \mu} C_v^* C_\mu <\Phi_v | V_{L.S} | \Phi_\mu >
\]

\[ V_{L.S} = \sum_i f_i + \sum_{ij} g_{ij} \]

Interaction between electric fields due to nuclei with each moving electron. (1 electron operator)

Interaction between electric fields due to all electrons with each moving electron. (2 electron operator)

Try: 
(1) All diagonal terms the same or \(|C_n|^2\) very small.
(2) Off diagonal terms small due to zero overlap or small \(C_n\)
NRLMOL: Linear Combination of Gaussian Orbitals

$$\Psi(r) = \sum_{i\sigma} C_i \exp[-\alpha_i (r-R_i)^2]|\sigma>$$

Place Gaussians on each atom in molecule or crystal

Reduce Problem to Finding Expansion Coefficients
Calculation of the Tunneling Barrier within DFT?

INCLUDE SPIN-ORBIT COUPLING VIA 2ND ORDER PERTURBATION THEORY

\[
\Delta_2 = \sum_{\sigma \sigma'} \sum_{xy} M_{\sigma \sigma'}^{xy} S_{\sigma \sigma}^{xy} S_{\sigma \sigma'}^{xy}
\]

\[
S_{\sigma \sigma'}^{xy} = \langle \chi_\sigma | S_x | \chi_\sigma \rangle
\]

\[
M_{\sigma \sigma'}^{xy} = M_{\sigma \sigma'}^{yx} = \sum_{ij} \frac{\langle \phi_{i \sigma} | V_x | \phi_{j \sigma'} \rangle < \phi_{j \sigma'} | V_y | \phi_{i \sigma} \rangle}{\varepsilon_{i \sigma} - \varepsilon_{j \sigma}}
\]

\[
= \sum_{ij} \frac{\frac{d \Phi}{dy} d\frac{d}{dz} - \frac{d \Phi}{dz} d\frac{d}{dy}}{|\phi_{i \sigma}|^2}
\]

\[
\equiv < \phi_{j \sigma'} | V_x | \phi_{i \sigma} > \frac{d \Phi}{dy} d\frac{d}{dz} - \frac{d \Phi}{dz} d\frac{d}{dy} |\phi_{i \sigma}|^2
\]
2nd-Order Anisotropy Hamiltonian

\[ |\chi_1\rangle = \cos(\frac{\theta}{2})|\uparrow\rangle + e^{i\beta}\sin(\frac{\theta}{2})|\downarrow\rangle \]
\[ |\chi_2\rangle = -e^{i\beta}\sin(\frac{\theta}{2})|\uparrow\rangle + \cos(\frac{\theta}{2})|\downarrow\rangle \]

\[ \Delta_2 = \sum_{xy} \gamma_{xy} \langle S_x \rangle \langle S_y \rangle \rightarrow \left[ -DS_z S_z - E(S_x S_x - S_y S_y) \right]/S^2 \]

Determine \( \gamma_{xy} \) from DFT, L.S and Perturbation Theory.
### Magnetic Reorientation Barriers in Molecules

**NRLMOL/PBE-GGA VS EXPERIMENT (1999-2003)**

(MRP, Khanna, Kortus, Baruah, Park, Ribas)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>S</th>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Mn}<em>{12}\text{O}</em>{12}(\text{O}<em>2\text{CH})</em>{16} (\text{H}_2\text{O})_4)</td>
<td>10</td>
<td>(-0.56^a)</td>
<td>(-0.56^b)</td>
</tr>
<tr>
<td>([\text{Fe}_8\text{O}<em>2(\text{OH})</em>{12}(\text{C}<em>6\text{H}</em>{15}\text{N}_3)_6 \text{Br}_6]^{2+})</td>
<td>10</td>
<td>(-0.53^c)</td>
<td>(-0.30^d)</td>
</tr>
<tr>
<td>([\text{Mn}_{10}\text{O}_4(2,2'\text{-biphenoxide})<em>4 \text{Br}</em>{12}]^{4-})</td>
<td>13</td>
<td>(-0.06^e)</td>
<td>(-0.05^f)</td>
</tr>
<tr>
<td>(\text{Co}_4(\text{CH}_2\text{C}_5\text{H}_4\text{N}_4)(\text{CH}_3\text{OH})_4 \text{Acl}_4)</td>
<td>6</td>
<td>(-0.64^g)</td>
<td>(-0.7 \text{ to } -0.9^h)</td>
</tr>
<tr>
<td>(\text{Fe}_4(\text{OCH}_2)_6(\text{C}<em>4\text{H}</em>{9}\text{ON})_6)</td>
<td>5</td>
<td>(-0.56^i)</td>
<td>(-0.57^j)</td>
</tr>
<tr>
<td>(\text{Cr}[\text{N}(\text{Si}(\text{CH}_3)_3)_2]_3)</td>
<td>3/2</td>
<td>(-1.15^i)</td>
<td>(-2.66^k)</td>
</tr>
<tr>
<td>(\text{Mn}<em>9\text{O}</em>{34}\text{C}_{32}\text{N}<em>3\text{H}</em>{35})</td>
<td>17/2</td>
<td>(-0.33^m)</td>
<td>(-0.32^l)</td>
</tr>
<tr>
<td>(\text{Ni}<em>4\text{O}</em>{16}\text{C}<em>{16}\text{H}</em>{40})</td>
<td>4</td>
<td>(-0.385)</td>
<td>(-0.40^m)</td>
</tr>
<tr>
<td>(\text{Mn}_4\text{O}_3\text{Cl}_4(\text{O}_2\text{CCH}_2\text{CH}_3)_3(\text{NC}_5\text{H}_5)_3)</td>
<td>9/2</td>
<td>(-0.58^n)</td>
<td>(-0.72^o)</td>
</tr>
</tbody>
</table>

**2004-2006: Additional challenges identified**
Wannier Description of Magnetic Core of Molecule

NB: Four equivalent sites lead to nearly degenerate LUMO "band"
Interaction of Electrons with Molecular Magnets

**BACKGROUND**

Addition of localized electron on crown Mn decreases anisotropy.
Park and Pederson, PRB 70 045416 (2004)

Additional of electron delocalized over entire molecule increases anisotropy

**QUESTIONS**

Can magnetism be controlled by shuttling electrons back and forth?

In transport, does the traversing electron change the molecule?

What other environmental effects?

---

**TABLE I: The GS properties from DFT: spin, energy and magnetic anisotropy energy as a function of charge**

<table>
<thead>
<tr>
<th>State</th>
<th>( Q )</th>
<th>Spin</th>
<th>Energy (eV)</th>
<th>MAE (K)</th>
<th>MAE (meV)</th>
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</thead>
<tbody>
<tr>
<td>Anion</td>
<td>-1</td>
<td>21/2</td>
<td>-3.08</td>
<td>137</td>
<td>11.8</td>
</tr>
<tr>
<td>Neutral</td>
<td>0</td>
<td>20/2</td>
<td>0.00</td>
<td>55</td>
<td>4.7</td>
</tr>
<tr>
<td>Cation</td>
<td>1</td>
<td>19/2</td>
<td>6.16</td>
<td>69</td>
<td>5.9</td>
</tr>
</tbody>
</table>
Addition of Localized Excess Electrons and Delocalized Excess Electrons can have very different effects!

Localized Electron:

Closes D Shell on Mn Ion
Quenches Local Anisotropy on (Temperature independent?)
Changes the Exchange-Coupling Between Neighbors
(K. Park)

Delocalized Electron:

Visits all four equivalent sites and/or 4-nearly degenerate bands
Spin-Orbit/Axis changes ordering/occupations of nearly degenerate states

Large Environmentally Dependent Change in Anisotropy
Electron/Spin Transport across a Nanomagnet?

Need Many Electron / Many Spin Method that accounts for all interactions

Must be Computationally “Fast”
Step 1: Many-Electron Wavefunctions from DFT
(Pederson and Canali, to be submitted)

“Order parameters” \( \{ p \} \) for Many-Electron Wavefunctions

\[
H(E, B, Q, \theta, \phi) = H_0(Q) + E \cdot r + B \cdot (L + 2S) + V_{L+S}(\theta, \phi)
\]

- Treat Self-Consistently for Reference Hamiltonians
- With or without SCF
- Non SCF (Exact Diagonalization)
- Noncollinear Spin Orbitals

\[
H(p) \phi_k(p) = \lambda_k(p) \phi_k(p)
\]

\[
\phi_k(p) = \phi_{k1}(p) \chi_1(\theta, \phi) + \phi_{k2}(p) \chi_2(\theta, \phi)
\]

Step 2: Many-Electron Wavefunctions from DFT

\[ \phi_k(p) = \phi_{k1}(p) \chi_1(\theta, \phi) + \phi_{k2}(p) \chi_2(\theta, \phi) \]

\[ |\chi_1\rangle = \cos(\theta/2)|+\rangle + e^{i\phi} \sin(\theta/2)|-\rangle \]

\[ |\chi_2\rangle = -e^{-i\phi} \sin(\theta/2)|+\rangle + \cos(\theta/2)|-\rangle \]

\[ \Phi(p, 1, 2, \ldots N) = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \phi_a(\tau_1) & \phi_a(\tau_2) & \phi_a(\tau_3) & \phi_a(\tau_4) & \ldots & \phi_a(\tau_N) \\ \phi_b(\tau_1) & \phi_b(\tau_2) & \phi_b(\tau_3) & \phi_b(\tau_4) & \ldots & \phi_b(\tau_N) \\ \phi_c(\tau_1) & \phi_c(\tau_2) & \phi_c(\tau_3) & \phi_c(\tau_4) & \ldots & \phi_c(\tau_N) \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ \phi_N(\tau_1) & \phi_N(\tau_2) & \phi_N(\tau_3) & \phi_N(\tau_4) & \ldots & \phi_N(\tau_N) \end{vmatrix} \]

GROUND AND EXCITED SLATER DETERMINANTS
Step 3: Many-Electron Overlaps and Energies

Good Estimate of Energies from Single Hubbard U and p-dependent eigenvalues.

\[ \Phi(p) = \frac{1}{(N!)^{1/2}} \begin{align*}
\phi_a(\tau_1) \phi_a(\tau_2) \phi_a(\tau_3) \phi_a(\tau_4) & \ldots \phi_a(\tau_N) \\
\phi_b(\tau_1) \phi_b(\tau_2) \phi_b(\tau_3) \phi_b(\tau_4) & \ldots \phi_b(\tau_N) \\
\phi_c(\tau_1) \phi_c(\tau_2) \phi_c(\tau_3) \phi_c(\tau_4) & \ldots \phi_c(\tau_N) \\
\phi_N(\tau_1) \phi_N(\tau_2) \phi_N(\tau_3) \phi_N(\tau_4) & \ldots \phi_N(\tau_N)
\end{align*} \]

Tunneling Probabilities and 1-Electron Green’s Function requires:

\[ \langle \Phi(p_i) | \Phi(p_j) \rangle \]

N.B.: Noncollinear spin-orbitals from different p’s are not orthonormal

(Still an \( N^3 \) operation!)
Energies as a function of $p$ and $Q'$

$$H(p) \phi_k(p) = \lambda_k(p) \phi_k(p)$$

$$E(p,Q;Q') = E_0(Q) + \sum_k q_k \lambda_k(p) + \frac{U}{2} (Q'-Q)^2$$

- **Ground state**: DFT for charge $Q$
- **Occupations numbers**: $Q' = \sum_k q_k$
- **Molecular Hubbard $U$ (Capacitance)** as calculated from DFT energy vs $Q$
Step 4: Many-Electron Wavefunctions from DFT

COMPUTATIONAL DETAILS

• Common Rep for Rigid “Core” and “Sub Valence” States.
• Common Rep for Valence/Conduction (Active) States.
• We use neutral Mn$_{12}$ for NC spin-orbital basis.

\[ \psi_1 \psi_2 \psi_3 \psi_4 \psi_5 \psi_6 \ldots \psi_N \]
Spin Selection Rules within a Semiclassical Magnetic State

FIG. 3: (Color online) Matrix elements for transitions between anionic and neutral charge states. (a) Giant-spin model; (b) SDFT results for transitions from neutral GS spin multiplet to anionic first excited multiplet; (c) SDFT results for transitions from neutral GS to anionic GS spin multiplets.
The theory of tunneling spectroscopy in a $Mn_{12}$ single-electron transistor by DFT methods

L. Michalak$^1$, C. M. Canali$^1$, M. R. Pederson$^2$, M. Paulsson$^1$, and V. G. Benza$^3$

$^1$Division of Physics, Department of Natural Sciences, Kalmar University, 391 82 Kalmar, Sweden
$^2$Naval Research Lab, Washington DC, USA and
$^3$Universita’ dell’ Insubria, Como, Italy

(Dated: December 5, 2008; Received textdate; Revised textdate; Accepted textdate; Published textdate)

$$\chi^{\pm}(\theta, \varphi) = \cos(\theta/2)|\pm\rangle \pm \sin(\theta/2)e^{\pm i}|\mp i.$$
## Conclusions

- Good Agreement with Experiment
- Some Verified Predictions within DFT

<table>
<thead>
<tr>
<th>Theoretical</th>
<th>Experiment</th>
<th>Prediction?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mag. Anisotropy / Barriers, Tunneling Fields</td>
<td>Good/Excellent</td>
<td>Yes</td>
</tr>
<tr>
<td>Exchange Parameters / Spin Excitations</td>
<td>Good</td>
<td>Yes</td>
</tr>
<tr>
<td>Electronic Structure/ Optical Conductivity</td>
<td>Usual DFT</td>
<td>Yes</td>
</tr>
<tr>
<td>Vibrational Spectra (IR/Raman)</td>
<td>Very Good</td>
<td>?</td>
</tr>
<tr>
<td>Incommensurate Ordering between 2\textsuperscript{nd}-order and 4\textsuperscript{th}-order axes</td>
<td>Qualitative Accord</td>
<td>Partially</td>
</tr>
<tr>
<td>Local Moments / Neutron Scattering</td>
<td>Qualitative Accord</td>
<td>Maybe</td>
</tr>
</tbody>
</table>

…Still Lots of Questions Remain
Computer Aided Design of a Biologically Inspired Organic Photovoltaic

OBJECTIVE:
Simulate light weight, disposable molecular scale devices for power sources and sensing applications.

NEW METHODS FOR:
• Electron Excitation Rates
• Coupling DFT with Monte Carlo
• Molecular Electron Phonon interactions

ACCOMPLISHMENT:
PREDICT TIME CONSTANT FOR SOLAR TO ELECTRIC ENERGY CONVERSION

Motivations: Simulation of Molecular Devices
Where Light Harvesting, Nanomagnetics and Photomagnetism meets

DoD HPCMO Challenge Project:
Predict Charge Transfer Rates & Recombination Rates in
Light Harvesting Molecular Triad
(Baruah & Pederson JCP 125 164706 2006)

Spin-Orbit Coupling and Magnetic Fields allow for Spin Forbidden Transitions
[Pederson and Baruah, Handbook of Magnetism ad Magnetic Materials (2007)]

News from:
Gust et al
Nature, 1 May 2008

Washington Post - 5 May 2008
Weak terrestrial magnetism influences recombination rate and allows for bionavigation
Origin of 4th-Order Anisotropy? (responsible for tunnel splittings)

4th-Order Contributions:
Can have different angular dependence and different scaling with $1/[\text{speed of light}]$

Spin-Orbit Only: Wrong Sign and Wrong Order of Magnitude

Experiment: 5-10 K  Electronic spin-orbit: -1 K
A Vibrational Contribution to Magnetic Anisotropies.

• Spin Orbit Interaction Depends on Electric Fields and Kohn-Sham Orbitals

• Electric Fields and Kohn-Sham Orbitals depend on Atomic Positions/ Vibrational Displacements

• Zero Point Energy of a Vibrational Mode Changes as a function of Spin Projection due to spin-orbit-vibron coupling.

• Lowest-Order effect is $1/[\text{Speed of Light}]^8$
SPIN-ORBIT MEDIATED SPIN VIBRON INTERACTION

\[ E = \frac{\omega}{2} + \gamma_{zz} M^2 - A + B M^2 \frac{2}{(2 \omega^2)} \]

\[ \frac{1}{2} S(S+1)[d/dQ(\gamma_{xx} + \gamma_{yy})] \]

\[ d/dQ[\gamma_{zz} - (\gamma_{xx} + \gamma_{yy})/2] \]

Depends on accurate calculation of zero-field splittings as function of atomic position and vibrational frequencies/vectors.
Large Mn-crown contributions in Region identified as field-dependent in IR experiments. (Sushkov et al)

Good agreement between predicted Raman and recent experimental measurements (North et al)
EVOLUTION OF 4TH-ORDER ENHANCEMENT WITH COUPLING TO VIBRONS

\[ \Delta(4) = 6K - 1K = 5K \]

EXPERIMENT: 5-10K

NRLMOL+GGA: 6K - 1K = 5K
Transverse 4th-order Anisotropy from spin-orbit-vibron

\[ H = D S_z S_z + G S_z S_z S_z S_z + H[ S_x S_x S_x S_x + S_y S_y S_y S_{zy}] \]

Translate D,G,H to Stephenson Polynomial Representation

Energies in Kelvin

<table>
<thead>
<tr>
<th></th>
<th>( A_1(4) )</th>
<th>( A_2(4) )</th>
<th>( B_1(4) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt</td>
<td>-8.35</td>
<td>-0.334</td>
<td>-0.43</td>
</tr>
<tr>
<td>Vibrational</td>
<td>-5.58</td>
<td>-0.008</td>
<td>-0.01</td>
</tr>
<tr>
<td>Electronic</td>
<td>0.68</td>
<td>0.0005</td>
<td>-0.002</td>
</tr>
</tbody>
</table>

Additional transverse terms required for tunnel splittings … probably due to some symmetry breaking at 2nd-order
NANOSCALE MOLECULAR MAGNETS
Classical Barrier Hopping

vs

Resonant Tunneling of Magnetization

Barrier changes continuously with B field

Yellow States Aligned with Blue States only if:

\[ B = \frac{[\Delta N] D}{2} \]

\[ \Delta W = MB - DM^2/2 \]

\[ <Sz> (M) \]

AKA: Zero-Field Splittings in atomic physics/radical chemistry
Molecular Magnets (Type 2): \([V_{15}As_6O_{42}(H_2O)] K_6\)

[Kortus, Hellberg, Pederson PRL 86, 3400 (2001)]

Couple NRLMOL and many-spin Heisenberg Hamiltonian

\[ H\Phi = \lambda\Phi \]

- Electronic Structure
- Spin Ordering
- Exchange Parameters

Effective Moment vs Temperature

Expt. DFT+ Heisenberg

Diagonalize Many-Spin Hamiltonian for excitation spectra.
MAGNETOMOLECULAR
ANISOTROPY ENERGY

\[ \Delta E \sim \frac{1}{4C^4} M^2 \]

\[ E = \text{DFT Energy} + (\Theta) \]

\[ (\Theta) = C^4 (3.5 \times 10^8) \]

Spin Orbit Energy

ME’s
Type 3: Electronic structure of the molecule-based magnet Mn[N(CN)2]2 from Theory and Experiment


- AF/FM Energy Splitting OK
- Magnetic Anisotropy OK
- Local Moments OK
- $L_2/L_3$ splitting OK
- Etc.

NRLMOL/VASP

EXPERIMENT
Schrödinger’s Equation with Spin-Orbit Coupling
\[ [H + \frac{V}{\hbar} \cdot \mathbf{S}] \psi_{i\sigma}’ = \epsilon_{i\sigma}’ \psi_{i\sigma} > \] \( \tag{6} \)

Second Order Energy Shift (PT)
\[ \Delta_2 = \sum_{\sigma'\tau} \sum_{x'z} M_{x'y}^{\sigma \sigma'} S_{x'}^\tau S_{y}^\tau \]
\[ M_{x'y}^{\sigma \sigma'} = M_{y'z}^{\sigma' \sigma} = -\sum_{ij} \frac{\langle \phi_{i\sigma} | V_z | \phi_{j\sigma'} > \langle \phi_{j\sigma'} | V_z | \phi_{i\sigma} >}{\epsilon_{i\sigma} - \epsilon_{j\sigma'}} \]
\[ S_{x'}^\tau = \langle \chi_{\sigma} | S_x | \chi’_{\sigma} > \] \( \tag{7} \)

Unitary Txn. between Minority/Majority Spinors and Quantized States
\[ |\chi_1 > = e^{i\gamma} [ \cos \frac{\theta}{2} | \uparrow > + e^{i\beta} \sin \frac{\theta}{2} | \downarrow > | \]
\[ |\chi_2 > = e^{-i\gamma} [ -e^{-i\beta} \sin \frac{\theta}{2} | \uparrow > + \cos \frac{\theta}{2} | \downarrow > | \] \( \tag{8} \)

For Closed Shell System With Uniaxial Symmetry:
\[ \Delta_2 = (M_{xx}^{11} + M_{xx}^{20} + M_{zz}^{12} + M_{zz}^{21}) \frac{\sin^2(\theta)}{4} \]
\[ + (M_{xx}^{11} + M_{xx}^{20} + M_{zz}^{12} + M_{zz}^{21}) \frac{\cos^2(\theta)}{4} \]
\[ = A + \frac{\gamma}{2} [\Delta N \cos \theta]^2 = A + \frac{\gamma}{2} <S_z>^2 \] \( \tag{9} \)

2ND ORDER ANISOTROPY BARRIER = $\frac{\gamma}{2} \times S^2$
Barrier vs Majority Filling Rigid Band Model
Mn$_{12}$-Acetate

Addition of Majority Spin Electrons (Fe/Mn sub?) should reduce barrier! (RBM)
SPIN ORBIT COUPLING:
CARTESIAN VS. L.S?

\[
U(r,p,S) = -\frac{1}{2c^2} S \cdot p \times \nabla \Phi(r)
\]

\[
U(r,L,S) = \frac{1}{2c^2} S \cdot L \left( \frac{1}{r} \frac{d\Phi(r)}{dr} \right)
\]

Most (all?) computational methods have used the L.S. representation.
"Slater Determinant" Ensures Wavefunction is Antisymmetric, Normalized and Managable

\[ \Phi(\tau_1, \tau_2, \tau_3 \ldots) = \frac{1}{(N!)^{1/2}} \]

\[ \phi_a(\tau_1) = \psi_\alpha(\vec{r}_1) \chi(\sigma_1) \]

IFF:

\[ \langle \phi_a(\tau) | \phi_b(\tau) \rangle = \delta_{ab} \]
Configuration Interaction

\[ |\Psi\rangle = C_0 |\Phi_0\rangle + C_1 |\Phi_1\rangle + C_2 |\Phi_2\rangle + C_3 |\Phi_3\rangle + \ldots \]

\[ |\Phi_I\rangle = |\phi_a \phi_b \phi_c \ldots \rangle = \frac{1}{(N!)^{1/2}} \phi_a(\tau_1) \phi_a(\tau_2) \phi_a(\tau_3) \phi_a(\tau_4) \ldots \phi_a(\tau_N) + \phi_b(\tau_1) \phi_b(\tau_2) \phi_b(\tau_3) \phi_b(\tau_4) \ldots \phi_b(\tau_N) + \phi_c(\tau_1) \phi_c(\tau_2) \phi_c(\tau_3) \phi_c(\tau_4) \ldots \phi_c(\tau_N) + \ldots + \phi_N(\tau_1) \phi_N(\tau_2) \phi_N(\tau_3) \phi_N(\tau_4) \ldots \phi_N(\tau_N) \]

\[ (\Phi_I | [H - E] | \Psi \rangle = (\Phi_I | [(\Sigma_i f_i + \Sigma_{ij} g_{ij}) - E] | \Psi \rangle = 0 \]

\[ \Sigma_J (\Phi_I | [(\Sigma_i f_i + \Sigma_{ij} g_{ij}) - E] | \Phi_J \rangle C_J = 0 \]

Many Electron Secular Eqn.
Multiconfigurational Contributions to Magnetic Anisotropy

\[ |\Psi\rangle = C_0 |\Phi_0\rangle + C_1 |\Phi_1\rangle + C_2 |\Phi_2\rangle + C_3 |\Phi_3\rangle + \ldots. \]

\[(\Psi| V_{L.S} |\Psi\rangle = \sum_v C_v^* C_v <\Phi_v| V_{L.S} |\Phi_v\rangle + \sum_{v\mu} C_v^* C_\mu <\Phi_v| V_{L.S} |\Phi_\mu\rangle\]

\[ V_{L.S} = \sum_i f_i + \sum_{ij} g_{ij} \]

Interaction between electric fields due to nuclei with each moving electron. (1 electron operator)

Interaction between electric fields due to all electrons with each moving electron. (2 electron operator)

Try: (1) All diagonal terms the same or $|C_n|^2$ very small.

(2) Off diagonal terms small due to zero overlap or small $C_n$
Excited Configurations of the Mn_{12}-Acetate Molecule

- Mn(3d) - Mn(3d) Majority Excitations: >0.44 eV
- Localized single spin flip: >1.00 eV
- Concerted local moment flips (3 or 4 3d e- at once): ~0.05 eV
- Charge-Transfer: ~6.00 eV (?)

Self Consistency Shows that Local Charges and Moment Size Unchanged
Flipping spins of all d wannier functions on a single site represents a triple/quaduple excitation:

\[ |\psi_l(r_1)\alpha_1\psi_m(r_2)\alpha_2\psi_n(r_3)\alpha_3>| \]

\[ |\psi_l(r_1)\beta_1\psi_m(r_2)\beta_2\psi_n(r_3)\beta_3>| \]

Direct off-diagonal L.S matrix element vanishes.
Type 3: Prussian-Blue and Analogs -- Magnetic Crystals derived from molecules (Photomagnetism)

Spin-Orbit Induced Energy Splittings

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<tr>
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<th>NRLMOL</th>
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Mn[N-(CN)₂]₂ Molecular Magnetic Material