Density-Functional-Based Investigation of Molecular Magnets

Mark R. Pederson
Washington DC

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Collaborators:

1998
- Shiv Khanna
- Jens Kortus
- Stephen Hellberg
- Tunna Baruah
- Kyungwha Park
- S. Richardson
- Noam Bernstein
- Jordi Ribas

Virginia Commonwealth University
TU Bergakademie Freiberg Germany
Naval Research Laboratory
NRL, Stoney Brook => Texas El Paso
Virginia Tech University
Howard University
Naval Research Laboratory
Barcelona, Spain

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Outline

• DFT For Molecular Magnets
  • Electronic Structure, Vibrational Spectra, Geometry
  • Magnetic Anisotropy Energies from Spin-Orbit Interaction.
  • Exchange Parameters for Heisenberg Hamiltonians
• Examples
  • $V_{15}$ - Small Anisotropy and “Large” Exchange Parameters
  • $\text{Mn}_{12}$-Acetate: “Large” Exchange Parameters and Small Anisotropy
• Response/Modification due to Fields, Electrons, Vibrons
• Many Electron Effects?
Density-Functional Theory...What is it ....What is it good for?

Hohenberg, Kohn, Sham (1964–1965)

Ground State Energy of Many Electron System Depends Only on a Electronic Density!

$E(\rho)$ is universal but an exact expression is not known.

$\mathbf{H} \Psi_{i\sigma} = \lambda_{i\sigma} \Psi_{i\sigma}$

$\rho(\mathbf{r}) = \sum_{i\sigma} |\Psi_{i\sigma}|^2$

Hellmann-Feynman Theorem (~1935)

If quantum mechanical motion of electrons is solved, forces on atoms are exactly what is expected from classical electricity and magnetism.

Forces due to Electric Fields of other nuclei and electrons.
NRLMOL: Linear Combination of Gaussian Orbitals

Place Gaussians on each atom in molecule or crystal

\[ \Psi_{i\sigma}(r) = \sum_i C_{i\sigma} \exp\left[-\alpha_i (r-R_i)^2\right]|\chi_{\sigma}\]
EARLY EXPERIMENTS ON RESONANT TUNNELING OF MAGNETIZATION

J.R. Friedman et al, PRL 76, 3830 (1996)

Energy/A

\[ H = -D S_z S_z + B_z S_z \]
\[ W(M) = MB - DM^2 \]

Yellow States Aligned with Blue States only if:
\[ B_z = [\Delta N]D \]

Barrier changes continuously with \( B_z \) field

AKA: Zero-Field Splittings in atomic physics/radical chemistry
Lower Symmetry Molecules (Fe\textsubscript{8}): Berry’s Phase Oscillations

Applied Magnetic Field

Log(Tunnel Splitting) (M=5)

Angle of Applied Transverse Field

\[ H = -DS_z S_z - E(S_x S_x - S_y S_y) + H_x S_x \]

A. Garg:
EPL 22, 205 (1993)

Period in transverse tunneling Experiments

\[ (k_B/gm_B)^2 [2E(E+D)]^{1/2} \]
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 a complex molecule be so simple?
• What relative energy scales allow for molecular magnetism?

Majority Spin Electrons

Minority Spin Electrons

\[ \text{Mn}_{12}\text{O}_{12}(\text{RCOO})_{16}(\text{H}_2\text{O})_4 \]

1.5 nanometers

Resonant Tunneling of Magnetization?
Two Spin-Dependent Interactions

Interionic Exchange:
Splits States with Different Total Spin

Spin-Orbit Coupling:
Splits (2S+1)-Fold Degeneracy of a Spin Manifold

What constraints on relative energy scales are required to yield single-spin behavior?
Exchange Coupling Parameters within Density Functional Theory?

Example: $V_{15}$

$E_1 = -JS^2$

$E_2 = JS^2$
Heisenberg Hamiltonian within DFT: $[V_{15}As_6O_{42}(H_2O)] K_6$

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

- Electronic Structure
- Spin Ordering
- Exchange Parameters

Effective Moment vs Temperature

Diagonalize Many-Spin Hamiltonian for excitation spectra.

Couple NRLMOL/DFT and many-spin Heisenberg Hamiltonian

$H \Phi = \lambda \Phi$

$H = \sum J_{ij} \vec{S}_i \cdot \vec{S}_j$
Intramolecular exchange interactions: $\text{Mn}_{12}$-acetate

- $\text{Mn}^{3+}(S=2)$
- $\text{Mn}^{4+}(S=3/2)$

- $S_4$ symmetry + 3 inequivalent Mn sites: $J_1, J_2, J_3, J_4$

- Consider low-energy collinear spin-excitations

- Use optimized ground-state geometry

\[
E = E_0 + \sum J_{ij} S_i S_j
\]

by DFT

unknowns

$\text{Mn}^{3+}$ $\text{O}^{2-}$
DFT calculated exchange constants: Mn$_{12}$-acetate

- $J_1$, $J_2$: dominant, antiferromag.

<table>
<thead>
<tr>
<th></th>
<th>DFT</th>
<th>Exp. (Ref.A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_1(K)$</td>
<td>140</td>
<td>119</td>
</tr>
<tr>
<td>$J_2(K)$</td>
<td>117</td>
<td>118</td>
</tr>
<tr>
<td>$J_3(K)$</td>
<td>7</td>
<td>-8</td>
</tr>
<tr>
<td>$J_4(K)$</td>
<td>24</td>
<td>23</td>
</tr>
</tbody>
</table>

DFT: K. Park et al., PRB (2004)

Qualitative Agreement with Experiment (50 %)
Spin excitation energetics

• Heisenberg Hamiltonian \( H = \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j \)

DFT determined

• Diagonalize \( H \) with DFT-determined \( J_{ij} \) to find ground state & excited spin multiplets [Lanczos method, Hellberg et al., JPSJ (1999).]

• Dimension of Hilbert space for Mn\(_{12}\)-acetate: 10\(^8\)
Calculated ground state & low-lying excited spin multiplets (Mn$_{12}$-acetate)


- Degeneracy can be lifted by including spin-orbit interaction

- Energy gap between S=10 and 1$^{\text{st}}$ excited S=9 < MAB of S=10 (= 66K)

Experimental energy gap = 35-40 K

Regnault et al., PRB (2002)

Petukhov et al., PRB (2004)

megagauss, EPR, neutron scattering
Each Spin Multiplets Splits due to LS Coupling

(S=9) - 33 K
(S=9) - 7 K
(S=9) - 41 K
(S=10)

(2S+1)-fold degeneracy
Magnetic Anisotropy in Nanomagnets?

Computing Magnetic Effects due to Spin-Orbit Coupling Possible within Density-Functional Theory

(Van Vleck 1937)
NRLMOL: Linear Combination of Gaussian Orbitals

Place Gaussians on each atom in molecule or crystal

\[ \Psi_{i\sigma}(r) = \sum_i C_{i\sigma} \exp[\alpha_i (r-R_i)^2] \chi_{\sigma} \]

Reduce Problem to Finding Expansion Coefficients

DENSITY FUNCTIONAL FORMALISM USED (PBE GGA)

\[ H \Psi_{i\sigma} = \lambda_{i\sigma} \Psi_{i\sigma} \]

\[ \rho(r) = \sum_{i\sigma} |\Psi_{i\sigma}|^2 \]
Anisotropy Hamiltonian
Pederson and Khanna PRB 1999
Effect on total energy due to spin-orbit L.S term
Dependent on axis of spin quantization

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

To lowest order:
(2nd order perturbation in L\cdot S)

Determine \( \gamma_{ab} \) from DFT

\[ \Delta_2 = \sum_{ab} \gamma_{ab} \langle S_a \rangle \langle S_b \rangle \to \]
\[ \Delta E_2 = -DS_zS_z - E(S_xS_x - S_yS_y) \]
MAGNETOMOLECULAR ANISOTROPY ENERGY

\[ \Delta E \sim (1/4C^4) M^2 \]

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

\[ \Theta = \delta \Psi_{\sigma}(r) = [\delta \Psi_{i1} |\chi_1\rangle + \delta \Psi_{i2} |\chi_2\rangle]/c^2 \]

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

Spin Orbit Energy

ME’s
Accuracy of Non-Relativistic DFT for Spin-Orbit?

<table>
<thead>
<tr>
<th>Element</th>
<th>NRLMOL</th>
<th>DIRAC</th>
<th>EXPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr 3d</td>
<td>1.282</td>
<td>1.303</td>
<td></td>
</tr>
<tr>
<td>Kr 3p</td>
<td>7.551</td>
<td>7.883</td>
<td></td>
</tr>
<tr>
<td>Kr 2p</td>
<td>50.97</td>
<td>53.43</td>
<td></td>
</tr>
<tr>
<td>Mn 2p</td>
<td>10.3</td>
<td></td>
<td>11-12</td>
</tr>
<tr>
<td>Ru 2p</td>
<td>121</td>
<td></td>
<td>125</td>
</tr>
</tbody>
</table>

Mn[N-(CN)$_2$]$_2$ Molecular Magnetic Material

Density of States for Passivated Mn$_{12}$O$_{12}$ Magnet

Minority Gap: 2.03 eV
Majority Gap: 0.43 eV

- No Mn (4s)
- S=10
- Ferrimagnetic

Expt: Gaps at 1.08 and 1.75 eV  [Oppenheimer et al, PRB 65 05449 (2002)]
Second Order Molecular Magnetic Anisotropy Barrier Theory vs. Experiment

All Electron GGA (NRLMOL): 55.7 K

Expt. (Barra et al, Fort et al): 55.6 K
In our formulation every ground-state electron relaxes due to the constraint of an imposed axis of quantization

<table>
<thead>
<tr>
<th>What happens if we go beyond a single determinant?</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT: Density….not Wavefunction</td>
</tr>
<tr>
<td>Empirical Observation: DFT wavefunctions not too different than SU HF</td>
</tr>
</tbody>
</table>
Wannier Description of Magnetic Core of Molecule

Lowest Electronic Excitation:
“band-like” d,eg - d,eg majority spin excitation
Other Contributions to Magnetic Anisotropy: Beyond Mean Field

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

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

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

Try: (1) All diagonal terms the same or \(|C_\nu|^2\) very small.

(2) Off diagonal terms small due to zero overlap or small \(|C_\nu|\)
Spin-Orbit Contributions to Many-Electron Hamiltonian (See Slater)

\[ V_{L.S} = \left[ \sum_{ij} q_j s_i \cdot \frac{(r_i - r_j)}{|r_i - r_j|^3} \times p_i \right] / [2c^2] \]

Sum of 1 body (nuclei-electron) and 2 body (electron-electron) operators
Excited Configurations of the Mn$_{12}$-Acetate Molecule

<table>
<thead>
<tr>
<th>Excitation Type</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(3d) - Mn(3d) Majority Excitations</td>
<td>&gt;0.44</td>
</tr>
<tr>
<td>Localized single spin flip</td>
<td>&gt;1.00</td>
</tr>
<tr>
<td>Concerted local moment flips (3 or 4 3d e$^-$ at once):</td>
<td>~0.05</td>
</tr>
<tr>
<td>Charge-Transfer</td>
<td>~6.00 (?)</td>
</tr>
</tbody>
</table>

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:

Direct off-diagonal L.S matrix element vanishes.
Spin Manifolds in Mn\textsubscript{12}-Acetate

Park, Pederson and Hellberg PRB \textbf{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>

N.B. None of these states are eigenstates of S\textsuperscript{2} !

Above states are NOT connected by one and two electron operators
How does Magnetization Barrier Depend on Addition of A single Electron?
Projected Onsite Anisotropies?

T. Baruah et al, CPL 360 144 (2002)

Majority Spin Insertion should decrease anisotropy

Local JT distortion

~1 Kelvin

~10 Kelvin

O²⁻
Additional Majority Spin Electrons Should Reduce Barrier?

Rough Prediction for $\text{Mn}_{12}\text{O}_{12}^{+14}$: $U \sim 31\text{K}$

Good Agreement with Experiment…but situation is more complicated
(See Park et al, PRB 2004)
Exchange Coupling also changes

Park and Pederson, PRB 70 054414, 2004