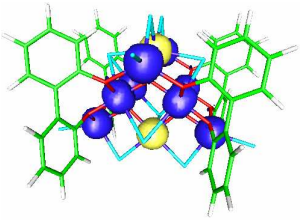
Density-Functional Based Simulation of Molecular Magnets



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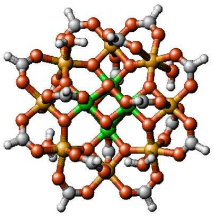
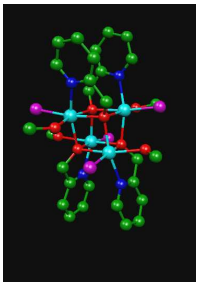


Collaborators: J. Kortus (MPI), T. Baruah (Georgetown/NRL), S. Hellberg (NRL), K. Park (Howard/NRL) and N. Bernstein (NRL), S.N. Khanna (VCU).



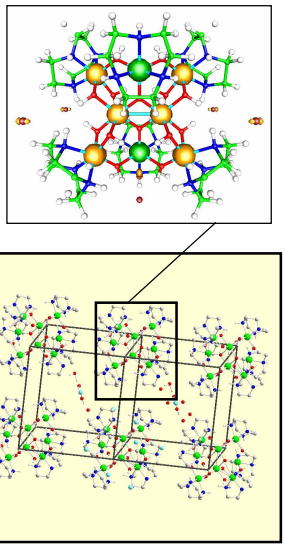
Supported by ONR, DOD HPCMP

Outline:

- Motivation: Practical considerations plus neat experiments.
- Method: DFT, NRLMOL, L.S Coupling
- Background on 2nd-order Barrier
- Examples: Mn_{12}, Mn_{10}, Fe_4, Fe_8 Cr_1, Co_4 (Good Agreement with Expt)
- What determines Axes and Barriers?
  - Pairing dependencies?
  - Global vs Local?
  - Total Moment?
  - Ligand Variation?
- Why does it work?
  - If GGA is exact.
  - If many-electron hamiltonian is starting point.
- 4th-order MAE via spin-orbit vibron interaction.

Molecular Magnetic Crystals -Type 1 : Anatomy and Challenges

From NRLMOL



From Cambridge Crystal Data Bank

- Individual molecular magnets are "isolated" magnetically and electronically.
- Six-Fold coordinated transition metal centers.
- Metal-metal superexchange interactions are strong compared to magnetic reorientation temperature.
- Well defined spin-ordering for each molecule (so far).

EARLY EXPERIMENTS ON RESONANT TUNNELING OF MAGNETIZATION

J.R. Friedman et al, Phys. Rev. Lett. 76, 3830 (1996)

L. Thomas et al, Nature 383, 245 (1996)

SOME MOLECULAR CRYSTALS OF CURRENT INTEREST:

"$Mn_{12}O_{12}$-Acetate" - Longitudinal Tunneling

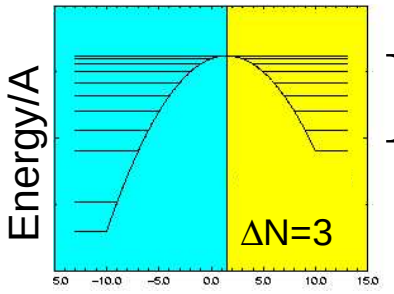
"Fe_8O_2-tacn" - Transverse Tunneling

Different Physics than Spin Dependent Transport and/or Tunneling!

NANOSCALE MOLECULAR MAGNETS

LONGITUDINAL FIELD

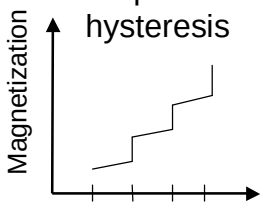
Classical Barrier Hopping vs. Resonant Tunneling of Magnetization



$\langle S_z \rangle$ (M)

Barrier changes continuously with B_z field

Steps in hysteresis



$\Delta W = MB - DM^2/2$

AKA: Zero-Field Splittings in atomic physics/radical chemistry

Yellow States Aligned with Blue States only if:

$B_z = [\Delta N]D/2$

Calculation of Anisotropy Hamiltonian within DFT, DFT+U, DFT-SIC or DMFT?

Electronic and Atomic Equations of Motion -DFT

$$E = \sum_{i\sigma} \langle \Psi_{i\sigma} | -\frac{\nabla^2}{2} + V_{nuc}(\vec{r}) | \Psi_{i\sigma} \rangle + \frac{1}{2} \int d\vec{r} d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} + \int d\vec{r} g(\rho_\uparrow \rho_\downarrow, \nabla\rho_\uparrow \nabla \rho_\downarrow, ...) + \frac{1}{2} \sum_{nm}{}' \frac{Z_n Z_m}{|R_n - R_m|}$$

$$\sum_k \langle \frac{d\Psi_{i\sigma}}{dq_k} | -\frac{\nabla^2}{2} + V_{eff}(\vec{r}) - \lambda_{i\sigma} | \Psi_{i\sigma} \rangle = 0$$

$$\Psi_{i\sigma}(\vec{r}) = \sum_{j\vec{A}} C_{j\vec{A}}^{i\sigma} \cdot P_{l_j}(\vec{r} - \vec{A}) \cdot \exp[-\alpha_j (r - A)^2]$$

$$\{q_k\} = \{\vec{A}, C_{j\vec{A}}^{i\sigma}, \alpha_j\}$$

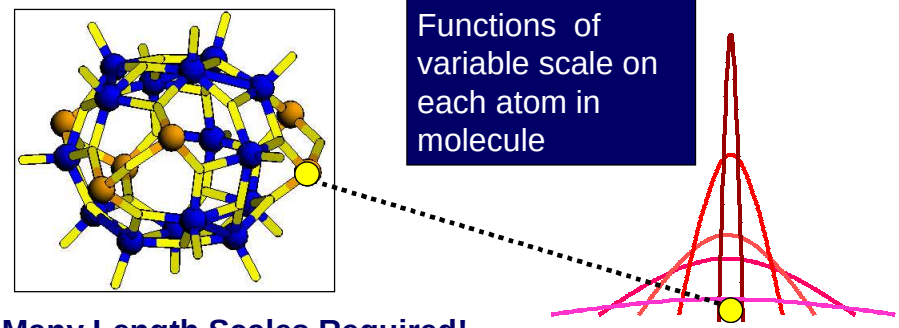
$$\nabla_n E = 0$$ **(Hellmann-Feynman Force)**

Vary Single-Electron Orbitals to Minimize Energy

$$\phi_a(\tau) = = \Sigma_{nlm,R} C(a)_{nlm,R} P_{lm}(r\text{-}R) R_{nl}[(\mathbf{r}\text{-}\mathbf{R})^2] \chi(\sigma_a)$$

C_{nj} $u_i(r)$

Place Trial Functions of variable scale on each atom in molecule



Many Length Scales Required!

NRLMOL: Computational Tool Developed at NRL

Recent Review:
MR Pederson, DV Porezag, J Kortus and D.C. Patton, Phys. Stat. Solidi B **217,** 197 (2000).

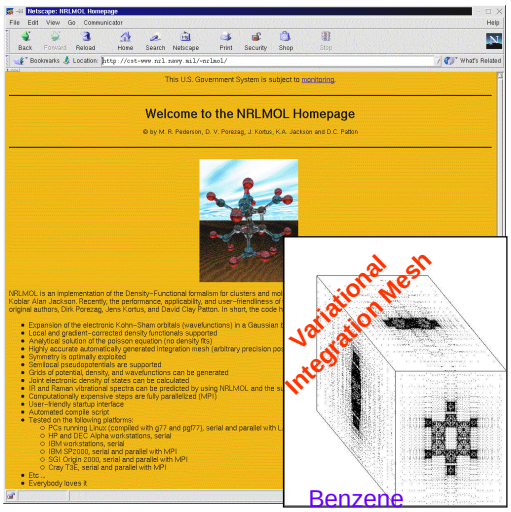
•Added Pseudopotentials [Porezag, Pederson and Liu, PRB **60**, 14132 (1999)].

•$Z^{10/3}$ theorem on gaussian basis set completeness, [Porezag and Pederson, PRA **60**, 2840 (1999).]

Study electronic, magnetic, structural and vibrational effects in molecules and clusters

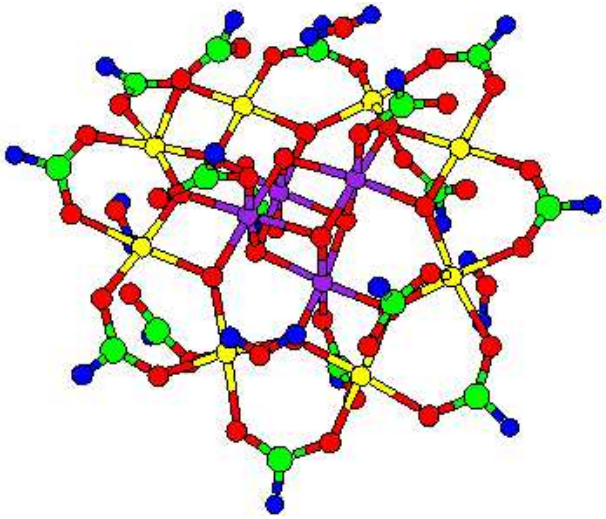
HONEY BEE ALGORITHMS

Automatic Dynamical Load Balancing on Homo- or Hetero-geneous Parallel Platforms



Massively Parallel NRLMOL: distributed to research community via CHSSI

$Mn_{12}O_{12}$-Acetate molecule

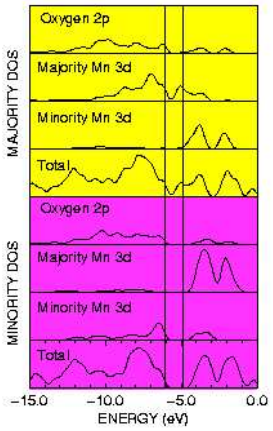


Ligands:

- **Separate Magnet Cores**
- **Six Fold Coordination of Mn Atoms**
- **Prevent Reconstruction of Magnetic Core.**
- **"Steal" Mn 3d and 4s electrons?**

$Mn_{12}O_{12}^{2-}(COOCH_3)_{16}^{1-}(H_2O)_4$

Density of States for Passivated $Mn_{12}O_{12}$ Magnet

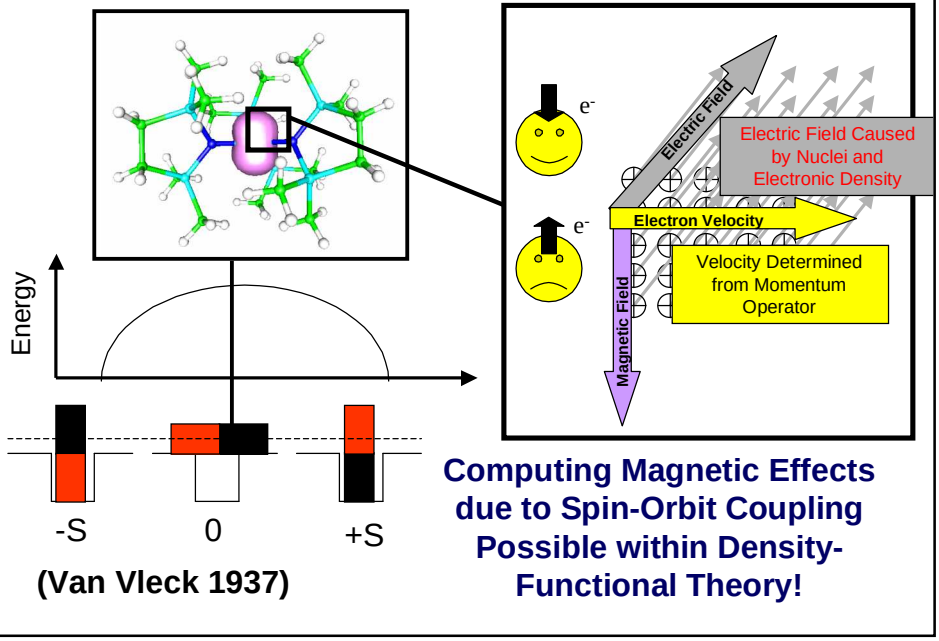


- **No Mn (4s)**
- **S=10**
- **Ferrimagnetic**

Minority Gap: 2.03 eV

Majority Gap: 0.43 eV

Magnetic Anisotropy in Nanomagnets



(Van Vleck 1937)

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

Anisotropy Hamiltonian

Pederson and Khanna PRB 1999

Effect on total energy due to spin-orbit L.S term

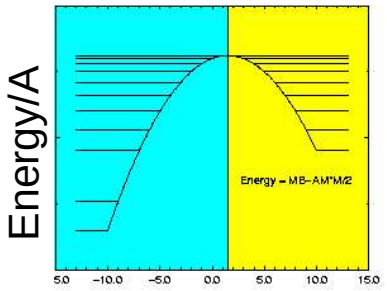
Dependent on axis of spin quantization

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

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

Determine γ_{ab} from DFT

$$\Delta_2 = \Sigma_{ab}\ \gamma_{ab} \langle S_a\rangle\langle S_b\rangle \rightarrow$$
$$\Delta E_2 = -DS_zS_z - E(S_xS_x - S_yS_y)$$



$\langle S_z\rangle$ (M)

MAGNETOMOLECULAR ANISOTROPY ENERGY

$$\Delta E \sim (1/4C^4)\, M^2$$

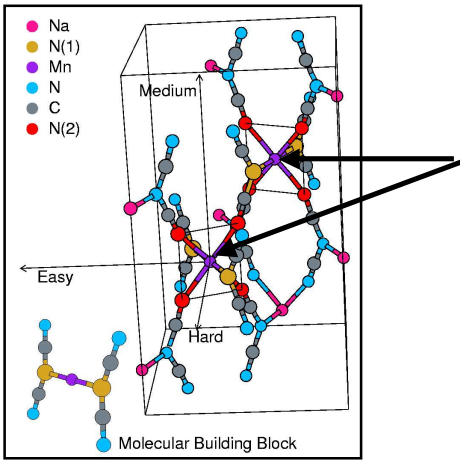
Θ

Spin Orbit Energy

E= DFT Energy + ■(Θ)

■(Θ) = ME's / C^4 (3.5×10^8)

Accuracy of Non-Relativistic DFT for Spin-Orbit?



	NRLMOL	DIRAC	EXPT
Kr 3d	1.282	1.303	
Kr 3p	7.551	7.883	
Kr 2p	50.97	53.43	
Mn 2p	10.3		11-12
Ru 2p	121		125

GAS PHASE

CRYSTALLINE PHASE

M.R. Pederson, A.Y. Liu, T. Baruah, E.Z. Kurmaev, A. Moewes, S Chiuzbidian, M. Neuman, C.R. Kmety, K.L. Stevenson and D.Ederer, To appear in **Phys. Rev. B 2002**

SPIN ORBIT COUPLING: CARTESIAN VS. L.S?

$$U(\mathbf{r},\mathbf{p},\mathbf{S}) = -\frac{1}{2c^2}\mathbf{S}\bullet\mathbf{p}\times\nabla\Phi(\mathbf{r})$$

$$U(r,\mathbf{L},\mathbf{S}) = \frac{1}{2c^2}\mathbf{S}\bullet\mathbf{L}\frac{1}{r}\frac{d\Phi(r)}{dr}$$

Most (all?) computational methods have used the L.S representation

WAVEFUNCTIONS ARE EXPANDED IN TERMS OF SOME BASIS SET

(GAUSSIANS, PLANEWAVES, MTOS, APWS ETC…)

$$\Psi_{\mathbf{is}}(\mathbf{r}) = \sum_{j\sigma} C_{j\sigma}^{is} \mathrm{f}_j(\mathbf{r}) \chi_\sigma$$

$$\left\langle \mathrm{f}_j \chi_\sigma \left| U(\mathbf{r},\mathbf{p},\mathbf{S}) \right| \mathrm{f}_k \chi_{\sigma'} \right\rangle = ?$$

MATRIX ELEMENTS FOR SPIN-ORBIT COUPLING OPERATOR

[M. R. Pederson - Submitted to PRB (1999)]

WAVEFUNCTIONS EXPANDED IN TERMS OF SPIN-ORBITAL PRODUCTS

$$\psi_{is}(\mathbf{r}) = \Sigma_{j\sigma} C_{j\sigma}^{is} f_j(\mathbf{r}) \chi_\sigma \qquad (1)$$

$$\begin{aligned} U_{j\sigma,k\sigma'} &= < f_j \chi_\sigma | U(\mathbf{r},\mathbf{p},\mathbf{S}) | f_k \chi_{\sigma'} > \\ &= \Sigma_\alpha \frac{-1}{i2c^2} < f_j | [\nabla \times \nabla\Phi(\mathbf{r})]_\alpha | f_k > < \chi_\sigma | S_\alpha | \chi_{\sigma'} > \\ &= \Sigma_\alpha \frac{1}{i} < f_j | V_\alpha | f_k > < \chi_\sigma | S_\alpha | \chi_{\sigma'} > \end{aligned} \qquad (2)$$

"STANDARD" CARTESIAN REPRESENTATION OF SPATIAL OPERATOR

$$< f_i | V_x | f_j > = \frac{1}{2c^2} < f_i | (\frac{d\Phi}{dy}\frac{d}{dz} - \frac{d\Phi}{dz}\frac{d}{dy}) | f_j > \qquad (3)$$

INTEGRATION BY PARTS:

$$\begin{aligned} < f_i | \frac{d\Phi}{dy}\frac{d}{dz} | f_j > &= \int d^3r \frac{d}{dy}[f_i \Phi \frac{df_j}{dz}] \\ &- < \frac{df_i}{dy} | \Phi | \frac{df_j}{dz} > - < f_i | \Phi | \frac{d^2 f_j}{dz dy} > \end{aligned} \qquad (4)$$

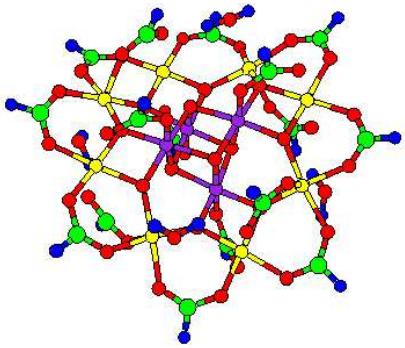
SIMPLIFIED REPRESENTATION FOR SPIN-ORBIT MATRIX ELEMENTS

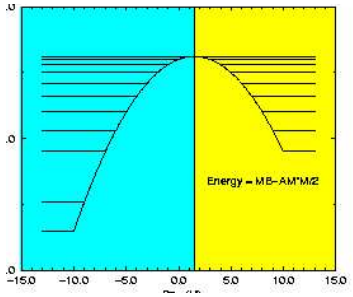
$$< f_i | V_x | f_j > = \frac{1}{2c^2} (< \frac{df_i}{dz} | \Phi | \frac{df_j}{dy} > - < \frac{df_i}{dy} | \Phi | \frac{df_j}{dz} >) \qquad (5)$$

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





What about correlations and multideterminental contributions to anisotropies?

What about spin contaminated wavefunctions?

What are the conditions for which existing approximations to DFT should be good enough?

THE ANATOMY OF A SLATER DETERMINANT

Many Electron Determinent

$$\Phi(\tau_1,\tau_2,\tau_3..) = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \phi_a(\tau_1)\ \phi_a(\tau_2)\ \phi_a(\tau_3)\ \phi_a(\tau_4)\ldots\ \phi_a(\tau_N) \\ \phi_b(\tau_1)\ \phi_b(\tau_2)\ \phi_b(\tau_3)\ \phi_b(\tau_4)\ldots\ \phi_b(\tau_N) \\ \phi_c(\tau_1)\ \phi_c(\tau_2)\ \phi_c(\tau_3)\ \phi_c(\tau_4)\ldots\ \phi_c(\tau_N) \\ \bullet\ \bullet\ \bullet \\ \phi_N(\tau_1)\ \phi_N(\tau_2)\ \phi_N(\tau_3)\ \phi_N(\tau_4)\ldots\phi_N(\tau_N) \end{vmatrix}$$

"Slater Determinant" Ensures Wavefunction is Antisymmetric, Normalized and *Managable*

IFF:

$$\langle\phi_a(\tau)|\ \phi_b(\tau)\rangle = \delta_{ab}$$

$$\phi_a(\tau_1) = \psi_\alpha(r_1)\chi(\sigma_1)$$

Single Electron Spin Orbital

Spatial part

Spin part

Configuration Interaction

$$|\Psi) = C_0|\Phi_0) + C_1|\Phi_1) + C_2|\Phi_2) + C_3|\Phi_3) + \ldots..$$

$$|\Phi_I) = |\phi_a\phi_b\phi_c\ldots) = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \phi_a(\tau_1)\ \phi_a(\tau_2)\ \phi_a(\tau_3)\ \phi_a(\tau_4)\ldots\ \phi_a(\tau_N) \\ \phi_b(\tau_1)\ \phi_b(\tau_2)\ \phi_b(\tau_3)\ \phi_b(\tau_4)\ldots\ \phi_b(\tau_N) \\ \phi_c(\tau_1)\ \phi_c(\tau_2)\ \phi_c(\tau_3)\ \phi_c(\tau_4)\ldots\ \phi_c(\tau_N) \\ \bullet\ \bullet\ \bullet \\ \phi_N(\tau_1)\ \phi_N(\tau_2)\ \phi_N(\tau_3)\ \phi_N(\tau_4)\ldots\phi_N(\tau_N) \end{vmatrix}$$

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

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

Many Electron Secular Eqn.

Multiconfigurational Contributions to Magnetic Anisotropy

$$|\Psi) = C_0|\Phi_0) + C_1|\Phi_1) + C_2|\Phi_2) + C_3|\Phi_3) + \ldots$$

$$(\Psi| V_{L.S} |\Psi) = \Sigma_\nu C^*_\nu C_\nu \langle\Phi_\nu| V_{L.S} | \Phi_\nu\rangle + \Sigma'_{\nu\mu} C^*_\nu C_\mu \langle\Phi_\nu| V_{L.S} | \Phi_\mu\rangle$$

$$V_{L.S} = \Sigma_i f_i + \Sigma'_{ij} g_{ij}$$

(See J.C. Slater)

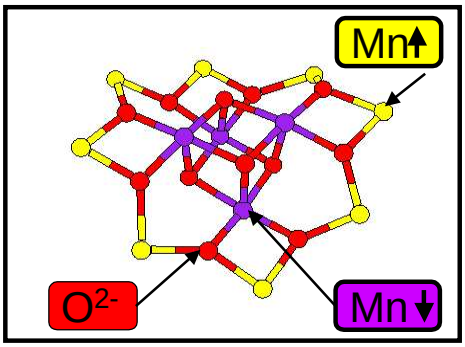
Interaction between electric fields due to nuclei with each moving electron. (1 electron operator)

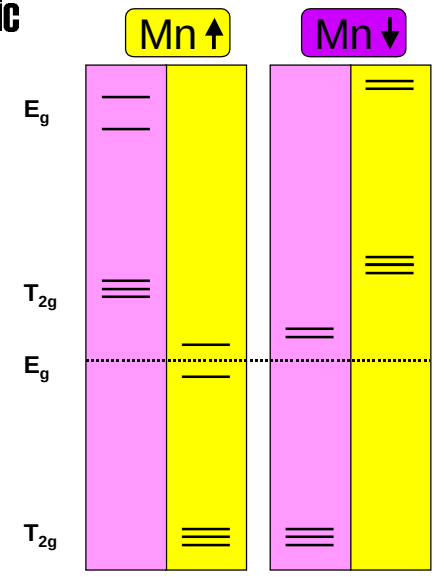
Interaction between electric fields due to all electrons with each moving electron. (2 electron operator)

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

(2) Off diagonal terms small due to zero overlap or small C_ν

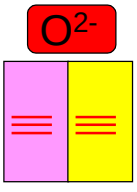
Wannier Description of Magnetic Core of Molecule





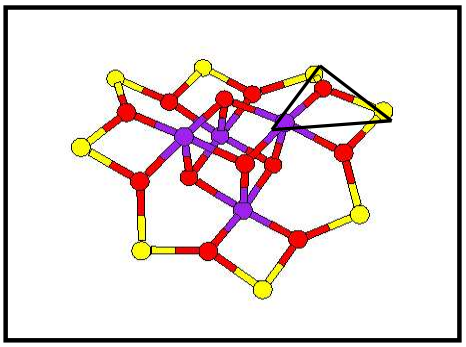
Lowest Electronic Excitation:

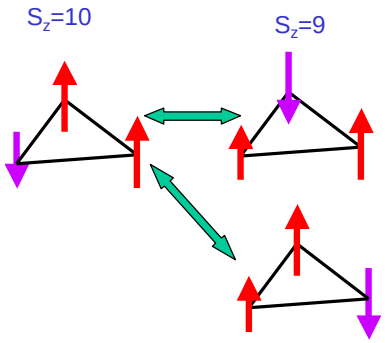
"band-like" d(eg) - d(eg) majority spin excitation



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 (?)

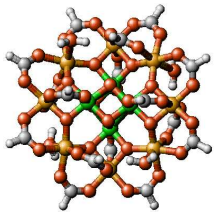


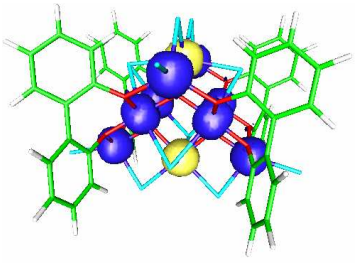


Self Consistency Shows that Local Charges and Moment Size Unchanged

Mn_{12} vs Mn_{10}?

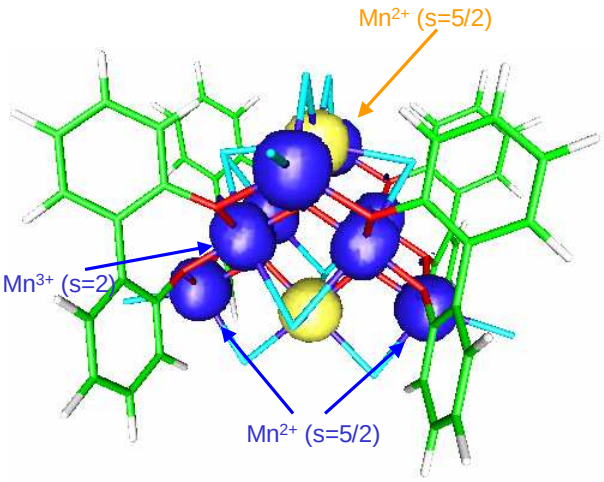
	Total Spin	Local Spins	Interference?	Anisotropy
Mn_{12}:	S=10	S=3/2 and S=2	Constructive	Large
Mn_{10}:	S=12/13	S=5/2	Destructive	Small





$[Mn_{10}O_4(2,2'\text{-biphenoxide})_4Br_{12}]^{4-}$

Kortus, Baruah, Bernstein Pederson, PRB (2002)



High spin single molecule magnet
Exp. : S=12
Theory: S=13

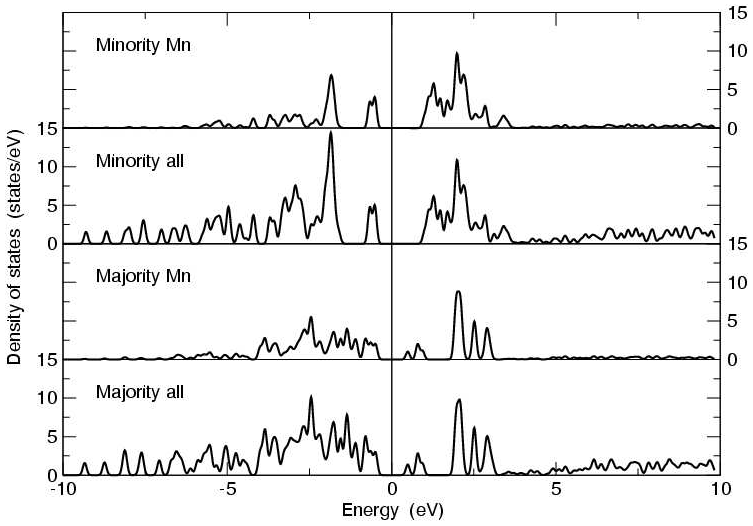
MAE:
9K NRLMOL
8K Experiment

Negatively charged cluster compensated by unit containing Mn atom $[Mn(CH_3CN)_4(H2O)_2]$
• easy-plane system
• MAE 0.1 K
• all magnetic properties due to Mn_{10}-cluster

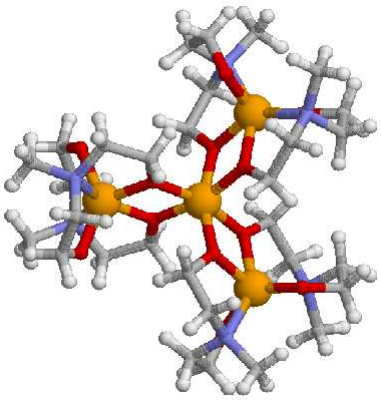
Exp.: Barra *et al.* J. Solid State Chem. **145**, 484 (1999)

Spin-density isosurfaces for 0.03 e/a_B^3

Density of states Mn_{10}-cluster



Ferric star
Kortus et al, (to be published)



The cluster ground state is ferrimagnetic with $S = 5$.

The three outer Fe(III) ions (s = 5/2) couple antiferromagnetic to the inner Fe(III) ion.

Fe-Fe(center) distances of 3.2 Å.

Theory	D=-0.56 K	|E|=0.064 K
Exp.	D=-0.57 K	|E|=0.056 K

Exp.: S. Schromm, O. Waldmann, P. Müller (Uni Erlangen)

Co_4 Based Molecular Magnet

Baruah and Pederson, CPL 2002

Magnetic moment: 12 μ_B

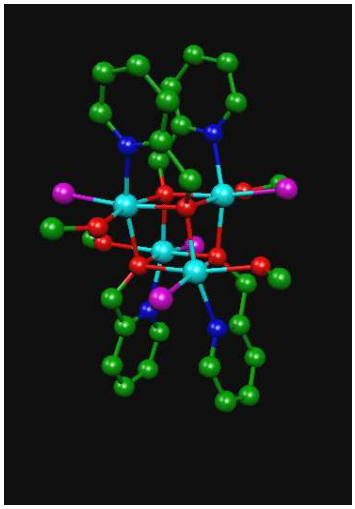
Local Co moment: 3 μ_B

Addition of 4 hydrogens reduced moment by 4 μ_B

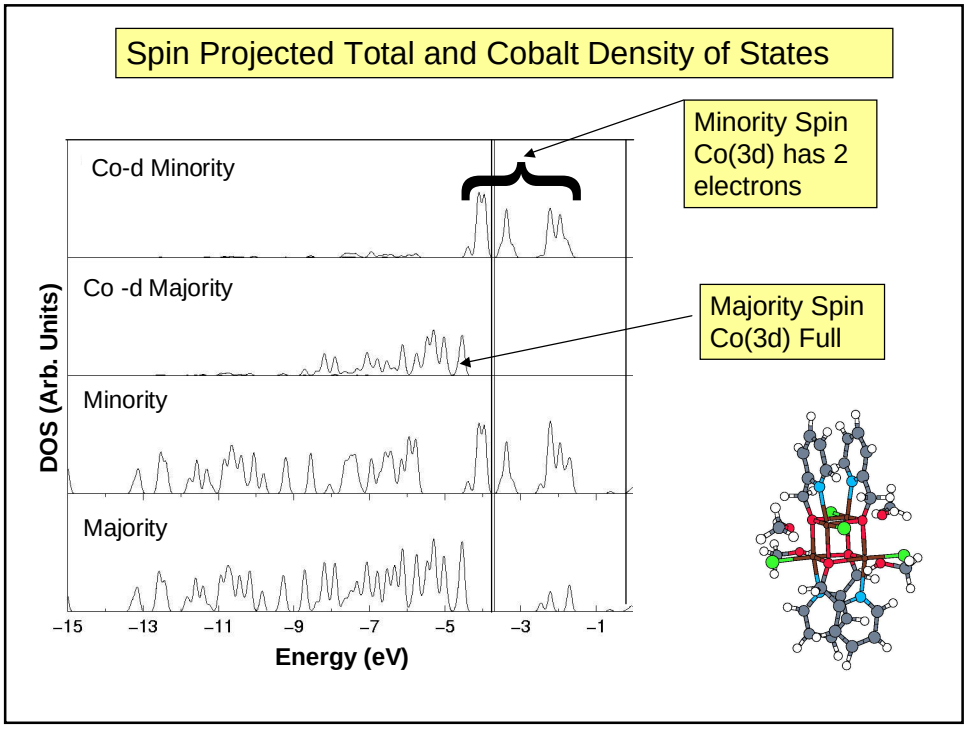
Anisotropy varies strongly with molecular distortions (23-60K)

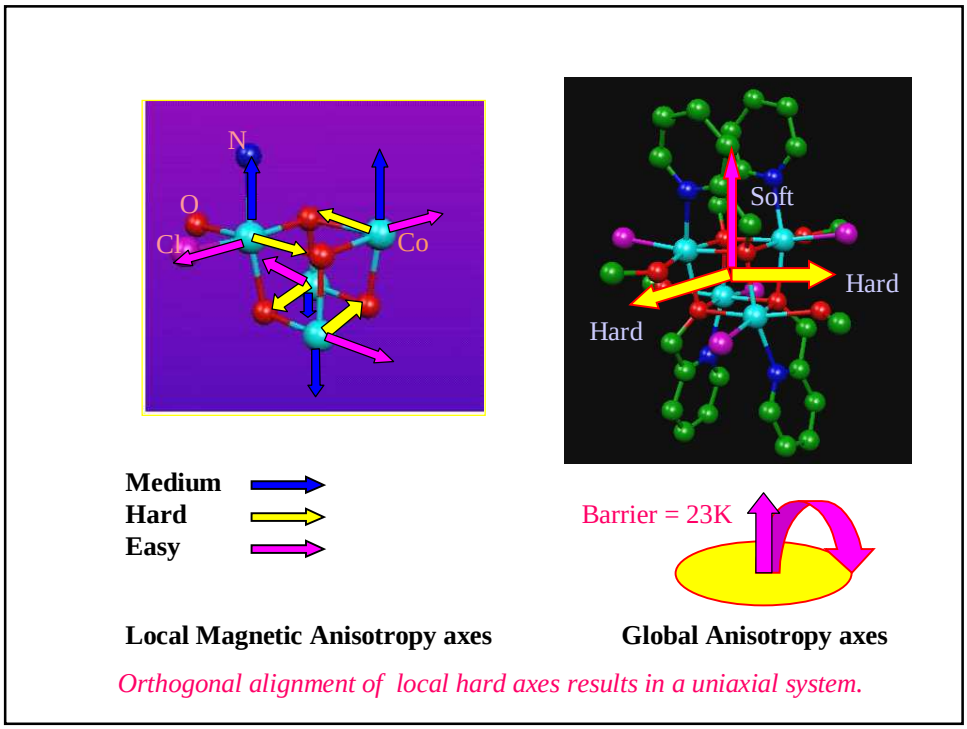
Uniaxial alignment

Global easy axis along Z



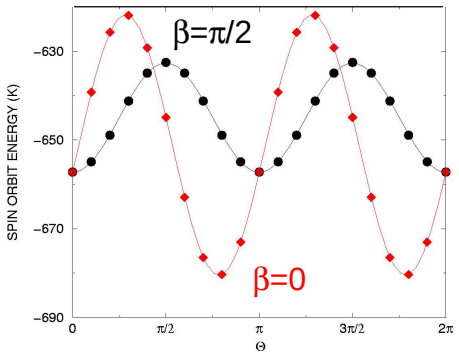
Lowest-energy staggered structure

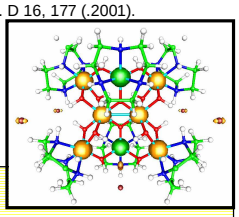

Spin Projected Total and Cobalt Density of States
Minority Spin Co(3d) has 2 electrons
Majority Spin Co(3d) Full
Co-d Minority
Co -d Majority
Minority
Majority
DOS (Arb. Units)
−15
−13
−11
−9
−7
−5
−3
−1
Energy (eV)


N
O
Cl
Co
Soft
Hard
Hard
Medium
Hard
Easy
Barrier = 23K
Local Magnetic Anisotropy axes
Global Anisotropy axes
Orthogonal alignment of local hard axes results in a uniaxial system.

Problem Case: $Fe_8O_2(OH)_{12}(C_6N_3H_{15})_6$

J. Kortus, M.R. Pederson, C.S. Hellberg and S.N. Khanna,, Eur. Phys. Jour. D 16, 177 (.2001).





ANISOTROPY HAMILTONIAN (Kelvin)

$\Delta_2 = -D\cos^2\Theta - E\sin^2\Theta\cos(2\beta)$

	EXPT	DFT
D	29.5	53
E	5.5	5.4

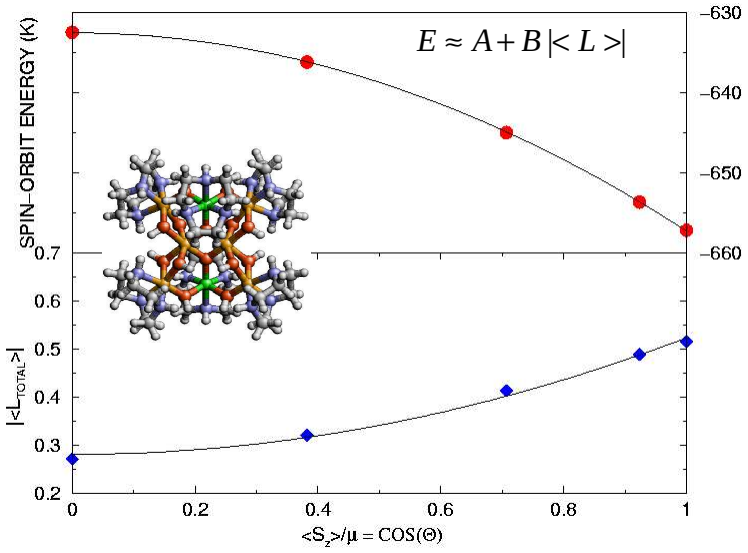
$|\chi_1\rangle = \cos(\theta/2)|\uparrow\rangle + e^{i\beta}\sin(\theta/2)|\downarrow\rangle$

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

$\Delta_2 = \Sigma_{xy}\,\gamma_{xy}\,\langle S_x\rangle\langle S_y\rangle \rightarrow [-DS_zS_z - E(S_xS_x - S_yS_y)]/S^2$

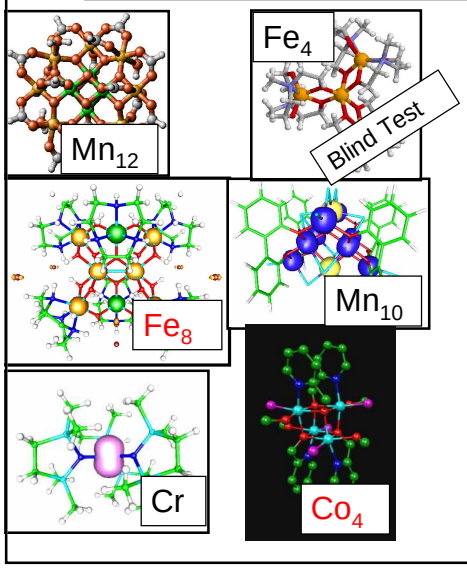
Excellent agreement between 2nd-order and exact diagonalization.
Small Gap…Case for DFT+U or SIC-LSD or DMFT?

Induced orbital moment and valence spin-orbit energy Fe_8



DFT Prediction: Spin Ordering, Magnetic Anisotropies and Resonant Tunneling of Magnetization in Nanomagnets.

2nd-Order Spin Orbit Energy Depends on Quantization Axis



$\Delta_2 = -D\cos^2\Theta + E\sin^2\Theta\cos(2\beta)$

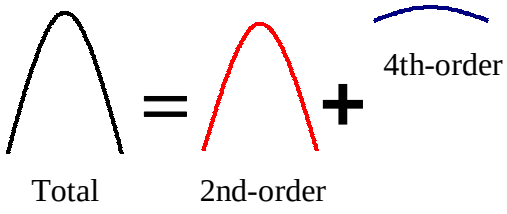
	GGA-DFT	EXPT
Mn_{12} (D)	55	55
Mn_{12} (E)	0	0
Fe_8 (E)	5.4	5.5
Fe_8 (D)	>50	29
Cr (D)	5.6	6.0
Mn_{10} (D)	9.5	8.0
Fe_4 (D)	14.0	14.3
Fe_4 (E)	1.6	1.4
Co_4 (D)	27	~100

Baruah, Kortus, Bernstein, Pederson

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/[Speed of Light]^8

4th-Order Anisotropy (responsible for tunnel splittings)



Higher order terms in L•S:

•exact electronic (non-self-consistent) total energy with L•S

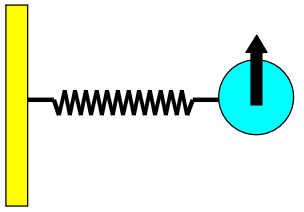
•coupling of spins to vibrations

$$\Delta E_4 = G\, S_z S_z S_z S_z + H\,[S_x S_x S_x S_x + S_y S_y S_y S_y] =$$
$$A_1(4)[S^2(S_z^2 - S^2/3)] + A_2(4)[3S^4 + 35S_z^4 + 30S^2 S_z^2] + \cdots \} \text{ cubic harmonics}$$
$$B_1(4)[S_x^4 + S_y^4 - 6S_x^2 S_y^2] + \ldots$$

Can have different angular dependence and different scaling with 1/[speed of light]

SPIN-ORBIT MEDIATED SPIN VIBRON INTERACTION

$$[P^2 + \omega^2 Q^2]/2 + \gamma_{zz} S_z^2 + Q \Sigma_{ab} (d\gamma_{ab}/dQ) S_a S_b$$



$$|\Psi\rangle = |\phi\rangle |SM\rangle$$

$$E = \omega/2 + \gamma_{zz} M^2 - (A + BM^2)^2/(2\omega^2)$$

$S(S+1)[d/dQ(\gamma_{xx}+\gamma_{yy})]/2$ $\qquad$ $d/dQ[\gamma_{zz} - (\gamma_{xx}+\gamma_{yy})/2]$

Compute total energy, forces, γ_{ab} for all atomic displacements

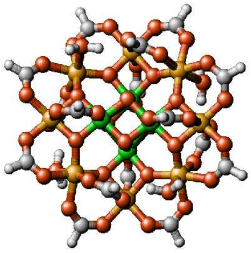
Extract: vibrations (IR, Raman) from dynamical matrix

vibration-spin coupling from d/dQ(γ_{ab})

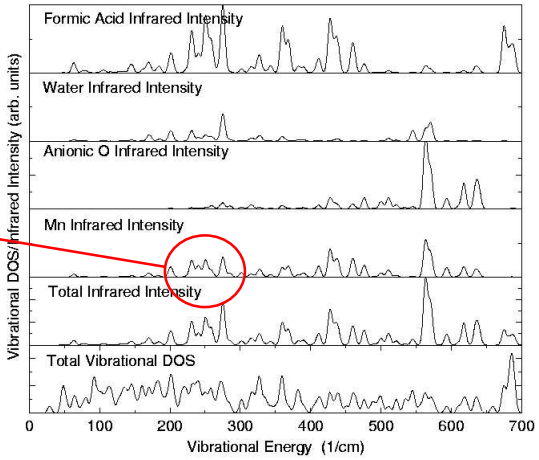
Difficult calculations (shortcuts): must compare to experiment

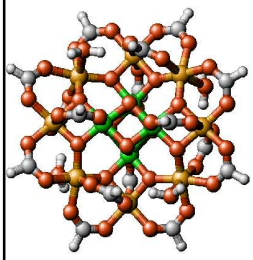
Calculated Total and Infrared DOS - Mn_{12}-Acetate

Pederson, Bernstein and Kortus, (to appear in PRL)

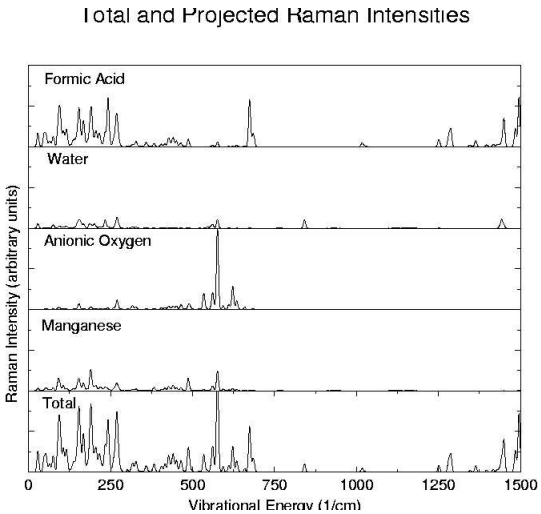


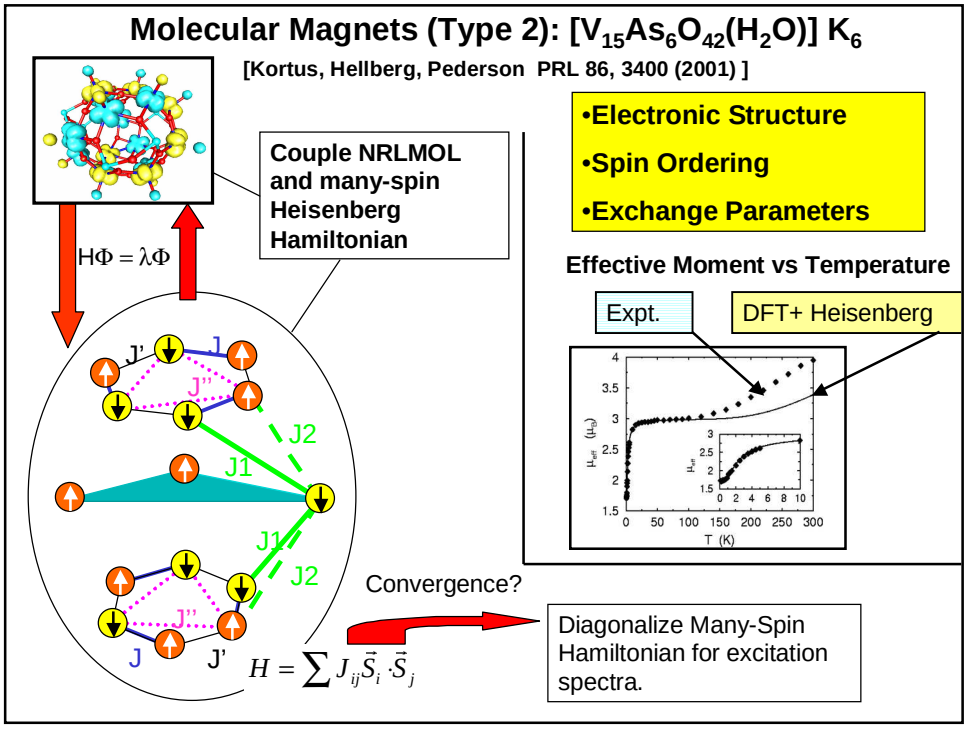
Large Mn-crown contributions in Region identified as field-dependent in IR experiments. (Sushkov et al)





Good agreement between predicted Raman and recent experimental measurements (North et al)





Conclusions

- MAE : barrier to spin flips, controlled by spin-orbit coupling
- Accurate calculation of 2nd order MAE using DFT
- Vibrational spectra (IR, Raman) good agreement with exper.
- 4th order MAE
  - electronic: wrong sign, magnitude
  - vibrational coupling: preliminary results good.
- Open questions:
  - Importance of this effect in other nanomagnets
  - Source of tunnel splittings:
    - other transverse terms
    - symmetry breaking terms at 2nd order. energy