

# Magnetic Properties of Transition Metal Complexes from Density Functional Theory

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# Outline

- Density Functional Theory in a Nutshell
- Molecular Magnets
- Magnetic Properties
- Fe<sub>7</sub> disks

# Density Functional Theory

Electrons and nuclei: Materials and Chemistry



Born-Oppenheimer approximation

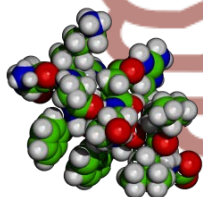
$$H = \sum_i^n (T_i - \sum_N \frac{Z_N}{r_i}) + \sum_{i,j} \frac{1}{r_{ij}}$$

Solve the SE

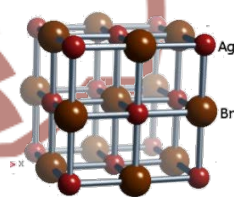


$$E, \psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_n)$$

Contains all the information needed to solve the many-electron problem.



Molecules



Crystals



Holy grail

# Density Functional Theory

$$H = \sum_i^n (T_i - \sum_N \frac{Z_N}{|\vec{r}_i - \vec{R}_N|}) + \sum_{i,j}^n \frac{1}{r_{ij}}$$



$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_n)$$

## Extremely difficult to solve in practice:

- Must include spin:  $\otimes \text{SU}(2)$ .
- $3n$  electronic coordinates. Complexity grows exponentially with that number.
- Solutions need to be antisymmetric with respect to particle exchange.



“the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble”

# Density Functional Theory

Hohenberg and Kohn (1964)

$$E = E[n(\vec{r})]$$

Energy is a functional of the one-electron density!

~~$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_n)$~~



$n(\vec{r})$  ✓

Now the problem reduces to 3 degrees of freedom!

Computational complexity:  $N^\alpha$



# Density Functional Theory

Kohn and Sham (1965)

$$n(\vec{r}) = \sum_{i \in occ} |\varphi_i(\vec{r})|^2$$

and

$$E = E_{ext} + T + E_{coul} + E_{xc}$$



We know how to calculate these



Unknown

(Nobel prize in Chemistry in 1998)

# Density Functional Theory

Bad news:

The functional  $E[n]$  is unknown...

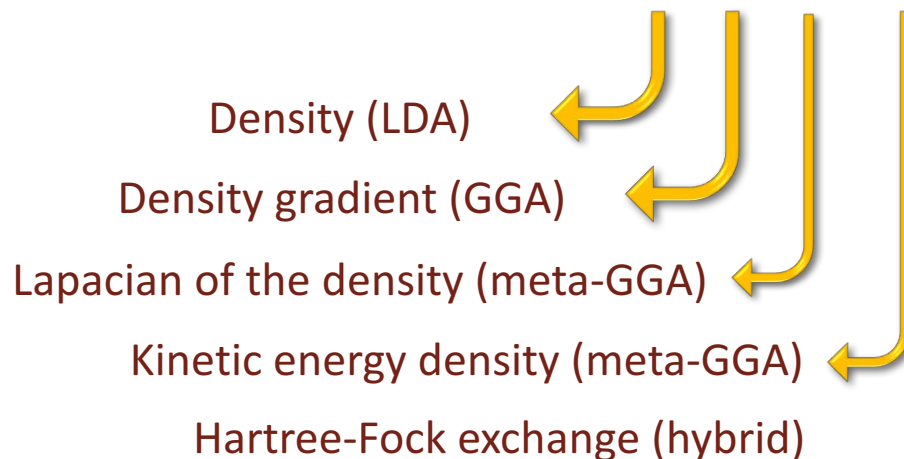


After more than 50 years and trying very hard....

# Density Functional Theory

...we have to use approximations

$$E = E_{ext} + T + E_{coul} + E_{xc}[n, \nabla n, \nabla^2 n, \text{etc.}]$$



- ⊕ Exact theory, in principle.
- ⊕ Computationally easy to implement.
- ⊕ Fast!




**Some widely used functionals:**

- **LDA: The first and simplest approximation (1980)**
- **GGAs : PW91, PBE, very successful in solid state (1991, 1997)**
- **Hybrid functionals (Becke, 1993): popular in chemistry: B3LYP**

**DFT is a theory for the ground state only!**

# Density Functional Theory in Practice

Linear combination of basis functions  $\rightarrow E = E(C_\mu^i) \rightarrow$  Minimize  $E$  (SCF)  $\rightarrow E, C_\mu^i$

- 
  - Plane waves
  - Localized Gaussians
  - Slater-type functions



## Evaluation of properties

$E \rightarrow$ 

- Dissociation energies
- IP and EA
- Relative stability

$\frac{\partial E}{\partial \mathbf{R}_N} \rightarrow$  Forces (equilibrium Structures, lattice properties)  
 $\frac{\partial E}{\partial \mathbf{F}} \rightarrow$  Dipolar moments

$\frac{\partial^2 E}{\partial \mathbf{R}_N^2}$   
 $\downarrow$   
 Harmonic frequencies

$\frac{\partial^2 E}{\partial \mathbf{F}^2}$   
 $\downarrow$   
 Hyper-polarizabilities

$\frac{\partial^2 E}{\partial \mathbf{B} \partial \mathbf{M}_A}$   
 $\downarrow$   
 NMR shieldings

$\frac{\partial^2 E}{\partial \mathbf{M}_A \partial \mathbf{M}_B}$   
 $\downarrow$   
 NMR spin-spin couplings

# Density Functional Theory in Practice

- ⇒ No **systematic** (in the mathematical sense) way of approaching the exact functional.
- ⇒ Known **exact properties** can be used.
- ⇒ Comparison:
  - ⇒ Very accurate **numerical** solutions.
  - ⇒ Very accurate **experiments**.

# Density Functional Theory in Practice

## Typical mean absolute errors:

Dissociation energies	~4 kcal/mol	B3LYP
Harmonic frequencies	~30 cm <sup>-1</sup>	VSXV
Bond lengths	~0.01Å	PBE hybrid
Lattice constants	~0.04Å	LDA
NMR <sup>13</sup> C shieldings	~3 ppm	B3LYP

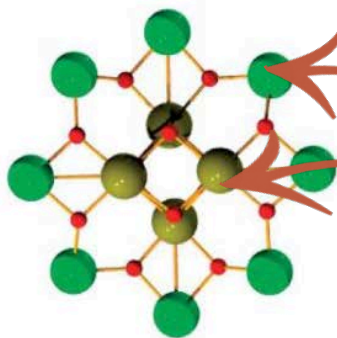
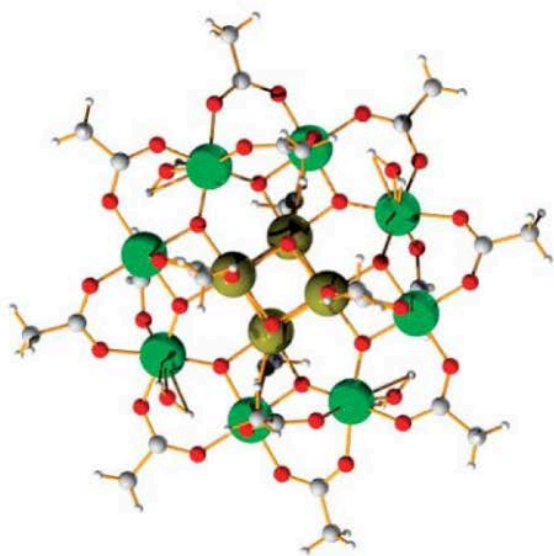
Ideally, we would like to use the one functional for all properties

However, functionals perform different for different properties

**Many spectacular failures and successes**

# Molecular Magnets

- Single molecule magnets (or molecular magnets) are a small group of paramagnetic metal ions bound together by simple groups like  $O^{2-}$ ,  $OH^-$ ,  $Cl^-$ ,  $OCH_3^-$ , etc.
- First SMM reported:  $Mn_{12}$  complex; Sessoli et al., Nature 365, 141 (1993).



- 8  $Mn^{3+}$  ( $s=2$ ) ↑
- 4  $Mn^{4+}$  ( $s=3/2$ ) ↓
- Total  $S=10$

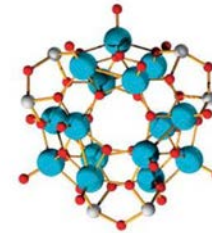
- Organic ligands keep the structure in place and shield the metal ions.
- The ions are typically  $3d$  transition metals.
- The ions are magnetically coupled (superexchange).

# Molecular Magnets

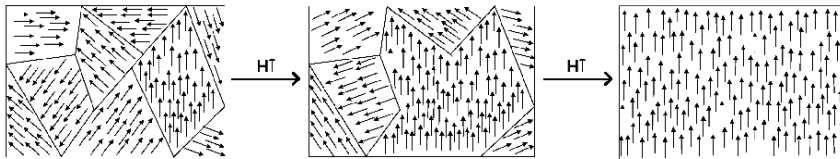
- These molecules show slow relaxation of the magnetization.
- As a consequence, it “remembers” its magnetization after a magnetic field is switched off, just like traditional magnets.



vs.

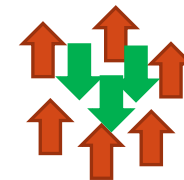


- This is a purely molecular property, **unlike macroscopic magnets**.



Domains  $\sim$  sub  $\mu\text{m}$

vs.



$\sim$  sub nm

# Molecular Magnets

## Applications:

- These are the smallest magnets that can be made: High density data storage.
- Spintronics: building devices that use the spin current to operate.
- Quantum computing: The spin state of a MM can be used as a qbit.



Mount Pleasant  
(Michigan)



- Science of Advanced Materials PhD
- Physics + Chemistry + Engineering
  
- Multidisciplinary program.
- Strong in electronic structure.
- Nice, quiet town.

Looking for enthusiastic students!



# Magnetic Properties

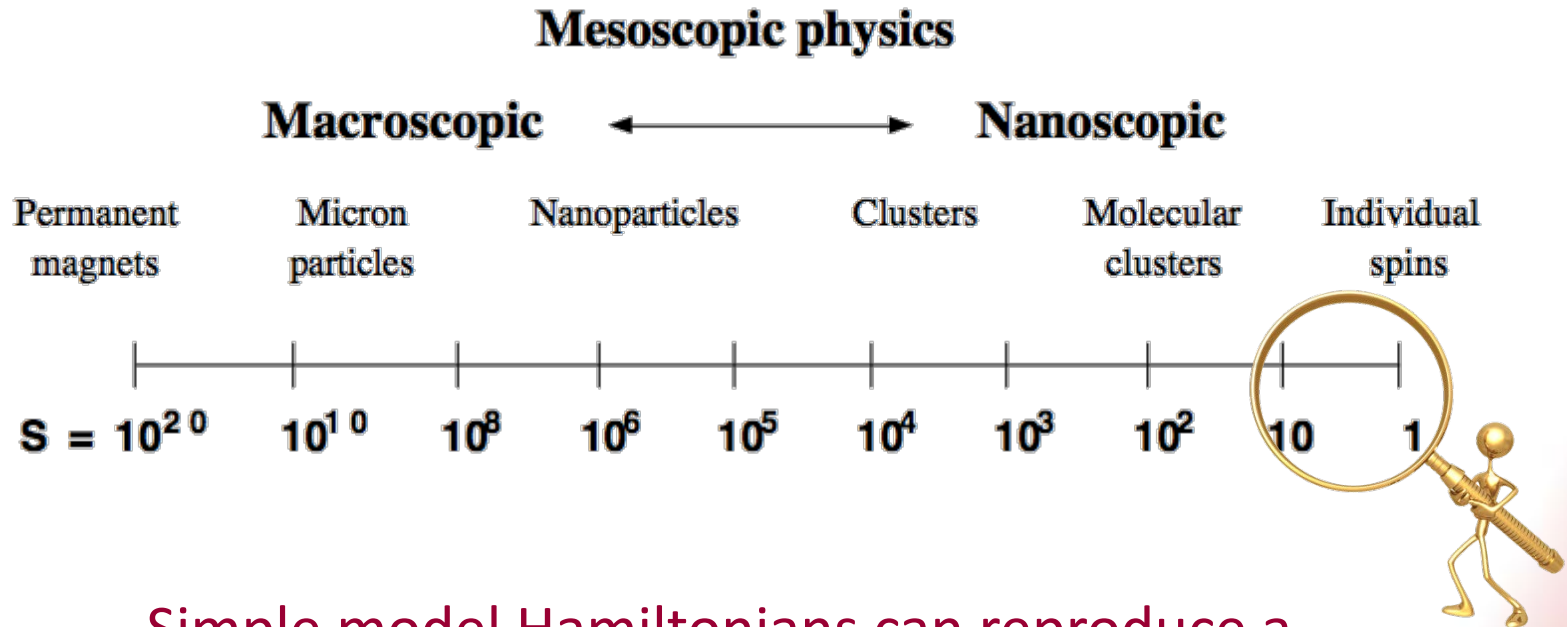
How can we model the magnetic behavior of a SMM?

- Model spin Hamiltonians (Heisenberg-Dirac-van Vleck) in most cases capture the physics

$$\hat{H} = -2 \sum_{\langle AB \rangle} J_{AB} \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B$$

- Quantum or classical
- Used to model a large number of problems in physics :
  - Spin waves, Ising model, etc.
- “Magnetism in Condensed Matter”, S. Blundell (Oxford, 2001)

# Magnetic Properties



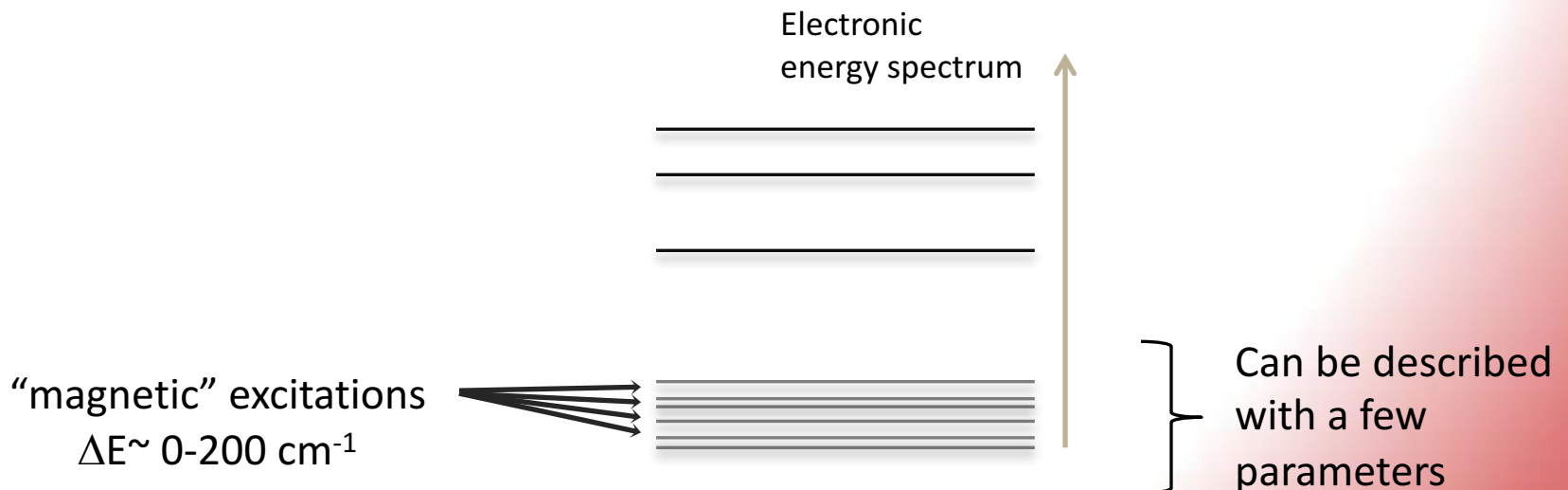
Simple model Hamiltonians can reproduce a huge range of scales!

# Magnetic Properties

- The success of this model is related to the ability to model the energetics of a large number of low-lying states.

$$H = -2 \sum_{\langle AB \rangle} J_{AB} \mathbf{S}_A \cdot \mathbf{S}_B$$

- “Magnetism in Condensed Matter”, S. Blundell (Oxford, 2001)



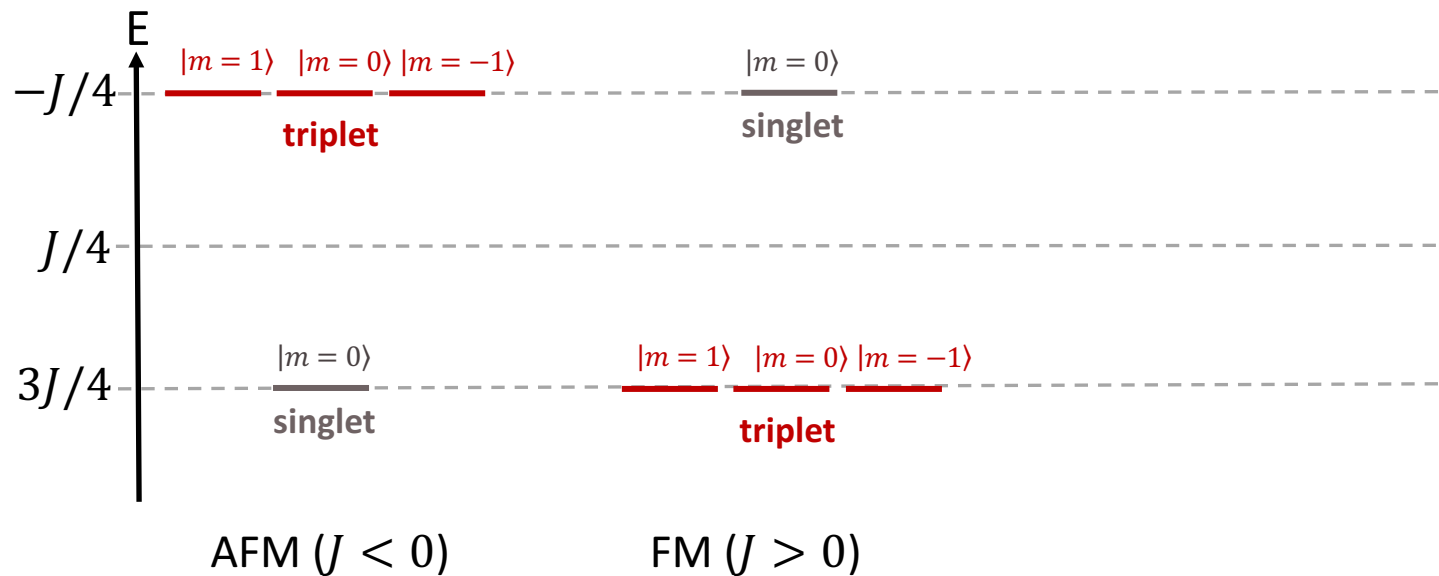
# Magnetic Properties

Example: Simple  $s=1/2$  dimer



Spin-1/2 dimer

$$\hat{H}_{HDVV} = -J \sum_{\langle ij \rangle} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$$



# Magnetic Properties

Zero field splitting:

- Magnetic Anisotropy Energy (spin-orbit)
- Magnetodipolar interactions (small  $\sim 0.1 \text{ cm}^{-1}$ )

$$\hat{H}_{HDVV} = -J \sum_{\langle ij \rangle} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + \hat{\mathbf{S}} \cdot \mathbf{D} \cdot \hat{\mathbf{S}}$$

3x3 tensor

Total molecular spin

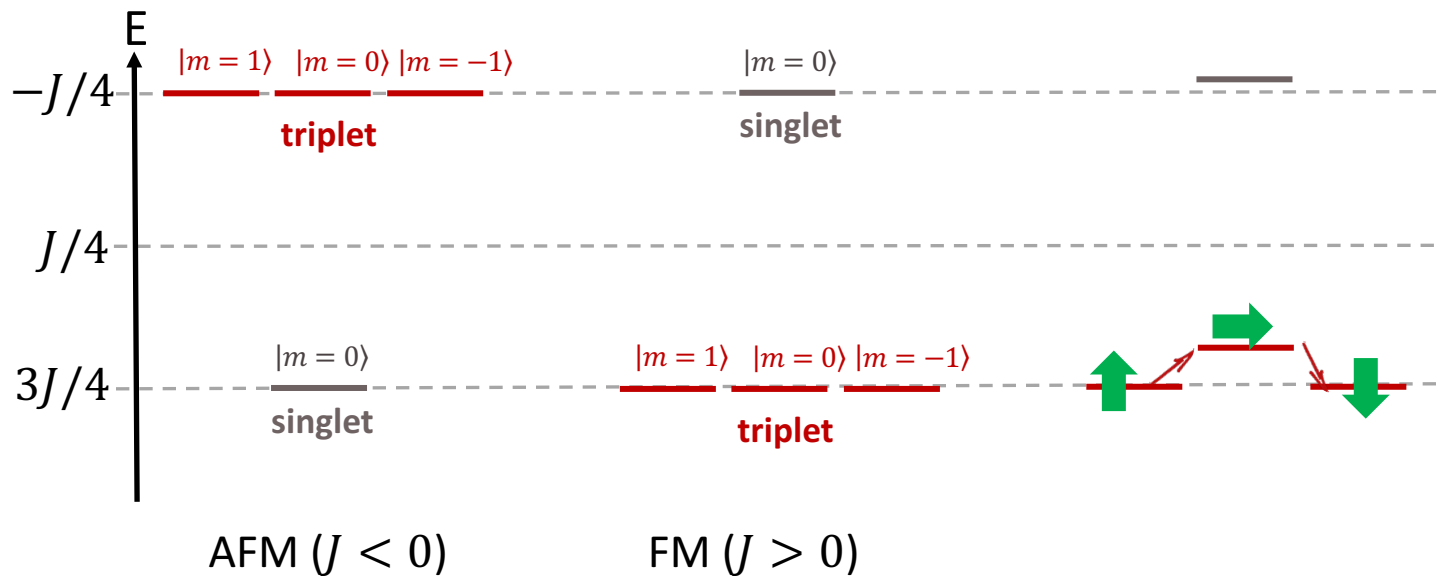
$$\hat{H}_{HDVV} = -J \sum_{\langle ij \rangle} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + E(\hat{\mathbf{S}}_x^2 - \hat{\mathbf{S}}_y^2) + D(\hat{\mathbf{S}}_z^2 - S(S+1)/3)$$

$\Delta M = 1$  or  $\Delta M = 2$

$$\text{With } D = \frac{3D_{zz}}{2} \text{ and } E = \frac{|D_{xx} - D_{yy}|}{2}$$

# Magnetic Properties

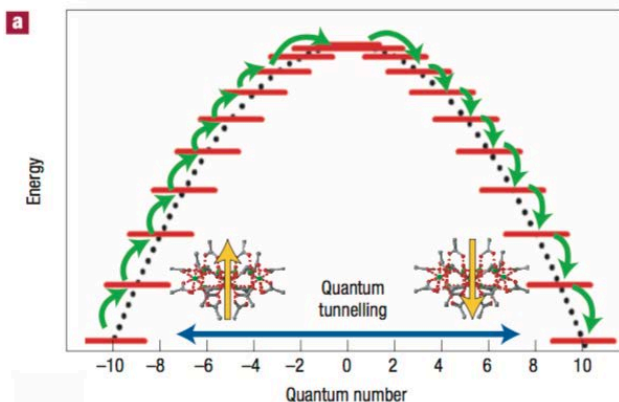
$$\hat{H}_{HDVV} = -J \sum_{\langle ij \rangle} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + E(\hat{\mathbf{S}}_x^2 - \hat{\mathbf{S}}_y^2) + D(\hat{\mathbf{S}}_z^2 - S(S+1)/3)$$



# Magnetic Properties

Real complexes:

- Exchange interactions are generally negative  $\sim 0-100 \text{ cm}^{-1}$ .
- Spin-orbit is responsible for the magnetic anisotropy.
- Orbital angular momentum does not contribute to magnetization (usually due to spin-orbit and Jahn-Teller distortion).
- Tens to hundreds atoms.
- Several transition metal centers:
  - $\text{Fe}_8$ : 8  $s=5/2$  centers  $\rightarrow \sim 10^6$  configurations
  - $\text{Mn}_{12}$ : 4  $s=3/2$  plus 8  $s=2$  centers  $\rightarrow \sim 10^8$  configurations
- Thermal spin inversion originates in the interactions with the environment: phonons.



$$U_{eff} \sim S^2 |D|$$

For  $\text{Mn}_{12}$

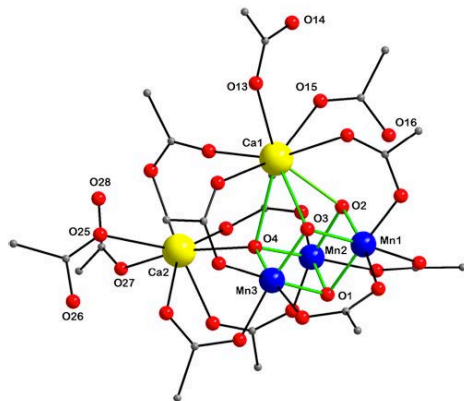
- $S = 10$
- $D = -0.5 \text{ cm}^{-1}$
- $U_{eff} \sim 50 \text{ cm}^{-1}$  or 60 K

# Magnetic Properties

## Experiments

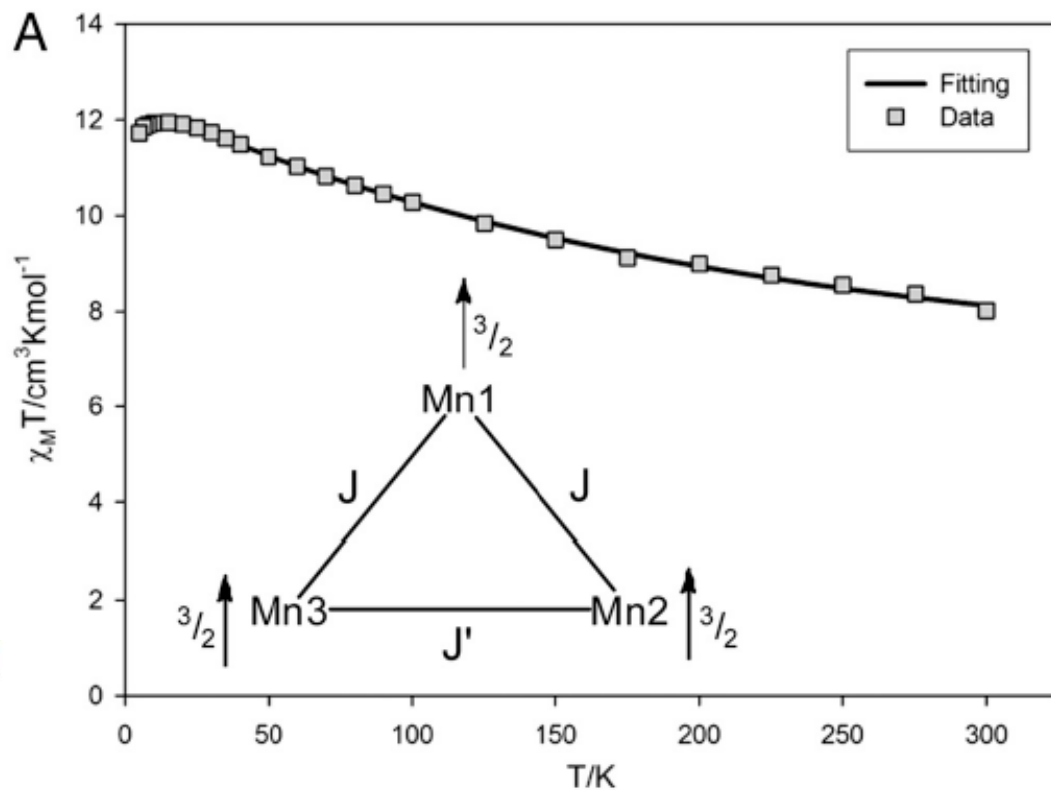
Example: Asymmetric  $[\text{Mn}_3\text{Ca}_2]$  Mukherjee et al., PNAS 109, 2257 (2012).

- $S_T$  determined from variable T DC and AC magnetic susceptibility.
- 2- $J$  model: 64 states, 12 unique energies.
- Fits experimental susceptibility very well with  $S_T=9/2$  and  $J=40 \text{ cm}^{-1}$   $J'=-11 \text{ cm}^{-1}$ .



Van Vleck equation:

$$\chi_M = \frac{Ng^2\beta^2}{3kT} \frac{\sum S_T(S_T+1)(2S_T+1)\Omega(S_T)\exp\left[-\frac{E(S_T)}{kT}\right]}{\sum (2S_T+1)\Omega(S_T)\exp\left[-\frac{E(S_T)}{kT}\right]}$$



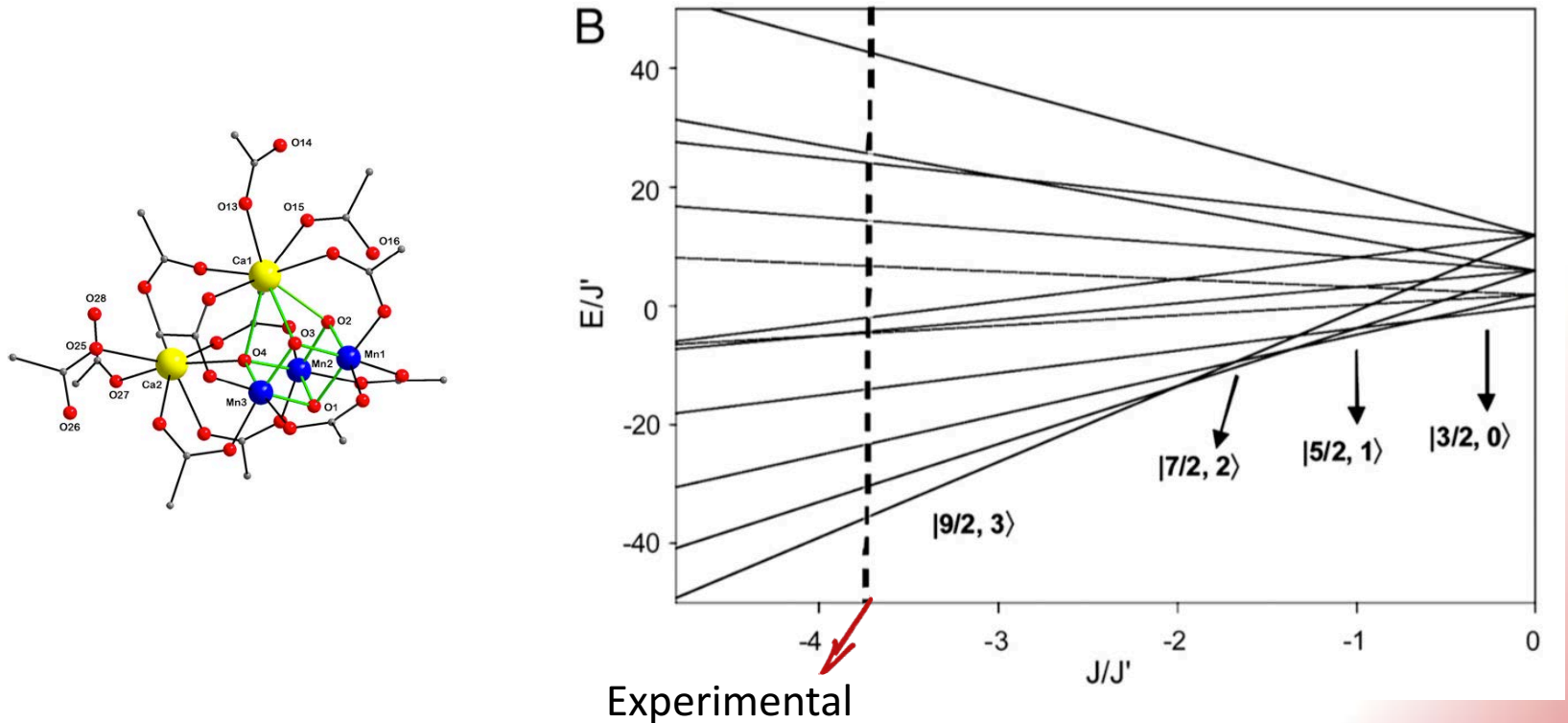


# Magnetic Properties

## Experiments

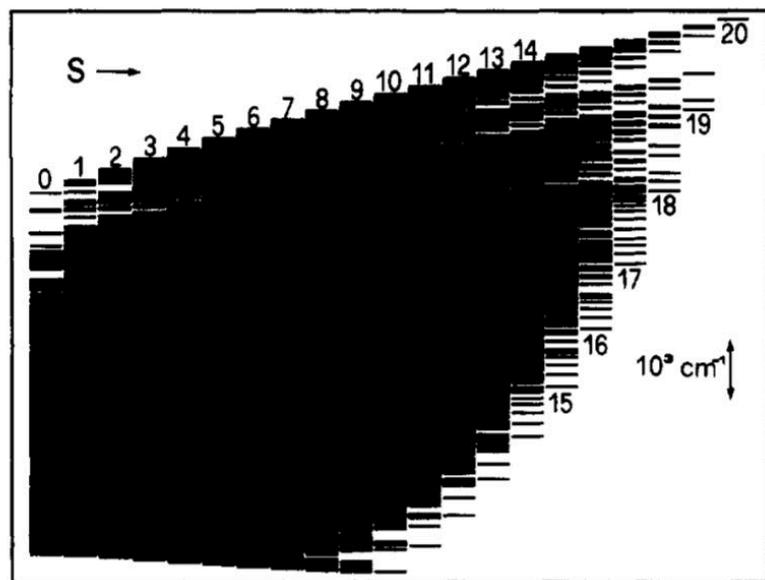
Example: Asymmetric  $[\text{Mn}_3\text{Ca}_2]$  Mukherjee et al., PNAS 109, 2257 (2012).

- $2\text{-}J$  model: 64 states, 12 unique energies.



- For large molecules with many  $J$ s, fitting becomes difficult
- Fitting is more difficult for FM coupling

Real complexes:

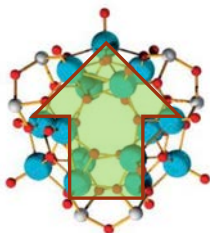


Quantum states of Fe<sub>8</sub>

- Clearly very difficult for electronic structure.
- What kind of information can we get from DFT?
  - Parameters in the HDVV Hamiltonian:  $J$  couplings and MAE

## Magnetic Anisotropy Energy

- Spin-orbit interaction (fine structure in atoms):
- For 3d elements it can be included as a perturbation.
  - Consider second-order perturbation theory with different directions for the spin of the reference state.
- For heavier elements (such as Lanthanides) perturbation theory is not a good approximation.
  - Fully self-consistent with spin-orbit: 2-components or “noncollinear” DFT.
  - Relativistic approaches: 4-components.
- The  $D$  parameter is affected by the “local” distortions. See Cirera et al., Chem. Eur. J. **15**, 4078 (2009).



Neese and Solomon, Inorg. Chem. **37**, 6568 (1998)  
Pederson and Khanna, Phys. Rev. B **59**, R693 (1999)  
van Wüllen, J. Chem. Phys. **130**, 194109 (2009)

# Molecular Magnets

Table 1. Calculated  $D$  values [ $\text{cm}^{-1}$ ] for mononuclear complexes obtained by using the PBE functional and NRLMOL code that only include the spin-orbit term.  $D$  values were also calculated with the ORCA code and included the spin-spin contributions. Experimental data obtained by EPR techniques are provided for comparison.

	$d^n$	$D_{\text{calcd(SO)}}$	$D_{\text{calcd(SO+SS)}}$	$D_{\text{exptl}}$	Ref.
[Mn(dbm) <sub>3</sub> ]	Mn <sup>III</sup> d <sup>4</sup>	-2.43	-3.49	-4.57	[43]
[Mn(acac) <sub>3</sub> ]	Mn <sup>III</sup> d <sup>4</sup>	-2.36	-3.28	-4.52 <sup>[a]</sup>	[12]
[MnF <sub>3</sub> (terpy)]	Mn <sup>III</sup> d <sup>4</sup>	-1.84	-2.65	-3.82 <sup>[a]</sup>	[44]
[MnF <sub>3</sub> (bpea)]	Mn <sup>III</sup> d <sup>4</sup>	-1.84	-2.63	-3.67 <sup>[a]</sup>	[44]
[Mn(N <sub>3</sub> ) <sub>3</sub> (terpy)]	Mn <sup>III</sup> d <sup>4</sup>	-1.65	-2.39	-3.29 <sup>[a]</sup>	[45]
[MnCl(Py)(TPP)]	Mn <sup>III</sup> d <sup>4</sup>	-1.28	-1.93	-3.00 <sup>[a]</sup>	[46]
[Fe(dpm) <sub>3</sub> ]	Fe <sup>III</sup> d <sup>5</sup>	-0.19	+0.26	-0.18	[47]
[Fe(mal) <sub>3</sub> ]	Fe <sup>III</sup> d <sup>5</sup>	-0.13	-0.11	±0.12	[48]
[Fe(acac) <sub>3</sub> ]	Fe <sup>III</sup> d <sup>5</sup>	+0.29	-0.22	+0.16	[48]
[Mn(bpea)(N <sub>3</sub> ) <sub>3</sub> ]	Mn <sup>III</sup> d <sup>4</sup>	+1.41	+2.07	+3.50 <sup>[a]</sup>	[44]
[Fe(SPh) <sub>4</sub> ] <sup>2-</sup>	Fe <sup>II</sup> d <sup>6</sup>	+2.18	+3.14	+5.48 <sup>[a]</sup>	[49]

[a] Values obtained from high-field EPR spectroscopy.

Table 3 Comparison of the calculated by NRLMOL and experimental magnetic anisotropy parameter  $D$  for the single molecule magnets. See theory references for computational details.

molecule	$S$	$D(\text{K})$	
		theory	experiment
Mn <sub>12</sub> O <sub>12</sub> (O <sub>2</sub> CH) <sub>16</sub> (H <sub>2</sub> O) <sub>4</sub>	10	-0.56 <sup>a</sup>	-0.56 <sup>b</sup>
[Fe <sub>8</sub> O <sub>2</sub> (OH) <sub>12</sub> (C <sub>6</sub> H <sub>15</sub> N <sub>3</sub> ) <sub>6</sub> Br <sub>6</sub> ] <sup>2+</sup>	10	-0.53 <sup>c</sup>	-0.30 <sup>d</sup>
[Mn <sub>10</sub> O <sub>4</sub> (2,2'-biphenoxide) <sub>4</sub> Br <sub>12</sub> ] <sup>4-</sup>	13	-0.06 <sup>e</sup>	-0.05 <sup>f</sup>
Co <sub>4</sub> (CH <sub>2</sub> C <sub>5</sub> H <sub>4</sub> N) <sub>4</sub> (CH <sub>3</sub> OH) <sub>4</sub> AcL <sub>4</sub>	6	-0.64 <sup>g</sup>	-0.7 - -0.9 <sup>h</sup>
Fe <sub>4</sub> (OCH <sub>2</sub> ) <sub>6</sub> (C <sub>4</sub> H <sub>9</sub> ON) <sub>6</sub>	5	-0.56 <sup>i</sup>	-0.57 <sup>j</sup>
Cr[N(Si(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub> ] <sub>3</sub>	3/2	-1.15 <sup>i</sup>	-2.66 <sup>k</sup>
Mn <sub>9</sub> O <sub>34</sub> C <sub>32</sub> N <sub>3</sub> H <sub>35</sub>	17/2	-0.33 <sup>m</sup>	-0.32 <sup>l</sup>
Ni <sub>4</sub> O <sub>16</sub> C <sub>16</sub> H <sub>40</sub>	4	-0.385	-0.40 <sup>m</sup>
Mn <sub>4</sub> O <sub>3</sub> Cl <sub>4</sub> (O <sub>2</sub> CCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub> (NC <sub>5</sub> H <sub>5</sub> ) <sub>3</sub>	9/2	-0.58 <sup>n</sup>	-0.72 <sup>o</sup>

# Magnetic Properties

## Magnetic Exchange Couplings

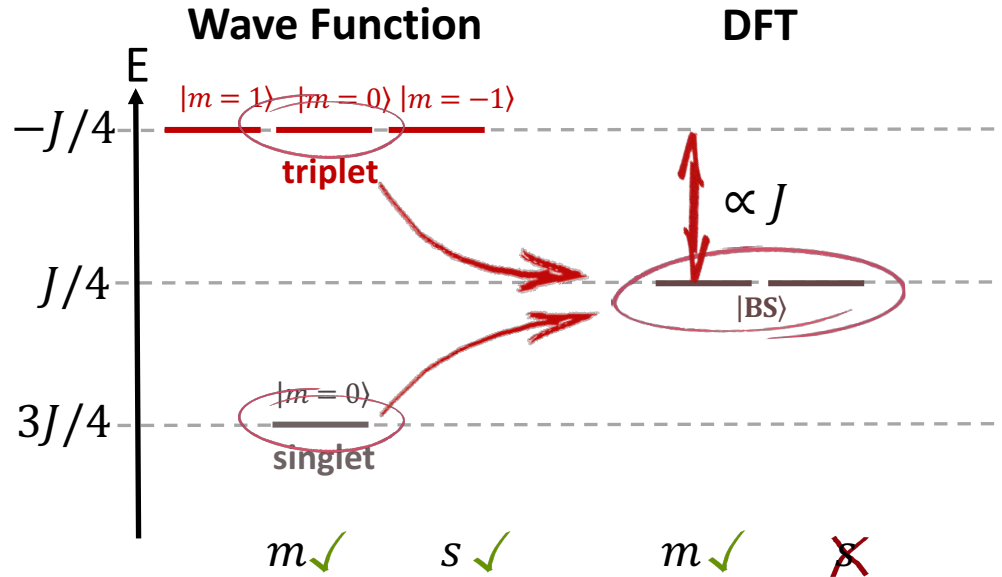
- Energy differences methods: The different states of the HDVV Hamiltonian are “mapped” into DFT solutions



Spin-1/2 dimer

$$\hat{H}_{HDVV} = -J \sum_{\langle ij \rangle} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$$

AFM ( $J < 0$ )



- It provides a **simple** scheme to extract J couplings
- It can be easily extended to other cases
- **Widely used** in the literature

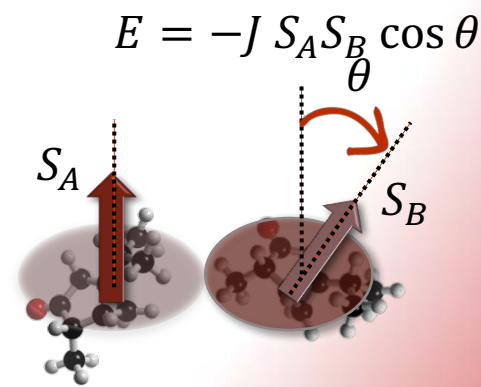
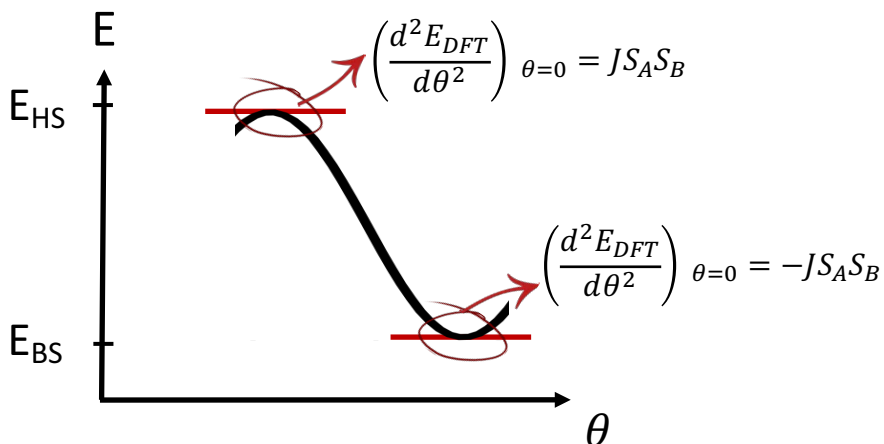
# Magnetic Properties

## Problems with the energy differences method

- Multicenter TM complexes can have several target states and convergence to these can be difficult.
- Cannot be done as a “black-box”.

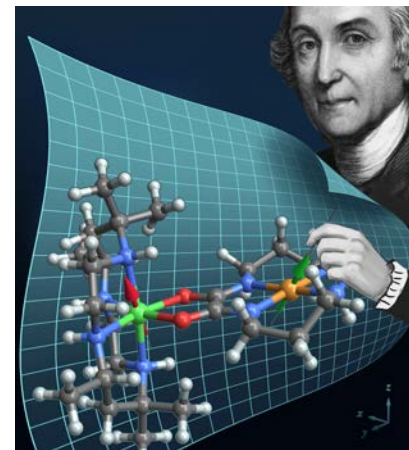
Can we extract  $J$  couplings in a more efficient way ?

Consider local spin rotations



# Magnetic Properties

- Implemented as a **constraint** using Lagrange multipliers
- Uses **analytical** linear response
- All couplings can be extracted from a **single reference** state
- Close to energy differences for “Heisenberg” like systems
- Works for multinuclear and heteronuclear complexes
- Needs noncollinear kernel



$$W = E^{DFT} - \lambda_{AB} (Q_{AB} - \theta_{AB}) \quad \text{where } \lambda_{AB} \text{ represents is a Lagrange multiplier}$$

$$\delta W = 0$$

...but we are interested in  $\frac{\partial^2 E}{\partial \theta_{AB}^2}$   $\longrightarrow$   $\mathcal{H}_\theta$  Hessian matrix

Since it can be shown that  $\mathcal{H}_\theta = \mathcal{H}_\lambda^{-1}$

All we need is  $\frac{\partial^2 E}{\partial \lambda_{AB} \partial \lambda_{CD}}$  that can be calculated using **perturbation theory**.

Other approaches:

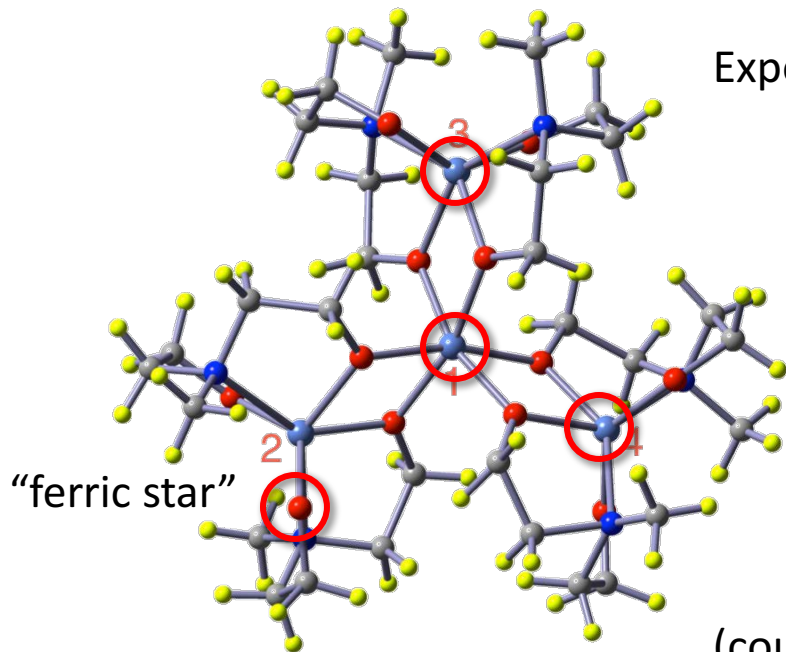
- Liechtenstein et al., J. Phys. F **14**, L125 (1984)
- Bruno, PRL **90**, 087205 (2003)
- Zhekova et al., JCTC **7**, 1858 (2011)



# Magnetic Properties

Experimental: Saalfrank et al., Dalton Trans. 2006, 2865

4-Fe(III) centers ( $S=5/2$  each)



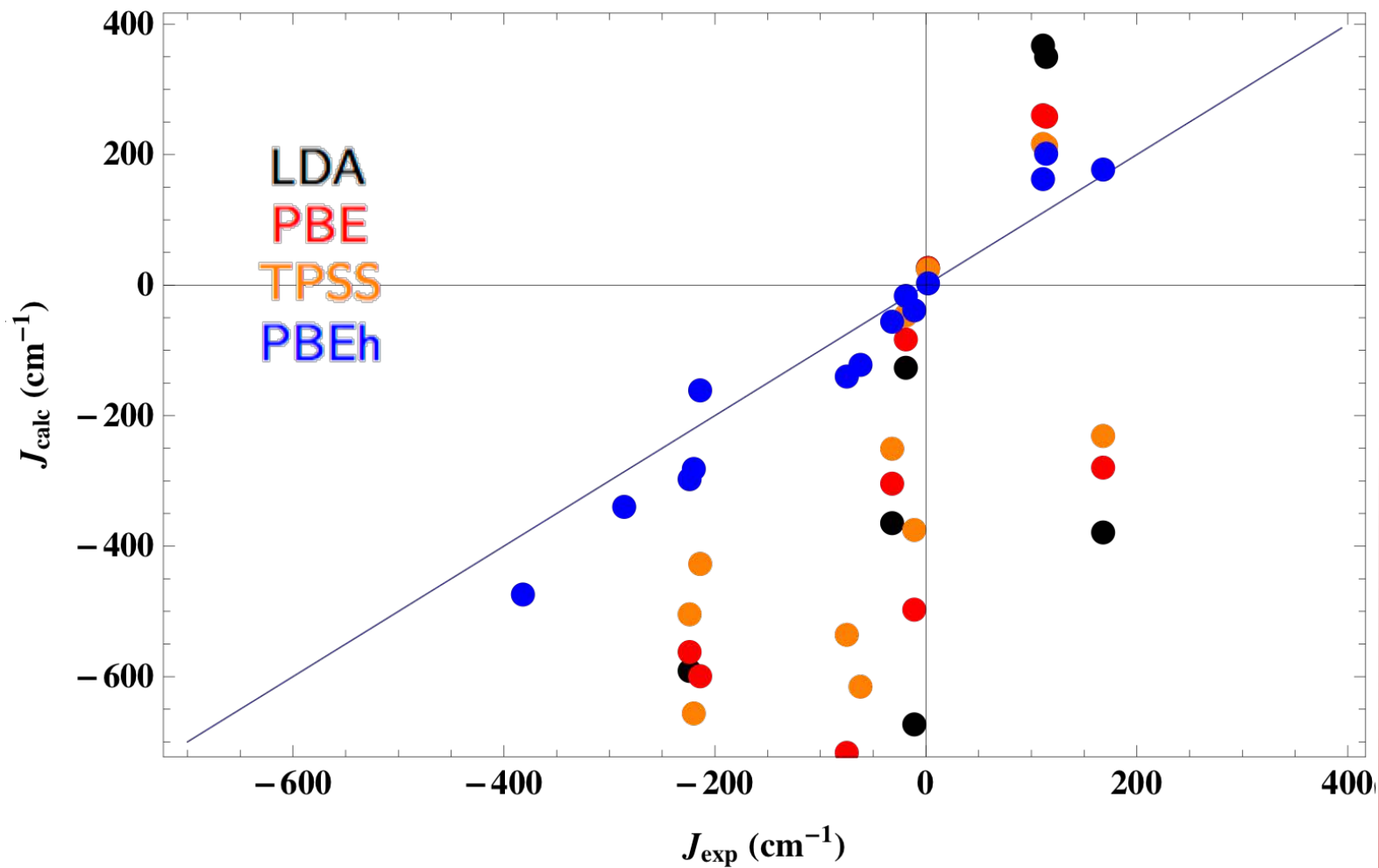
(couplings in  $\text{cm}^{-1}$ )

	LSDA	+15%HFx	+30%HFx	Exp.
$J_{12}$	-102	-41	-21	-21
$J_{13}$	-96	-41	-21	-21
$J_{14}$	-103	-44	-22	-21
$J_{23}$	-2	-1	$\sim 0$	small
$J_{24}$	-3	-2	$\sim 0$	small
$J_{34}$	-3	0	$\sim 0$	small



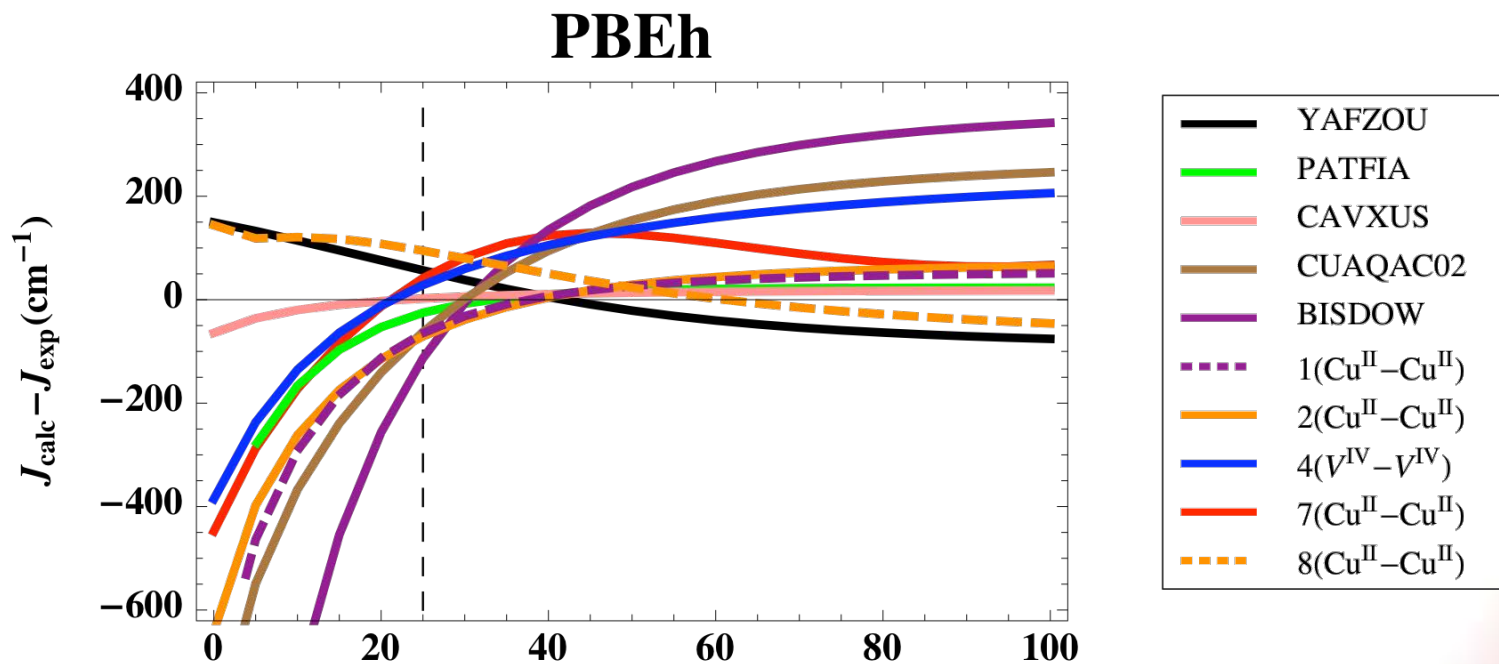
# Magnetic properties

$J$  couplings: Performance of DFT



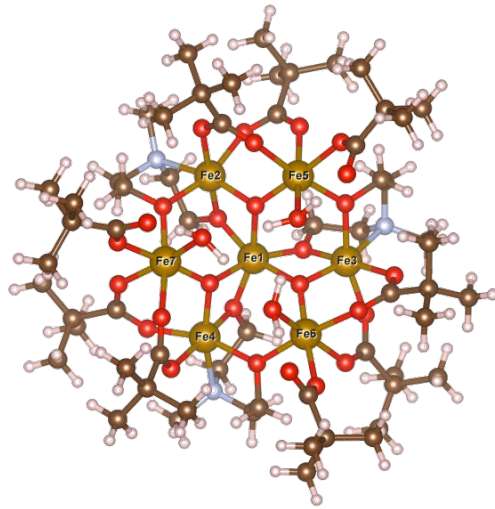
# Magnetic properties

Assessment in a set of 16 bimetallic TM complexes with accurate experimental reference values



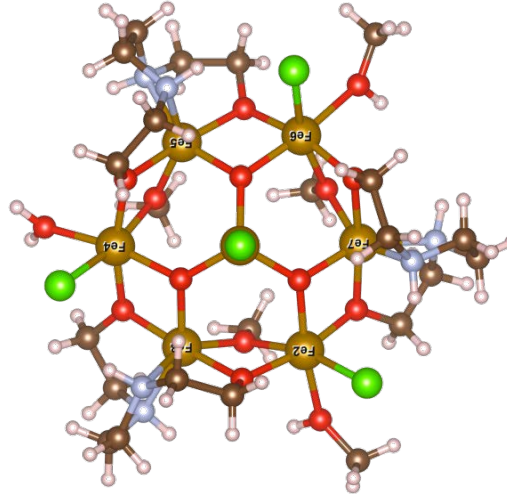
# Fe<sub>7</sub> disks

Fe(III)<sub>7</sub> disks: Mukherjee et al., Inorg. Chem. 50, 3849 (2011)



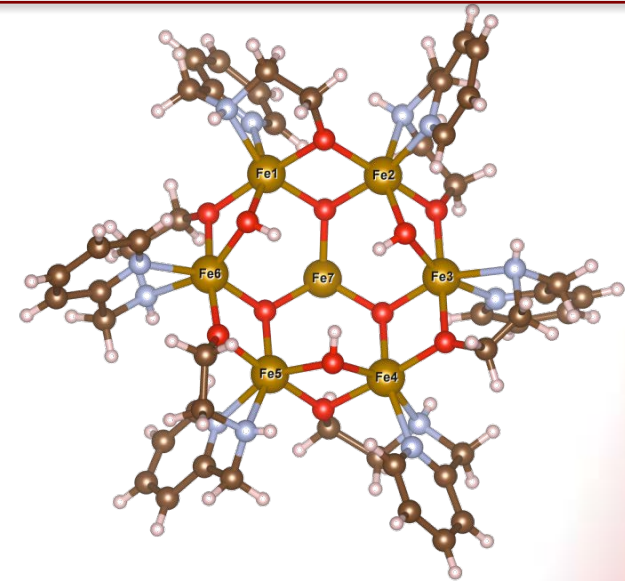
Complex 1

S=5/2 ground state



Complex 2

High-spin ground state



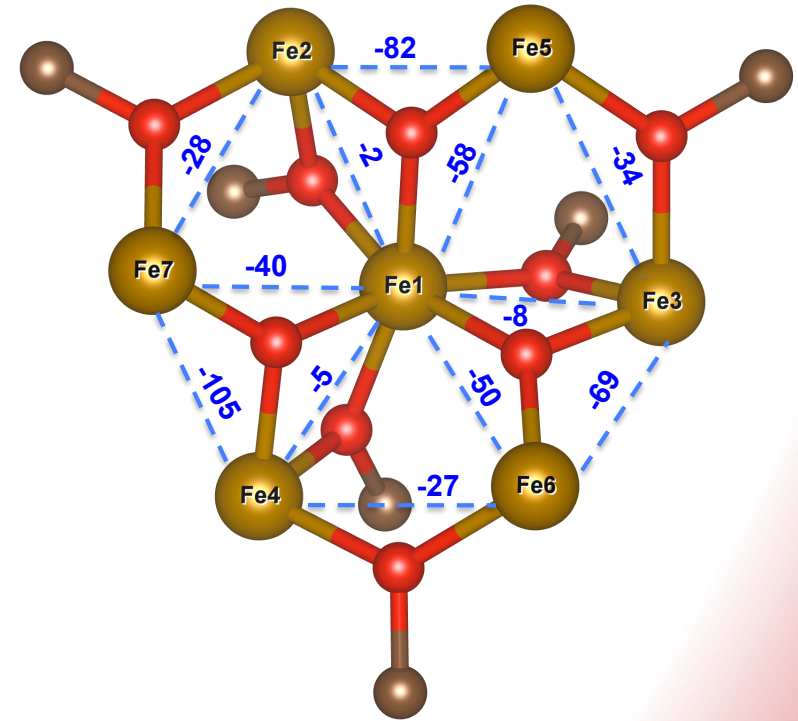
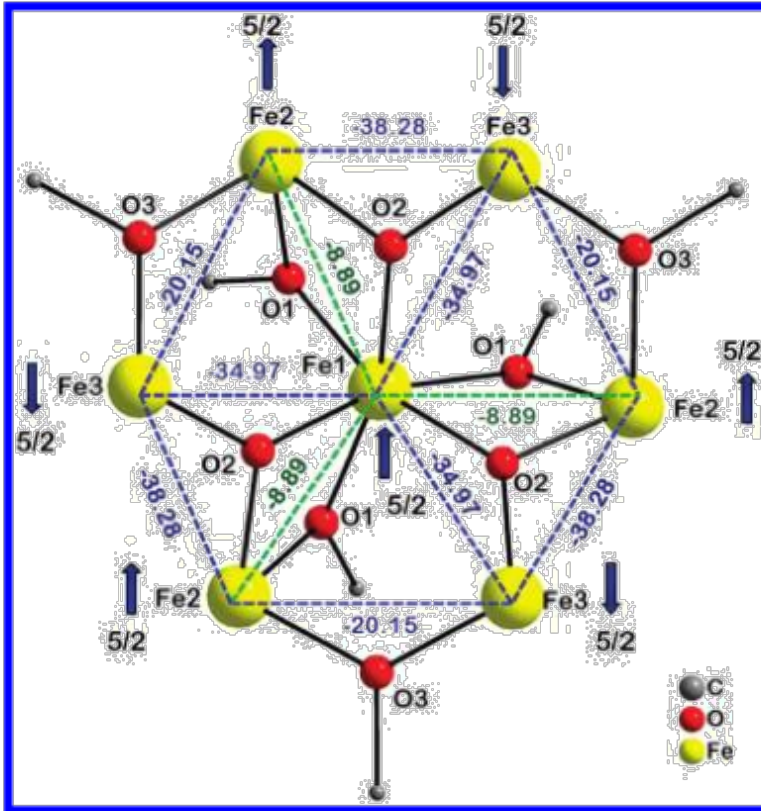
Complex 3

- Fe(III) typically exhibits antiferromagnetic coupling
- Too many Fe centers to fit susceptibility data:  
Couplings are very difficult/impossible to determine experimentally

# Fe<sub>7</sub> disks

## Complex 1

Couplings in cm<sup>-1</sup>



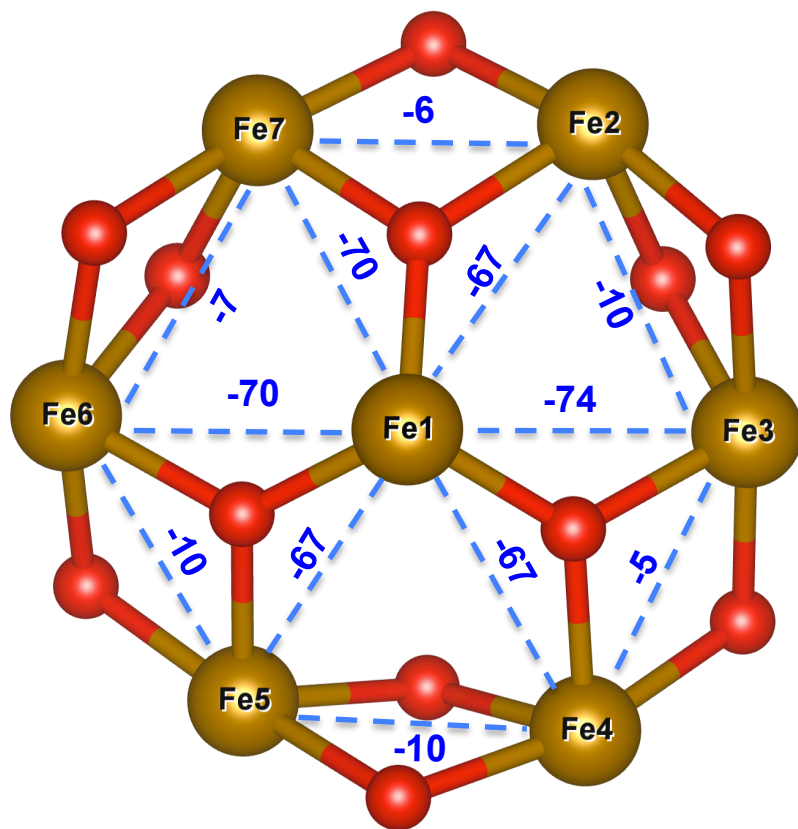
DFT

From magneto-structural data [Mukherjee et al., Inorg. Chem. **50**, 3849 (2011)]

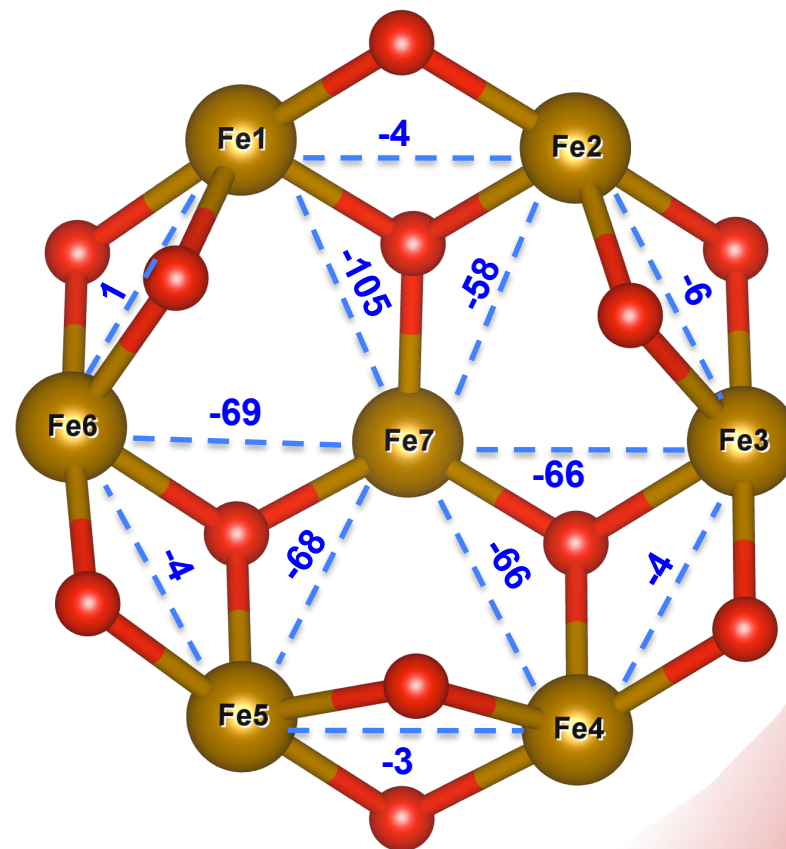
Alternated strong and weak couplings

# Fe<sub>7</sub> disks

Couplings in cm<sup>-1</sup>



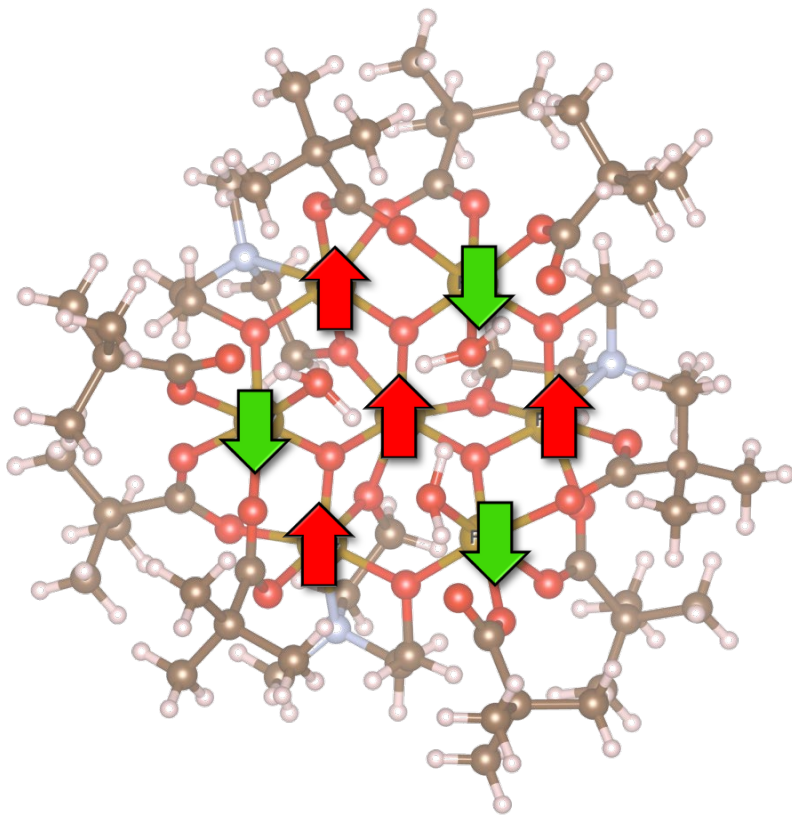
Complex 2



Complex 3

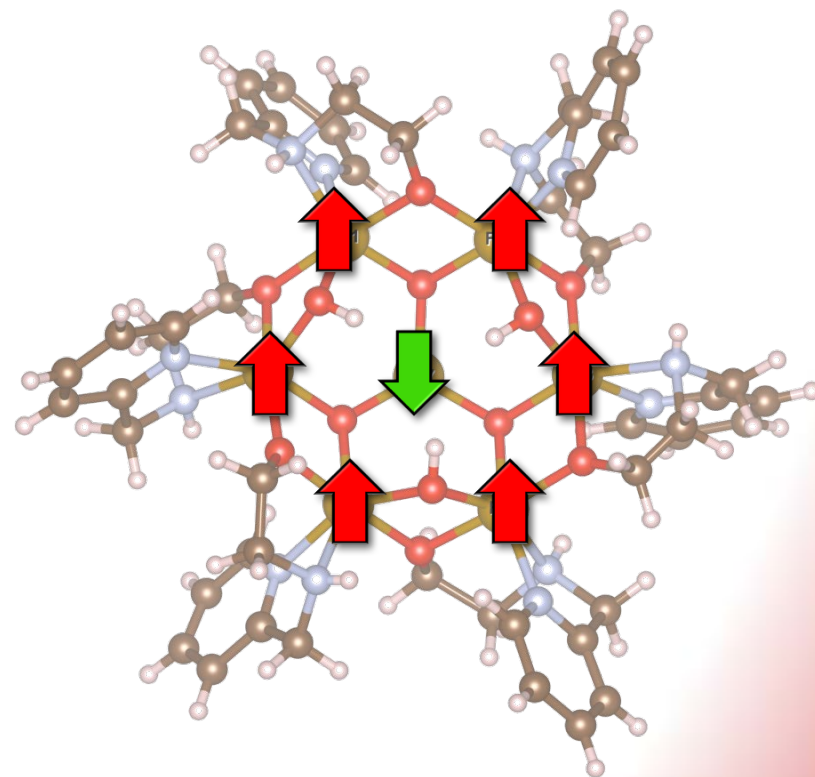
Strong AF "radial"  
couplings

# Fe<sub>7</sub> disks



Complex 1  
 $S=5/2$

Alternated coupling dominates

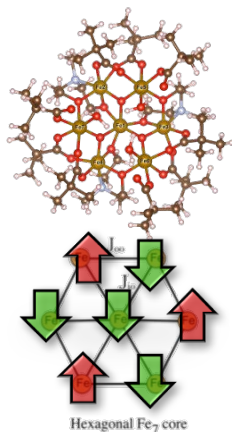


Complex 3  
high-spin

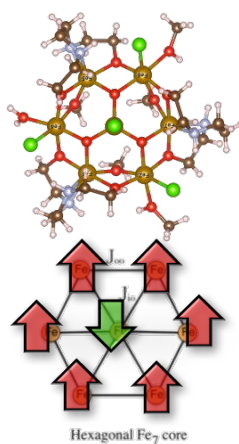
Radial coupling dominates



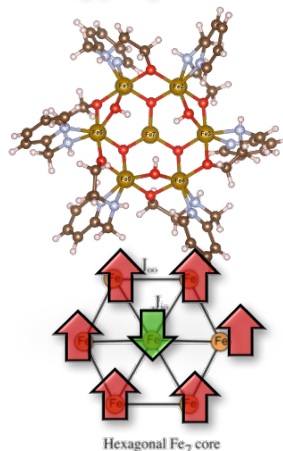
# Fe<sub>7</sub> disks



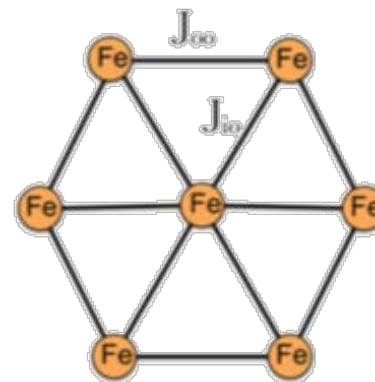
**(1) Low spin**  
( $S=5/2$ )



**(2) High spin**  
( $S=15/2$ )

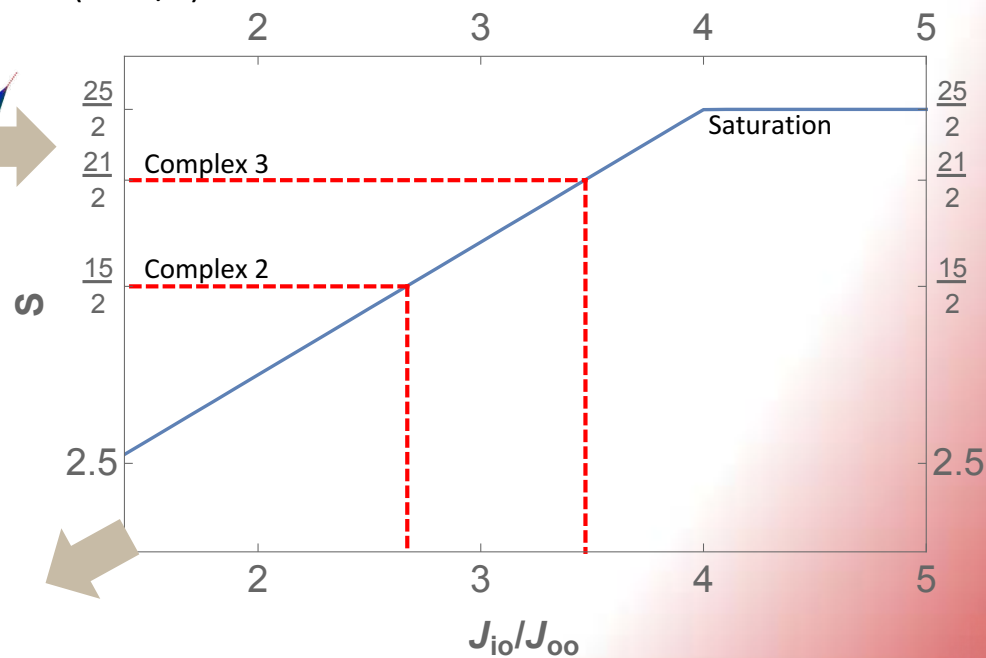
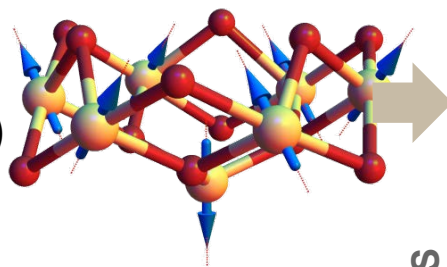


**(3) High spin**  
( $S=21/2$ )



Hexagonal Fe<sub>7</sub> core

From a classical spin model  
(poor man's approximation)



Complex	$J_{io}/J_{oo}$		
	DFT	Magneto-structural	Experimental (spin model)
2	8.5	4.0	2.7
3	10.0	3.6	3.5

# Summary

- DFT is a **powerful** tool for materials science, chemistry, and physics.
- It provides **fast**, sometimes accurate **computational** results.
- This is also the case for **magnetic** properties, although **more work** needs to be done.

## Acknowledgements



Questions? Comments?



