Magnetic Exchange Couplings in Transition Metal Complexes from Density Functional Theory

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Outline

Road map

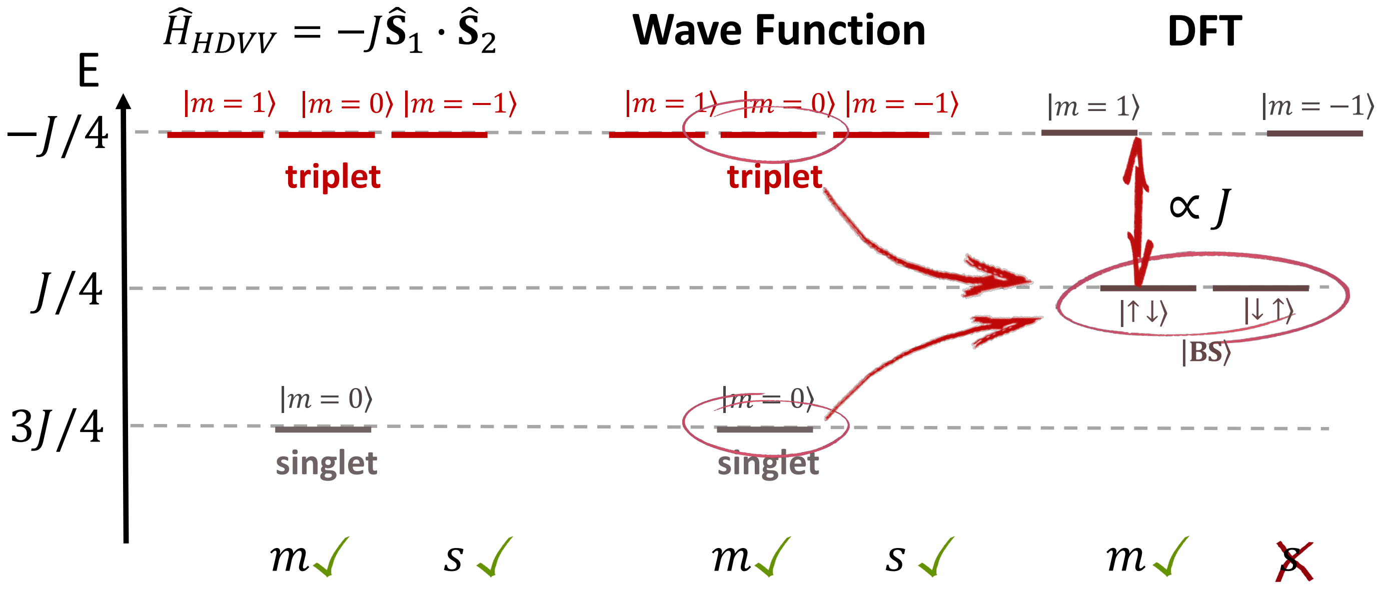
- Performance of DFT
- Magnetic Exchange Couplings from Local Rotations
- Fe_7 disks
- Spin Dynamics from DFT

J Couplings

Magnetic Exchange Couplings

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

Spin-1/2 dimer AFM ($J < 0$)

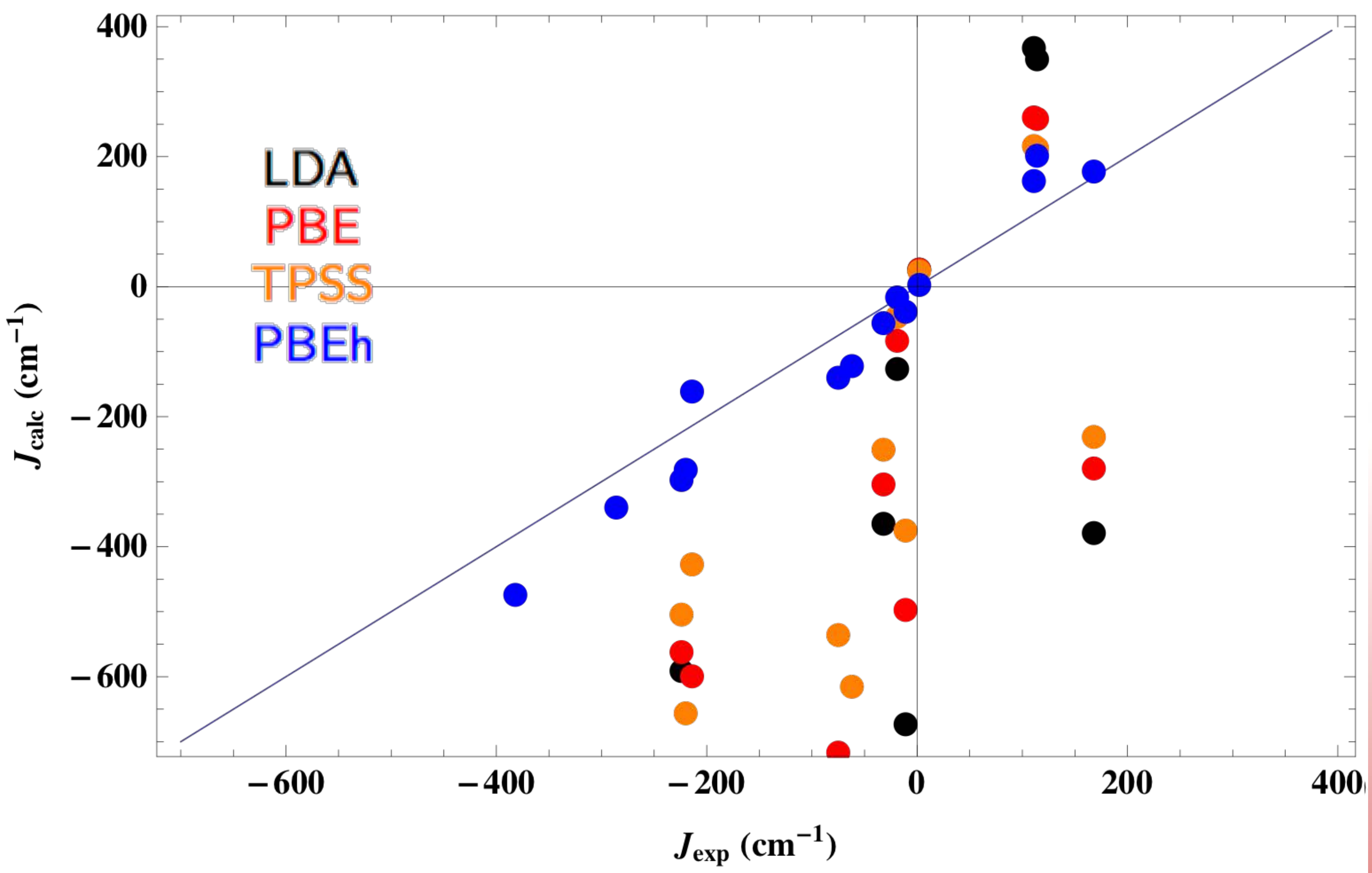


$$\hat{H}_{HDVV} = -J\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$$

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

Noodleman, JCP 74, 5737 (1981)

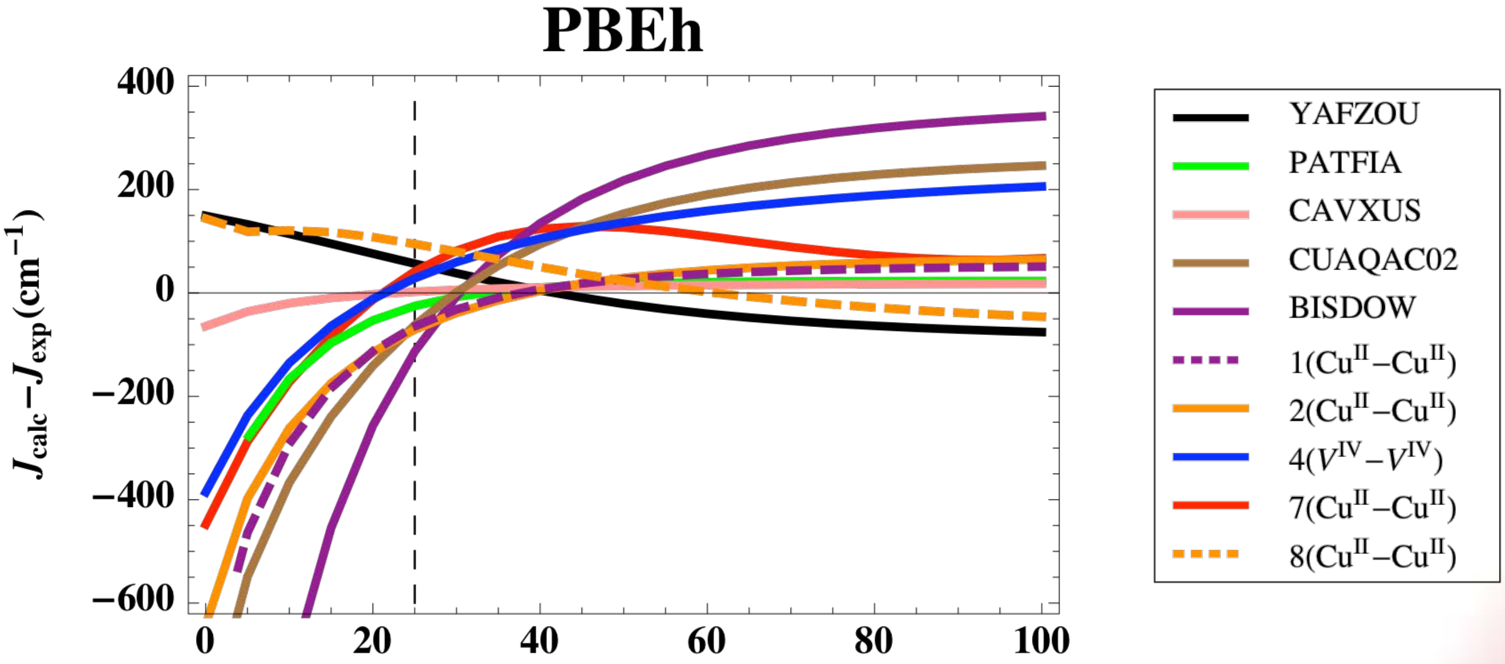
J couplings: Performance of DFT



Phillips and Peralta, J. Chem. Phys. 134, 034108, (**2011**)

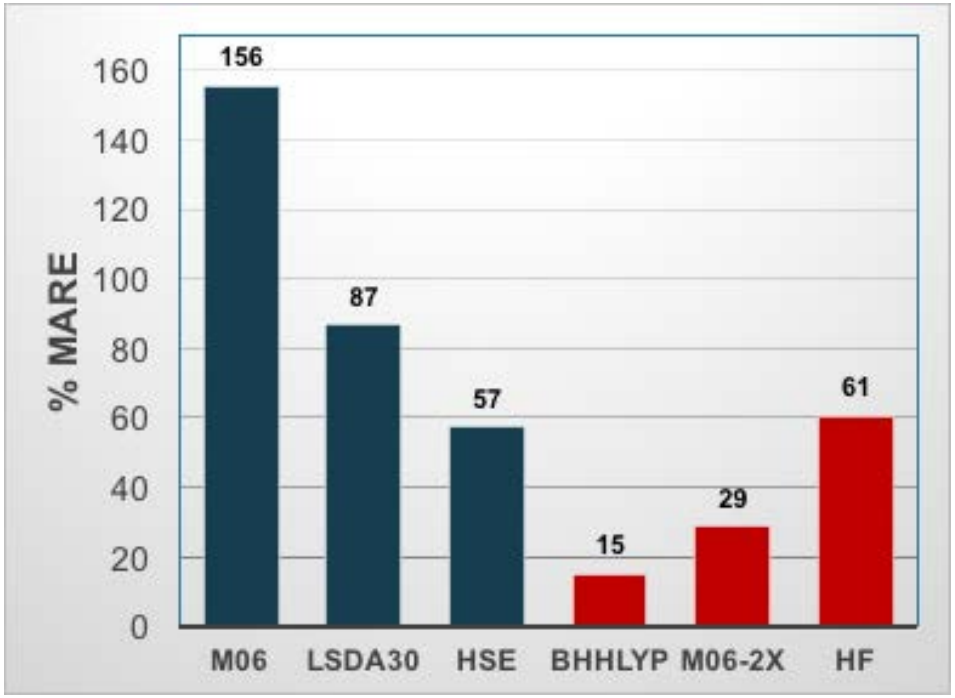
J couplings: Performance of DFT

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



J couplings: Performance of DFT

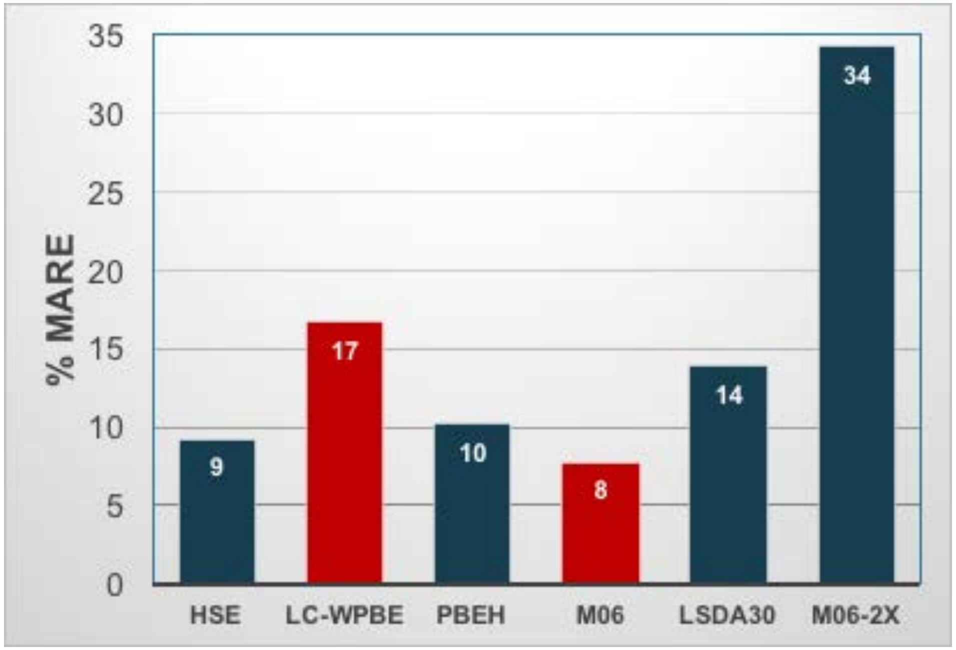
- **Cu-Cu couplings**
  - 7 triply bridged Cu-Cu complexes.
  - Exp. values from 73 to104 cm^{-1}.



Wannarit et al., PCCP 6, 1966 (2013)
Phillips and Peralta, JPCA 118, 5841 (2014)

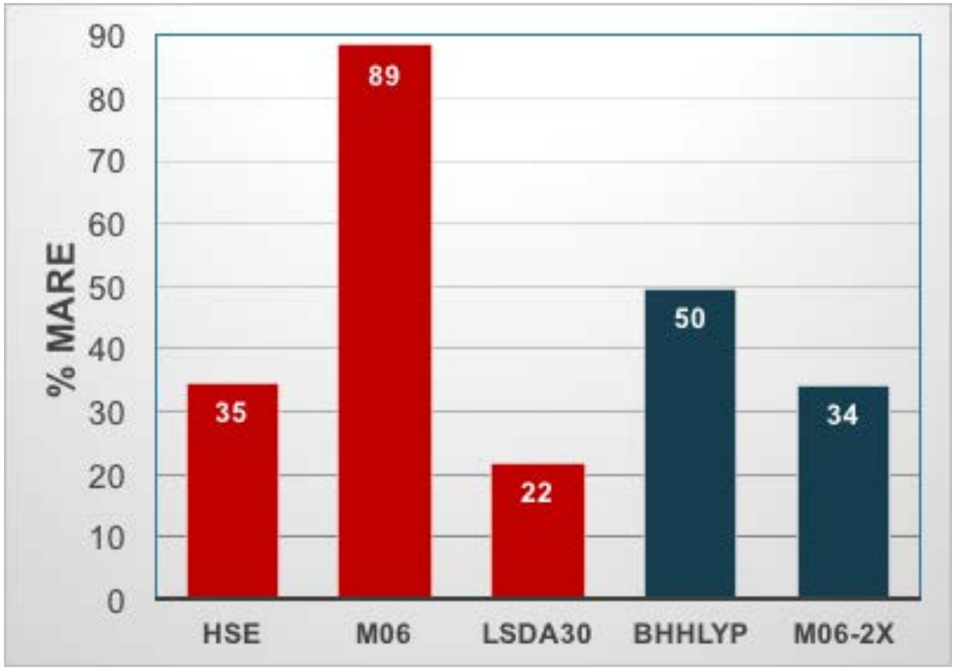
J couplings: Performance of DFT

- **Fe-Fe couplings**
  - 7 oxo-bridged Fe(III)-Fe(III) complexes.
  - Exp. values from -132 to -78 cm^{-1}.



J couplings: Performance of DFT

- **Heterodinuclear complexes**
  - 6 heterodinuclear complexes (Ni, Cu, V)
  - Exp. values from -117 to +118 cm^{-1}.



Joshi et al., JCTC 12, 1728 (2016)

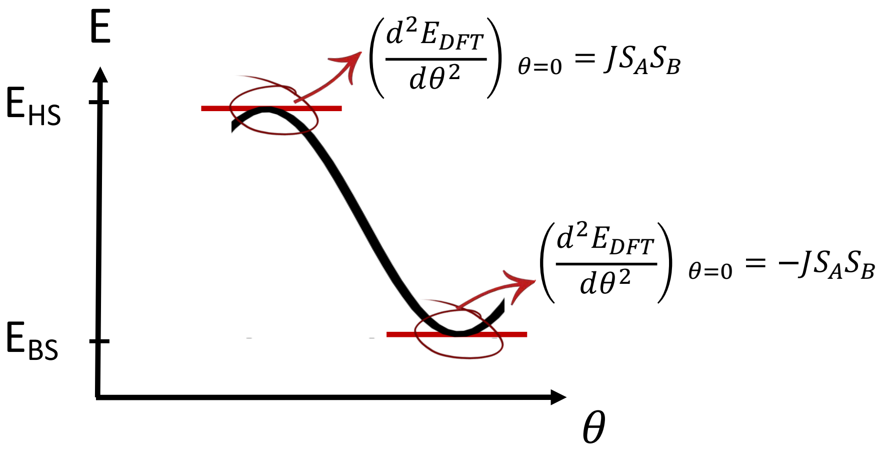
J couplings: Local Spin rotations

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".

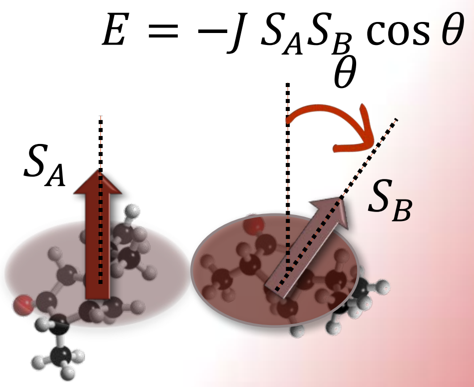
Can we extract *J* couplings in a more efficient way ?

Consider local spin rotations



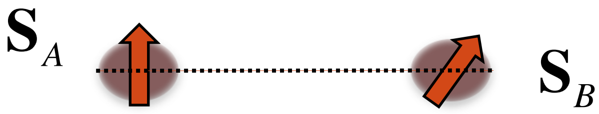
$$\left(\frac{d^2E_{DFT}}{d\theta^2}\right)_{\theta=0} = JS_AS_B$$

$$\left(\frac{d^2E_{DFT}}{d\theta^2}\right)_{\theta=0} = -JS_AS_B$$



$$E = -J\,S_AS_B\cos\theta$$

J couplings: Local Spin rotations



In order to **"twist"** by a certain angle **local magnetic moments**, we define

$$\mathbf{Q}_{AB} = (\mathbf{S}_A \times \mathbf{S}_B) / S_A S_B$$

where $\mathbf{S}_X$ is the total magnetization vector of atom X.

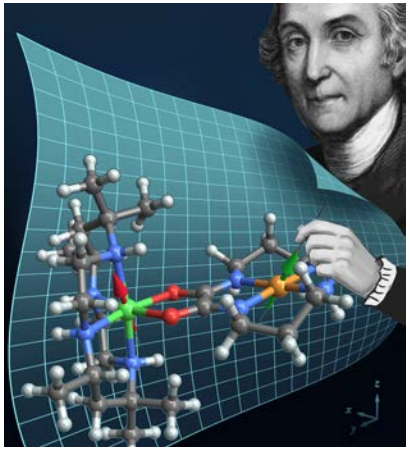
$$\mathbf{S}_X = \left\langle \hat{\mathbf{S}} \right\rangle_X$$

and **minimize** the electronic energy with the constraint

$$\mathbf{Q}_{AB} = \theta_{AB} \hat{\mathbf{y}} \qquad \text{(for small } \theta_{AB}\text{)}$$

J couplings: Local Spin rotations

- 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



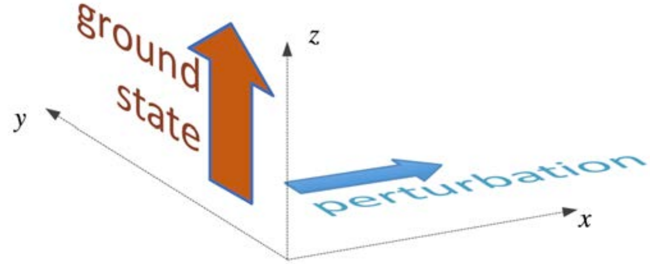
$W = E^{DFT} - \lambda_{AB}(Q_{AB} - \theta_{AB})$ where λ_{AB} represents is a Lagrange multiplier

$$\delta W = 0$$

…but we are interested in $\dfrac{\partial^2 E}{\partial \theta_{AB}^2}$ → $\mathbb{H}_\theta$ Hessian matrix

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

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

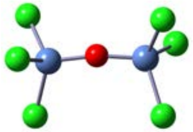


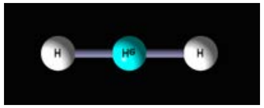
Other approaches:

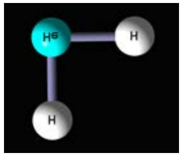
- Liechtenstein et al., J. Phys. F **14,** L125 (1984
- Bruno, PRL **90**, 087205 (2003)
- Zhekova et al., JCTC **7**, 1858 (2011)

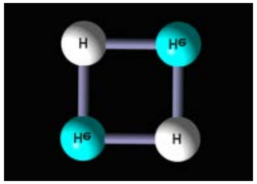
J couplings: Local Spin rotations

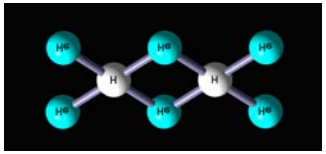
Proof-of-concept









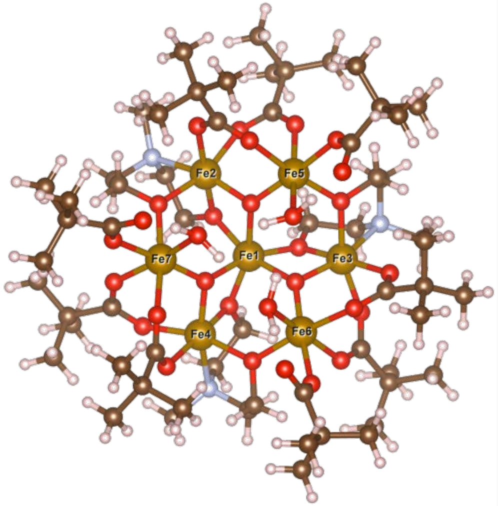


	J_{SP} (cm^{-1}) energy diff.	J_{CP} (cm^{-1}) high spin	J_{CP} (cm^{-1}) broken symm.
$[Cu_2Cl_6]^{2-}$	46	46	46
$[Fe_2OCl_6]^{2-}$	-64	-65	…
H-He-H (linear)	-3961	-4066	-3860
H-He-H (bent)	835	847	832
H-He_2-H (square)	-4784	-4843	-4723
He_2-H-He_2-H-He_2	-401	-403	-398
H-Ne-H (linear)	-603	-603	-602

Fe_7 disks

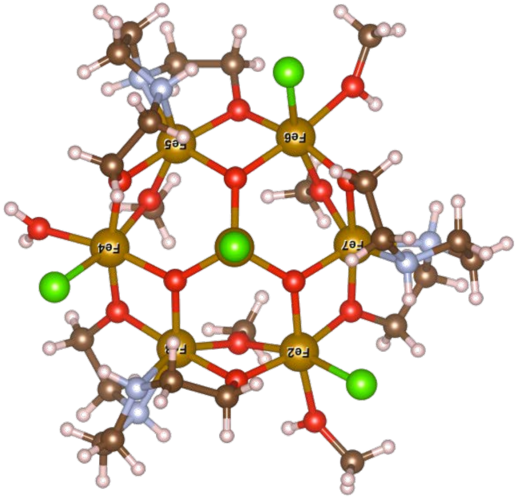
Fe_7 disks

Fe(III)$_7$ disks: Mukherjee et al., Inorg. Chem. 50, 3849 (2011)



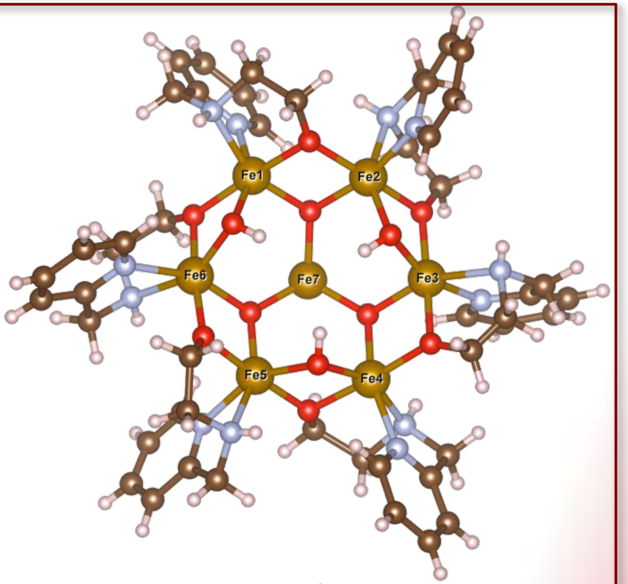
Complex 1

S=5/2



Complex 2

S=15/2



Complex 3

S=21/2

Low-spin ground state

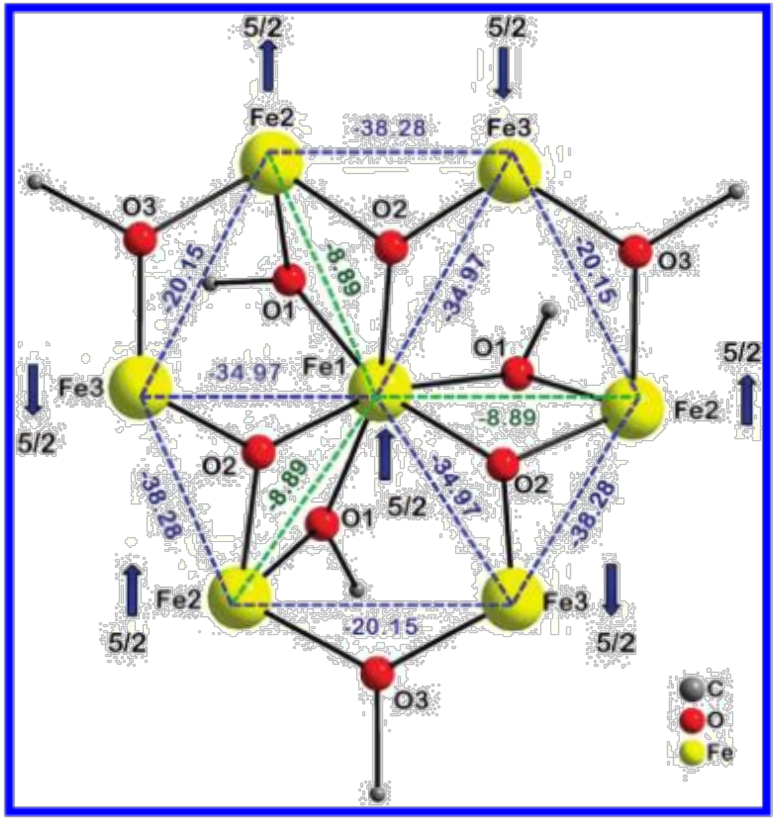
High-spin ground state

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

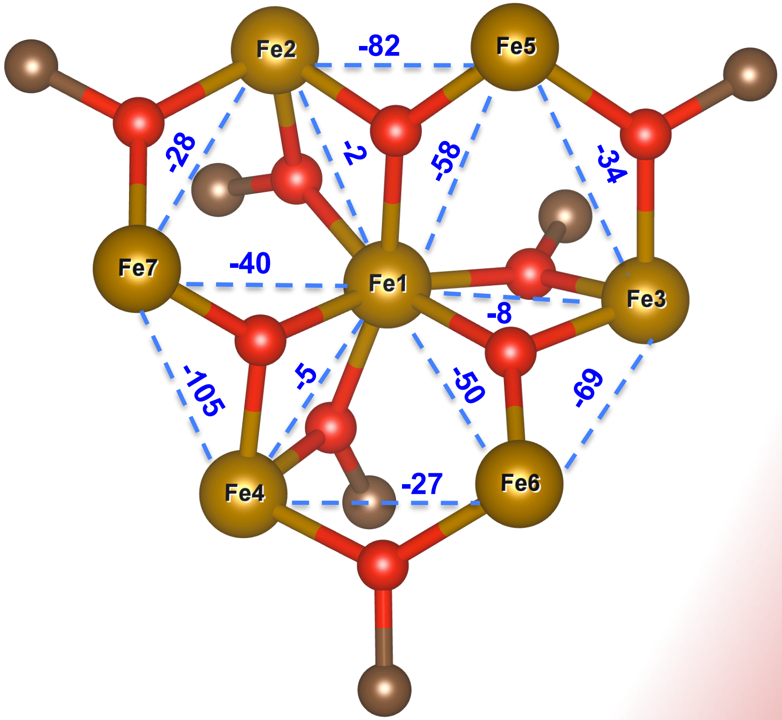
Fe_7 disks

Complex 1

Couplings in cm^{-1}



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

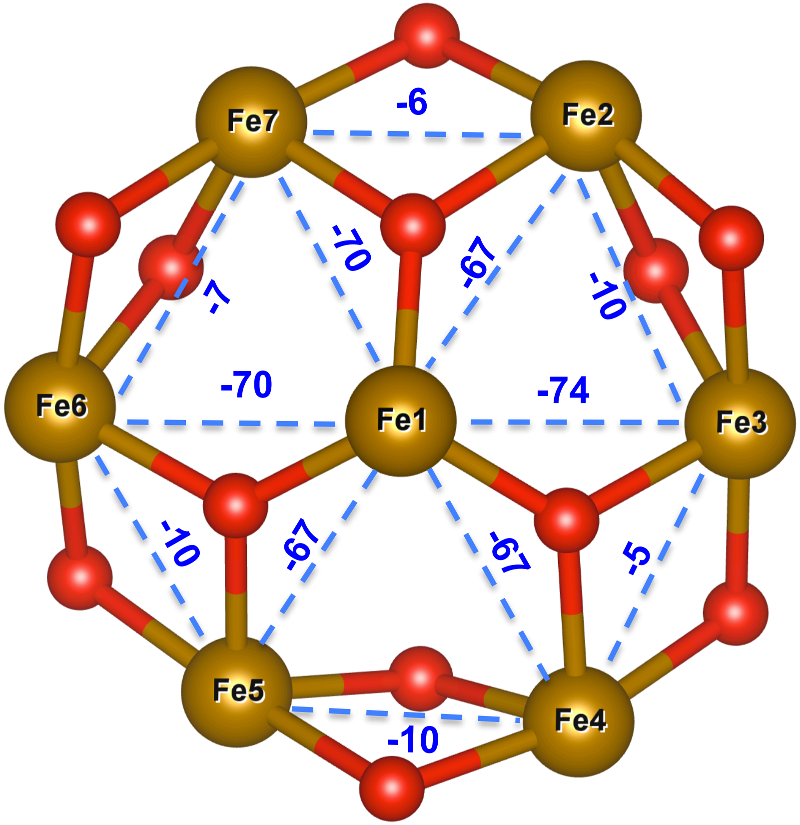


DFT

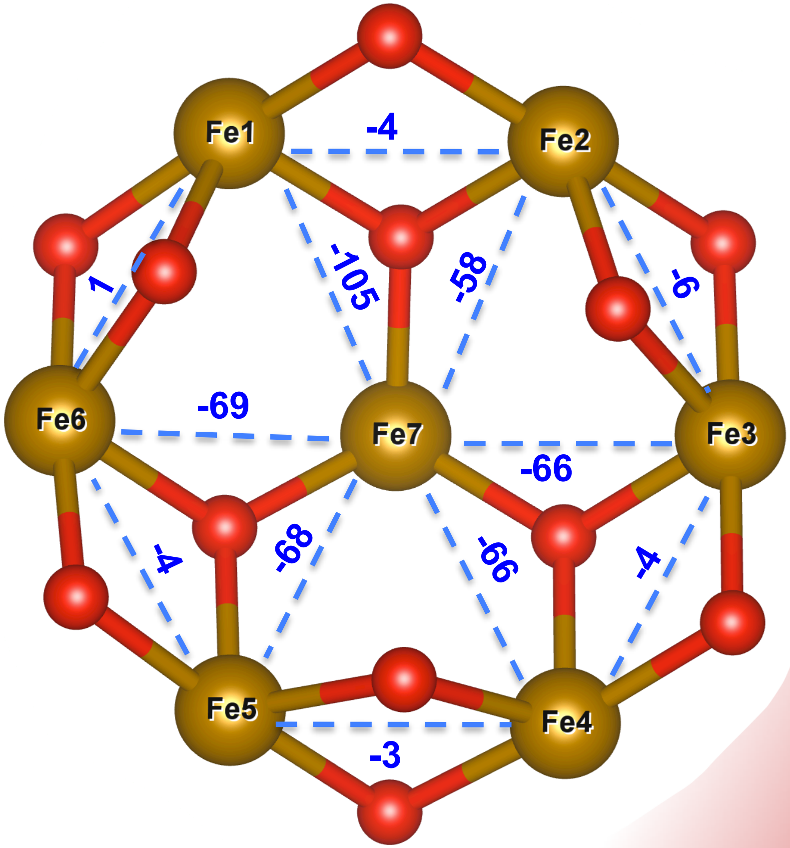
Alternated strong and weak couplings

Fe_7 disks

Couplings in cm^{-1}



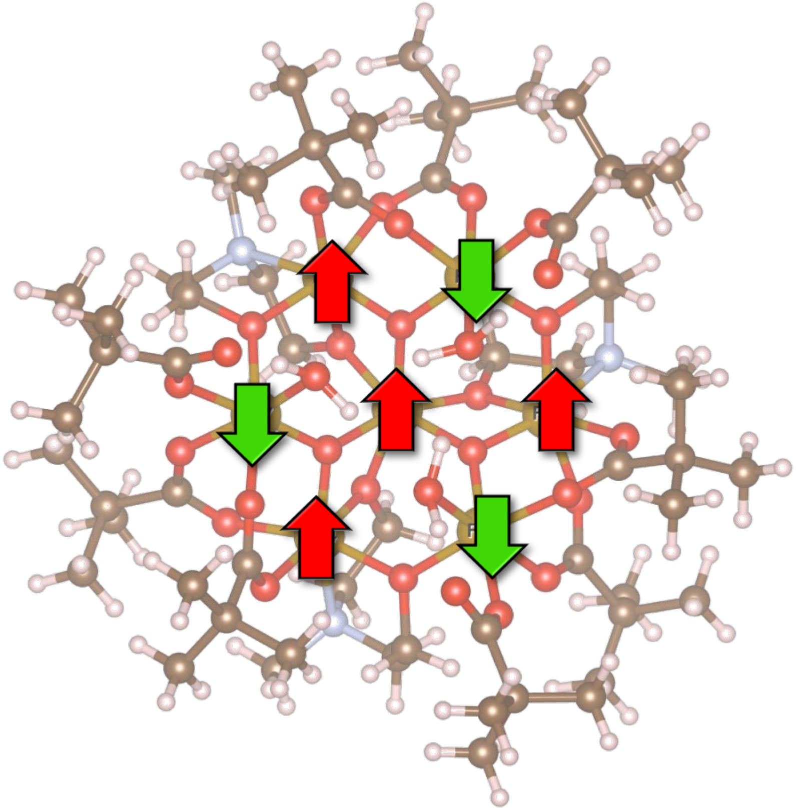
Complex 2



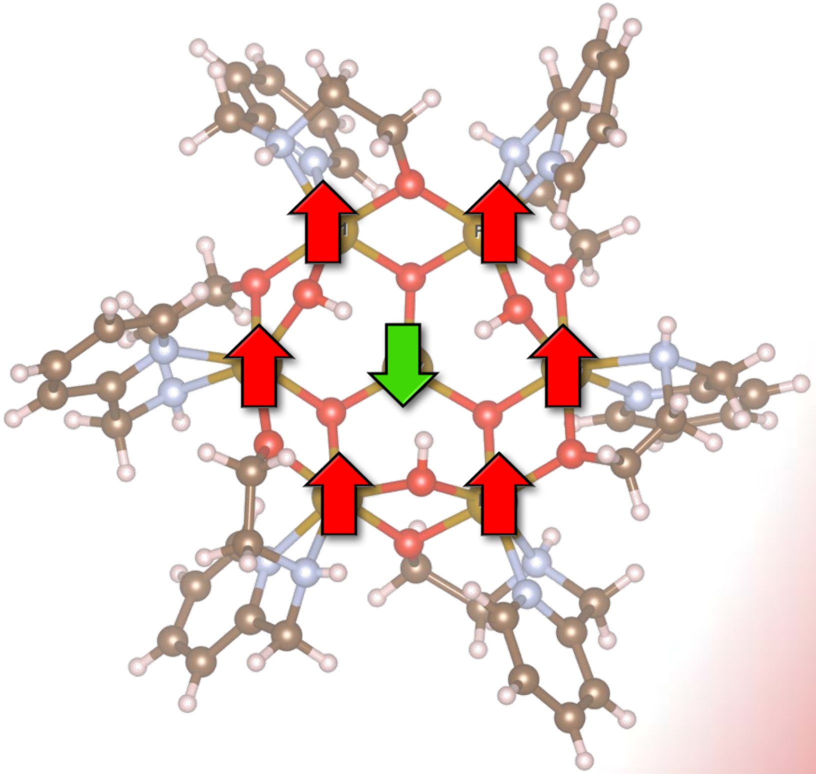
Complex 3

Strong AF “radial” couplings

Fe$_7$ disks



Complex 1
S=5/2

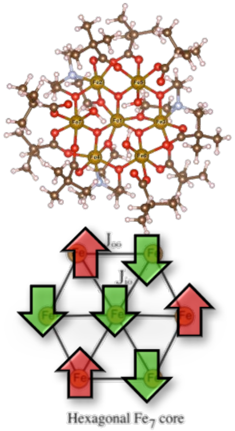


Complex 3
high-spin

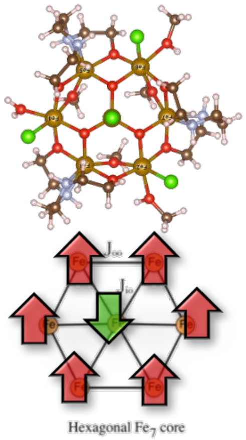
Alternated coupling dominates

Radial coupling dominates

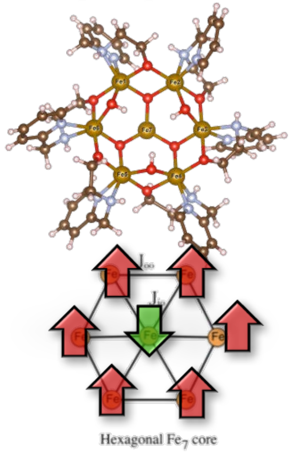
Fe$_7$ disks



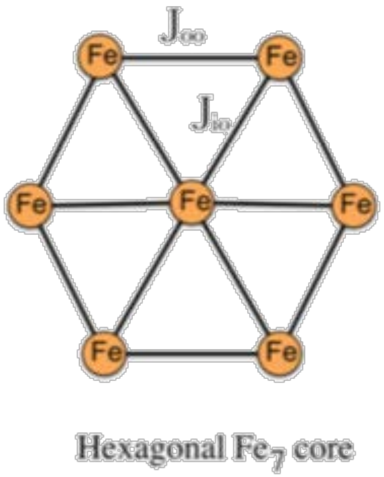
(1) Low spin
(S=5/2)



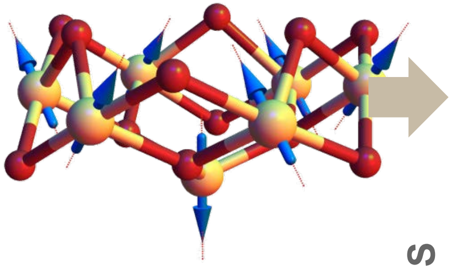
(2) High spin
(S=15/2)

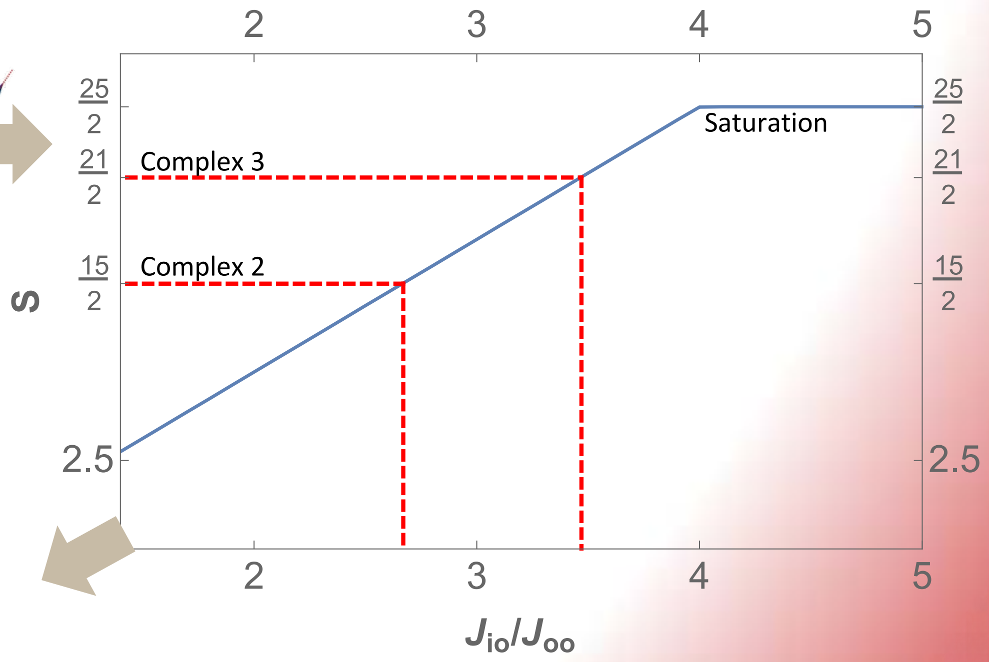


(3) High spin
(S=21/2)



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

TD-DFT

TD-DFT

- Liouville-von Neumann equation

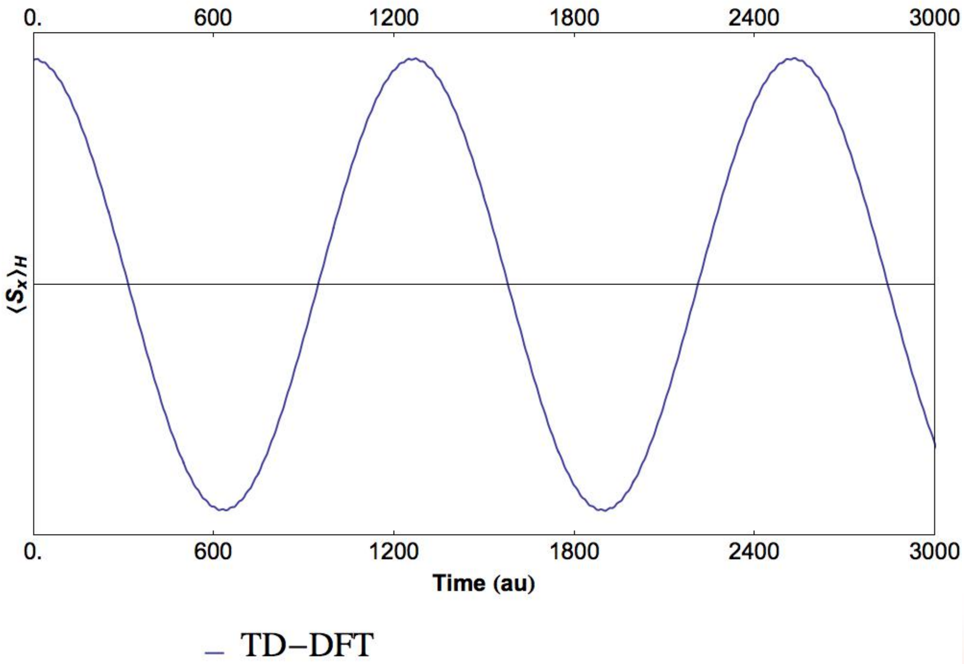
$$\dot{p} = -i\left[H_{KS}, p\right] \qquad p = n + \boldsymbol{\sigma}.\mathbf{m}$$

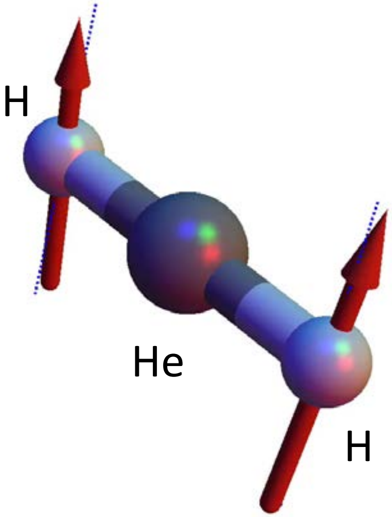
- Propagates the **charge** density and **spin** density vector simultaneously
- Propagation in the AO basis
- Integrator: Second-order Magnus expansion
- Exponential: Scaling and squaring
- Non-collinear V_{XC} in H_{KS}
- Implemented in an in-house version of Gaussian
- How to initiate dynamics: Drive the system off equilibrium

Peralta, Hod, Scuseria, JCTC 11, 3661 (2015).

TD-DFT

- Propagation step: 0.5 au = 0.012 fs
- PBE functional, 6-31G** basis
- Dynamics started from an off-equilibrium noncollinear spin configuration
- At each step $<\mathbf{S}>_A$ is recorded



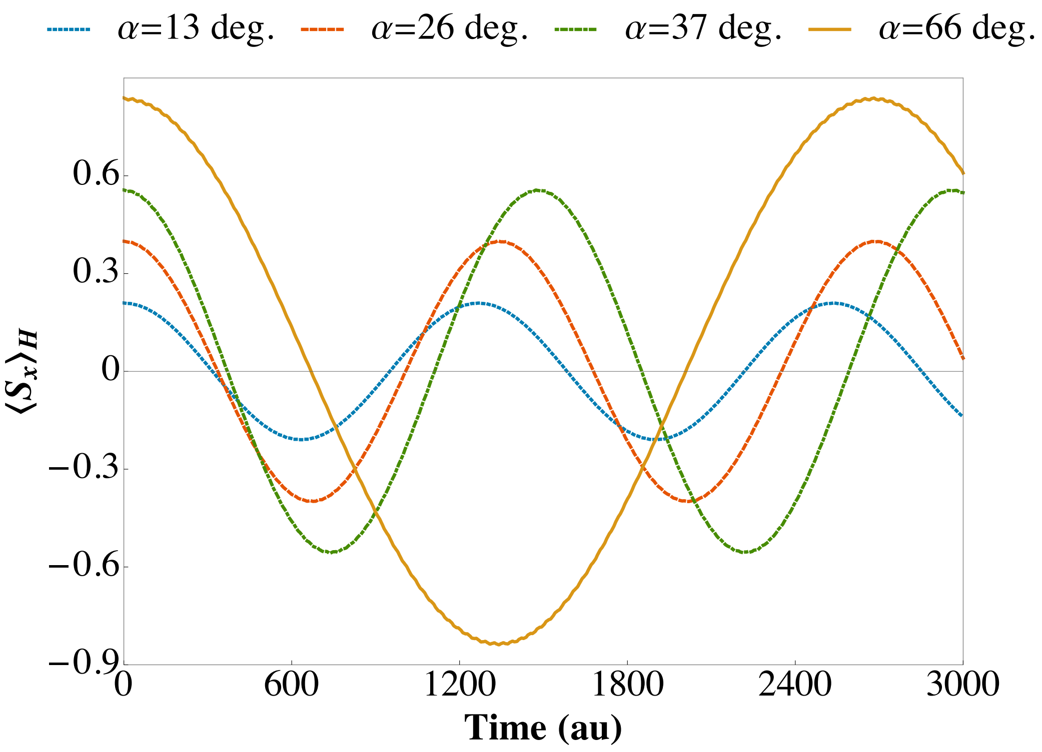


- Classical spin precession
- J can be obtained comparing to the dynamics of a classical HDVV model

$$\dot{\mathbf{S}}_A = J\ \mathbf{S}_A \times \mathbf{S}_B$$

Stamenova and Sanvito, PRB (2013)

TD-DFT



- Start dynamics with different constraint angles α
- Frequency ω increases with α
- J can be calculated from ω and total magnetization

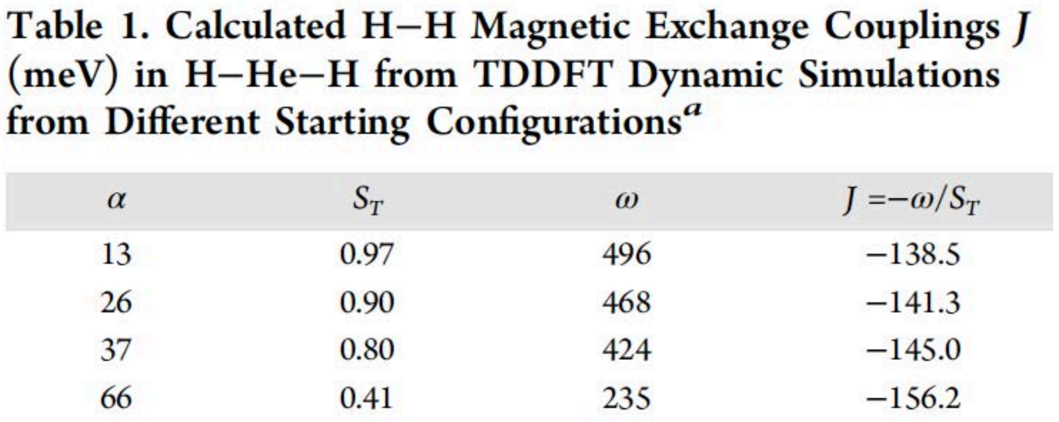
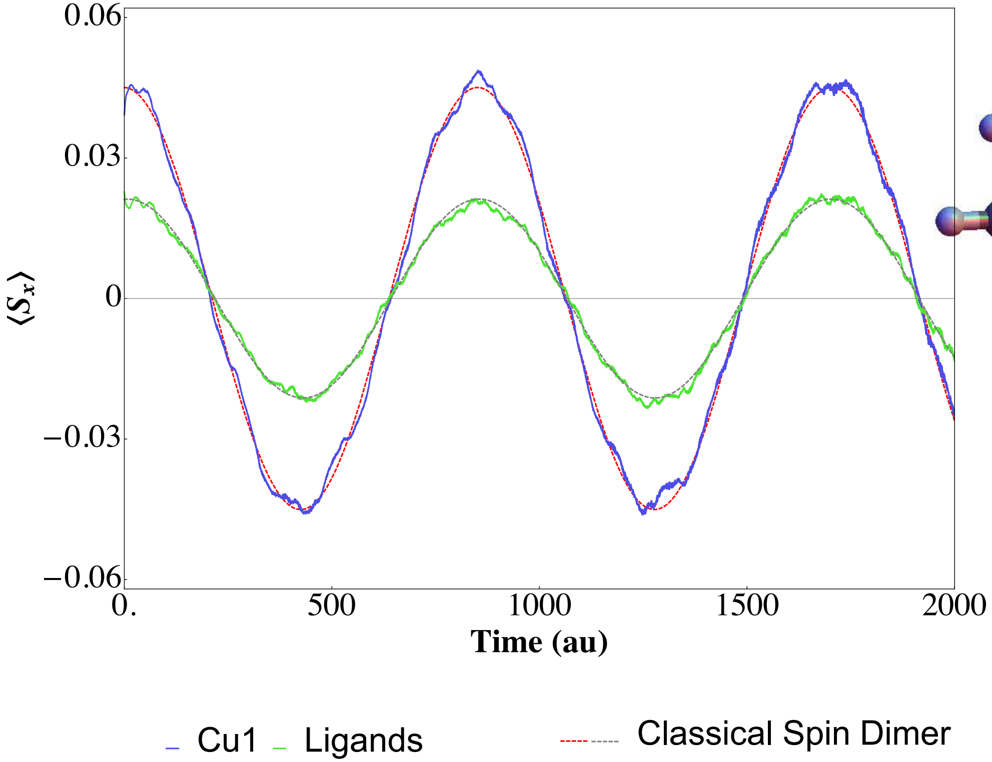
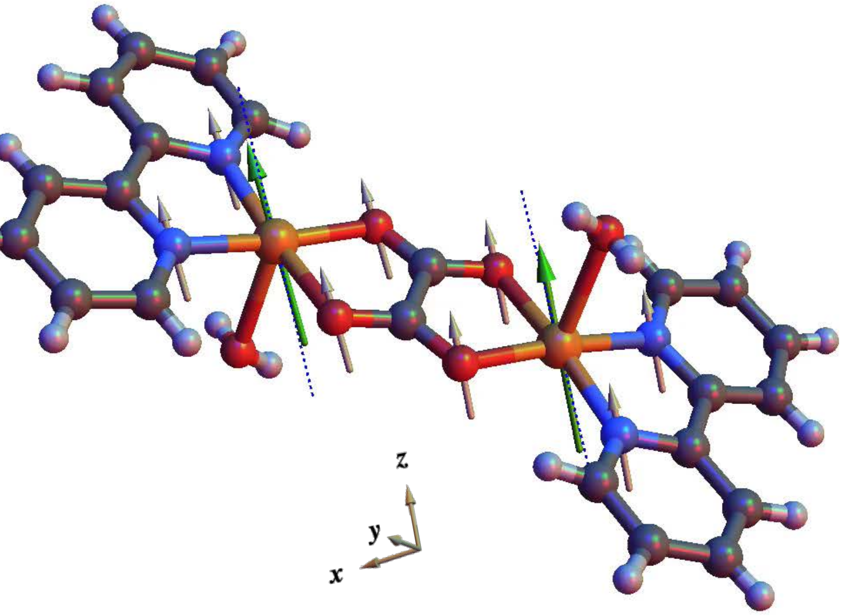


Table 1. Calculated H−H Magnetic Exchange Couplings J (meV) in H−He−H from TDDFT Dynamic Simulations from Different Starting Configurations[a]

α	S_T	ω	$J = -\omega/S_T$
13	0.97	496	−138.5
26	0.90	468	−141.3
37	0.80	424	−145.0
66	0.41	235	−156.2

TD-DFT





- Cu_2 BISDOW Complex
- PBE with 6-31G* basis for Cu, 6-31G for others
- $\Delta t = 0.0048$ fs ($t_{max} = 48$ fs)

Energy Differences	$J = -0.23\ eV$
Dynamics	$J = -0.20\ eV$

Summary

- HFX dominant factor for *J* couplings
- Current DFT approximations give large errors for *J* couplings (ideas?)
- Local spin rotations
- Dynamics including spin : spin precession

Acknowledgements

U.S. DEPARTMENT OF ENERGY

NSF

RESEARCH CORPORATION *for* SCIENCE ADVANCEMENT

CMU

Questions? Comments?