Spin-forbidden processes and molecular magnetism: Theory and applications

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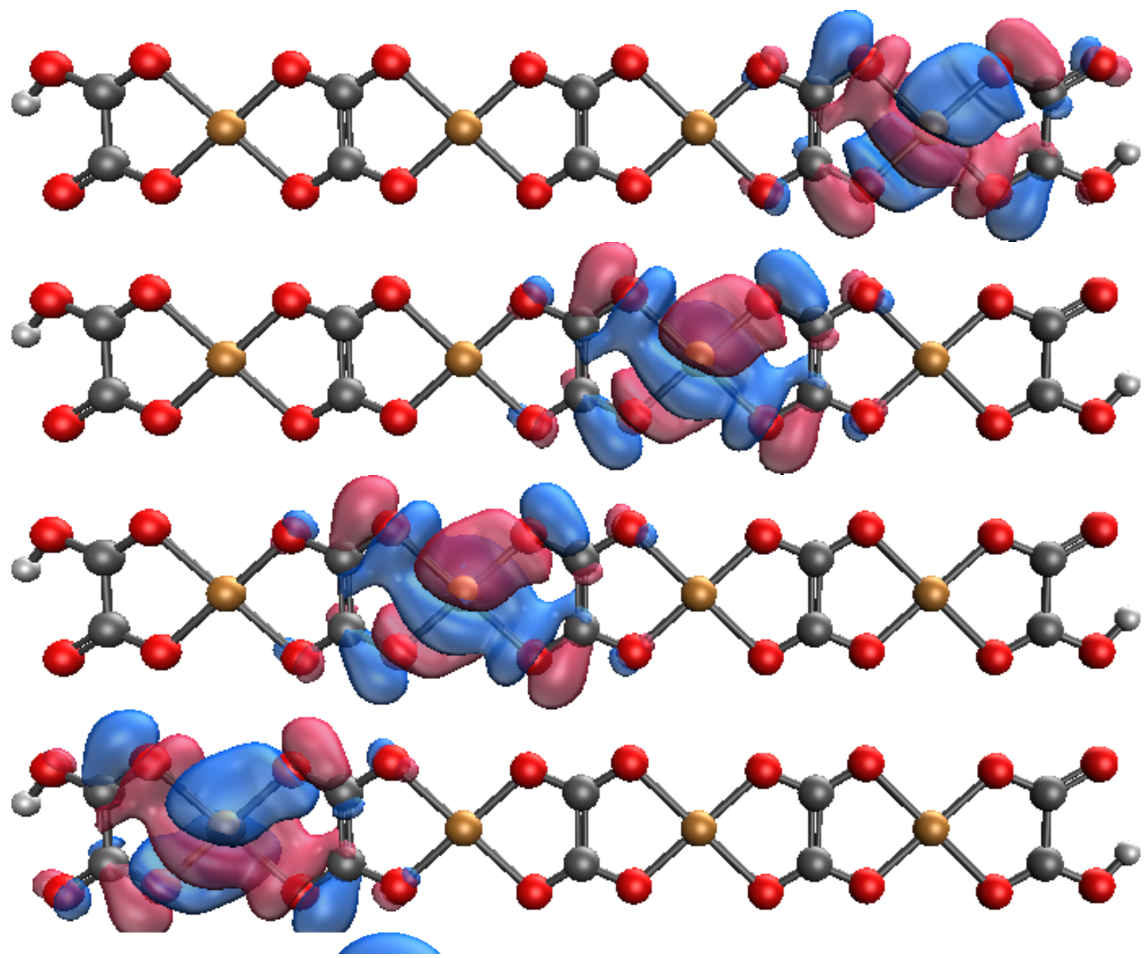
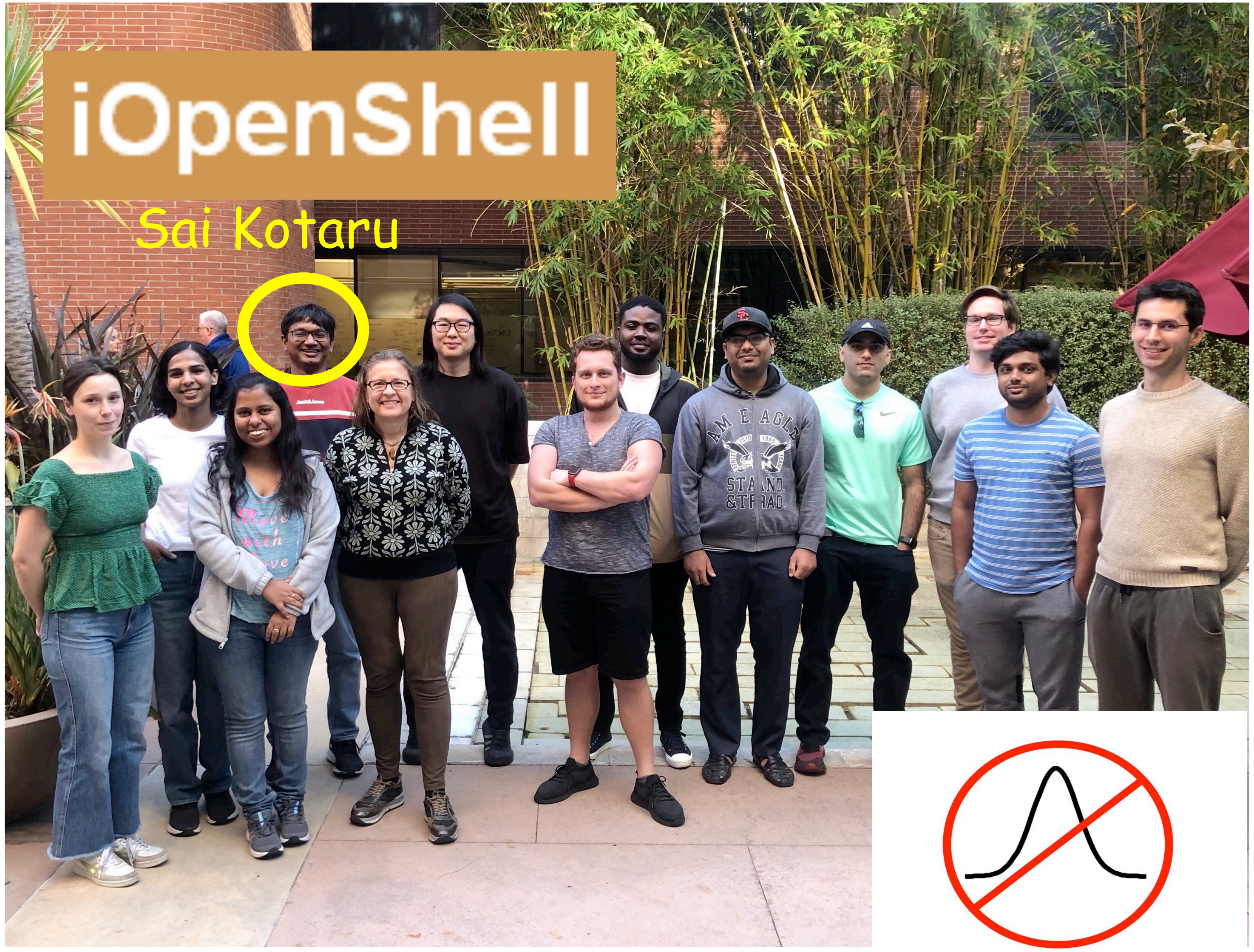


Virtual Computational Molecular Science Seminar
Skoltech, March 2023



Dr. Pavel Pokhilko

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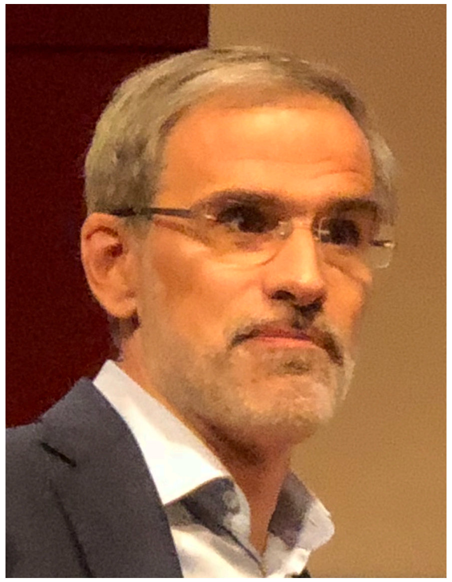

Professor Juergen Gauss (Mainz, Germany)

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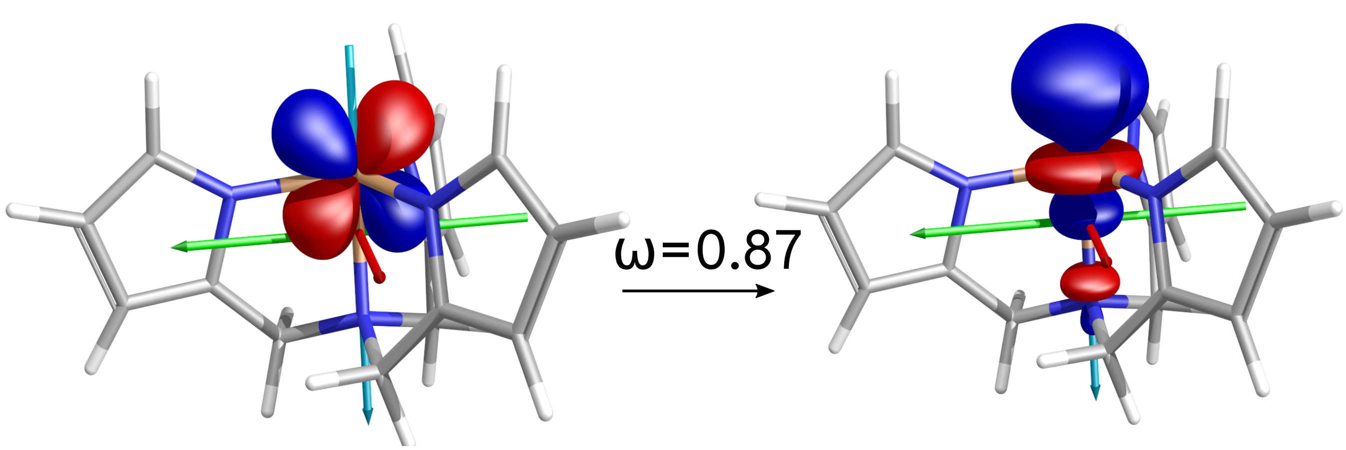
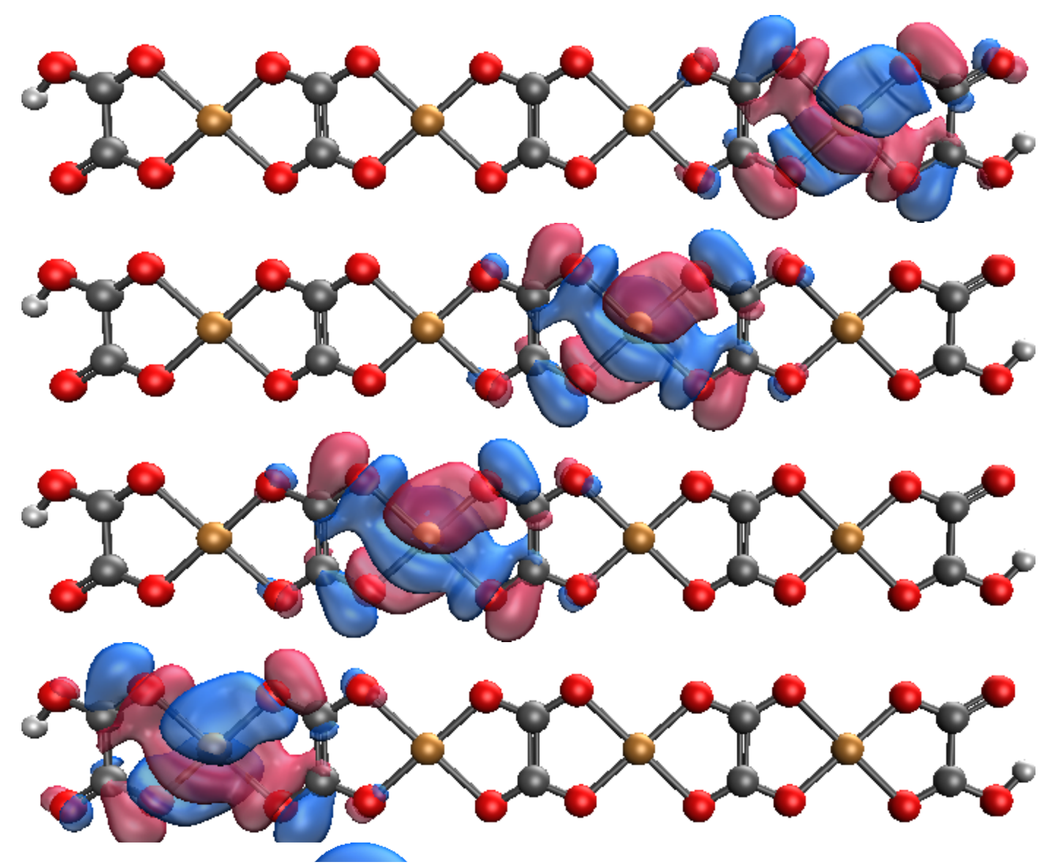
Dr. Xintian Feng (Q-Chem, Inc)

Outline

1. Spin-orbit coupling: What is it and why do we care?
2. What makes a magnet?
3. Theoretical tools for treating magnetic systems:
   - How to handle electron correlation;
   - How to compute SOCs;
   - How to make sense out of numbers: Quantitative molecular orbital theory of spin-forbidden transitions;
   - How to compute macroscopic properties.
4. From molecules to materials: Coarse-graining strong correlation.
5. Conclusions.



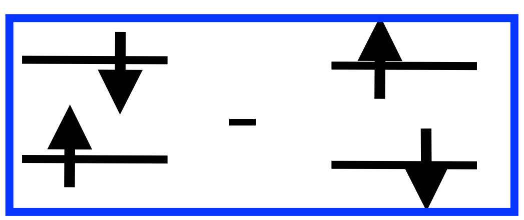


Spin in non-relativistic quantum mechanics

$$\Phi(x_1, x_2, \ldots, x_n) = -\Phi(x_2, x_1, \ldots, x_n) = \ldots$$

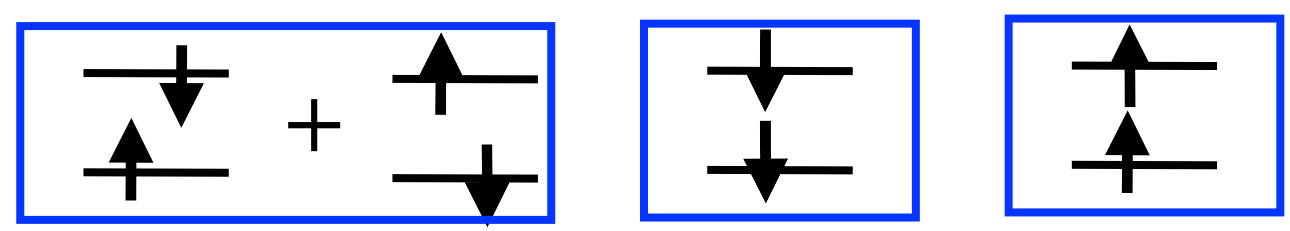
- Fermionic statistics leads to Pauli principle 
- Spin determines spatial part of the wfn and affects energies/properties: singlets are different from triplets

Singlet



$\langle S_z \rangle=0$
$\langle S^2 \rangle=0$

Triplet



$\langle S_z \rangle=0$, $\langle S^2 \rangle=2$ | $\langle S_z \rangle=-1$, $\langle S^2 \rangle=2$ | $\langle S_z \rangle=1$, $\langle S^2 \rangle=2$

- States of different multiplicities cannot interact, e.g., transitions between singlets and triplets, are forbidden;
- Different components of a multiplet are degenerate.

When relativity is turned on: Spin can interact with charge

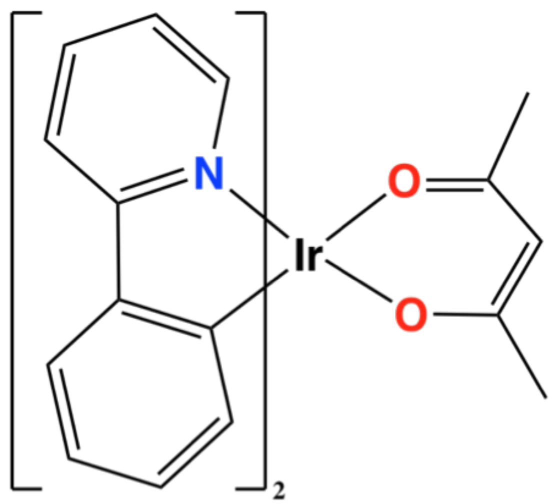
Spin-orbit coupling (SOC): $\sim \dfrac{Z(\mathbf{r} \times \mathbf{p}) \cdot \mathbf{s}}{|r|^3} = \dfrac{Z}{|r^3|}(\mathbf{L} \cdot \mathbf{s})$

- Describes interaction of the magnetic moment of the moving electron with the orbital motion and the field due to the nucleus;
- Is relatively weak in light elements, but:

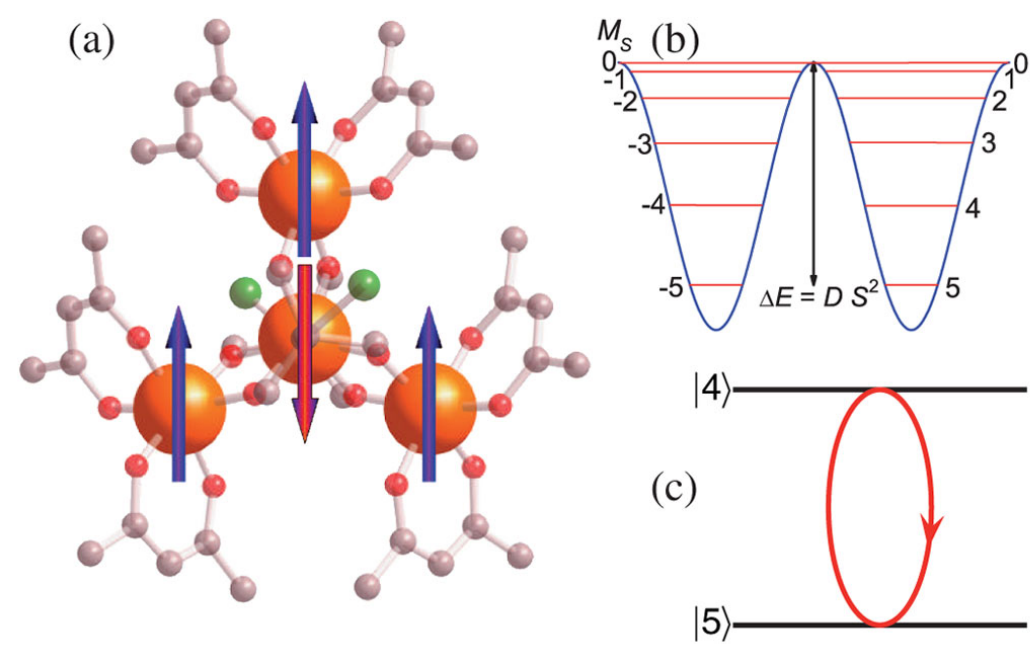
  - Splits the degeneracy within multiplets;
  - Couples the states of different multiplicity causing intensity borrowing and spin-forbidden transitions;
  - Creates barrier for reorienting spins (molecular magnetism).

Spin-orbit enables phenomena exploited in

- Many spectroscopies;
- Sensors and magneto-reception in birds;
- Combustion (reactions with oxygen) and catalysis;
- Photosensitezation, production of ROS (photodynamic therapy);
- Photovoltaics (OLEDs);
- Molecular magnetism.



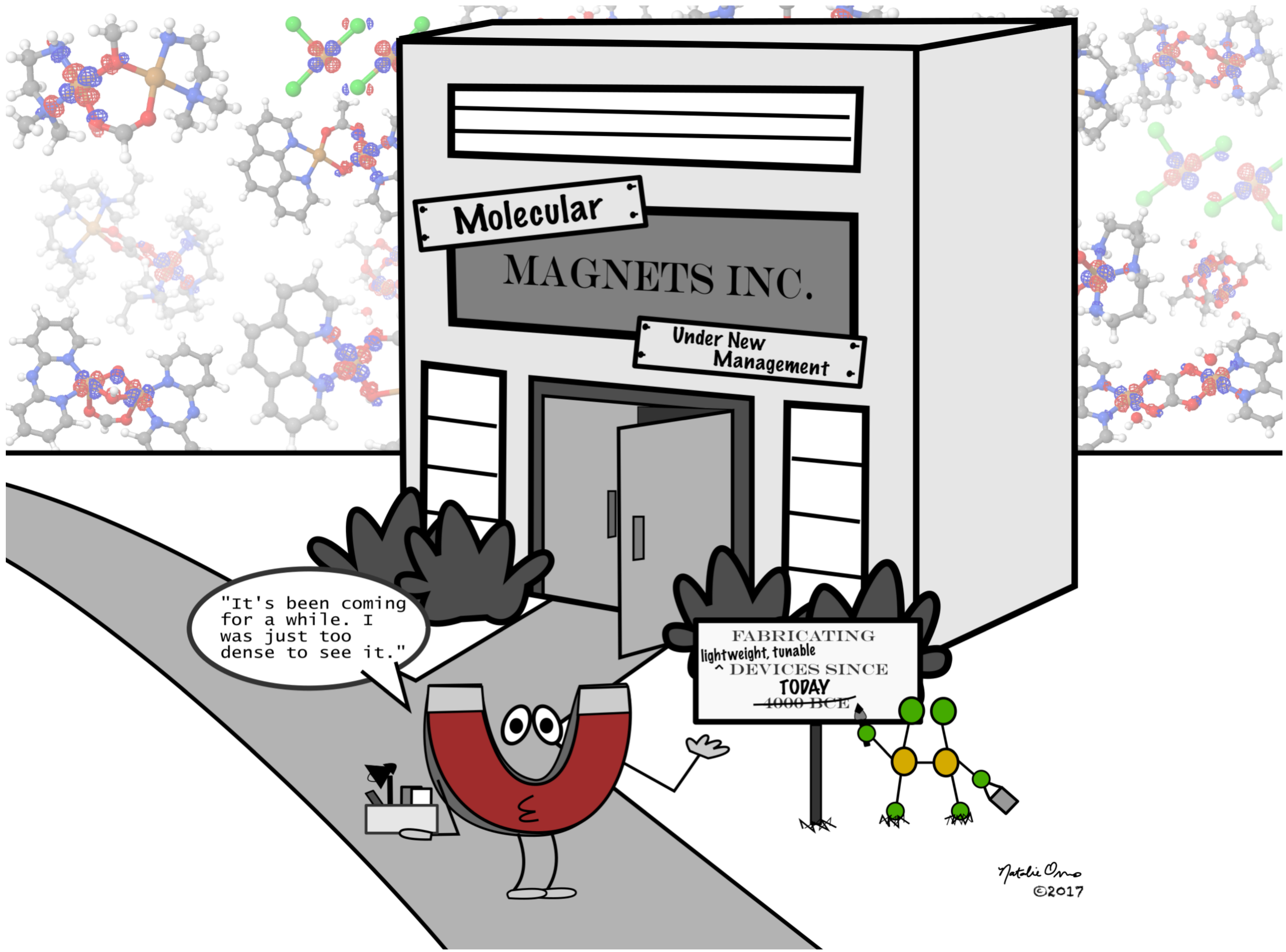
$Ir(ppy)_2(acac)$



OLED's function depends on SOC between singlet and triplet excited states.

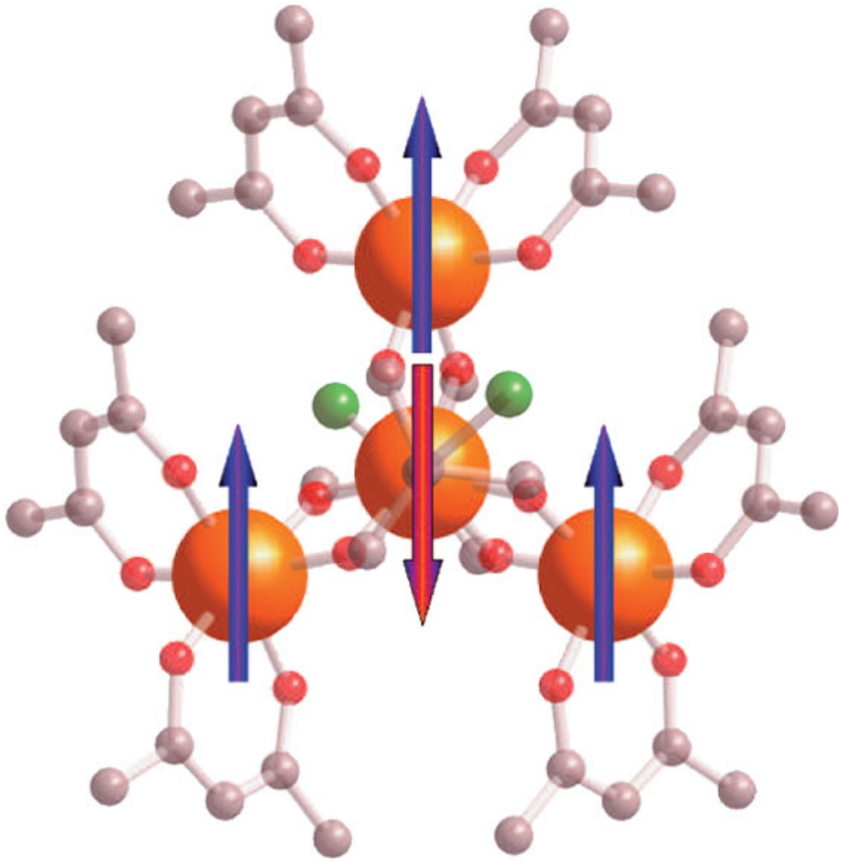
Fe_4 (S=5) SMM as a qubit.

Single-molecule magnets and anti-ferromagnets

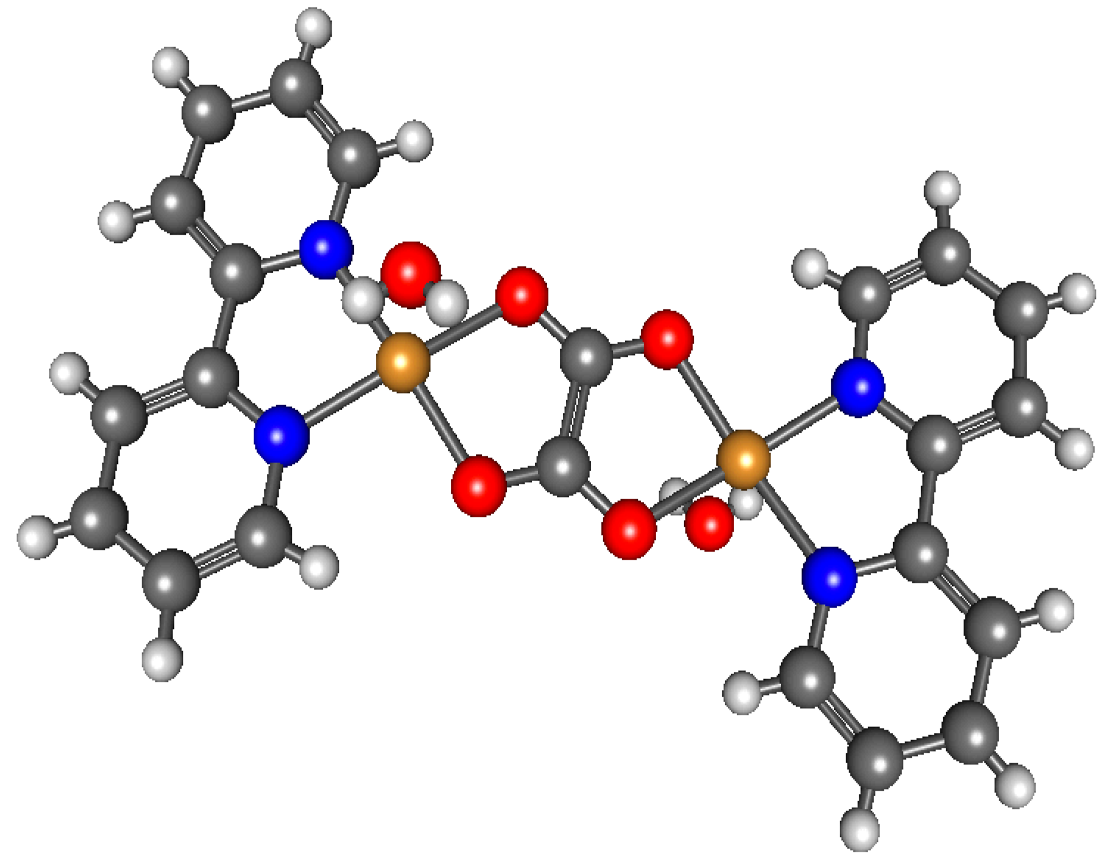


Applications: Spintronics, high-density memory storage, quantum information science (qubits)

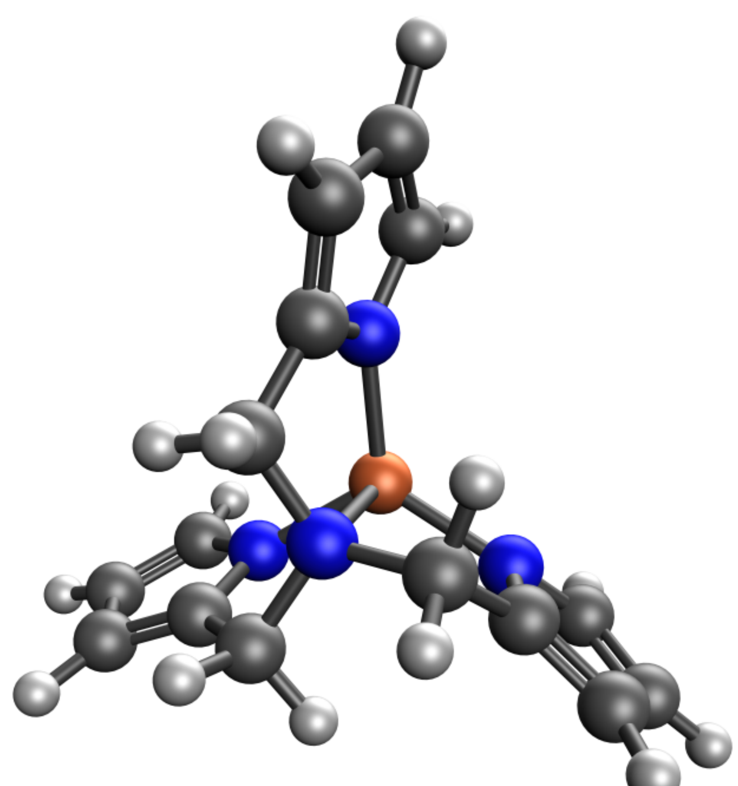
Examples of SMMs



$(Fe)_4$



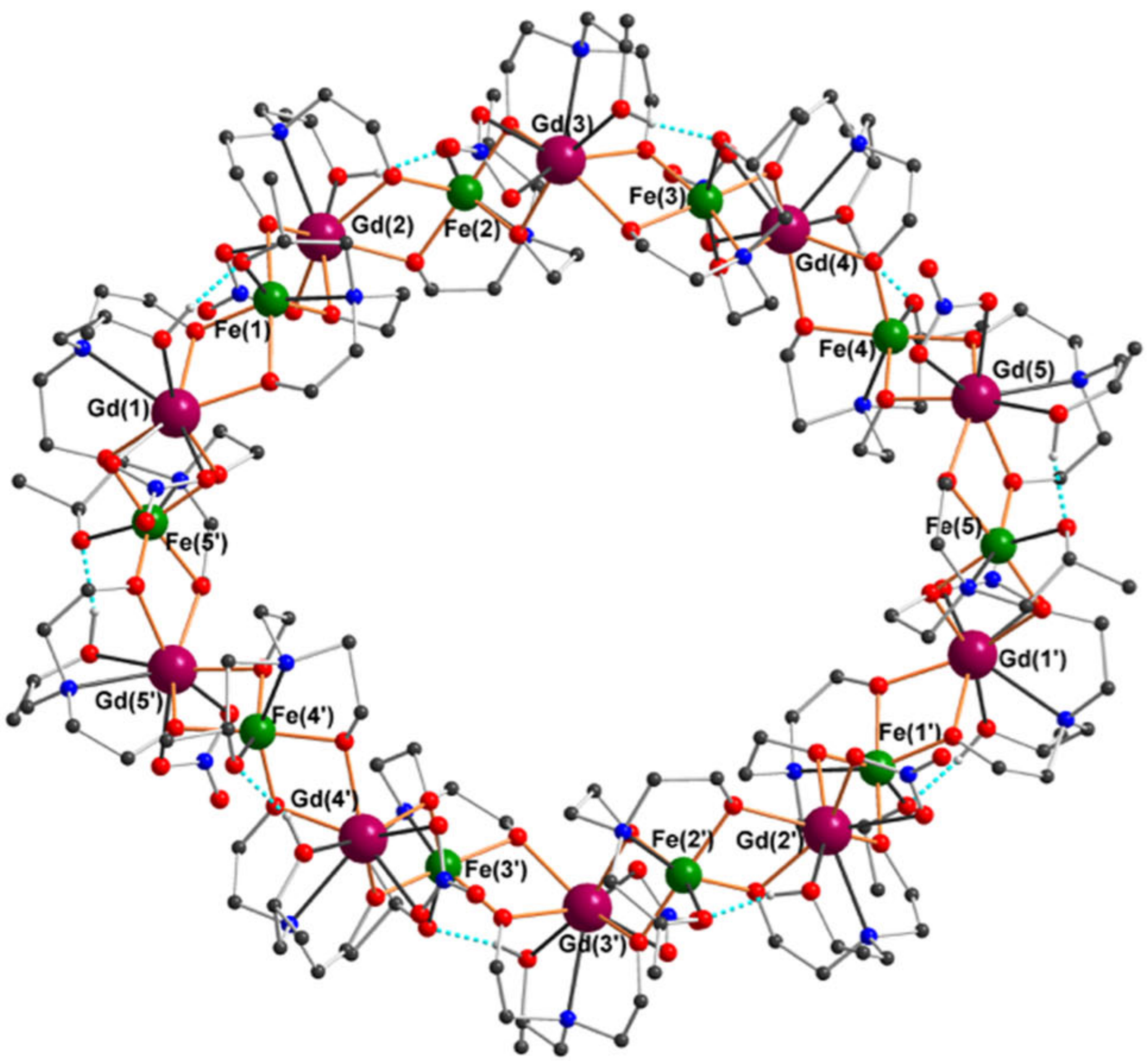
$(Cu)_2$

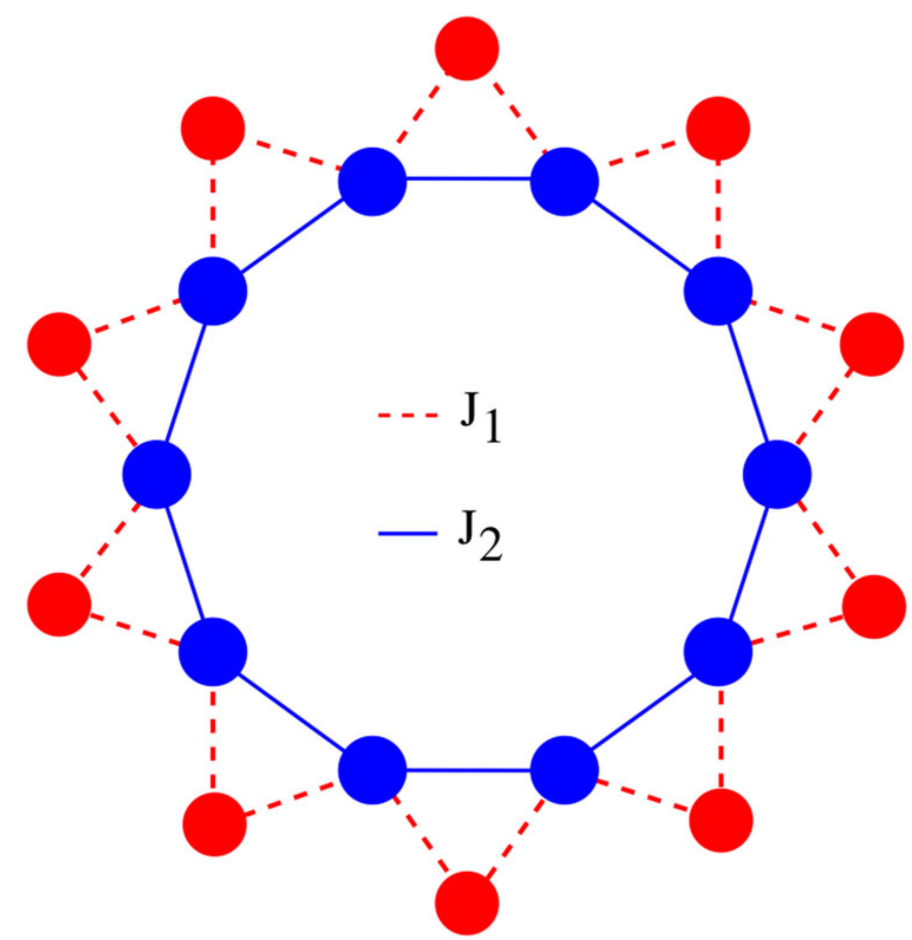


Fe(II)

SMM with the largest ground-state spin

$Fe_{10}Gd_{10}$ magnet with S=60





Baniodeh, Magnani, Lan, Buth, Anson, Richter, Affronte, Schnack, and Powell, Quantum Mat. **3**, 1 (2018).

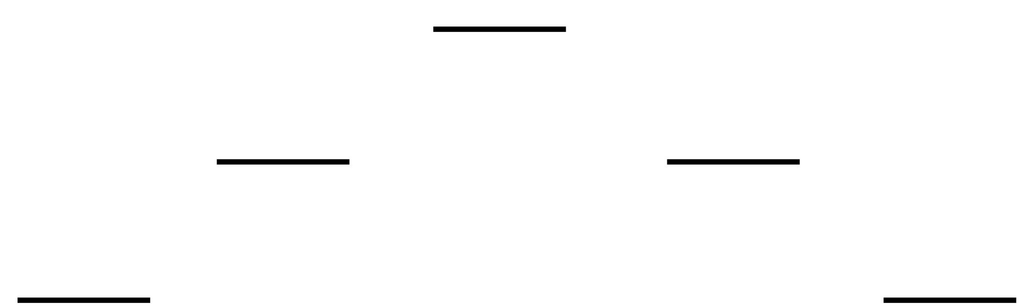
What makes an SMM?

Need to be able to be magnetized and retain magnetic state for some time

- **non-zero ground-state spin**
- **magnetic anisotropy (non-degenerate components of a multiplet)**

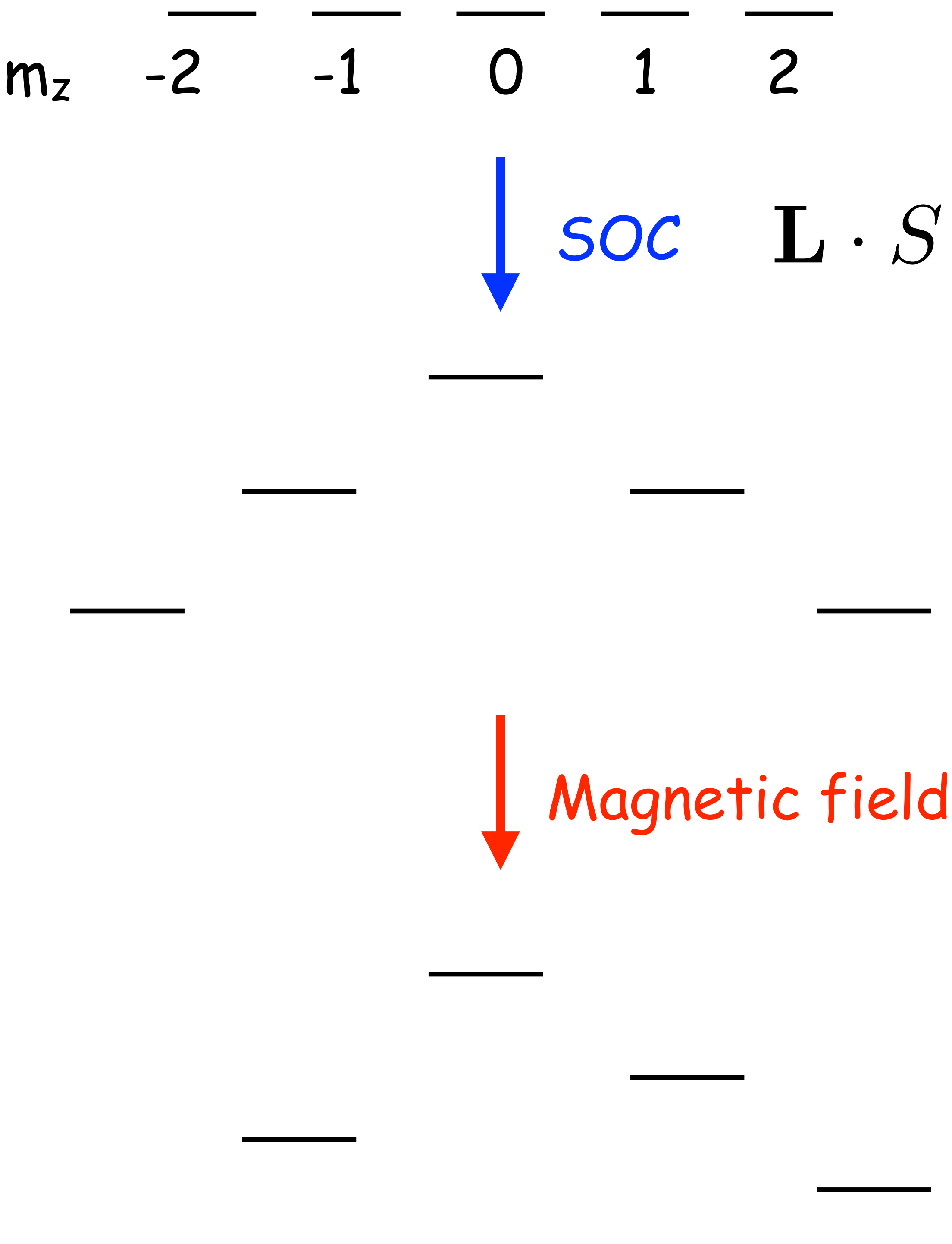
Quintet state: s=2 m_z=-2,-1,0,1,2

No anisotropy (not a magnet)



With anisotropy (can be a magnet)

Fe(II) SMM (quintet state)



SOC $\mathbf{L} \cdot S$

Zero-field splitting of multiplet

Magnetic field (Zeeman) $\mathbf{H}(\mathbf{L}_z + g\mathbf{S}_z)$

Methodological challenges and solutions

1. Robust and accurate black-box treatment of open-shell species:

    - EOM-CC methods, Spin-Flip, RAS-SF, SF-DFT.

2. Compute and analyze spin-related properties:

    - method-agnostic theory for computing SOC;

    - quantitative molecular orbital theory distilled from many-body calculations;

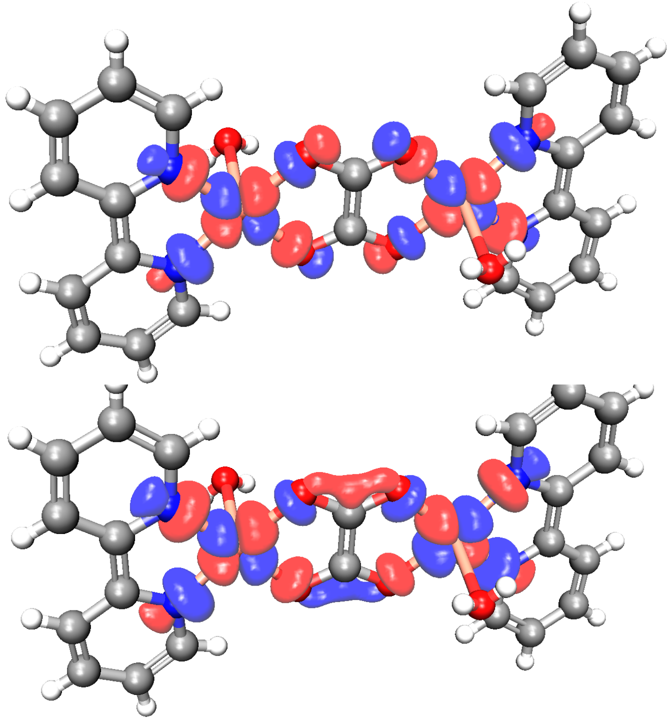
    - framework for macroscopic properties.

3. From molecules to materials:

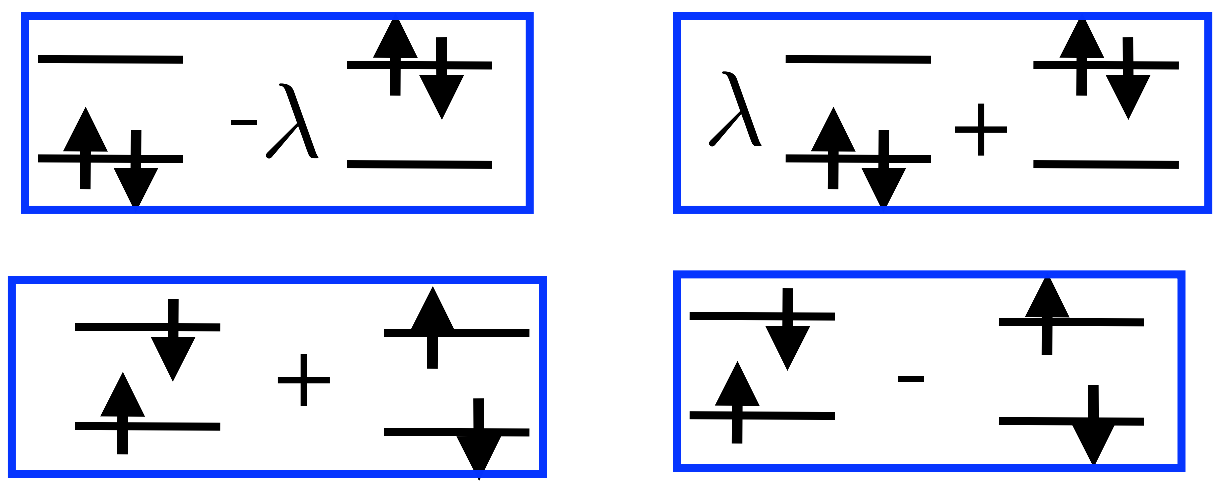
    - effective Hamiltonian approach for coarse-graining strong correlation.

Strong correlation: Bi-copper SMM example

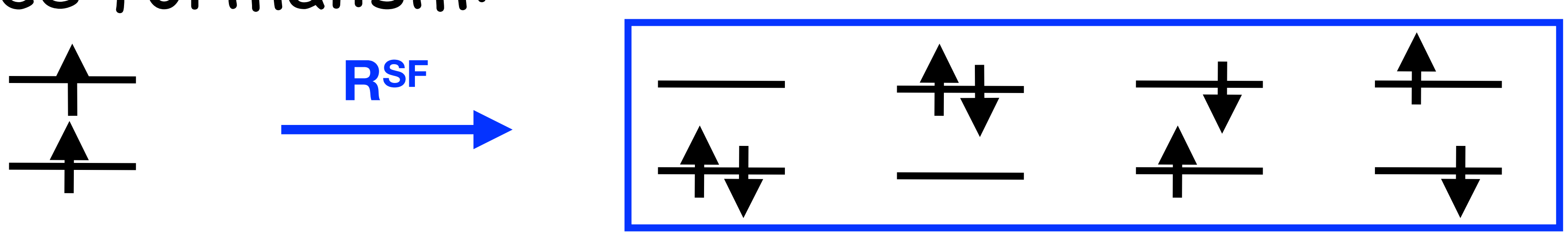
Degenerate frontier orbitals result in multi-configurational wave functions



Possible M_s=0 states:



Spin-Flip method treats multi-configurational wfns in single-reference formalism:

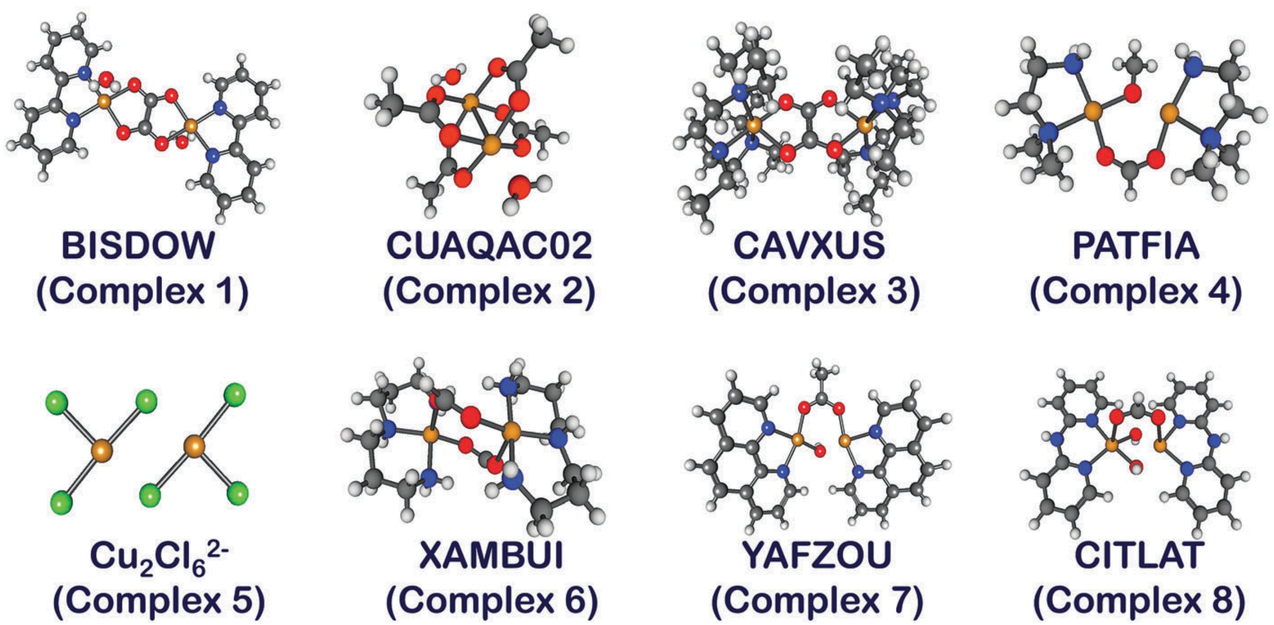


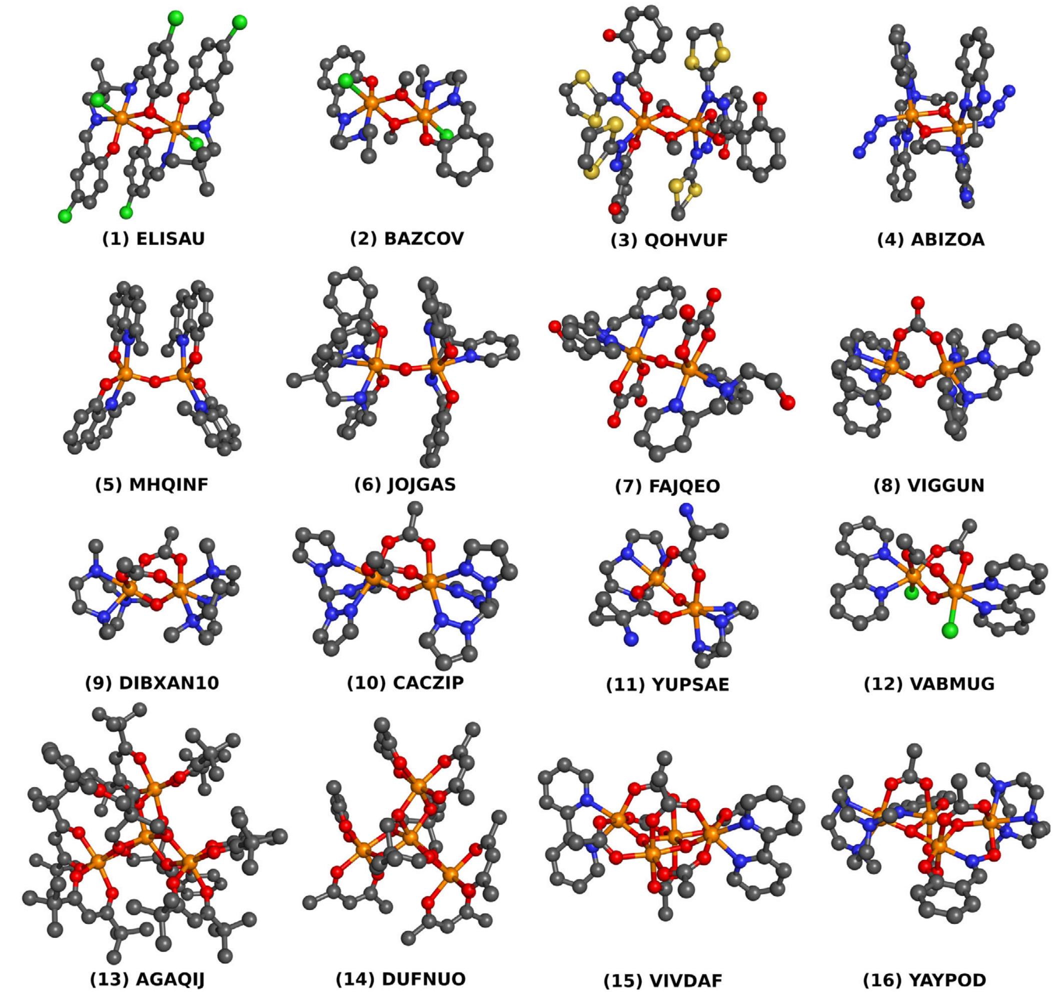
High-spin (M_s=1) reference state

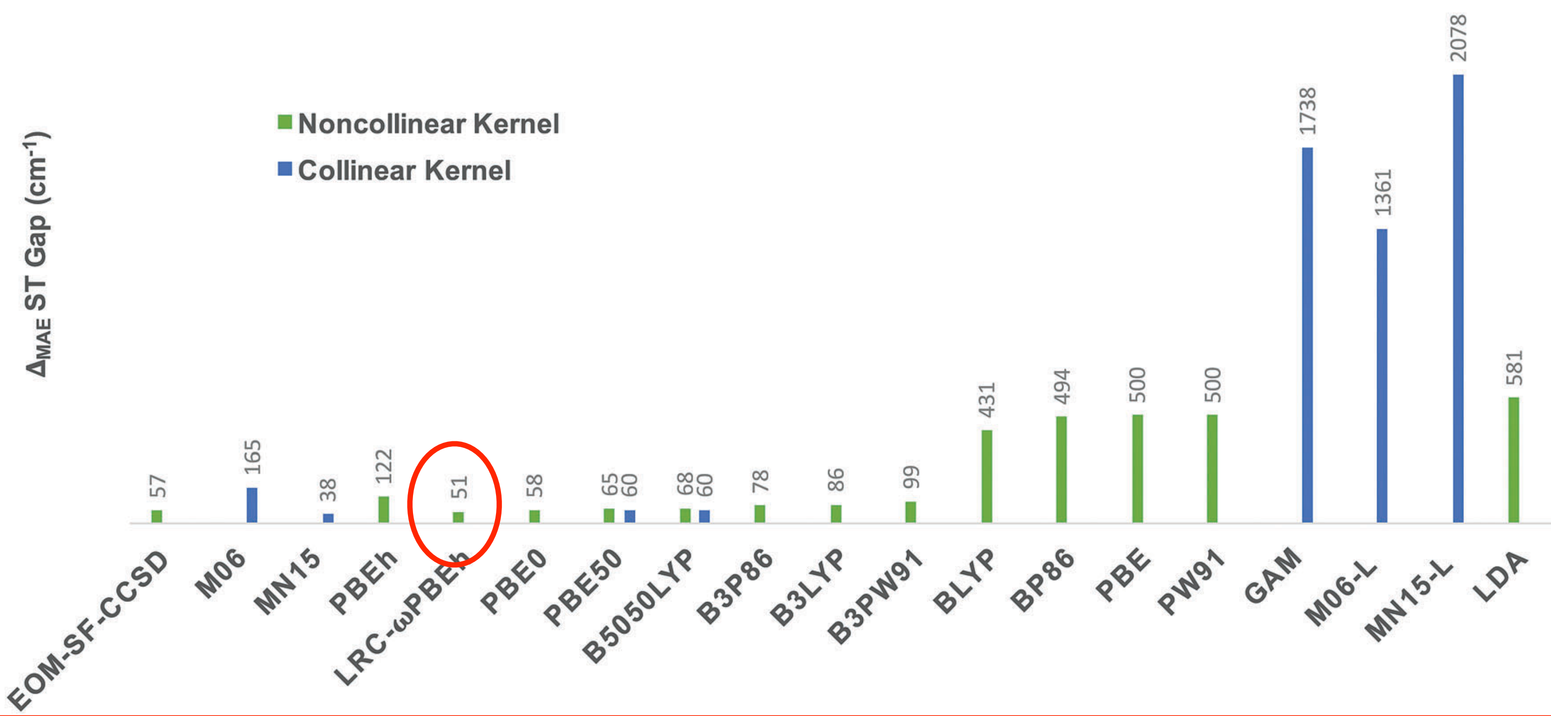
Low-spin (M_s=0) target states

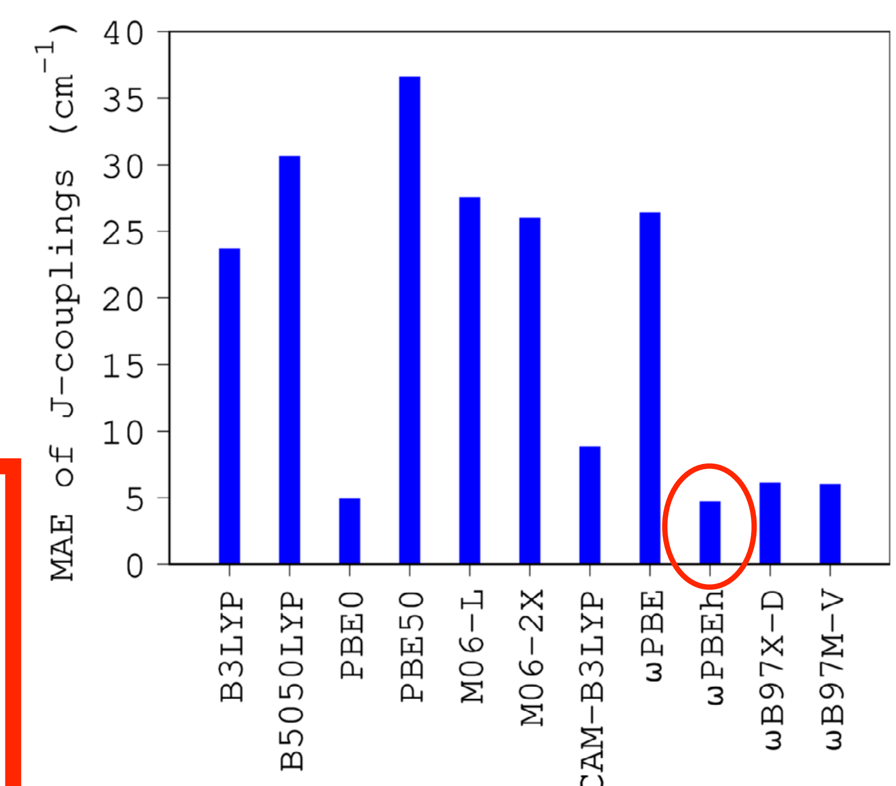
Krylov, CPL **338** 375 (2001); Krylov, Acc. Chem. Res. **39** 83 (2006); Casanova, Krylov, PCCP **22** 4326 (2020).

SF methods for SMMs









- SF-TDDFT is robust and yields accurate J-couplings (energy gaps) and densities
- wPBEh functional consistently delivers the best performance

Methodological challenges and solutions

1. Robust and accurate black-box treatment of open-shell species:
   - EOM-CC methods, Spin-Flip, RAS-SF, SF-DFT.
2. Compute and analyze spin-related properties:
   - method-agnostic theory for computing SOC;
   - quantitative molecular orbital theory distilled from many-body calculations;
   - framework for macroscopic properties.
3. From molecules to materials:
   - effective Hamiltonian approach for coarse-graining strong correlation.

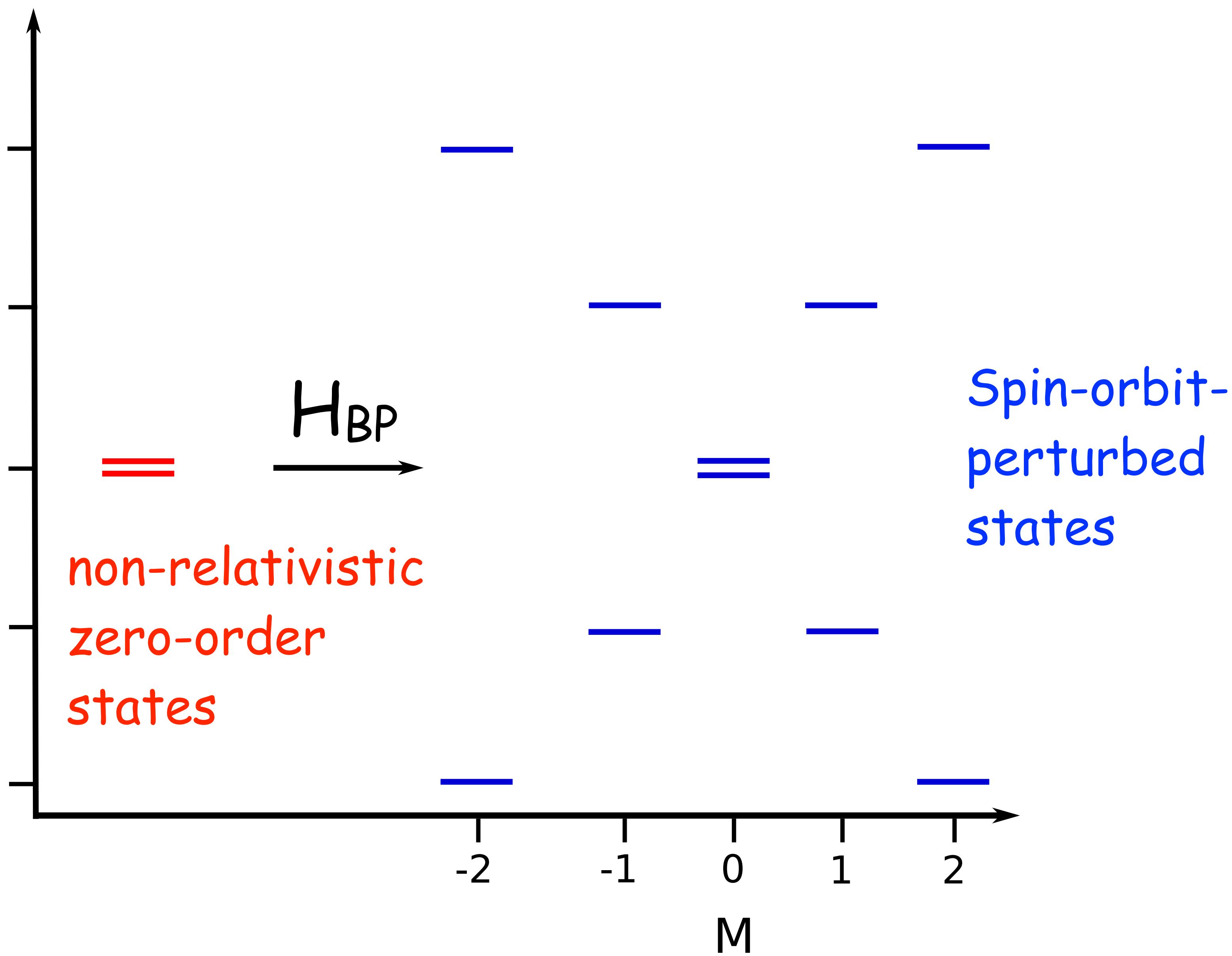
Theory of SOCs: State-interaction approach

Breit-Pauli Hamiltonian:

$$H_{BP}^{SO} = \frac{1}{2c^2}\left(\sum_i \mathbf{h}^{SO}(i)\cdot\mathbf{s}(i) - \sum_{i\neq j}\mathbf{h}^{SOO}(i,j)\cdot(\mathbf{s}(i)+2\mathbf{s}(j))\right)$$

$$\mathbf{h}^{SO} = \sum_K \frac{Z_K(\mathbf{r}_i-\mathbf{R}_K)\times\mathbf{p}_i}{|\mathbf{r}_i-\mathbf{R}_K|^3} = \sum_K \frac{Z_k}{r_{iK}^3}(\mathbf{r}_{iK}\times\mathbf{p}_i),$$

$$\mathbf{h}^{SOO}(i,j) = \frac{(\mathbf{r}_i-\mathbf{r}_j)\times\mathbf{p}_i}{|\mathbf{r}_i-\mathbf{r}_j|^3} = \sum_{i\neq j}\frac{1}{r_{ij}^3}(\mathbf{r}_{ij}\times\mathbf{p}_i),$$

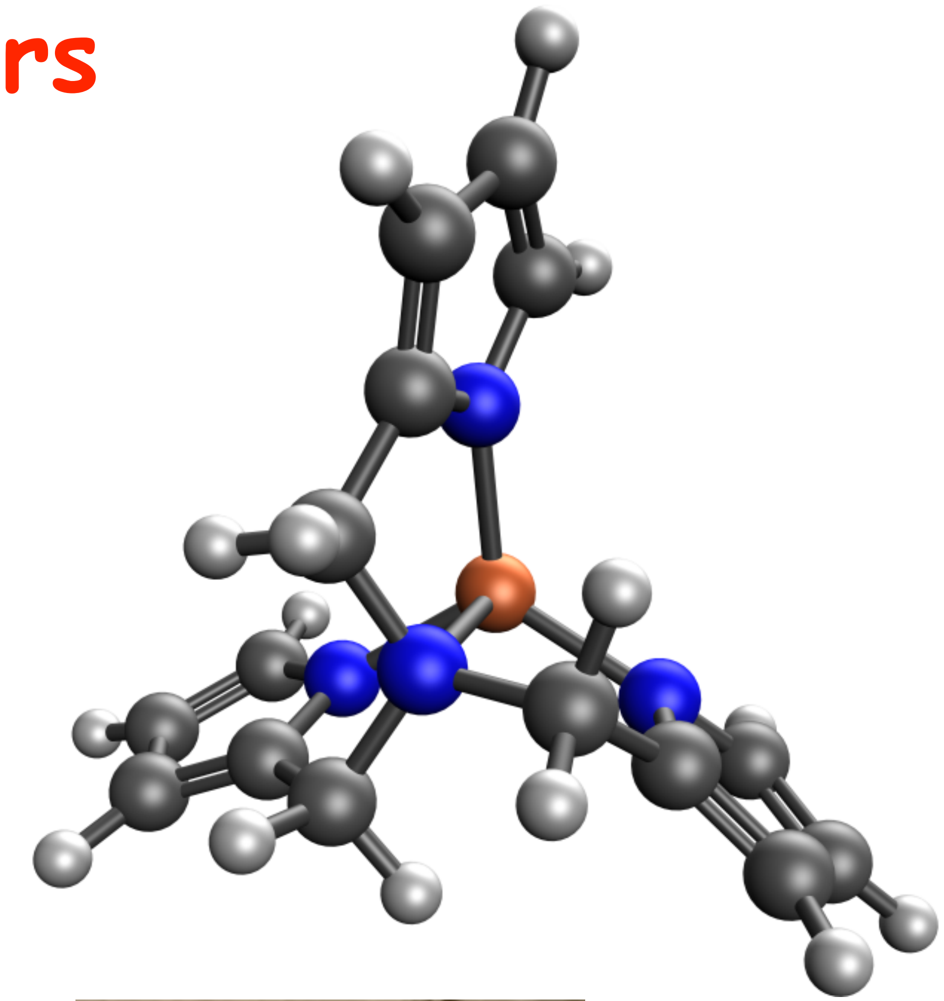


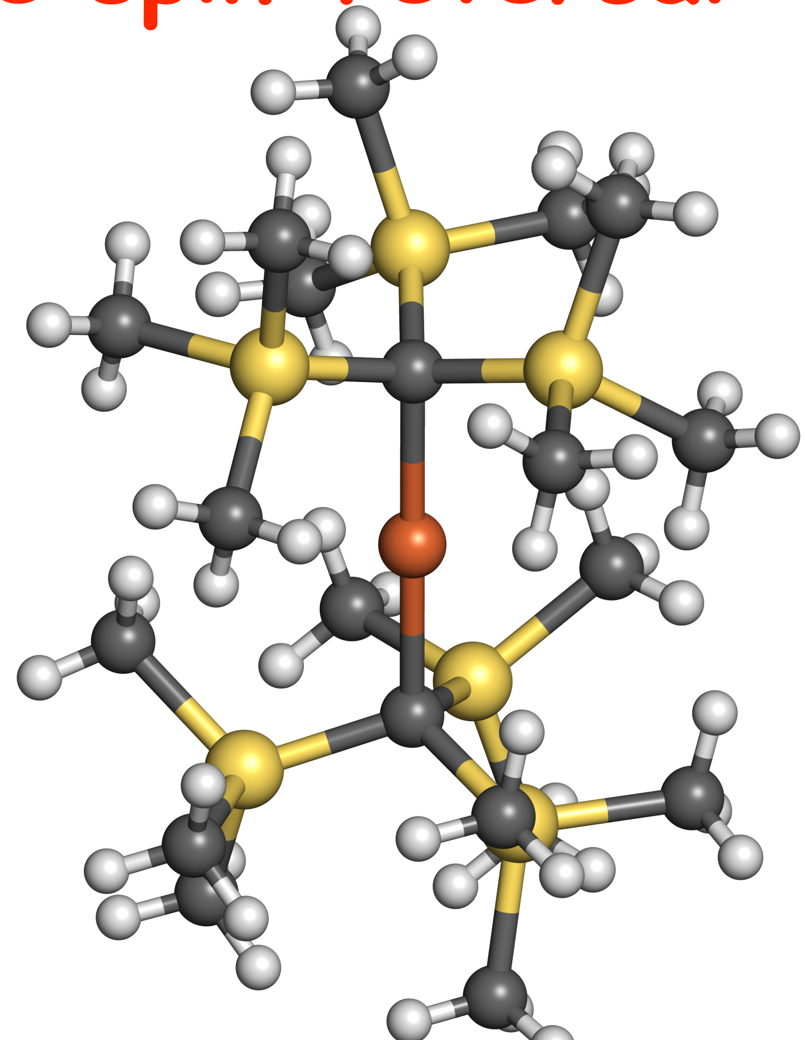
Our implementation is based on Wigner theorem, reduced density matrices, and natural orbitals:

- ansatz-agnostic;
- rigorous molecular orbital picture distilled from many-body calculations.

Epifanovsky, Klein, Stopkowicz, Gauss, Krylov, JCP **143** 064102 (2015); Pokhilko, Epifanovsky, Krylov, JCP **151** 034106 (2019); Pokhilko, Krylov, JPCL **10** 4857 (2019); Krylov, JCP **153** 080901 (2020); Kotaru, Pokhilko, Krylov, JCP **157** 224110 (2022).

Examples: Fe(II) SMMs with large spin-reversal barriers





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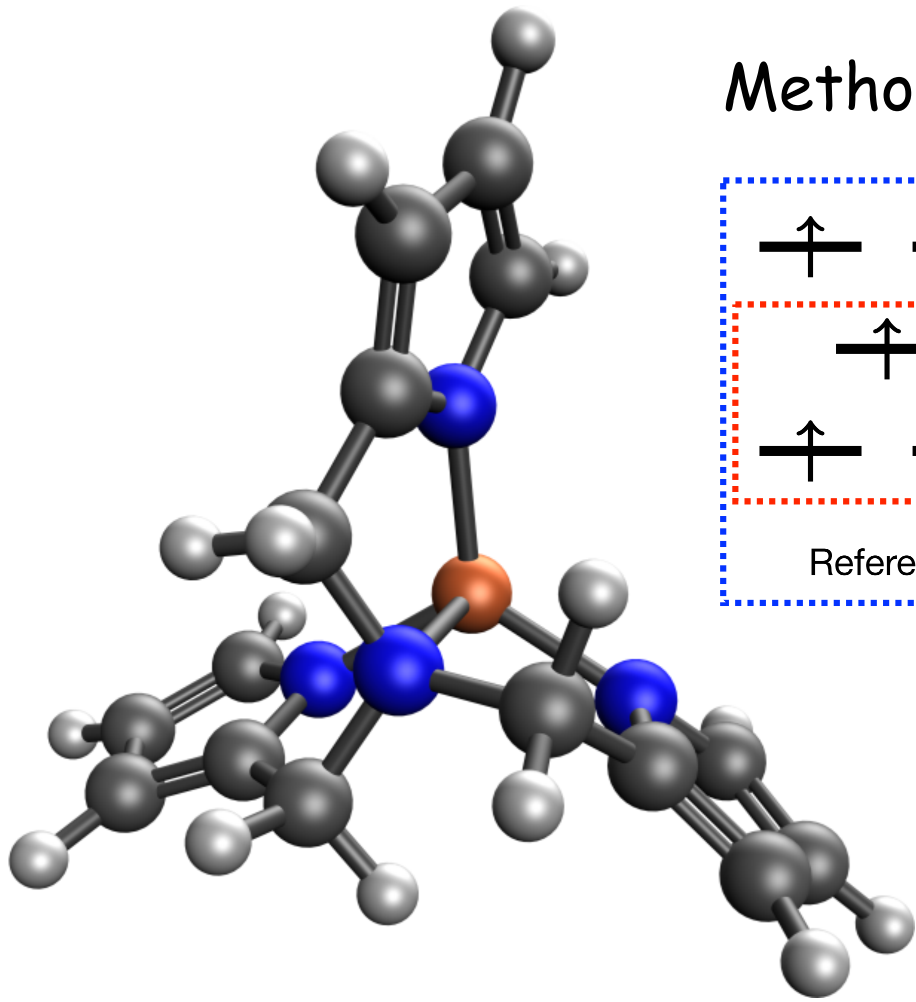
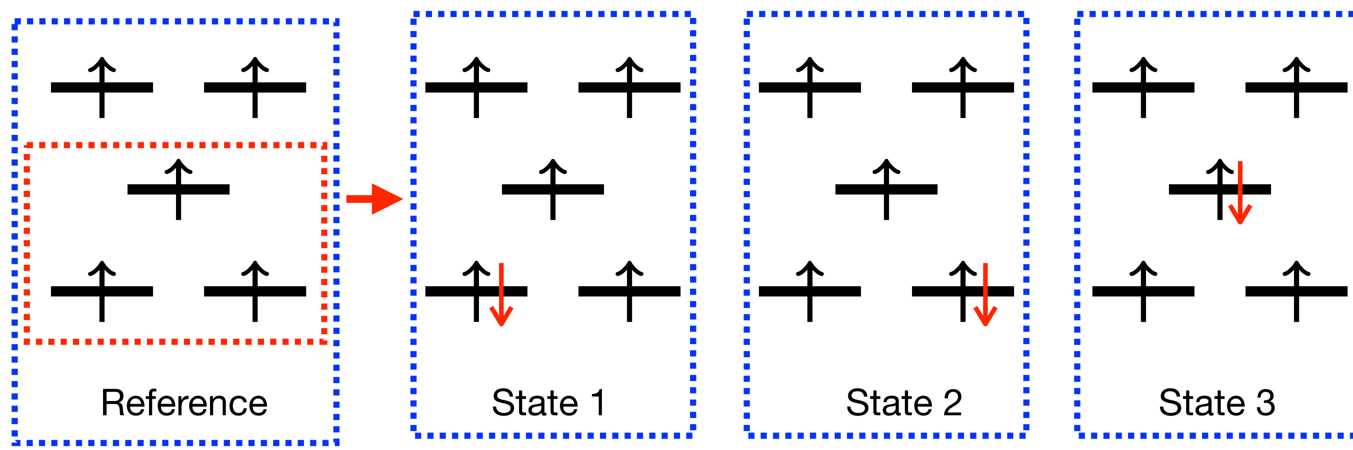
Pokhilko, Epifanovsky, Krylov, JCP **151** 034106 (2019); Alessio, Krylov, JCTC **17** 4225 (2021).

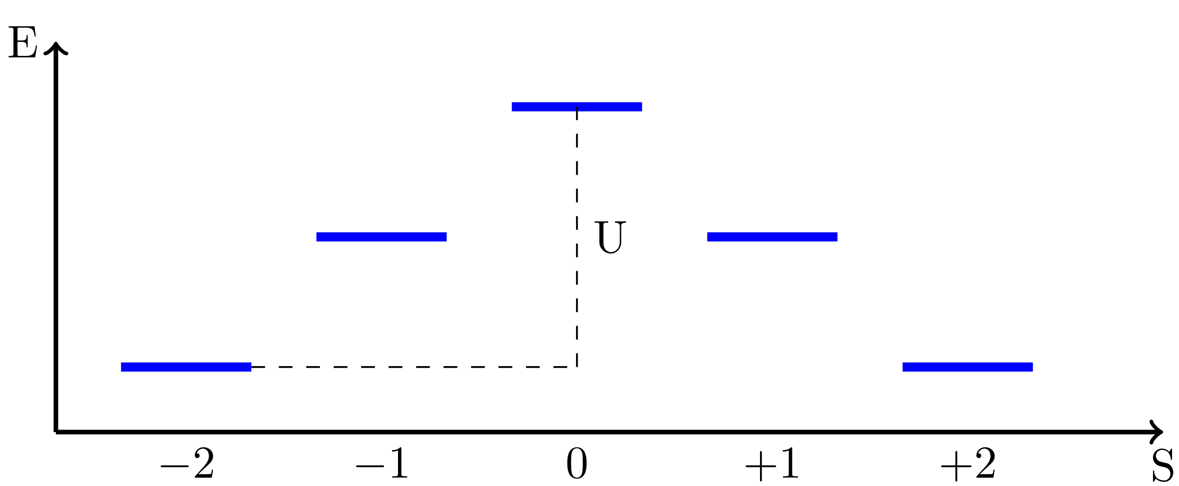
Fe(II) SMM



Method: EOM-EA-MP2/cc-pVDZ



Fe(II): d^6



El. multiplets	Barrier, cm^{-1}
2	173
3	158
5	157

Experiment: 158 cm^{-1}

Experiment: Freedman, Harman, Harris, Long, Chang, Long, JACS **132** 1224 (2010).

Connection to macroscopic properties

Magnetization: Response to external magnetic field H

$$M = -\frac{\partial E}{\partial H}$$

E is energy of the system perturbed by the field

1. Solve $\hat{H} = \hat{H}^0 + \hat{H}^{SO} + \hat{H}^Z$ with $\hat{H}^Z = \mu_B \mathbf{H}(g_e \hat{\mathbf{S}} + \hat{\mathbf{L}})$

to find perturbed state energies E_{nH}

2. Compute Boltzmann populations $p_{n_H} = e^{-E_{n_H}/kT}$

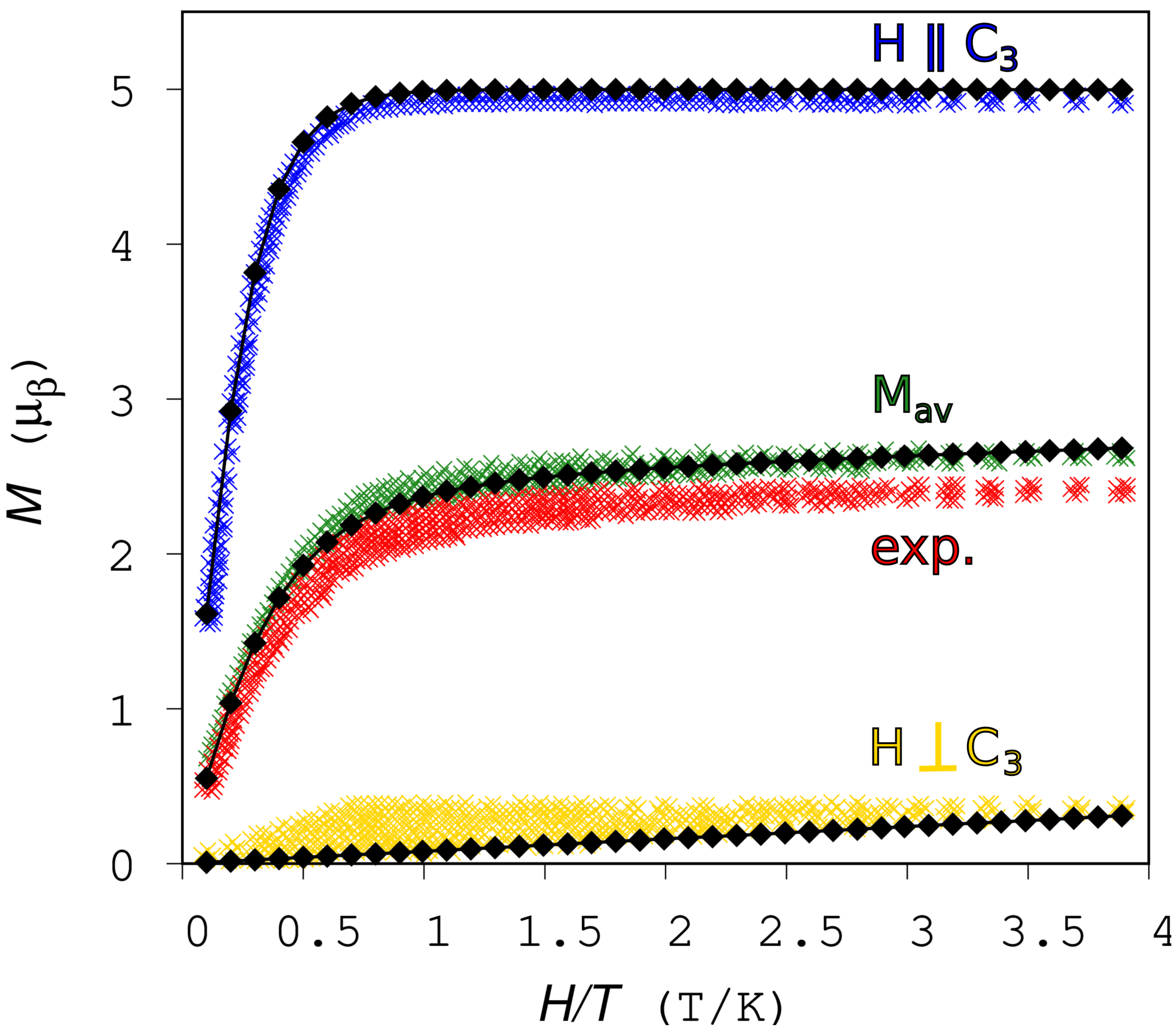
and partition function $Z = \sum_n e^{-E_{n_H}/kT}$

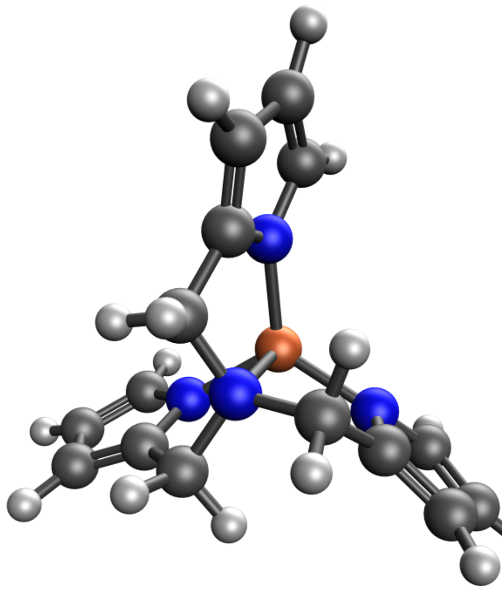
3. Take derivative: $\frac{\partial \ln(Z)}{\partial H} = \frac{1}{kT} \sum_n \left(-\frac{\partial E_{n_H}}{\partial H} \right) p_{n_H}$

$$M(H) = NkT \frac{\partial \ln Z(H)}{\partial H}$$

4. Average as appropriate.

From microscopic properties to macroscopic observables: Fe(II) SMM





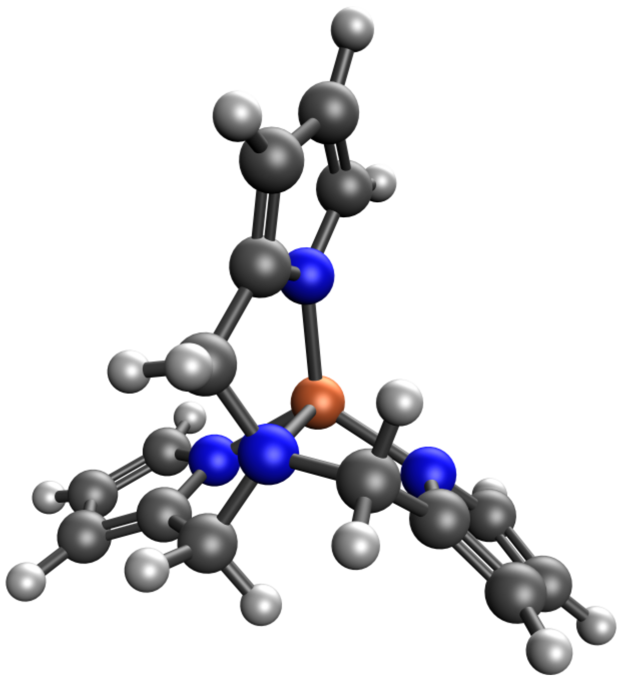
Black: our calculations (EOM-EA-MP2)

Red: experiment

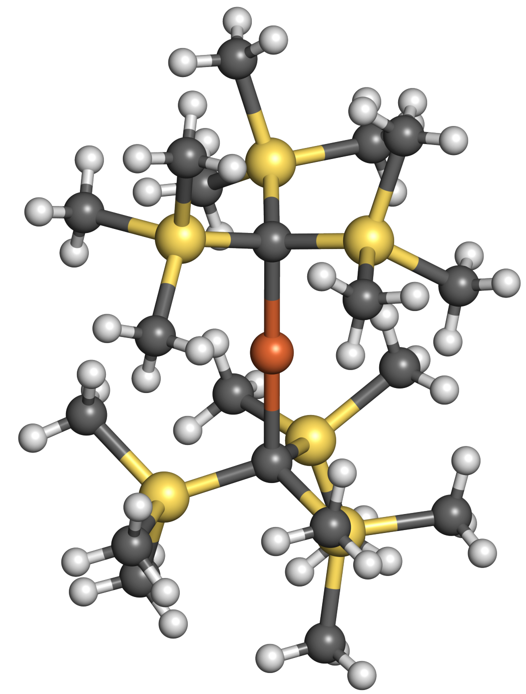
Other: Neese and co-workers (NEVPT2)

Atanasov, Ganyushin, Pantazis, Sivalingam, Neese, Inorg. Chem. **50** 7460 (2011);
Freedman, Harman, Harris, Long, Chang, Long, JACS **132** 1224 (2010).

Using magnetic NTOs to understand trends in spin-reversal barriers in Fe(II) SMMs



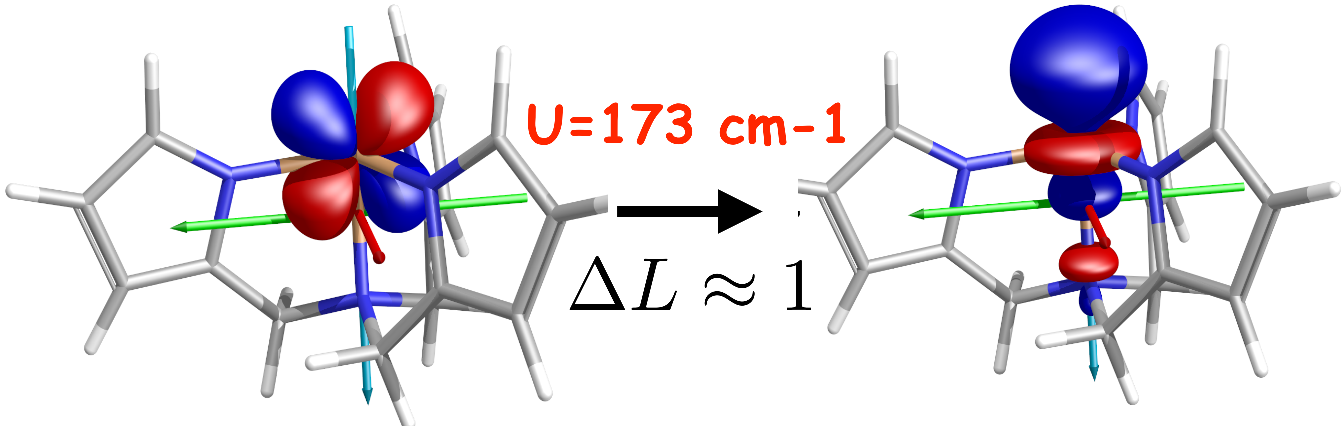
U=173 cm^{-1}

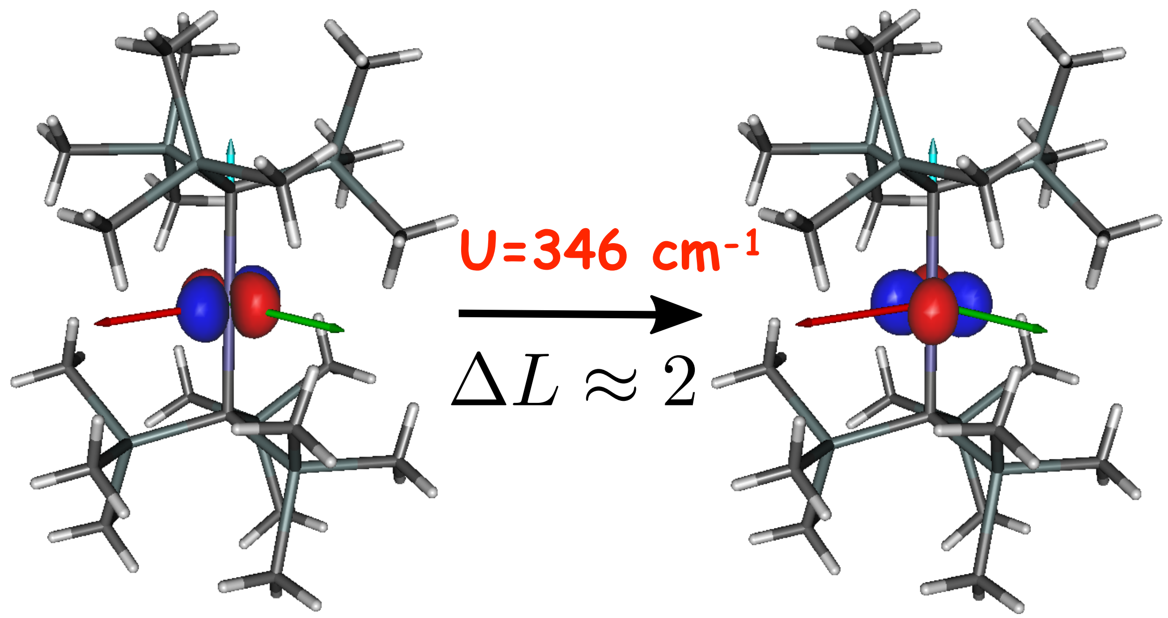


U=346 cm^{-1}

Why the barriers are so different?
Look at NTOs connecting spin-orbit coupled states to understand different magnitude SOCs.

Magnetic NTOs in Fe(II) SMMs





$$\text{SOC} \sim \frac{Z(\mathbf{r}\times\mathbf{p})\cdot\mathbf{s}}{|r|^3} = \frac{Z}{|r^3|}(\mathbf{L}\cdot\mathbf{s})$$

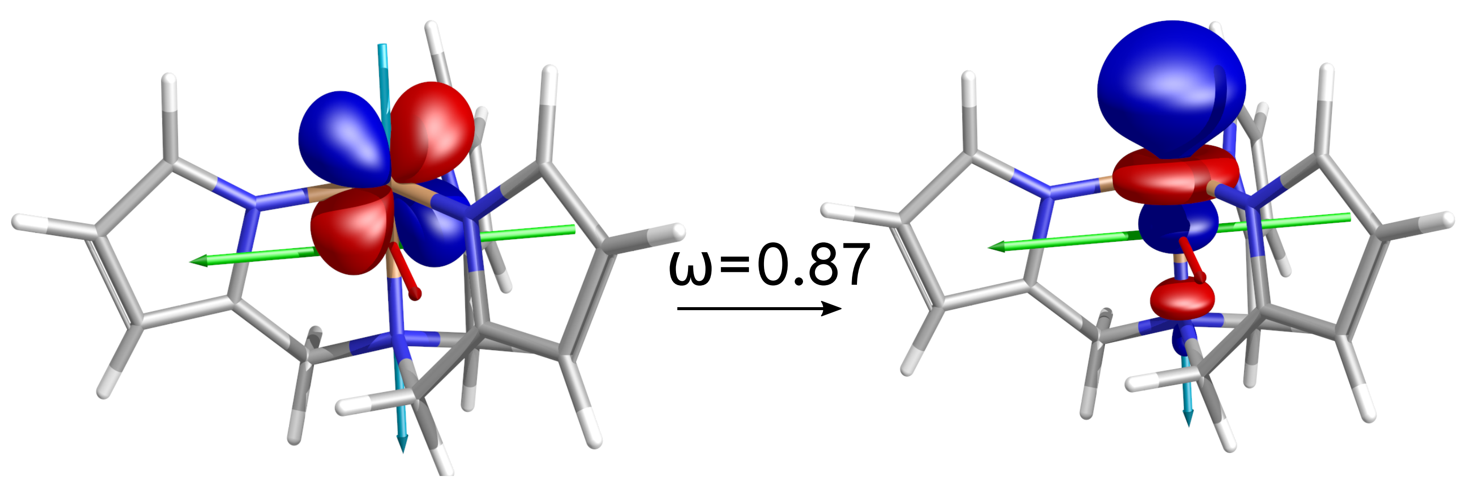
El-Sayed rules: large SOC is achieved when the orientation of p-orbitals changes, e.g. px → pz.

El-Sayed, Acc. Chem. Res. **1** 8 (1968); Salem, Rowland, Angew. Chem. Int. Ed. **11** 92 (1972).

- NTOs show different change in angular momentum - different SOC;
- Quantitative MO picture of the SOC: El-Sayed rules distilled from many-body wave-functions (EOM-EA-MP2) explain difference in spin-reversal barriers.

Summary:

1. Ansatz-agnostic formalism and implementation of SOC: can be used for any method that can produce one-particle transition DM for one multiplet component.
   - Available for all EOM-CC/MP2, CVS-EOM, RASCI, (SF)-TDDFT;
   - Includes 2-el part via SOMF (cheap and accurate).
2. Analysis of SOCs in terms of spinless DMs and their NTOs - molecular orbital picture and insight.
3. Protocol for computing macroscopic observables - direct connection with the experiments.



Pokhilko, Epifanovsky, Krylov, JCP **151** 034106 (2019); Vidal, Pokhilko, Krylov, Coriani, JPCL **11** 8314 (2020); Carreras, Jiang, Pokhilko, Krylov, Zimmerman, Casanova, JCP **153** 214107 (2020); Alessio, Krylov, JCTC **17** 4225 (2021).

Methodological challenges and solutions

1. Robust and accurate black-box treatment of open-shell species:
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2. Compute and analyze spin-related properties:
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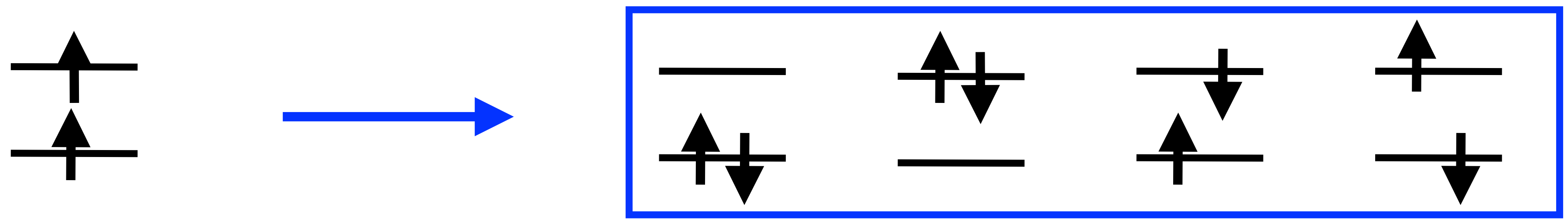
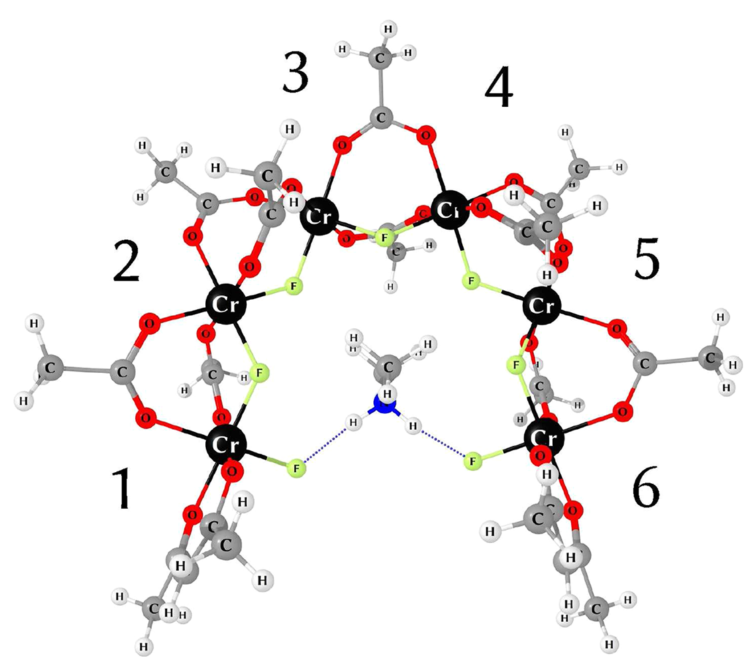
3. From molecules to materials:
    - effective Hamiltonian approach for coarse-graining strong correlation.

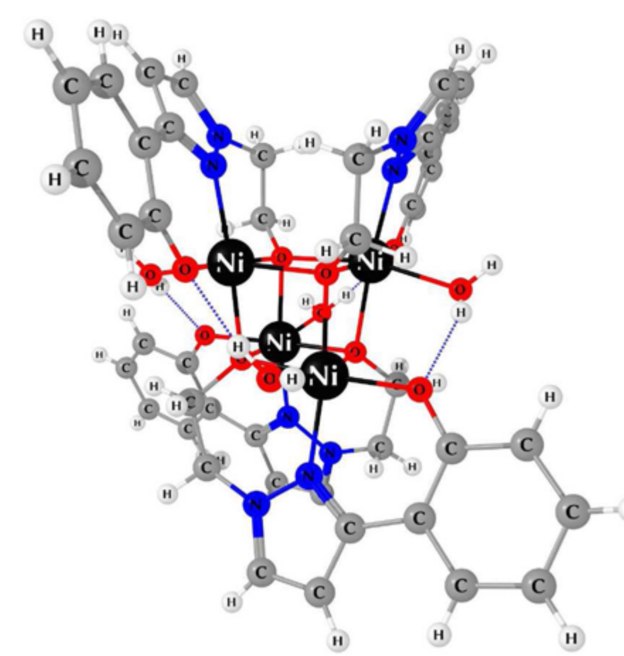
How do we tackle systems with more than 3 unpaired electrons?



1. Use multiple spin-flips: Works, but leads to cost/scaling increase.
2. Mayhall and Head-Gordon approach: Use single spin-flip calculation to parameterize a model Hamiltonian (e.g., Heisenberg) and solve coarse grained problem to find the entire manifold of states.

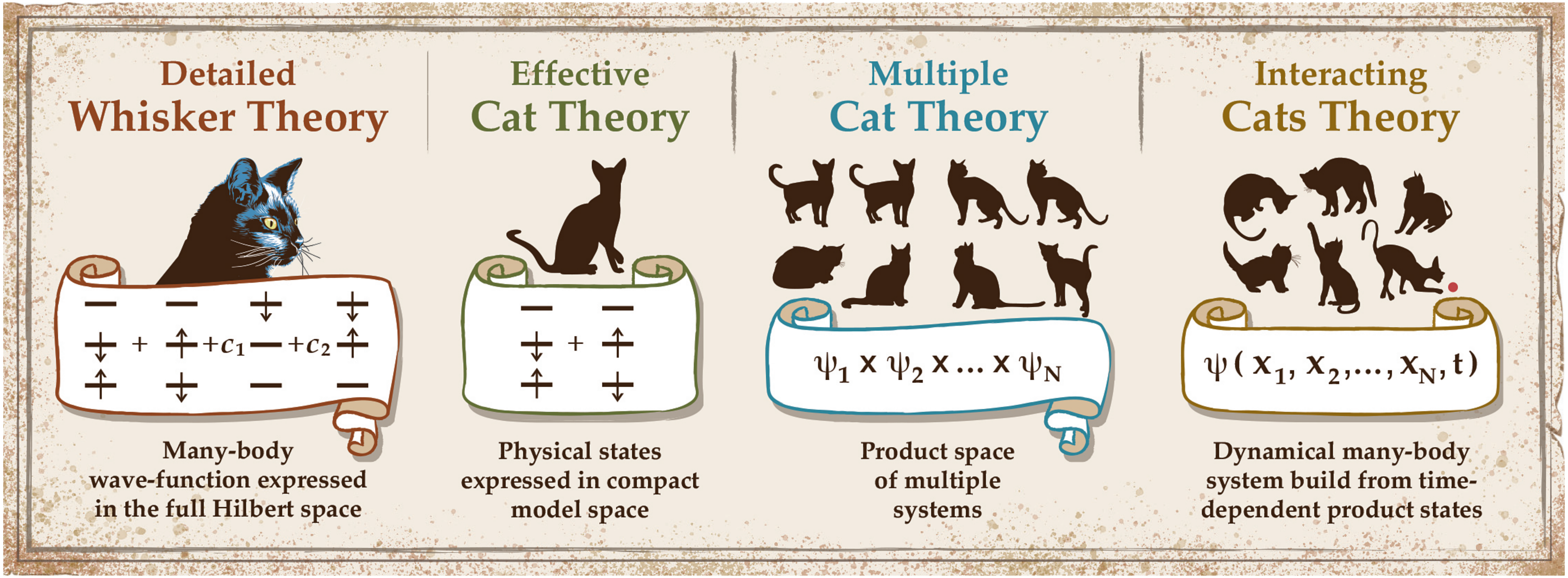
$$\hat{H} = -\sum_{ij} J_{ij}\hat{S}_i\hat{S}_j$$





Mayhall and Head-Gordon, JCP **141** 134111 (2014); Mayhall and Head-Gordon, JPCL **6** 1982 (2015).

Effective Hamiltonians approach: A way to coarse-grain strong correlation



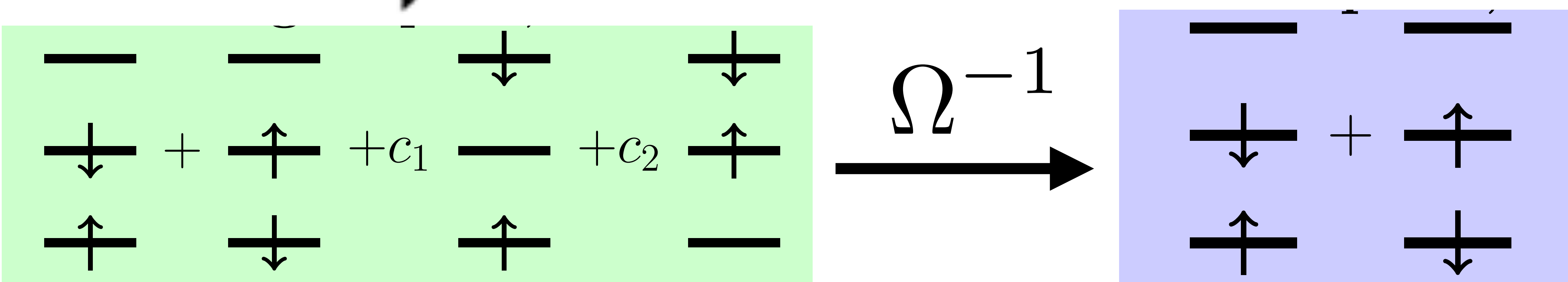
Graphics from: Clark, Adams, Hernandez, Krylov, Niklasson, Sarupria, Wang, Wild, Yang, ACS Central Sci. **7** 1271 (2021) - inspired by Pavel Pokhilko's PhD thesis.

Effective Hamiltonians derived from equation-of-motion coupled-cluster wave-functions

$$H\Omega P_0 = \Omega P_0 H^{eff} P_0$$

Detailed whisker theory

Effective cat theory



EOM-CC wave-function (SF, DIP, etc)

Heisenberg Hamiltonian

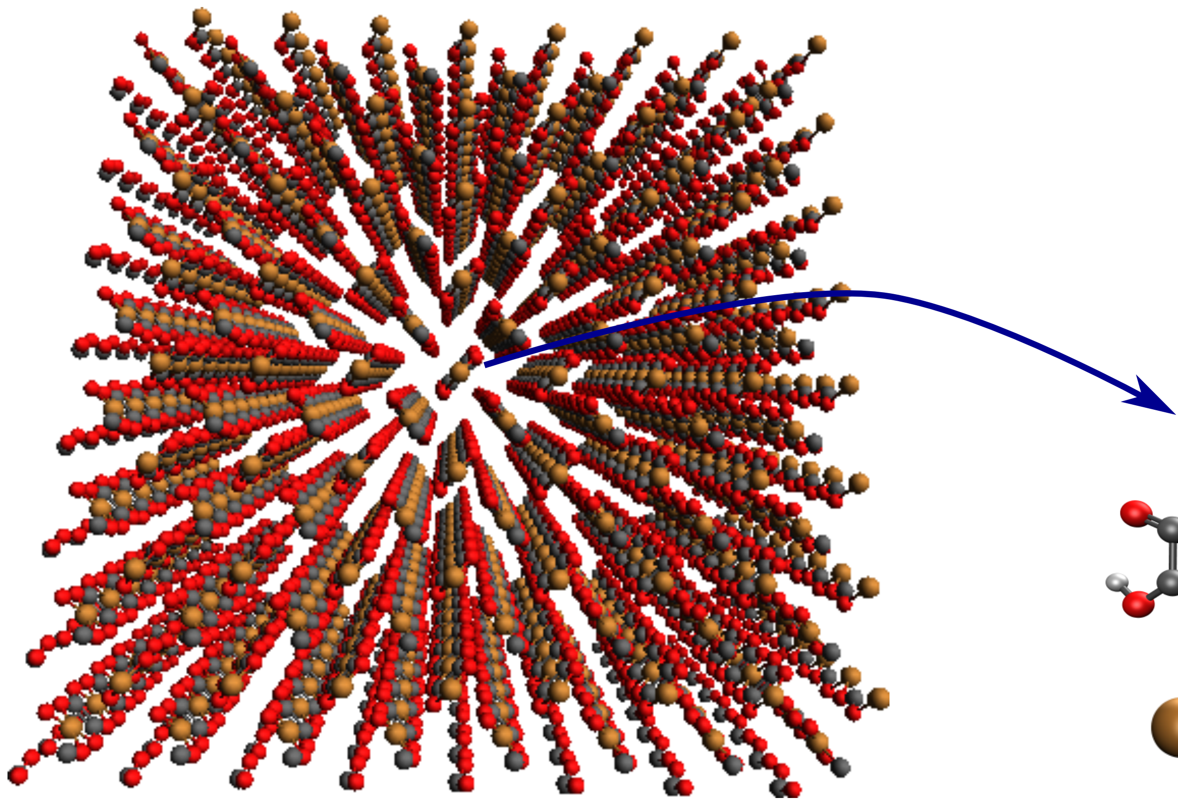
$$H_{Heis} = -\sum_{A<B} J_{AB}\mathbf{S}_A\mathbf{S}_B$$

Same energies by construction + diagnostic of the validity via generalized overlap

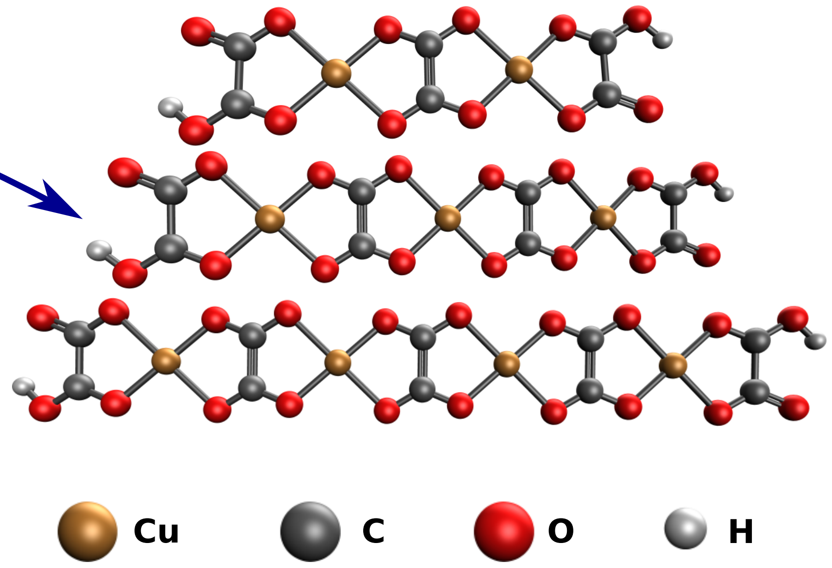
Mayhall and Head-Gordon, JCP **141** 134111 (2014); Mayhall and Head-Gordon, JPCL **6** 1982 (2015); Pokhilko and Krylov, JCP **152** 094108 (2020).

Example: Thermodynamic properties of strongly correlated infinite spin chains from first principles

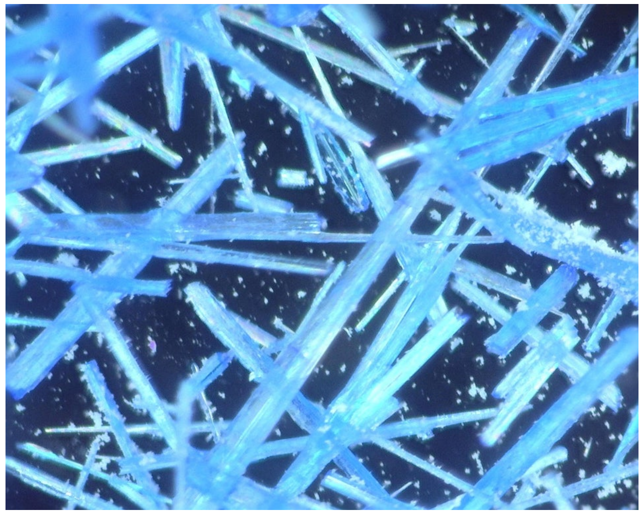
Dr. Pavel Pokhilko

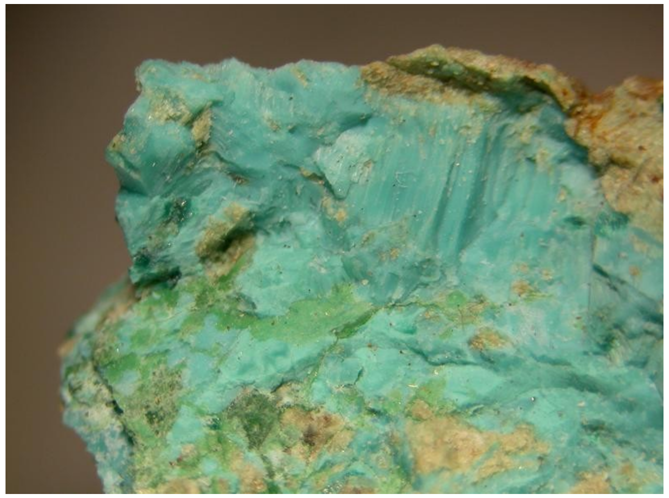


Copper oxalate crystal



Cu(II): d^9

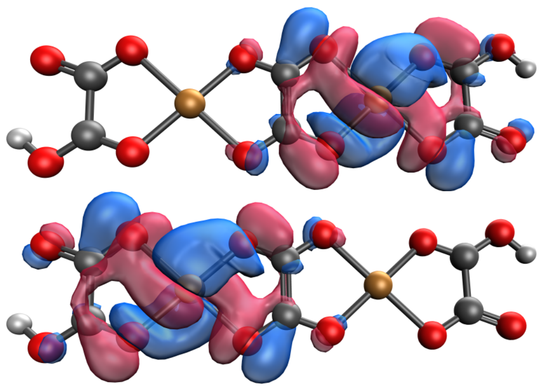


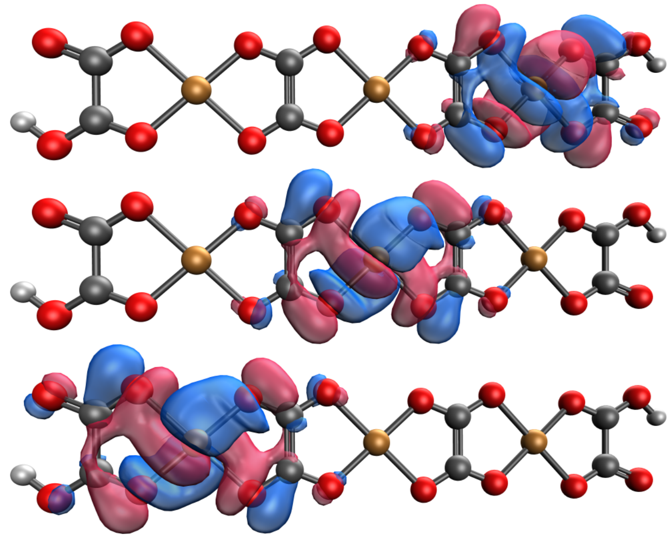


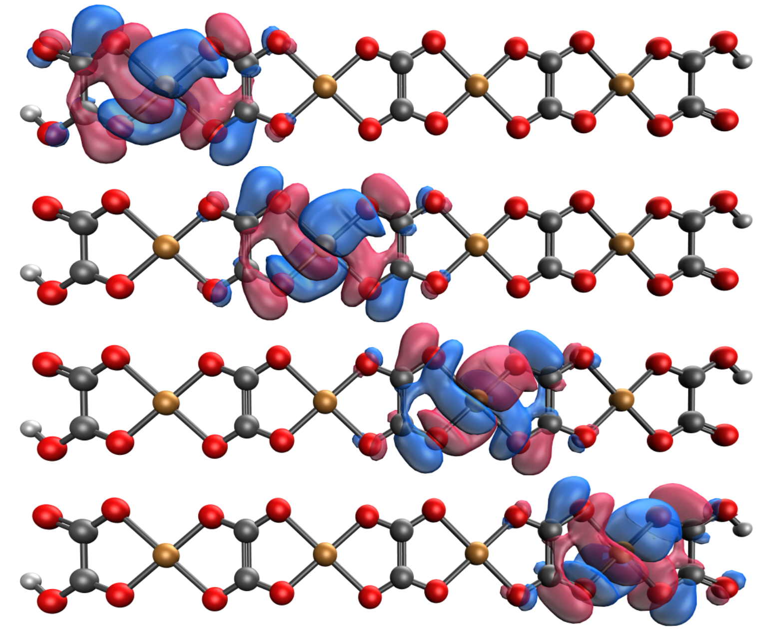
Moolooite

Pokhilko, Bezrukov, Krylov, JPCC **125** 7502 (2021).

Spin chains in copper oxalate: convergence of effective exchange







	OS	OS
OS	0.79	88.52
OS	88.52	-0.79

	OS	OS	OS
OS	26.45	88.43	0.19
OS	88.43	-54.79	88.30
OS	0.19	88.30	28.34

	OS	OS	OS	OS
OS	40.36	88.67	0.34	0.62
OS	88.67	-40.72	89.04	0.36
OS	0.34	89.04	-40.19	88.63
OS	0.62	0.36	88.63	40.55

- Nearest-neighbor Heisenberg Hamiltonian can be used:

$$H_{Heis} = -\sum_{A<B} J_{AB}\mathbf{S}_A\mathbf{S}_B \longrightarrow H = -J\sum_i \mathbf{S}_i\mathbf{S}_{i+1}$$

- Effective J converges fast: two-center model is sufficient.

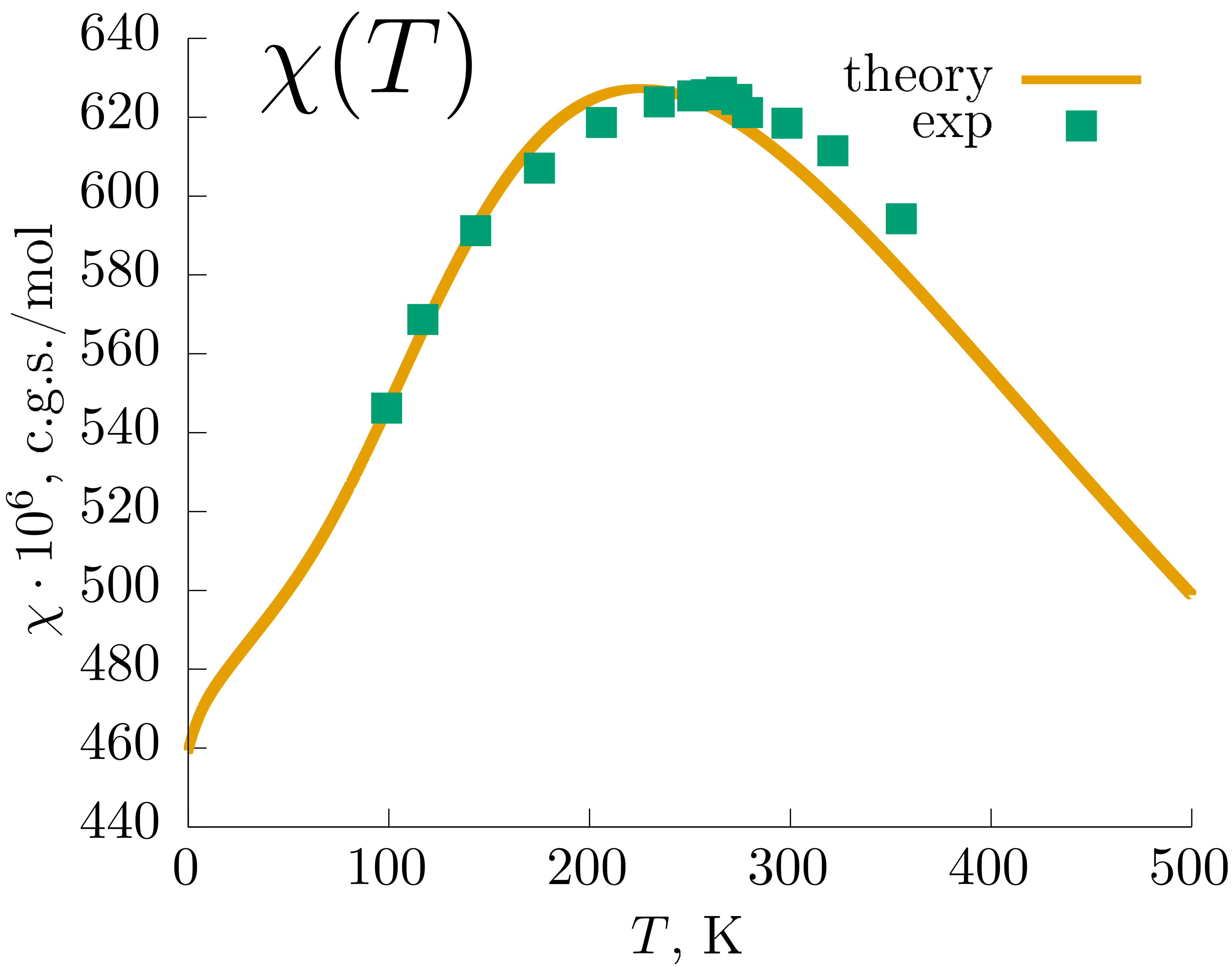
Spin chains in copper oxalate

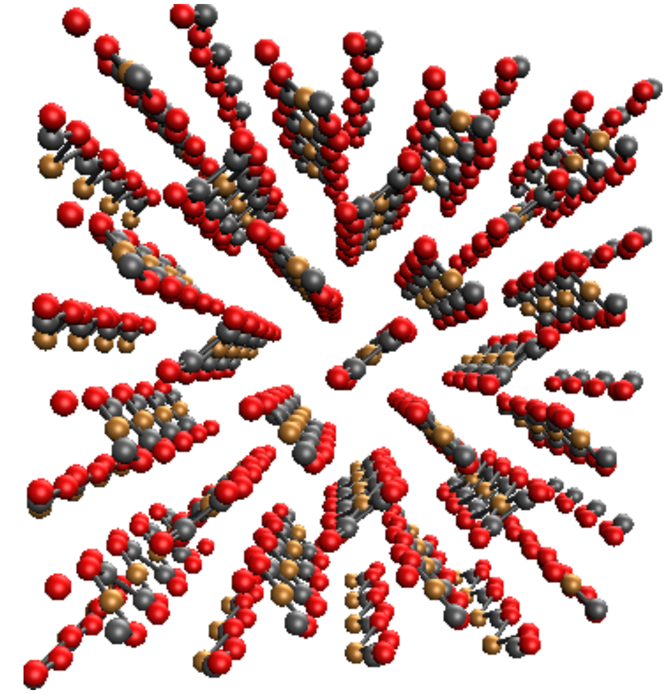
	Delta J	$\|J\|$, cm^{-1}
2-Cu		177.0
3-Cu	-0.1	176.9
4-Cu	1.2	178.1
triples	42.7	220.8
SOC	32.0	252.8
basis	-8.5	244.3

- Both strong and week correlations are important;
- SOC gives substantial contributions.

Methods: Energies by EOM-SF-CCSD/cc-pVDZ; SOCs by EOM-DIP-CCSD; Basis: cc-pVDZ->cc-pVTZ.

Spin chains in copper oxalate

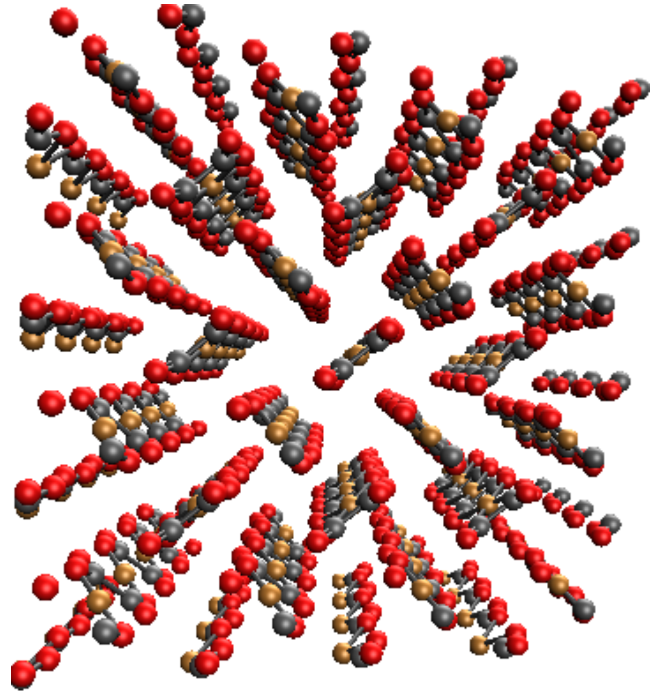


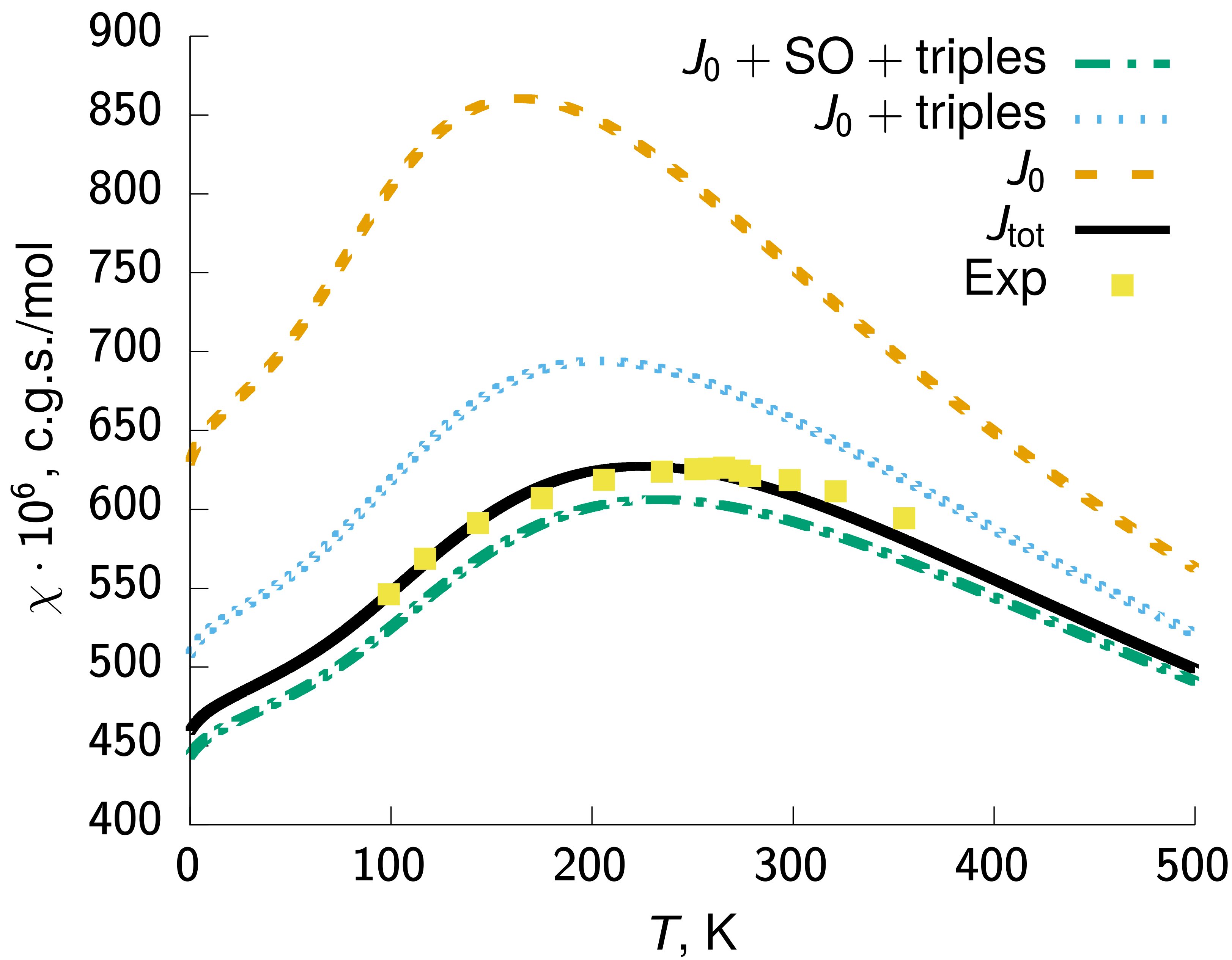


Excellent agreement with experiment!

Dubicki, Harris, Kokot, Inorg. Chem. **5** 93 (1966).

Spin chains in copper oxalate

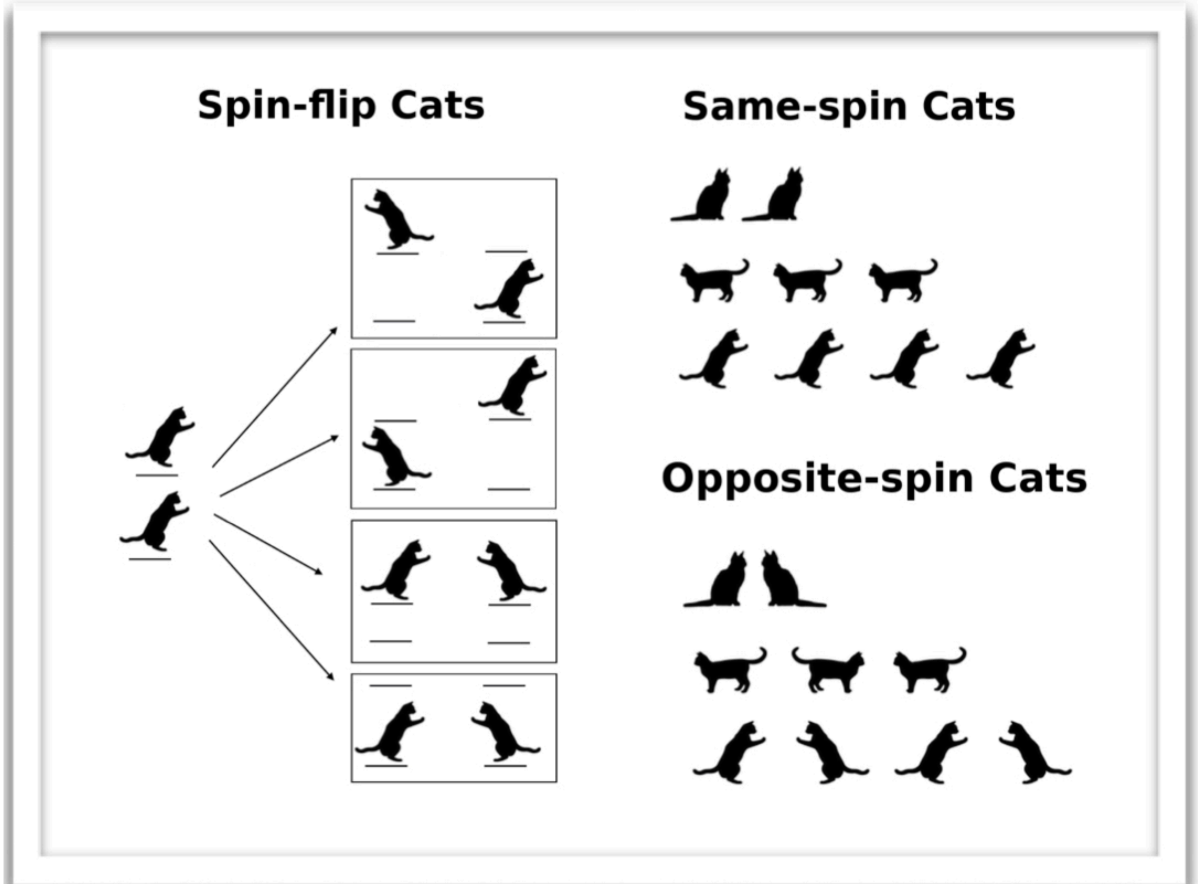




Systematic convergence: Right answer for the right reason!

Conclusions

1. SF approach treats strong correlation in a single-reference framework.
2. NOs and NTOs: A vehicle for understanding complex electronic structure.
3. Effective Hamiltonians extend the SF approach to large (and even infinite) systems.



"Chemistry with Cats: From Schrödinger's Paradox to Quantum Computing" on HxSTEM substack