Targeting Real chemical accuracy at the EXascale

Some peculiarities of spin-adaptation in quantum chemistry: the impact of orbital ordering

aka

Compact description of strongly correlated spin systems

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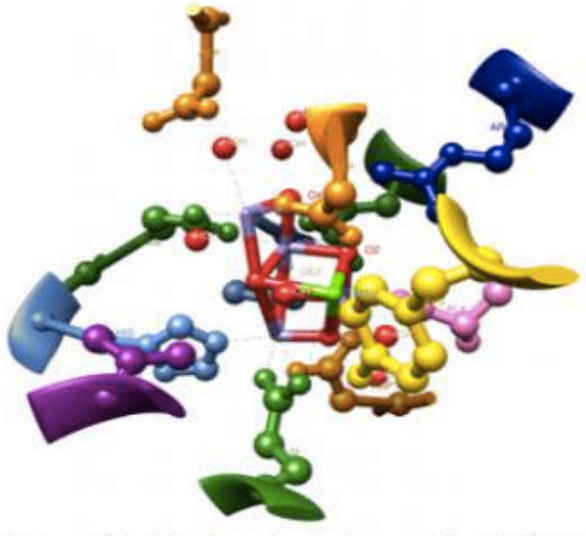
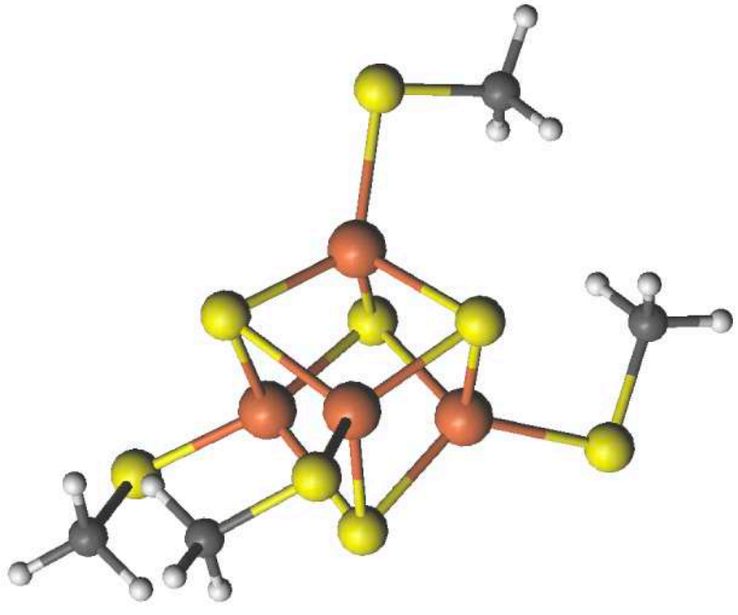
Polynuclear 3d transition metal complexes

There are numerous important biological catalysts whose active sites contain **multiple magnetic centres (eg Fe,Mn,Co ions), typically arranged in a cubane configuration with O or S bridging ligands.**

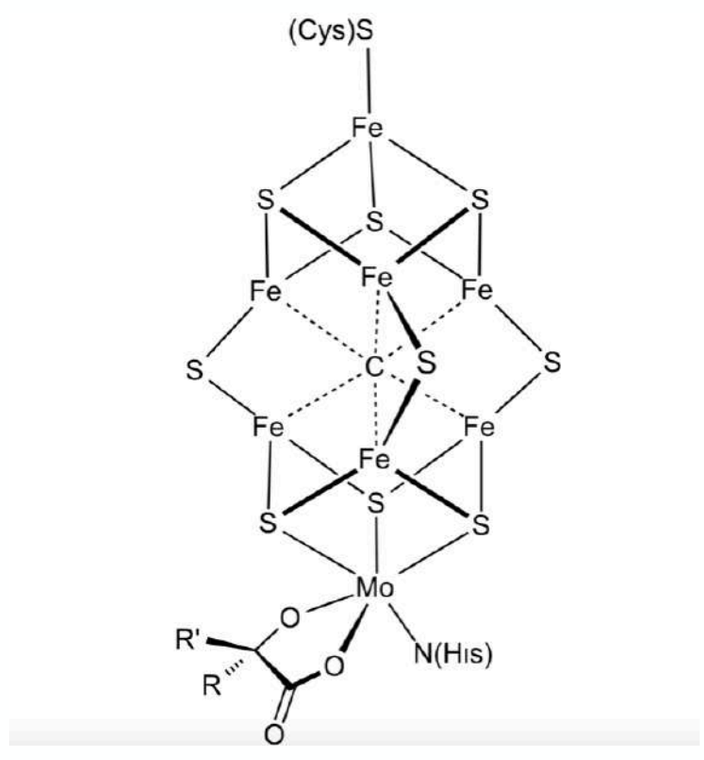
There molecules are implicated in **electron transport** and catalysis of **spin-forbidden reactions** (water splitting). Others are involved in nitrogen splitting (nitrogenase)



{Mn_4O_5Ca} cluster @ PSII



[Fe4S4]



Challenges

- Although the magnetic centres are high-spin (for example S=5/2 in the case of Fe(III)), the overall spin of is low. These are examples of extreme **multi-reference** systems.
- There is typically strong **anti-ferromagnetic** coupling between the magnetic sites, induced by various **exchange** and **super-exchange** mechanisms, which involve the ligands
- The cubane structure implies **frustration** in the magnetic interactions.
- There is a complex low-energy spectrum, with small gaps between states with the same low spin, and also between different spins. **These are hallmarks of strong electron correlation.**
- The structures of the molecules are distorted, indicative of Jahn-Teller effects. Nuclear dynamics is quite possibly non-adiabatic.

What do we want to understand?

- There are two levels of description we are after:
- On the one hand, a detailed **ab initio** description, starting from the Schrödinger equation, would seem desirable, but this is not sufficient for such complex systems. We might get accurate numbers, but what about understanding?
- Phenomenologically, these systems are described by **spin models**, such as Heisenberg models and extensions

$$\hat{H}_{Heisenberg+} = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{ijkl} K_{ijkl} (\mathbf{S}_i \cdot \mathbf{S}_j)(\mathbf{S}_k \cdot \mathbf{S}_l)$$

The exchange parameters J_{ij}, K_{ijkl} are to be obtained from ab initio calculations

The typical energy scale of the J are on the order of a few tens meV

Spin degeneracy

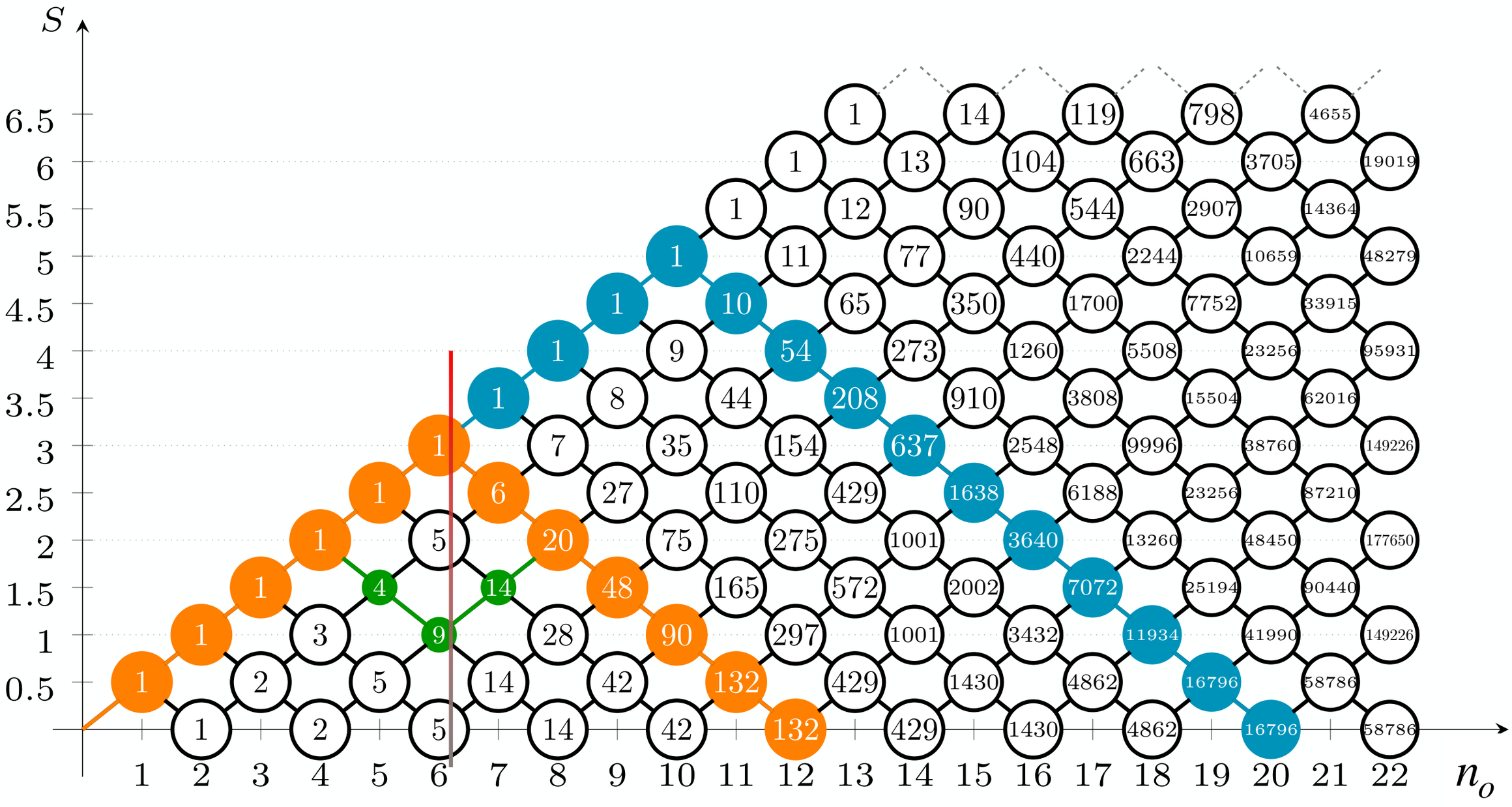
- **Low-spin open-shell** systems represent extreme examples of multi-reference wave functions, with a high degree of **spin-degeneracy**
- The multi-reference character of a wave function can be assessed via the so-called van-Vleck-Sherman formula, that gives the number of open-shell spin-eigenfunctions (with n_o open-shell orbitals and spin S) that can be constructed

$$g(n_o, S) = \binom{n_o}{n_o/2 - S} - \binom{n_o}{n_o/2 - S - 1}.$$

In a system with n_O open-shell electrons, the ground-state wavefunction with spin S consists of $g(n_O, S)$ leading CSFs

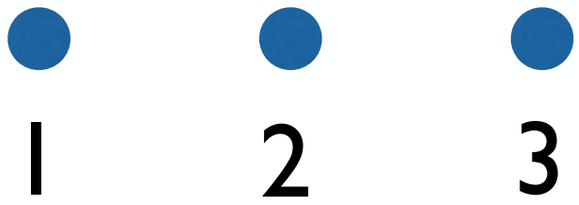
The expected spin-degeneracy in cubanes from the Van-Vleck-Sherman Formula

For a Fe(III) cubane, there are 20 open-shell electrons



Heisenberg Spin Chain

$$\hat{H} = J(\hat{\mathbf{S}}_1 . \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_2 . \hat{\mathbf{S}}_3)$$



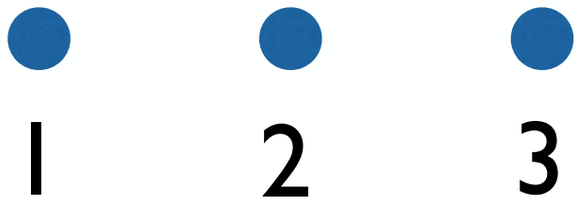
The two S=1/2, Ms=1/2 CSFs are:

$$|uud\rangle = \frac{1}{\sqrt{6}}\left(2|\uparrow\uparrow\downarrow\rangle - |(\uparrow\downarrow + \downarrow\uparrow)\uparrow\rangle\right)$$

$$|udu\rangle = \frac{1}{\sqrt{2}}|(\uparrow\downarrow - \downarrow\uparrow)\uparrow\rangle$$

Heisenberg Spin Chain

$$\hat{H} = J(\hat{\mathbf{S}}_1 . \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_2 . \hat{\mathbf{S}}_3)$$



It is implicity assumed that the spins are coupled in “natural order”

$$|u_1 u_2 d_3\rangle = \frac{1}{\sqrt{6}}\left(2|\uparrow_1 \uparrow_2 \downarrow_3\rangle - |(\uparrow_1 \downarrow_2 + \downarrow_1 \uparrow_2)\uparrow_3\rangle\right)$$

$$|u_1 d_2 u_3\rangle = \frac{1}{\sqrt{2}}|(\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2)\uparrow_3\rangle$$

“Natural order”

Consider the action of a permutation operator

$$P_{23}\,|\,u_1u_2d_3\rangle = |\,u_1u_3d_2\rangle$$

$$= \frac{1}{\sqrt{6}}\left(2|\uparrow_1\uparrow_3\downarrow_2\rangle - |(\uparrow_1\downarrow_3 + \downarrow_1\uparrow_3)\uparrow_2\rangle\right)$$

$$= -\frac{1}{2}\,|\,u_1u_2d_3\rangle + \frac{\sqrt{3}}{2}\,|\,u_1d_2u_3\rangle$$

$$P_{23}\,|\,u_1d_2u_3\rangle = |\,u_1d_3u_2\rangle$$

$$= \frac{\sqrt{3}}{2}\,|\,u_1u_2d_3\rangle + \frac{1}{2}\,|\,u_1d_2u_3\rangle$$

The action of permutation operators is to generate unitary transformations of the CSFs!

Why is this interesting?

$$\hat{H} = J(\hat{\mathbf{S}}_1 . \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_2 . \hat{\mathbf{S}}_3)$$

$$H^{123} = -\begin{pmatrix} \frac{5}{4} & \frac{\sqrt{3}}{4} \\ \frac{\sqrt{3}}{4} & \frac{3}{4} \end{pmatrix},$$

Expressed in terms of the “132” CSF basis

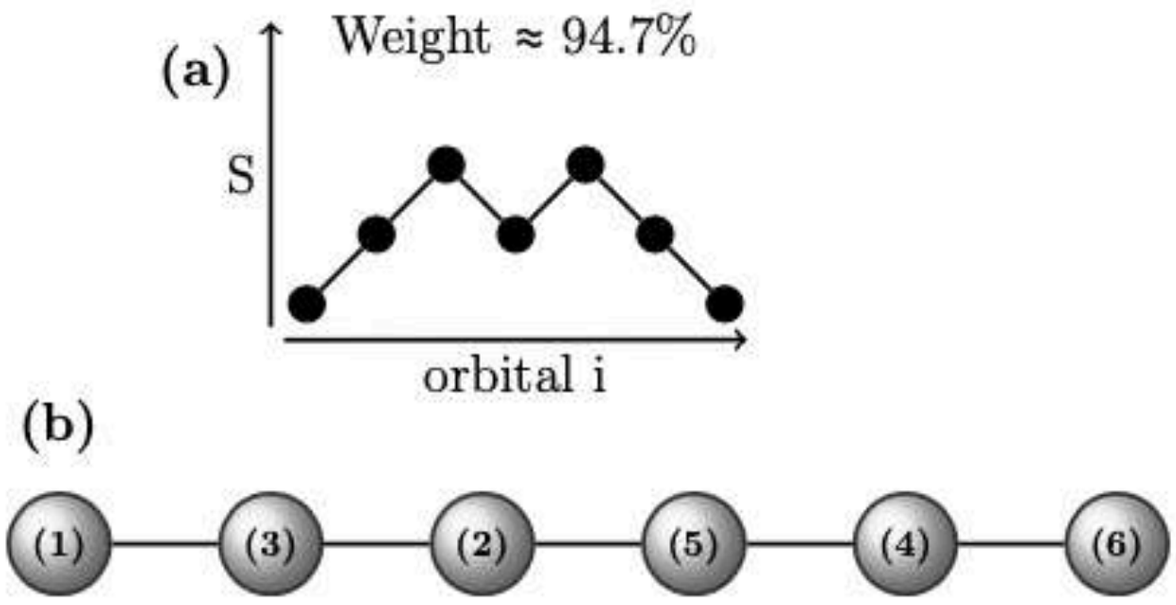
$$H^{132} = \begin{pmatrix} -\frac{3}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix}.$$

i.e. through a simple process of re-ordering we have diagonalised the Hamiltonian!

What happens in longer chains?

TABLE I. 6-site orderings and leading CSF weights.

Order		Ref. CSF	CI coefficient [%] PBC	OBC
Natural	1-2-3-4-5-6	$\|u_1 d_2 u_3 d_4 u_5 d_6\rangle$	77.9	92.2
Bipartite	1-3-5-2-4-6	$\|u_1 u_3 u_5 d_2 d_4 d_6\rangle$	95.7	89.9
Compact	1-3-2-5-4-6	$\|u_1 u_3 d_2 u_5 d_4 d_6\rangle$	97.1	94.7
SDs Néel state		$\|\uparrow_1\downarrow_2\uparrow_3\downarrow_4\uparrow_5\downarrow_6\rangle$	47.9	44.9



Propagating a doublet “meta-spin" down the chain

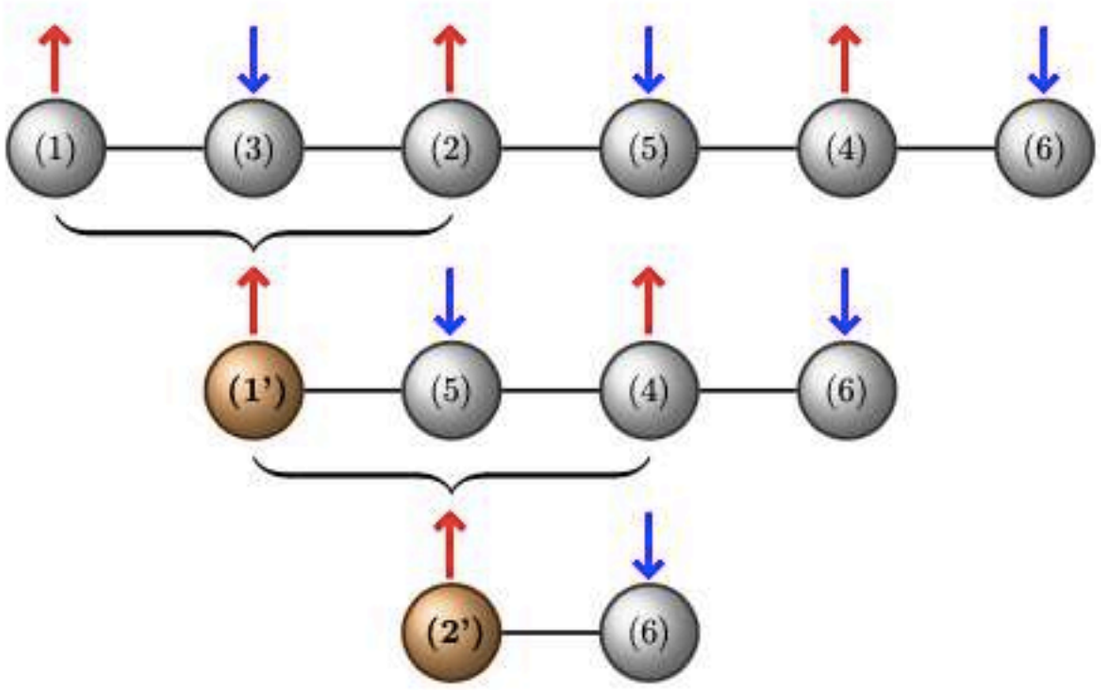
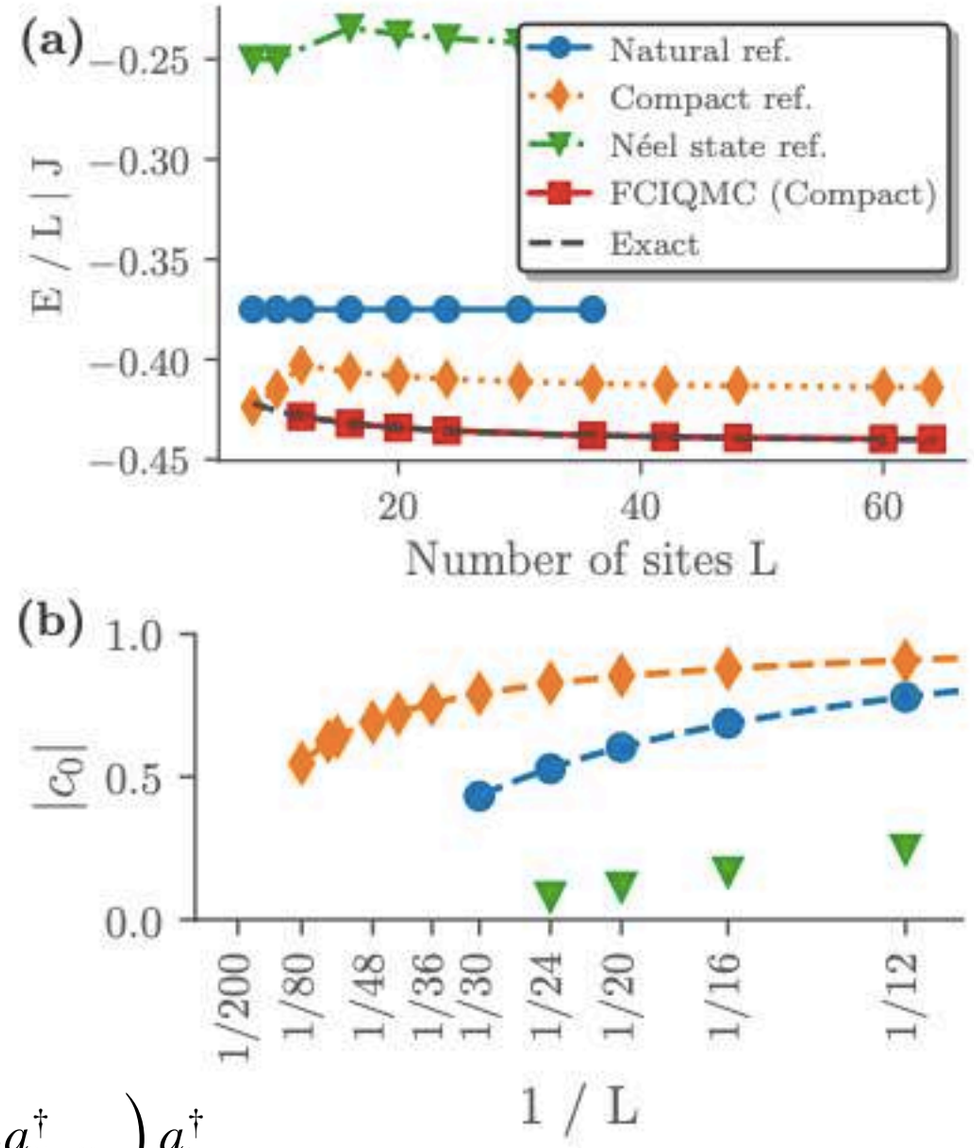


FIG. 2. Cumulative doublet coupling of “meta-spin-$\frac{1}{2}$” in the most compact order.



$$\psi_{i\sigma} = C_{\sigma}^{uud}\psi_{(i-2)\sigma}a^{\dagger}_{(i-1)\sigma}a^{\dagger}_{i\bar{\sigma}} + C_{\sigma}^{udu}\left(\psi_{(i-2)\sigma}a^{\dagger}_{(i-1)\bar{\sigma}} + \psi_{(i-2)\bar{\sigma}}a^{\dagger}_{(i-1)\sigma}\right)a^{\dagger}_{i\sigma}$$

Dobrautz et al, Phys Rev B **105**, 195123 (2022)

Spin-Spin correlation functions

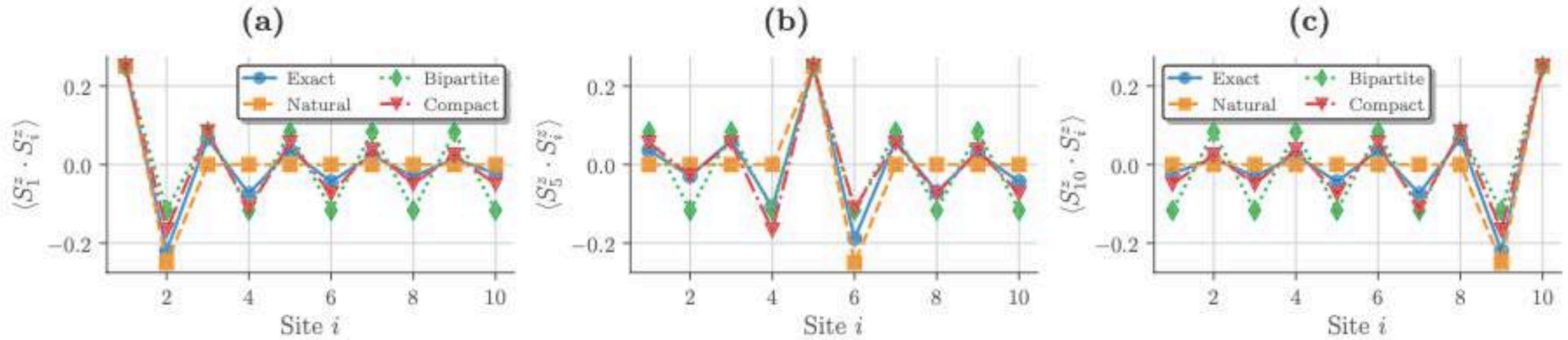


FIG. 5. (a) $\langle S_1^z \cdot S_x^z \rangle$, (b) $\langle S_5^z \cdot S_x^z \rangle$, and (c) $\langle S_{10}^z \cdot S_x^z \rangle$ exact and single-CSF spin-spin correlation functions for the 10-site chain with OBC.

Development of spin-adapted GUGA-FCIQMC

Dobrautz, Smart, Alavi, J. Chem. Phys. 151, 094104 (2019)

Spin adaptation is exact imposition of $[\hat{H}, \hat{S}^2] = 0$

$$\hat{H} = \sum_{ij} t_{ij} \hat{E}_{ij} + \frac{1}{2} \sum_{ij,kl} V_{ij,kl} \hat{e}_{ij,kl} \,.$$

Spin-summed Excitation operators:

$$\sum_{\sigma} a^{\dagger}_{i\sigma} a_{j\sigma} = \hat{E}_{ij}$$

$$\sum_{\sigma\tau} a^{\dagger}_{i\sigma} a^{\dagger}_{k\tau} a_{l\tau} a_{j\sigma} = \hat{E}_{ij}\hat{E}_{kl} - \delta_{jk}\hat{E}_{il} = \hat{e}_{ij,kl} \,.$$

$$[\hat{E}_{ij}, \hat{E}_{kl}] = \delta_{jk} \hat{E}_{il} - \delta_{il} \hat{E}_{kj}$$

…which satisfy the commutation relations of the generators of the unitary group U(n)

Moshinsky 1968, Paldus 1974

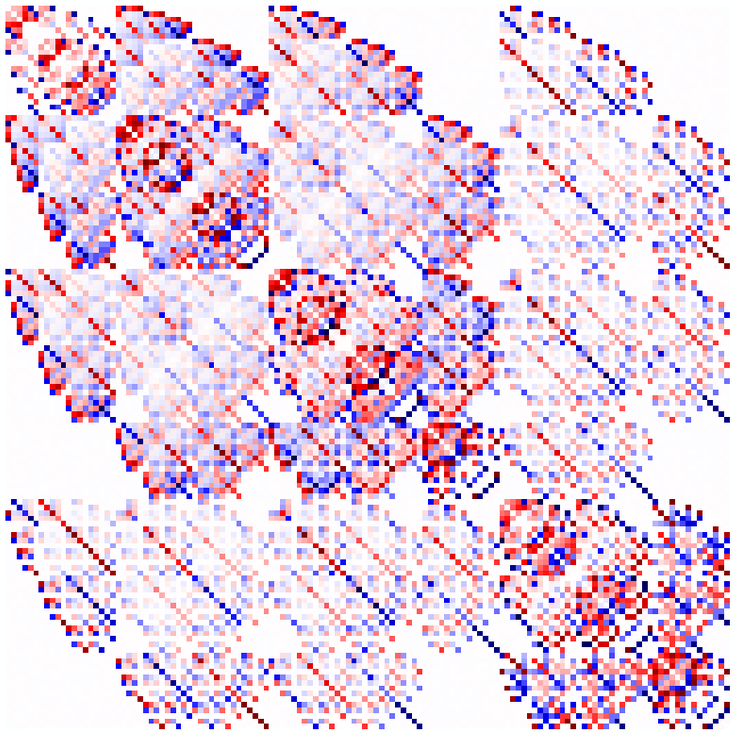
Acting with this H enables one to dynamically preserve SU(2) symmetry, i.e. the spin, of the stochastically evolving wave function.

Extremely powerful approach for systems with small spin gaps - typical of many strongly correlated systems.

Block diagonalisation of UGA-represented Hamiltonian using appropriately ordered orbitals

UGA Hamiltonian matrix of the S=0 sector of a model of 4 separated N atoms (S_A=3/2) in an expanded tetrahedral geometry

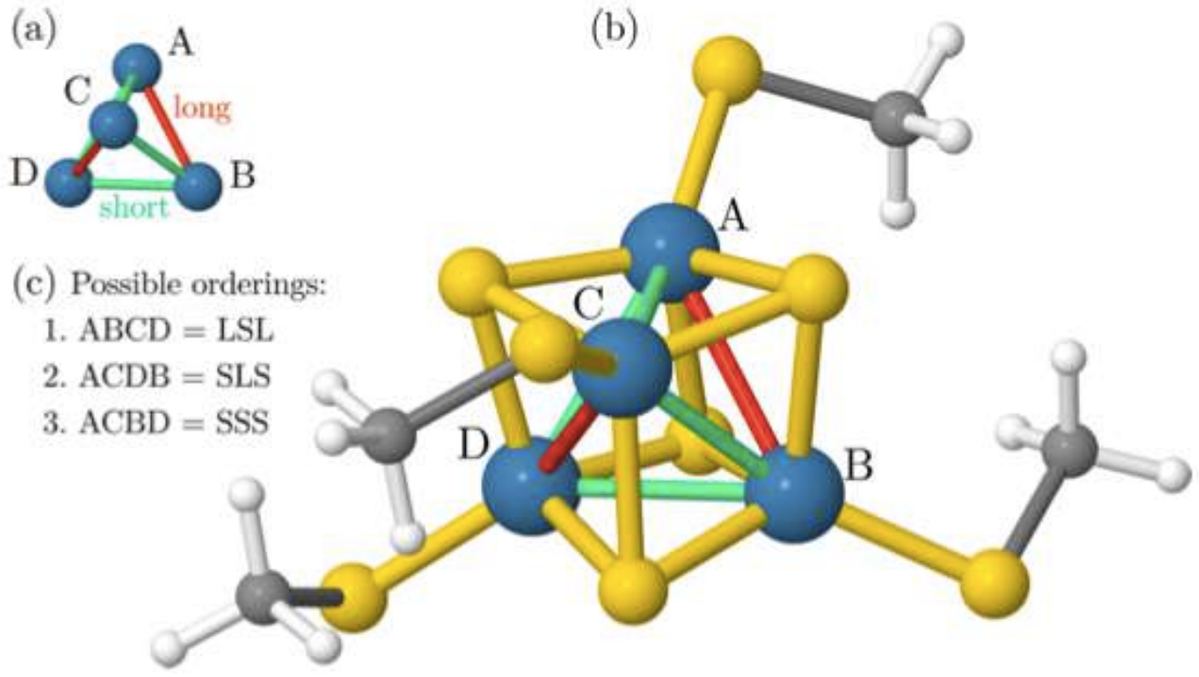
$$p_x^A p_x^B p_x^C p_x^D p_y^A \ldots p_z^D$$

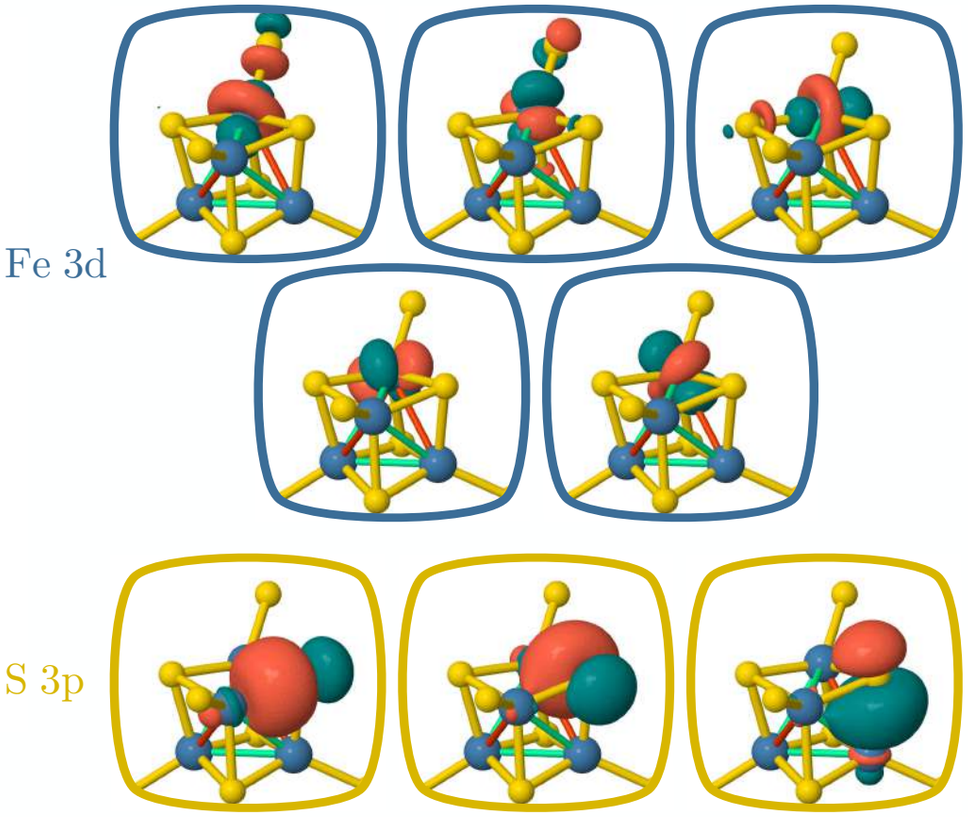


$$p_x^A p_y^A p_z^A p_x^B p_y^B p_z^B \ldots p_z^D$$

[Fe(III)$_4$S$_4$] complexes

Electron transfer catalysts in biological systems

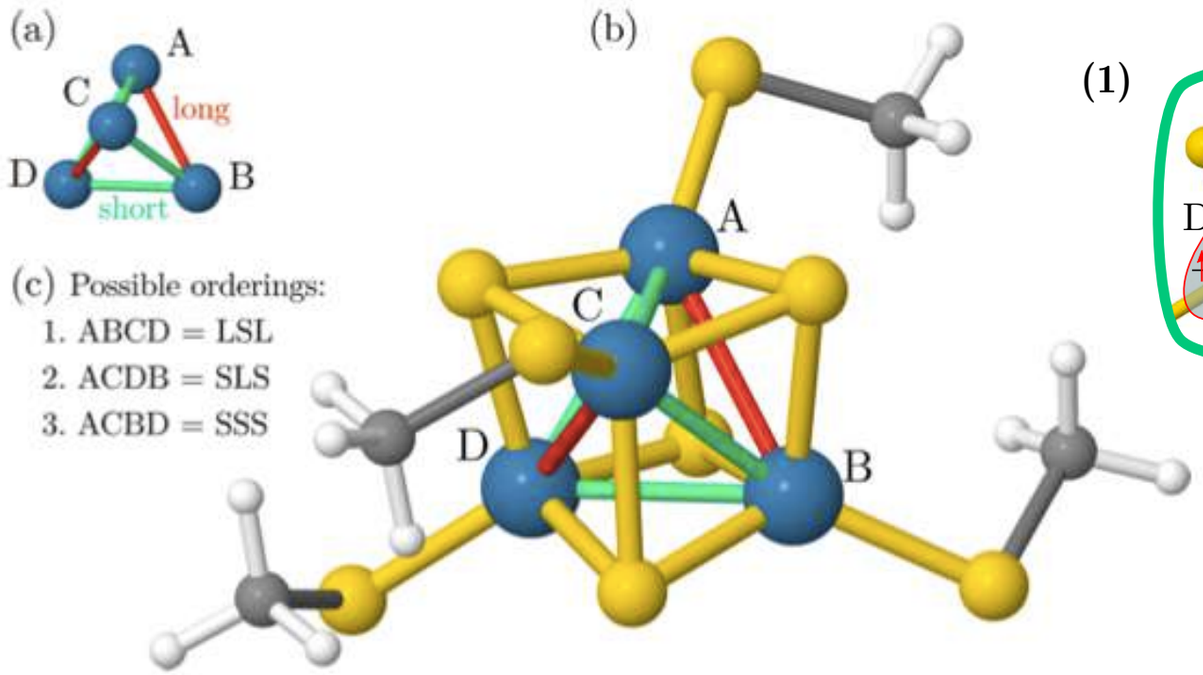


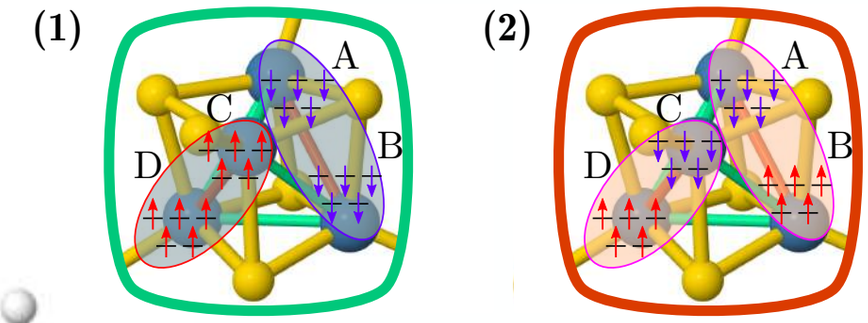


$[Fe(III)_4S_4]$ complexes

Electron transfer catalysts in biological systems, but also geometrically frustrated quantum antiferromagnets

Each centre is dominated by a high-spin d^5 configuration (S_A=5/2)





Internal dimer
can take $S = 0 \rightarrow 5$

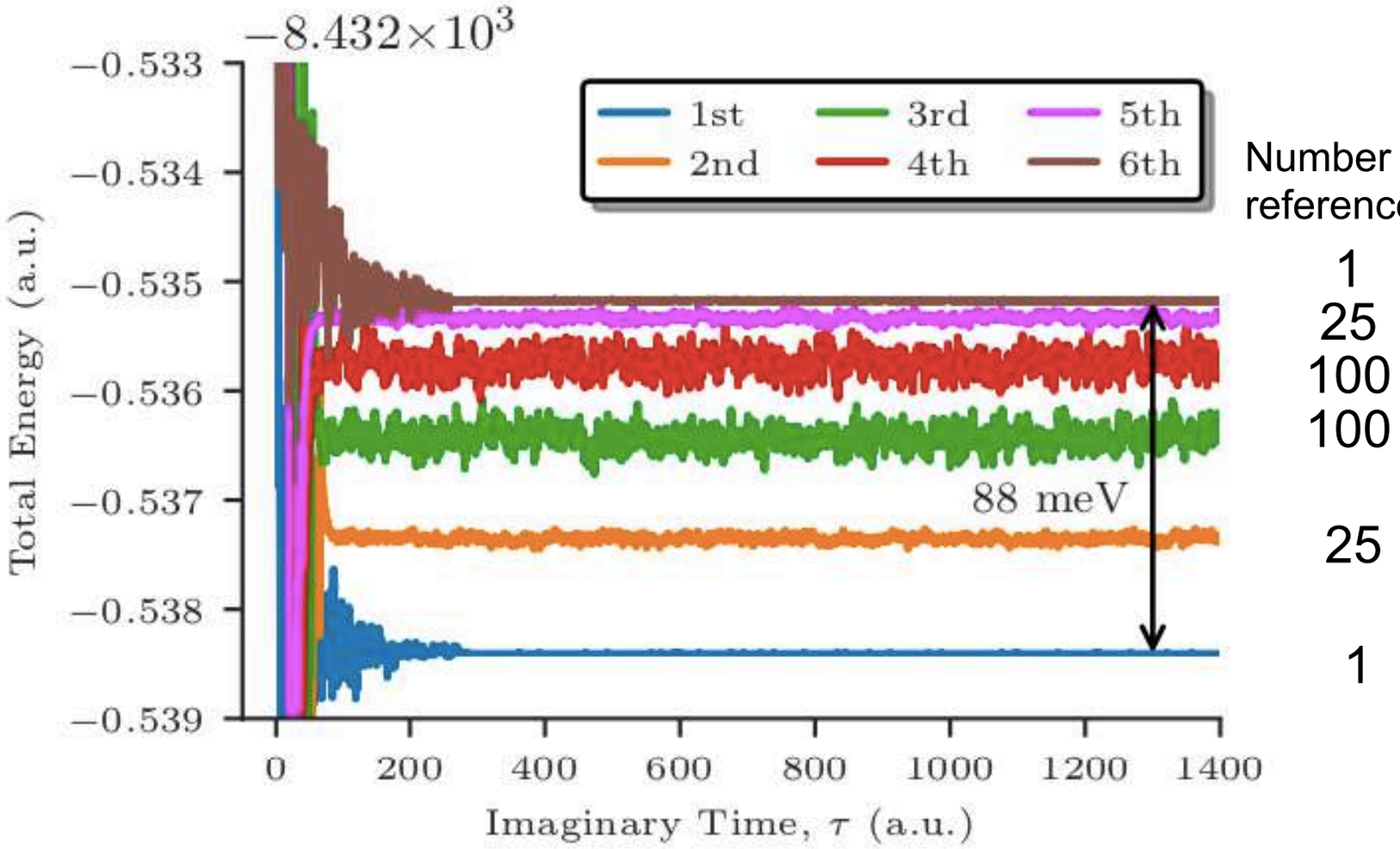
Correlating 3d electrons and orbitals only, number of determinants= $\binom{20}{10}^2 = 3 \times 10^{10}$

Including Sulfur 3p electrons and orbitals= $\binom{32}{22}^2 = 4 \times 10^{15}$

Application of GUGA-FCIQMC to [Fe(III)4S4]

Li Manni et al, J. Phys. Chem. A, **125**, 4727–4740 (2021)

6 lowest energy singlet states in complete-active-spaces of
CAS(20e,20o) [Fe 3d only] and CAS(44e,32o) [+S 3p]

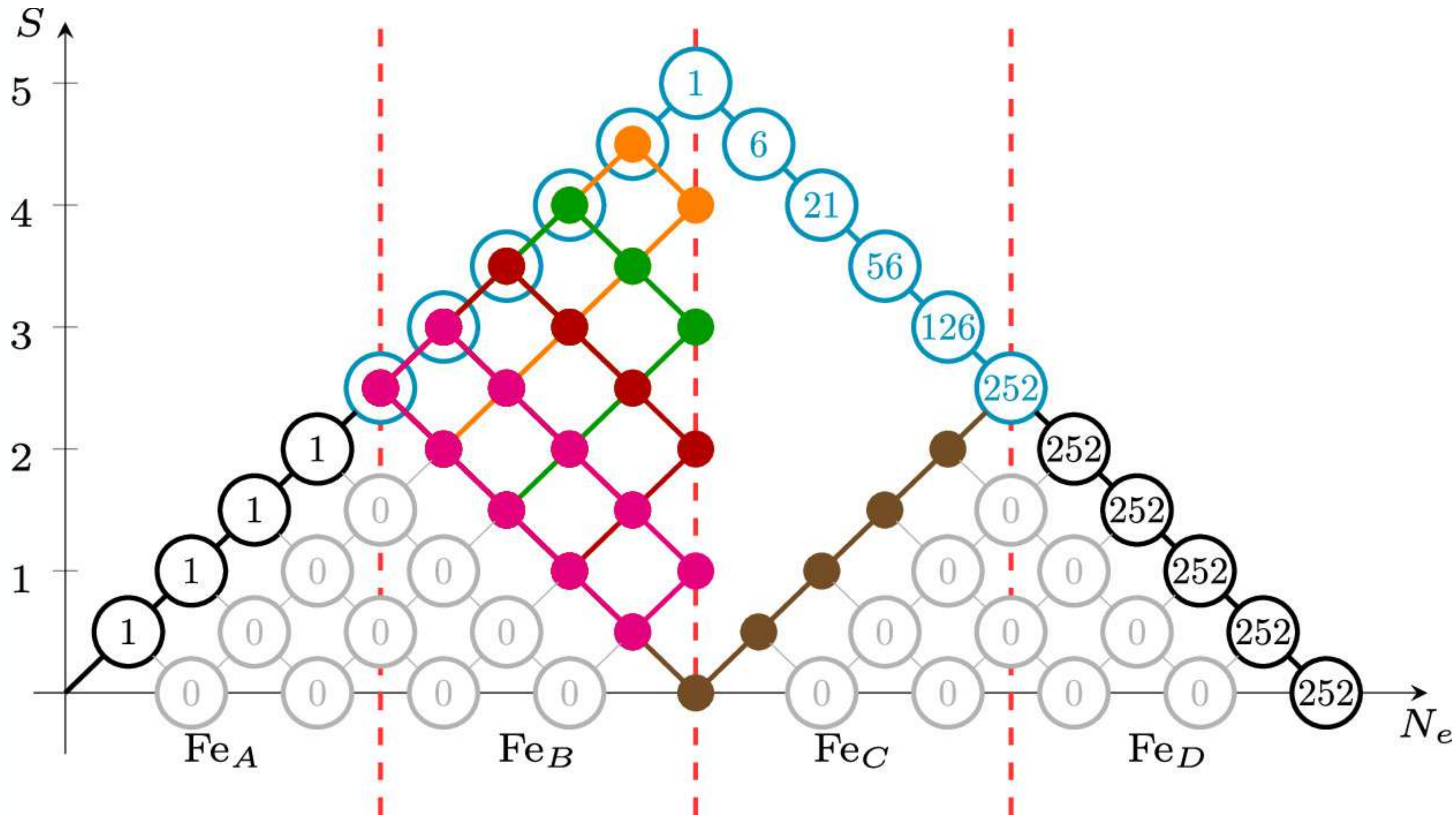


Number of reference CSFs

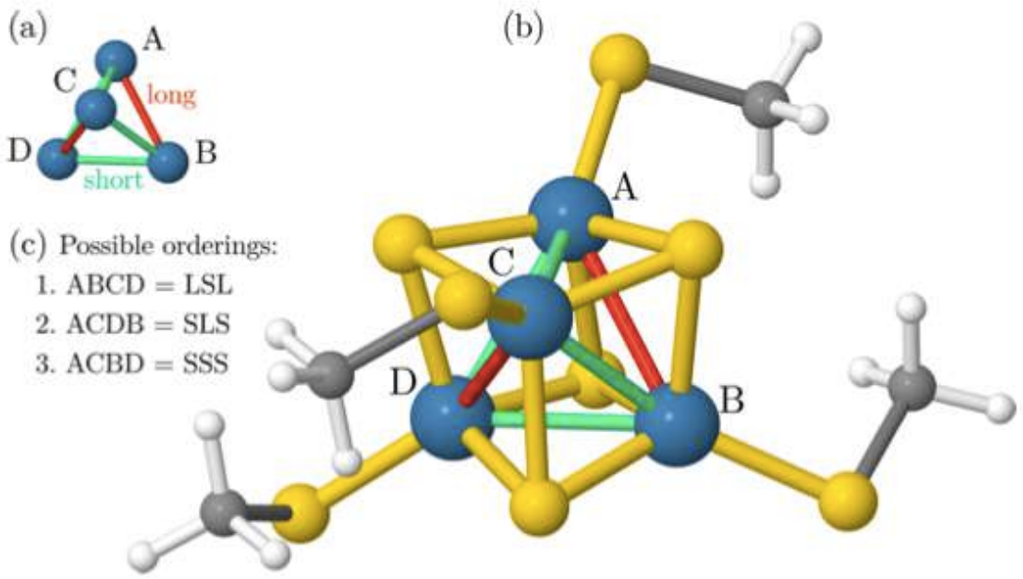
1
25
100
100
25
1

With the appropriate ordering of the orbitals, sorted by magnetic centres (ABCD), the *S*=0 ground state and 5th excited state turn out to be single reference!

Spin-branching diagram for the 4 Fe(III) centres



A (distorted) tetrahedral (S=5/2) Heisenberg spin system



$$\hat{\mathcal{H}}_{\mathrm{mod}} = J_{2\mathrm{B}}(\hat{\mathbf{S}}_{\mathbf{A}}\cdot\hat{\mathbf{S}}_{\mathbf{B}} + \hat{\mathbf{S}}_{\mathbf{C}}\cdot\hat{\mathbf{S}}_{\mathbf{D}}) + J_{4\mathrm{B}}(\hat{\mathbf{S}}_{\mathbf{A}}\cdot\hat{\mathbf{S}}_{\mathbf{D}} + \hat{\mathbf{S}}_{\mathbf{B}}\cdot\hat{\mathbf{S}}_{\mathbf{C}} + \hat{\mathbf{S}}_{\mathbf{A}}\cdot\hat{\mathbf{S}}_{\mathbf{C}} + \hat{\mathbf{S}}_{\mathbf{B}}\cdot\hat{\mathbf{S}}_{\mathbf{D}})$$

In case of the perfect tetrahedron $J_{4B} = J_{2B}$, the S=0 spin sector spans $A_1 \oplus A_2 \oplus 2E$, i.e. is six-fold degenerate (partly accidental).

The presence of the $2E$ states means that Jahn-Teller distortions with symmetry $(E \otimes E)_+ = A_1 \oplus E$ can lower symmetry, break the degeneracy, and lower the energy.

Computed Heisenberg exchange constants: comparison with experiment

Table 3. Parameters [cm^{-1}] of the Model Hamiltonian (eq 8) Extracted from the *Ab Initio* Calculations for Compounds (1) and (2), and the Experimentally Obtained for (2) from Ref 16

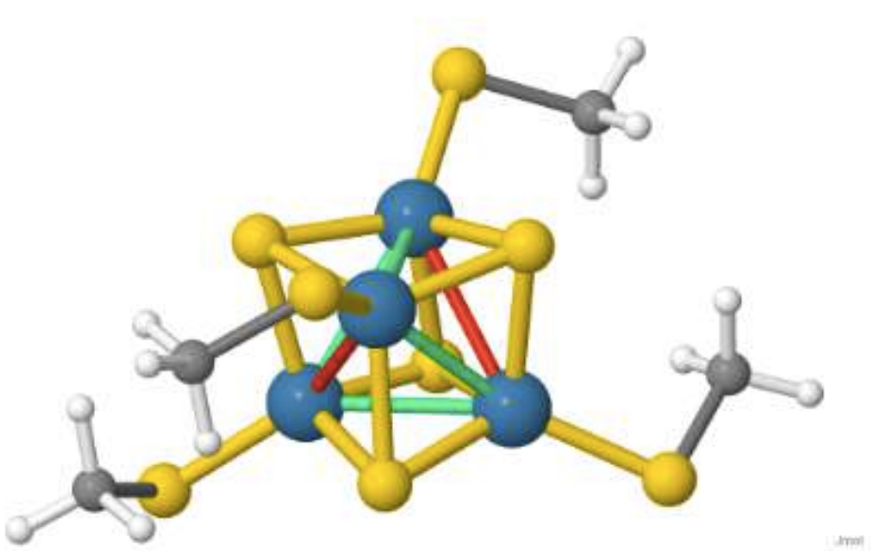
	Compound (1)		Compound (2)		
	(20e,20o)	(44e,32o)	(20e,20o)	(44e,32o)	Exp.[16]
J_{4B}	55.5	90.3	41.5	72.7	70
J_{2B}	32.0	49.8	58.9	87.3	82
$J4B - J2B$	23.5	40.5	−17.5	−14.6	−12

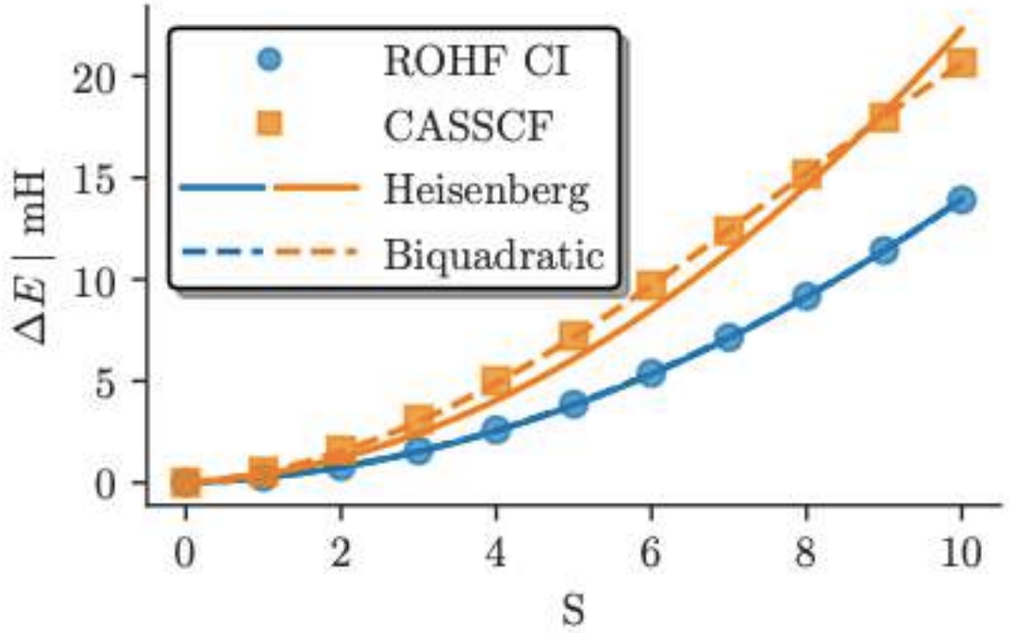
Spin ladder of [Fe(III)4S4]

The effect of CASSCF

Dobrautz et al, JCTC, **17**, 5684 (2021)

$$\hat{H} = \sum_{ij} J_{ij} \mathbf{S}_i \,.\, \mathbf{S}_j + \sum_{ij} K_{ij} (\mathbf{S}_i \,.\, \mathbf{S}_j)^2$$





Conclusions and future work

- Orbital re-ordering proves to be a very powerful trick to induce compactness into spin-adapted wavefunction expansions
- Many previously considered multi-reference systems can be rendered single-reference
- Extension of these methods beyond active-space calculations remains challenging
- Transcorrelation framework, which incorporates real-space Jastrow functions, to capture out-side of active correlation is being developed.

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