Spin-pure Stochastic-CASSCF Method Applied to Iron-Sulfur Clusters

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MAX PLANCK INSTITUTE
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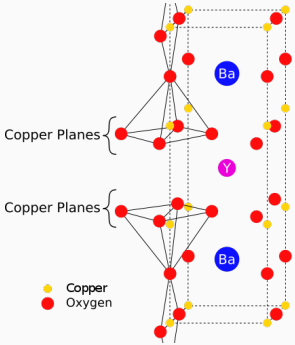
Outline

- Motivation
- Methods: CASSCF and FCIQMC
- Spin Symmetry via the Graphical Unitary Group Approach
- Results: Fe_2S_2 and Fe_4S_4 clusters
- Conclusion and Outlook

Motivation

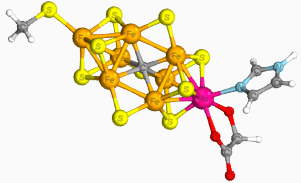
(Polynuclear) Transition Metal Compounds

Challenging systems for quantum chemical investigations

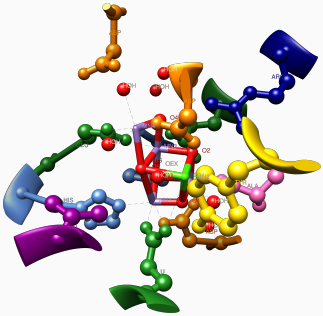


YBCO*: Unconventional high-T_c superconductivity

Iron-Sulfur clusters: electron transfer proteins



FeMoCo†: primary cofactor of nitrogenase



Mn_4O_5Ca in Photosystem II†: oxygen-evolving complex in photosynthesis process

Images from: *commons.wikimedia.org, †G. Li Manni

Electronic Structure Theory

Goals:

- *High accuracy ab initio* calculations for strongly correlated systems
- We want: accuracy, predictability and interpretability to compare with experiment → **groundstate energy and wavefunction**
- Beyond mean-field HF & DFT: ⇒ Combine embedding methods (CASSCF) with highly accurate *ab initio* CI-solver[†] (FCIQMC) for large active spaces

Problems: Narrow and dense spin spectrum

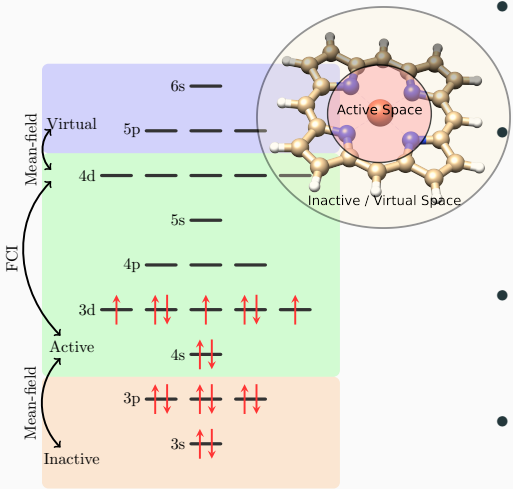
- small (near-degenerate) spin-gaps and spin-contamination problematic for convergence of projective techniques (like FCIQMC)
- no control and insight of total spin quantum number with Slater determinant formulation (hard to interpret)

Formulate FCIQMC in a spin-adapted basis[*] and perform spin-pure CASSCF

[†]Li Manni, Smart, Alavi, JCTC **12**, 3, 1245 (2016); [*]Dobrautz, Weser, Bogdanov, Alavi, Li Manni, arXiv:2106.07775 (submitted to JCTC)

Methods: CASSCF and FCIQMC

Complete active space self-consistent field method (CASSCF)



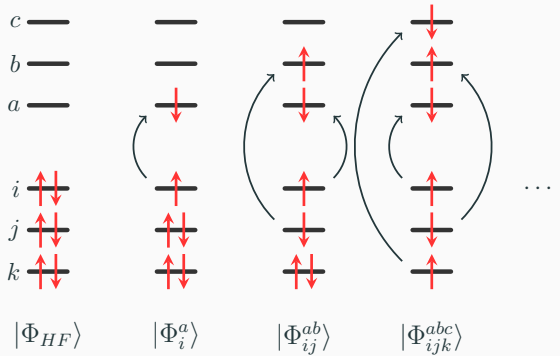
- Well-established **embedding method** in quantum chemistry for the treatment of strongly correlated electron systems
- **Active space** consisting of the most important orbitals and electrons treated exactly. Configuration interaction solver (**FCIQMC**) yields ground state energy and wavefunction $|\Psi_0\rangle$
- Effect of the **environment** (Inactive/Virtual space) accounted for at the mean-field level by orbital rotations.
- **One- and two-body reduced density matrices** in the active space are needed!

$$\rho_{ij}^{\sigma} = \langle \Psi_0 | a_{i\sigma}^{\dagger} a_{j\sigma} | \Psi_0 \rangle$$

Roos, Taylor, Sigbahn, Chem. Phys., **48, 2**, 157 (1980)

Problems for accurate description: Exponential scaling of Full Configuration Interaction

FCI $\Rightarrow |\Psi\rangle = \sum_I c_I |D_I\rangle \Rightarrow$ exact solution in a given basis set



All possible excitations from HF determinant

Number of possible states for given number of electrons and orbitals

#orbitals	#electrons	#states
2	2	4
4	4	36
8	8	4900
12	12	$\sim 8 \cdot 10^5$
16	16	$\sim 16 \cdot 10^6$
18	18	$\sim 2 \cdot 10^9$

Full Configuration Interaction Quantum Monte Carlo

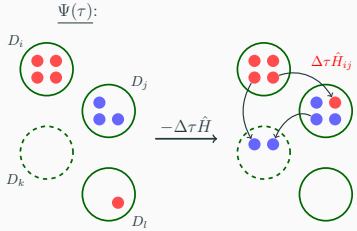
- *Projector MC method* based on the **imaginary-time Schrödinger equation**, stochastically sampling FCI wavefunction. Integration leads to an iterable equation:

$$\frac{\partial |\Psi\rangle}{\partial \tau} = -\hat{H}|\Psi\rangle \quad \rightarrow \quad |\Psi_0\rangle \propto \lim_{\tau\to\infty} \mathrm{e}^{-\tau\hat{H}}|\Phi\rangle$$

- *First order* Taylor expansion $\mathrm{e}^{-\Delta\tau\hat{H}} \approx 1 - \Delta\tau\hat{H}$ leads to the *working equation:*

$$c_i(\tau + \Delta\tau) = [1 - \Delta\tau H_{ii}]\, c_i(\tau) - \Delta\tau \sum_{j\neq i} H_{ij} c_j(\tau)$$

- Solved stochastically by the *population dynamics* of **"walkers"** in the discrete Slater determinant (SD) Hilbert space.
- **Multireference method** and highly accurate solutions for system sizes $> (50e, 50o)$ possible.



Booth, Thom, and Alavi, JCP, **131**, 054106 (2009), Guther *et al.*, JCP, **153**, 034107 (**2020**)

Spin Symmetry via the Graphical Unitary Group Approach

Spin Symmetry

Inherent to spin-preserving, non-relativistic Hamiltonians:

$$[\hat{H}, \hat{\mathbf{S}}^2] = 0$$

often not directly imposed, due to *impractical implementation.*

Benefits of a spin-symmetry adapted basis:

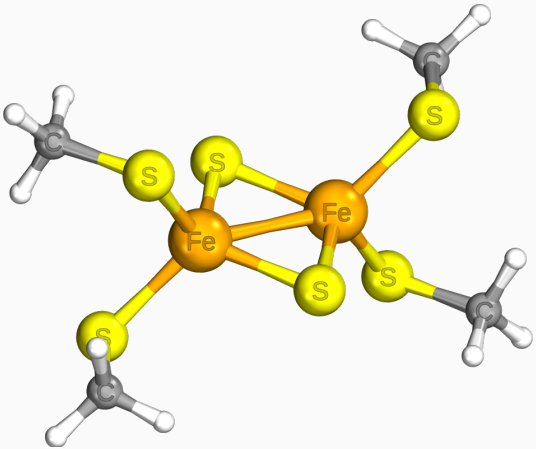
- target specific spin-states (singlet, triplet,...)
- no spin-contamination
- reduce Hilbert space size!
- resolve (near-)degeneracies of different spin-sectors

Efficient spin-adapted formulation of FCIQMC[†] possible with the graphical unitary group approach (GUGA)[‡] → spin-pure RDM sampling and CASSCF[*]

[†]Dobrautz, Smart and Alavi, JCP, **151**, 094104 (2019); [‡]Paldus, J. Chem. Phys. **61**, 5321 (1974) + Shavitt, Int. J. Quantum Chem., **12**, 131 (1977) [*]Dobrautz, Weser, Bogdanov, Alavi, Li Manni, arXiv:2106.07775 (2020) (submitted and accepted by JCTC)

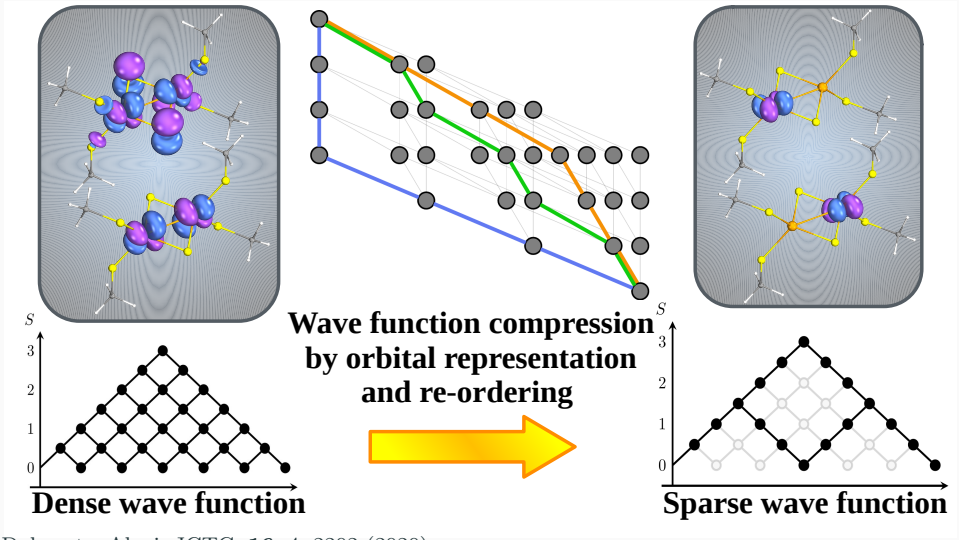
Results: Fe_2S_2 and Fe_4S_4 clusters

$[Fe_2^{(III)}S_2]^{2-}$ - Model System

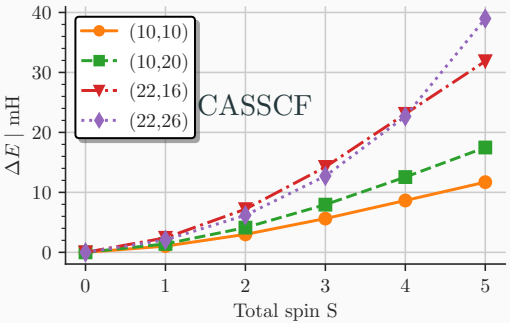


- CAS(10,10): 10 iron valence 3d orbitals
- CAS(10,20): 10 iron valence 3d and 10 double-shell d' orbitals
- CAS(22,16): 10 iron valence 3d and 6 3p bridging sulfur orbital
- Largest considered active space here: 22 electrons in 26 orbital, containing the 20 iron valence 3d and double-shell d' and the 6 3p orbitals of the bridging sulfurs

Importance of Localized and Ordered Orbitals



Results: Iron-sulfur clusters – Fe_2S_2

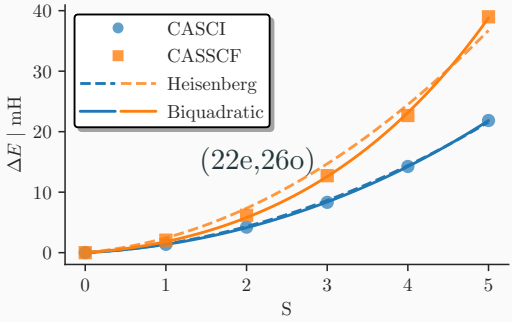


Linear Heisenberg

$$\hat{H} = J\,\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B$$

CASCI: $J = 1.44$ mH

CASSCF: $J = 2.45$ mH



Biquadratic Heisenberg

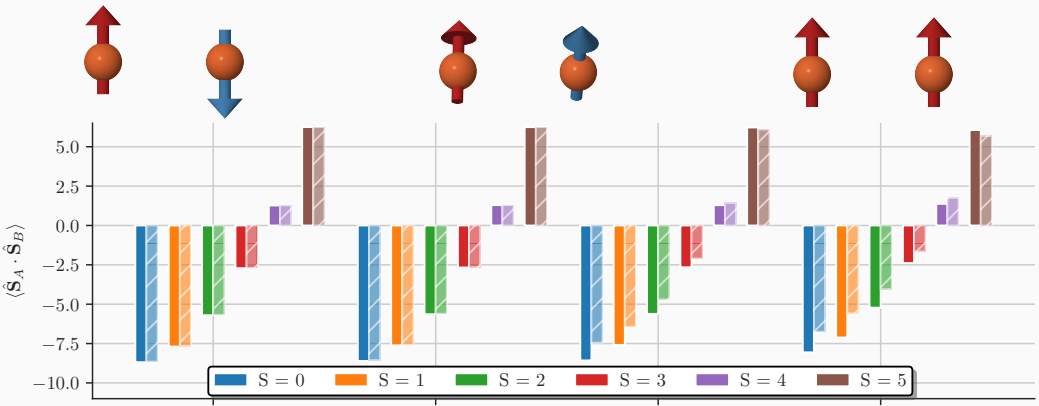
$$\hat{H} = J'\,\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B + K\left(\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B\right)^2$$

CASCI: $J' = 1.47$ mH and $K = 0.007$ mH

CASSCF: $J' = 2.70$ mH and $K = 0.054$ mH

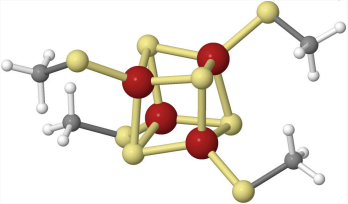
Results: Iron-sulfur clusters – Fe_2S_2 – Spin-spin correlation

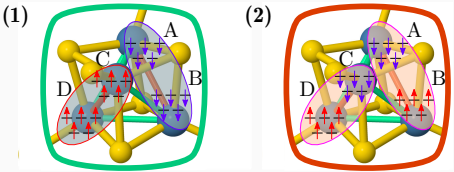
Properties via RDMs: Spin-spin correlation between irons: $\langle \sum_{i \in \mathrm{Fe}_A} \hat{\mathbf{S}}_i \cdot \sum_{j \in \mathrm{Fe}_B} \hat{\mathbf{S}}_j \rangle$



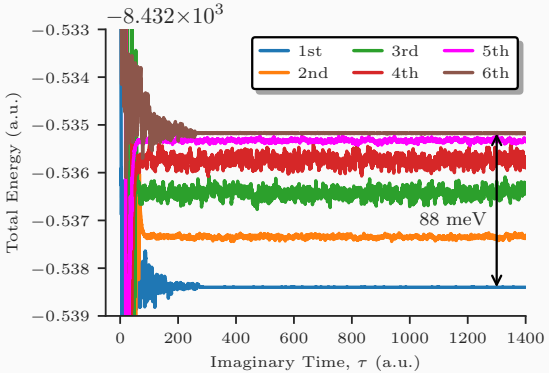
Results: Iron-sulfur clusters – Fe_4S_4 – CASCI

Six lowest singlet states resolved within ≈ 3 mH. Low spin state with 20 open shell orbitals. Calculations up to (44e,32o) active spaces





Reveals magnetic coupling of ground- and excited states



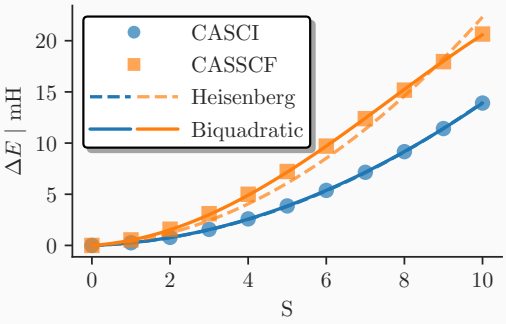
(20,20) active space

G. Li Manni, W. Dobrautz, N. Bogdanov, K. Guther, A. Alavi, JCP A, **125**, 22 4727 (2021)

Results: Iron-sulfur clusters – Fe_4S_4 – CASSCF

- (20e,20o) active space of Fe_4S_4 model system
- Reveals necessary higher order terms in mapping to spin-model (biquadratic Heisenberg)

Method	$J^{(\prime)}$ | mH	K | mH
CASCI	249.9	—
	259.2	-0.11
CASSCF	410.1	—
	470.0	-2.61



Conclusion and Outlook

Conclusion and Summary

- FCIQMC is an accurate and efficient stochastic multireference method for **large active spaces**
- Efficient spin-adapted implementation via the GUGA
- Enables to **target** specific spin states, **reduces** the Hilbert space size and **removes** spin contamination
- Orbital localization and reordering scheme causes wave function **compression**
- **Spin-adapted Stochastic-CASSCF** and properties via density matrices
- Spin-adapted CASSCF reveals need for **higher order** Heisenberg terms for FeS systems
- Allows spin-adapted state-specific / state-averaged / excited states CASSCF calculations for **large actice spaces**
- Allows the study of strongly correlated polynuclear transition metal compounds

Acknowledgments

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Thank you for your attention!

Integration with OpenMolcas

Stochastic-CASSCF for SDs implemented by G. Li Manni and S. Smart[†]

Additional input for a stochastic GUGA-FCIQMC CASSCF calculation:

fciqmc.input:

```
SYSTEM
   nonuniformrandexcits pchb
   guga 2S
ENDSYS
LOGGING
   print-molcas-rdms
ENDLOG
```

Produces `DMAT, PSMAT, PAMAT` and `NEWCYCLE` files containing the **spin-free** RDMs and the RDM energy used by `Molcas`

molcas.input:

```
&RASSCF
   neci
   guga
```

Produces the `$Project.FciDmp` file containing the new molecular integrals used by our FCIQMC code `NECI`, with output:

```
Run spin-free GUGA NECI externally.
Get the ASCII formatted FCIDUMP:
cp $MOLCAS_RUN_DIR/$Poject.FciDmp $NECI_RUN_DIR

When finished do:
cp PSMAT PAMAT DMAT NEWCYCLE $MOLCAS_RUN_DIR
```

[†]Li Manni, Smart, Alavi, JCTC **12**, 3, 1245 (2016)

The Gel'fand-Tsetlin Basis

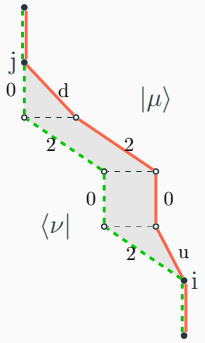
CSF given by step-vector $|\mu\rangle = |d_1, d_2, \ldots, d_n\rangle$.

For each *spatial* orbital (i) **step-value** d_i encodes:

- ΔN_i : change in total electron number
- ΔS_i : change in total spin with $S \geq 0$
- 2 bit per spatial orbital, like SD
- Can be represented graphically

4 ways of coupling a orbital:

d_i	ΔN_i	ΔS_i
0	0	0
u	1	$1/2$
d	1	$-1/2$
2	2	0



Paldus, J. Chem. Phys. **61**, 5321 (1974); Gel'fand and Tsetlin, Doklady Akad. Nauk SSSR, **71**, 1017 (1950)

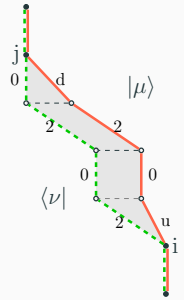
Matrix Elements via the Graphical UGA

Calculate matrix elements with the **Graphical** UGA:

$$\langle \nu | \hat{H} | \mu \rangle = \sum_{ij}^{n} t_{ij} \langle \nu | \hat{E}_{ij} | \mu \rangle + \frac{1}{2} \sum_{ijkl}^{n} V_{ijkl} \langle \nu | \hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il} | \mu \rangle$$

Matrix elements only depend on **loop** enclosed by CSFs, and have a **product** form

$$\langle \mu' | \hat{E}_{ij} | \mu \rangle = \prod_{k=i}^{j} W(d'_k, d_k, S_k)$$



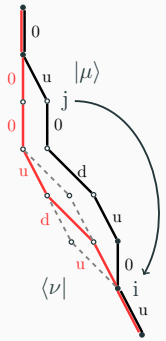
I. Shavitt, Int. J. Quantum Chem., **12**, 131 (1977)

Excitations via the Graphical UGA

$\hat{E}_{ij}$ moves electron from j to i with **all symmetry allowed** spin-recouplings, opposed to SD **more than one** excitation possible:

$$\hat{E}_{ij} |\mu\rangle = \sum_n C_n |\mu'_n\rangle$$

$$\hat{E}_{ij} |\mu\rangle \longrightarrow \begin{cases} |\mu'_1\rangle \\ |\mu'_2\rangle \\ |\mu'_3\rangle \end{cases}$$



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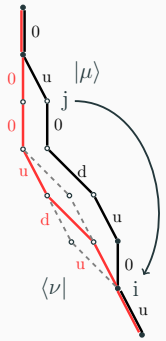


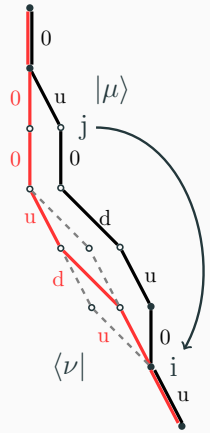
In FCIQMC we only need **one** connected state!
⇒ Loop over $i \to j$: select *one* excitation randomly through **branching tree** and calculate matrix element *on the fly!*

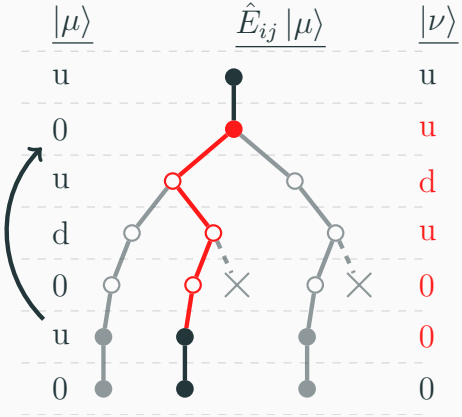
$$\hat{E}_{ij}\,|\mu\rangle \longrightarrow \begin{cases} |\mu'_1\rangle \\ |\mu'_2\rangle \\ |\mu'_3\rangle \end{cases}$$

I. Shavitt, Int. J. Quantum Chem., **12**, 131 (1977)

The Branching Tree

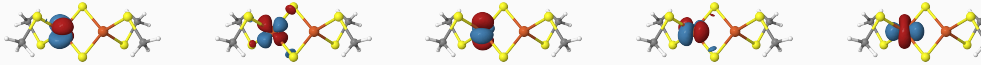
- Branching option at every singly occupied orbital in *excitation range* $i \to j$
- Randomly choose excitation and calculate matrix element **on-the-fly**



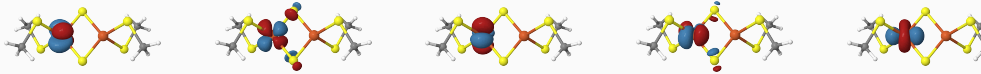


CASSCF Effect on orbitals

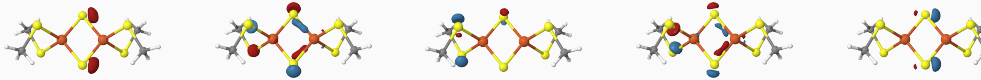
ROHF:



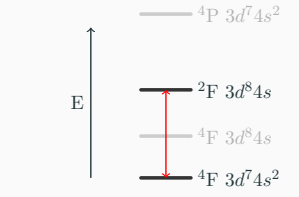
CASSCF:

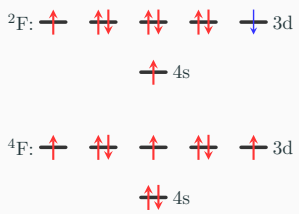


Difference:



Motivation: Potential Problems of a Slater determinant formulation:





Cobalt atom

- small (near-degenerate) spin-gaps and spin-contamination problematic for convergence of projective techniques
- no control and insight of total spin quantum number with Slater determinants (hard to interpret)
- No access to low-spin excited states for systems with a high-spin groundstate:
  -Restricting m_s converges to high-spin GS
- Open-shell low-spin excited state:
  multi-reference character of ^{2}F state problematic for single-reference methods

Spin-free RDMs with GUGA-FCIQMC cont.

- Coupling coefficients $\langle \mu' | \hat{E}_{ij} | \mu \rangle = \prod_{k=i}^{j} W(d'_k, d_k, S_k)$:

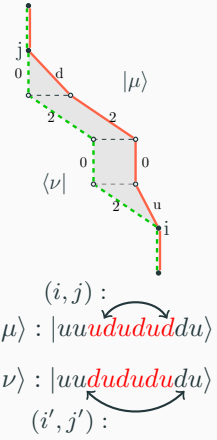
  More complicated as for SDs, but already calculated **on-the-fly** in *excitation generation*

- Additional information on excitation type:

  Excitation identification, like the involved spatial indices (i, j, k, l), more costly as for SDs (but already available)

- 'original' probability $p(\mu \to \nu | i, j, k, l)$:

  Different *exchange* type double excitations $\hat{E}_{ij}\hat{E}_{ji}$ can lead to same $|\mu\rangle \to |\nu\rangle$. Needs to be considered for unique total *generation probability*, but for RDM sampling we need to unbias this



$\Rightarrow$ We need to communicate **three additional 64bit integers**. Communicating accumulated data every *1000 iterations* **only** $\approx$**10%** increase in time per iteration!

Interfaced with `OpenMolcas`

Dobrautz, Weser, Bogdanov, Alavi, Li Manni, arXiv:2106.07775 (2020) (submitted to JCTC)