Spin-pure Stochastic-CASSCF applied to iron-sulfur clusters

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MAX PLANCK INSTITUTE
FOR SOLID STATE RESEARCH

Outline

- Motivation
- Full Configuration Interaction Quantum Monte Carlo
- Spin Symmetry via the Graphical Unitary Group Approach
- Results: Fe_2S_2 and Fe_4S_4 clusters
- Conclusion and Outlook

Motivation

Electronic Structure Theory

Goals:

- *High accuracy ab initio* calculations for strongly correlated systems
- We want: accuracy, predictability and interpretability to compare with experiment
- Beyond HF & DFT: $\Rightarrow$ Combine CASSCF with FCIQMC as CI-solver[†] for large active spaces

Problems:

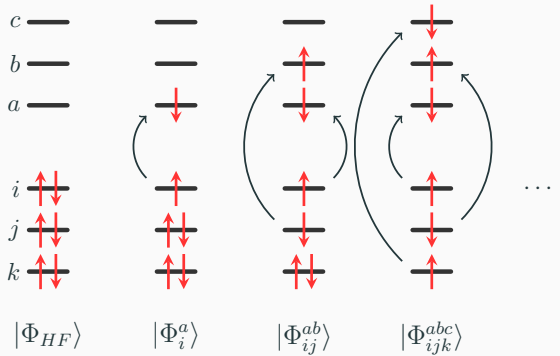
- small (near-degenerate) spin-gaps and spin-contamination problematic for convergence of projective techniques (like FCIQMC)
- no control and insight of total spin quantum number with Slater determinant formulation (hard to interpret)

Idea: Formulate FCIQMC and sample RDMs in a spin-adapted basis[*]

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

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

Full Configuration Interaction Quantum Monte Carlo

- *Projector MC method* based on the **imaginary-time Schrödinger equation**, stochastically sampling FCI wavefunction.
  Formal 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:*

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

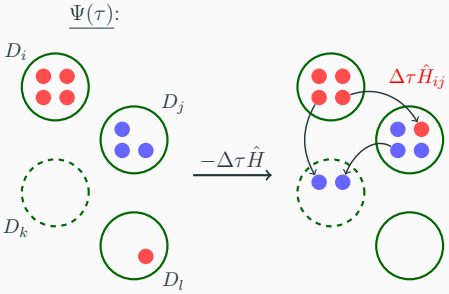
- Solved stochastically by the *population dynamics* of **"walkers"** in the discrete Slater determinant (SD) Hilbert space.
- **Multireference method** and highly accurate solutions for system sizes $> (50e, 50o)$ possible.

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

Population dynamics of walkers governed by:

$$c_i(\tau + \Delta\tau) = \underbrace{[1 - \Delta\tau H_{ii}]\, c_i(\tau)}_{\text{death/cloning}} - \underbrace{\Delta\tau \sum_{j \neq i} H_{ij} c_j(\tau)}_{\text{spawning}}$$

Spawning step: $|D_i\rangle \rightarrow |D_j\rangle$ with $p_{gen} = \frac{\Delta\tau |H_{ij}|}{p(D_j|D_i)}$



Need *efficient* H_{ij}
matrix element calculation,
excitation generation,
and **RDM sampling**
for excitation $|D_i\rangle \rightarrow |D_j\rangle$

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

Idea: Formulate FCIQMC in a spin-adapted basis[†]

[†]Dobrautz, Smart and Alavi, JCP, **151**, 094104 (2019)

The (Graphical) Unitary Group Approach

- **Spin-free** formulation of non-relativistic Hamiltonian:

$$\hat{H} = \sum_{ij}^{n} t_{ij}\, \hat{E}_{ij} + \frac{1}{2} \sum_{ijkl}^{n} V_{ijkl} \left(\hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il} \right)$$

- Spin-preserving excitation operators:

$$\hat{E}_{ij} = \hat{c}^{\dagger}_{i\uparrow} \hat{c}_{j\uparrow} + \hat{c}^{\dagger}_{i\downarrow} \hat{c}_{j\downarrow}, \quad \text{with} \quad [\, \hat{E}_{ij}, \hat{\mathbf{S}}^2 \,] = 0$$

- *Same commutation relations* as **generators** of the Unitary Group $U(n)$
- Gel'fand-Tsetlin (GT) basis: **invariant** and **irreducible**, same storage cost as SDs
- **Efficient** matrix element calculation and excitation generation entirely in CSFs via the Graphical Unitary Group Approach (GUGA)*, without reference to SDs

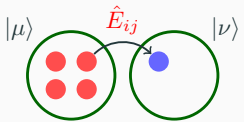
Paldus, J. Chem. Phys. **61**, 5321 (1974); Gel'fand and Tsetlin, Doklady Akad. Nauk SSSR, **71**, 1017 (1950) *Shavitt, Int. J. Quantum Chem., **12**, 131 (1977

Spin-free RDMs with GUGA-FCIQMC

One- and two-body RDMs:

$$\rho_{ij} = \langle \Psi | \hat{E}_{ij} | \Psi \rangle = \sum_{\mu\nu} c_\mu^{(\mathrm{I})} c_\nu^{(\mathrm{II})} \langle \nu | \hat{E}_{ij} | \mu \rangle, \quad \Gamma_{ij,kl} = \frac{1}{2} \langle \Psi | \hat{E}_{ij} \hat{E}_{kl} - \delta_{jk} \hat{E}_{il} | \Psi \rangle$$

Replica trick*: two statistically independent simulations (I and II) for unbiased RDMs necessary! (Twice the computational cost)

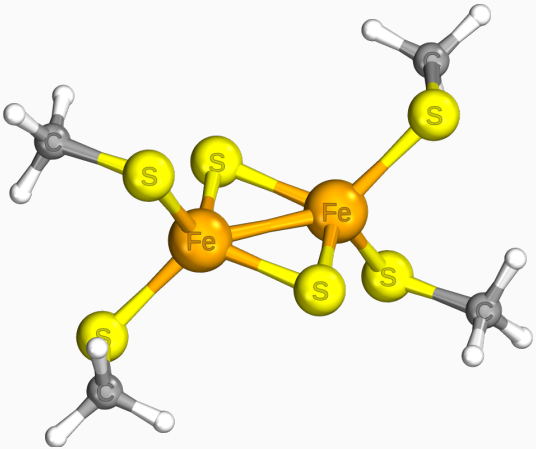


- Sample ρ_{ij} and $\Gamma_{ij,kl}$ in the *random excitation process* $|\mu\rangle \rightarrow |\nu\rangle$
- Already for SDs: store 'parent' state $|\mu\rangle$, coefficient c_μ and source (I,II) along $|\nu\rangle$
- New for GUGA: store *coupling coefficient* $\langle \nu | \hat{E}_{ij} | \mu \rangle$, information of the excitation type and 'original' probability $p(\mu \rightarrow \nu | i,j,k,l)$
- Moderate computational overhead and interfaced with `OpenMolcas`†

*Overy, Booth, Blunt, Shepherd, Cleland, Alavi, JCP, **141**, 244117 (2014); †Dobrautz, Weser, Bogdanov, Alavi, Li Manni, arXiv:2106.07775 (2020) (submitted to JCTC)

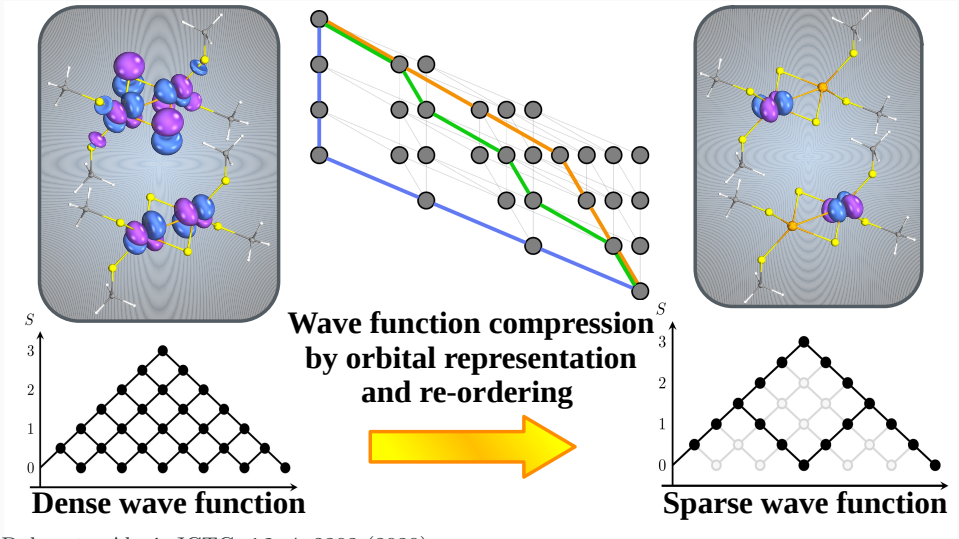
Results: Fe_2S_2 and Fe_4S_4 clusters

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

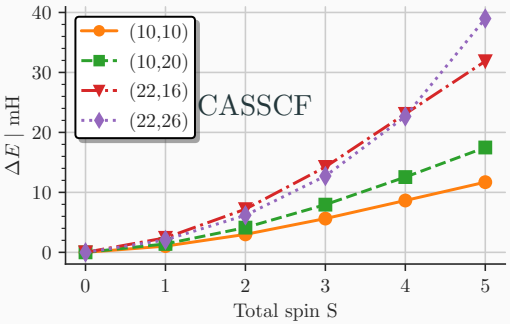


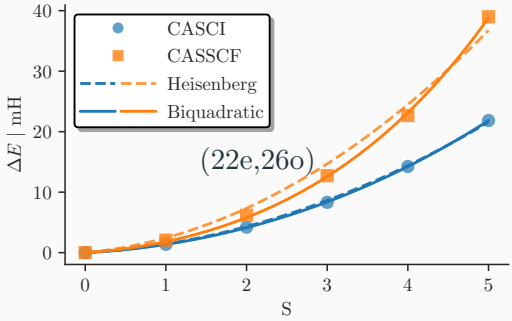
- CAS(10,10): 10 iron valence 3d orbitals
- CAS(10,20): 10 iron valence 3d and 10 double-shell d' orbitals
- CAS(22,16): 10 iron valence 3d and 6 3p bridging sulfur orbital
- Largest considered active space here: 22 electrons in 26 orbital, containing the 20 iron valence 3d and double-shell d' and the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

Importance of Localized and Ordered Orbitals

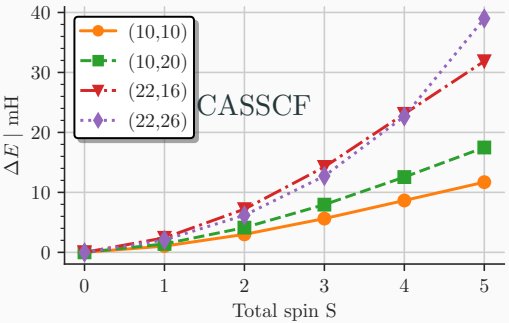


Results: Iron-sulfur clusters – Fe_2S_2





Results: Iron-sulfur clusters – Fe_2S_2

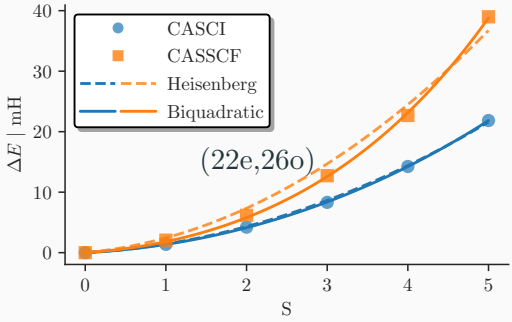


Linear Heisenberg

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

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

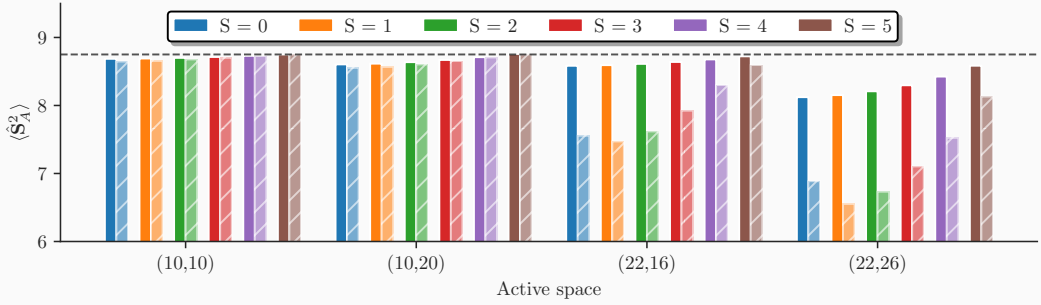
CASSCF: $J' = 2.70$ mH and $K = 0.054$ mH

Results: Iron-sulfur clusters – Fe_2S_2 – Local spin

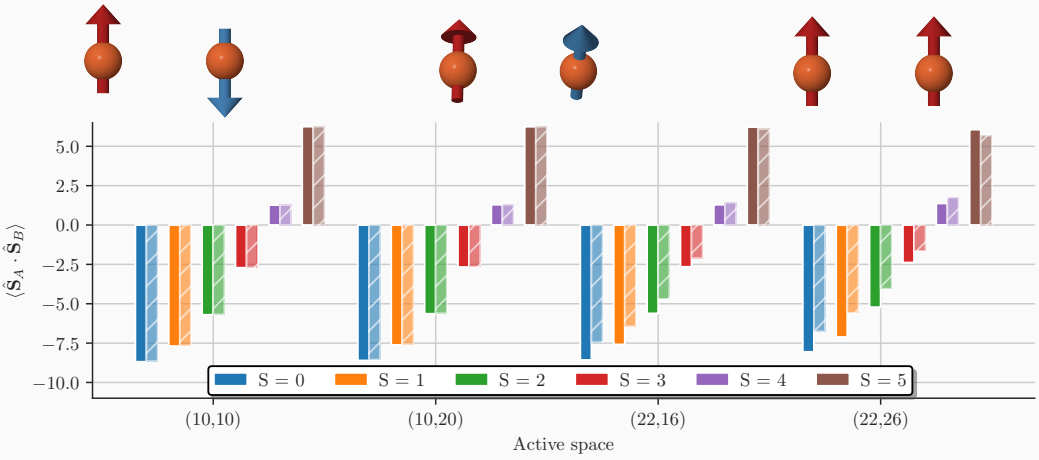
Local spin of magnetic Fe orbitals: $\langle(\sum_{i\in \mathrm{Fe}_A} \hat{\mathbf{S}}_i)^2\rangle$

$S^2_{max} = \frac{5}{2}(\frac{5}{2}+1) = 8.75$

$S^2_{min} \approx 6.5 \rightarrow S_{min} \approx 2$



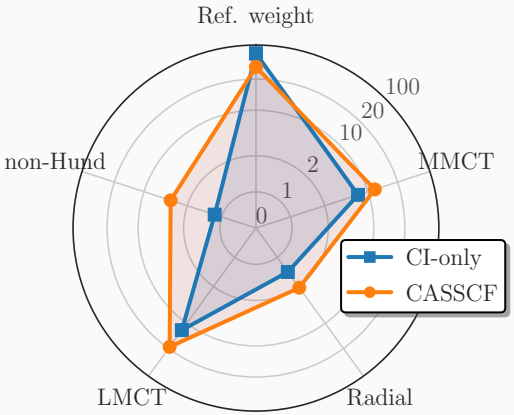
Results: Iron-sulfur clusters – Fe_2S_2 – Spin-spin correlation



Results: Iron-sulfur clusters – Fe_2S_2 – Wavefunction character

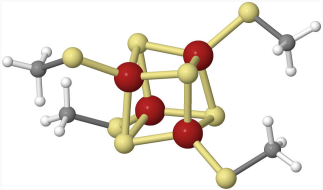
Singlet state

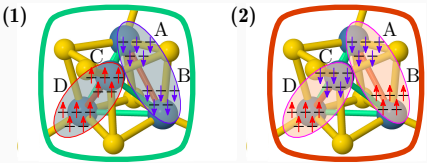
Active space	(22e, 26o)	
	CASCI	CASSCF
Ref. weight [%]	74.4	**46.1**
MMCT d→d [%]	6.9	**12.9**
Radial d→d'[%]	1.5	**2.1**
LMCT [%]	13.4	**27.9**
non-Hund [%]	1.2	**3.7**



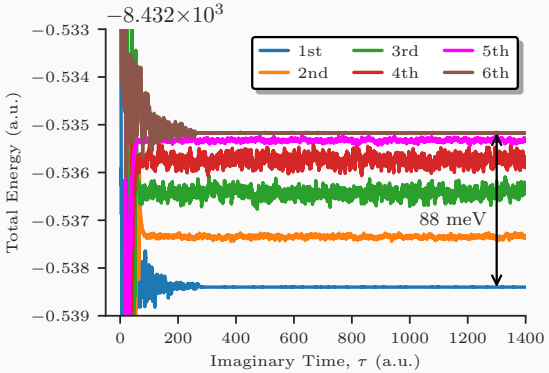
Results: Iron-sulfur clusters – Fe_4S_4 – CASCI

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



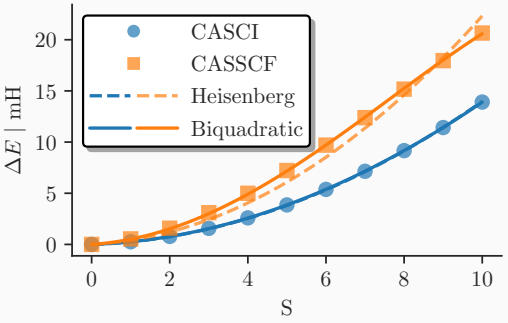
(20,20) active space

G. Li Manni, W. Dobrautz, N. Bogdanov, K. Guther, A. Alavi, JCP A, 2021, accepted

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 interfaced with `OpenMolcas`
- 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**

Acknowledgments

Ali Alavi

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Nikolay Bogdanov

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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

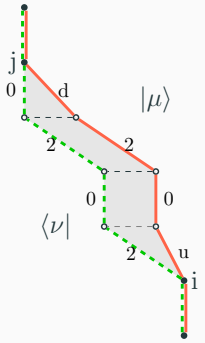
CSF given by step-vector $|\mu\rangle = |d_1, d_2, \ldots, d_n\rangle$.

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)

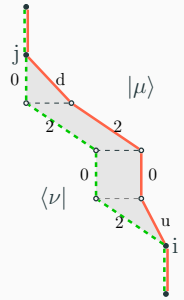
Matrix Elements via the Graphical UGA

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

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



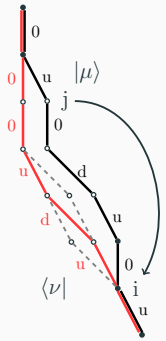
I. Shavitt, Int. J. Quantum Chem., **12**, 131 (1977)

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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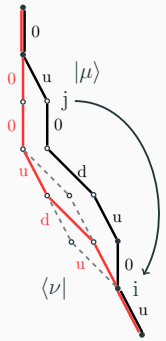


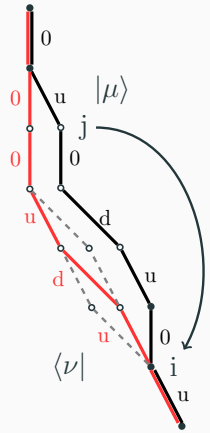
In FCIQMC we only need **one** connected state!
⇒ Loop over $i \to j$: select *one* excitation randomly through **branching tree** and calculate matrix element *on the fly!*

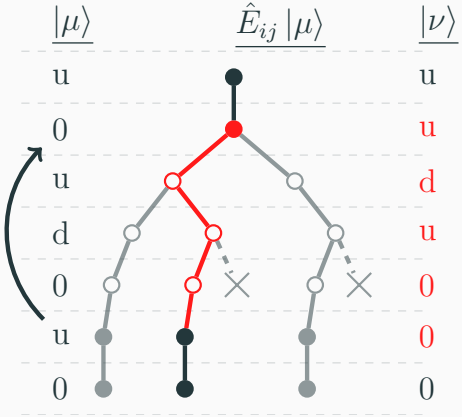
$$\hat{E}_{ij}\,|\mu\rangle \longrightarrow \begin{cases} |\mu'_1\rangle \\ |\mu'_2\rangle \\ |\mu'_3\rangle \end{cases}$$

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

The Branching Tree

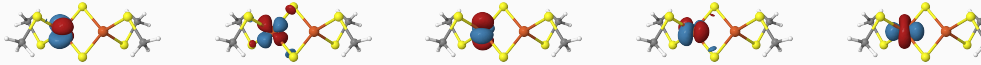
- Branching option at every singly occupied orbital in *excitation range* $i \to j$
- Randomly choose excitation and calculate matrix element **on-the-fly**



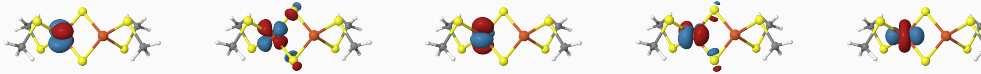


CASSCF Effect on orbitals

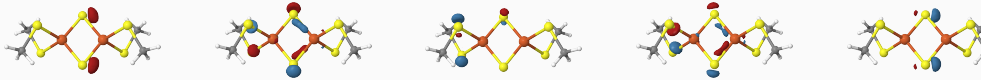
ROHF:



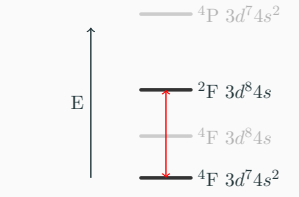
CASSCF:

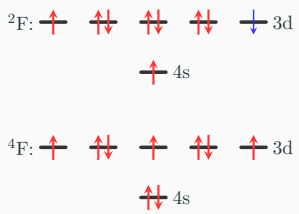


Difference:



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

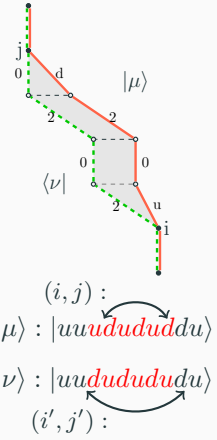
  More complicated as for SDs, but already calculated **on-the-fly** in *excitation generation*

- 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)