Spin-pure Stochastic-CASSCF in OpenMolcas via spin-adapted FCIQMC (GUGA-FCIQMC)

applied to the $[Fe_2^{(III)}S_2]^{2-}$ model system

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Max Planck Institute for Solid State Research

Outline

- Motivation
- Theory and Implementation
- Results for the $[Fe_2^{(III)}S_2]^{2-}$ model system
- Conclusion, Summary 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[†]

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)

Theory and Implementation

FCIQMC

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

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

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

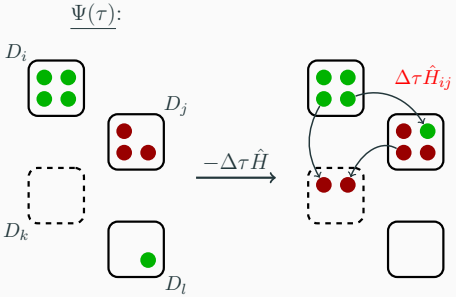
$$c_i(\tau+\Delta\tau) = \underbrace{\left[1-\Delta\tau H_{ii}\right] c_i(\tau)}_{\text{diagonal}} \underbrace{- \Delta\tau \sum_{j\neq i} H_{ij} c_j(\tau)}_{\text{off-diagonal}}$$

- *Population dynamics* of **"walkers"** simulate the working equation.

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

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

→ Use **configuration state functions (CSFs)** in FCIQMC[†]

[†]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 $U(n)$.
  Invariant and **irreducible** basis† $\Rightarrow$ **CSFs**

- Efficient *matrix element computation* and *excitation generation* with **Graphical** UGA (GUGA)*

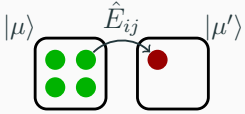
Paldus, JCP **61**, 5321 (1974); Gel'fand and Tsetlin, Dokl. Akad. Nauk SSSR, **71**, 1017 (1950)†; Shavitt, Int. J. Quantum Chem., **12**, 131 (1977)*

Spin-free RDMs with GUGA-FCIQMC

One- and two-body RDMs:

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

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



- Sample ρ_{ij} and $\Gamma_{jl,ik}$ in the *random excitation process* $|d\rangle \rightarrow |d'\rangle$
- Already for SDs: store 'parent' state $|d\rangle$, coefficient c_d and source (I,II) along $|d'\rangle$
- New for GUGA: store *coupling coefficient* $\langle d' | \hat{E}_{ij} | d \rangle$, information of the excitation type and 'original' probability $p(d \rightarrow d' | i, j, k, l)$

*Overy, Booth, Blunt, Shepherd, Cleland, Alavi, JCP, **141**, 244117 (2014)

Spin-free RDMs with GUGA-FCIQMC cont.

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

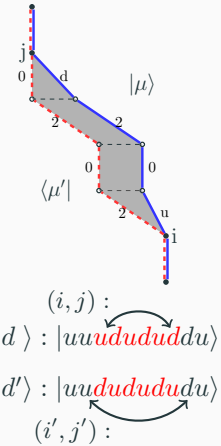
  More complicated as for SDs, but already calculated **on-the-fly** in *excitation generation*

- 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 $p(d \to d'|i, j, k, l)$:

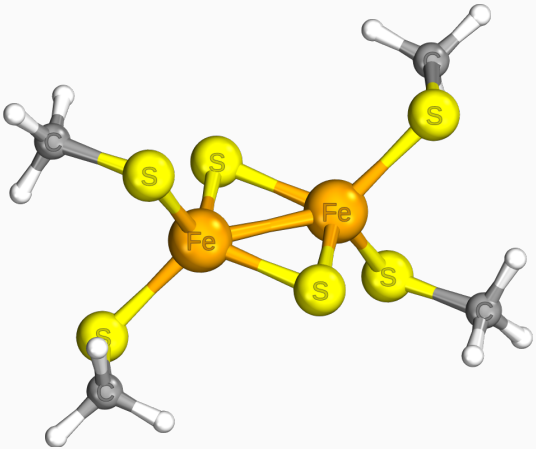
  Different *exchange* type double excitations $\hat{E}_{ij}\hat{E}_{ji}$ can lead to same $|d\rangle \to |d'\rangle$. Needs to be considered for unique total *generation probability*, but for RDM sampling we need to unbias this



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

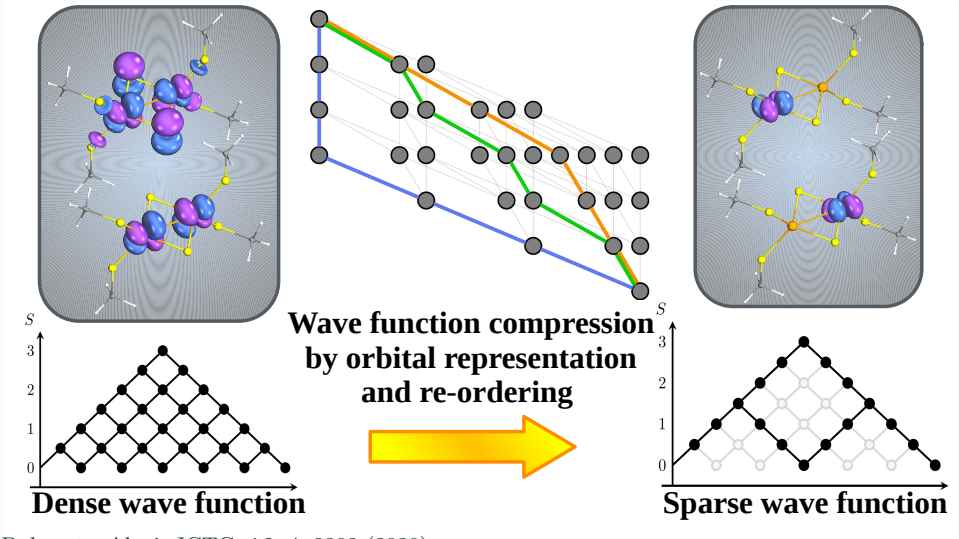
Results for the $[Fe_2^{(III)}S_2]^{2-}$ model system

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

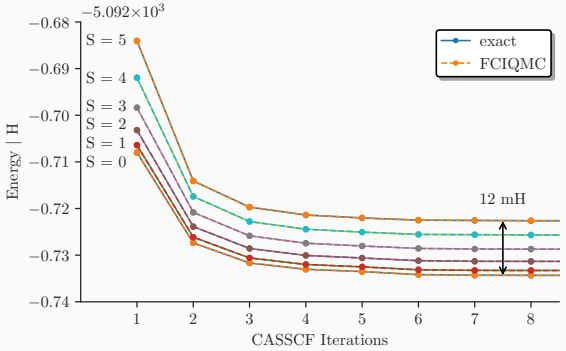


- Largest considered active space here: 22 electrons in 26 orbital, containing the 20 iron valence 3d and double-shell d' and the 6 3p orbitals of the bridging sulfurs
- CAS(10,10): 10 iron valence 3d orbitals
- CAS(10,12): 10 iron valence 3d and 2 4s orbitals
- CAS(10,20): 10 iron valence 3d and 10 double-shell d' orbitals
- CAS(22,16): 10 iron valence 3d and 6 3p bridging sulfur orbital

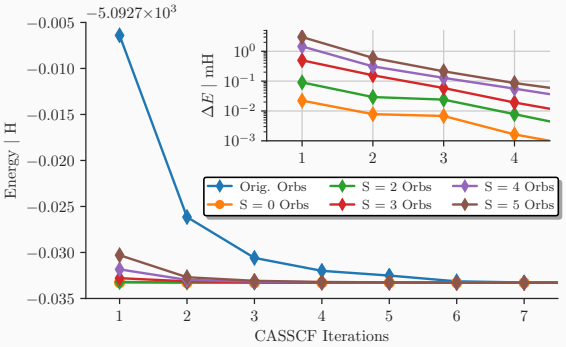
Importance of Localized and Ordered Orbitals



Results - CAS(10,10) Test-case

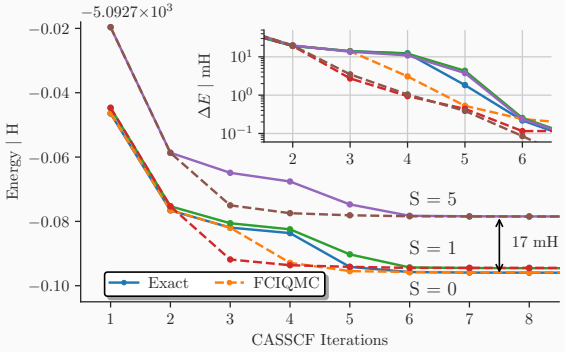


Starting from the **SD-based optimized CAS(22,26) 'singlet' orbitals.**

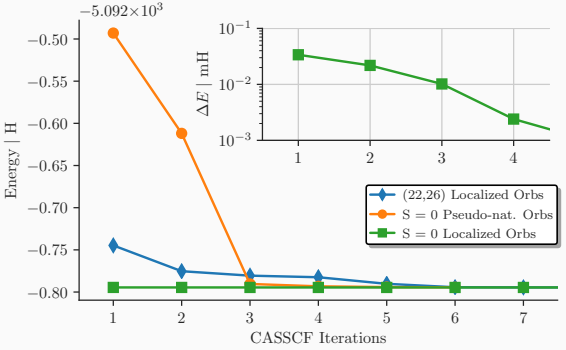


Deterministic triplet CASSCF starting from the **CSF-based optimized CAS(10,10)** of different spin-states.

Results - CAS(10,20)

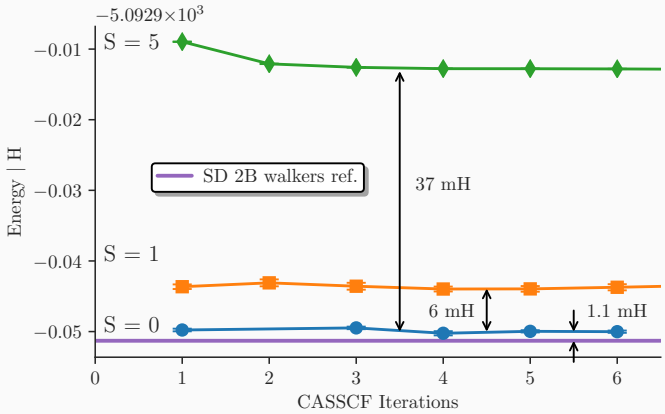


Singlet, Triplet and 11-tet CASSCF starting from the **CAS(22,26) SD-optimized 'singlet' orbitals.**



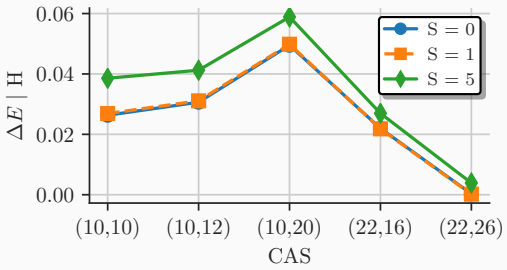
Deterministic triplet CASSF starting from the **CSF-optimized pseudo-natural** and **localized CAS(10,20) pure singlet orbitals.**

Results - CAS(22,26)

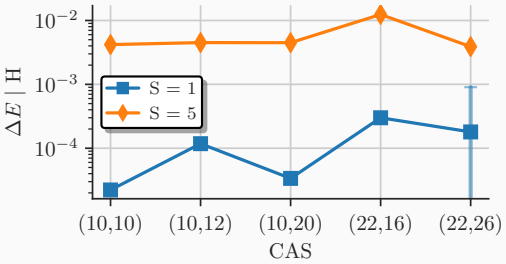


Singlet, triplet and 11-tet spin-pure stochastic CASSCF calculations with **50M walkers** starting from the **CAS(22,26) SD-optimized 'singlet' orbitals.**

$[Fe_2^{(III)}S_2]^{2-}$ Orbital Relaxation versus Active Space Size

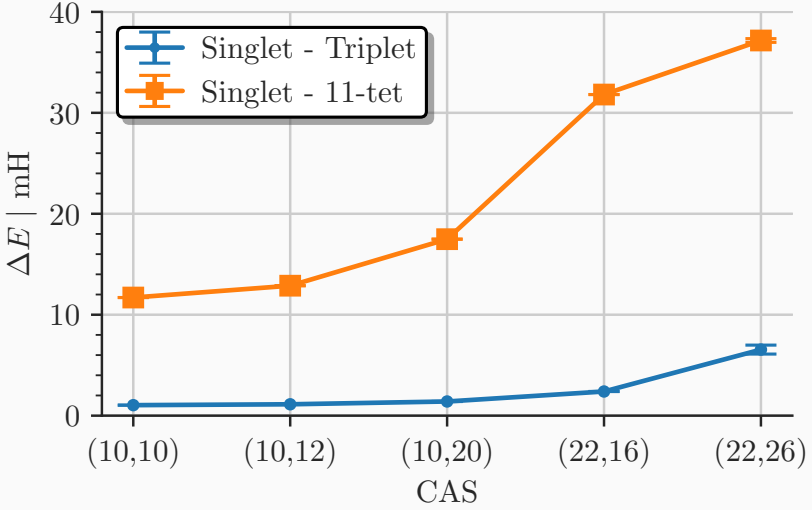


Orbital relaxation from **CAS(22,26) SD-optimized orbitals.**



Orbital relaxation from **GUGA-optimized singlet-orbitals within active space** (Except (22,26)!)

$[Fe_2^{(III)}S_2]^{2-}$ Spin-gaps versus Active Space Size



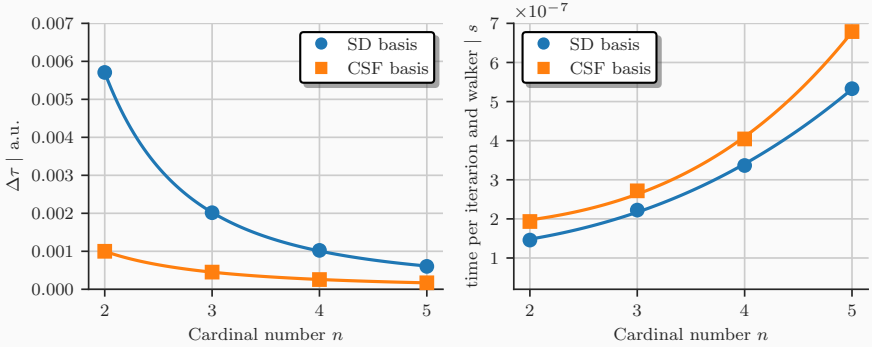
Conclusion, Summary and Outlook

Conclusion and Summary

- **Spin-pure Stochastic-CASSCF** with spin-free RDMs from GUGA-FCIQMC, used as the CI-solver interfaced with `OpenMolcas` for large active space sizes
- Allows to **target specific spin-states** with **no spin-contamination** and **resolve even near-degenerate spin-states**
- Manageable computational overhead (only $\approx 10\%$ increased time per iteration)
- Spin-gaps and orbital relaxation effect for $[Fe_2^{(III)}S_2]^{2-}$ model system as a function of active space size
- Fast CASSCF convergence starting from 'neighboring' spin-state orbitals
- Stochastic noise in GUGA-FCIQMC RDMs **can** be beneficial for CASSCF convergence
- @ Vera Krewald talk today: In principle we can do state-averaged spin-pure CASSCF in `Molcas` now

Outlook

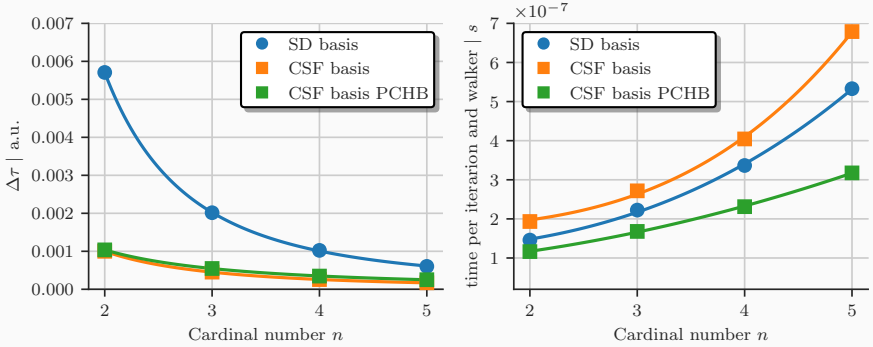
Target more realistic (bigger) systems ⇒ algorithmic advances!



Time-step $\Delta\tau$ and time per iteration for N_2 at 4.2Å separation versus basis set size.
10 electrons in a cc-pVnZ basis.

Outlook

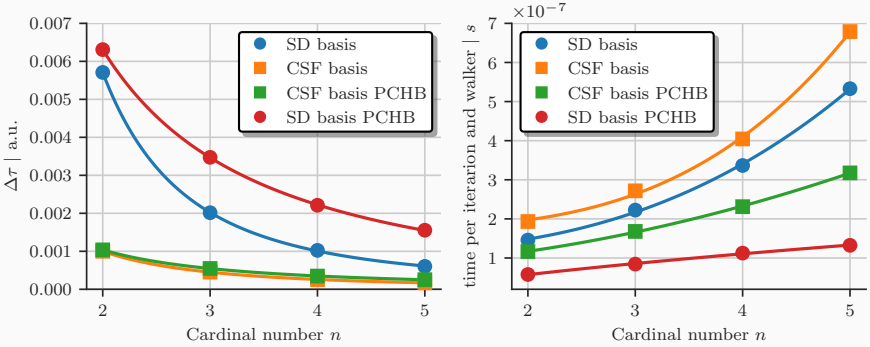
Target more realistic (bigger) systems ⇒ algorithmic advances!



Heat-bath† excitation generation for GUGA-FCIQMC!

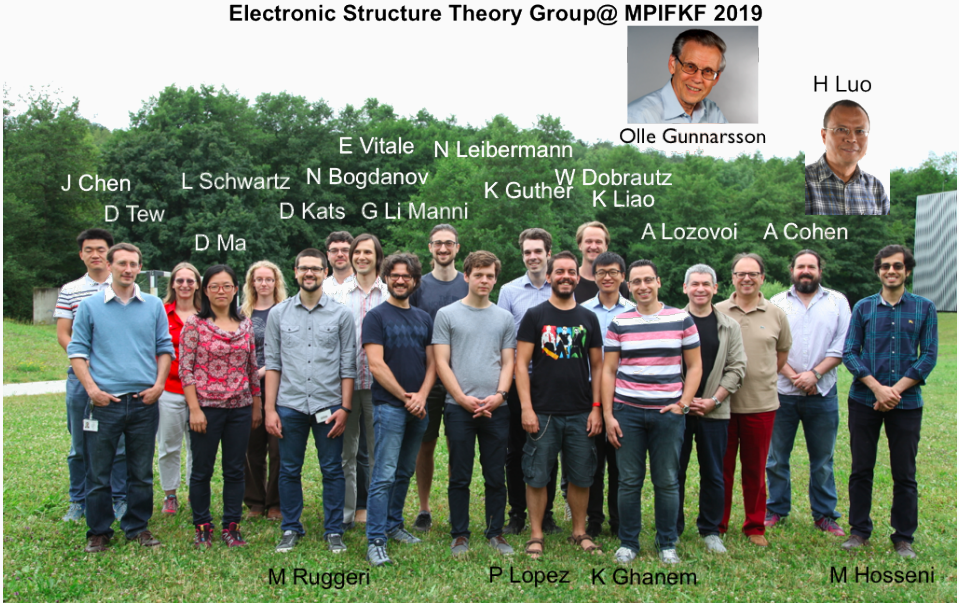
Outlook

Target more realistic (bigger) systems ⇒ algorithmic advances!



But also for SD-based FCIQMC...

Acknowledgment



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
```

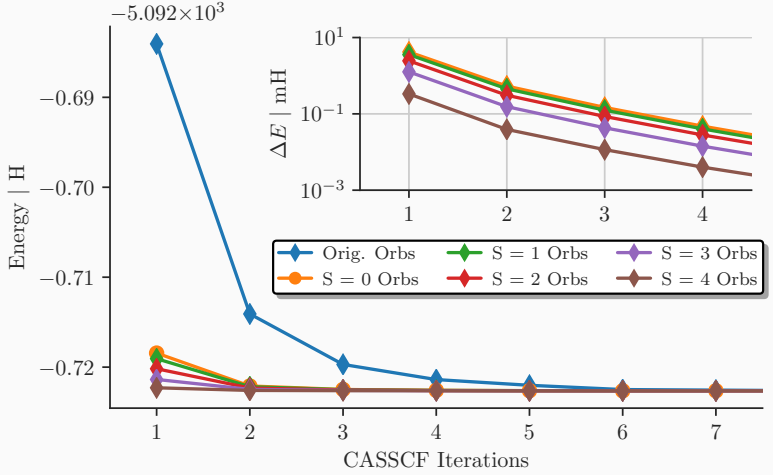
Produces the `$Project.FciDmp` file containing the new molecular integrals used by our FCIQMC code `NECI`, with output:

```
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
```

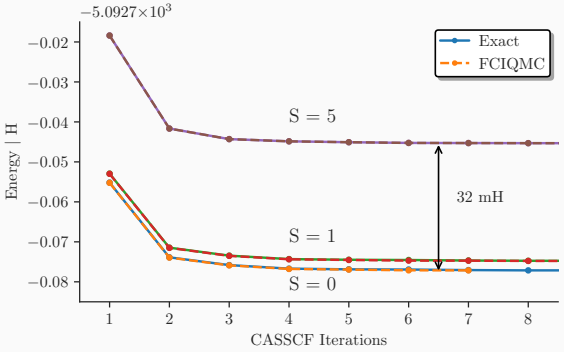
[†]Li Manni, Smart, Alavi, JCTC **12**, 3, 1245 (2016)

Results - CAS(10,10) Test-case

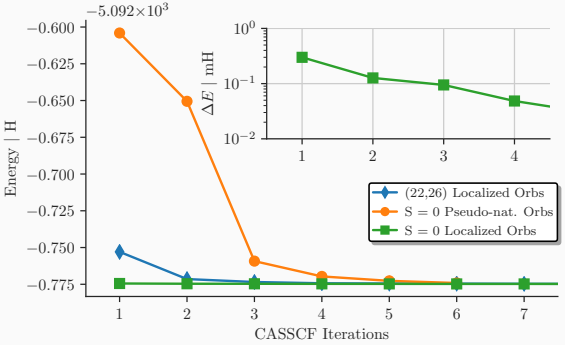


Deterministic 11-tet CASSCF starting from the **CSF-based optimized CAS(10,10)** of different spin-states.

Results - CAS(22,16)

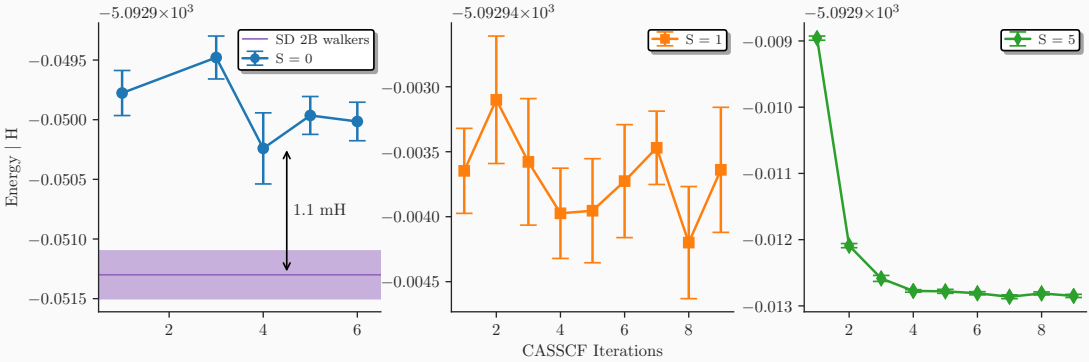


Singlet, Triplet and 11-tet CASSCF starting from the CAS(22,26) SD-optimized 'singlet' orbitals.



Deterministic triplet CASSF starting from the pseudo-natural and localized CAS(22,16) singlet orbitals.

Results - CAS(22,26) cont.



Singlet (left), triplet (middle) and 11-tet (right) spin-pure stochastic CASSCF calculations with **50M walkers** starting from the **CAS(22,26) SD-optimized 'singlet' orbitals.**

Li Manni, Dobrautz, Alavi, JCTC, **16**, 4, 2202 (2020)

The Gel'fand-Tsetlin Basis

4 ways of coupling a orbital:

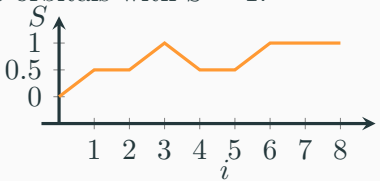
d_i		ΔN_i	ΔS_i
0	0	0	0
u	1	1	$1/2$
d	2	1	$-1/2$
2	3	2	0

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

CSF given by step-vector $|d\rangle$. E.g. 8 e^- in 8 orbitals with S = 1:

$$|d\rangle = |1,0,1,2,3,1,0,3\rangle$$
$$\equiv |u,0,u,d,2,u,0,2\rangle$$



Matrix Elements and Excitations via the Graphical UGA

Calculate MEs and generate excitations with **Graphical** UGA:

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

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

$$\hat{E}_{ij} |d\rangle = \sum_{n} C_n |d'_n\rangle$$

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

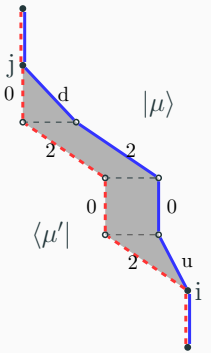
Matrix Elements and Excitations via the Graphical UGA

Single excitations

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

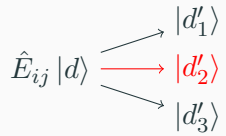
Double excitations

$$\langle d'|\hat{E}_{ij}\hat{E}_{kl} - \delta_{jk}\hat{E}_{il}|d\rangle = \sum_{x=0,1} \prod_{k} W_x(d'_k, d_k, S_k)$$



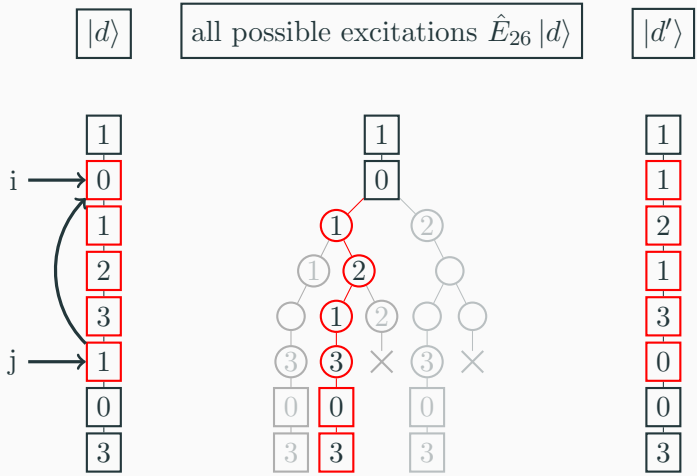
In FCIQMC we only need **one** connected state!

$\Rightarrow$ Loop over $i \rightarrow j$: select *one* excitation randomly through **branching tree** and calculate matrix element *on the fly!*



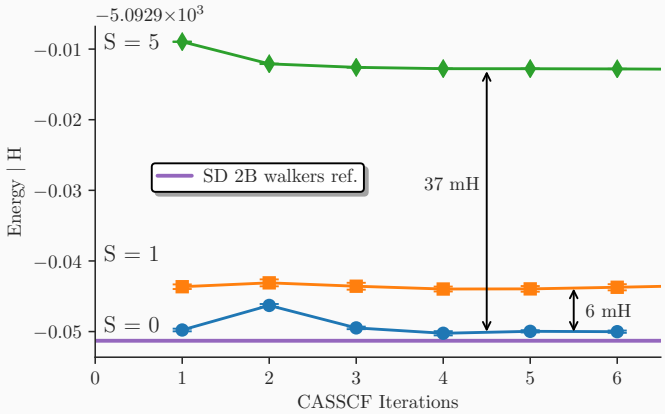
Shavitt, Int. J. Quantum Chem., **12**, 131 (1977)

The Branching Tree



Randomly chosen excitation and on-the-fly ME calculation

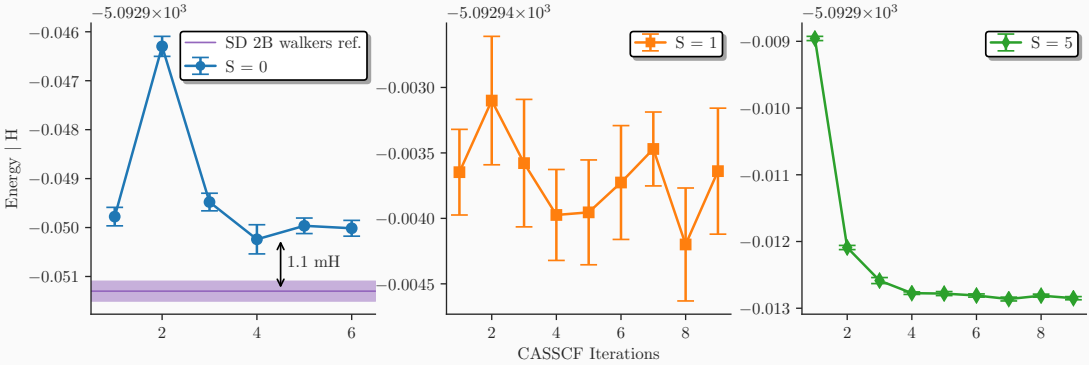
Results - CAS(22,26)



Singlet, triplet and 11-tet spin-pure stochastic CASSCF calculations with **50M walkers** starting from the **CAS(22,26) SD-optimized 'singlet' orbitals.**

Li Manni, Dobrautz, Alavi, JCTC, **16**, 4, 2202 (2020)

Results - CAS(22,26) cont.



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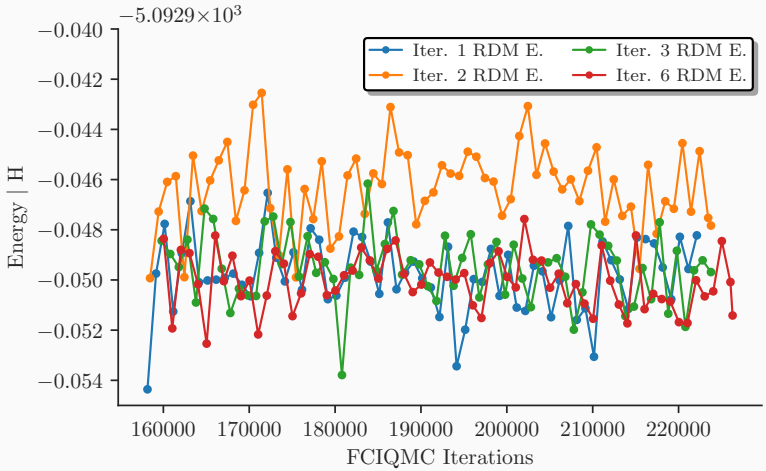
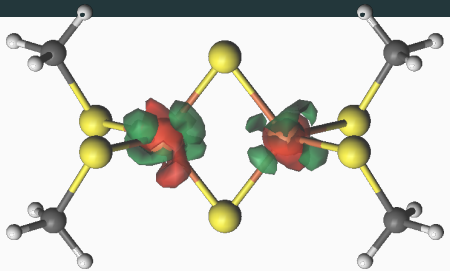
Results - CAS(22,26) cont.

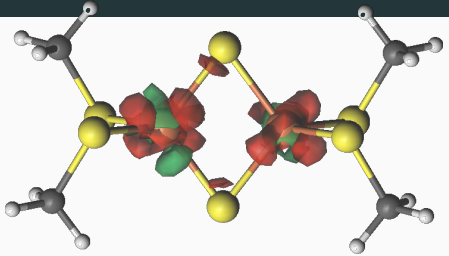


CAS(22,26) Singlet GUGA-FCIQMC RDM energies.

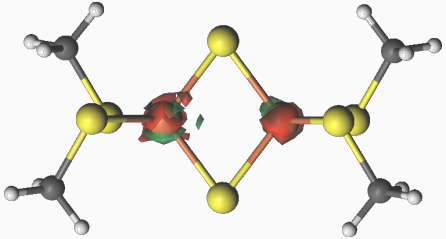
Results - CAS(22,26) Singlet Orbital Differences (Isovalue level: 0.0001)



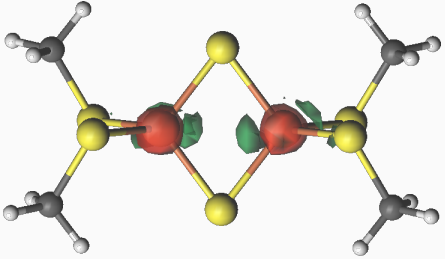
Singlet: Cycle 1 - Cycle 2



Singlet: Cycle 2 - Final



Singlet: Cycle 1 - Final



Final Singlet - Triplet difference