Spin-adapted FCIQMC using the Graphical Unitary Group Approach

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Max Planck Institute for Solid State Research

Outline

- Motivation
- Spin Symmetry and the Graphical Unitary Group Approach
- Results
- Histogram-based time-step optimization
- 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: $\Rightarrow$ stochastic wavefunction theory

Problems:

- 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)

Idea: Formulate FCIQMC in a spin-adapted basis

Spin Symmetry and the Graphical Unitary Group Approach (GUGA)

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

The 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 $U(n) \rightarrow$ find **invariant** and **irreducible** basis
- Sequential orbital coupling based on group chain:

$$U(1) \subset U(2) \subset \cdots \subset U(n-1) \subset U(n)$$

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

The Gel'fand-Tsetlin Basis

4 ways of coupling a orbital:

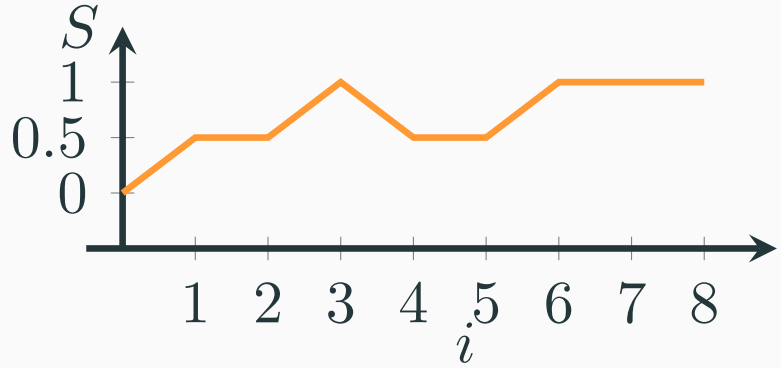
d_i		ΔN_i	ΔS_i
0	0	0	0
u	1	1	$1/2$
d	2	1	$-1/2$
2	3	2	0

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:

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



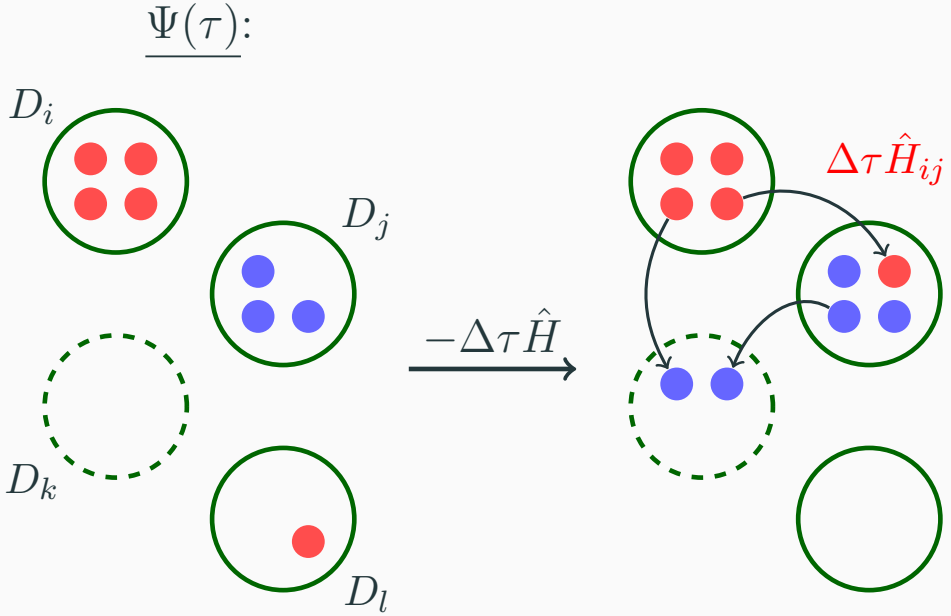
Intermezzo: Excitation generation in FCIQMC

FCIQMC

Population dynamics of walkers governed by:

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

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



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

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:

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

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

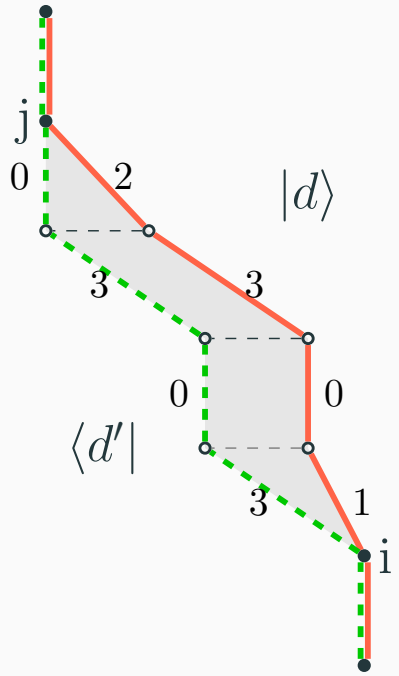
Matrix Elements and Excitations via the Graphical UGA

Single excitations

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

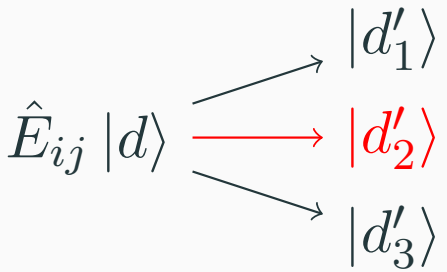
Double excitations

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



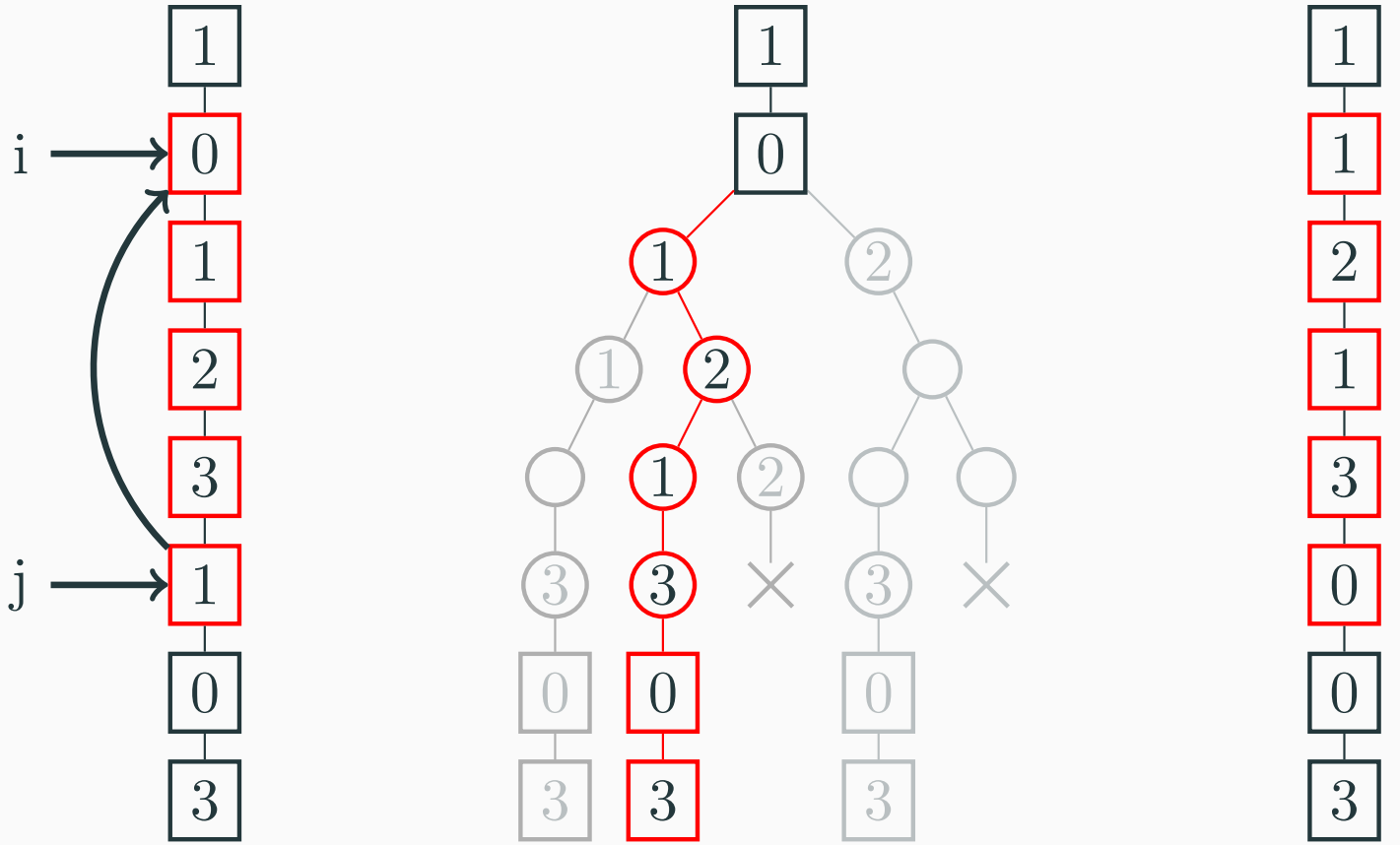
In FCIQMC we only need **one** connected state!

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



The Branching Tree

$|d\rangle$ | all possible excitations $\hat{E}_{26}\,|d\rangle$ | $|d'\rangle$

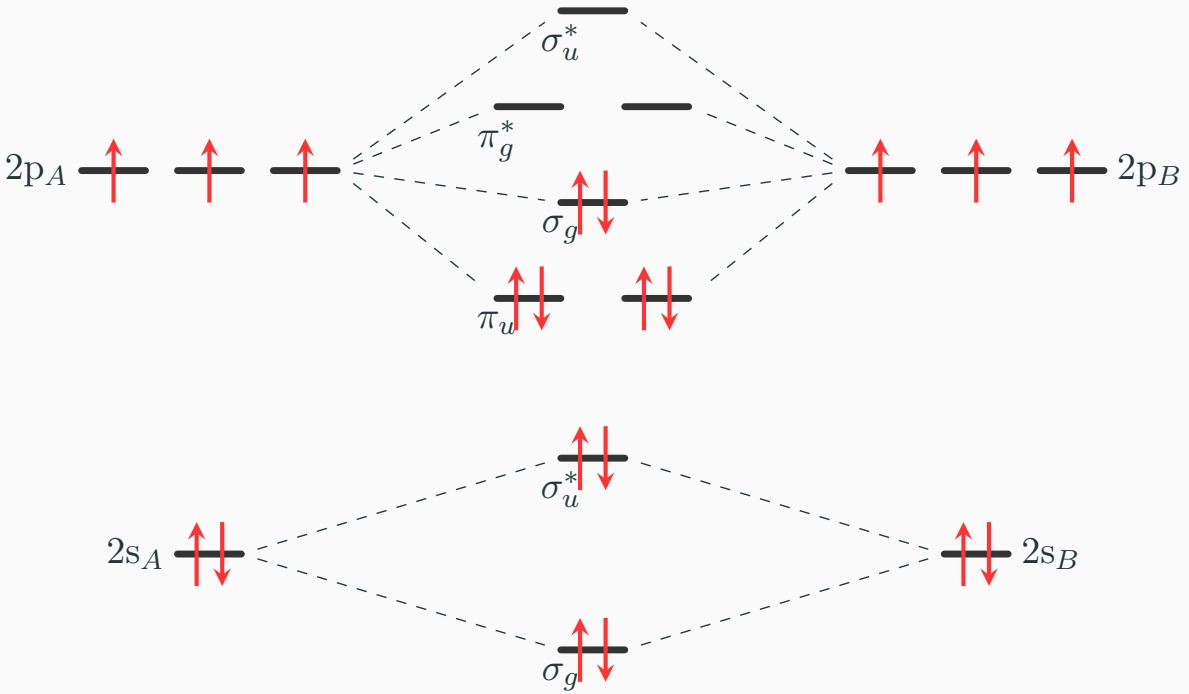


Randomly chosen excitation and on-the-fly ME calculation

Results

Nitrogen Dimer - Spin-resolved binding curve

- Optimal test case for spin-adapted approach
- 4 degenerate spin states at dissociation
- Spin-resolved binding curve in a cc-pVDZ basis
- Dissociation energy within chemical accuracy



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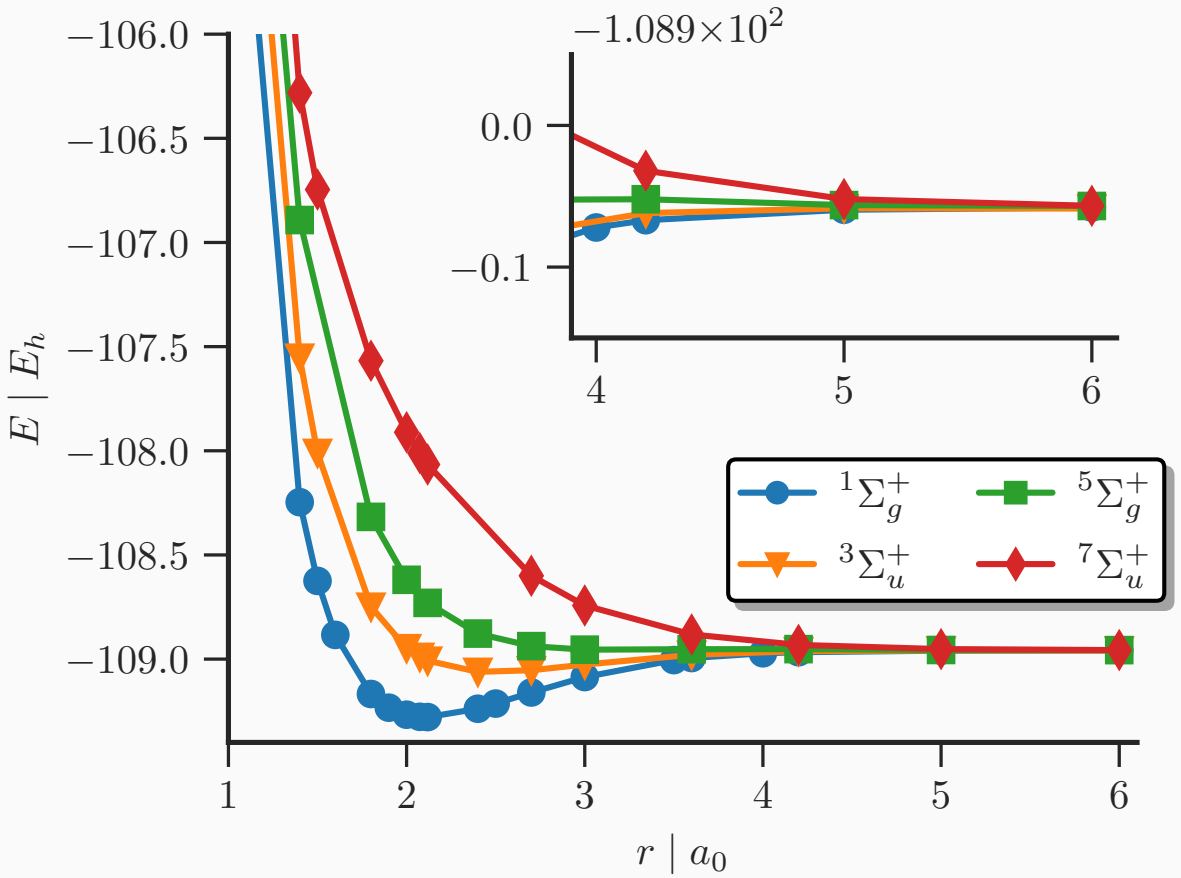
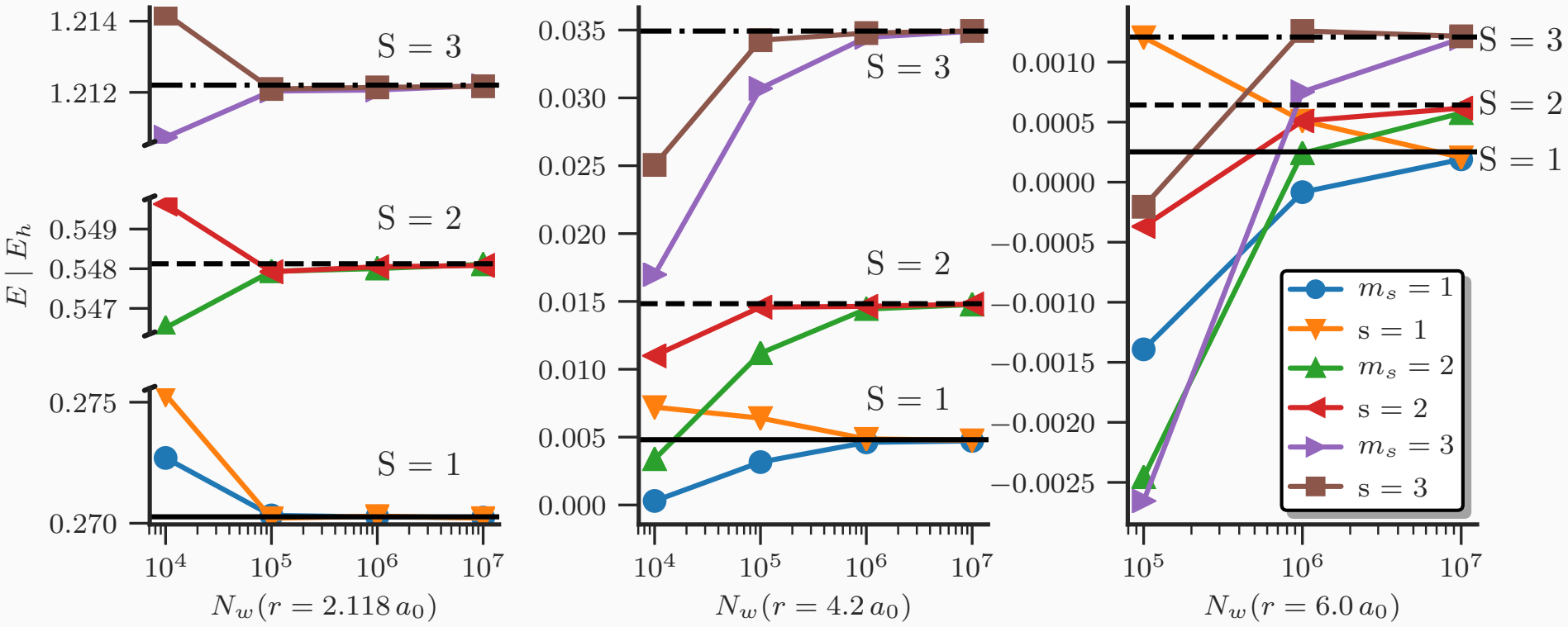


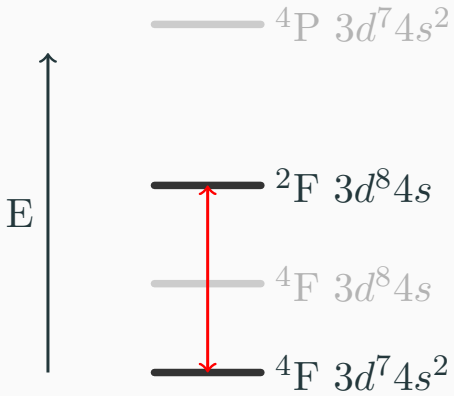
Nitrogen Dimer

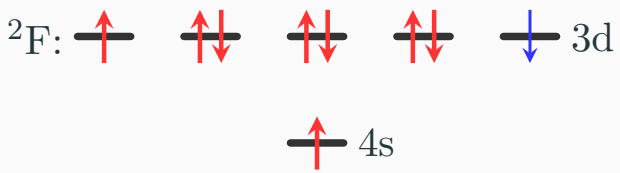
Improved convergence of small spin-gaps with GUGA-FCIQMC

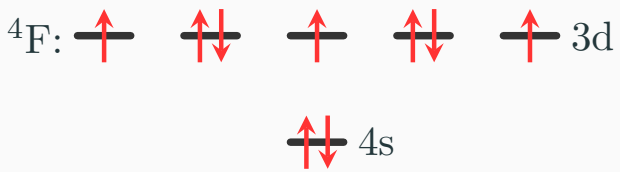


Comparison with m_s restricted SD based FCIQMC calculations

Results: Spin-Gap of the Cobalt Atom

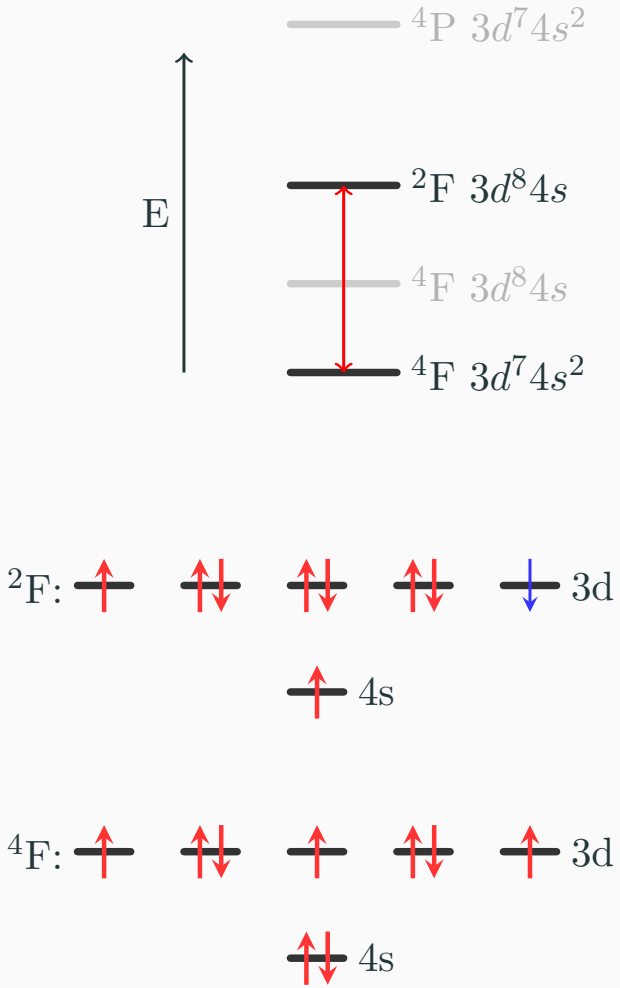


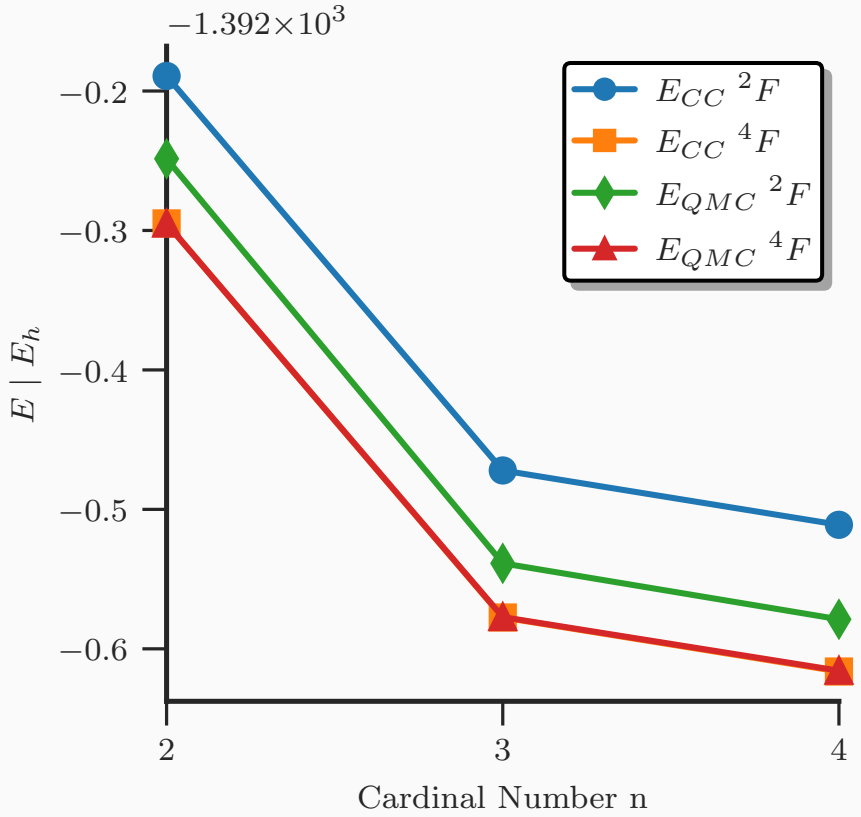




- Difficulties:
  -Restricting m_s converges to high-spin GS
  -Inaccessible by previous spin-adaptation, due to odd numbers of electrons
- Open-shell low-spin excited state: multi-reference character of ^{2}F state problematic for single-reference methods

Results: Spin-Gap of the Cobalt Atom



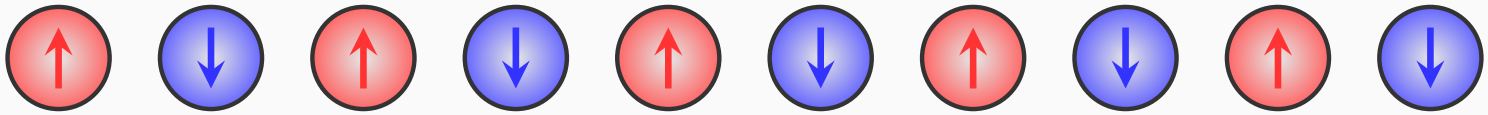


GUGA-FCIQMC and UCCSD(T) spin-gap vs. cardinal number of basis set

- Spin-gap $\Delta E_{D-Q}(TQ) = 21.17 \pm 0.59$ kcal/mol
  $\Delta E_{exp} = 20.26$ kcal/mol [Sugar and Corliss, 1985]

Pushing the limits: Hydrogen chain at dissociation

Number of open-shell orbitals is the restricting factor in spin-adapted approaches. Worst case:
Hydrogen chain (in a minimal basis) at dissociation:



L	S	$\Delta E \mid mE_h$
10	0	-0.00084(88)
10	1	-0.0059(10)
10	2	-0.00020(95)
20	0	-0.03719(35)
20	1	-0.0055(22)
20	2	-0.0026(15)
30	0	-1.1623(43)*

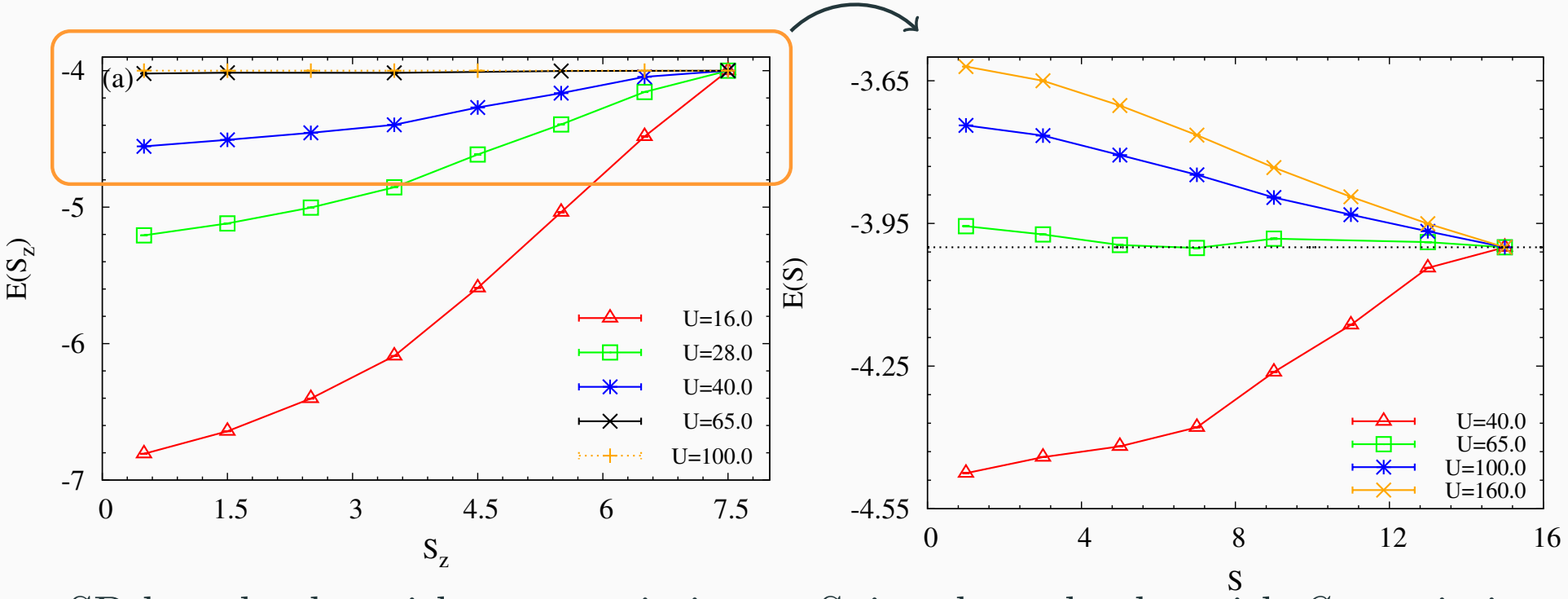
$S = 0, 1$ and 2 groundstate energy of a L-hydrogen chain at $r = 3.6\,a_0$ in a STO-6G basis set compared to DMRG and MRCI+Q reference results.

Wavefunction is **highly multiconfigurational** and dominated by all-open-shell CSFs.

* better accuracy with non-initiator calculation!

Pushing the limits: large U Hubbard model in a real-space basis - the Nagaoka Ferromagnetism

Groundstate energy as function of S_z (left) and S (right) for increasing U/t for 15 e^- on a 4×4 square lattice



SD-based calc. with m_s restriction

Spin-adapted calc. with S restriction

SD-based calculation converges to high-spin groundstate!

Histogram-based time-step optimization

Conventional time-step "optimization"

- Adapt $\Delta\tau$ to ensure the number of spawned walkers:

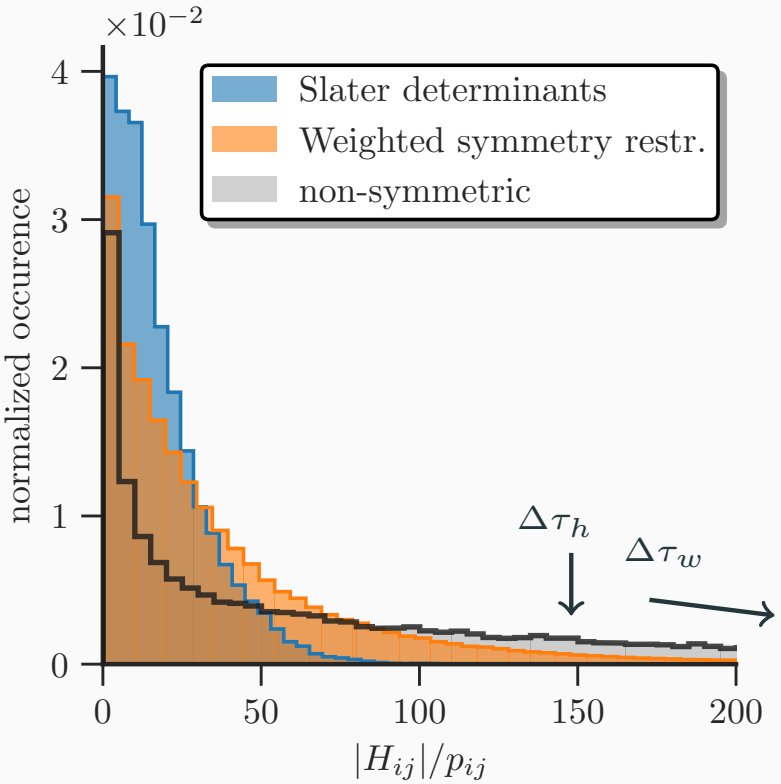
$$\Delta\tau \frac{|H_{ij}|}{p(j|i)} \approx 1.$$

- As a consequence the **global** time-step is determined by a **single** "worst-case" $\frac{|H_{ij}|}{p(j|i)}$ ratio, once and for all.
- This also implies a very rare spawn, $p(j|i) \ll 1$, determines the dynamics of the entire simulation.
- Especially damaging in the spin-adapted GUGA approach, with lower $p(j|i)$ due to the increased connectivity in a CSF basis.

Histogram-based time-step optimization

Instead of using worst-case $\frac{|H_{ij}|}{p(j|i)}$: histogram all occurrences and integrate to cover a chosen threshold (Default: 99.99%)

$\Rightarrow$ Almost all excitation are covered and time-step is not dominated by worst-case outliers!



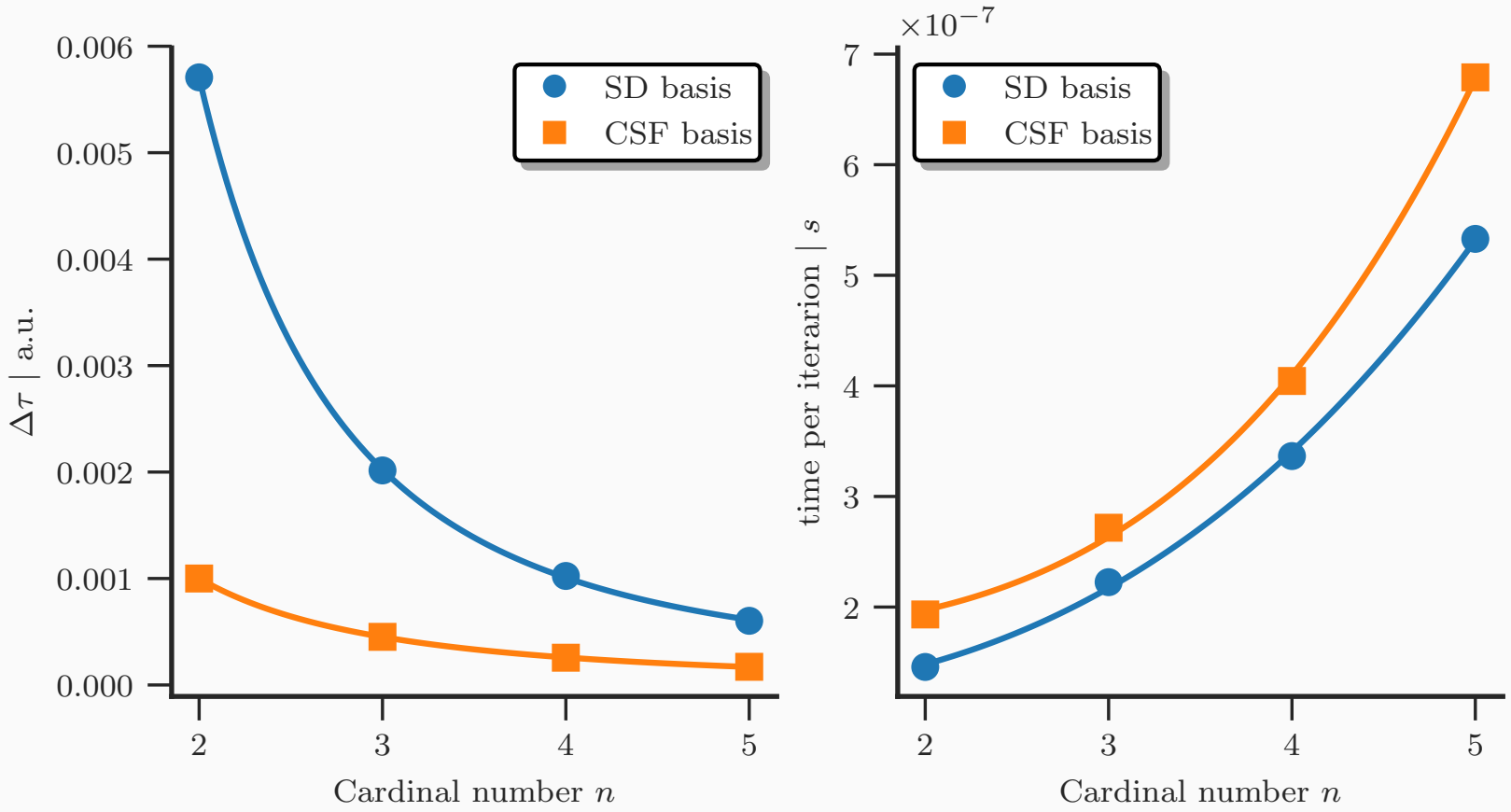
Worst case, $\Delta\tau_w$, and histogrammed time-step $\Delta\tau_h$ (99.99%) for the SD- and CSF-based N_2 calc. at equilibrium.

Basis	$\Delta\tau_w$	$\Delta\tau_h$	$\Delta\tau_h/\Delta\tau_w$
SD	$5.59 \cdot 10^{-3}$	$6.20 \cdot 10^{-3}$	1.11
CSF	$5.20 \cdot 10^{-5}$	$1.12 \cdot 10^{-3}$	21.50
Ratio	107.51	5.55	

Computational Cost

Performance penalty of spin-adapted FCIQMC implementation:

Additional scaling cost of $\approx \mathcal{O}(n^{1.3})$, with cardinal number n



Time-step $\Delta\tau$ (left) and time per iteration (right) vs. cardinal number of cc-pVnZ basis set for N_2 at $r = 4.2\,a_0$

Summary and Outlook

Summary and Outlook

Spin-adapted FCIQMC

- Efficient implementation via the GUGA
- Target specific spin states, reduce Hilbert space size and remove spin contamination
- Improve convergence for systems with small spin-gap
- Spin gap of cobalt in good agreement with experiment and systems with up to 30 open-shell orbitals possible

Outlook:

- Spin-pure RDMs to allow for fully spin-adapted Stochastic CASSCF calculations (Giovanni is desperately waiting for it, sorry...)
- Spin-free formulation of t-J and Heisenberg model (Optimization necessary to push lattice sizes)

Thank you for your attention!

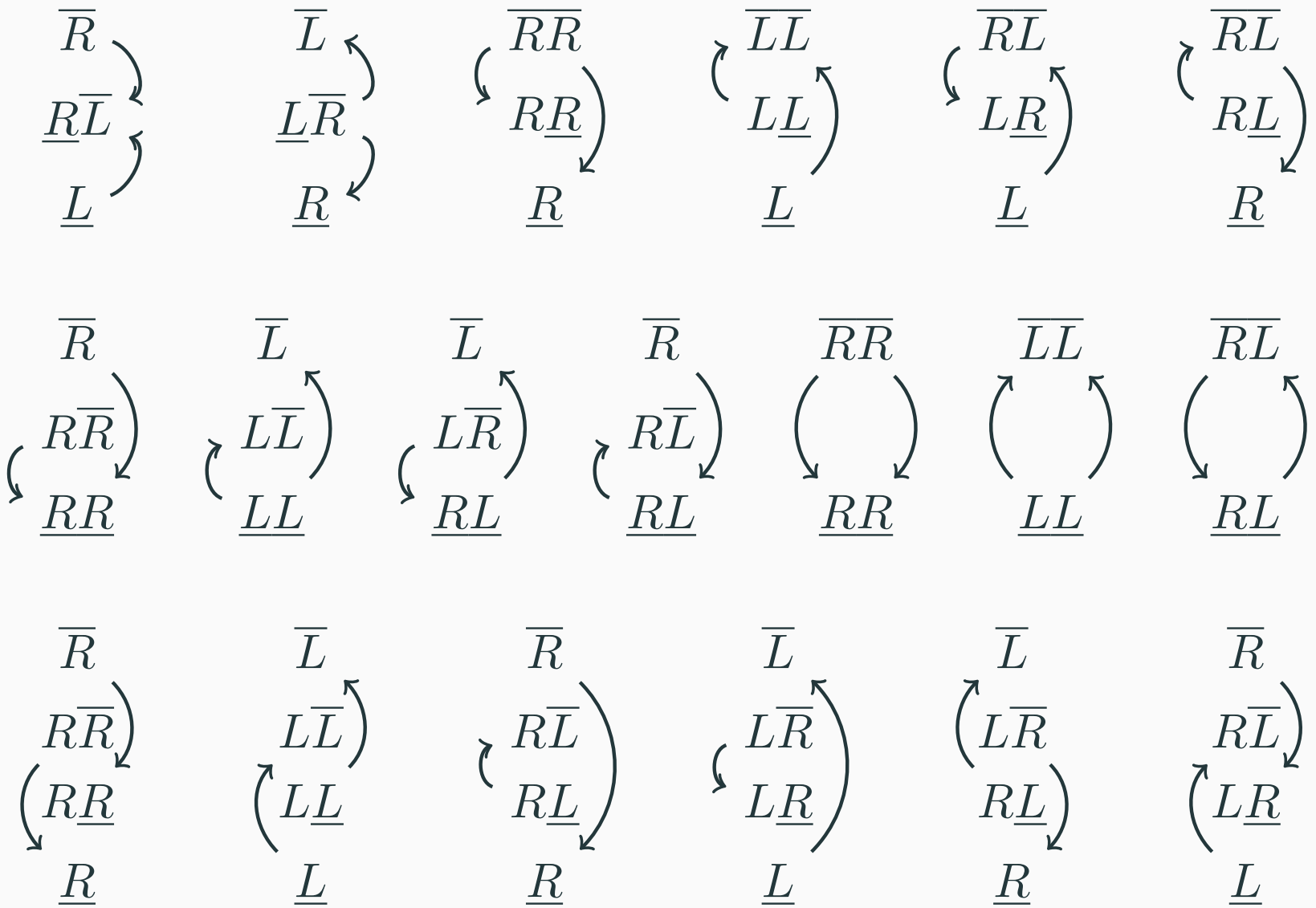
Double Excitations

- Excitations and matrix elements for two-body term

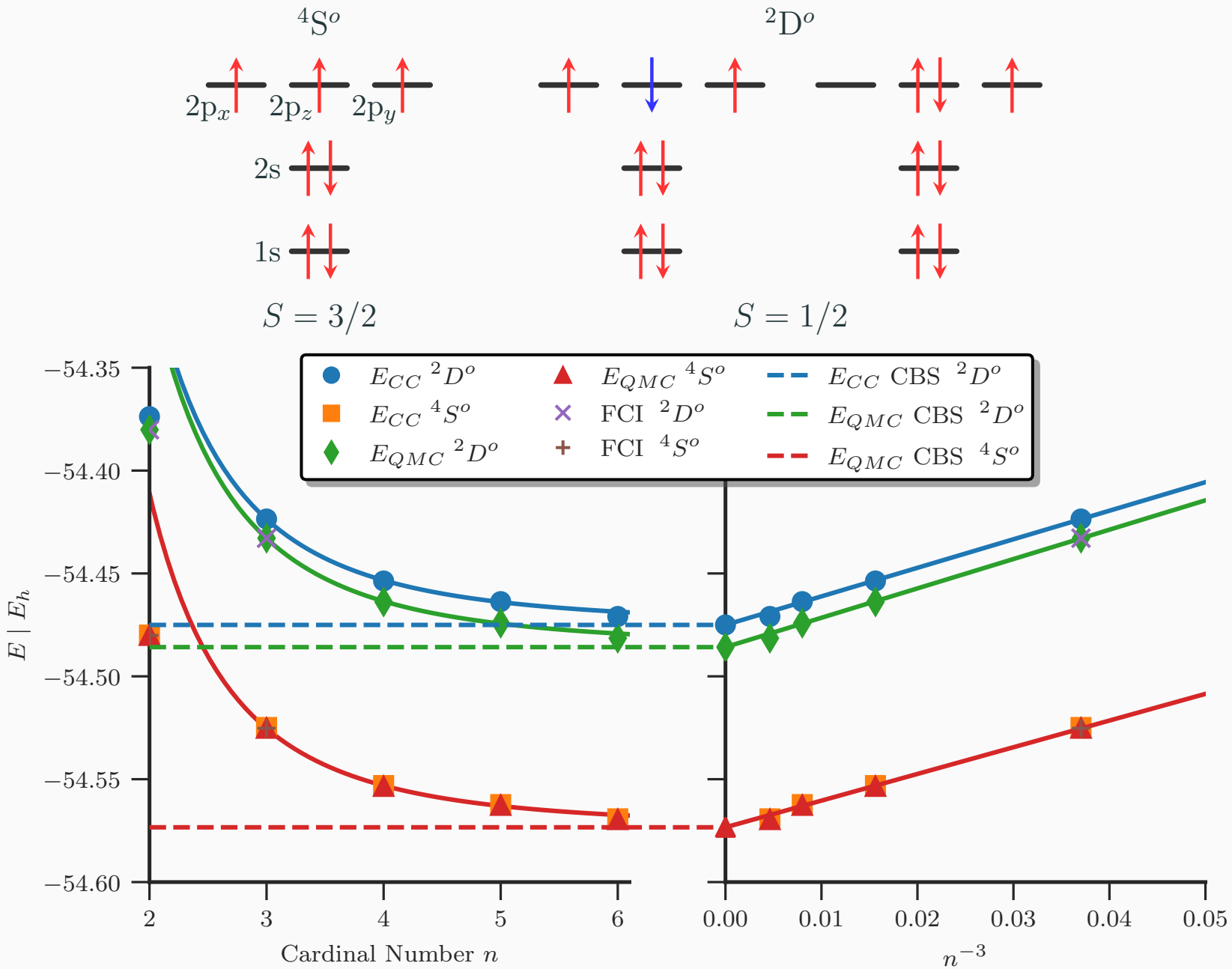
$$\langle d'|\hat{E}_{ij}\hat{E}_{kl} - \delta_{jk}\hat{E}_{il}|d\rangle$$

  much more complicated
- Classification of generators as raising (R) if $i < j$ or lowering (L) if $i > j$
- 19 types of distinct combinations, depending on order of indices (i, j, k, l)
- Branching tree and on-the-fly matrix element calculation still applicable

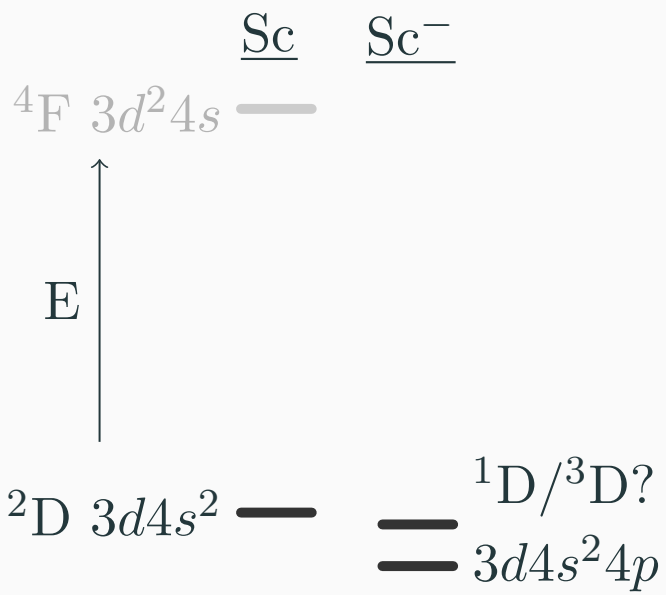
Double Excitations



Nitrogen Atom - Spin-gap



Result: Spin-Gap and EA of Scandium



- Surprising occupation of 4p orbital of Sc^-
- Experimental uncertain ordering of Sc^- bound states
- Open shell singlet or triplet GS?
- Multi-reference character of open-shell singlet problematic for single-reference methods

C. W. Bauschlicher, S. R. Langhoff, and P. R. Taylor, Chem. Phys. Let., **158**, 245 (1989); G. Jeung, Phys. Let. A, **113**, 73 (1985)

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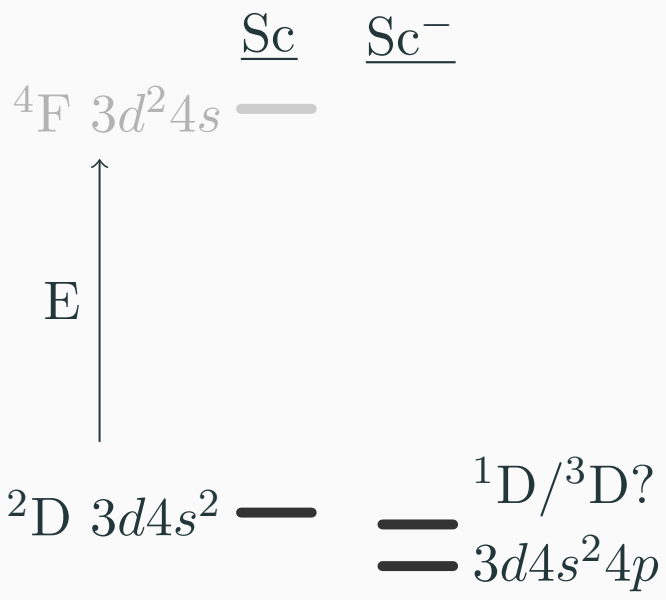

Electron affinities and Sc^- singlet-triplet spin-gap vs. cardinal number of basis set in mE_h

n	$^2D - {}^1D$	$^2D - {}^3D$	Sc^- $^1D - {}^3D$
2	7.740(75)	0.380(77)	7.341(76)
3	7.34(54)	2.572(77)	4.99(33)
4	6.67(75)	2.381(65)	4.80(42)
CBS	6.2 ±1.4	2.24 ±0.13	4.66 ±0.76
Exp.	6.95 ±0.74	1.54 ±0.74	5.40 ±1.47
ΔE	0.8 ±2.1	-0.70 ±0.86	0.7 ±2.2

- Electron affinities and spin-gap in good agreement with experiment [Feigerle et al., 1981, Sugar and Corliss, 1985]
- Singlet ^1D state undisputed ground state

C. W. Bauschlicher, S. R. Langhoff, and P. R. Taylor, Chem. Phys. Let., **158**, 245 (1989); G. Jeung, Phys. Let. A, **113**, 73 (1985)