GUGA-FCIQMC

Orbital Reordering in Lattice Models and Properties via RDMs

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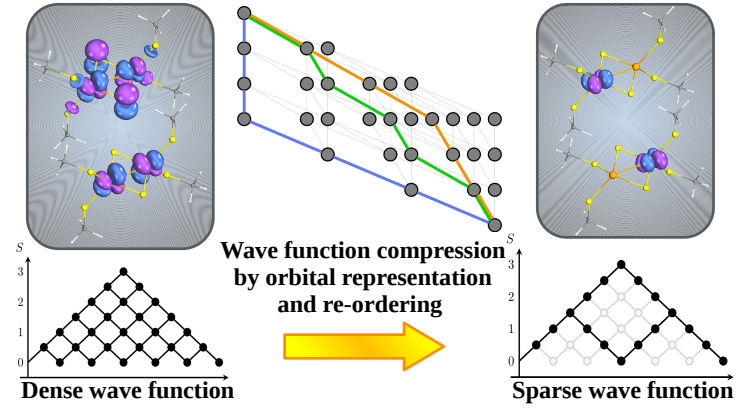
Max Planck Institute for Solid State Research

Outline

- Motivation: Wave Function Compression by Orbital Reordering
- Orbital Reordering: Application to Lattice Models
- Spin-pure RDM Sampling in GUGA-FCIQMC: CASSCF and Properties
- Scaling to Larger Systems and Extension to Hubbard and *ab initio* Systems
- Conclusions and Outlook

Motivation: Wave Function Compression by Orbital Reordering

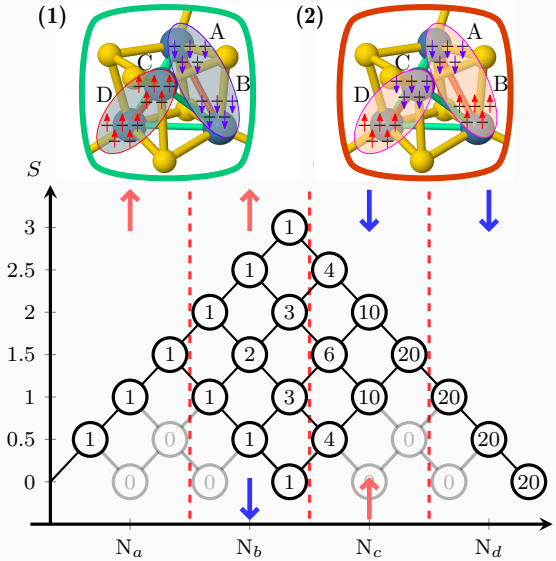
Compression by reordering – Iron-Sulfur Clusters



- Physically motivated ordering
- Locality
- Induced sparseness in Hamiltonian
- Compact ground state

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

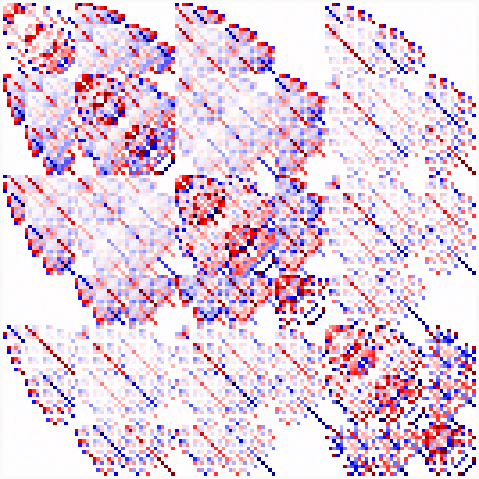
Compression by reordering



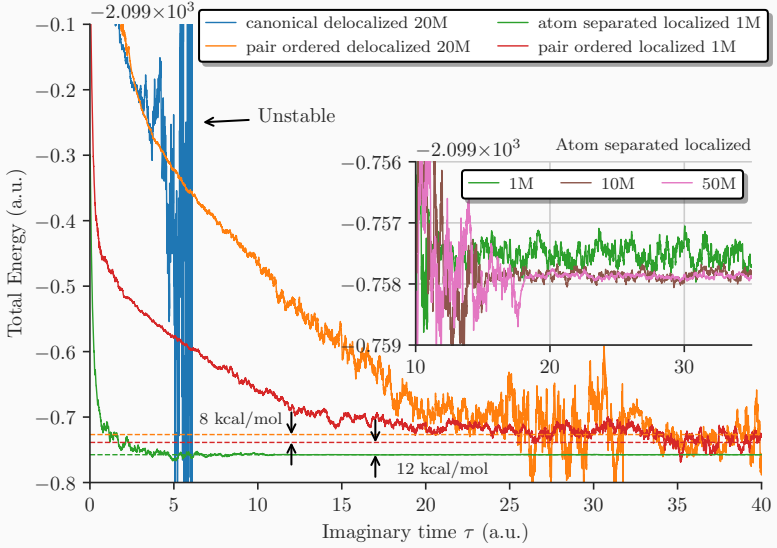
- Localized orbitals on each magnetic site
- captures local high-spin state
- (anti-)ferromagnetic interaction between magnetic centers, $\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$
- Compact excited states

Example: N_4 Compactness, Sparseness and quasi-Block-diagonalization

Open-shell CSFs of N_4 (12e,12o) active space in localized orbitals



Example: Chromium dimer CAS(24,48) at dissociation

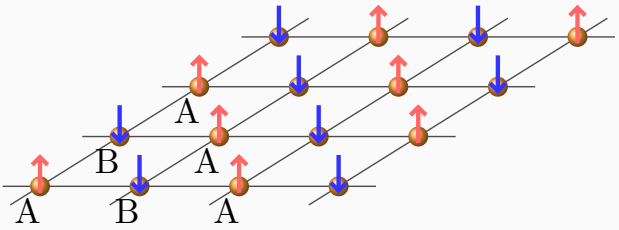


Orbital Reordering: Application to Lattice Models

Lattice models – Bipartite graphs

Heisenberg model: $\hat{H} = 2J \sum_{\langle i,j \rangle} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j$

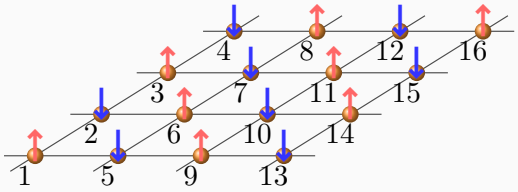
Spin-free GUGA form: $\hat{H} = J \sum_{\langle i,j \rangle} \hat{e}_{ij,ji} - \frac{JN_b}{2}$



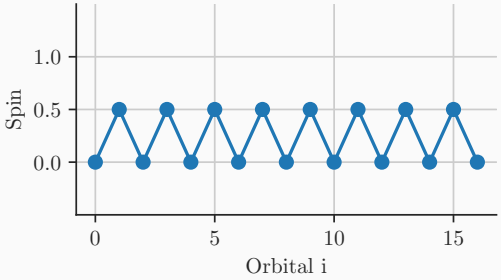
- Physically motivated ordering
- Bipartite: Every A has only B neighbors and v.v.
- E.g. used in sign-problem free formulation of Hubbard model at half-filling
- 'Unfrustrated'

4×4 Heisenberg model: Natural ordering

Intuitive straight-forward ordering used for SDs:



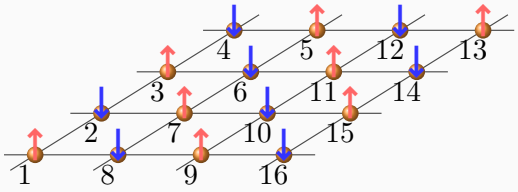
Reference CSF:



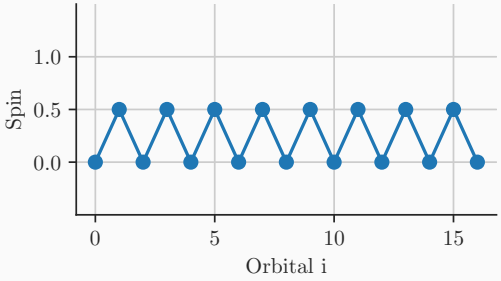
Problem across boundary (e.g. 4 - 5) already, since $S \geq 0$

4×4 Heisenberg model: Snake-like ordering

Snake-like ordering:



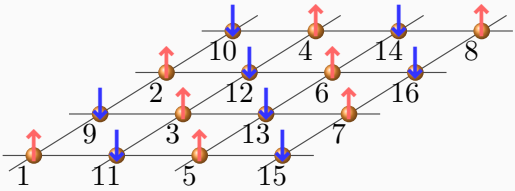
Reference CSF:

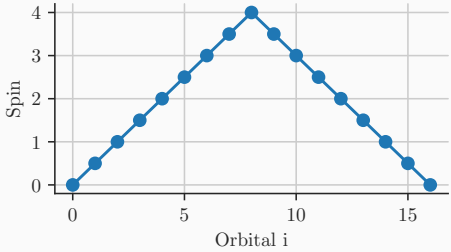


Problem across boundary (e.g. 4 - 5) resolved.

4×4 Heisenberg model: Bipartite ordering

Bipartite ordering:





Reference CSF (as for FeS/N systems!)

Order	reference weight [%]
Natural	30%
Snake	30%
Bipartite	**86**%

Question, as bipartite is not unique:

What is the ‘best’ ordering?

Can we use additional physically-motivated concepts like locality?

3 site Heisenberg chain

3-site Heisenberg chain with $S = \frac{1}{2}$: two possible CSFs: $|uud\rangle$ and $|udu\rangle$.

$$|u_1u_2d_3\rangle = \frac{1}{\sqrt{6}}(2\,|\uparrow_1\uparrow_2\downarrow_3\rangle - |(\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2)\uparrow_3\rangle)$$
$$|u_1d_2u_3\rangle = \frac{1}{\sqrt{2}}\,|(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)\uparrow_3\rangle$$

Equivalent set of spin eigenfunctions by applying the permutation operator P_{23}:

$$P_{23}\,|u_1u_2d_3\rangle = |u_1u_3d_2\rangle = -\frac{1}{2}\,|u_1u_2d_3\rangle + \frac{\sqrt{3}}{2}\,|u_1d_2u_3\rangle$$
$$P_{23}\,|u_1d_2u_3\rangle = |u_1d_3u_2\rangle = \frac{\sqrt{3}}{2}\,|u_1u_2d_3\rangle + \frac{1}{2}\,|u_1d_2u_3\rangle$$

3 site Heisenberg chain with OBC

$$\hat{H} = \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_3$$

In GUGA-CSF basis and natural (1-2-3) order:

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

whilst with the second (1-3-2) order, it is *already* diagonal:

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

A permutation (symmetric group) diagonalizes the (unitary group) Hamiltonian!

4 site Heisenberg chain – Periodic Boundary conditions

$$\hat{H} = \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_3 \cdot \hat{\mathbf{S}}_4 + \hat{\mathbf{S}}_4 \cdot \hat{\mathbf{S}}_1$$

The $S = 0$ CSF Hilbert space is still only 2 dimensional ($g(4, 0) = 2$), with the two states $|uudd\rangle$ and $|udud\rangle$. Employing the natural order 1-2-3-4, we obtain the Hamiltonian

$$H^{1234} = -\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{3}{2} \end{pmatrix}$$

whilst the order 1-3-2-4 yields the diagonal Hamiltonian

$$H^{1324} = -\begin{pmatrix} 2 & 0 \\ 0 & 0 \end{pmatrix},$$

Note: 4 site Heisenberg with PBC is 'biggest' system with single CSF ground state

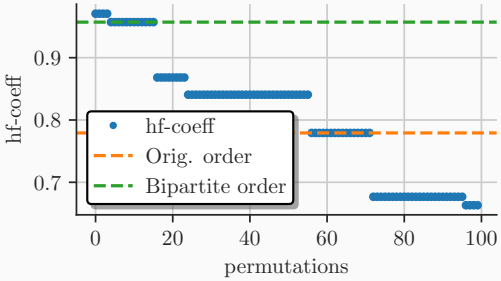
What is the ‘best’ ordering → extensive search

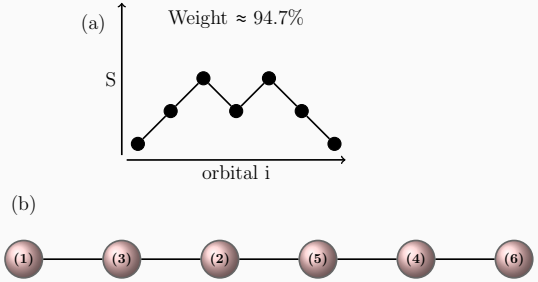
Workflow:

- Create all $n!$ permutations for n-site chain/ring (**very** rapidly growing!)
- Create the CSF Hilbert space for chosen spin ($S = 0$ for now)
- Loop over all permutations and create the Hamiltonian for chosen perm.
- Reminder: Order **DOES** matter in GUGA (difference to Slater dets.)
- Diagonalize the Hamiltonian, analyze and store interesting quantities (reference weight, etc.)

6 site Heisenberg chain – Compact Ordering and CSF

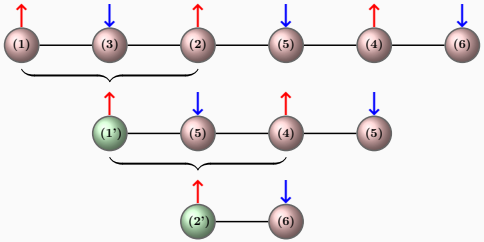
Reference weight in GS





Weight and reference for the compact ordered 6 site chain with OBC.

6 site Heisenberg chain – Renormalization

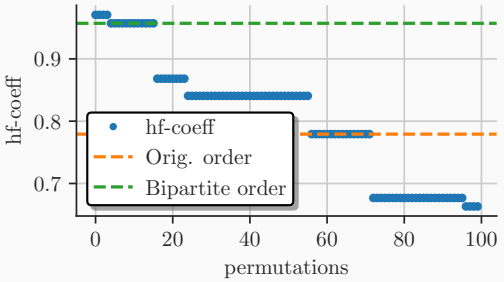


Cumulative doublet coupling of "meta-spin-1/2" in the most compact order.

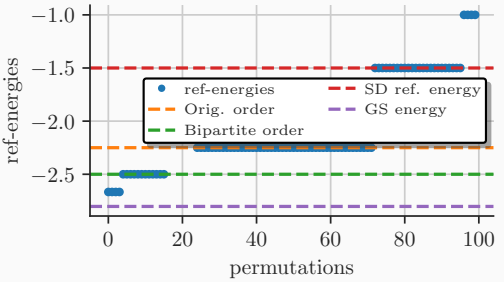
Order		Ref. CSF	CI coefficient [%] PBC	OBC
Natural	1-2-3-4-5-6	$\|u_1 d_2 u_3 d_4 u_5 d_6\rangle$	77.9	92.2
Bipartite	1-3-5-2-4-6	$\|u_1 u_3 u_5 d_2 d_4 d_6\rangle$	95.7	89.9
Compact	1-3-2-5-4-6	$\|u_1 u_3 d_2 u_5 d_4 d_6\rangle$	**97.1**	**94.7**
SDs Néel state		$\|\uparrow_1\downarrow_2\uparrow_3\downarrow_4\uparrow_5\downarrow_6\rangle$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

Combinatorial number of permutations: Need cheap indicator

For nearest neighbor Heisenberg model, the reference energy is a 'cheap' indicator for the largest weight!



Reference weight in GS



Reference energy of ref. CSF

Combinatorial number of permutations: Need cheap indicator

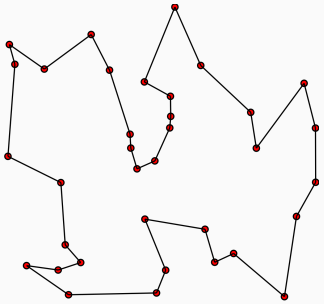
Need to minimize over all permutations, S_n, and CSFs, $|\mu\rangle$:

$$\min_{S_n} \min_{\mu} \langle \mu | \hat{H} | \mu \rangle$$

Heisenberg diagonal elements in the GUGA approach:

$$\langle \mu | \hat{H} | \mu \rangle \sim \sum_{j>i} V_{ij} X_{ij}(\mu), \quad V_{ij} = \begin{cases} J & \text{for nearest neighbors} \\ 0 & \text{else} \end{cases}$$

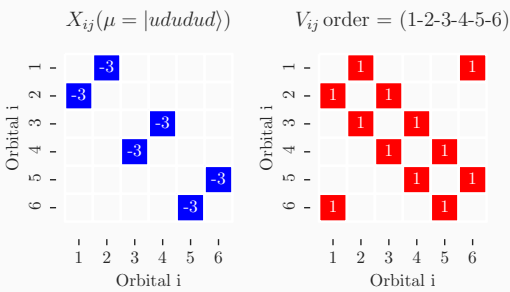
For nearest neighbor only: related to the traveling salesman problem (TSP)



Traveling Salesman Problem

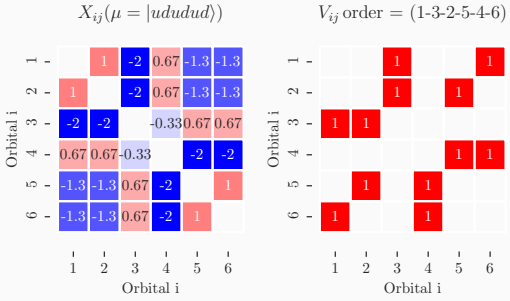
Cost function X_{ij} ('distance') and connectivity V_{ij} (chosen route)

Natural order:



Reference energy ≈ -9

Compact order:



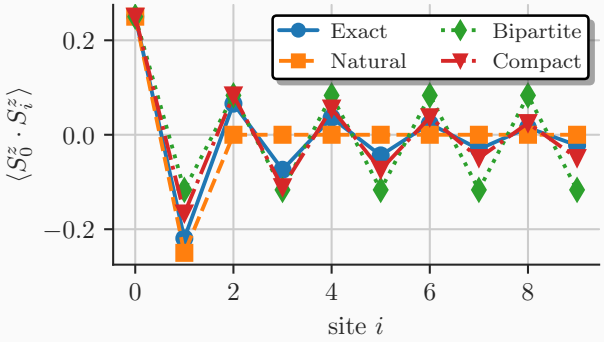
Reference energy ≈ -10.6

Used **Simulated Annealing** and state-of-the-art TSP solvers to verify compact order via renormalization for large number of sites

Physical motivation: Spin-spin correlation function

$$H = 2J \sum_{\langle i,j \rangle} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \sim J \sum_{\langle i,j \rangle} \hat{E}_{ij} \hat{E}_{ji} \qquad \rightarrow \quad \langle S_i^z \cdot S_j^z \rangle \sim \langle \hat{E}_{ij} \hat{E}_{ji} \rangle$$

Approximate with the single reference CSF $|\mu_0\rangle = \sum_i c_i |D_i\rangle$, which is still a linear combination of many SDs!



- Natural:
  $|\mu_0\rangle = |ududududud\rangle$
- Bipartite:
  $|\mu_0\rangle = |uuuuudddddd\rangle$
- Compact:
  $|\mu_0\rangle = |uudududududd\rangle$

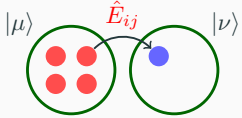
Spin-pure RDM Sampling in GUGA-FCIQMC: CASSCF and Properties

Spin-free RDMs with GUGA-FCIQMC: CASSCF and Properties

One- and two-body RDMs:

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

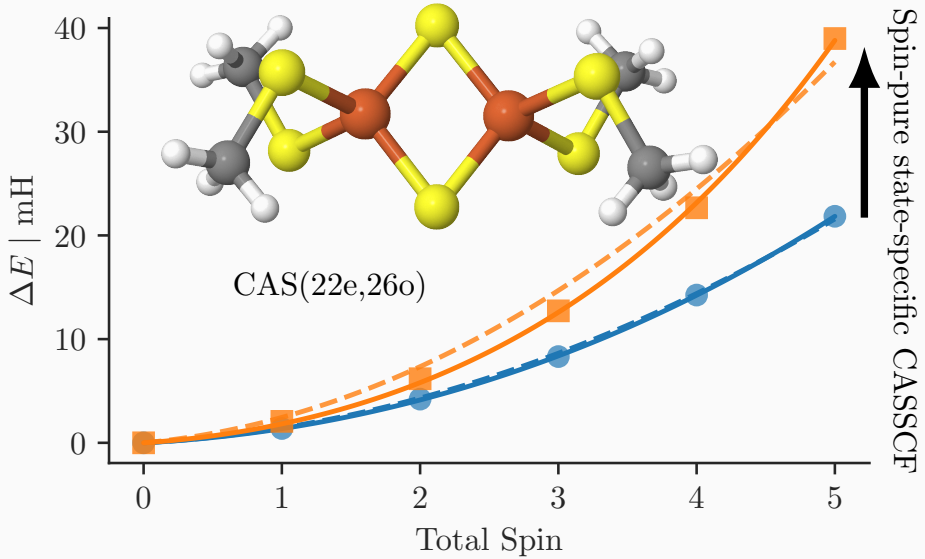
Replica trick*: two statistically independent simulations (I and II) for unbiased RDMs necessary! (Twice the computational cost)



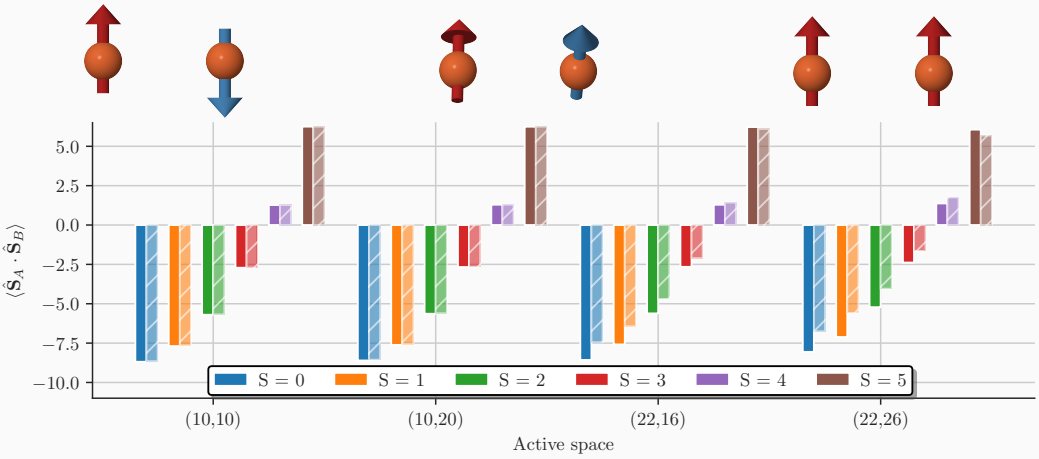
- Sample ρ_{ij} and $\Gamma_{ij,kl}$ in the *random excitation process* $|\mu\rangle \rightarrow |\nu\rangle$
- Already for SDs: store 'parent' state $|\mu\rangle$, coefficient c_μ and source (I,II) along $|\nu\rangle$
- New for GUGA: store *coupling coefficient* $\langle \nu | \hat{E}_{ij} | \mu \rangle$,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

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

Spin-pure state-specific CASSCF – Fe_2S_2



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

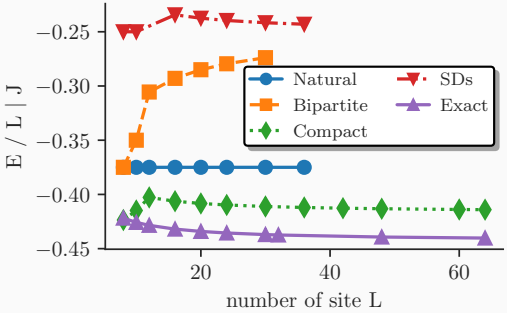


Back to the Heisenberg model

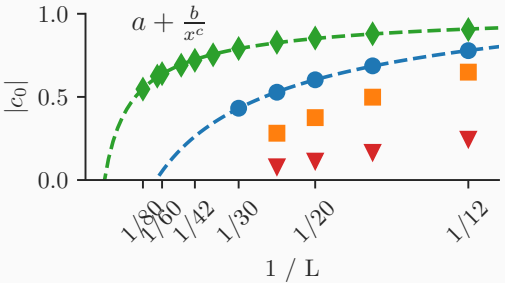
Scaling to Larger Systems and Extension to Hubbard and *ab initio* Systems

Scaling to larger systems: Reference energy and weight

Reference energy:

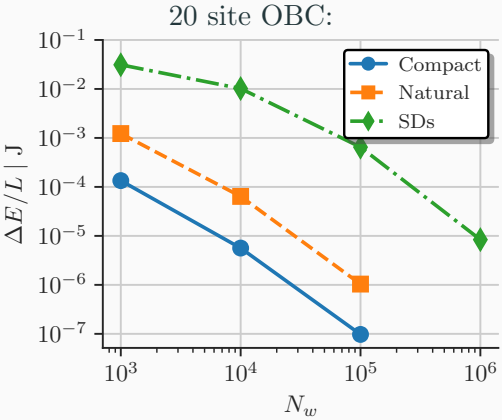


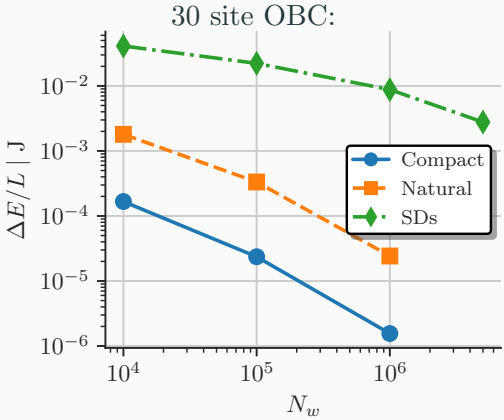
Reference weight:



Scaling to Larger Systems: FCIQMC accuracy

Difference to exact energy vs. number of walkers N_w:

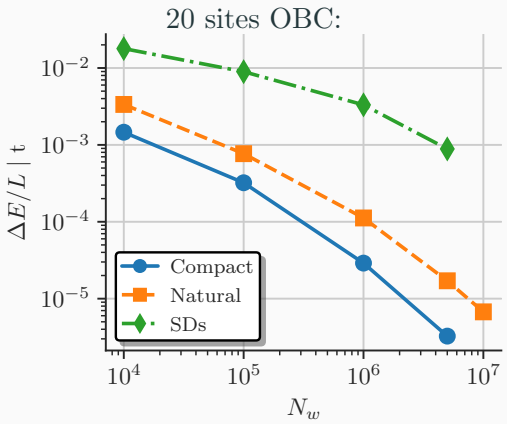


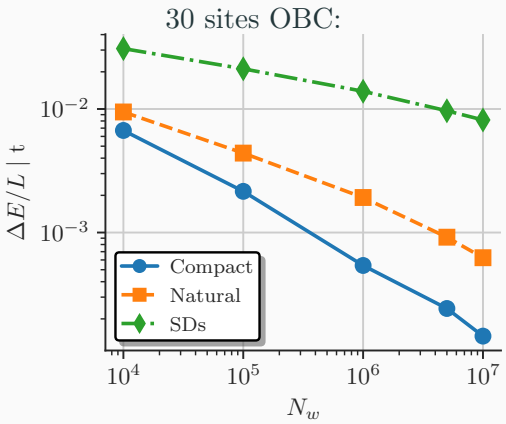


1D real-space Hubbard Chains

Real-space, half-filled Hubbard model, $U = 16$:

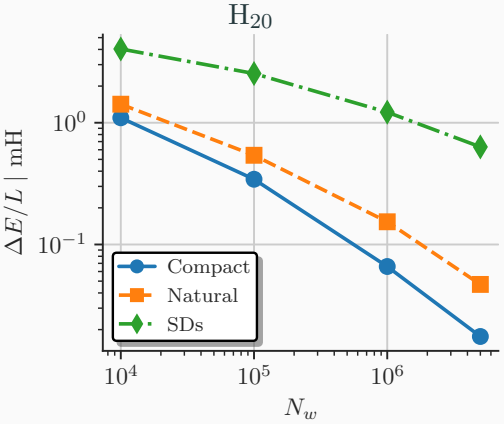
Difference to exact energy vs. number of walkers N_w:

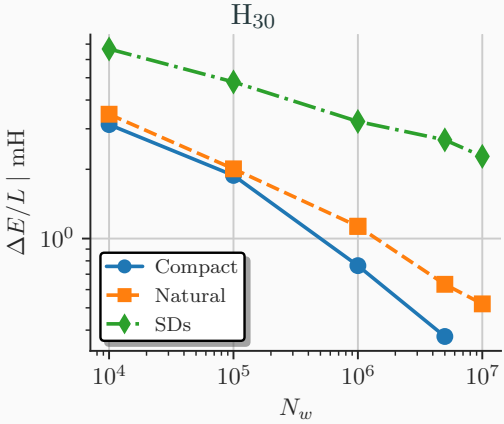




1D Hydrogen Chains in a minimal basis

3.6Å separated hydrogen chain in a minimal basis and localized orbitals:
Difference to exact energy vs. number of walkers N_w:





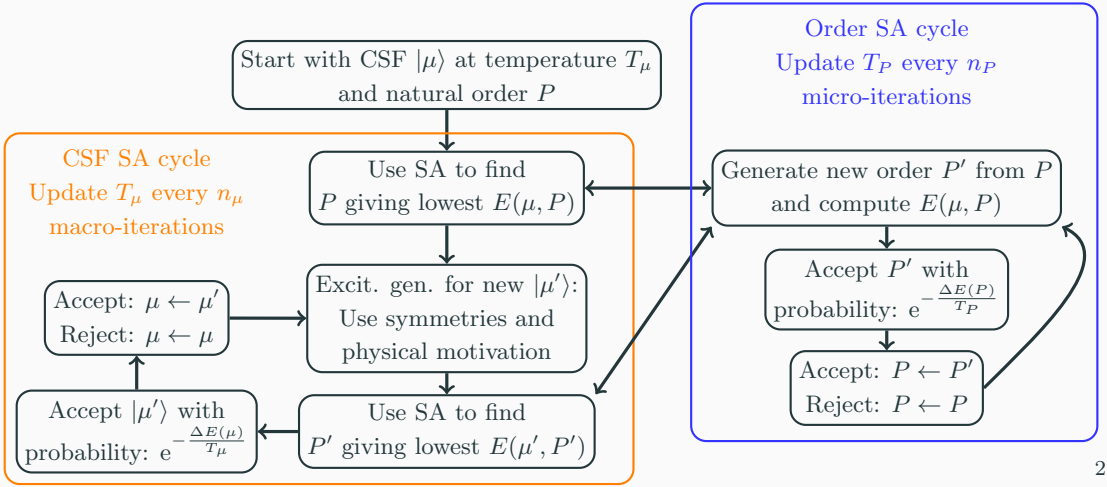
Summary: Reference weight

Weight of the reference state [%] for the Heisenberg, Hubbard and Hydrogen chains with OBC for the natural and compact ordering.

Order	Heisenberg		Hubbard			Hydrogen		
# sites	20	30	10	20	30	10	20	30
Natural	60.2	43.0	78.9	54.7	43.3	67.2	41.3	36.1
Compact	**85.4**	**79.0**	**87.3**	**77.1**	**68.4**	**74.0**	**54.9**	**46.8**

Target Larger Systems: Simulated Annealing + Excitation Generation

Use a mix of Simulated Annealing (SA) and GUGA-FCIQMC excitation generation to search for the 'best' CSF, $|\mu\rangle$ and corresponding permutation (order), P:



Conclusions and Outlook

Conclusions and Outlook

Conclusions:

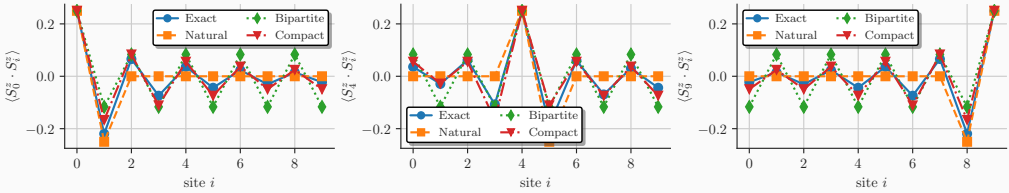
- Simple reordering of orbitals increases compactness of GUGA Ansatz
- Not only locality, but renormalization underlying concept (different than DMRG!)
- Mimics properties of exact solution (Reference energy and spin-spin correlations)
- Increased compactness of GS. Sparseness and block-diagonalization of Hamiltonian
- Orders of magnitude increased accuracy for initiator FCIQMC
- Combination of SA and excitation generation for larger systems

Outlook:

- Vamshi: Next-nearest neighbor interaction, frustrated systems and higher dimensions
- Giovanni: Application to *ab initio* systems
- Sujun: Real-space Hubbard model

Thank you for your attention!

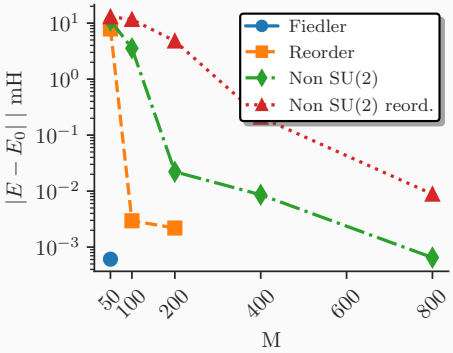
Scaling to larger systems



Difference to DMRG Reordering

Locality and entanglement are important concepts for DMRG orbital order.

Increased compactness by orbital reordering in GUGA is different!



30-site hydrogen chain DMRG energy difference to $M = 500$ Fiedler reference result for different orbital ordering with and without spin-adaptation versus matrix dimension M.

Spin-free RDMs with GUGA-FCIQMC cont.

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

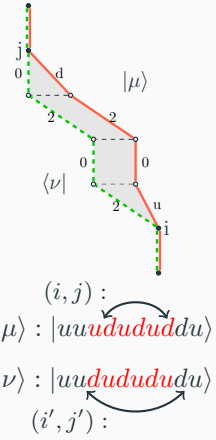
  More complicated as for SDs, but already calculated **on-the-fly** in *excitation generation*

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

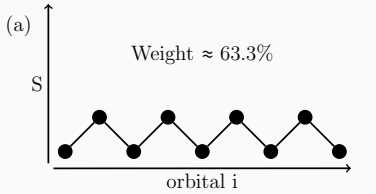
  Different *exchange* type double excitations $\hat{E}_{ij}\hat{E}_{ji}$ can lead to same $|\mu\rangle \to |\nu\rangle$. Needs to be considered for unique total *generation probability*, but for RDM sampling we need to unbias this



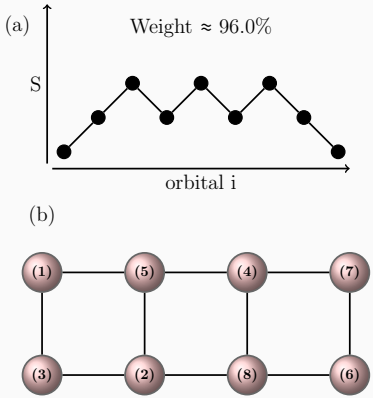
$\Rightarrow$ We need to communicate **three additional 64bit integers**. Communicating accumulated data every *1000 iterations* **only ≈10%** increase in time per iteration!

Interfaced with `OpenMolcas`

4×2 Heisenberg Ladder

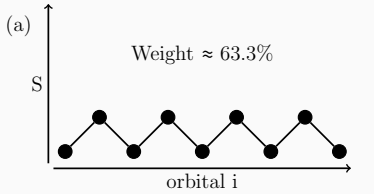


Natural order reference weight.

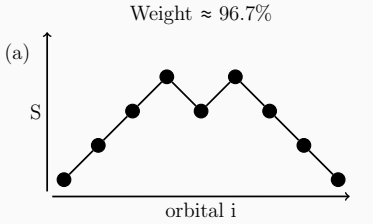


Compact order reference weight with OBC.

4×2 Heisenberg Ladder



Natural order reference weight.



Compact order reference weight with PBC.