SU(2) Symmetry in FCIQMC

using the Graphical Unitary Group Approach

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Motivation

Goal:

- *High accuracy* ab-initio calculations for large *strongly correlated* systems
- Beyond Hartree-Fock, DFT $\rightarrow$ *Wavefunction theory*

Problem:

- Small spin-gaps, near degeneracies, spin-contamination problematic for *rate of convergence* of projective methods

Idea:

- Formulate in a *symmetry adapted basis:* $[\,\hat{H}, \hat{S}^2\,] = 0 \rightarrow$ **Configuration State Functions**
- target specific spin-states, no spin-contamination, reduce Hilbert space size

Full Configuration Interaction Quantum Monte Carlo

- FCI $\leftrightarrow$ Exact Diagonalization in given basis set
- *Projector method* based on the imaginary-time Schrödinger equation, stochastically sampling FCI wavefunction:

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

- *First order difference* approximation $\mathrm{e}^{-\delta\tau H} \approx 1 - \delta\tau H$ leading to the *working equation:*

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

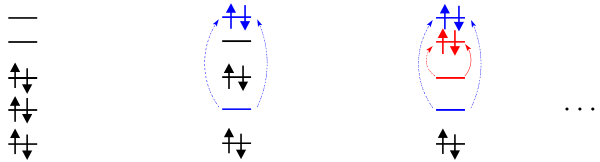
- *Population dynamics* of 'walkers' simulate the working equation.

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

- Coefficients proportional to signed walkers on state $c_i \propto N_i$
- No storage of full Hilbert space! Only "snapshot" of occupied states!

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

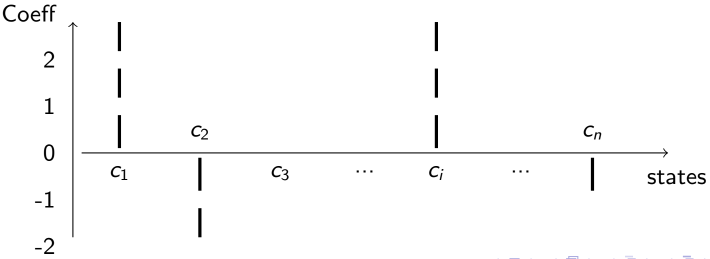
"The Hilbert space":



$|\Phi_0\rangle$ $\quad |\Phi_{ij}^{ab}\rangle$ $\quad |\Phi_{kl}^{cd}\rangle$ $\quad \ldots$

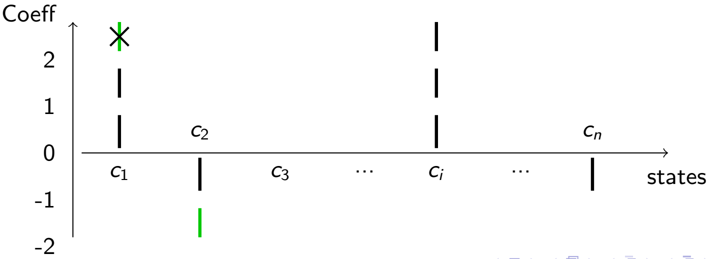
$$c_i(\tau + \delta\tau) = \underbrace{[1 - \delta\tau H_{ii}]\, c_i(\tau)}_{\text{death/cloning}} \underbrace{- \delta\tau \sum_{j \neq i} H_{ij} c_j(\tau)}_{\text{spawning}}$$

- *Three* algorithmic steps each time-step for each walker $|\Phi(\tau)\rangle$:



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

1: **Death/Cloning:** Die with $p_d = \delta\tau H_{ii}$ if $p_d > 0$



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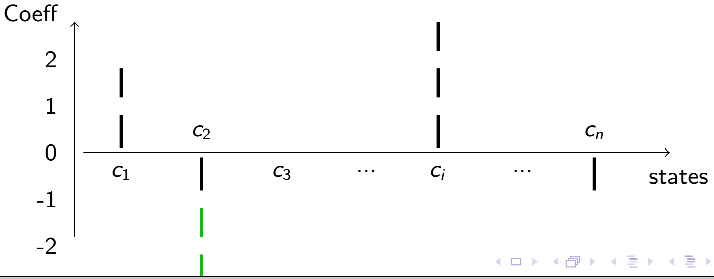
1: **Death/Cloning:** If $p_d < 0$ clone with $p_c = |p_d|$



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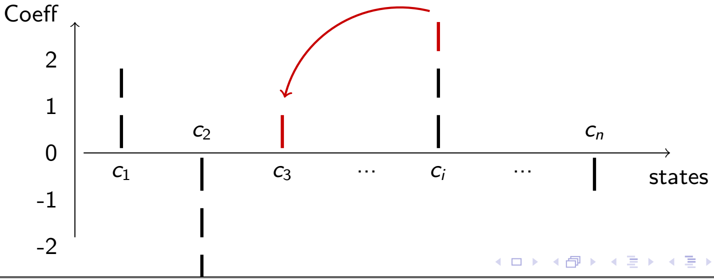
2: **Spawning:** with $p_s = \frac{\delta\tau |H_{ij}|}{p(j|i)}$, sign given by H_{ij}



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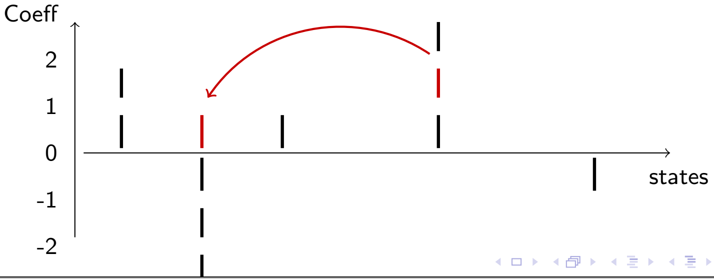

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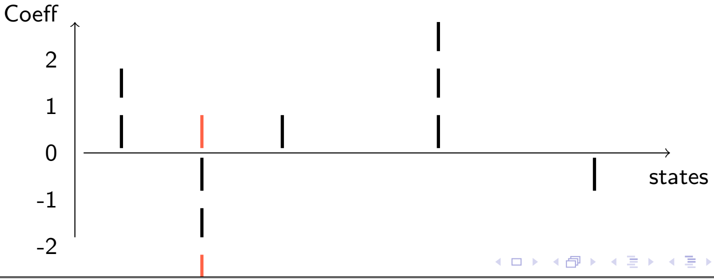
3: **Annihilation:** Walkers with opposite sign on same state are removed!



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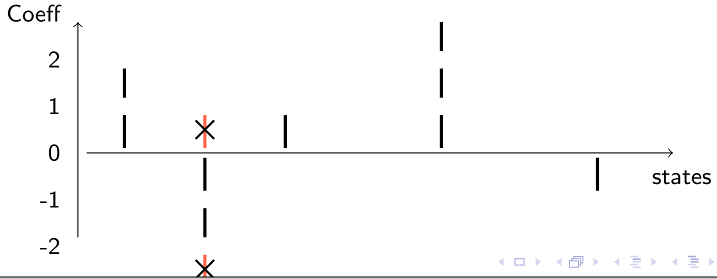

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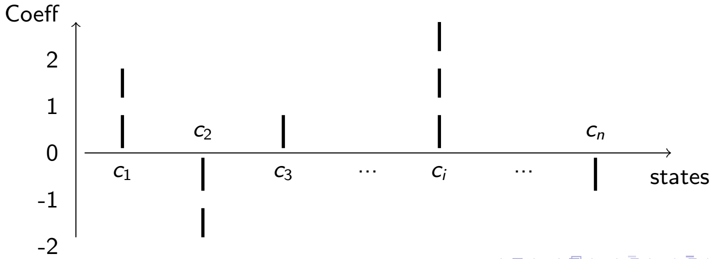
- $|\Phi(\tau + \delta\tau)\rangle$:



The Unitary Group Approach

- **Total spin symmetry:** inherent to spin-preserving, non-relativistic Hamiltonians:

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

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

$$\hat{H} = \sum_{ij}^{n} t_{ij} E_{ij} + \frac{1}{2} \sum_{ijkl}^{n} [ij;kl] \left(E_{ij} E_{kl} - \delta_{jk} E_{il} \right)$$

- with Spin-preserving substitution operators:

$$E_{ij} = c_{i\uparrow}^{\dagger} c_{j\uparrow} + c_{i\downarrow}^{\dagger} c_{j\downarrow}, \quad \text{with} \quad [E_{ij}, E_{kl}] = \delta_{jk} E_{il} - \delta_{il} E_{kj}$$

- *same commutation relations* as **generators** of the Unitary Group U(n) → find **invariant and irreducible** basis under action of E_{ij}

Gelfand-Tsetlin Basis

Sequential orbital coupling based on group subduction chain:

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

4 ways of coupling a orbital:

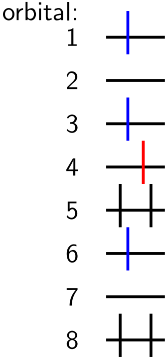
d_i	ΔN_i	ΔS_i
0	0	0
1	1	$1/2$
2	1	$-1/2$
3	2	0

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 $|d\rangle$

Gelfand-Tsetlin Basis

Example: 8 electrons in 8 spatial orbitals with S=1:



$\vert d \rangle$
1
0
1
2
3
1
0
3

Graphical Unitary Group Approach

Calculate matrix elements with **Graphical** UGA:

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

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

$$E_{ij}|d\rangle = \sum_n C_n |d'_n\rangle, \quad \text{with} \quad \langle d' | E_{ij} | d \rangle = \prod_{k=i}^{j} W(d'_k, d_k, S_k)$$

$$E_{ij}|d\rangle \rightarrow |d'_1\rangle, \; |d'_2\rangle, \; |d'_3\rangle$$

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But in FCIQMC we only need **one** connected state!

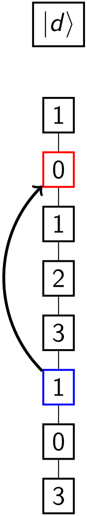
- Loop over $i \to j$: select *one* excitation randomly through **branching tree** and calculate matrix element *on the fly!*

Branching Tree

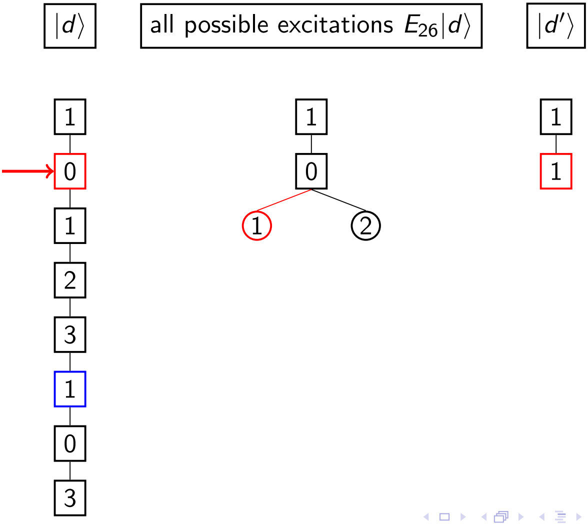
Example: 8 Electrons in 8 orbitals with S=1 and excitation from orbital $j = 6$ to $i = 2$ E_{26}:

$$E_{26}|1, 0, 1, 2, 3, 1, 0, 3\rangle$$

Branching Tree



Branching Tree



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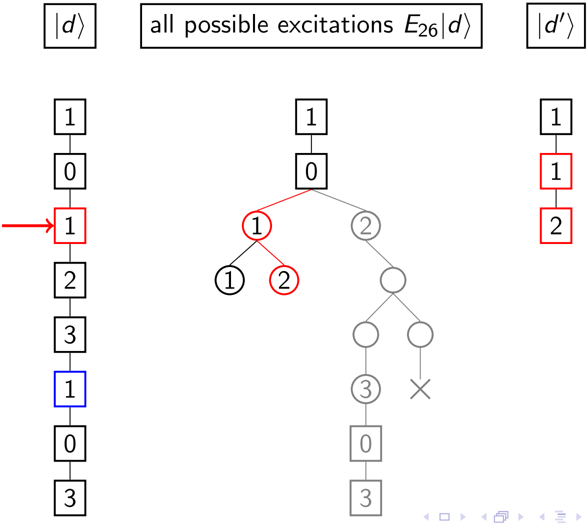
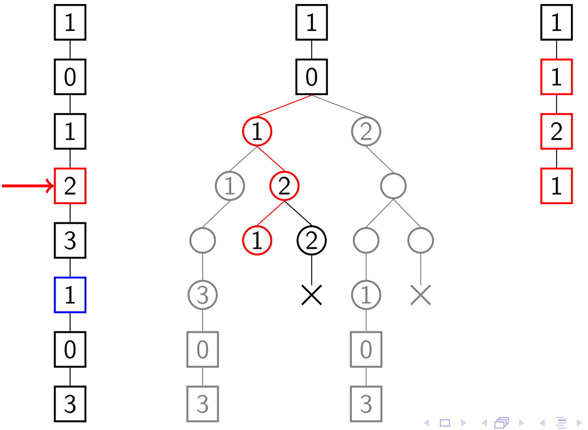


Branching Tree

$|d\rangle$ | all possible excitations $E_{26}|d\rangle$ | $|d'\rangle$



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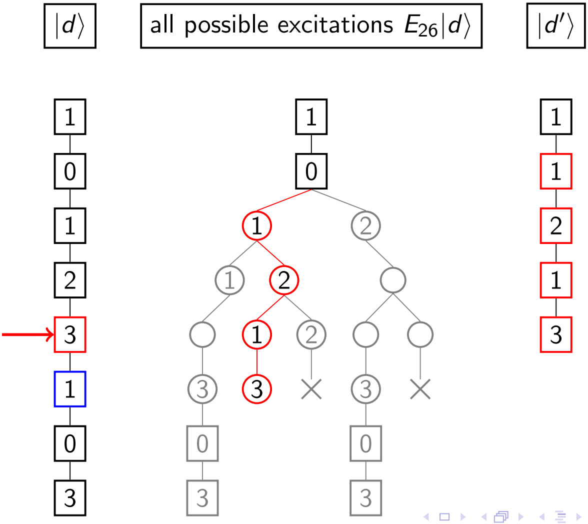

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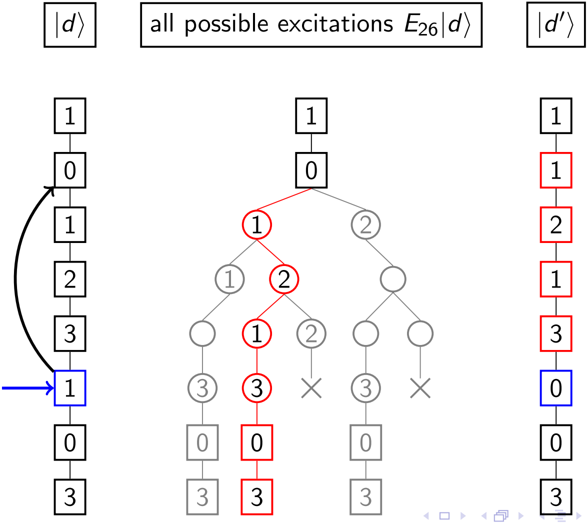
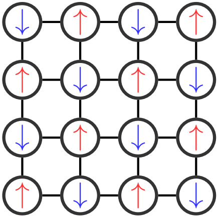


Two-dimensional real-space Hubbard model

$$\hat{H} = -t \sum_{\langle i,j \rangle,\sigma} \left(c^{\dagger}_{i,\sigma} c_{j,\sigma} + h.c. \right) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}$$

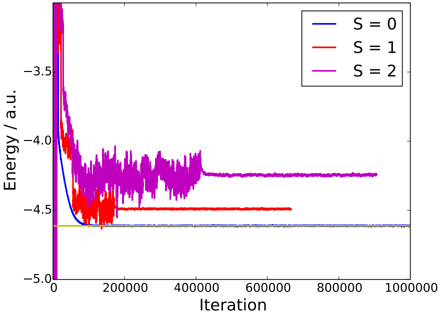


At Large Coulomb Repulsion U:

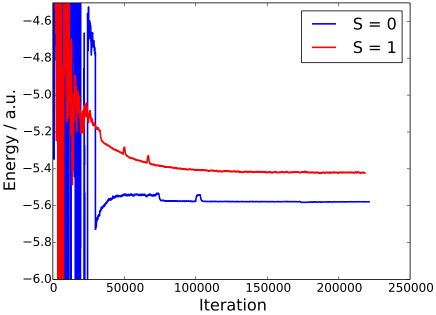
- dominant Anti-ferromagnetic Néel state
- Almost only open-shell orbitals
- Advantage: only single excitations
- Target low-spin eigenstates!

Two-dimensional real-space Hubbard model

16-site U=16, half-filled



20-site U=16, half-filled

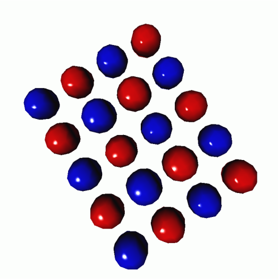


20-site Hilbert space size: 34B, Number of walkers: 500M

Hydrogen "lattice"

Full Ab-initio Hamiltonian:

$$\hat{H} = \sum_{ij}^{n} \sum_{\sigma=\uparrow,\downarrow} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{1}{2} \sum_{ijkl}^{n} \sum_{\sigma,\tau=\uparrow,\downarrow} [ij;kl] c_{i\sigma}^{\dagger} c_{k\tau}^{\dagger} c_{l\tau} c_{j\sigma}$$

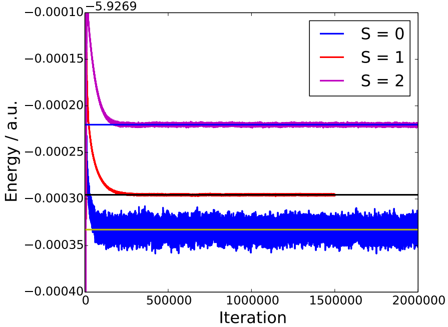


Large atomic separation in localized basis

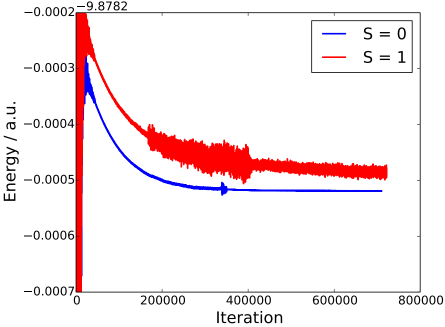
- Almost only singly occupied orbitals
- Single excitations predominant
- But also double excitations possible
- Open-boundary conditions

Hydrogen "lattice"

H_{12} at 4Å in a minimal basis set



H_{20} at 4Å in a minimal basis set



20-site Hilbert space size: 34B, Number of walkers: 10M

Thank you for your attention!