Non-unitary similarity transformation of the electronic Schrödinger equation via Gutzwiller and Jastrow factorization

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Outline

- Motivation
- Non-unitary Similarity Transformations
- Full Configuration Interaction Quantum Monte Carlo
- Gutzwiller Wavefunction Ansatz for the Hubbard Model
- Jastrow Factorization for ab-initio Models
- Conclusion and Summary

Motivation

Electronic Structure Theory

- **Electronic properties:** Energy differences, polarization, response functions, ...
- What we seek: Accuracy, predictability and interpretability
- Task: Solve the Schrödinger equation (ab-initio)

$$\hat{H}\Psi(\mathbf{x_1}, \ldots, \mathbf{x_n}) = E\Psi(\mathbf{x_1}, \ldots, \mathbf{x_n})$$

- **High complexity** $\rightarrow$ *Computational Physics and Chemistry*

Electronic Correlation

Weakly correlated systems:

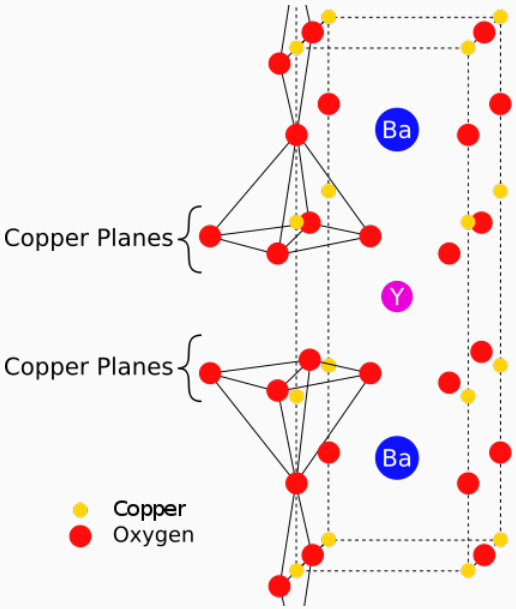
- Near-equilibrium geometry molecules, large electronic gap
- Single important electronic configuration
- Well described in a effective, mean-field approach
- Hartree-Fock, DFT, PT work well → Routine calculations for large systems possible

Strongly correlated systems:

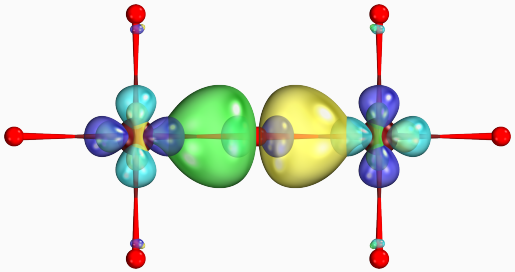
- Transition metal systems, non-equilibrium geometries, excited states, ...
- Multiple important electronic configurations
- Beyond mean-field: multi-reference methods

→ **Stochastic wavefunction theory**

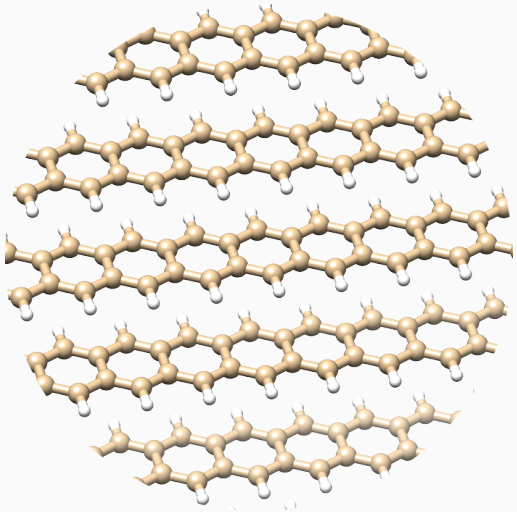
A few examples of Applications



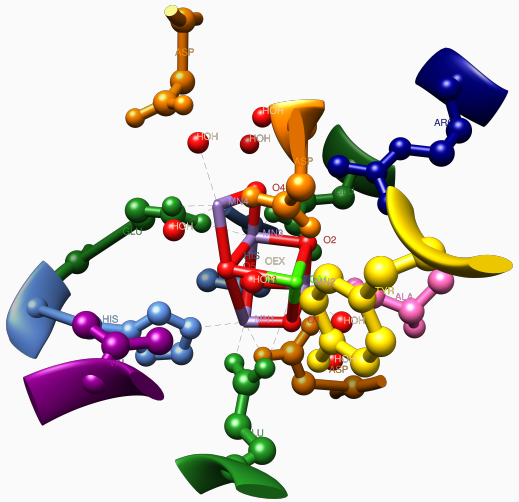
YBCO*



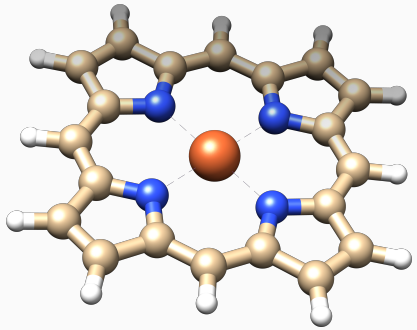
Cu-O-Cu‡



Polyacene†



Photosystem II†

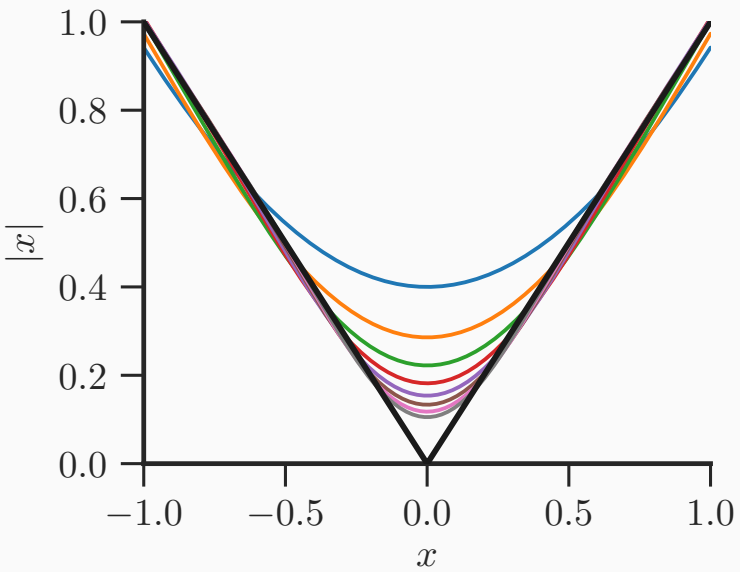


Metal Porphyrin†

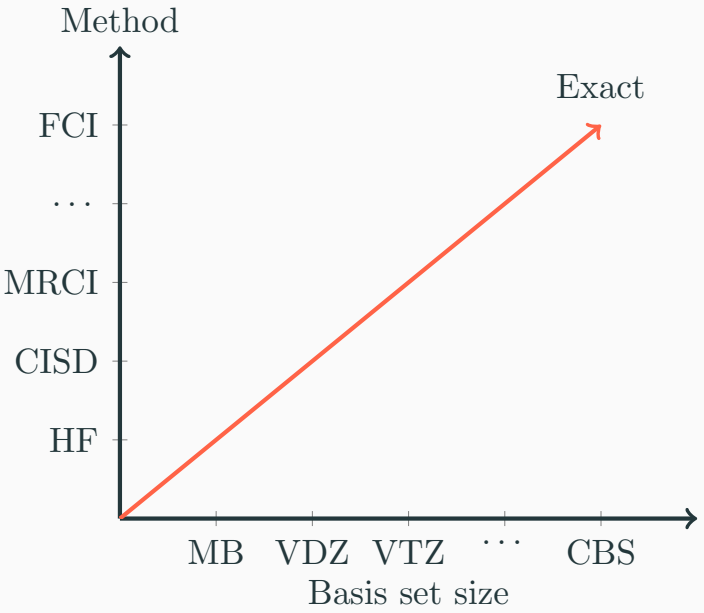
Images from: *`commons.wikimedia.org`, †G. Li Manni, ‡N. Bogdanov

Problems for accurate description: Cusp condition and hierarchy of methods and basis set size

Cusp condition: $$\lim_{r_{ij}\to 0}\left(\frac{\partial\Psi}{\partial r_{ij}}\right)_{av} = \frac{1}{2}\Psi(r_{ij}=0)$$



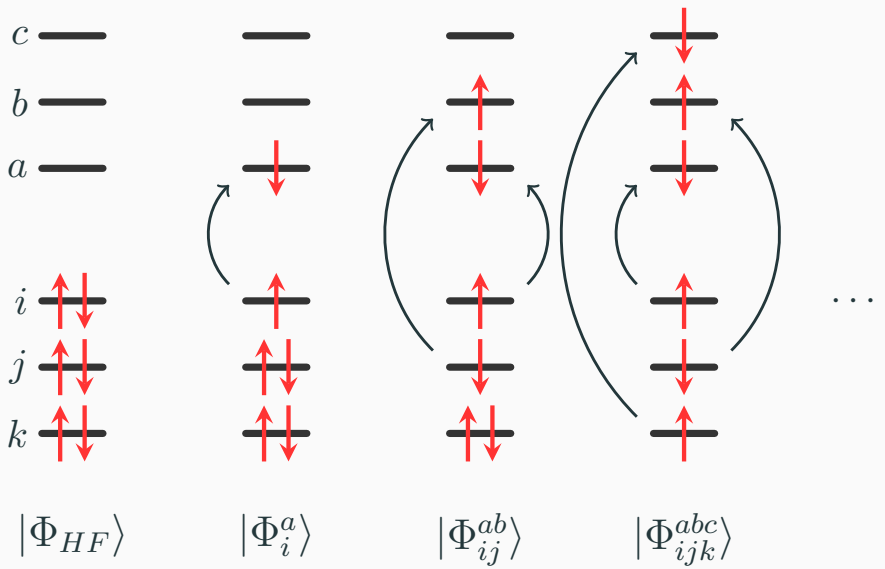
Non-differentiable behaviour at electron coalescence ⇒ large basis set expansion necessary



Hierarchy of methods and basis set size ⇒ detrimental scaling with number of orbitals of more accurate methods

Problems:
Exponential scaling of Full Configuration Interaction (FCI)

$\text{FCI} \Rightarrow |\Psi\rangle = \sum_I c_I |D_I\rangle \Rightarrow$ 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	$\sim 2 \cdot 10^9$

Non-unitary Similarity Transformations

Non-unitary Similarity Transformations

Describe the cusp condition and/or capture part of correlation with a correlated wavefunction Ansatz:

$$|\Psi\rangle = \mathrm{e}^{\hat{\tau}} |\Phi\rangle , \quad \text{with} \quad \hat{\tau} = \hat{\tau}^{\dagger}$$

And instead of:

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$

solve the similarity transformed (s.t.) problem:

$$\left(\mathrm{e}^{-\hat{\tau}} \hat{H} \mathrm{e}^{\hat{\tau}}\right) |\Phi\rangle = \bar{H} |\Phi\rangle = E |\Phi\rangle$$

Baker-Campbell-Hausdorff (BCH) exp. to obtain s.t. Hamiltonian:

$$\bar{H} = \mathrm{e}^{-\hat{\tau}} \hat{H} \mathrm{e}^{\hat{\tau}} = \hat{H} + [\hat{H}, \hat{\tau}] + \frac{1}{2} [[\hat{H}, \hat{\tau}], \hat{\tau}] + \ldots$$

The Similarity Transformed Hamiltonian

Consequences:

- Sim. transf. $\bar{H}$ is non-Hermitian ($[\,\hat{H}, \hat{\tau}\,], \ldots$)
- 3-body interactions (and possibly higher order)
- Similarity transformation **does not** change spectrum

Questions:

1. Does the commutator series terminate?
2. Can it be resummed?
3. Can the ST Hamiltonian be evaluated? (Do the 3-body terms cause problems?)
4. Does the non-Hermiticity pose a problem? (lack of lower bound for variational approaches)
5. What are the advantages?

Does the commutator series terminate or can it be resummed?

Two Forms of Correlators

1. The **Gutzwiller** correlator:
   Applied to the Hubbard model; starts in 2nd quantization

$$\hat{\tau} = J \sum_i n_{i\uparrow} n_{i\downarrow}$$

   $\Rightarrow$ BCH exp. can be exactly **resummed** up to infinite order!

2. The **Jastrow** correlator:
   Applied to ab-initio Hamiltonians; starts in 1st quant.

$$\tau(\mathbf{R}) = \sum_{i<j} u(\mathbf{r}_i, \mathbf{r}_j), \quad \text{with} \quad \mathbf{R} = \{\mathbf{r}_1, \ldots \mathbf{r}_N\},$$

   where $u(\mathbf{r}_i, \mathbf{r}_j)$ is symmetric, but not necessarily merely a function of $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$.
   $\Rightarrow$ BCH expansion **terminates** at 2nd order!

Gutzwiller, PRL, **10**, 159 (1963); Jastrow, Phys. Rev. **98**, 1479 (1955).

Can $\bar{H}$ be evaluated and does the non-Hermiticity pose a problem?

Other Approaches

Transcorrelated approach of Boys and Handy: optimize Slater-Jastrow form, orbitals of a single det. and Jastrow parameters

$$|\Psi_{BH}\rangle = \mathrm{e}^{\tau}\, D[\{\phi\}]$$

Problematic because on non-Hermitian nature of $\bar{H}$

Variational quantum Monte Carlo: minimize variational energy, by optimizing trial-wf. parameters (accuracy limited by trial-wf.)

$$E_{VMC} = \min \frac{\langle \Psi_T | \hat{H} | \Psi_T \rangle}{\langle \Psi_T \,|\, \Psi_T \rangle}, \quad |\Psi_T\rangle = \mathrm{e}^{\tau}\, |\Psi_0\rangle$$

Explicitly correlated methods (R12/F12): use correlating functions of the interelectronic distance $r_{12} = |r_1 - r_2|$

$$|\Psi_{F12}\rangle = (1 + \lambda \hat{Q}_{12} f(r_{12}))\, |\Phi_{HF}\rangle + \sum_{ijab} c_{ij}^{ab}\, |\Phi_{ij}^{ab}\rangle$$

Our Approach:
Solve for right eigenvector of $\bar{H}$ by projection

We keep the orbitals and the Gutzwiller/Jastrow parameters fixed and solve for the **right** eigenvector of non-Hermitian $\bar{H}$

$$|\Psi\rangle = \mathrm{e}^{\hat{\tau}}\,|\Phi\rangle \quad \Rightarrow \quad \bar{H} = \mathrm{e}^{-\hat{\tau}}\,\hat{H}\,\mathrm{e}^{\hat{\tau}}$$

with an unchanged spectrum and

$$\langle\Phi_0^L|\,E = \langle\Phi_0^L|\,\bar{H}, \quad \bar{H}\,|\Phi_0^R\rangle = E\,|\Phi_0^R\rangle \quad \text{and} \quad \left\langle \Phi_i^L \,\middle|\, \Phi_j^R \right\rangle = \delta_{ij}$$

where $|\Phi\rangle$ is expanded in a linear combination of SDs $|\Phi^R\rangle = \sum_i c_i\,|D_i\rangle$ and $|\Phi_0^R\rangle$ is obtained as the right eigenvector of $\bar{H}$ by a projective FCI calculation $\Rightarrow$ FCIQMC

Full Configuration Interaction Quantum Monte Carlo (FCIQMC)

FCIQMC

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

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

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

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

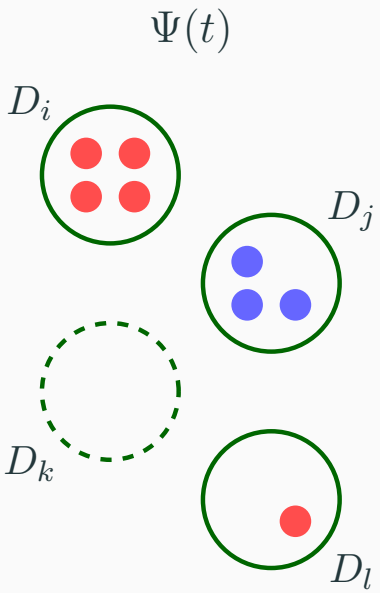
- *Population dynamics* of **"walkers"** simulate the working equation.

Full Configuration Interaction Quantum Monte Carlo

Population dynamics of walkers governed by:

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

Stochastic snapshot $|\Psi(t)\rangle$:



Full Configuration Interaction Quantum Monte Carlo

Population dynamics of walkers governed by:

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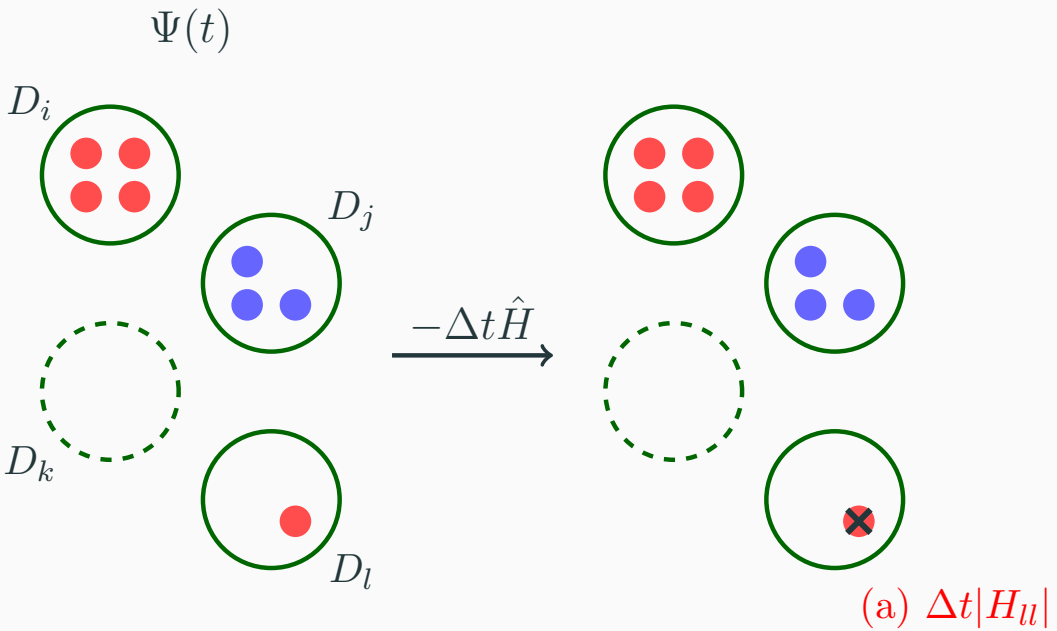
(a) Death/cloning step: die with $p_d = \Delta t H_{ll}$



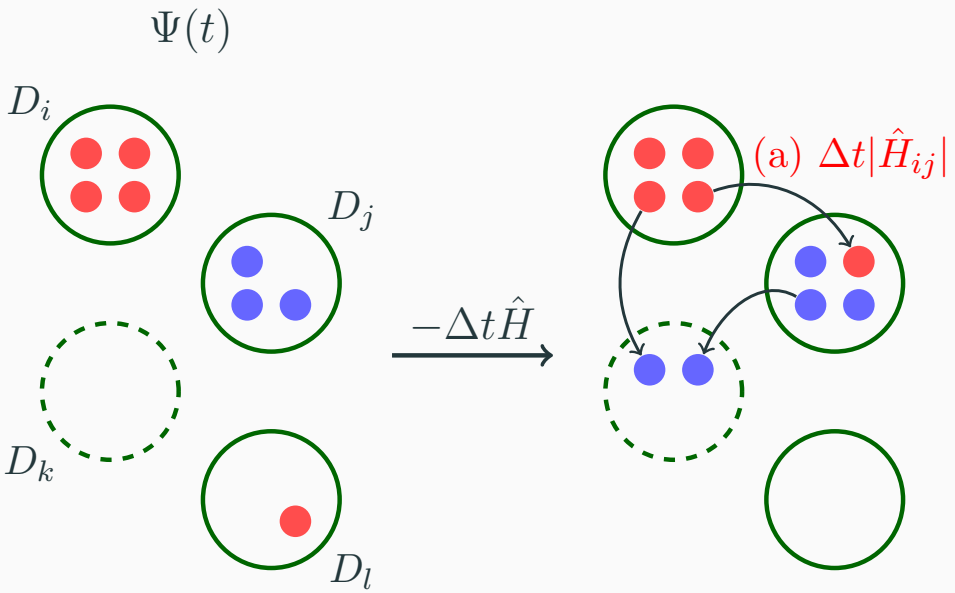
(a) $\Delta t|H_{ll}|$

Full Configuration Interaction Quantum Monte Carlo

Population dynamics of walkers governed by:

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

(b) Spawning step: $|D_i\rangle \rightarrow |D_j\rangle$ with $p_s = \frac{\Delta t |H_{ij}|}{p(j|i)}$

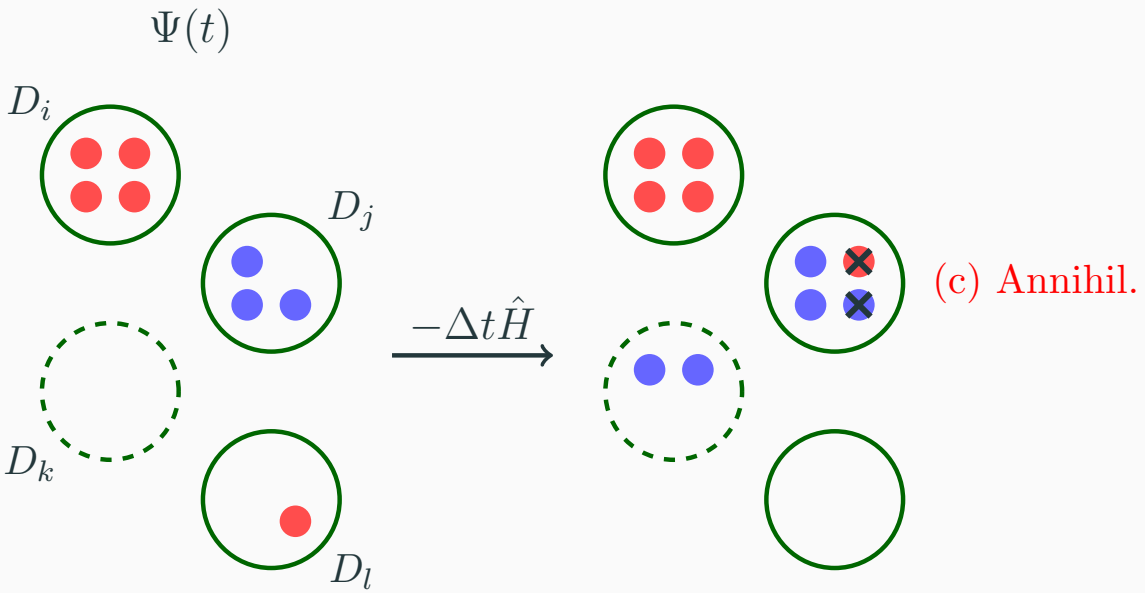


Full Configuration Interaction Quantum Monte Carlo

Population dynamics of walkers governed by:

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

(c) Annihilation step: walkers with opposite sign cancel

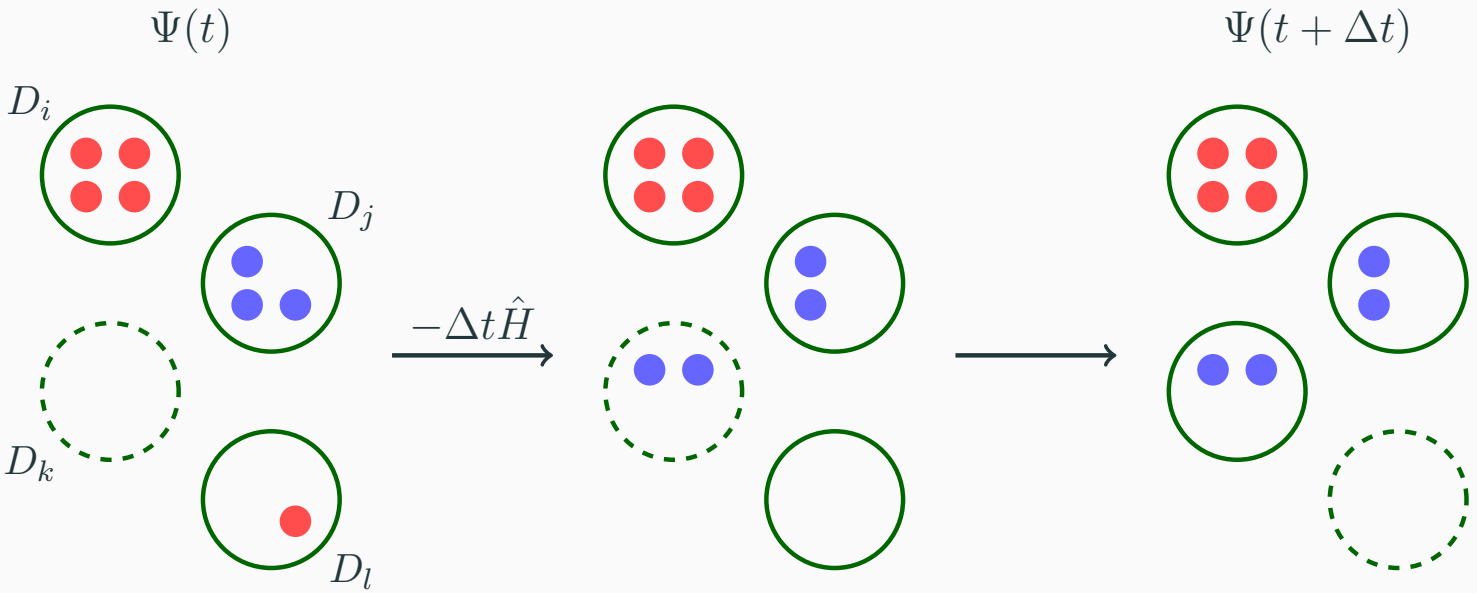


Full Configuration Interaction Quantum Monte Carlo

Population dynamics of walkers governed by:

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

Wavefunction at time-step $|\Psi(t+\Delta t)\rangle$:



Similarity transformed FCIQMC

FCIQMC readily applicable to solve for right eigenvector of non-Hermitian $\bar{H}$

Conditions:

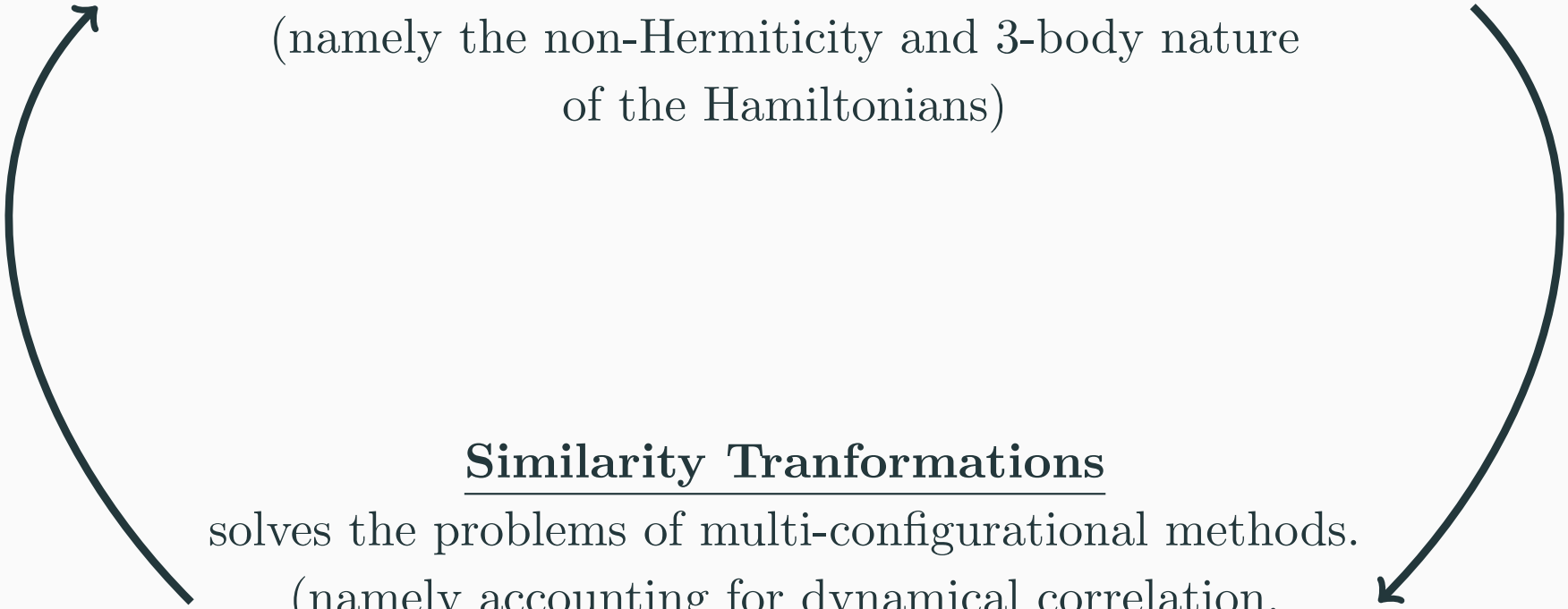
- Respect non-Hermiticity of $\bar{H}$: $\bar{H}_{ij} \neq \bar{H}_{ji}$
- Adapt algorithm to deal with higher order interactions (3-body at most for now):
  Implement spawning step for triple excitations

What are the advantages?

A Virtuous Circle

Projective Multi-configurational methods (FCIQMC)

solve the problems of sim. transf. methods.
(namely the non-Hermiticity and 3-body nature
of the Hamiltonians)

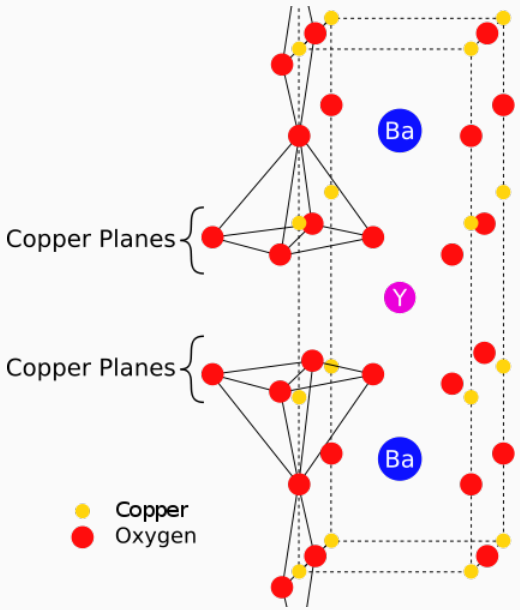


Similarity Tranformations

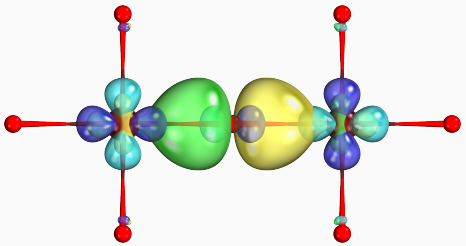
solves the problems of multi-configurational methods.
(namely accounting for dynamical correlation,
describe the cusp behaviour and
compactifying CI solutions)

Gutzwiller Wavefunction Ansatz for the Hubbard Model

High-T_C Superconductors and the Hubbard Model

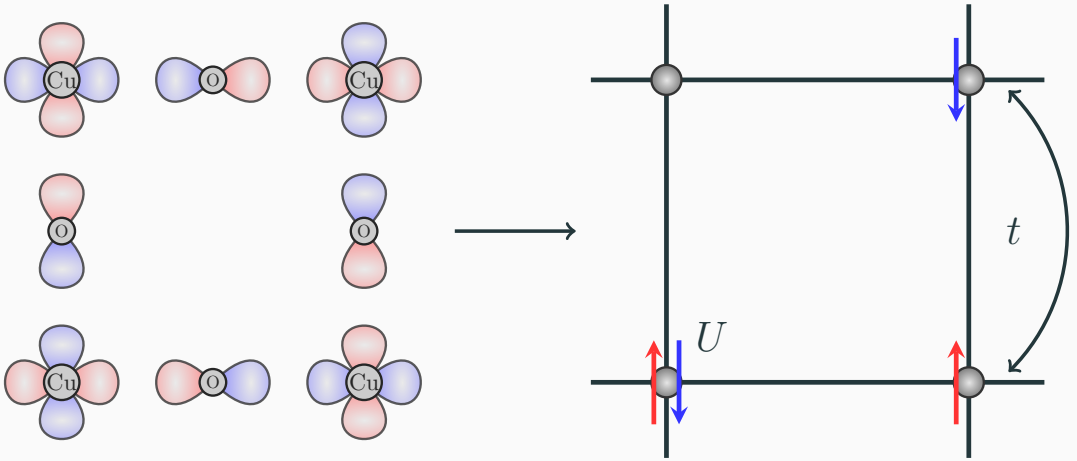


YBCO



Cu-O-Cu

Mapping to an effective lattice model:



The Hubbard Hamiltonian

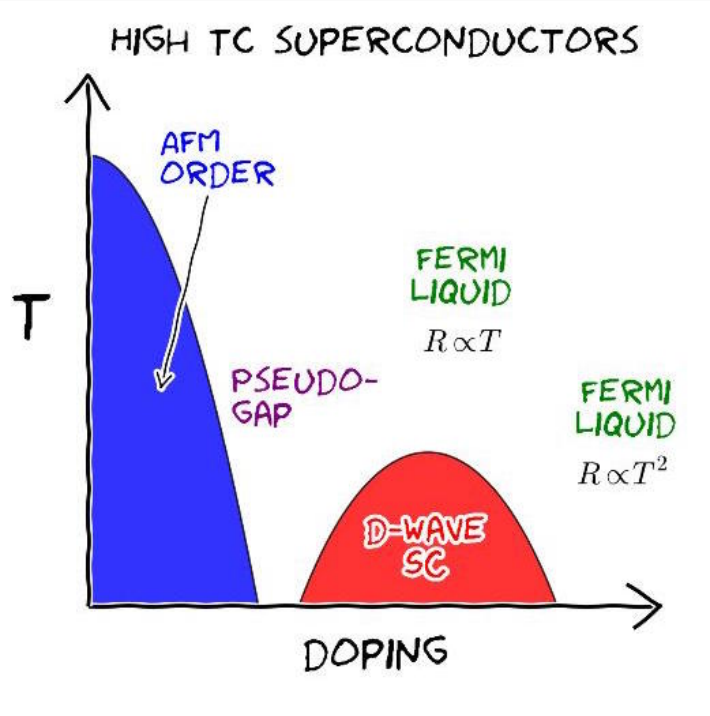
$$\hat{H} = -t \sum_{\langle i,j \rangle, \sigma} \left(c^{\dagger}_{i,\sigma} c_{j,\sigma} + h.c. \right) + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}$$

Strong interaction $\Rightarrow$ highly multiconfigurational

Hubbard, 1963; Kanamori, 1963; Gutzwiller; 1963; Anderson, 1987; Emery, 1987; Zhang and Rice, 1988; Bednorz and Müller, 1986

The Hubbard Model

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



- Minimal model for itinerant electrons
- High-T_C superconductivity in cuprates
- Rich phase diagram as function of temperature, interaction strength and doping
- Anti-ferromagnetism, Mott metal-insulator transition, unconventional superconductivity, ...

Similarity Transformation based on the Gutzwiller Ansatz

- Suppress energetically unfavourable double occupancies via the *Gutzwiller* Ansatz:

$$|\Psi\rangle = \mathrm{e}^{\hat{\tau}} |\Phi\rangle , \quad \hat{\tau} = J \sum_i n_{i\uparrow} n_{i\downarrow}$$

- Perform an exact *similarity transformation* (ST) of the Hubbard Hamiltonian $\hat{H}$:

$$\bar{H} |\Phi\rangle = \left(-t \sum_{\langle i,j \rangle, \sigma} \mathrm{e}^{-\hat{\tau}} a^\dagger_{i\sigma} a_{j\sigma} \mathrm{e}^{\hat{\tau}} + U \sum_i n_{i\uparrow} n_{i\downarrow} \right) |\Phi\rangle = E |\Phi\rangle$$

Gutzwiller, PRL 10, **159** (1963); Tsuneyuki, Prog. Theor. Phys. Supp., **176**, 134 (2008); Scuseria et al., PRB, **91**, 041114 (2015)

For the Gutzwiller correlator applied to the Hubbard model the BCH expansion does not terminate but can be resummed up to infinite order, due to the **idempotency** of the number operator

$$n_{i\sigma} = n_{i\sigma}^2$$

$$\bar{H} = -t \sum_{\langle i,j \rangle, \sigma} a_{i\sigma}^\dagger a_{j\sigma} \mathrm{e}^{J(n_{j\bar{\sigma}} - n_{i\bar{\sigma}})} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

- t is **reduced** if two opposite spins are coming together

- t is **enhanced** if two opposite spins are comping apart

Additionally, the exponential $\mathrm{e}^{J(n_{j\bar{\sigma}}-n_{i\bar{\sigma}})}$ can be exactly linearized, due to the idempotency of $n_{i\sigma}$:

$$(n_{j\sigma}-n_{i\sigma})^{2m-1} = n_{j\sigma}-n_{i\sigma}, \quad \text{and}$$

$$(n_{j\sigma}-n_{i\sigma})^{2m} = n_{j\sigma}+n_{i\sigma}-2n_{i\sigma}n_{j\sigma}$$

leading to non-Hermitian $\bar{H}$ with up to 3-body interactions

$$\bar{H} = \hat{H} - t\sum_{\langle i,j\rangle,\sigma} a^{\dagger}_{i\sigma}a_{j\sigma}\left[(\mathrm{e}^{J}-1)n_{j\bar{\sigma}} + (\mathrm{e}^{-J}-1)n_{i\bar{\sigma}} - 2(\cosh(J)-1)n_{i\bar{\sigma}}n_{j\bar{\sigma}}\right]$$

Tsuneyuki, Prog. Theor. Phys. Supp., **176**, 134 (2008); Scuseria et al., PRB, **91**, 041114 (2015)

Hubbard model in momentum space

The Gutzwiller Ansatz is more suitable in the low to intermediate U/t regime*, where a momentum space representation is preferable

With a plane-wave Ansatz

$$a_{\mathbf{r},\sigma} = \frac{1}{\sqrt{M}} \sum_{\mathbf{k}} \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}}\, c^{\dagger}_{\mathbf{k},\sigma}$$

the original Hubbard Hamiltonian in momentum-space is given by

$$\hat{H} = -t \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} n_{\mathbf{k},\sigma} + \frac{U}{2M} \sum_{\mathbf{pqk},\sigma} c^{\dagger}_{\mathbf{p}-\mathbf{k},\sigma} c^{\dagger}_{\mathbf{q}+\mathbf{k},\bar{\sigma}} c_{\mathbf{p},\bar{\sigma}} c_{\mathbf{p},\sigma}$$

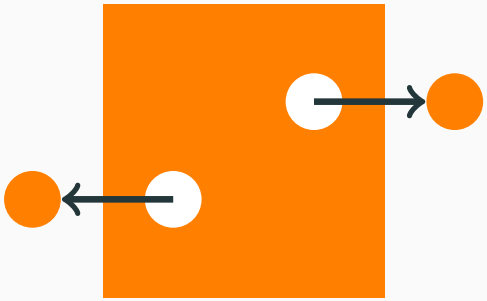
*Kaplan, Horsch, Fulde, PRL **49**, 889 (1982); Metzner and Vollhardt, PRL 59, **121** (1987).

Similarity Transformed Hamiltonian in k-space

$$\bar{H}(J) = -t \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} n_{\mathbf{k},\sigma} + \frac{1}{2M} \sum_{\mathbf{pqk},\sigma} \omega(J,\mathbf{p},\mathbf{k}) c^{\dagger}_{\mathbf{p-k},\sigma} c^{\dagger}_{\mathbf{q+k},\bar{\sigma}} c_{\mathbf{q},\bar{\sigma}} c_{\mathbf{p},\sigma}$$
$$+2t \frac{\cosh(J)-1}{M^2} \sum_{\mathbf{pqskk'},\sigma} \epsilon_{\mathbf{p-k+k'}} c^{\dagger}_{\mathbf{p-k},\sigma} c^{\dagger}_{\mathbf{q+k'},\bar{\sigma}} c^{\dagger}_{\mathbf{s+k-k'},\bar{\sigma}} c_{\mathbf{s},\bar{\sigma}} c_{\mathbf{q},\bar{\sigma}} c_{\mathbf{p},\sigma}$$

with

$$\omega(J,\mathbf{p},\mathbf{k}) = U - 2t\left[(\mathrm{e}^{J}-1)\epsilon_{\mathbf{p-k}} + (\mathrm{e}^{-J}-1)\epsilon_{\mathbf{p}}\right]$$



- For excitations removing electrons from Fermi det. ($\mathbf{p} \to \mathbf{p}-\mathbf{k}$) U is reduced
- For the reverse process U is increased

$\Rightarrow$ this leads to a right eigenvector dominated by the HF det. even in the strong correlation regime

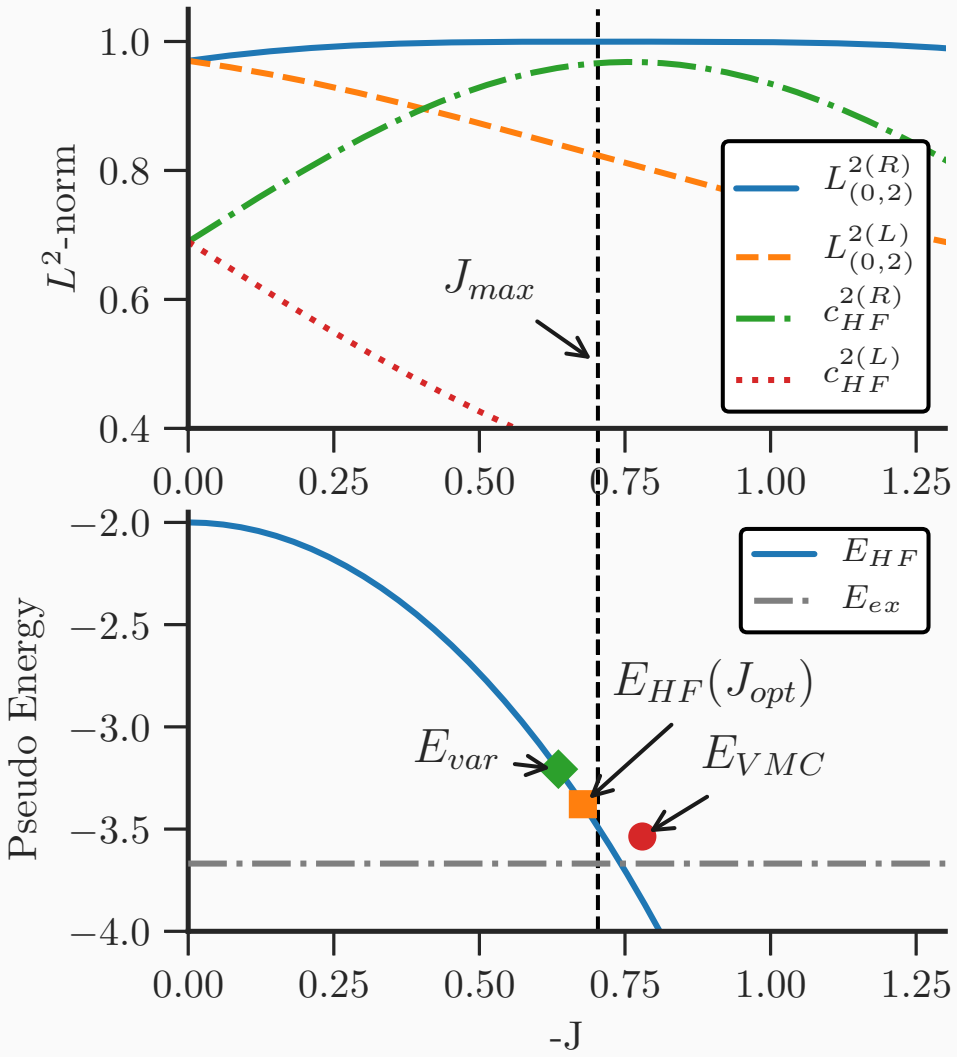
Results obtained by projection on single det.

Similar to the optimization of coupled cluster amplitudes we want to solve for the single parameter J by projection.

$$\langle \Phi_{HF} | \hat{\tau}^{\dagger} (\bar{H} - E) | \Phi_{HF} \rangle = 0$$

M	U/t	n_{el}	J_{opt}	e_{ex}	e_J	$e_J/e_{ex}[\%]$
18	2	18	-0.27053	-1.32141	-1.31697	99.7
18	4	18	-0.52345	-0.95847	-0.92697	96.7
36	2	36	-0.28683	-1.20831	-1.19904	99.3
36	4	36	-0.55295	-0.87306	-0.81145	92.9
36	4	24	-0.52372	-1.18530	-1.16457	98.3
50	2	50	-0.28298	-1.22278	-1.21523	99.4
50	4	50	-0.54600	-0.87966	-0.82601	93.9
50	4	46	-0.55208	-0.99114	-0.95008	95.9
50	4	42	-0.54324	-1.08002	-1.04765	97.0
50	4	26	-0.51076	-1.11564	-1.09946	98.6

Results: Increased Compactness of Right Eigenvector



- ED study on a 6-site chain:
- Optimization of J based on a single det. with

$$\left\langle (\hat{\tau} - \langle \hat{\tau} \rangle)^\dagger \bar{H} \right\rangle_{HF} = 0$$

- E_{var} obtained by minimizing the variance*

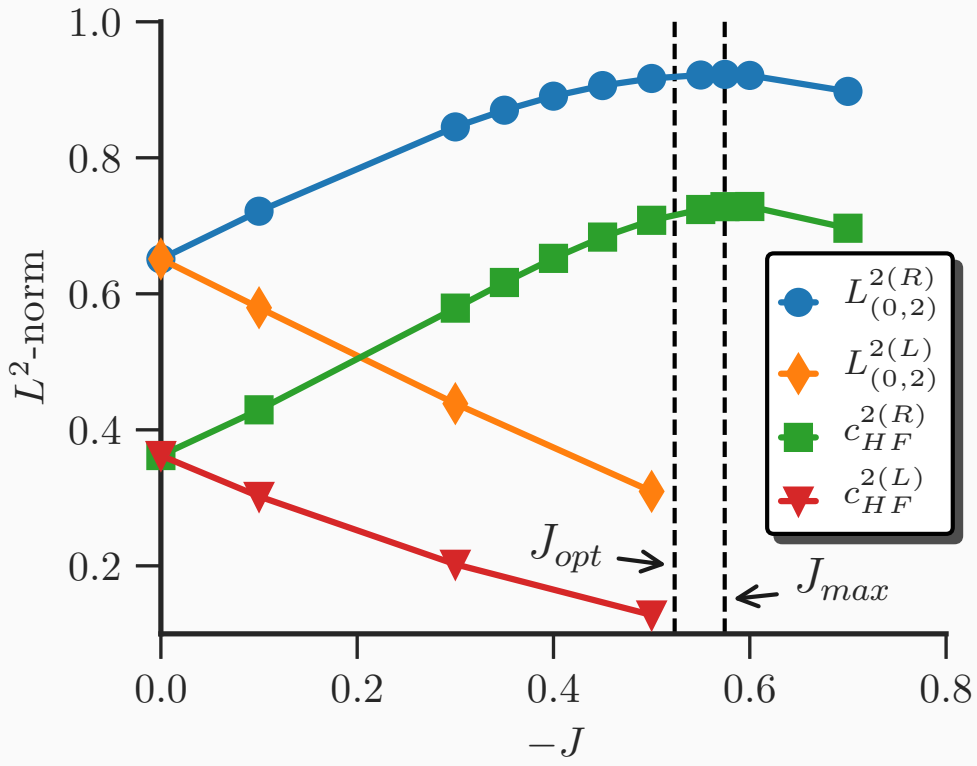
$$\min \left\langle (\bar{H} - \langle \bar{H} \rangle)^2 \right\rangle_{HF}$$

- E_{VMC} obtained by VMC† optimization of J

*S. Tsuneyuki, Prog. Theor. Phys. Supp., **176**, 134 (2008), †P. L. Rios

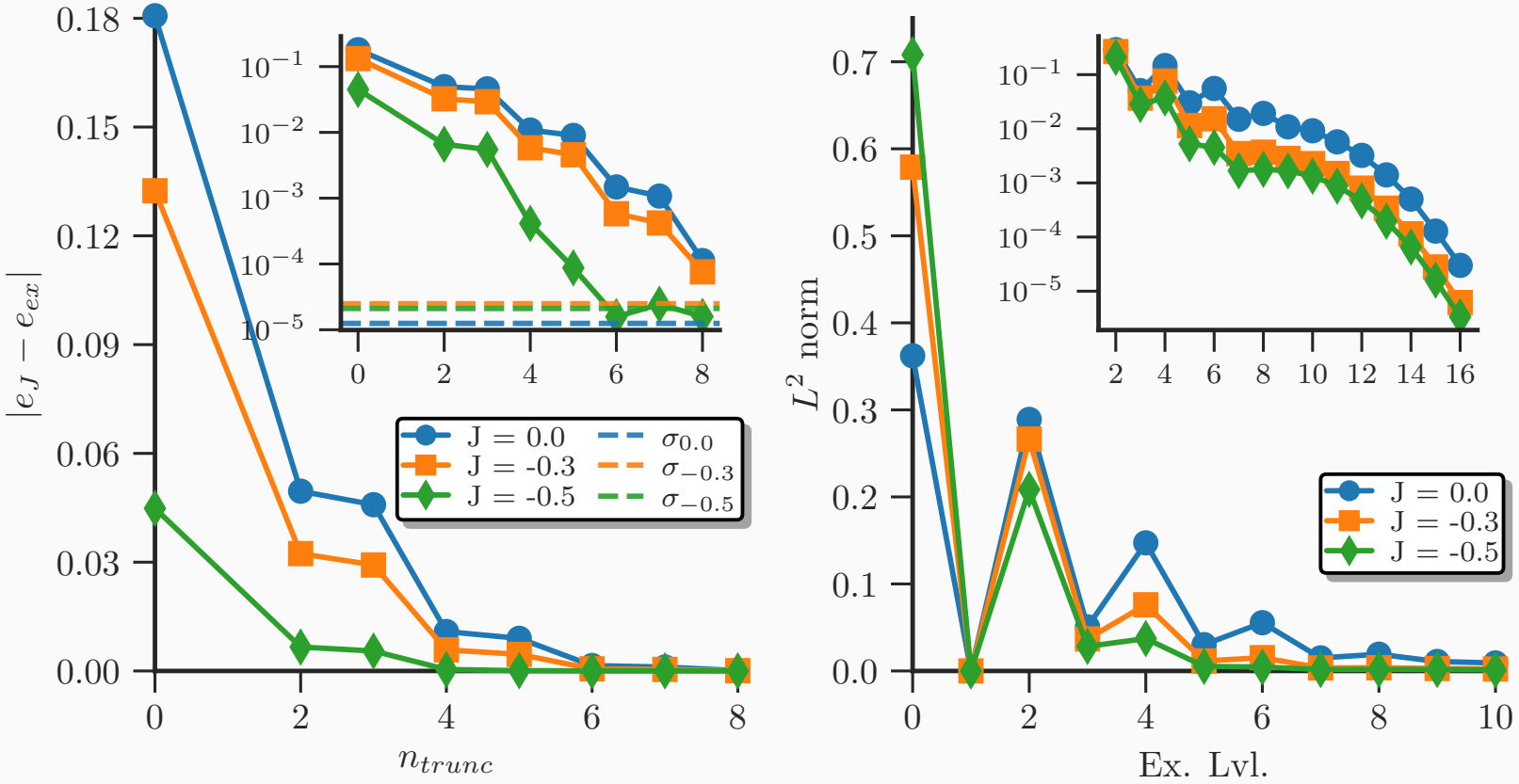
Results: Increased Compactness - 18-site system

- FCIQMC able to solve for left and **right** eigenvectors $|\Phi_0^{R/L}\rangle$
- More efficient sampling, due to **increased compactness**
- Applicable up to—previously unreachable —lattice sizes



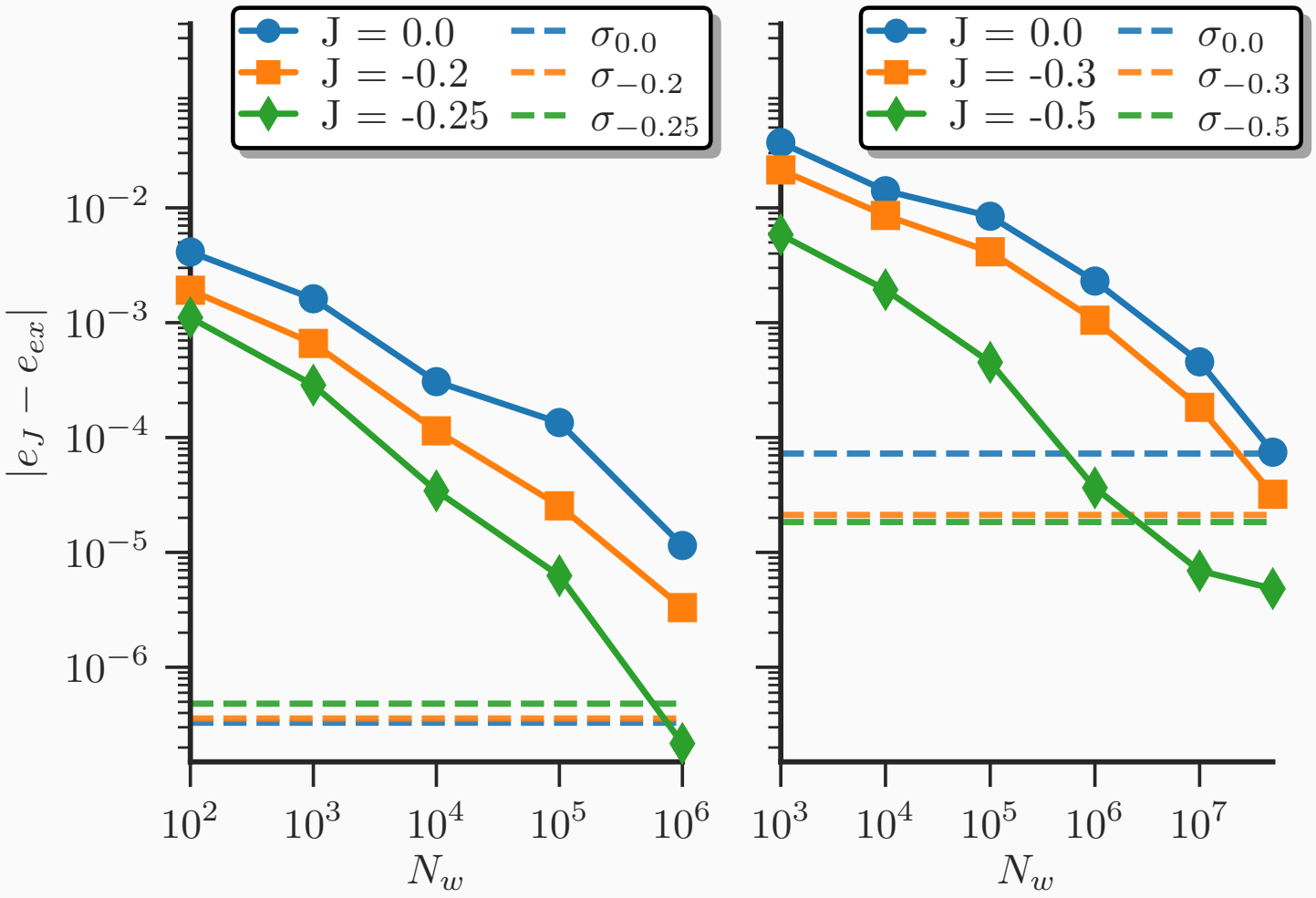
HF coefficient and L^2 norm within doubles of $|\Phi_0^{R/L}\rangle$ vs. J. 18 e$^-$ in 18 orbitals, $U/t = 4$

Results: Increased Compactness - 18-site system



(left) Absolute errror of energy per site vs. excitation level truncation. (right) L^2 norm contained in specific excitation levels relative to HF det. for the half-filled 18-site Hubbard model at $U/t = 4$.

Results: Accelerated convergence - 18-site system



Convergence of the absolute error vs. walker number N_w for the $U/t = 2$ (left) and $U/t = 4$ (right) half-filled 18-site Hubbard model.

Results: Ground state energy of the 36 and 50 site lattice

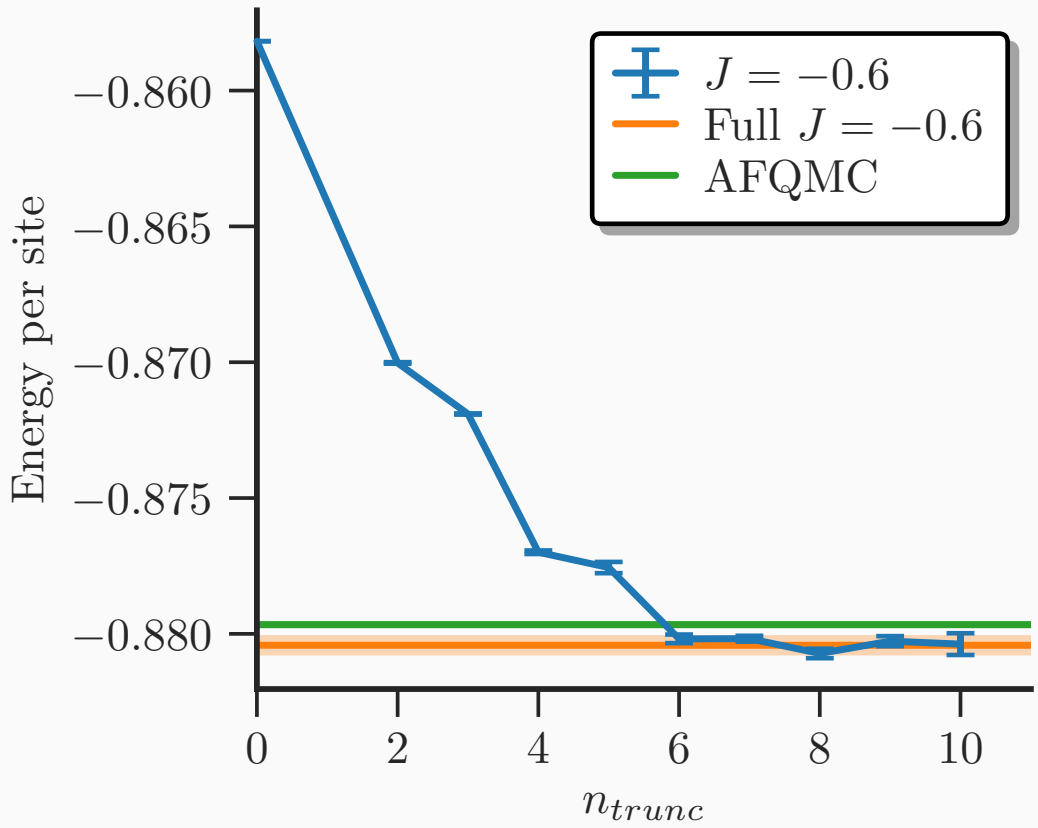
Ground state energy of the orginal $J = 0$ and similarity transformed J_{opt} FCIQMC calculations compared to AFQMC reference results*.

M	U/t	n_{el}	E^*_{ref}	$\Delta E_{J=0}$	$\Delta E_{J_{opt}}$
36	4	24	-1.18525(4)	0.003247(97)	0.000039(45)
36	2	36	-1.208306(56)	0.000230(60)	0.000048(58)
36	4	36	-0.87306(56)	0.025480(64)	0.00045(61)
50	2	50	-1.22278(17)	0.00219(19)	-0.00006(18)
50	4	50	-0.879660(20)	0.04565(17)	-0.000997(80)
50	4	46	-0.9911420(86)	0.03564(24)	0.00058(18)
50	4	42	-1.079276(66)	0.02552(13)	0.00037(14)
50	4	26	-1.115640(20)	0.001766(36)	-0.000262(24)

*Qin, Shi, and Zhang, PRB, **94**, 085103 (2016); Sorella, PRB, **84**, 241110 (2011)

Results: Apparent size-consistency 50-site system

- Excellent agreement with reference results up to interaction of $U/t = 4$
- Applicable to problematic doped regime
- Seemingly size-consistent behaviour of truncated CI calculations



Truncated CI of 50 e$^-$ in 50 orbitals, $U/t = 4$

Jastrow Factorization for ab-initio Models

Jastrow-based factorization of the Hamiltonian

Incorporate cusp condition and induce compactness of right eigenvector with

$$\tau(\mathbf{R}) = \sum_{i<j} u(\mathbf{r}_i, \mathbf{r}_j), \quad \mathbf{R} = \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$$

where $u(\mathbf{r}_i, \mathbf{r}_j)$ is symmetric, but not necessarily merely a function of $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$.

BCH expansion terminates at 2nd order (only kinetic energy operators in $\hat{H}$ do not commute with τ)

$$\begin{aligned}\bar{H} &= \hat{H} - \sum_i \left(\frac{1}{2}\nabla_i^2 \tau + (\nabla_i \tau)\nabla_i + \frac{1}{2}(\nabla_i \tau)^2 \right) \\ &= \hat{H} - \sum_{i<j} \hat{K}(\mathbf{r}_i, \mathbf{r}_j) - \sum_{i<j<k} \hat{L}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)\end{aligned}$$

Hirschfelder, JCP, **39**, 3145 (1963), Boys and Handy, 1969

Boys-Handy form of u

$$u(\mathbf{r}_i, \mathbf{r}_j) = \sum_{\substack{mno \\ m+n+o \leq 6}} c_{mno}(\bar{r}_i^m \bar{r}_j^n + \bar{r}_j^m \bar{r}_i^n)\bar{r}_{ij}^o,$$

where $\bar{r}_i^m$ is distance of electrons from nuclei and $\bar{r}_{ij}^o$ the relative distance between electrons:
Includes $e-e$, $e-n$ and $e-e-n$ terms

$$\bar{r} = \frac{r}{1+r} \quad \Rightarrow \quad \text{desired cusp behaviour:}$$

$$\bar{r} \approx r - r^2 \quad \text{for small } r$$

$$\bar{r} \approx 1 - 1/r \to 1 \quad \text{for large } r$$

17 parameters of u obtained by VMC variance minimization by Schmidt and Moskowitz, JCP, **93**, 4172 (1990)

Jastrow s.t. Hamiltonian in 2nd quantised form

$$\bar{H} = \sum_{pq,\sigma} h_q^p a_{p,\sigma}^\dagger a_{q,\sigma} \frac{1}{2} \sum_{pqrs} (V_{rs}^{pq} - K_{rs}^{pq}) \sum_{\sigma,\tau} a_{p,\sigma}^\dagger a_{q,\tau}^\dagger a_{s,\tau} a_{r,\sigma}$$
$$- \frac{1}{6} \sum_{pqrstu} L_{stu}^{pqr} \sum_{\sigma\tau\lambda} a_{p,\sigma}^\dagger a_{q,\tau}^\dagger a_{r,\lambda}^\dagger a_{u,\lambda} a_{t,\tau} a_{s,\sigma}$$

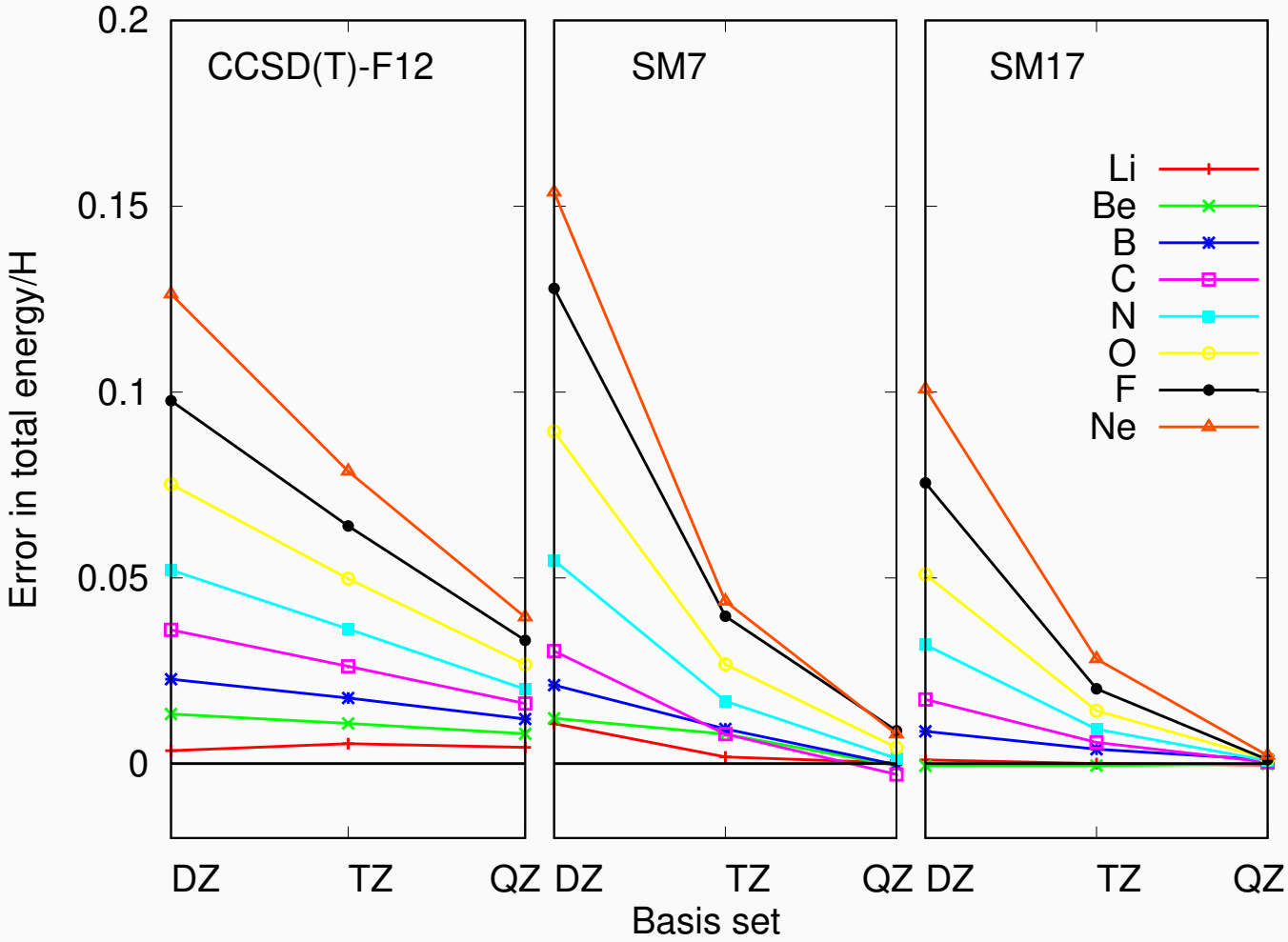
with

$$K_{rs}^{pq} = \langle \phi_p \phi_q | \hat{K} | \phi_r \phi_s \rangle$$
$$L_{stu}^{pqr} = \langle \phi_p \phi_q \phi_r | \hat{L} | \phi_s \phi_t \phi_u \rangle \quad \text{(48-fold symmetry in } L \text{ for real orbitals)}$$

Both integrals K and L are computed numerically using standard DFT grids over gaussian orbitals. The main problem is the storage of L. Current limit ≈ 80 orbitals

Results: Errors in total energies of first-row atoms

SM7: u without $e-e-n$ terms; SM17: full parametrization (cc-pVnZ basis set)



Core functions

Energies of the cations of Ne using SM17 vs. CCSD(T) and CCSD(T)-F12

method	basis	Ne^{4+}	Ne^{3+}	Ne^{2+}	Ne^{+}	Ne
CCSD(T)	cc-pV5Z	-120.7011	-124.2757	-126.6027	-128.1067	-128.8989
CCSD(T)	cc-pCV5Z	-120.7275	-124.3027	-126.6303	-128.1346	-128.9269
CCSD(T)-F12	cc-pCV5Z	-120.7303	-124.3062	-126.6359	-128.1420	-128.9360
ST-FCIQMC	cc-pVQZ	-120.7288	-124.3045	-126.6334	-128.1397	-128.9355
Expt*		-120.7312	-124.3068	-126.6366	-128.1431	-128.9376

$\Rightarrow$ Due to $e - e - n$ term in u no tight core functions needed in basis set $\Rightarrow$ even smaller basis sets are necessary for an accurate description!

*Chakravorty et al., PRA, **47**, 3649 (1993)

Conclusion and Summary

Conclusion and Summary

Gutzwiller factorization for the Hubbard model

- Exact similarity transformation based on the Gutzwiller Ansatz
- Efficient sampling of non-Hermitian Hamiltonian with 3-body interactions, due to increased compactness
- Excellent agreement with reference results up to 50 sites and $U/t = 4$, even off half-filling

Jastrow factorization for ab-initio models

- FCIQMC is a good projective solver, can handle the 3-body terms efficiently
- Extremely rapid basis set convergence
- Core-electron correlation accounted for by the $e - e - n$ Jastrow factor, obviating the need for tight functions
- No projection operators are needed (unlike R12/F12 methods)

Thank you for your attention!

Imaginary-time propagation with s.t. Hamiltonians

Why is the FCIQMC method applicable?

$$|\Psi(\beta)\rangle = \mathrm{e}^{-\beta(\hat{H}-E_0)}\,|\Psi(0)\rangle \quad \rightarrow \quad |\Psi_0\rangle = \lim_{\beta\to\infty} \mathrm{e}^{-\beta(\hat{H}-E_0)}\,|\Psi(0)\rangle$$

$$\text{with} \quad |\Psi(\beta)\rangle = \mathrm{e}^{\hat{\tau}}\,|\Phi(\beta)\rangle$$

$$|\Phi(\beta)\rangle = \mathrm{e}^{-\beta(\bar{H}-E_0)}\,|\Phi(0)\rangle \quad \rightarrow \quad |\Phi_0\rangle = \lim_{\beta\to\infty} \mathrm{e}^{-\beta(\bar{H}-E_0)}\,|\Phi(0)\rangle$$

Proof:

$$\mathrm{e}^{\hat{\tau}}\,|\Phi(\beta)\rangle = |\Psi(\beta)\rangle = \mathrm{e}^{-\beta(\hat{H}-E_0)}\,|\Psi(0)\rangle = \mathrm{e}^{-\beta(\hat{H}-E_0)}\,\mathrm{e}^{\hat{\tau}}\,|\Phi(0)\rangle$$

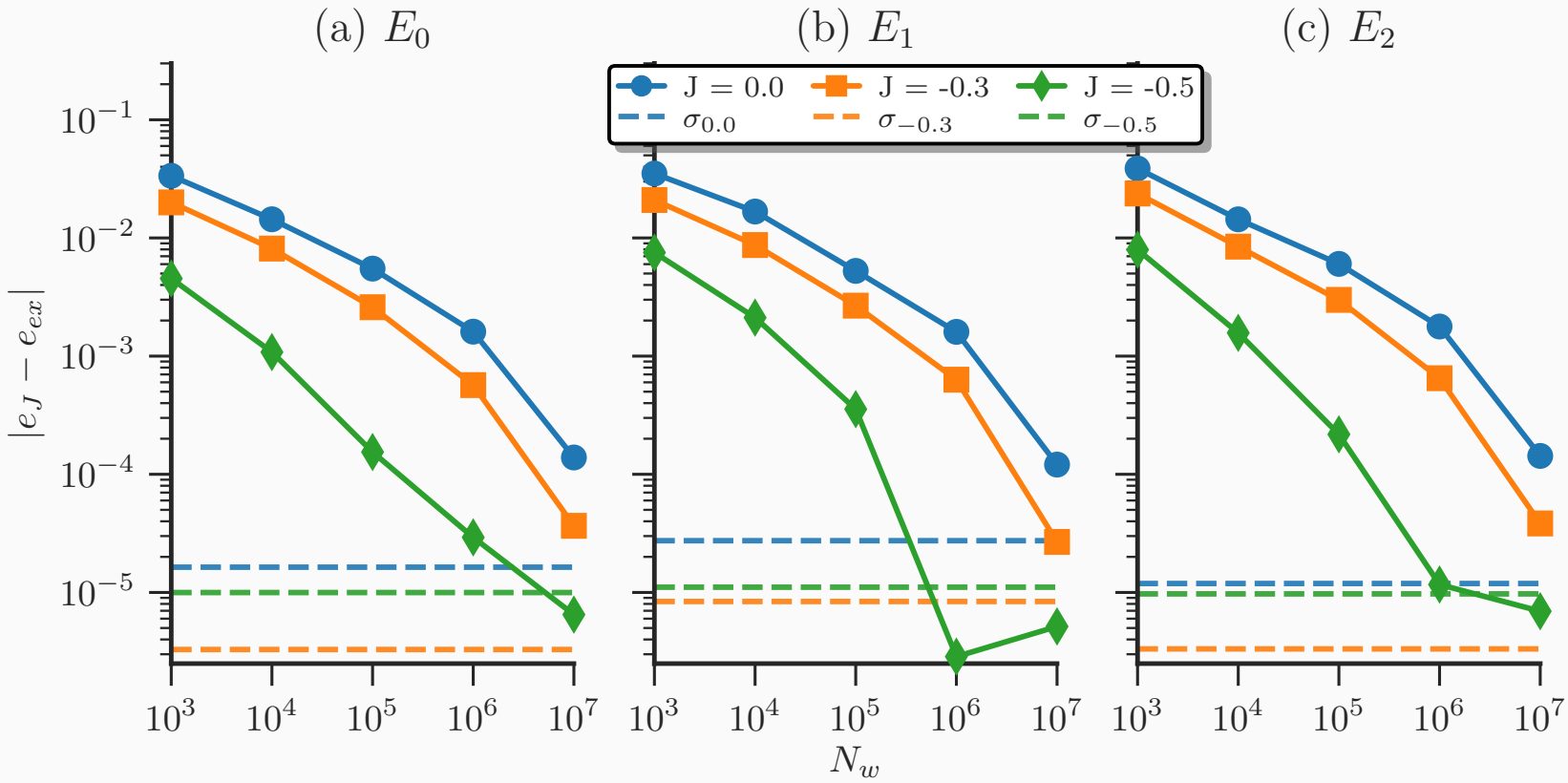
$$\Rightarrow |\Phi(\beta)\rangle = \mathrm{e}^{-\hat{\tau}}\,\mathrm{e}^{-\beta(\hat{H}-E_0)}\,\mathrm{e}^{\hat{\tau}}\,|\Phi(0)\rangle$$

$$= \lim_{m\to\infty} \mathrm{e}^{-\hat{\tau}} \left(1 - \frac{\beta}{m}(\hat{H}-E_0)\right)^m \mathrm{e}^{\hat{\tau}}\,|\Phi(0)\rangle$$

$$= \lim_{m\to\infty} \underbrace{\mathrm{e}^{-\hat{\tau}}}_{\rightarrow} \left(1 - \frac{\beta}{m}(\hat{H}-E_0)\right) \underbrace{\mathrm{e}^{\hat{\tau}}}_{\leftarrow} \mathrm{e}^{-\hat{\tau}} \left(1 - \frac{\beta}{m}(\hat{H}-E_0)\right) \ldots \mathrm{e}^{\hat{\tau}}\,|\Phi(0)\rangle$$

Excited States

Excited states of 14 e^- in 18 sites, $U/t = 4$



Shift energy remains good energy estimate even for excited states!

Jastrow-based factorization of the Hamiltonian

$$\bar{H} = \hat{H} - \sum_{i<j} \hat{K}(\mathbf{r}_i, \mathbf{r}_j) - \sum_{i<j<k} \hat{L}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$$

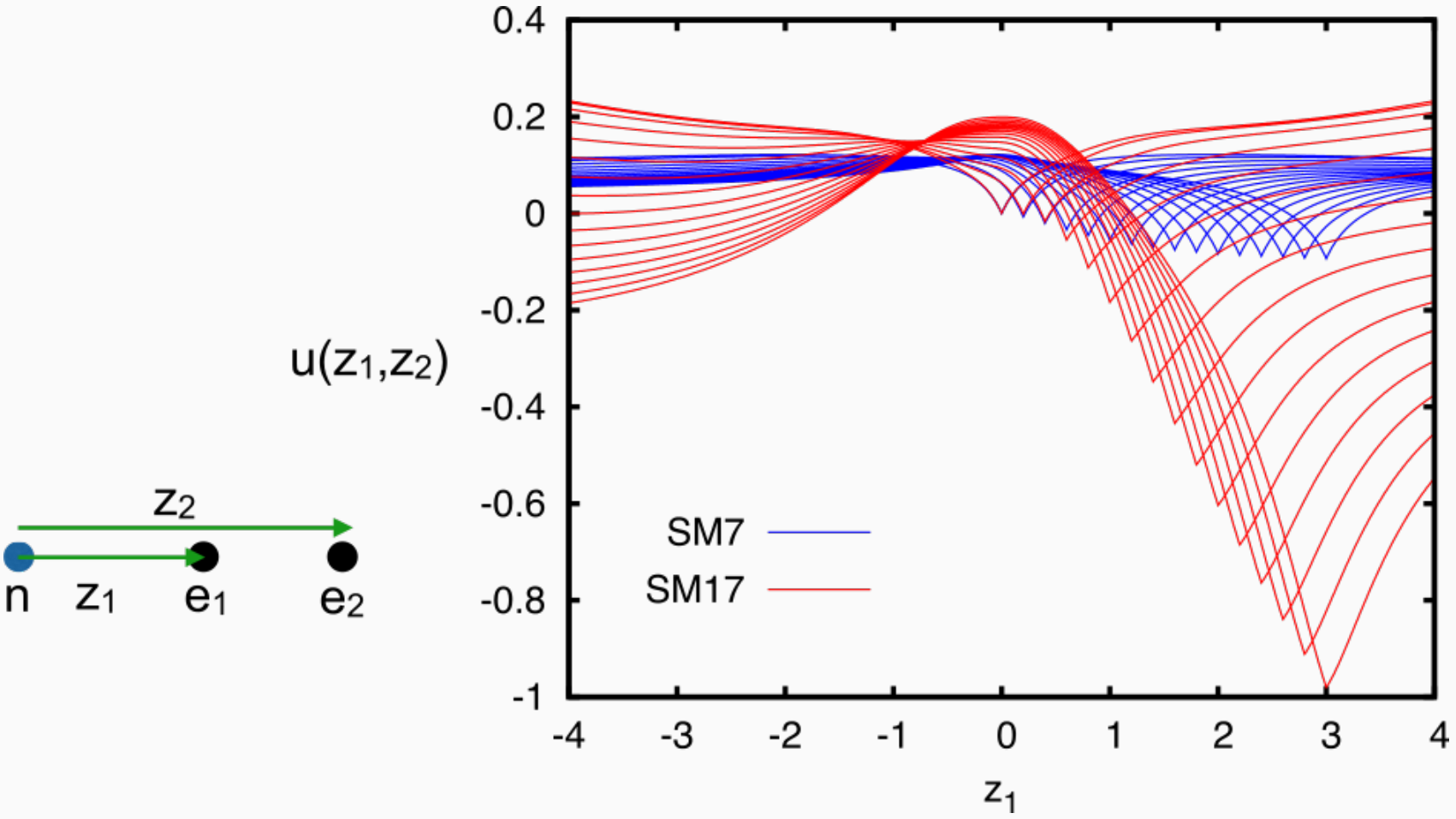
with

$$\hat{K}(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{2}\Big(\underbrace{\nabla_i^2 u + \nabla_j^2 u}_{\text{screens Coulomb singularity in } \hat{H}} + (\nabla_i u)^2 + (\nabla_j u)^2 \Big)$$

$$+ \underbrace{\nabla_i u \cdot \nabla_i + \nabla_j u \cdot \nabla_j}_{\text{non-Hermitian gradient terms} \rightarrow \text{induce compactness}}$$

$$\hat{L}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = \nabla_i u_{ij} \cdot \nabla_i u_{ik} + \nabla_j u_{ji} \cdot \nabla_j u_{jk} + \nabla_k u_{ki} \cdot \nabla_k u_{kj}$$

Correlation Factor



Correlation factor (Ne) with and without e-e-n term (SM17 vs SM7)
The cusps locate the position of e_2