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

Werner Dobrautz

Max Planck Institute for Solid State Research

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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*

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

Cusp condition: $\lim_{r_{ij} \to 0} \left(\dfrac{\partial \Psi}{\partial r_{ij}} \right)_{av} = \dfrac{1}{2} \Psi(r_{ij} = 0)$
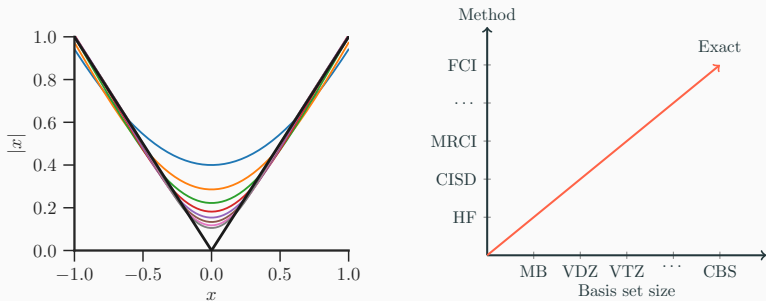
Non-differentiable behaviour at electron coalescence $\Rightarrow$ large basis set expansion necessary
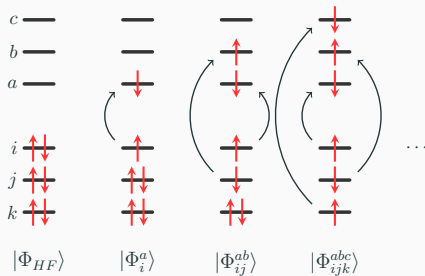
Hierarchy of methods and basis set size $\Rightarrow$ detrimental scaling with number of orbitals of more accurate methods

Problems:
Exponential scaling of Full Configuration Interaction (FCI)

FCI $\Rightarrow |\Psi\rangle = \sum_I c_I |D_I\rangle \Rightarrow$ exact solution in a given basis set

$|\Phi_{HF}\rangle \quad |\Phi_i^a\rangle \quad |\Phi_{ij}^{ab}\rangle \quad |\Phi_{ijk}^{abc}\rangle$

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	$\sim 2 \cdot 10^9$

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Problems: Electronic Correlation $\leftrightarrow$ Multi-configurationality

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 $\rightarrow$ 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

$\Rightarrow$ Problematic for many approaches (PT, CC, ...)

$\Rightarrow$ **Idea:**

Use a correlated wf. Ansatz to describe the cusp/capture part of correlation energy ("more single reference")

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Non-unitary Similarity Transformations

Non-unitary Similarity Transformations

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

$$|\Psi\rangle = e^{\hat{\tau}} |\Phi\rangle, \quad \text{with} \quad \hat{\tau}^{\dagger} = \hat{\tau}, \quad (\text{unitary: } \hat{\tau}^{\dagger} = -\hat{\tau})$$

And instead of:

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

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

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

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

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

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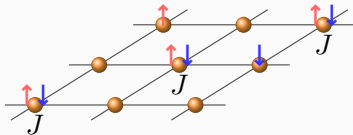4. What are the advantages?

Does the commutator series terminate or can it be resummed?

Two Forms of Correlators

1. <u>The **Gutzwiller** correlator:</u>
   Applied to the Hubbard model

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

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

2. <u>The **Jastrow** correlator:</u>
   Applied to ab-initio Hamiltonians

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

   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

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

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.)

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

Explicitly correlated methods (R12/F12): use correlating functions of the interelectronic distance to describe electronic cusp

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

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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)

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

$$\frac{\partial \ket{\Psi}}{\partial t} = -\hat{H} \ket{\Psi} \quad \rightarrow \quad \ket{\Psi_0} \propto \lim_{t \to \infty} e^{-t\hat{H}} \ket{\Phi}$$

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

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

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

Population dynamics of walkers governed by:

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

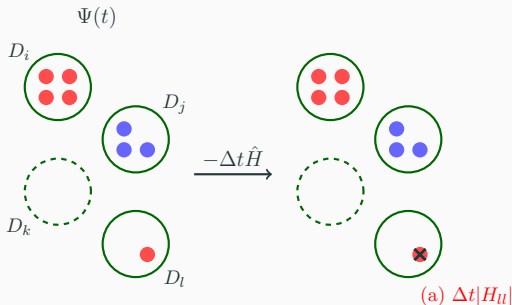Stochastic snapshot $|\Psi(t)\rangle$:

Population dynamics of walkers governed by:

$$c_i(t + \Delta t) = \underbrace{[1 - \Delta t H_{ii}]\, c_i(t)}_{\text{death/cloning}} - \underbrace{\Delta t \sum_{j \neq i} H_{ij} c_j(t)}_{\text{spawning}}$$
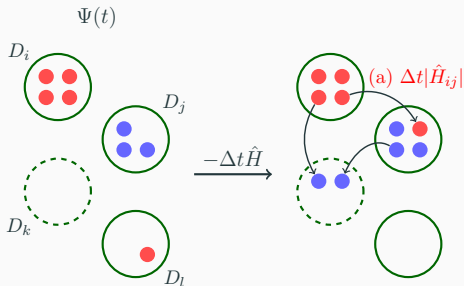
(a) Death/cloning step: die with $p_d = \Delta t H_{ll}$

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

Population dynamics of walkers governed by:

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

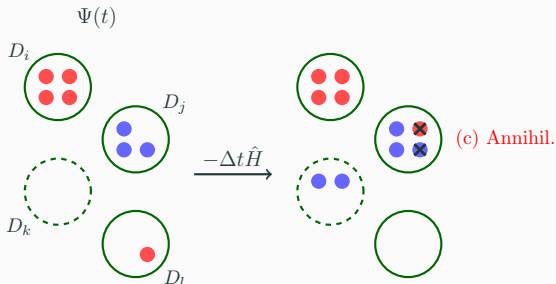(b) Spawning step: $|D_i\rangle \to |D_j\rangle$ with $p_s = \dfrac{\Delta t |H_{ij}|}{p(j|i)}$

Population dynamics of walkers governed by:

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

(c) Annihilation step: walkers with opposite sign cancel

$\Psi(t)$

D_i D_j
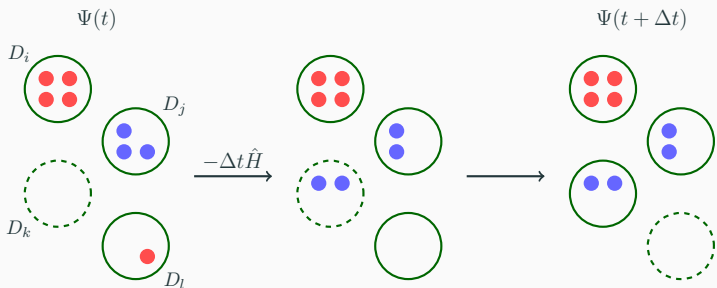
$-\Delta t \hat{H}$

(c) Annihil.

D_k D_l

Full Configuration Interaction Quantum Monte Carlo

Population dynamics of walkers governed by:

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

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

$\Rightarrow$ efficiently possible due to stochastic nature of algorithm

What are the advantages?

A Virtuous Circle

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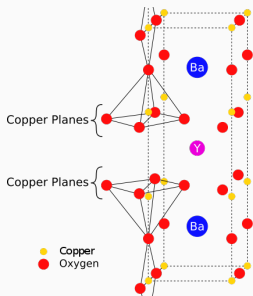(namely the non-Hermiticity and 3-body nature
of the Hamiltonians)

Similarity Tranformations
solves the problems of multi-configurational methods.
(namely accounting for dynamical correlation,
describe the cusp behaviour and
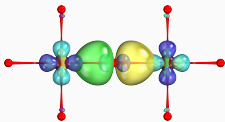compactifying CI solutions)
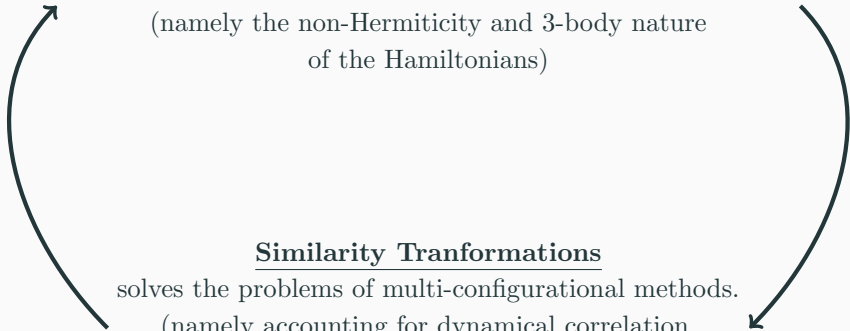
Gutzwiller Wavefunction Ansatz for the Hubbard Model

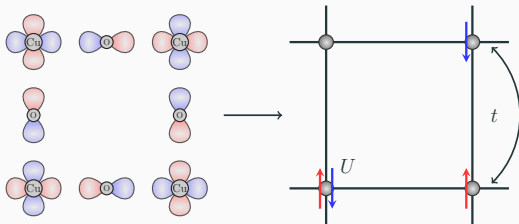# High-T$_C$ Superconductors and the Hubbard Model

YBCO

Cu-O-Cu

Mapping to an effective lattice model:

The Hubbard Hamiltonian

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

Strong interaction $\Rightarrow$ highly multiconfigurational

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

Similarity Transformation based on the Gutzwiller Ansatz

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

$$|\Psi\rangle = \mathrm{e}^{\hat{\tau}} |\Phi\rangle, \quad \hat{\tau} = J \sum_i n_{i\uparrow} n_{i\downarrow}$$
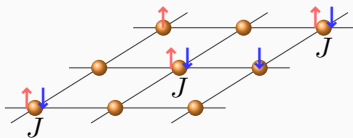
- Perform an exact *similarity transformation* (ST) of the Hubbard Hamiltonian $\hat{H}$:

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

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

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

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

Results in a *renormalized* hopping:

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

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

Additionally, the exponential $e^{J(n_{j\bar{\sigma}} - n_{i\bar{\sigma}})}$ 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

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

Tsuneyuki, Prog. Theor. Phys. Suppl., **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 for a stochastic sampling

With a plane-wave Ansatz

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

the **original** Hubbard Hamiltonian in momentum-space is given by

$$\hat{H} = -t \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} n_{\mathbf{k},\sigma} + \frac{U}{2M} \sum_{\mathbf{pqk},\sigma} c_{\mathbf{p}-\mathbf{k},\sigma}^{\dagger} c_{\mathbf{q}+\mathbf{k},\bar{\sigma}}^{\dagger} c_{\mathbf{p},\bar{\sigma}} c_{\mathbf{p},\sigma}$$
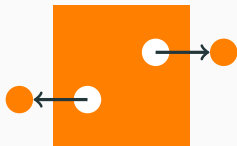
[*]Kaplan, Horsch, Fulde, PRL **49**, 889 (1982); Metzner and Vollhardt, PRL 59, **121** (1987). 18

Similarity Transformed Hamiltonian in k-space

$$\bar{H}(J) = -t \sum_{\mathbf{k},\sigma} \epsilon_{\mathbf{k}} n_{\mathbf{k},\sigma} + \frac{1}{2M} \sum_{\mathbf{pqk},\sigma} \omega(J,\mathbf{p},\mathbf{k}) c^{\dagger}_{\mathbf{p}-\mathbf{k},\sigma} c^{\dagger}_{\mathbf{q}+\mathbf{k},\bar{\sigma}} c_{\mathbf{q},\bar{\sigma}} c_{\mathbf{p},\sigma}$$

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

with

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

- 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

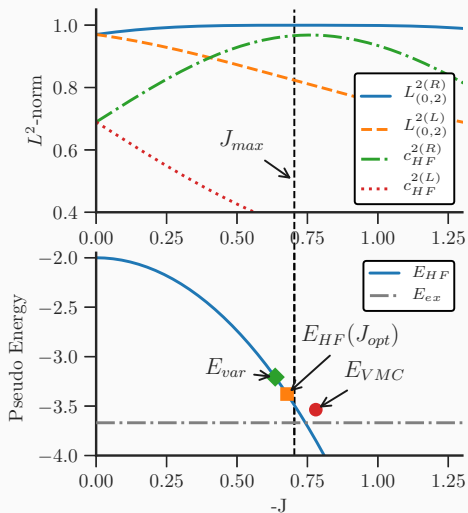Dobrautz, Luo, and Alavi PRB **99**, 075119 (2019)

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 on $\langle \Phi_{HF} | \hat{\tau}^\dagger$:

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

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

- <u>ED study on a 6-site chain:</u>

- Optimization of J based on a single det. with

$$\langle (\hat{\tau} - \langle \hat{\tau} \rangle)^\dagger \bar{H} \rangle_{HF} = 0$$
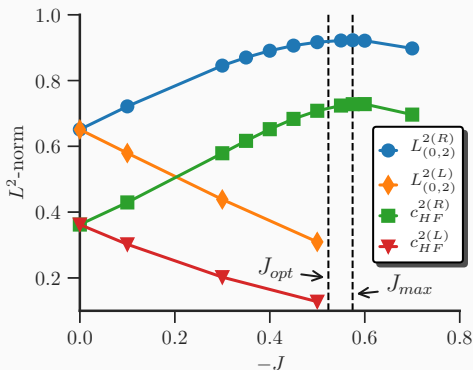
- E_{var} obtained by minimizing the variance[*]

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

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

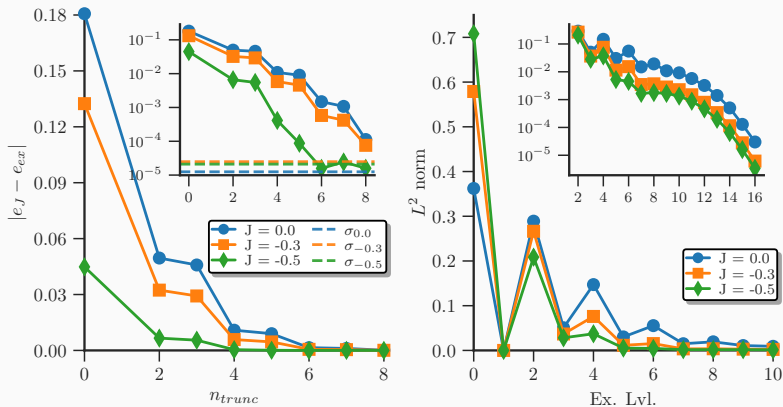[*]S. Tsuneyuki, Prog. Theor. Phys. Supp., **176**, 134 (2008), [†]P. L. Rios

- FCIQMC able to solve for left and **right** eigenvectors $|\Phi_0^{R/L}\rangle$: $\bar{H}(J)^\dagger = \bar{H}(-J)$

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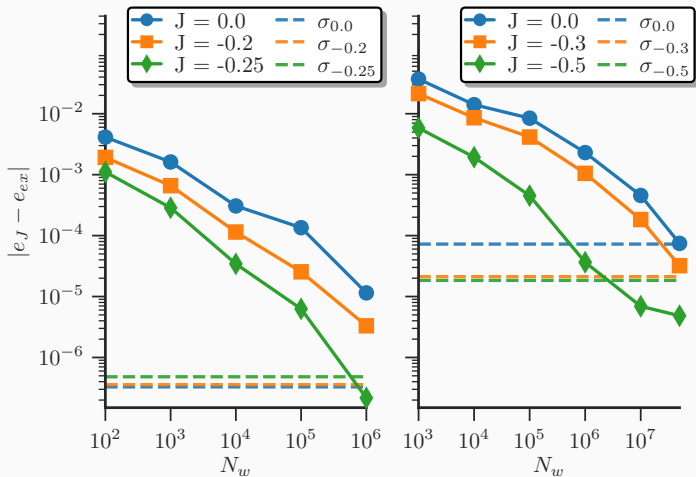
(left) Absolute errror of energy per site vs. excitation level truncation.
(right) L^2 norm contained in specific excitation levels relative to HF det.
for the half-filled 18-site Hubbard model at $U/t = 4$.

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)

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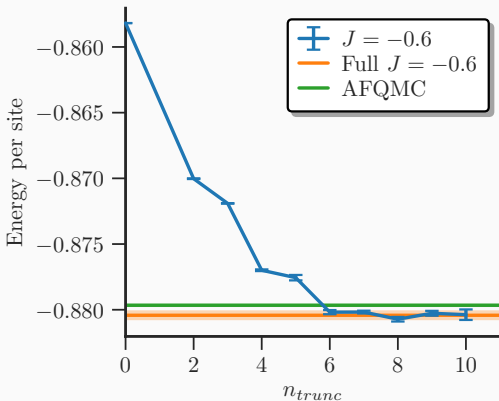
Truncated CI of 50 e$^-$ in 50 orbitals, $U/t = 4$

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)

$$\bar{H} = \hat{H} - \sum_i \left(\frac{1}{2}\nabla_i^2\tau + (\nabla_i\tau)\nabla_i + \frac{1}{2}(\nabla_i\tau)^2 \right)$$

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

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

$$\bar{r} = \frac{r}{1+r} \quad \Rightarrow \quad \text{desired cusp behaviour:}$$
$$\bar{r} \approx r - r^2 \quad \text{for small } r$$
$$\bar{r} \approx 1 - 1/r \rightarrow 1 \quad \text{for large } r$$

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

$$\bar{H} = \sum_{pq,\sigma} h_q^p a_{p,\sigma}^\dagger a_{q,\sigma} + \frac{1}{2} \sum_{pqrs} (V_{rs}^{pq} - K_{rs}^{pq}) \sum_{\sigma,\tau} a_{p,\sigma}^\dagger a_{q,\tau}^\dagger a_{s,\tau} a_{r,\sigma}$$

$$- \frac{1}{6} \sum_{pqrstu} L_{stu}^{pqr} \sum_{\sigma\tau\lambda} a_{p,\sigma}^\dagger a_{q,\tau}^\dagger a_{r,\lambda}^\dagger a_{u,\lambda} a_{t,\tau} a_{s,\sigma}$$
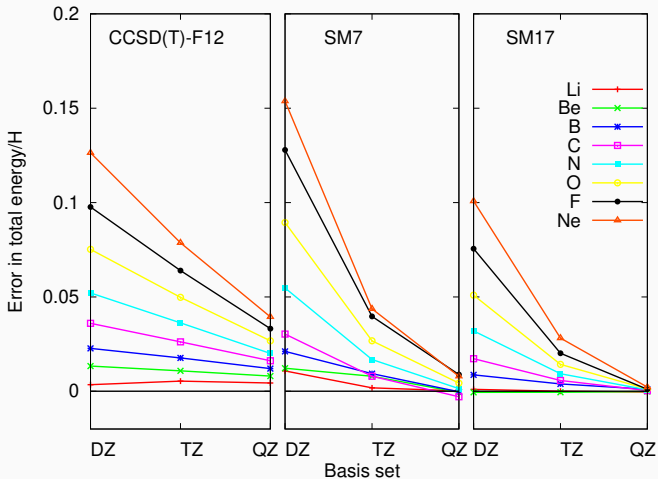
with

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

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

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

No need for core functions

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!

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

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, due to **correct cusp behavior**
- Core-electron correlation accounted for by the $e - e - n$ Jastrow factor, obviating the need for tight core functions

Thank you for your attention!

Imaginary-time propagation with s.t. Hamiltonians

Why is the FCIQMC method applicable?

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

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

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

Proof:

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

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

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

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

Optimization of Correlation Parameter

Optimization of J based on the HF state:

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

The Ansatz:

$$e^{-\hat{\tau}} \hat{H}(J) e^{\hat{\tau}} |\Phi_{HF}\rangle = \bar{H} |\Phi_{HF}\rangle = E |\Phi_{HF}\rangle$$

projecting onto $\langle\Phi_{HF}|$ yields

$$\langle\Phi_{HF}|\bar{H}(J)|\Phi_{HF}\rangle = E_{HF}(J) = E$$

and projecting onto $\langle\Phi_{HF}|\hat{\tau}^\dagger$ yields

$$\langle\Phi_{HF}|\hat{\tau}^\dagger\bar{H}(J)|\Phi_{HF}\rangle = E_{HF}(J)\langle\Phi_{HF}|\hat{\tau}^\dagger|\Phi_{HF}\rangle$$

Excited States

The n-th excited state in FCIQMC is obtained by

$$|\Phi_n(t + \delta t)\rangle = \hat{P}_n(t + \delta t) \left[\mathbf{1} - \delta t \left(\hat{H} - E_n^S \right) \right] |\Phi_n(t)\rangle$$

with Gram-Schmidt orthogonalization

$$\hat{P}_n(t) = \mathbf{1} - \sum_{m < n} \frac{|\Phi_m(t)\rangle \langle \Phi_m(t)|}{\langle \Phi_m(t) \,|\, \Phi_m(t)\rangle}, \quad E_m < E_n,$$

however, $\left\langle \Psi_i^L \,\middle|\, \Psi_j^R \right\rangle = \delta_{ij}$ for non-Hermitian $\bar{H}$.
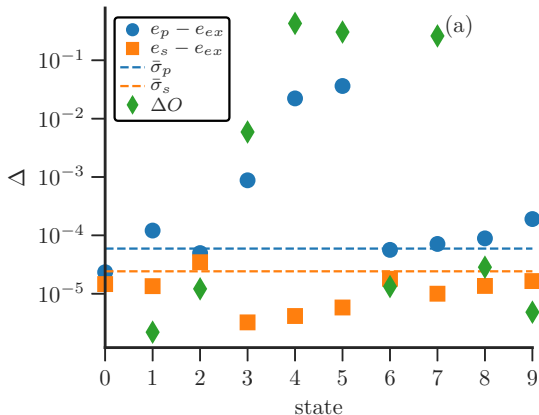
Right eigenvalue equation for a general $\hat{H}$ for i-th excited state

$$\hat{H} |\Psi_i\rangle = E_i |\Psi_i\rangle,$$

There exists a vector $|\Phi_i\rangle = \hat{P}_i |\Psi_i\rangle$, which is a eigenvector of the composite operator $\hat{P}_i \hat{H}$ with the same eigenvalue E_i

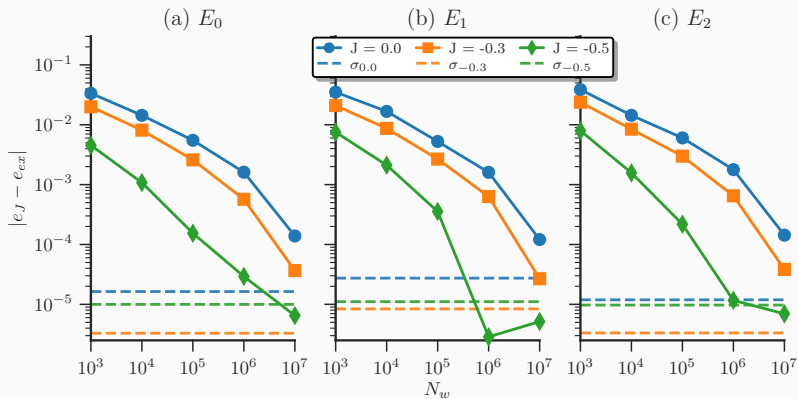$$\hat{P}_i \hat{H} |\Phi_i\rangle = E_i |\Phi_i\rangle.$$

Excited States

Error of the first 10 eigenstate energies obtained by the projected energy e_p and shift energy e_s for the 6 e^- in 6 site 1D periodic Hubbard model at $U/t = 4$ and $J = -0.1$.

Excited States

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

(a) E_0 (b) E_1 (c) E_2

Legend: J = 0.0, J = -0.3, J = -0.5, $\sigma_{0.0}$, $\sigma_{-0.3}$, $\sigma_{-0.5}$

y-axis: $|e_J - e_{ex}|$; x-axis: N_w

Shift energy remains good energy estimate even for excited states!

Jastrow-based factorization of the Hamiltonian

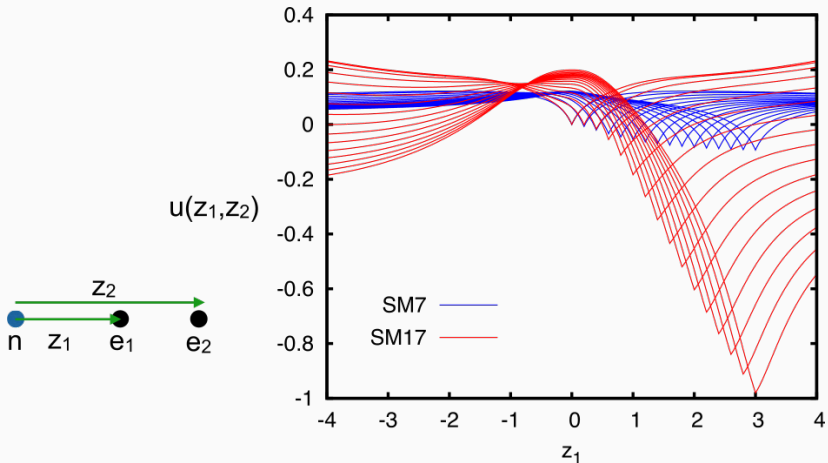$$\bar{H} = \hat{H} - \sum_{i<j} \hat{K}(\mathbf{r}_i, \mathbf{r}_j) - \sum_{i<j<k} \hat{L}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$$

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