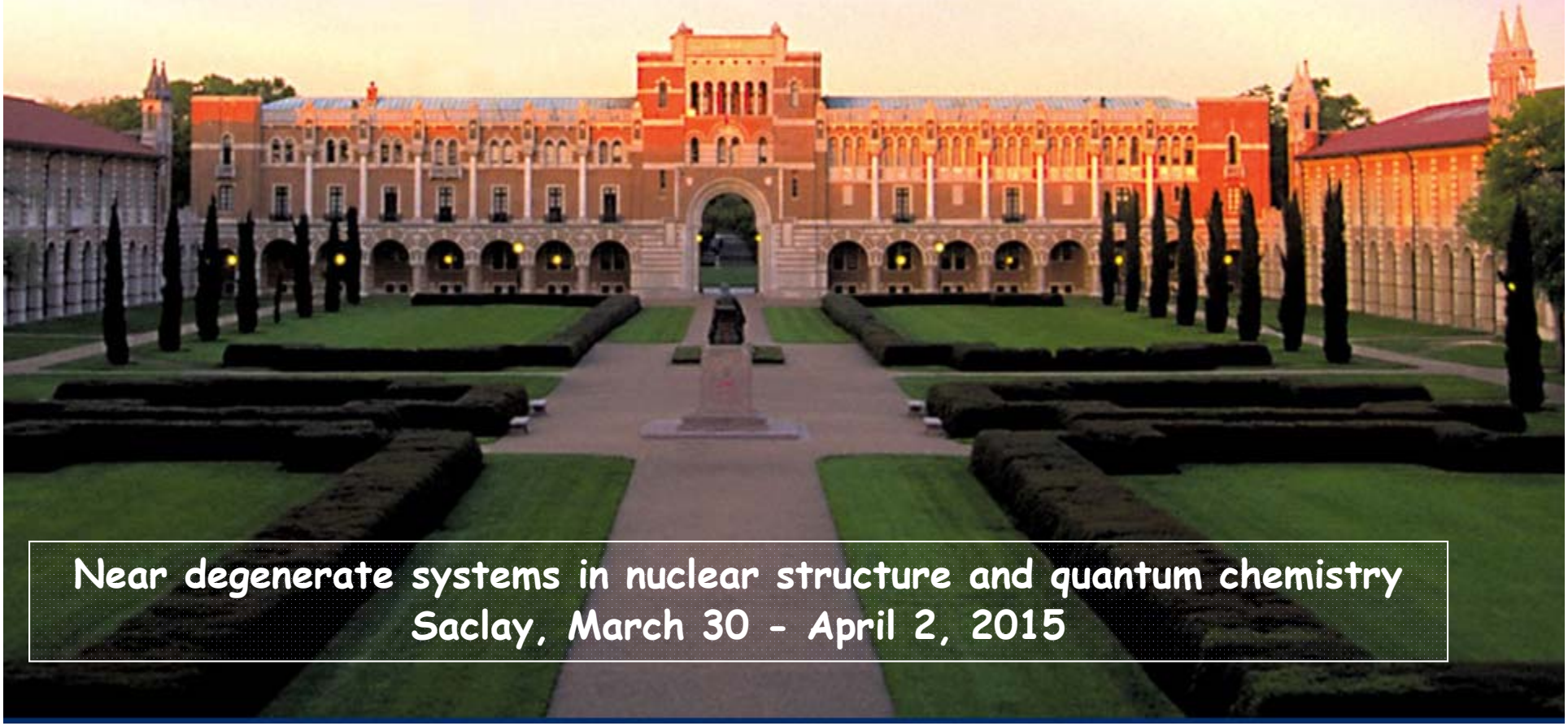
Low cost generalized CC models for strong and weak correlations

Gustavo E. Scuseria



Near degenerate systems in nuclear structure and quantum chemistry
Saclay, March 30 - April 2, 2015

QC Wavefunction Theory

- **Weak ("dynamic")** and **static/strong** correlations are different
- In weakly correlated systems, **HF** is a good approximation
- **Static** correlation appears from **near degeneracies** among and between occupied and unoccupied orbitals; **HF** breaks down
- The **weak** correlation problem has been **solved**: **SR CCSD(T)**
- "**Solved**": polynomial cost approach with controlled errors (albeit not inexpensive, cost ~ N^6 - N^7)
- The **static/strong correlation** problem remains wide open
- Ideal wavefunction theory needs:
  - Low computational cost
  - Address the static/strong correlation problem in a black-box manner

Outline

- **Pair coupled cluster** theory for **static** correlation
- **Lie algebraic similarity transformation** theory for **weak** correlation
- **Their marriage**
- All with **low** polynomial computational cost

coupled cluster theory

CC theory

- **Coupled Cluster** theory is based on a **particle-hole excitation** construction of the Hilbert space: **singles + doubles + triples + …**

$$T = T_1 + T_2 + T_3 + \ldots \qquad T_2 = \sum_{ijab} t_{ij}^{ab} c_a^\dagger c_b^\dagger c_i c_j$$

$$\left|\Psi\right\rangle = e^T \left|\Phi\right\rangle \qquad He^T \left|\Phi\right\rangle = Ee^T \left|\Phi\right\rangle$$

i,j : occ; ***a,b***: unocc in reference determinant $|\Phi\rangle$

- Hamiltonian is similarity transformed to non-hermitian form

$$\overline{H} = e^{-T} H e^T; \qquad \overline{H}\left|\Phi\right\rangle = E\left|\Phi\right\rangle$$

$$E = \left\langle \Phi \right| \overline{H} \left| \Phi \right\rangle$$

- This is a canonical transformation but the energy is unbound
- Cluster coefficients are determined left-projecting Schrodinger eqn:

$$0 = \left\langle {}_{ij}^{ab} \right| \overline{H} \left| \Phi \right\rangle$$

CC theory (cont.)

- This is equivalent to making the energy variance zero over the projected subspace of the full Hilbert space:

$$\sigma^2 = \left\langle \overline{H}^2 \right\rangle - \left\langle \overline{H} \right\rangle^2 = 0$$

- **Mathematically**: constrained energy functional ***L*** is made stationary

$$L\left(t_{ij}^{ab}, z_{ab}^{ij}\right) = \left\langle \Phi \left| \left(I + Z\right) e^{-T} H e^{T} \right| \Phi \right\rangle$$

$$Z = \sum_{ijab} z_{ab}^{ij} c_i^{\dagger} c_j^{\dagger} c_a c_b, \qquad \frac{\partial L}{\partial t_{ij}^{ab}} = \frac{\partial L}{\partial z_{ab}^{ij}} = 0$$

with different **right** $\left|\Phi\right\rangle$ and **left** eigenvectors $\left\langle \Phi \right|\left(I + Z\right)$

- ***CC*** has **polynomial scaling** with system size: ***CCSD*** is N^6; ***CCSDT*** is N^8
- **Size extensive** theory
- ***CCSD(T)*** is the "**gold standard**" for **weak correlation** in quantum chemistry, **but** for **strongly correlated** systems where high-order excitations become important, **single-reference CCSD(T) falls dead**

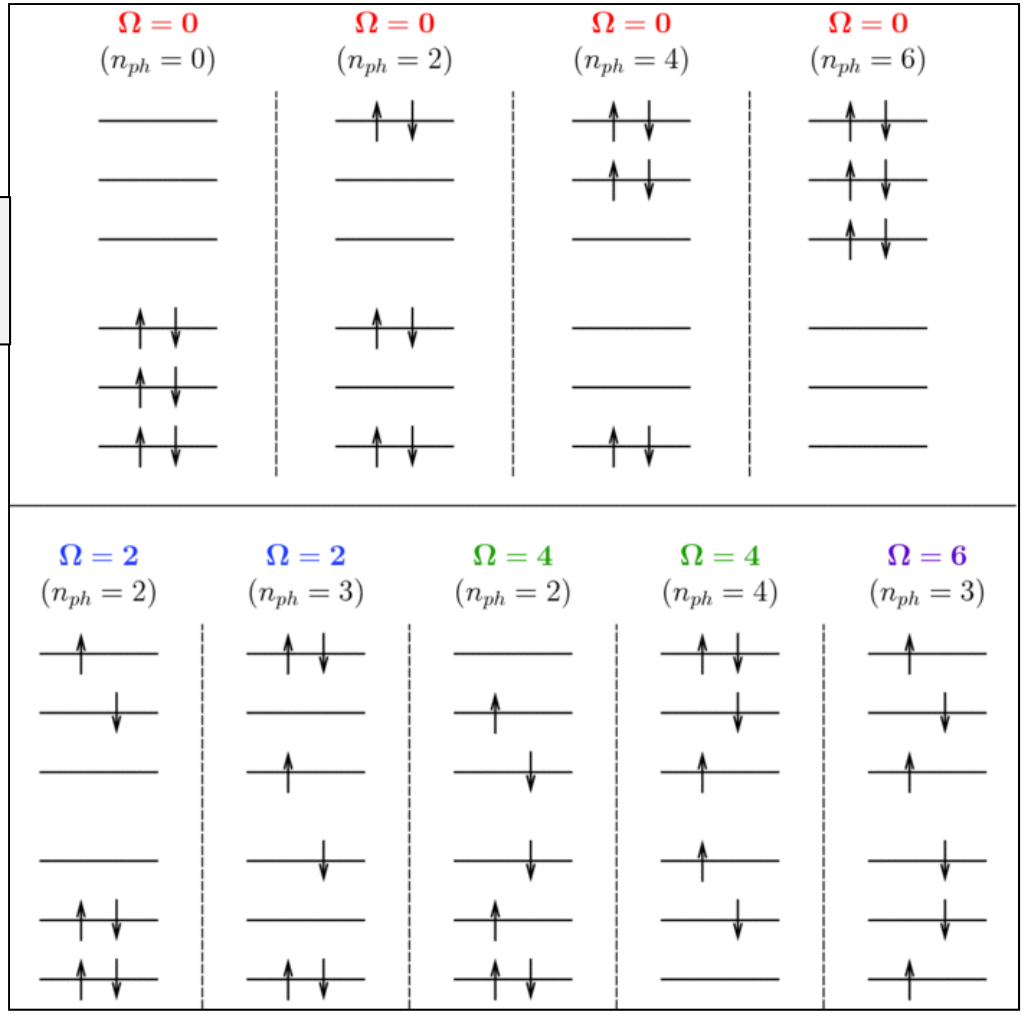
pair coupled cluster theory

Lots of "pair" theories in the literature…
What is different about this one ?

- Concept of **seniority**
- **High quality** results for **static** correlation
- **Mean-field** computational cost

Seniority Ω vs. ph excitations

reference determinant



Ω = N – 2D, where **N** = particle number, **D** = number of pairs.
Ω is the number of **unpaired** electrons.

pCCD

- **Coupled Cluster** theory with a **simplified** **pair** excitation operator

$$T = \sum_{ia} t_i^a c_{a\alpha}^\dagger c_{a\beta}^\dagger c_{i\beta} c_{i\alpha} = \sum_{ia} t_i^a P_a^\dagger P_i$$

- **orbital optimization**: make ***CC*** energy stationary with respect to **all** orbital rotations. **This is crucial to properly define the pairs.**

$$L\left(t_i^a, z_j^b, \kappa_{pq}\right) = \left\langle \Phi \left| \left(I + Z\right) e^{-T} e^{-\kappa} H e^{\kappa} e^{T} \right| \Phi \right\rangle$$

$$\kappa = \sum_{pq} \kappa_{pq} \left(c_p^\dagger c_q - c_q^\dagger c_q \right), \qquad \kappa_{pq} = \kappa_{qp}^*, \qquad \frac{\partial L}{\partial t_i^a} = \frac{\partial L}{\partial z_j^b} = \frac{\partial L}{\partial \kappa_k^c} = 0$$

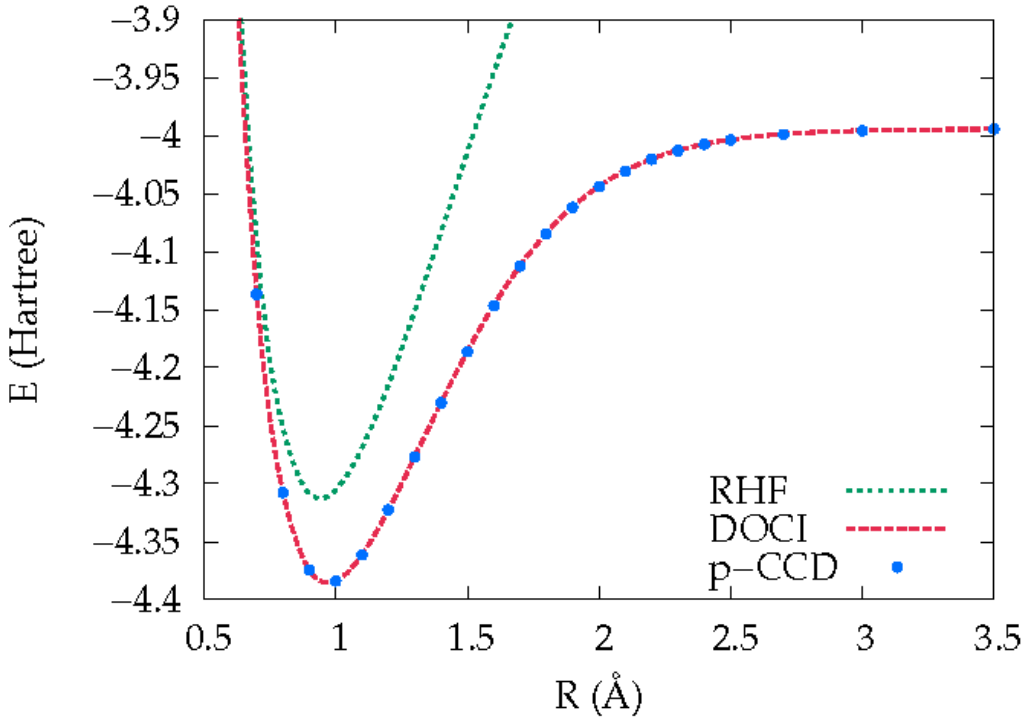
- **Ayers et al.**: **oo-pCCD** results match **oo-DOCI = full CI of pairs !**

- **pCCD** has **mean-field** computational cost: **$O(N^3)$**
  (if we ignore the integral transformation)

- **DOCI has combinatorial cost** (and is size extensive like ***CC***)

H_8 dissociation

cc-pvdz basis



A combinatorial cost wave function (**DOCI**)
is remarkably well approximated by **O(N³) pCCD**

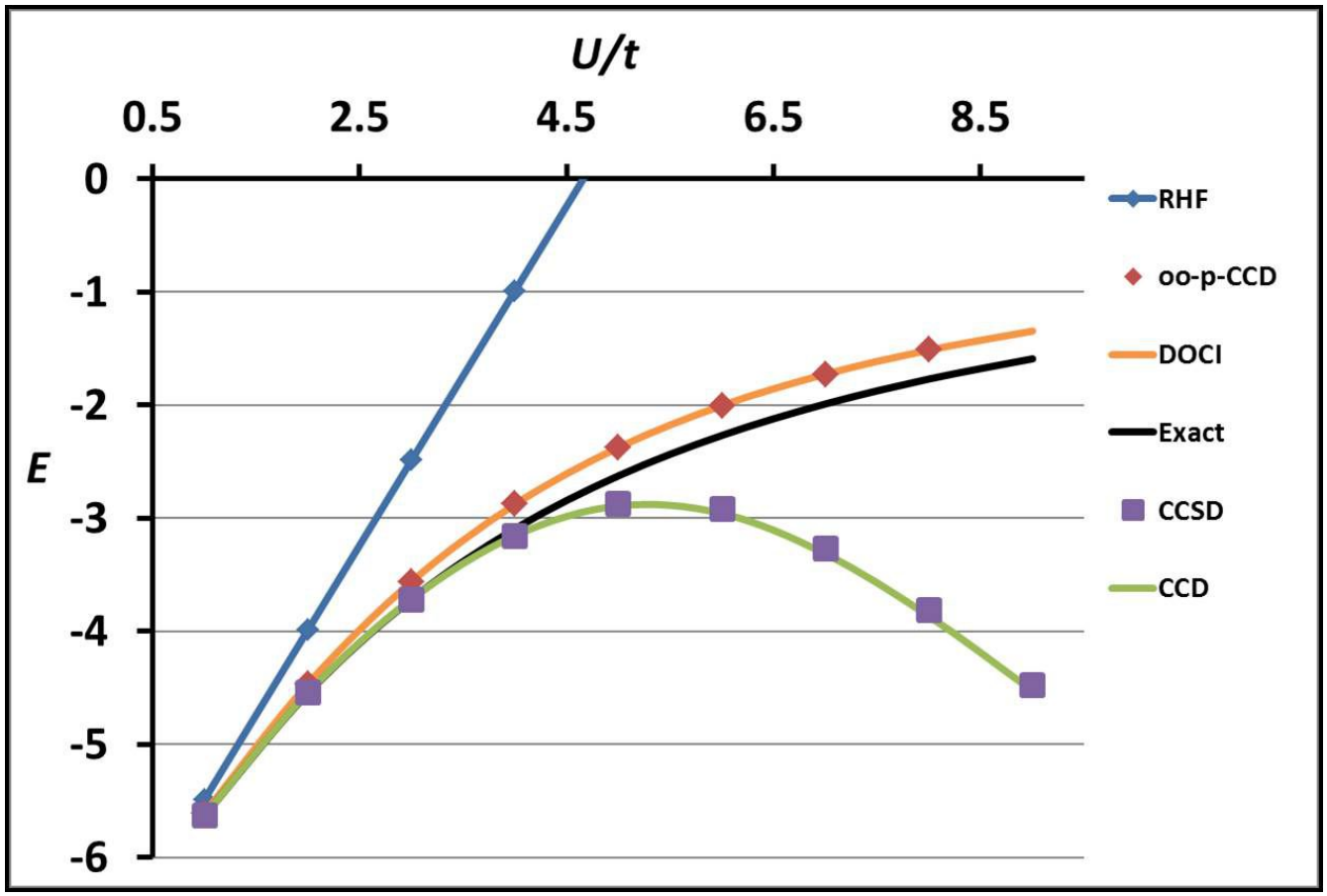
Hubbard model

$$H = -t \sum_{<i,j>\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} c^{\dagger}_{i\uparrow} c_{i\uparrow} c^{\dagger}_{i\downarrow} c_{i\downarrow}$$

- U = 0 => **RHF** is exact
- U small => **weakly** correlated
- U large => **strongly** correlated
- Exact solution known in 1D => Bethe ansatz
- Very rich physics (Mott transition, hiTc cuprates)

oo-pCCD vs. RHF based CC

1D Hubbard chain; 16 sites; half-filling

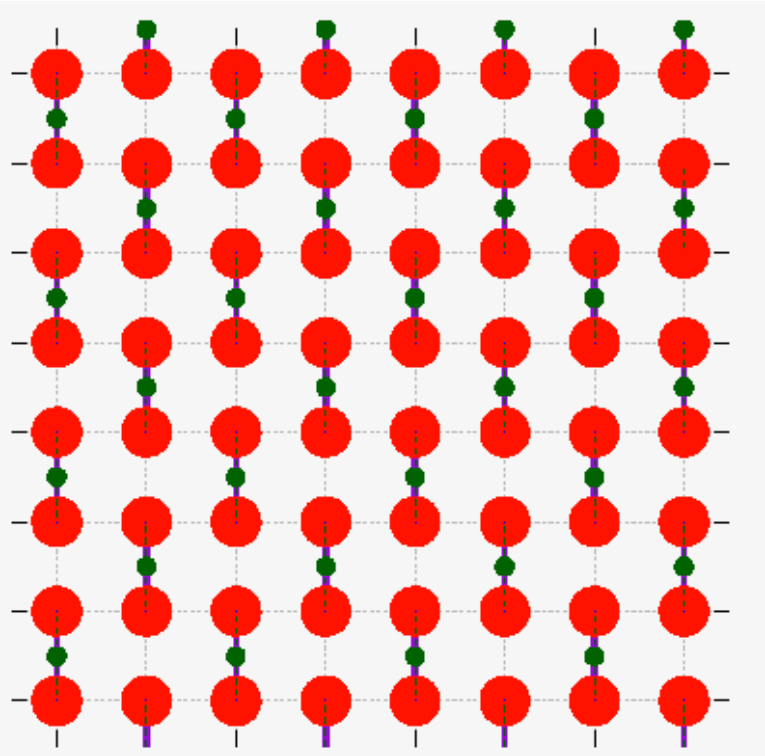


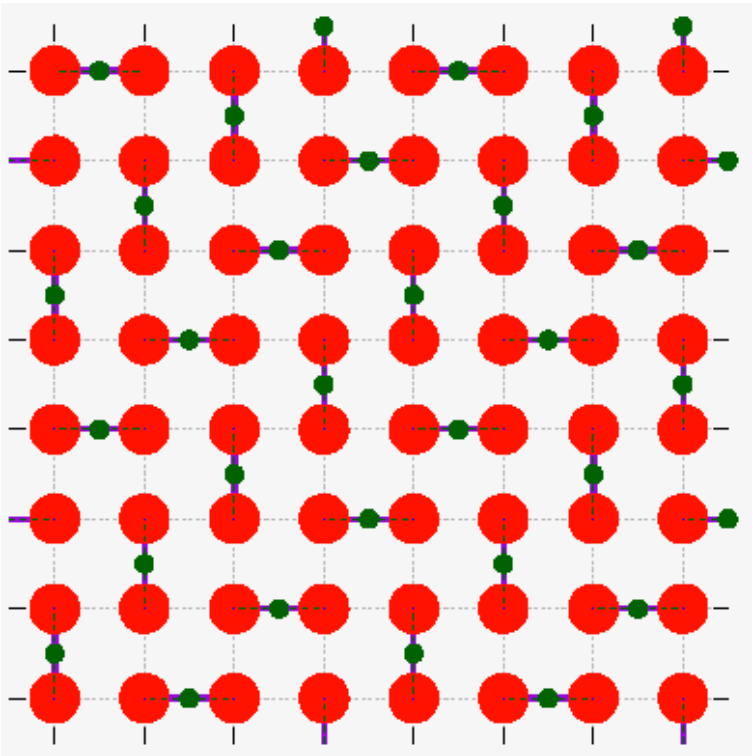
- Orbital optimization (**oo**) is important for matching **DOCI**
- Optimized orbitals become localized for large **U**
- Note **catastrophic failure** of **CCD**/**CCSD** w/ **RHF** orbitals

T. Stein, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys.* **140**, 214113 (2014)

2D Hubbard at half-filling

8x8 structures
pCCD ground state is quasi degenerate





These two structures are degenerate at **U=0** and **infinity**.
Their energy difference is maximum at **U=4** but tiny.
DOCI-QMC calculations (James Shepherd) confirm **pCCD** results.

How does pCCD match DOCI ?

- **DOCI** only has **n** even C_n excitations:

$$C_2 = T_2, \quad C_4 = T_4 + \frac{1}{2!}T_2^2$$

$$C_6 = T_6 + T_4 T_2 + \frac{1}{3!}T_2^3, \quad C_n = \ldots$$

- For repulsive systems, it appears that Ω=0 connected excitations higher than T_2 are negligible in **DOCI**

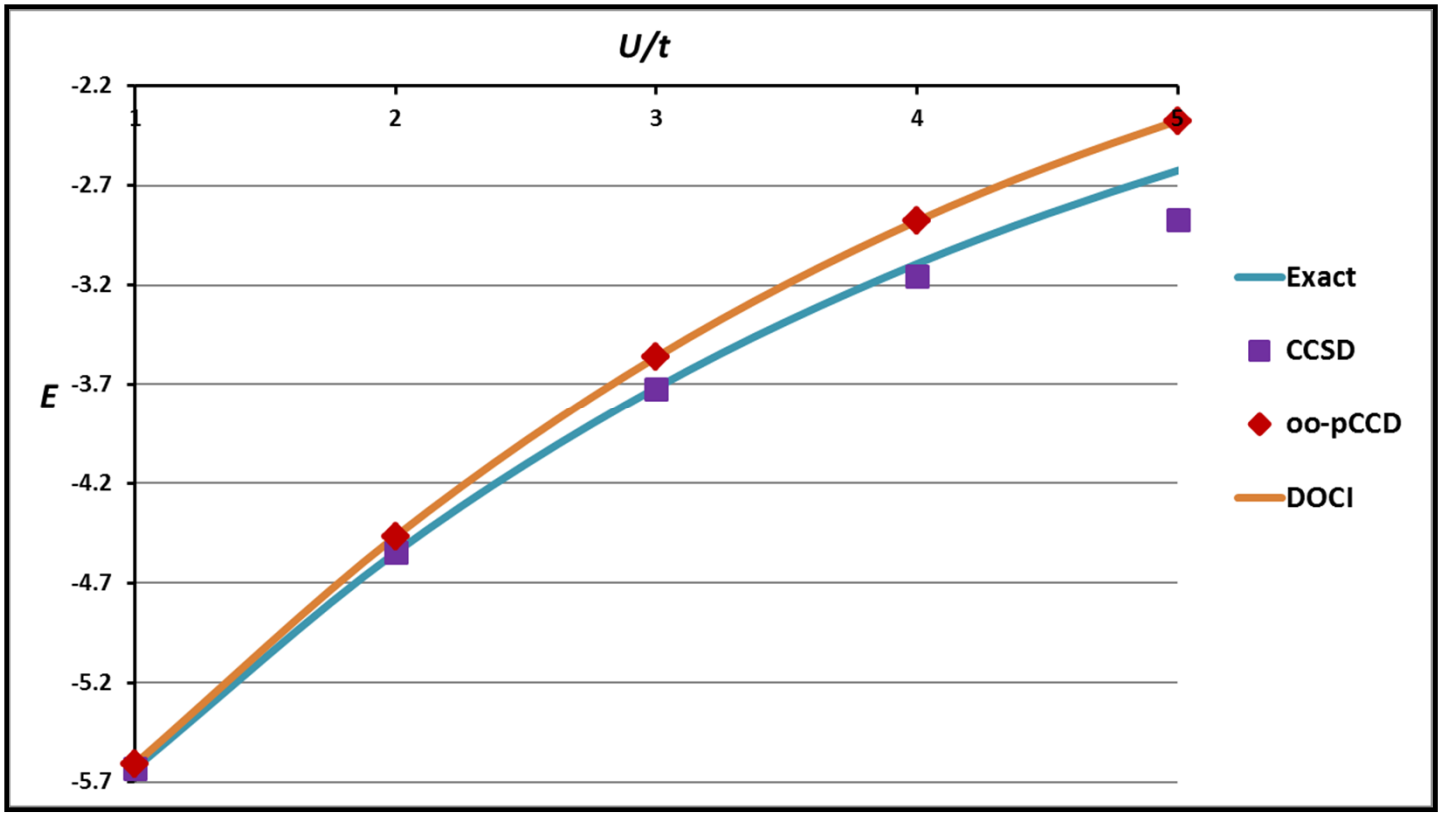
$$C_2 \sim T_2, \quad C_4 \sim \frac{1}{2!}T_2^2, \quad C_6 \sim \frac{1}{3!}T_2^3, \quad C_n \sim \frac{1}{(n/2)!}T_2^{n/2}$$

- This is ***not true*** in **attractive** systems:

Quasiparticle coupled cluster theory for pairing interactions,
T. M. Henderson, G. E. Scuseria, J. Dukelsky, A. Signoracci, and T. Duguet,
Phys. Rev. **C 89**, 054305 (2014).

How good is oo-pCCD for weak correlation?

1D Hubbard chain; 16 sites; half-filling



Not nearly as good as **CCSD**. Breaking pairs is important.
Ne atom: **DOCI/pCCD** recover ~30% of Ec

pCCD: Lessons learned

- **Pairing in an optimized particle-hole basis** is good for **static** correlation
- In repulsive systems, **DOCI**, a combinatorial cost wavefunction, is exquisitely well approximated by **pCCD**
- **pCCD = mean-field cost theory of correlated pairs**
- We are missing **broken-pair** correlations
- **How do we include these correlations?**

Broken-pair correlations

frozen-pair (fp) CCSD approach:

- Do oo-**pCCD**
- Freeze the pair amplitudes
- Solve for all other **CCSD** amplitudes.

$$\exp(T_1 + T_2) = \exp[T_1 + T_2(\textit{pairs}) + T_2(\textit{broken pairs})]$$

T_1 : *changes seniority by* 2

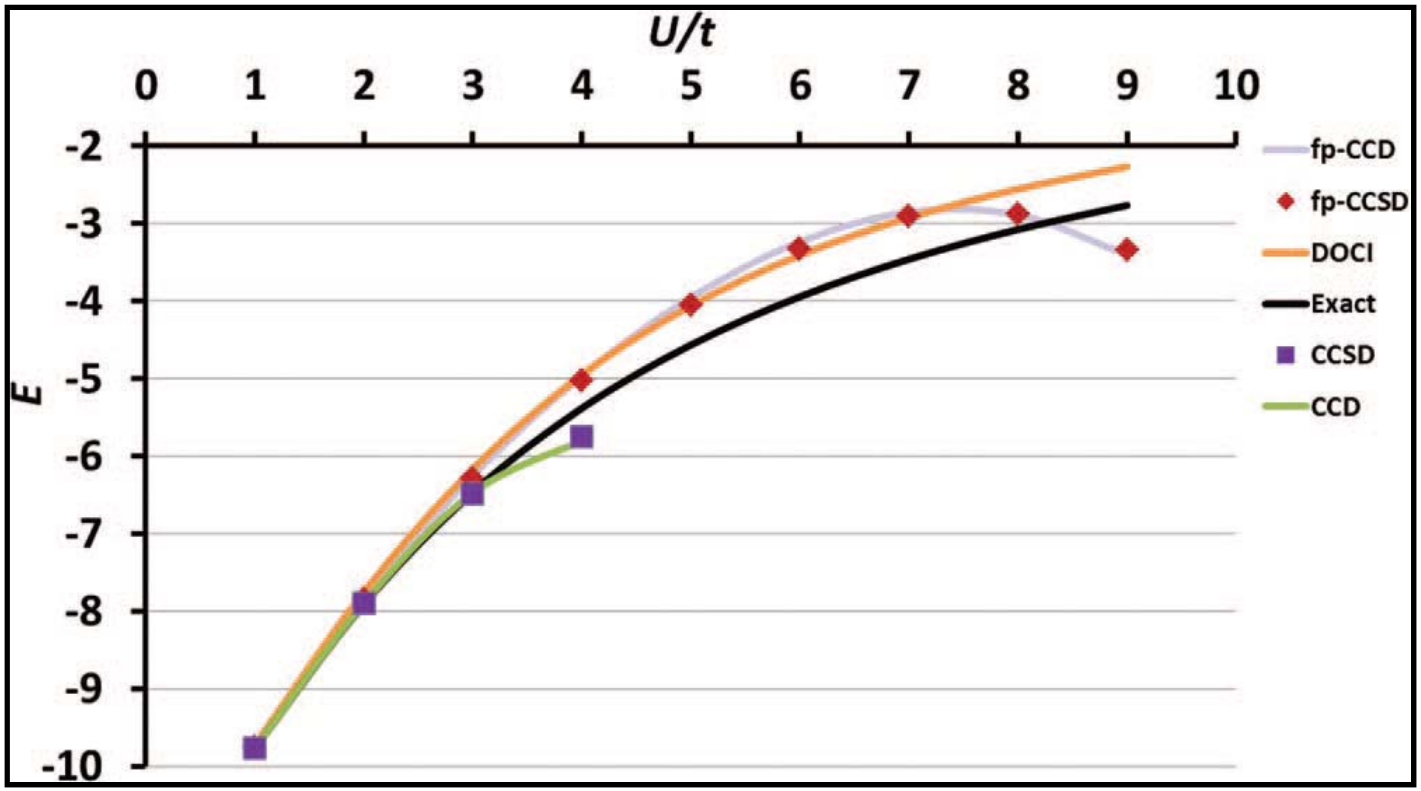
$T_2(\textit{pairs})$: *preserves seniority*

$T_2(\textit{broken pairs})$: *changes seniority by* 2 *or* 4

T. Stein, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys.* **140**, 214113 (2014).
T. M. Henderson, I. W. Bulik, T. Stein, and G. E. Scuseria, *J. Chem. Phys.* **141**, 244104 (2014).

Freezing & breaking ph pairs

1D Hubbard chain; 10 sites; half-filling



It does not work well in strongly correlated regime:
High seniority **CI** coefficients are not well factorized by the exponential of T_2 (*broken-pairs*)

T. Stein, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys.* **140**, 214113 (2014)

Lie algebraic similarity transformation theory

A novel form of CC theory

- Jastrow type correlator is written in **on-site basis** where **ph pairs are broken**
- **High quality** results for **weak** correlation
- **Low** computational cost

Lie algebraic interpretation of similarity transformations

- Traditional ***CC*** theory yields Hausdorff series that truncates:

$$\overline{H} = \mathrm{e}^{-T} H \mathrm{e}^{T} = H + [H,T] + [[H,T],T] + \ldots + 0$$

- In ***CCD***, a **2**-body ***H*** is renormalized into a **6**-body $\overline{H}$
- Key concept is **nilpotency** of **u(n)** **shifts** $\left(c_a^\dagger c_i\right)^2 = 0$
- **Question**: Are there any other types of similarity transformations that yield a closed formula?
- **Answer: YES !**
- Correlators based on **Cartan** generators lead to Hausdorff series that can be summed analytically.
- Key concept is **idempotency** of **u(n)** Cartans $\left(c_p^\dagger c_p\right)^2 = c_p^\dagger c_p$

J. Wahlen-Strothman, C. A. Jimenez-Hoyos, T. M. Henderson, G. E. Scuseria, PRB **91**, 041114(R) (2015)

Lie Algebraic Similarity Transformations

- In ***CC***, ***T*** is non-hermitian and defined by **ph** excitations from **|Φ >**
- New correlator ***J*** is hermitian and written in **on-site** basis
- ***J*** in the **ph** basis does not change seniority (not good !)
- Our goal here is: $\overline{H} = \mathrm{e}^{-J} H \mathrm{e}^{J}, \quad J^{\dagger} = J, \quad E = \left\langle \Phi \left| \overline{H} \right| \Phi \right\rangle$
- Like CC, this a canonical transformation yielding a non-hermitian $\overline{H}$
- Size extensive theory
- **QMC** community: $\widetilde{H} = \mathrm{e}^{J} H \mathrm{e}^{J}$, J hermitian, size extensive

Previous related work from:
S. Tsuneyuki, Prog. Theor. Phys. Suppl. **176**, 134 (2008)
E. Neuscamman et al., PRB **84**, 205132 (2011)

Lie algebraic similarity transformation theory

$$J = \sum_{ij\sigma\sigma'} \alpha_{i\sigma,j\sigma'} n_{i\sigma} n_{j\sigma'} \sim D_i, N_i N_j, S_i^z S_j^z, S_i^z N_j, N_i S_j^z$$

$$\overline{H} = e^{-J} H e^{J}, \qquad n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}, \qquad \sigma = \uparrow, \downarrow$$

$$e^{-J} c_{p\sigma}^{\dagger} c_{q\sigma} e^{J} = e^{-J_{p\sigma}} c_{p\sigma}^{\dagger} c_{q\sigma} e^{J_{q\sigma}}, \qquad J_{q\sigma} = \sum_{r} \alpha_{q\sigma,r\sigma} n_{r\sigma}$$

- Expansions $n_i n_j n_k n_l \ldots$ do not truncate but are resummed into orbital dependent rotations $J_{q\sigma}$
- Correlator parameters $\alpha_{i\sigma,j\sigma'}$ are solved projectively:

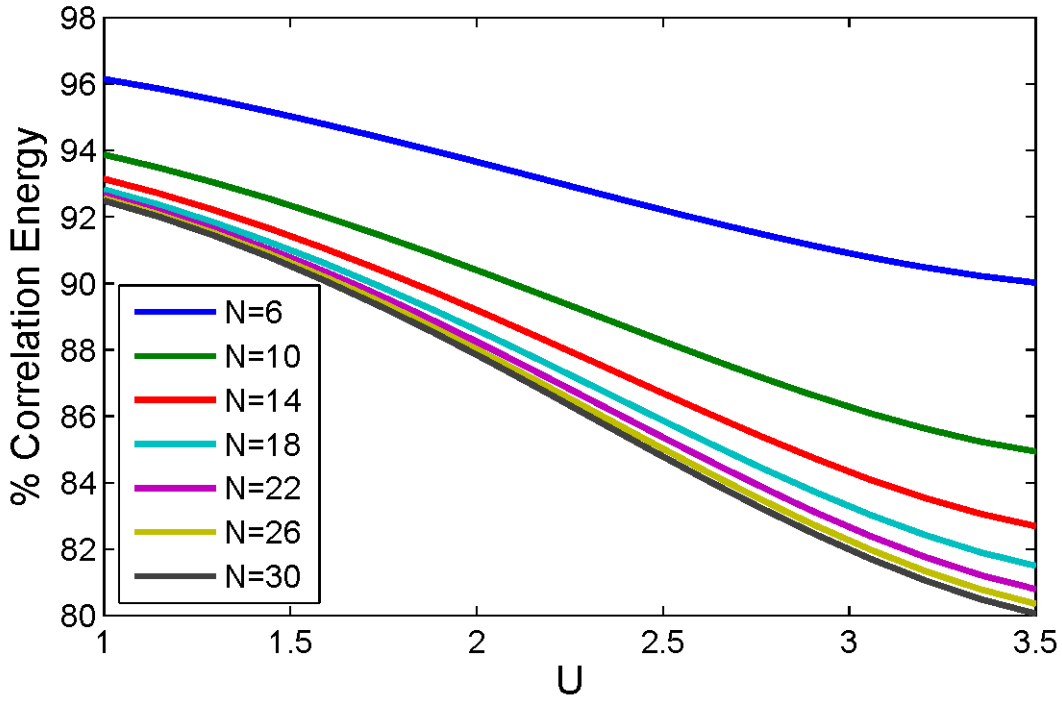
$$L\left(\alpha_{i\sigma,j\sigma'}, \eta_{i\sigma,j\sigma'}\right) = \left\langle \Phi \middle| \left(I + \tilde{J}\right) \overline{H} \middle| \Phi \right\rangle - \left\langle \Phi \middle| \overline{H} \middle| \Phi \right\rangle \left\langle \Phi \middle| \tilde{J} \middle| \Phi \right\rangle$$

$$\tilde{J} = \sum_{ij\sigma\sigma'} \eta_{i\sigma,j\sigma'} n_{i\sigma} n_{j\sigma'}, \qquad \frac{\partial L}{\partial \alpha_{i\sigma,j\sigma'}} = \frac{\partial L}{\partial \eta_{i\sigma,j\sigma'}} = 0$$

J. Wahlen-Strothman, C. A. Jimenez-Hoyos, T. M. Henderson, G. E. Scuseria, PRB **91**, 041114(R) (2015)

Ec as a function of U

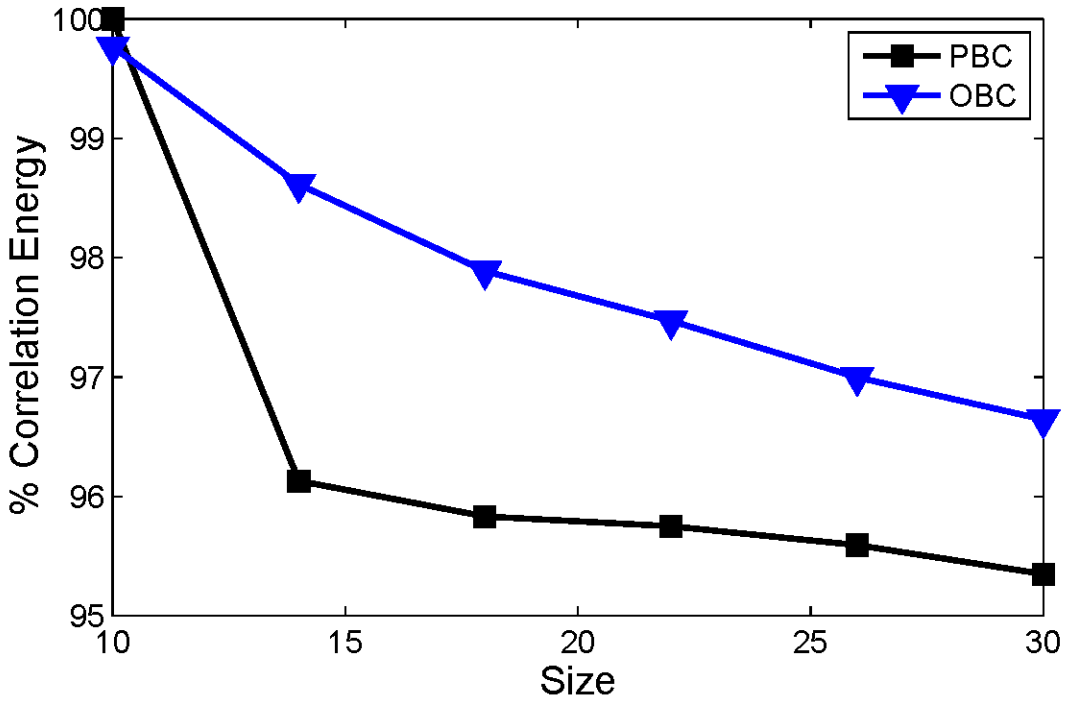
1D Hubbard chain; N=6-30; half-filling; RHF ref



Very accurate for small **U**. Less accurate for large **U**.
Model recovers mostly **weak/dynamical** correlation.

Doping at U=2

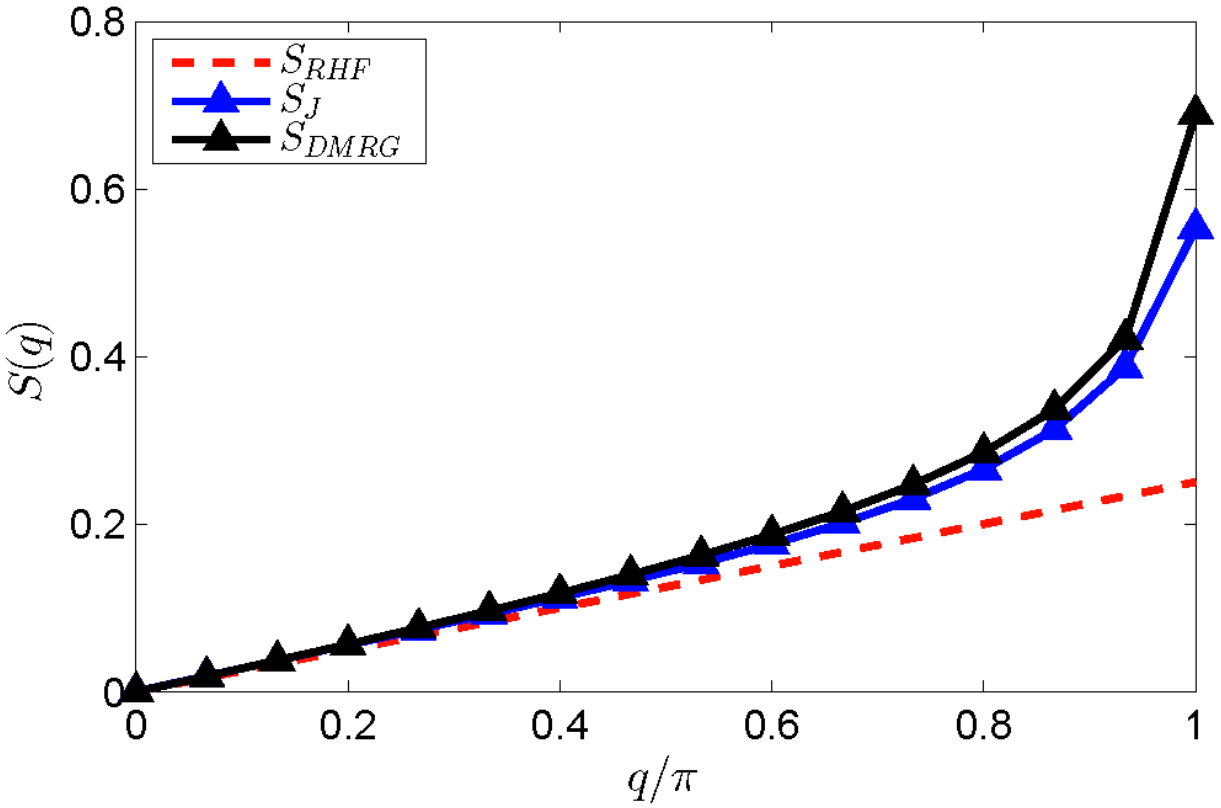
1D Hubbard chain; 8 holes; RHF reference



LAST recovers ~**95%** of **Ec** for **30** sites at **25%** hole doping

Spin-spin correlation function

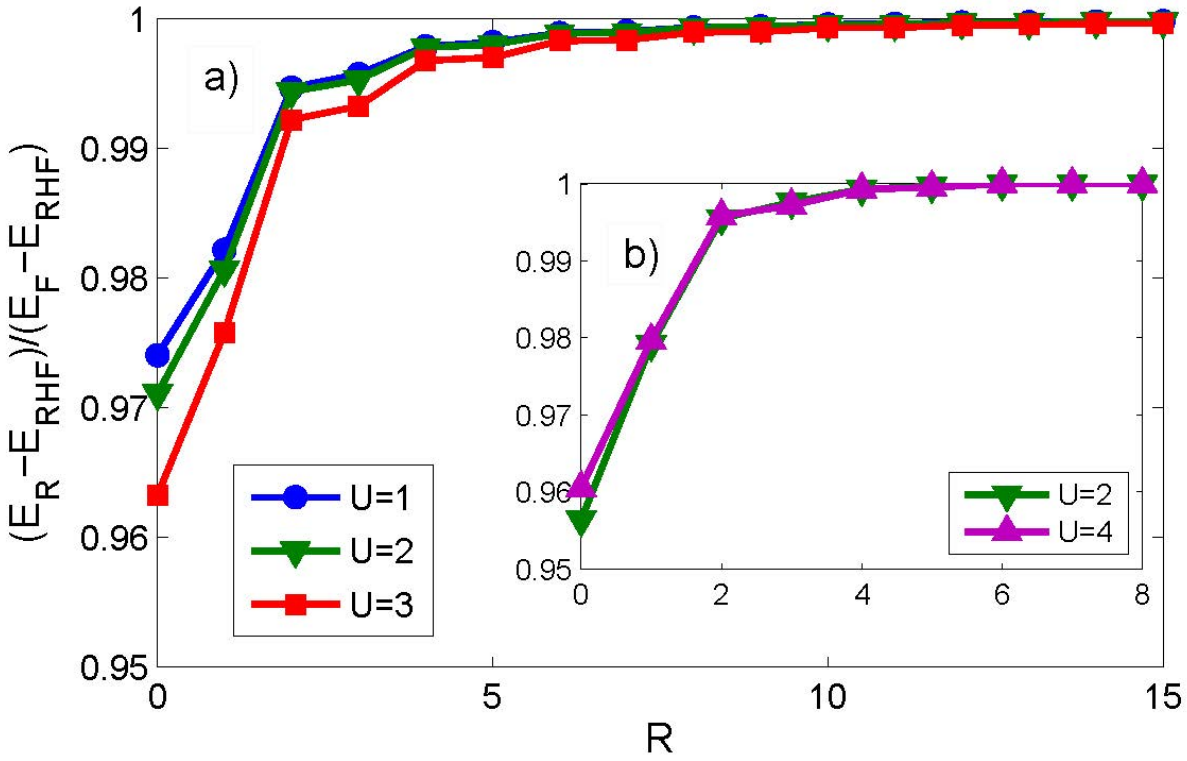
1D Hubbard PBC, N=30; ½ filled; U=3; RHF ref



Good agreement with **DMRG**

LAST correlator range

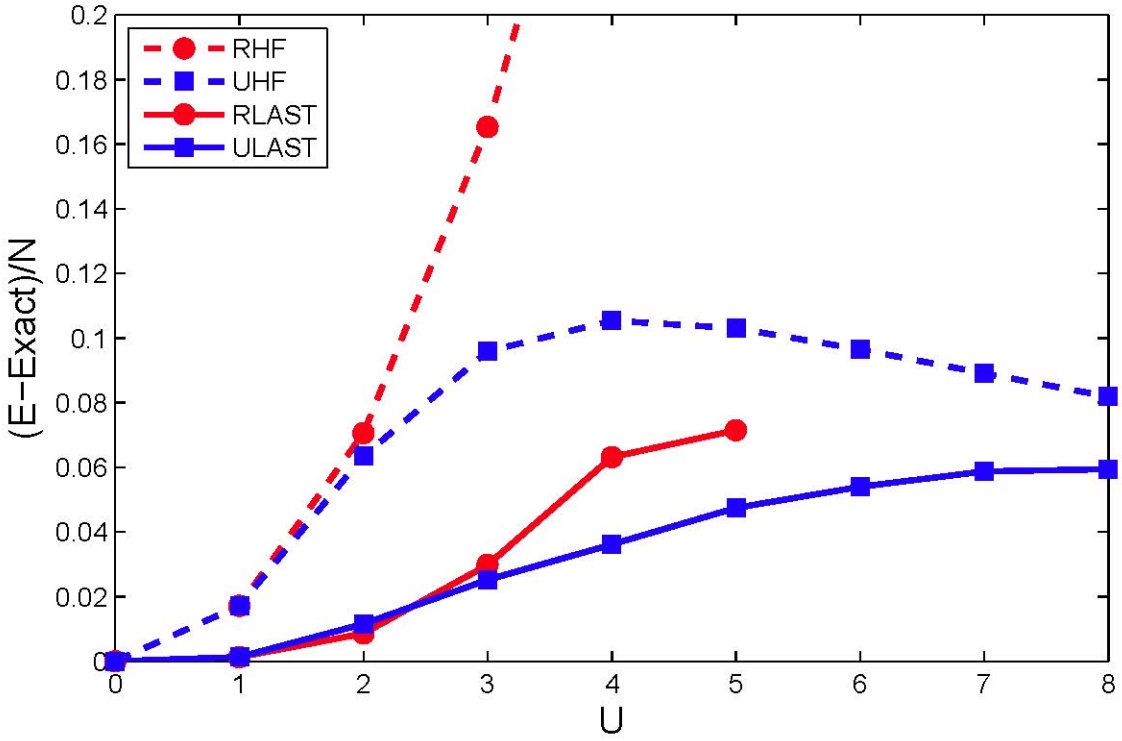
a) 1D Hubbard PBC, N=70; ½ filled
b) 8x8; ½ filled



Correlation parameters are short-range

RHF vs UHF based LAST

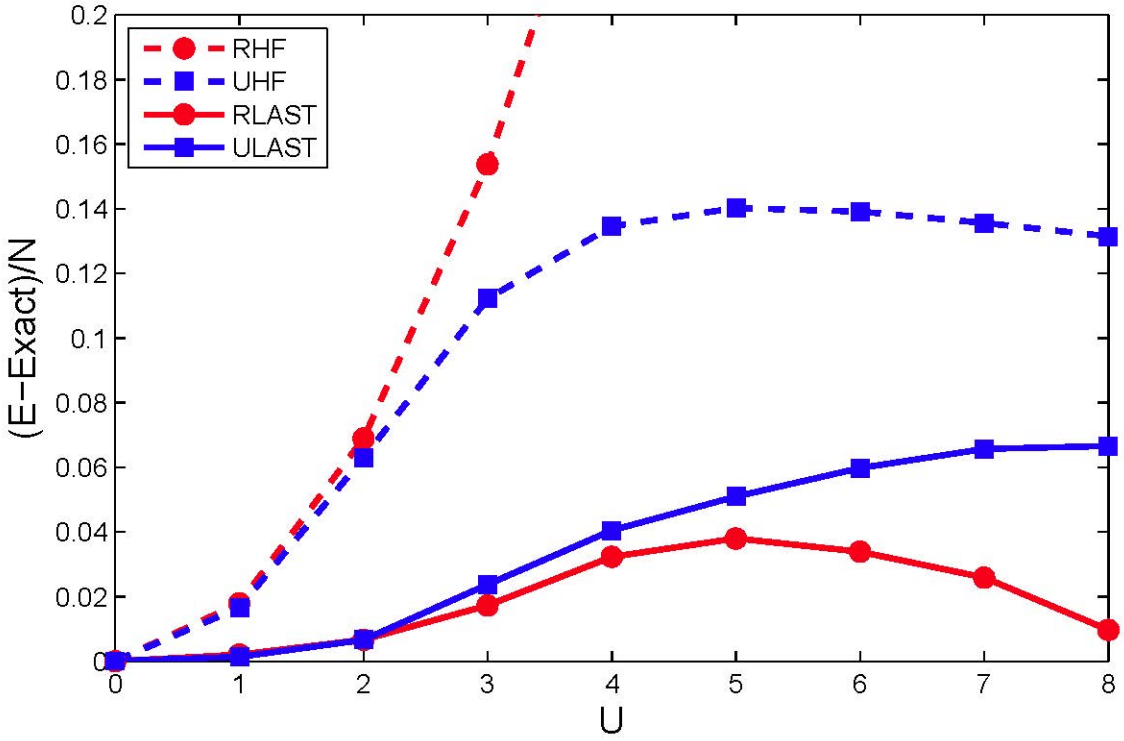
1D Hubbard PBC, N=30; ½ filled



ULAST provides better energies.
RLAST stops converging past **U=5**.

RHF vs UHF based LAST

1D Hubbard PBC, N=30; 2 holes



RLAST turns the corner around **U~5**
ULAST recovers **~half Ec** from **UHF**

RHF vs UHF based LAST for 2D

4x4 lattice where exact diagonalization is doable.
Half-filling and two-holes.

U	N_o	RHF	UHF	R-LAST	U-LAST	Exact
2	16	-1.0000	-1.0973	-1.0509	-1.1188	-1.1261
4	16	-0.5000	-0.7854	-0.6931	-0.8270	-0.8514
8	16	0.5000	-0.4619	-0.2235	-0.4873	-0.5293
2	14	-1.1172	-1.1644	-1.1634	-1.1920	-1.1982
4	14	-0.7344	-0.8808	-0.9018	-0.9595	-0.9840
8	14	0.0313	-0.5921	-0.5354	-0.6691	-0.7418

U-LAST energies are much better than **R-LAST** for large **U**.
UHF itself yields good energies for large **U**.
U-LAST develops spin contamination.

LAST: Lessons learned

- **Pairing in the onsite basis** is good for **dynamic** correlation; correlators are **short-range**
- **Pairing in the onsite basis** corresponds to breaking particle-hole pairs of **all** seniorities
- **LAST** yields excellent results for small **U** but deteriorates for large **U**
- **ULAST** is better than **RLAST** for large **U**
- **Can we put together pCCD & LAST ? YES**

Marriage of LAST & pCCD

- The two theories can be married:

$$L(t,z,\alpha,\eta)=\left\langle \Phi\left|\left(I+Z+\tilde{J}\right)e^{-T}e^{-J}He^{J}e^{T}\right|\Phi\right\rangle-\left\langle \Phi\left|e^{-T}e^{-J}He^{J}e^{T}\right|\Phi\right\rangle\left\langle \Phi\left|\tilde{J}\right|\Phi\right\rangle$$

- T : pair **ph** correlations **(pCCD)**
- J : broken pair **ph** correlations **(LAST)**
- **Dual basis**: **particle-hole (T)** and **on-site (J)**
- Each theory is **paired** in its own basis but **breaks pairs** in the other basis !

Gutzwiller similarity transformation

- **GST** is the simplest **LAST** form with **J ~ double occupancy**

$$H = -t\sum_{\langle ij\rangle\sigma}(c^{\dagger}_{i\sigma}c_{j\sigma} + c^{\dagger}_{j\sigma}c_{i\sigma}) + U\sum_{i} n_{i\uparrow}n_{i\downarrow}$$

$$J = \alpha\sum_{i} n_{i\uparrow}n_{i\downarrow}; \qquad n_{i\sigma} = c^{\dagger}_{i\sigma}c_{i\sigma}; \qquad \sigma = \uparrow,\downarrow$$

$$e^{-J}He^{J} = -t\sum_{\langle ij\rangle\sigma}\left([1+(e^{-\alpha}-1)n_{i\bar{\sigma}}]\,c^{\dagger}_{i\sigma}c_{j\sigma}\,[1+(e^{\alpha}-1)n_{j\bar{\sigma}}]\right) + U\sum_{i} n_{i\uparrow}n_{i\downarrow}$$

- Jastrow series expansion can be resummed into a 3-body $\overline{H}$

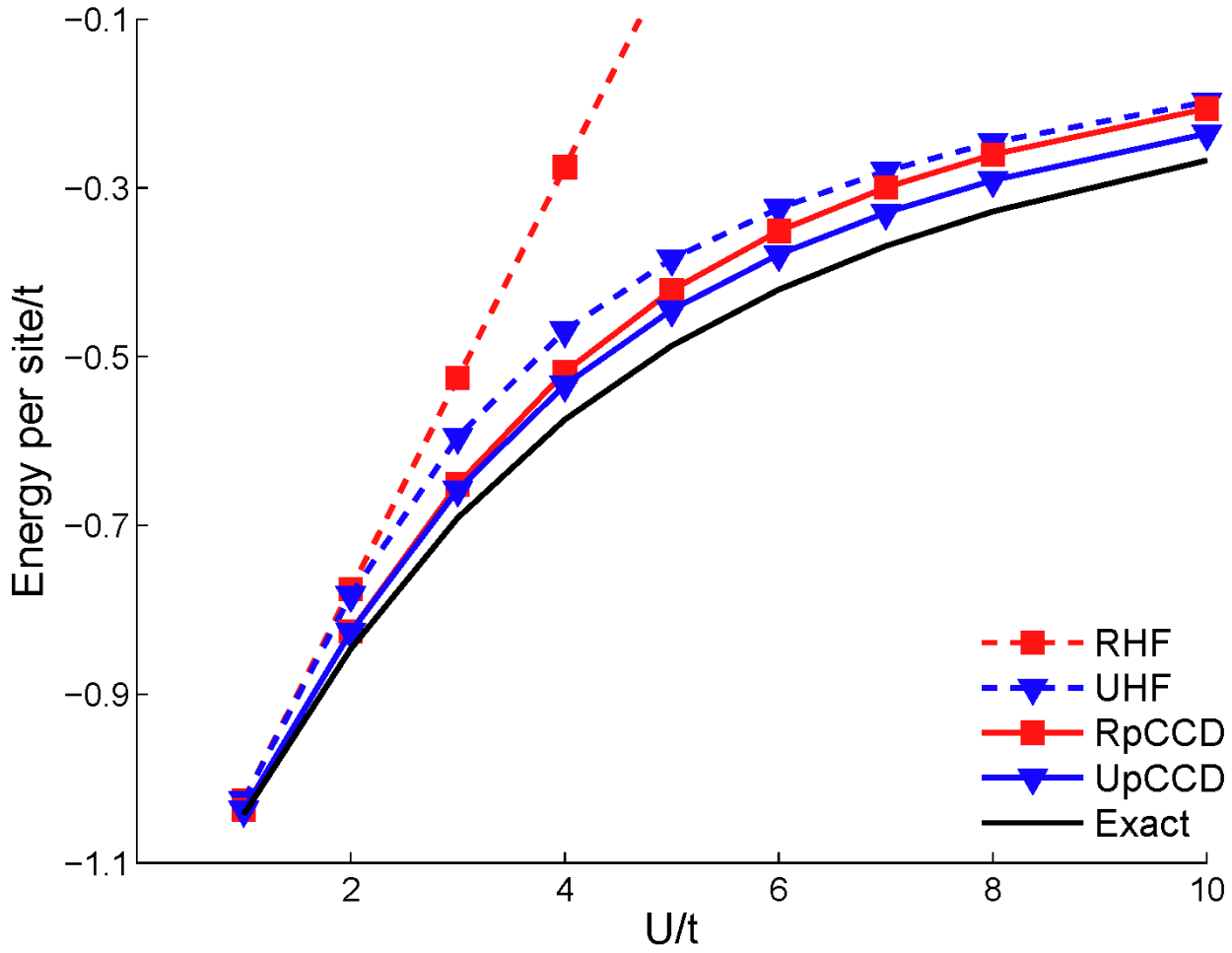
- In the following, the **GST** **3**-body Hamiltonian is reduced to rank **2** via mean-fielding over the reference determinant

S. Tsuneyuki, Prog. Theor. Phys. Suppl. **176**, 134 (2008)

J. Wahlen-Strothman, C. A. Jimenez-Hoyos, T. M. Henderson, G. E. Scuseria, PRB **91**, 041114(R) (2015)

Unrestricted orbital optimized pCCD

1D Hubbard chain; 30 sites; half-filling

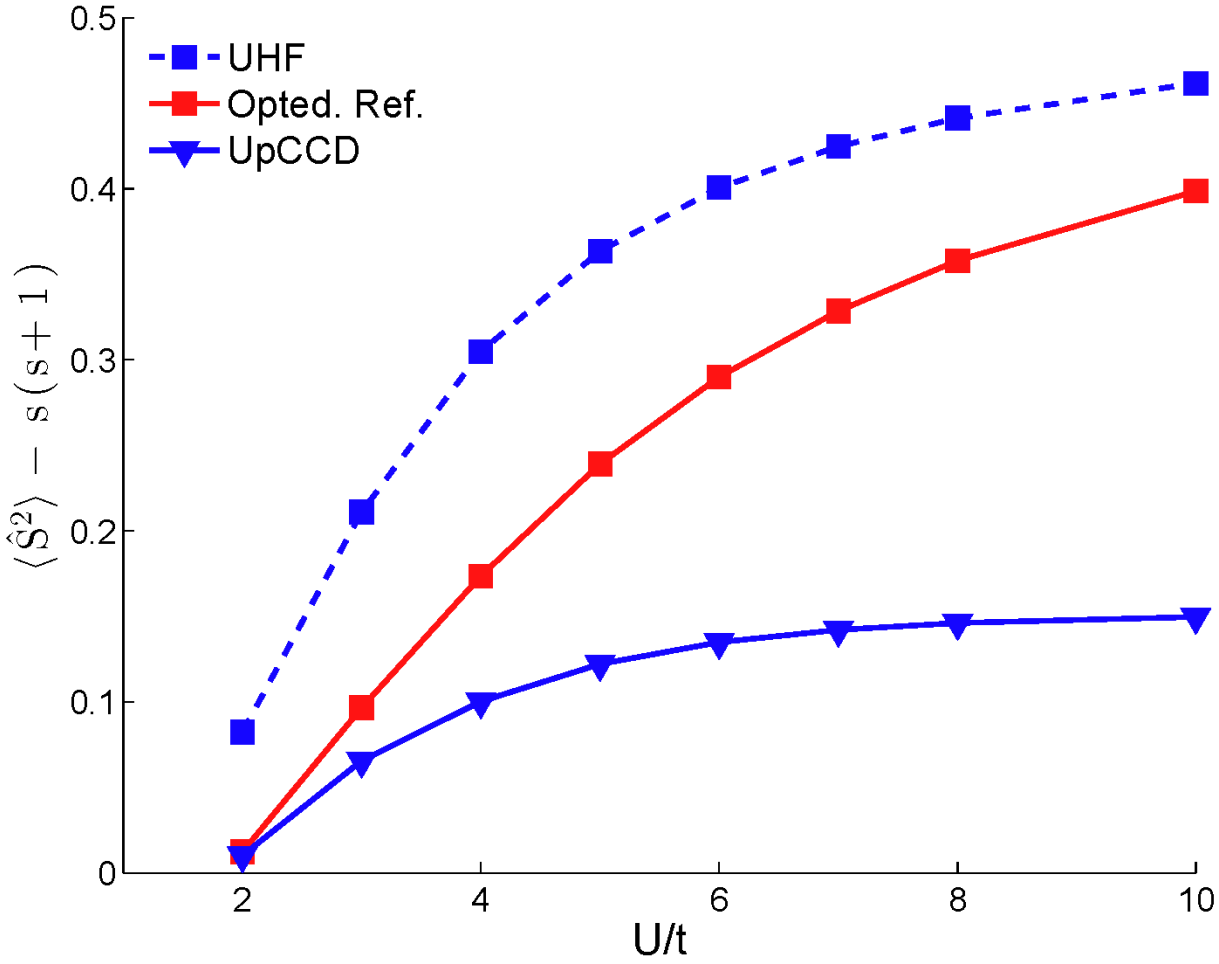


UpCCD energies are better than **RpCCD**

Ethan Qiu, Irek Bulik & GES, in preparation

Spin contamination in UpCCD

1D Hubbard chain; 30 sites; half-filling

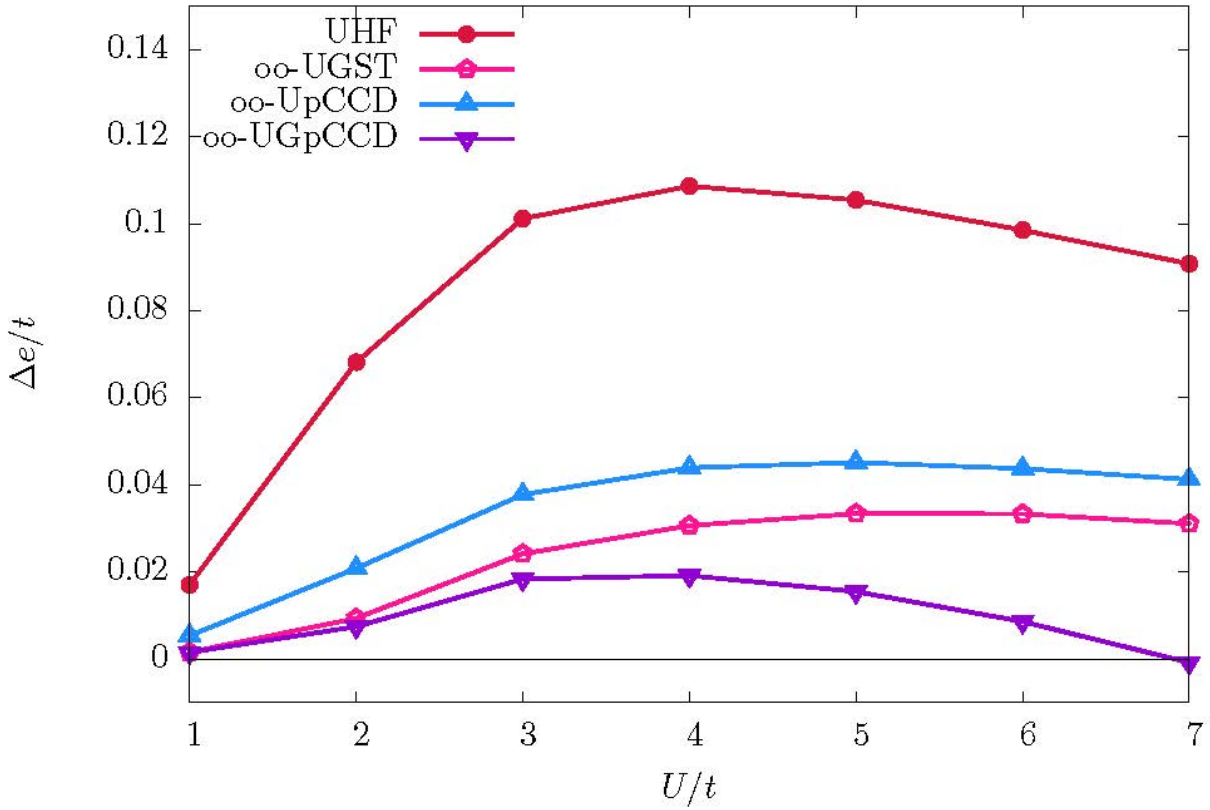


Small **per site** spin contamination

Ethan Qiu, Irek Bulik & GES, unpublished

UGST + UpCCD

1D Hubbard PBC, N=14; ½ filling

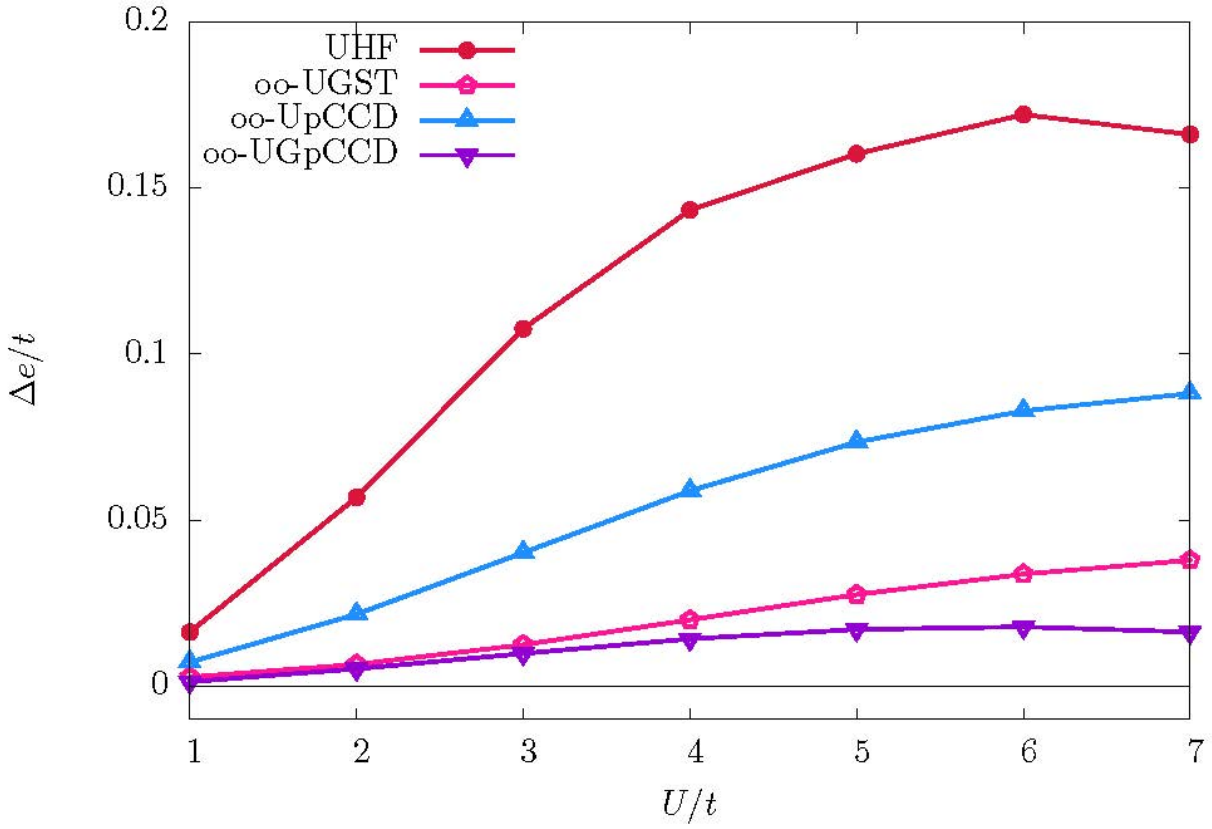


UGST recovers more correlation than **UpCCD**.
UGST + UpCCD is even better.

Irek Bulik, Tom Henderson & GES, unpublished

UGST + UpCCD

1D Hubbard PBC, N=14; 2 holes

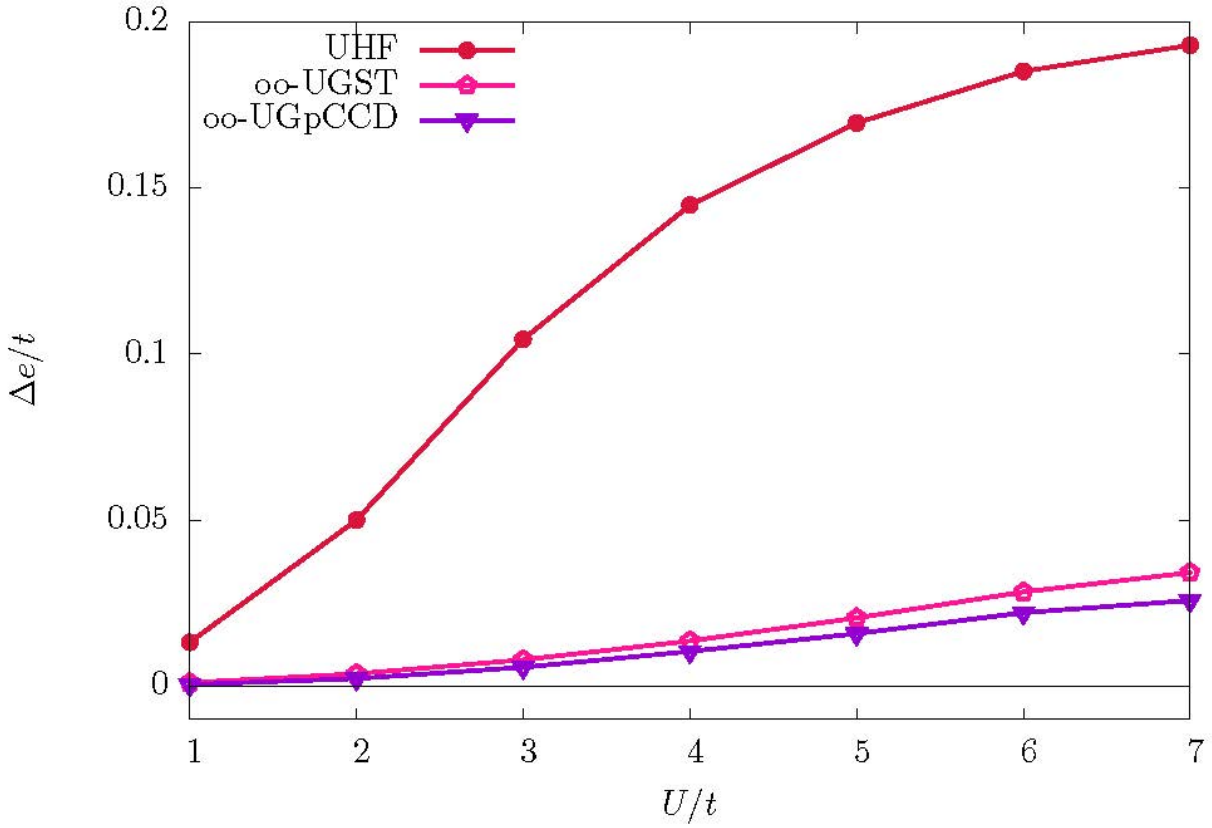


UGST recovers more correlation than **UpCCD**.
UGST + UpCCD is even better.

Irek Bulik, Tom Henderson & GES, unpublished

UGST + UpCCD

1D Hubbard PBC, N=14; 4 holes



UGST recovers substantial correlation.
UpCCD adds very little.

Irek Bulik, Tom Henderson & GES, unpublished

Summary

- **Pair coupled cluster** theory for **static** correlation
- **Lie algebraic similarity transformation** theory for **weak** correlation
- **Their marriage (generalized CC theory)**
- All with **low** polynomial computational cost

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$ DOE, NSF, Welch Foundation