Unconventional Coupled Cluster Theories for Strong and Weak Correlations

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coupled cluster theory

CCSD(T)

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

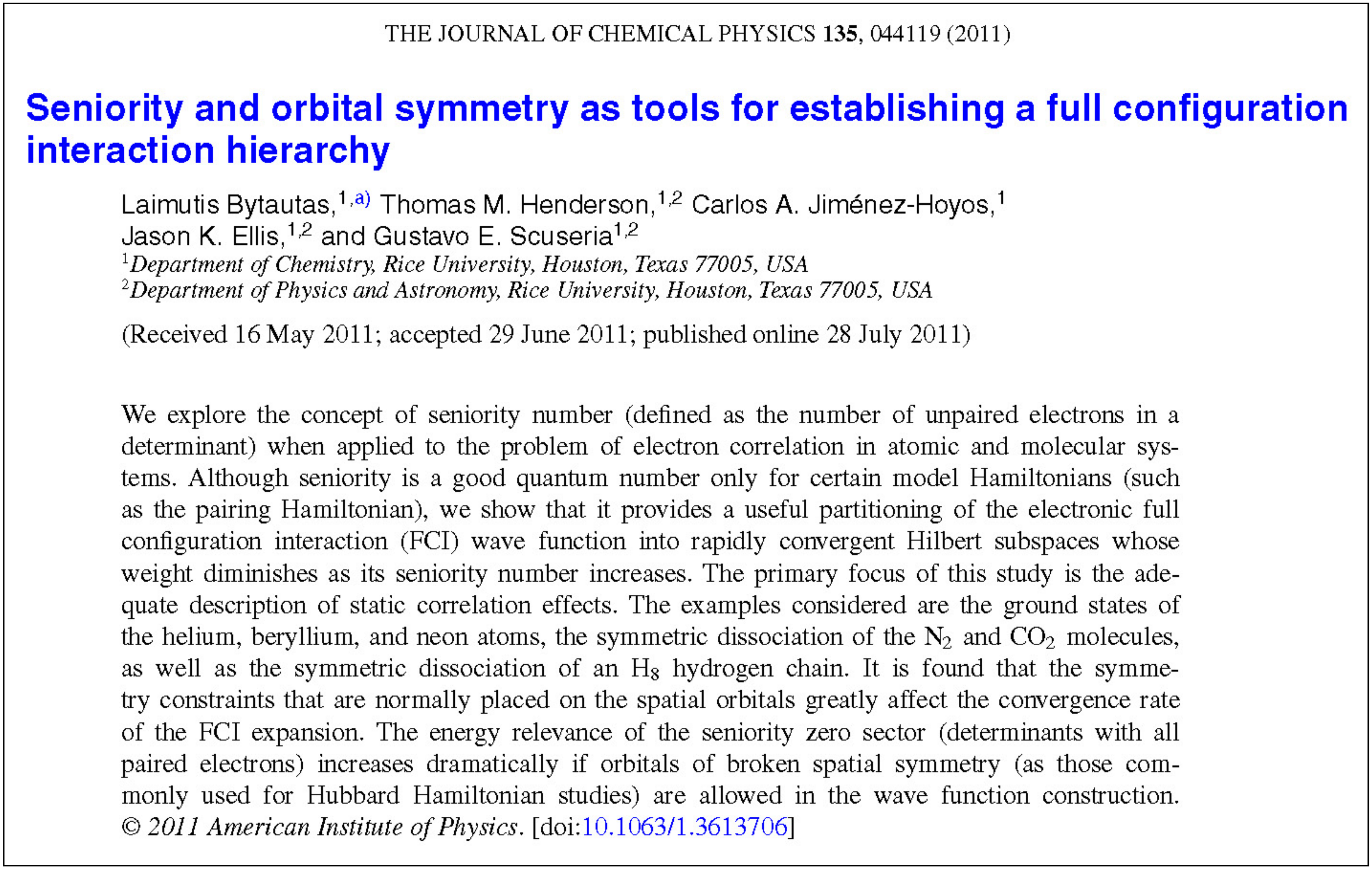
$$\overline{H} = e^{-T} H e^{T}; \qquad E = \langle 0 | \overline{H} | 0 \rangle; \qquad 0 = \langle {}_{ij}^{ab} | \overline{H} | 0 \rangle$$

- **Coupled Cluster** theory is the "**gold standard**" for **weakly correlated** systems in quantum chemistry
- It is based on a **particle-hole excitation** construction of the Hilbert space: singles + doubles + triples + quadruples +…
- It has **polynomial scaling** with system size: **CCSD** is **N**^{6}; **CCSDT** is **N**^{8}
- For **strongly correlated** systems where collective excitations become important, <u>**single-reference CC falls dead**</u>
- **(T)** means that triple excitations are treated perturbatively

pair coupled cluster theory

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

Seniority



THE JOURNAL OF CHEMICAL PHYSICS **135**, 044119 (2011)

Seniority and orbital symmetry as tools for establishing a full configuration interaction hierarchy

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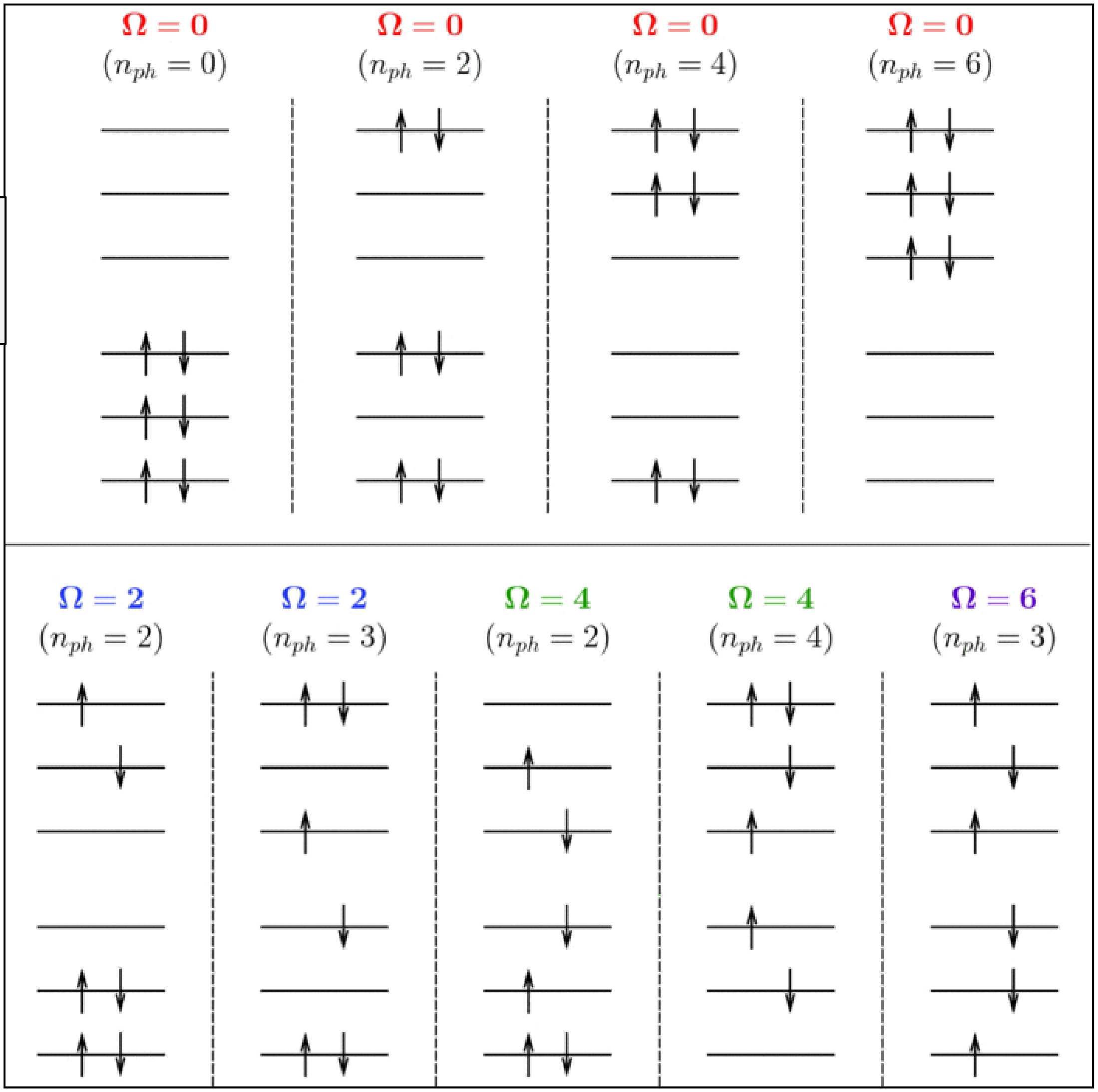
We explore the concept of seniority number (defined as the number of unpaired electrons in a determinant) when applied to the problem of electron correlation in atomic and molecular systems. Although seniority is a good quantum number only for certain model Hamiltonians (such as the pairing Hamiltonian), we show that it provides a useful partitioning of the electronic full configuration interaction (FCI) wave function into rapidly convergent Hilbert subspaces whose weight diminishes as its seniority number increases. The primary focus of this study is the adequate description of static correlation effects. The examples considered are the ground states of the helium, beryllium, and neon atoms, the symmetric dissociation of the N_2 and CO_2 molecules, as well as the symmetric dissociation of an H_8 hydrogen chain. It is found that the symmetry constraints that are normally placed on the spatial orbitals greatly affect the convergence rate of the FCI expansion. The energy relevance of the seniority zero sector (determinants with all paired electrons) increases dramatically if orbitals of broken spatial symmetry (as those commonly used for Hubbard Hamiltonian studies) are allowed in the wave function construction.
[doi:10.1063/1.3613706]

Seniority Ω vs. ph excitations

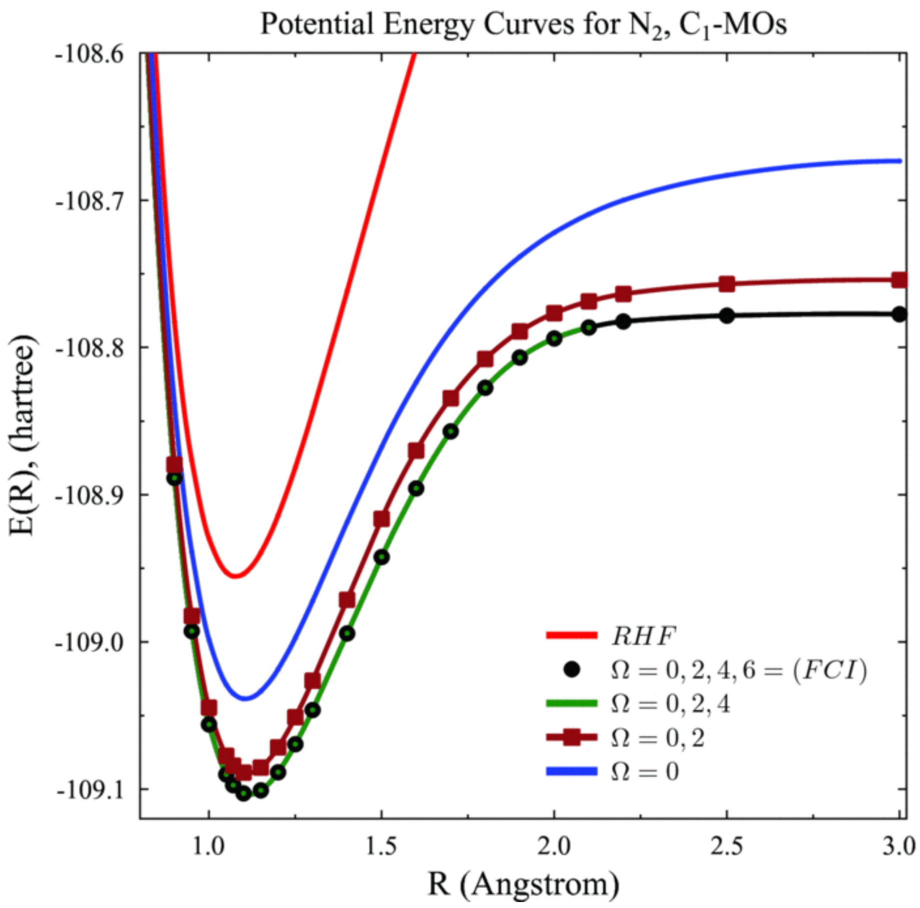
reference determinant

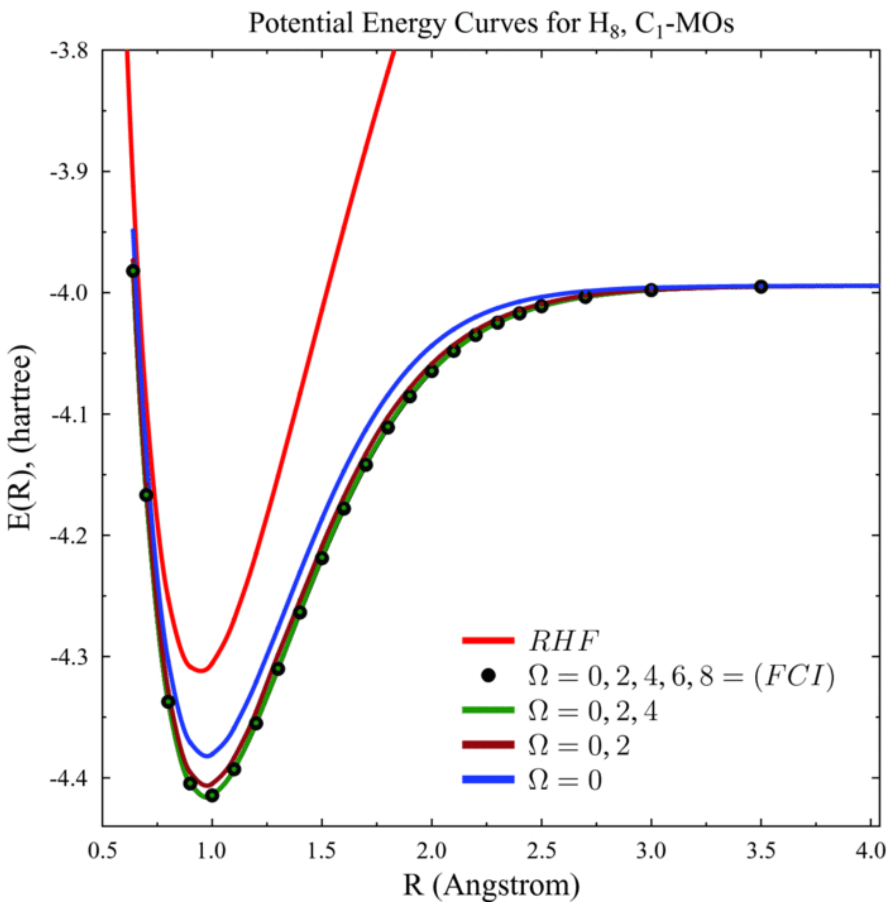


Ω = N – 2D, where **N** is particle number and **D** number of pairs.
Ω is the number of unpaired electrons.

Seniority Ω = 0, 2, 4...

N_2 and H_8 dissociations; cc-pVDZ





Ω=0 is **FCI** of paired excitations w/ **orbital optimization** (**DOCI**).
Breaking spatial symmetry yields faster seniority convergence.

Seniority

Bytautas et al., *J. Chem. Phys.* **135**, 044119 (2011).

Introduction:

"Thus, our objective is to see if the seniority-based method of partitioning Hilbert space is capable of offering new insights on how to generate compact wave functions that converge rapidly toward the FCI limit as the seniority number is increased."

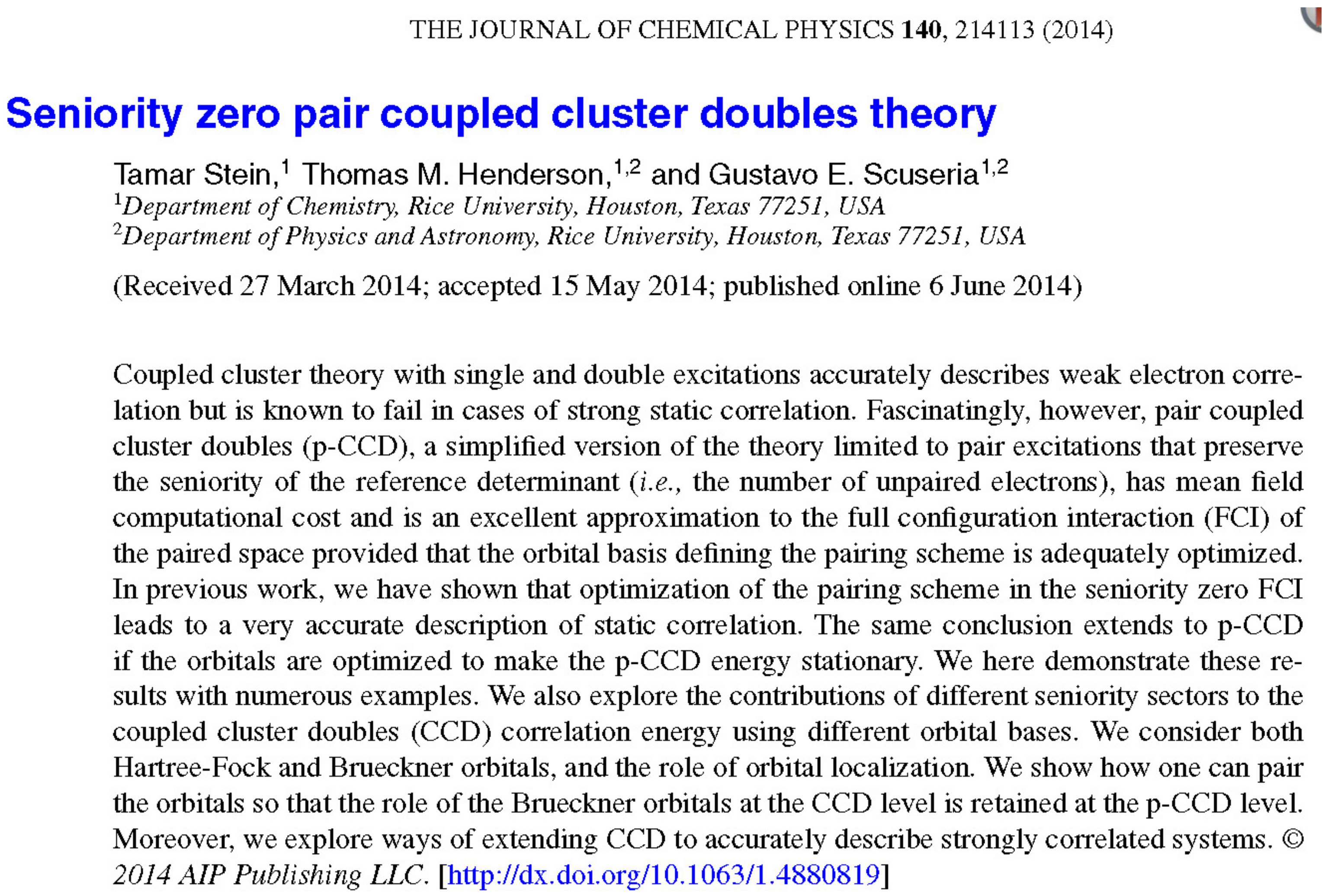
Conclusions:

"When the single-determinant reference is a good zeroth order wave function (the correlation energy is essentially *dynamic*), the traditional, excitation-based configuration selection procedure seems to be more efficient than a seniority based selection procedure. However, for the cases which exhibit *strong* (static) correlation (such as the beryllium atom or the symmetric dissociation of N_2, CO_2, and H_8 molecules), a seniority-based selection procedure is considerably more efficient..."

Seniority zero FCI (DOCI)

- **Seniority** is not a symmetry.
- But **DOCI** describes **strong** correlation very well.
- It has **combinatorial** cost.
- **Not good** for weakly correlated systems.
- "**Dual**" to **particle-hole number** (neither a symmetry).
- Is there a simple form that approximates **seniority zero FCI (DOCI) accurately?**
- **YES:** recent work by **Ayers/Bultinck/Van Neck** & in **my group**.

Seniority zero pair CCD



THE JOURNAL OF CHEMICAL PHYSICS **140**, 214113 (2014)

Seniority zero pair coupled cluster doubles theory

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Coupled cluster theory with single and double excitations accurately describes weak electron correlation but is known to fail in cases of strong static correlation. Fascinatingly, however, pair coupled cluster doubles (p-CCD), a simplified version of the theory limited to pair excitations that preserve the seniority of the reference determinant (*i.e.*, the number of unpaired electrons), has mean field computational cost and is an excellent approximation to the full configuration interaction (FCI) of the paired space provided that the orbital basis defining the pairing scheme is adequately optimized. In previous work, we have shown that optimization of the pairing scheme in the seniority zero FCI leads to a very accurate description of static correlation. The same conclusion extends to p-CCD if the orbitals are optimized to make the p-CCD energy stationary. We here demonstrate these results with numerous examples. We also explore the contributions of different seniority sectors to the coupled cluster doubles (CCD) correlation energy using different orbital bases. We consider both Hartree-Fock and Brueckner orbitals, and the role of orbital localization. We show how one can pair the orbitals so that the role of the Brueckner orbitals at the CCD level is retained at the p-CCD level. Moreover, we explore ways of extending CCD to accurately describe strongly correlated systems. © *2014 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4880819]

A simplified version of **CCD** does static correlation very well
if **orbitals defining the pairing scheme are optimized !**

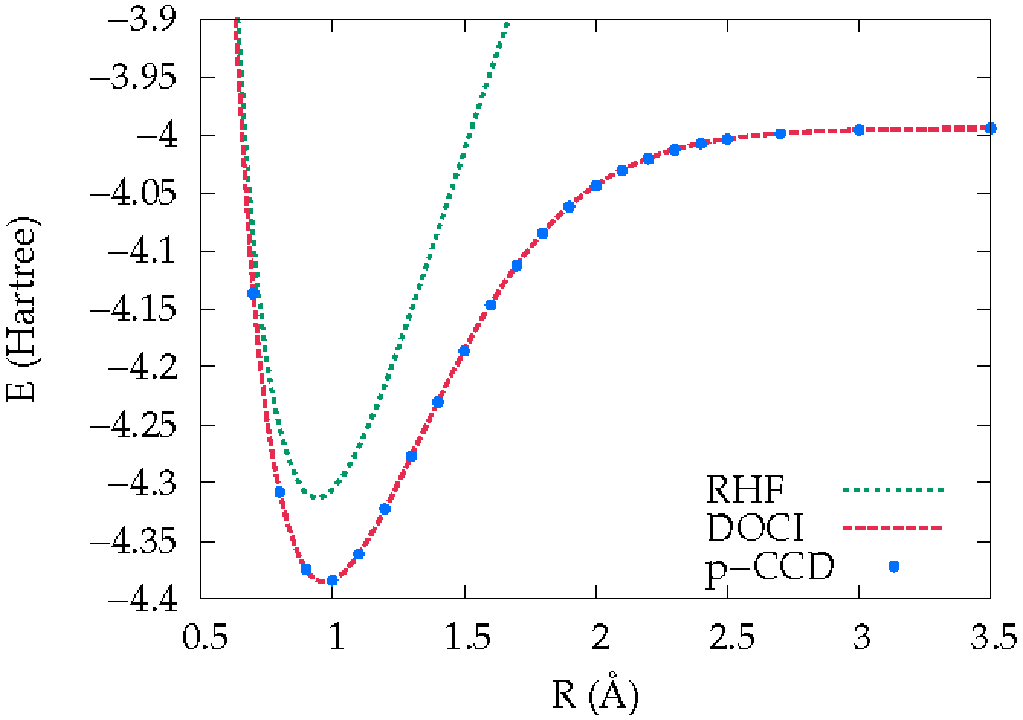
oo-pCCD

$$T_2 = \sum_{ia} t_i^a c_{a\alpha}^\dagger c_{a\beta}^\dagger c_{i\beta} c_{i\alpha} = \sum_{ia} t_i^a P_a^\dagger P_i$$

$$\left[P_n, P_m^\dagger \right] = \delta_{nm} \left(I - N_m \right)$$

- **Coupled Cluster** theory with a **simplified** cluster operator.
- Every occupied pair can be excited onto any unoccupied pair.
- Wavefunction $|\Psi\rangle = \exp(T_2)\,|\Phi\rangle$ is an entangled pair product state.
- **Orbital optimization**: make ***CC*** energy stationary with respect to orbital rotations (Scuseria & Schaefer, 1987). **This is crucial.**
- Excellent **oo-p-CCD** results compared to **DOCI**.
- Method has **mean-field** computational cost: **$O(N^3)$**
  (if we ignore the integral transformation)

H_8 dissociation (dz basis)



A combinatorial cost wave function (**DOCI**)
is remarkably well approximated by **$O(N^3)$ p-CCD**

Hubbard model

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

- **U = 0** => **RHF** is exact
- **U small** => **weakly** correlated
- **U large** => **strongly** correlated
- Exact solution known in **1D** => Bethe ansatz
- Equivalent to minimum basis hydrogen chains with **R ~ U/ t**
- Very rich physics

Performance on 1D Hubbard chains

Percent of exact correlation energy

Half-filling

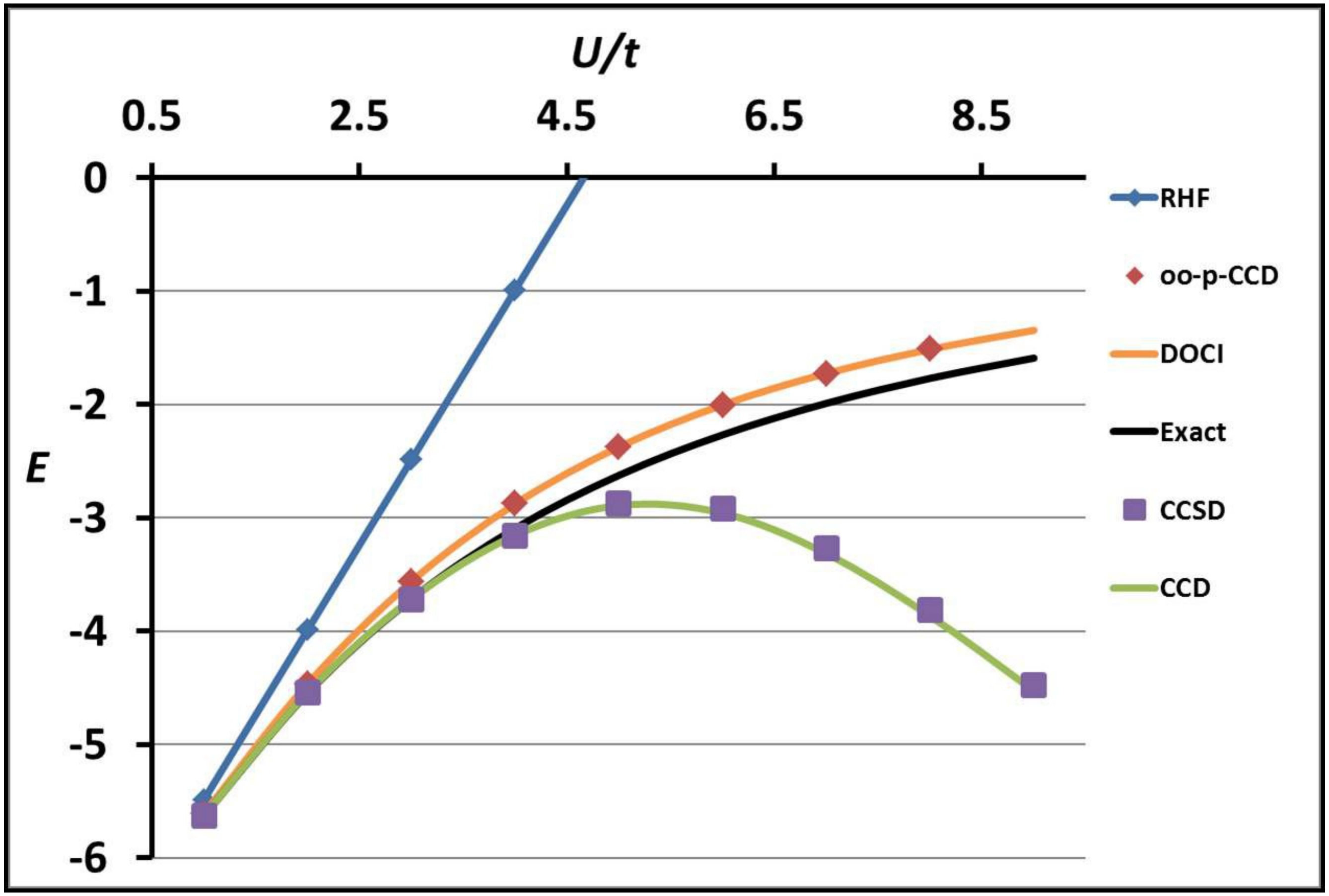
	6 sites		8 sites		10 sites		14 sites	
U	oo-p-CCD	DOCI	oo-p-CCD	DOCI	oo-p-CCD	DOCI	oo-p-CCD	DOCI
2	85.46%	85.48%	83.41%	83.42%	81.99%	82.00%	80.09%	80.10%
5	92.02%	92.02%	90.74%	90.75%	89.91%	89.92%	88.89%	88.90%
9	96.97%	96.97%	96.51%	96.51%	96.23%	96.23%	95.88%	95.88%

oo-p-CCD closely follows **DOCI**, which is close to the exact answer for large **U** (strong correlation)

It is crucial to **optimize** the orbitals, i.e., make energy stationary with respect to **all (occ+vir)** orbital rotations

oo-p-CCD vs. RHF based CC

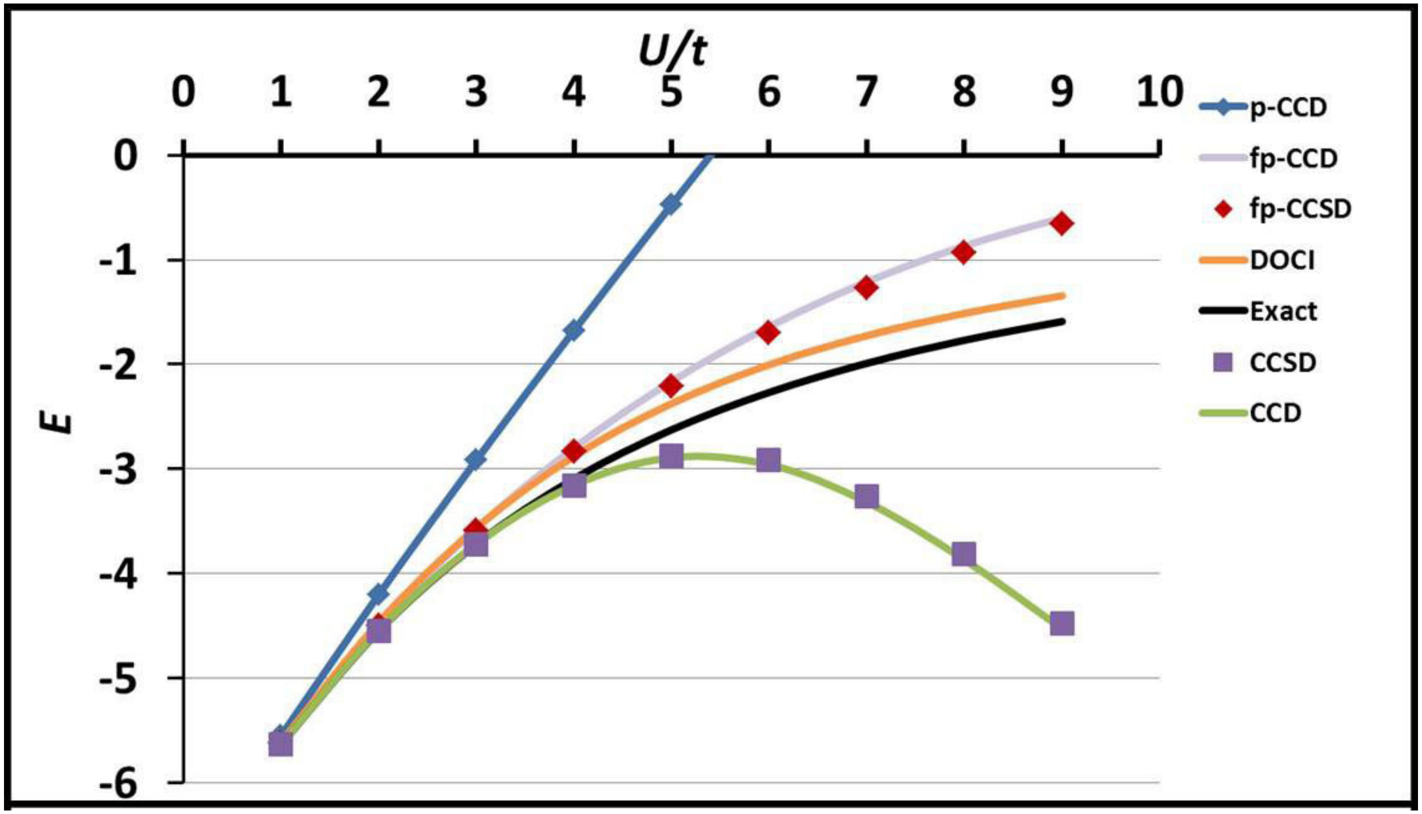
1D Hubbard chain; 16 sites; half-filling



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

Freezing & breaking pairs

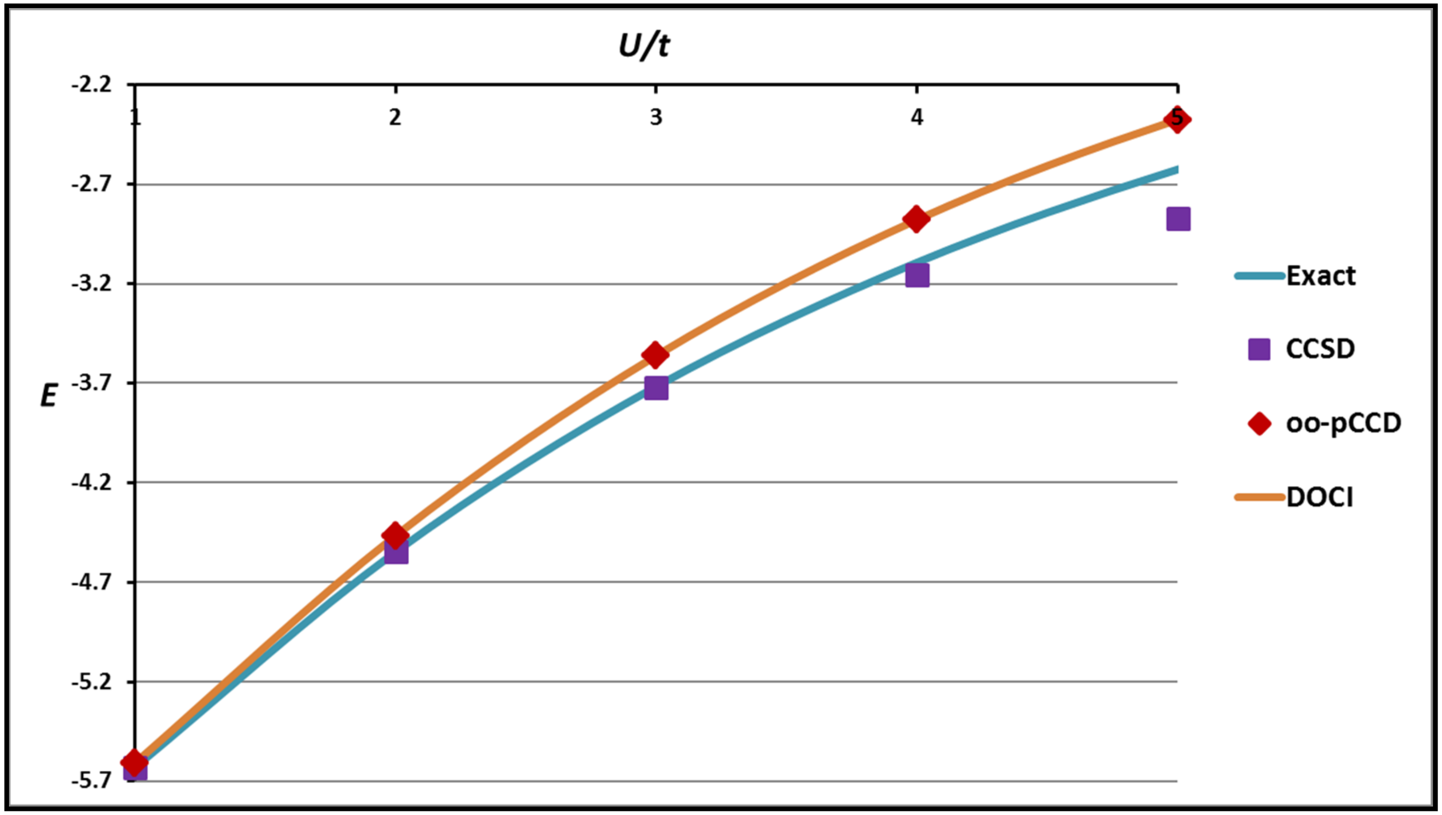
Do **p-CCD** with RHF orbitals.
Freeze the pair amplitudes.
Solve for all other amplitudes.
Much closer to **oo-p-CCD** (~**DOCI**).



1D Hubbard chain; 16 sites; half-filling

How good is oo-p-CCD for weak correlation?

1D Hubbard chain; 16 sites; half-filling



Not nearly as good as **CCSD**
(breaking pairs is important)

Lessons learned

- **Pairing in the particle-hole basis** is good for **strong** correlation.
- A combinatorial cost wavefunction can be very well approximated by a **low polynomial cost method**.
- **How do we include weak correlations?**

similarity transformation theory

Hamiltonian Similarity Transformations

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

- Our goal here is: $\overline{H} = \mathrm{e}^{-J}\, H\, \mathrm{e}^{J}, \quad J^{\dagger} = J, \quad E = \langle \Phi \,|\, \overline{H} \,|\, \Phi \rangle$
- Non-unitary similarity transformations are canonical.
- They lead to **non-hermitian** effective Hamiltonians.
- Except for coupled cluster theory, very little has been done.
- In **CC**, the cluster operator ***T*** is non-hermitian.
- Variational **MC** community: $\overline{H} = \mathrm{e}^{J}\, H\, \mathrm{e}^{J}$

Gutzwiller similarity transformation

$$H = \sum_{ij\sigma} t_{ij}(c^\dagger_{i\sigma} c_{j\sigma} + c^\dagger_{j\sigma} c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

$$\overline{H} = e^{-J} D e^{J}; \qquad J = \eta \sum_i n_{i\uparrow} n_{i\downarrow} = \eta D, \qquad e^{-J} D e^{J} = D$$

$$e^{-J} c^\dagger_{i\sigma} c_{j\sigma} e^{J} = [1 + (e^{-\eta} - 1) c^\dagger_{i\bar{\sigma}} c_{i\bar{\sigma}}]\, c^\dagger_{i\sigma} c_{j\sigma}\, [1 + (e^{\eta} - 1) c^\dagger_{j\bar{\sigma}} c_{j\bar{\sigma}}]$$

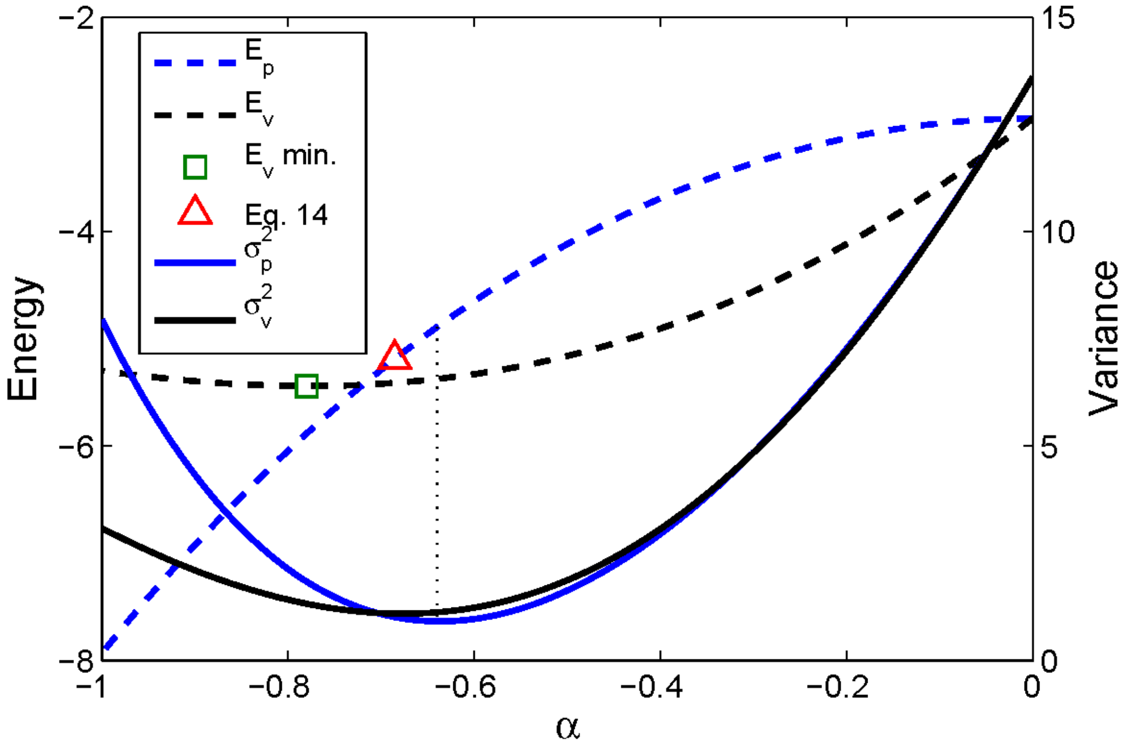
- Hausdorff transformation can be resummed.
- Similar to "**transcorrelation**" but done in Hilbert, not real space.
- Energy is **unbound**.
- η is an adjustable parameter
- Solved via **energy variance:** $\min\left(\left\langle \overline{H}^\dagger \overline{H} \right\rangle - |E|^2\right)$
- Or via **projective equations**: $\left\langle 0 \,|\, n_{i\uparrow} n_{i\downarrow} \overline{H} \,|\, 0 \right\rangle = 0$

J. Wahlen-Strothman, C. A. Jimenez-Hoyos, T. M. Henderson, G. E. Scuseria, arxiv: 1409.2203

Variational and projective energies are very close

$$J = \exp(\eta \sum_i n_{i\uparrow} n_{i\downarrow}), \quad E_p = \left\langle \Phi \right| e^{-J} H e^{J} \left| \Phi \right\rangle, \quad E_v = \frac{\left\langle \Phi \right| e^{J} H e^{J} \left| \Phi \right\rangle}{\left\langle \Phi \right| e^{2J} \left| \Phi \right\rangle}$$

Hubbard chain
10 sites
half-filling
U=4
RHF



Projective energy is unbound and has no stationary points.
Projective energy variance minimum is close to the variational one.

Lie algebraic similarity transformation theory

(Correlators are Cartan generators of an enveloping algebra)*

$$J = \sum_{ij\sigma\sigma'} \alpha_{i\sigma, j\sigma'} n_{i\sigma} n_{j\sigma'}$$

$$J \sim D_i, N_i N_j, S_i^z S_j^z, S_i^z N_j, N_i S_j^z$$

$$\overline{H} = e^{-J} H e^{J}$$

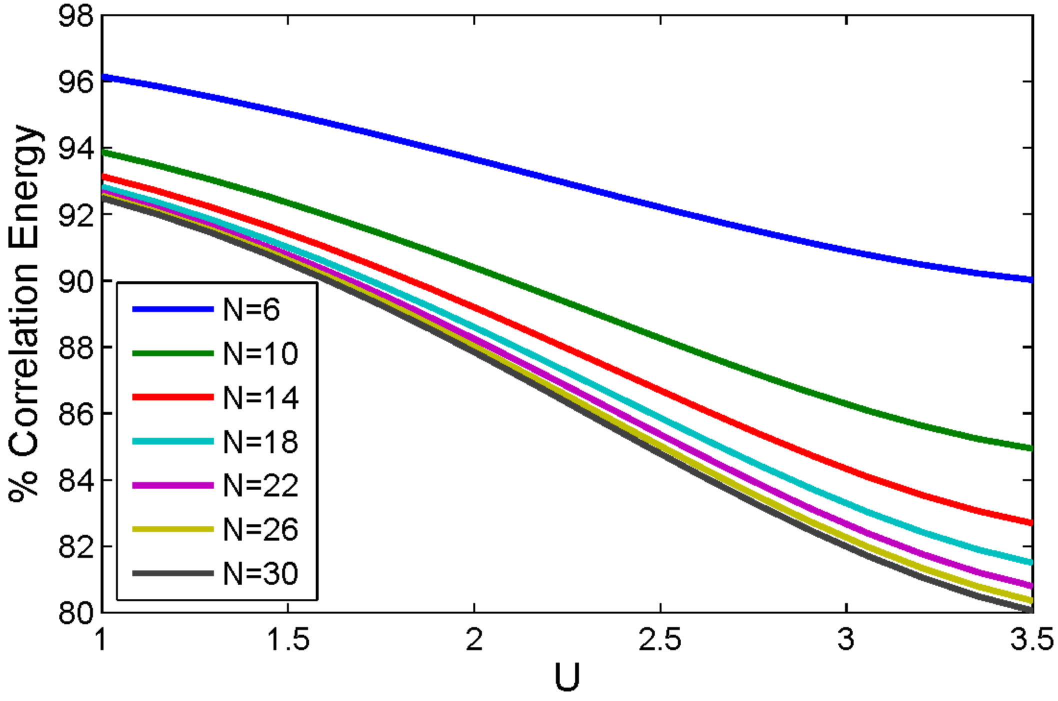
- All **J** are two-body Hermitian correlators.
- Closed renormalization.‡ No truncation in $\overline{H}$.
- Adjustable parameters $\boxed{\alpha_{i\sigma, j\sigma'}}$ are solved projectively.

* J. Zhao and G. E. Scuseria, in preparation.

‡ J. Wahlen-Strothman, C. A. Jimenez-Hoyos, T. M. Henderson, G. E. Scuseria, arxiv: 1409.2203

Ec as a function of U

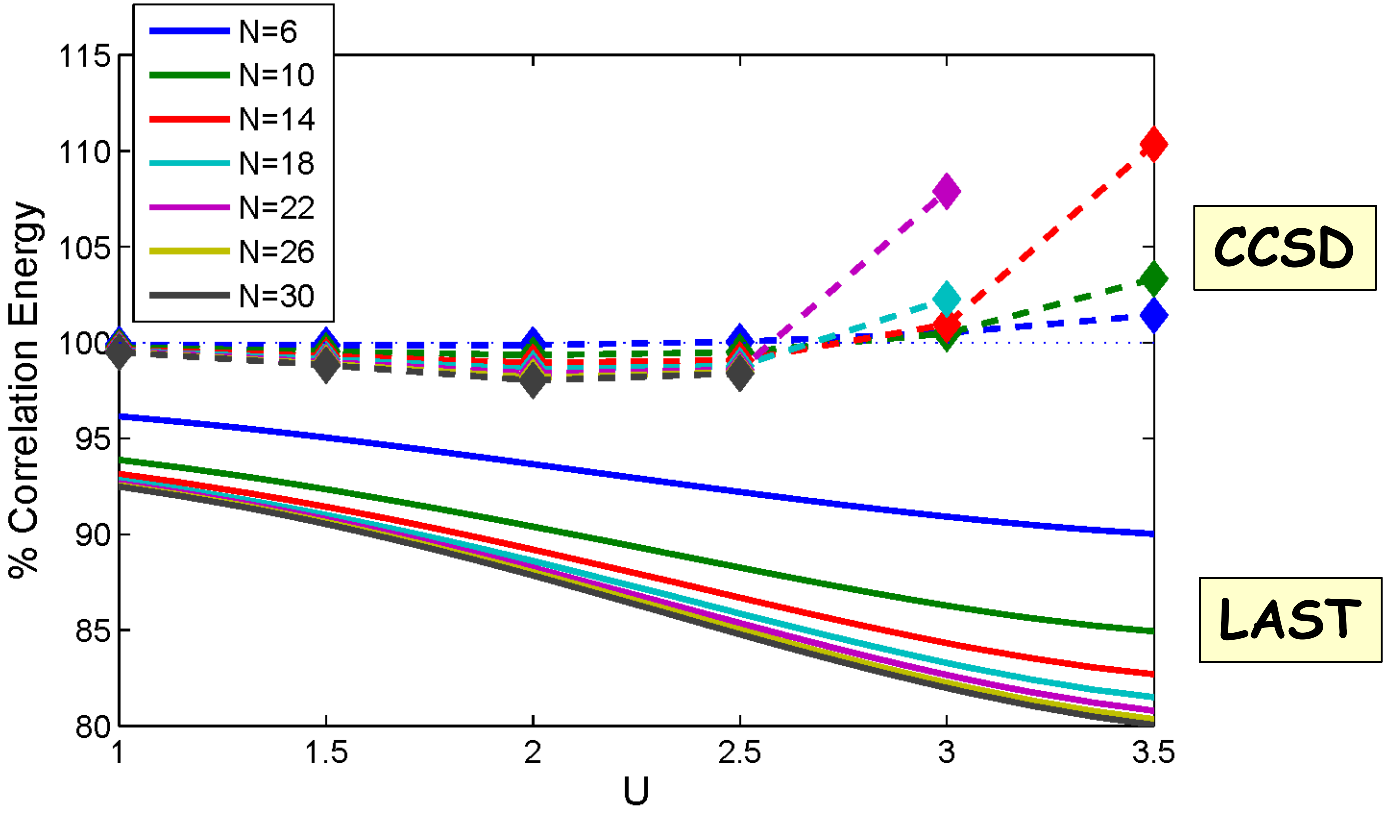
1D Hubbard chain; N=10-26; half-filling



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

Comparison w/ CCSD

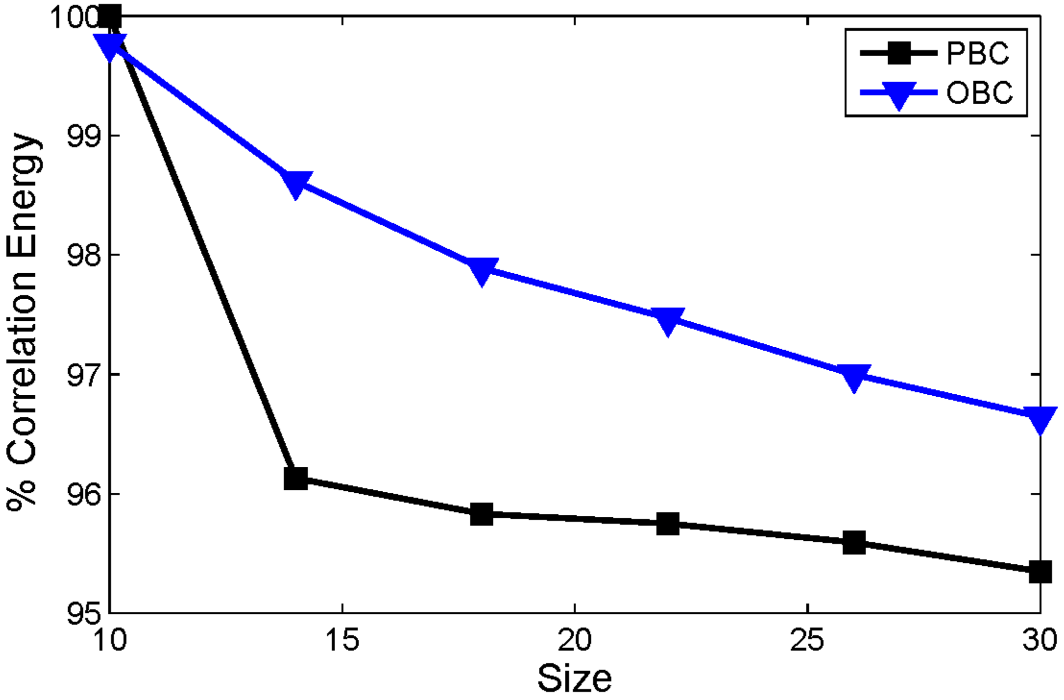
1D Hubbard chain; N=6-30; half-filling



CCSD does better for small U but deteriorates quickly beyond U ~2.5

Doping at U=2

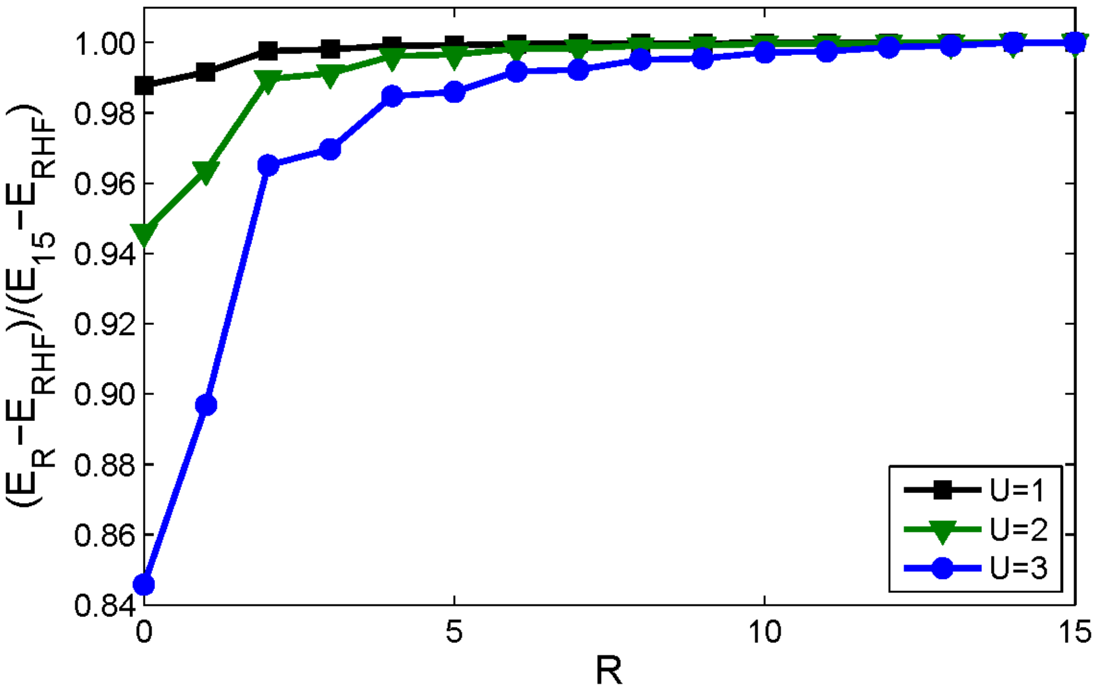
1D Hubbard chain; 8 holes



We recover ~**95%** of **Ec** for **30** sites at **25%** hole doping

Correlator range

1D Hubbard PBC, N=30; ½ filled



Correlation parameters are short-range

Projective vs. variational

1D Hubbard PBC, N=14; ½ filled

U	E_p	E_v	Exact	RHF	$\sigma^2{}_p$	$\sigma^2{}_v$
1	-14.698	-14.700	-14.715	-14.476	0.053	0.053
2	-11.849	-11.877	-11.954	-10.976	0.258	0.244
3	-9.393	-9.506	-9.749	-7.476	0.743	0.674
4	-7.469	-7.475	-8.088	-3.976	1.969	1.992
5	-5.494	-6.076	-6.853	-0.476	3.346	2.428
6	-3.766	-4.863	-5.917	3.024	5.254	3.579

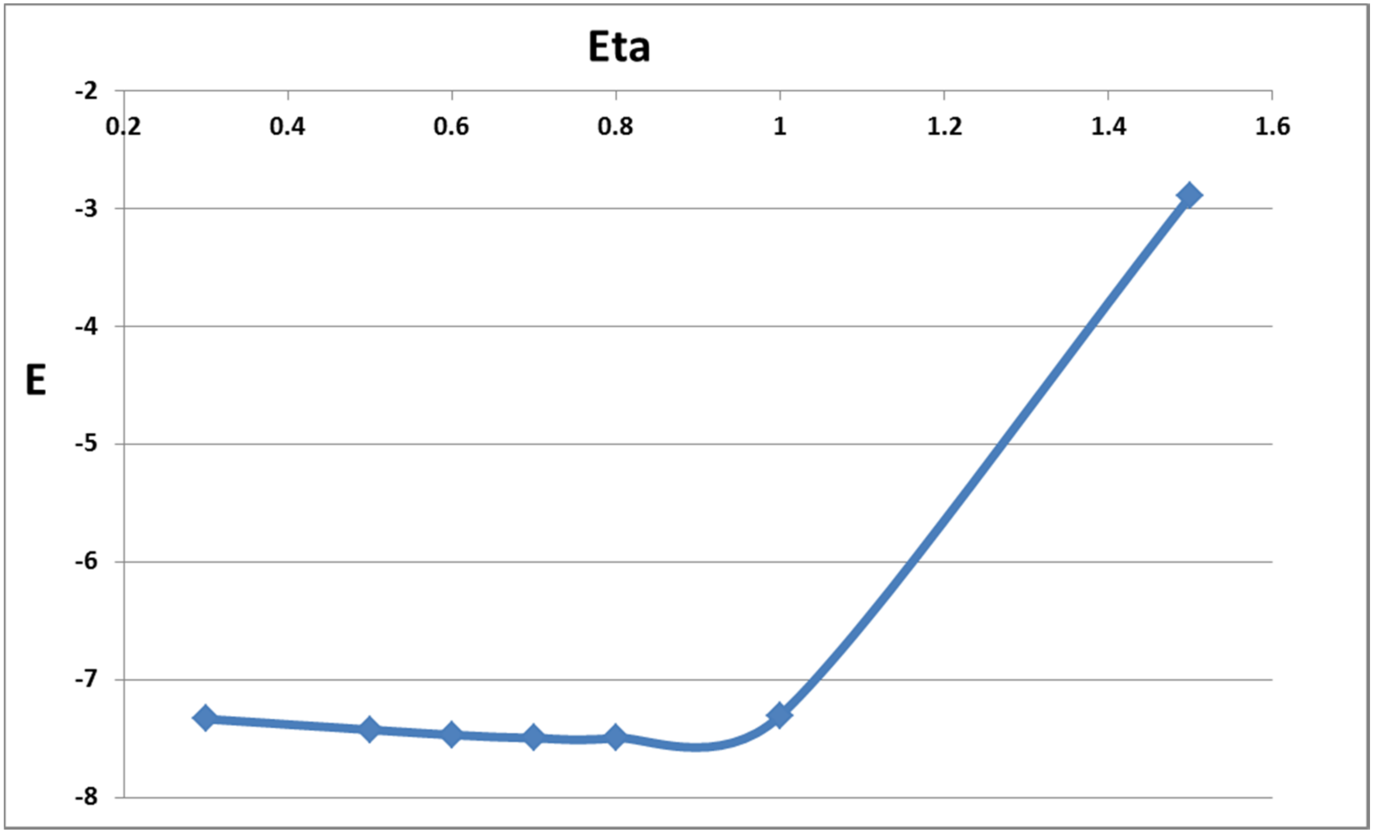
For small **U**, projective and variational results are very close.
For large **U**, the deviation is large but projective results are very good compared to **RHF**.
Variational cost is combinatorial whereas projective is polynomial.

marriage of Gutzwiller & pCCD

(preliminary results)

Energy (n)

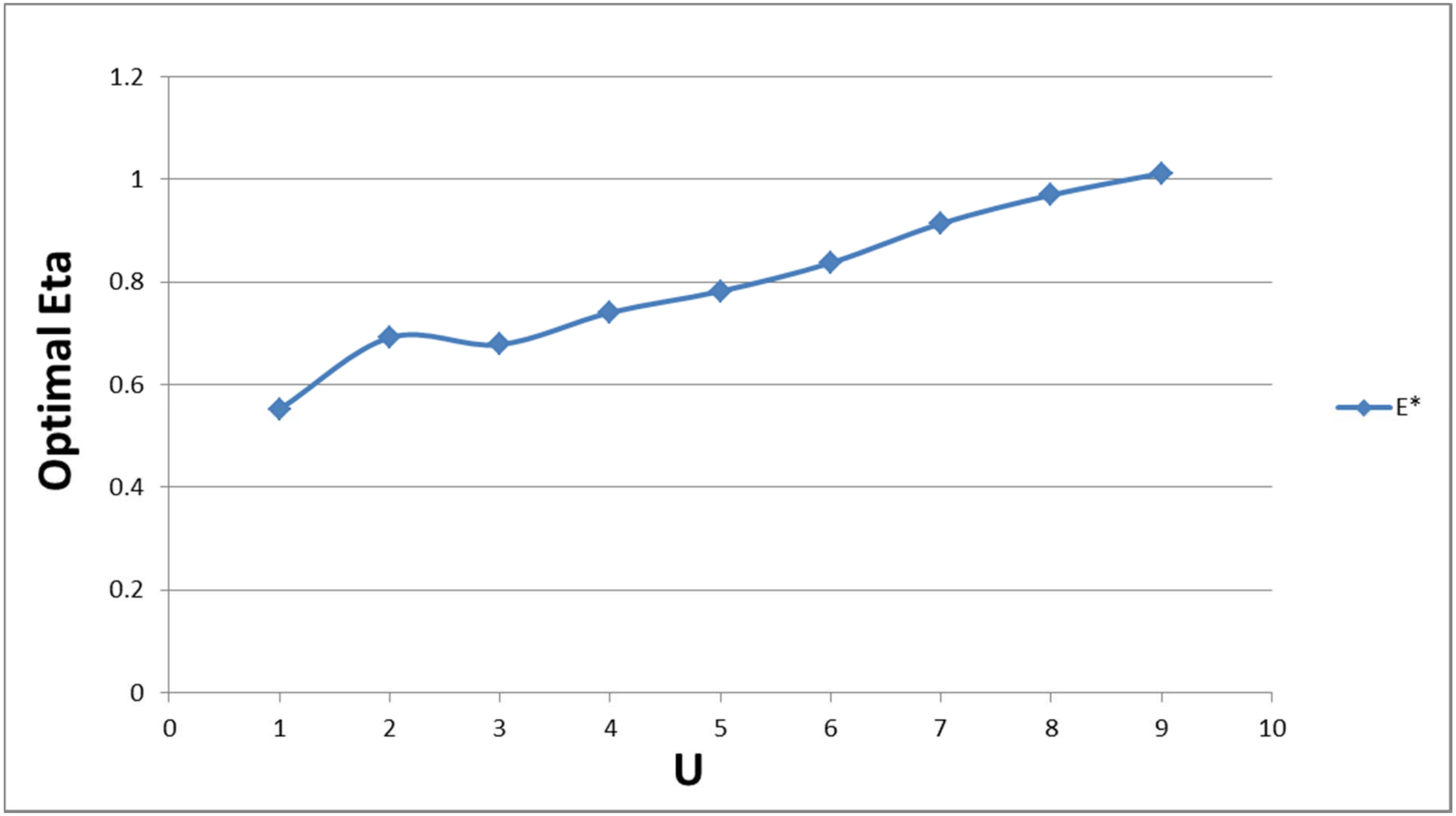
1D Hubbard, N=14; ½ filled; U=4



$$E_p\left(\eta\right)=\left\langle \Phi \,|\, e^{-T}e^{-J(\eta)}H\,e^{J(\eta)}e^{T}\,|\,\Phi\right\rangle$$

Optimum η(U)

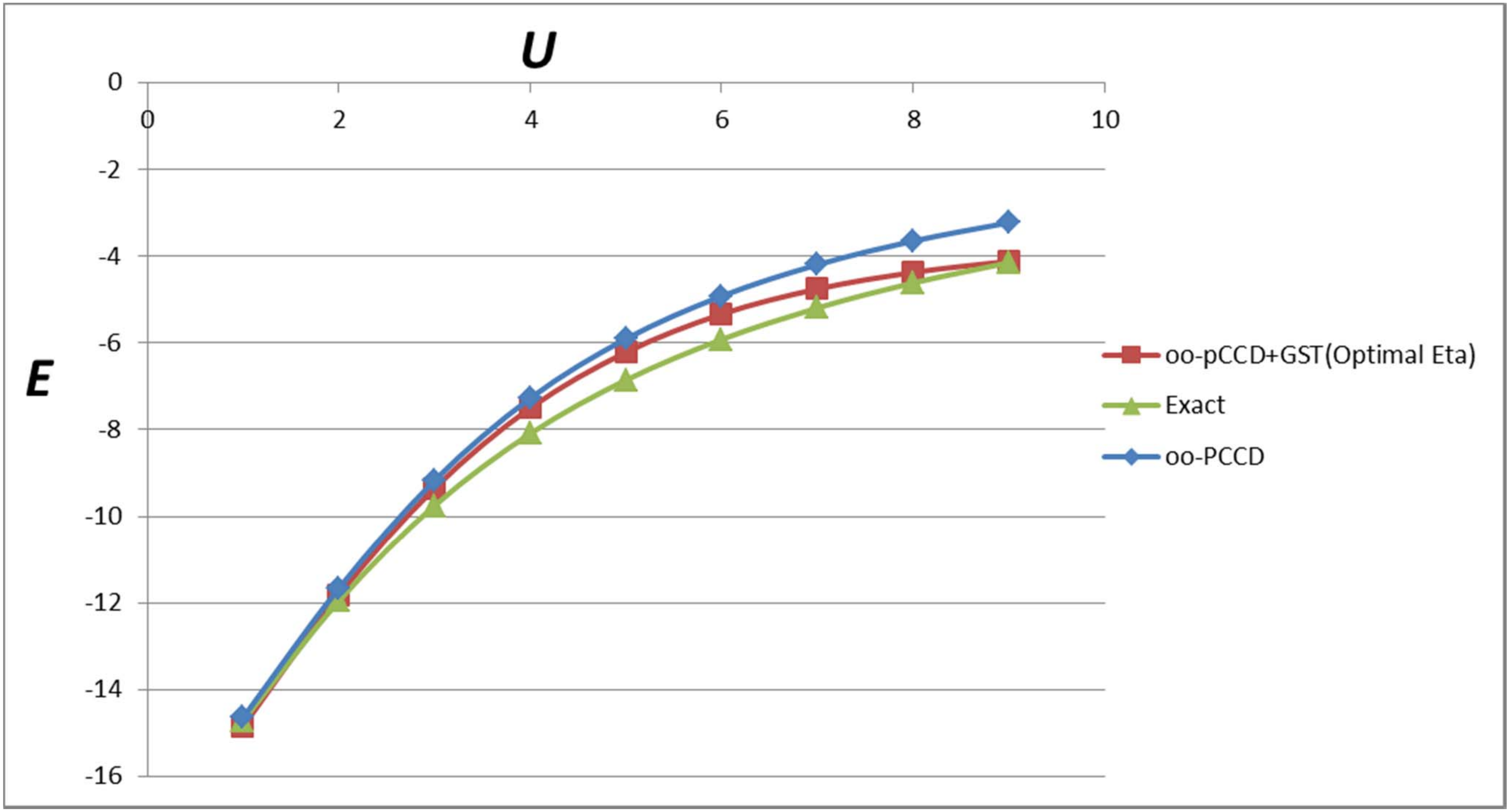
1D Hubbard, N=14; ½ filled; U=4



$$E_p(\eta) = \left\langle \Phi \,|\, e^{-T} e^{-J(\eta)} H \, e^{J(\eta)} e^{T} \,|\, \Phi \right\rangle$$

$E = E(U, \eta_{opt})$

1D Hubbard, N=14; ½ filled



Energy as a function of U

1D Hubbard, N=14; ½ filled

U	%Ec (oo-PCCD + GST)	%Ec (oo-PCCD)
1	112.25%	93.04%
2	92.60%	83.98%
3	87.11%	81.39%
4	88.05%	83.48%
5	91.13%	86.82%
6	94.02%	89.78%
7	96.52%	92.06%
8	98.42%	93.76%
9	99.82%	95.01%

Improvements for all **U**, except **U=1**

extension to quasiparticles

Pairing Hamiltonian

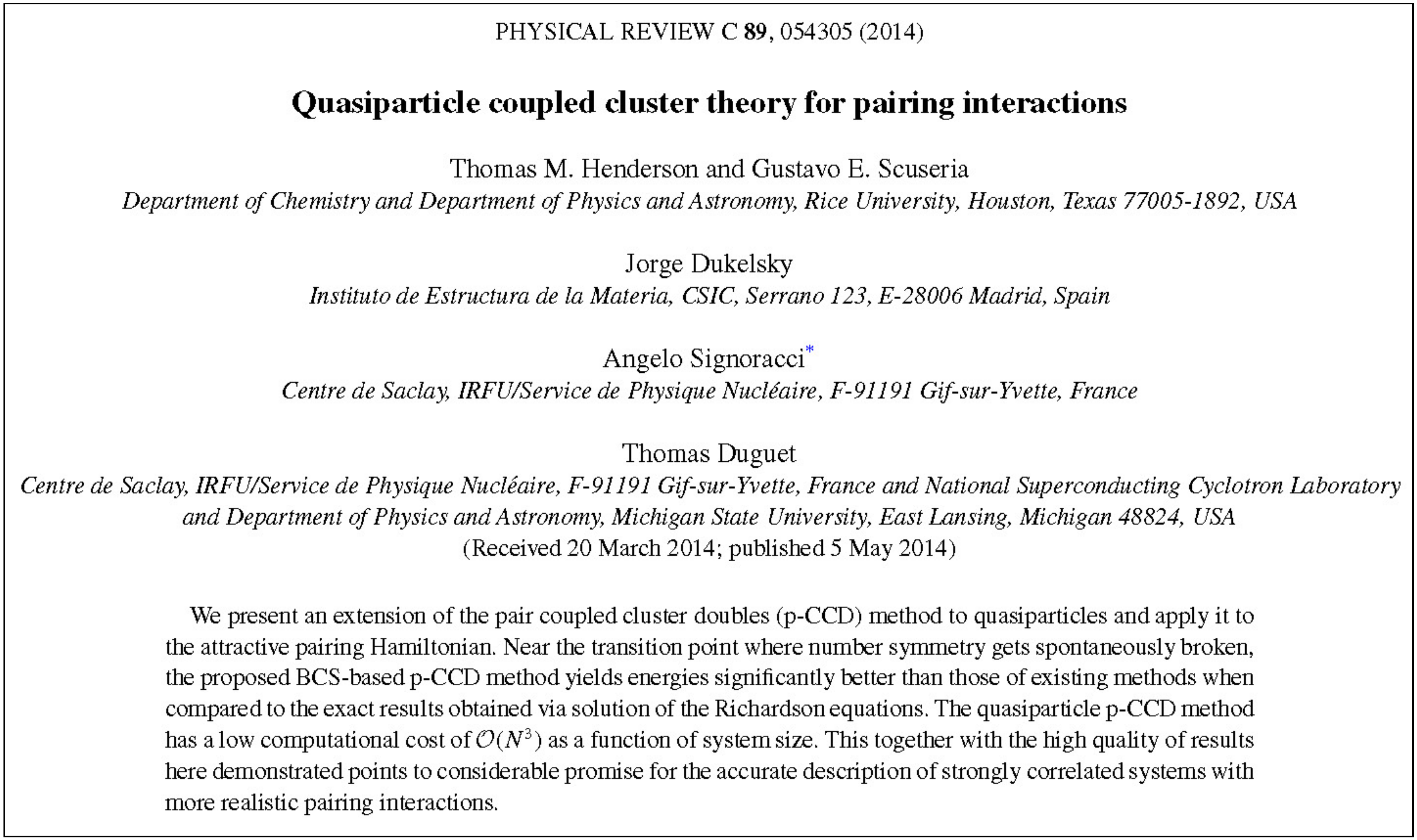
$$H = \sum_p \varepsilon_p N_p - G \sum_{pq} P_p^\dagger P_q$$

$$\left[P_p, P_q^\dagger \right] = \delta_{pq} \left(1 - N_p \right)$$

$$\left[N_p, P_q^\dagger \right] = 2\delta_{pq} P_q^\dagger$$

- **Integrable** by Bethe ansatz (Richardson)
- **G>0** (attractive) describes **superfluidity** in nuclei
- Model breaks **number symmetry** for large enough ***G***
- Interesting for studying role reversal between spin and number

Extension of p-CCD to quasiparticles



PHYSICAL REVIEW C **89**, 054305 (2014)

Quasiparticle coupled cluster theory for pairing interactions

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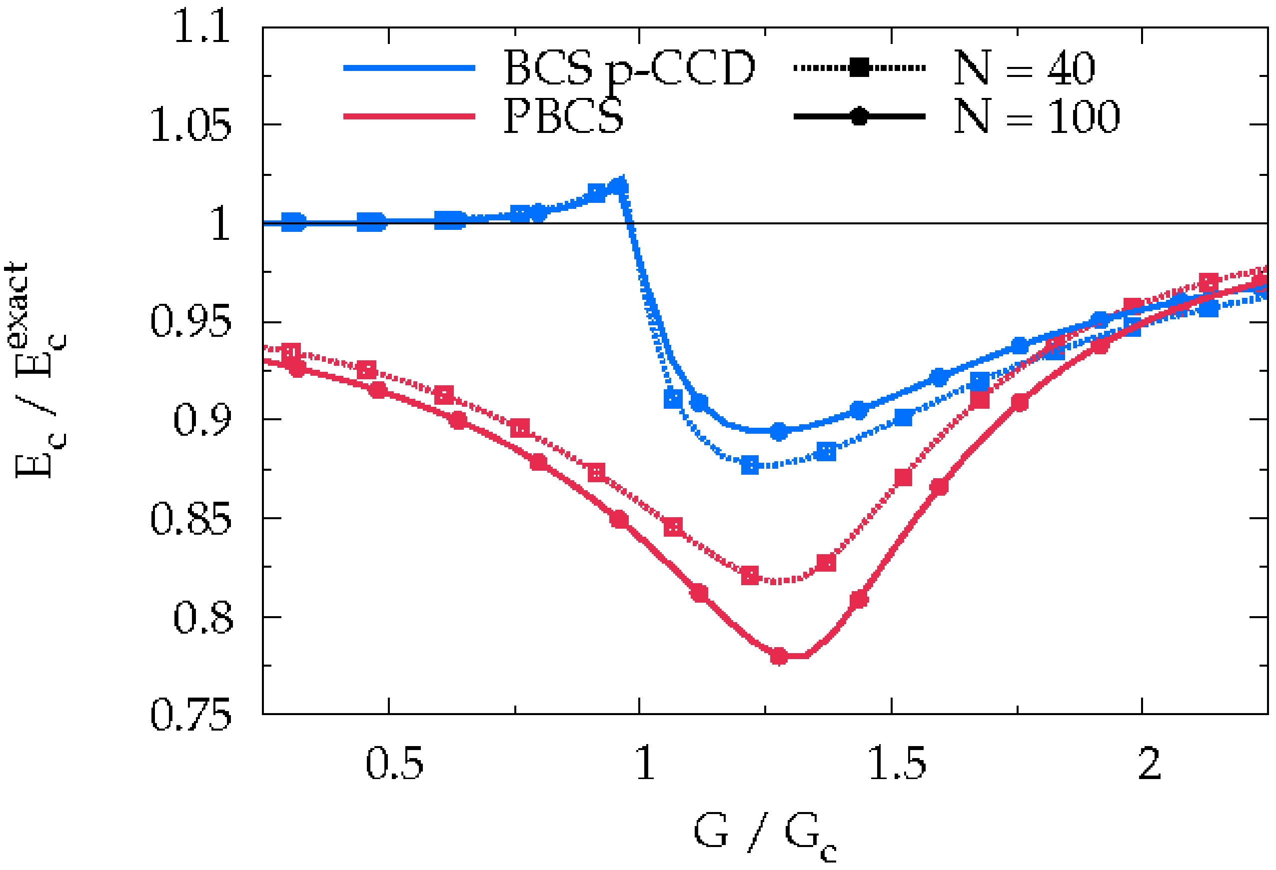
We present an extension of the pair coupled cluster doubles (p-CCD) method to quasiparticles and apply it to the attractive pairing Hamiltonian. Near the transition point where number symmetry gets spontaneously broken, the proposed BCS-based p-CCD method yields energies significantly better than those of existing methods when compared to the exact results obtained via solution of the Richardson equations. The quasiparticle p-CCD method has a low computational cost of $\mathcal{O}(N^3)$ as a function of system size. This together with the high quality of results here demonstrated points to considerable promise for the accurate description of strongly correlated systems with more realistic pairing interactions.

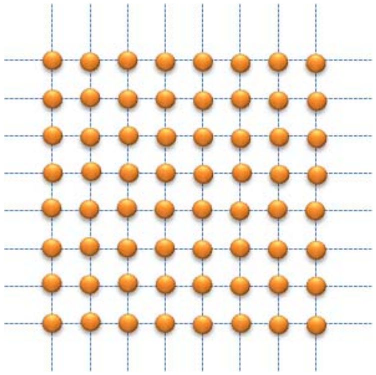
Attractive Pairing Hamiltonian



- At **$G=G_c$**, **HF** breaks number symmetry => **BCS**
- **pCCD** is better than **PBCS** but not great
- Exact **DOCI** results from Richardson solution

cluster mean-field theory
& beyond

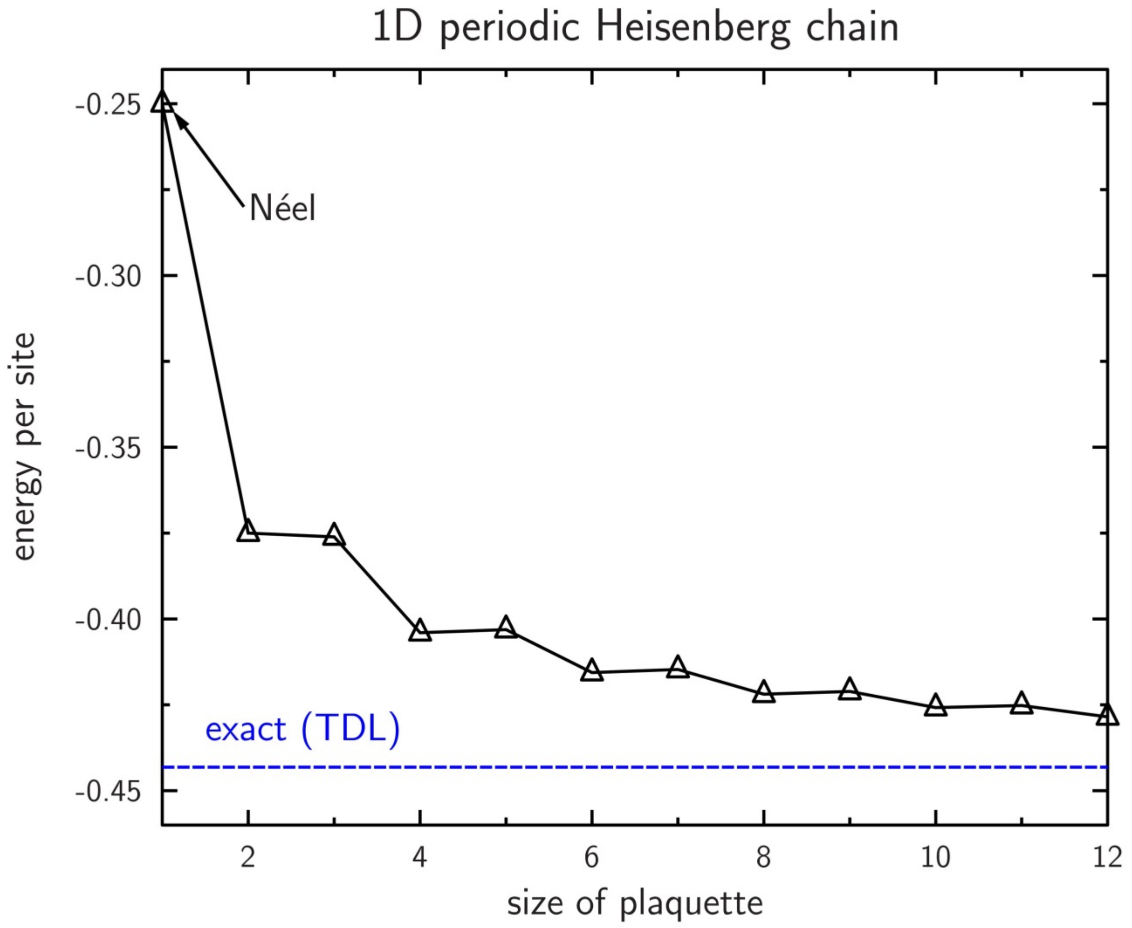
Cluster mean-field theory



- Consider a system product state made of plaquette states: $|\Psi > = |g_1\, g_2\, g_3 \ldots g_M >$
- Plaquette states g_i are **internally entangled**.
- But do not interact (**strong orthogonality**).
- They provide a tiling of the physical system.
- Minimize the energy: $E = < \Psi | H | \Psi >$; i.e., solve for the optimal plaquette states.
- Energy is size extensive and upper bound.
- Increase size of plaquette…
- **Hierarchical mean-field theory** for spin systems: Isaev, Dukelsky, Ortiz, PRB (2009).

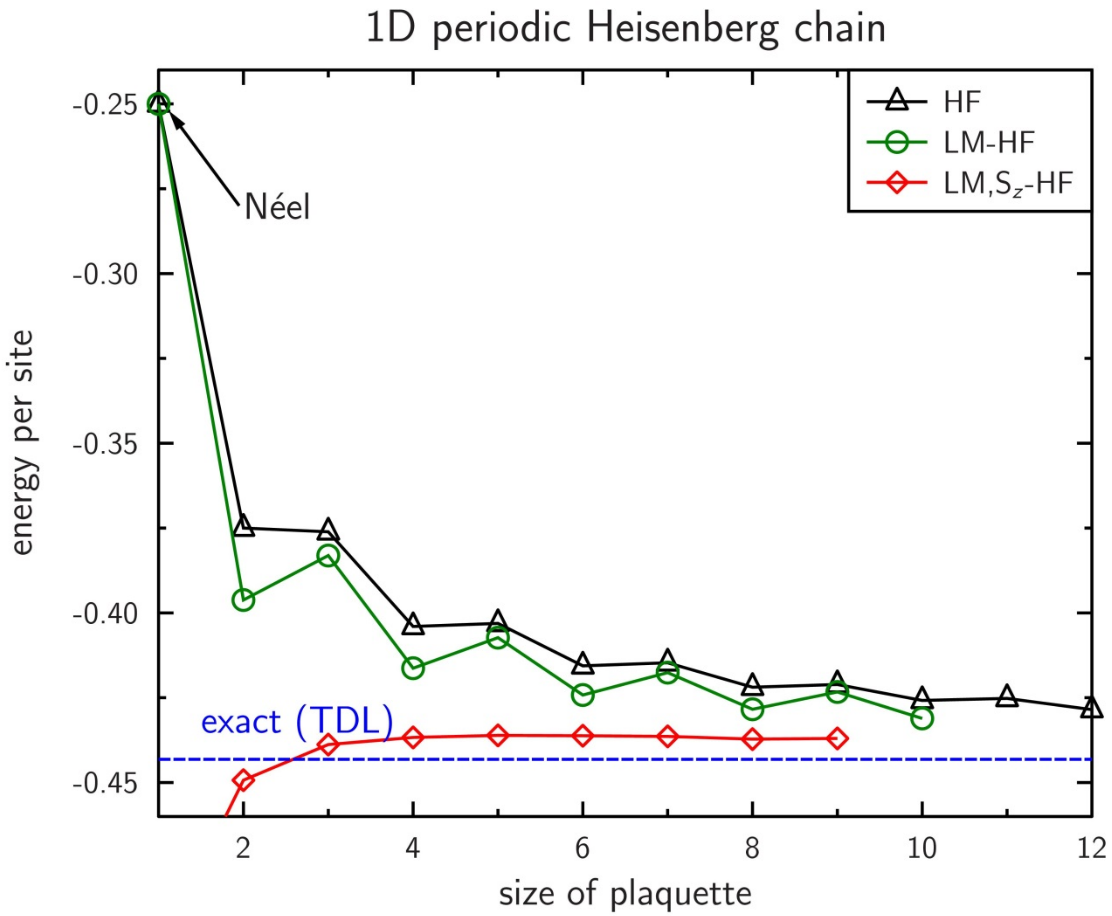
Cluster mean-field theory

$$H = J \sum_{<i,j>} \vec{S}_i \cdot \vec{S}_j$$



Variational: all energies are upper bounds to the exact result but convergence is not monotonic (because of even-odd alternation)

Add symmetry breaking & restoration



LM: Linear Momentum

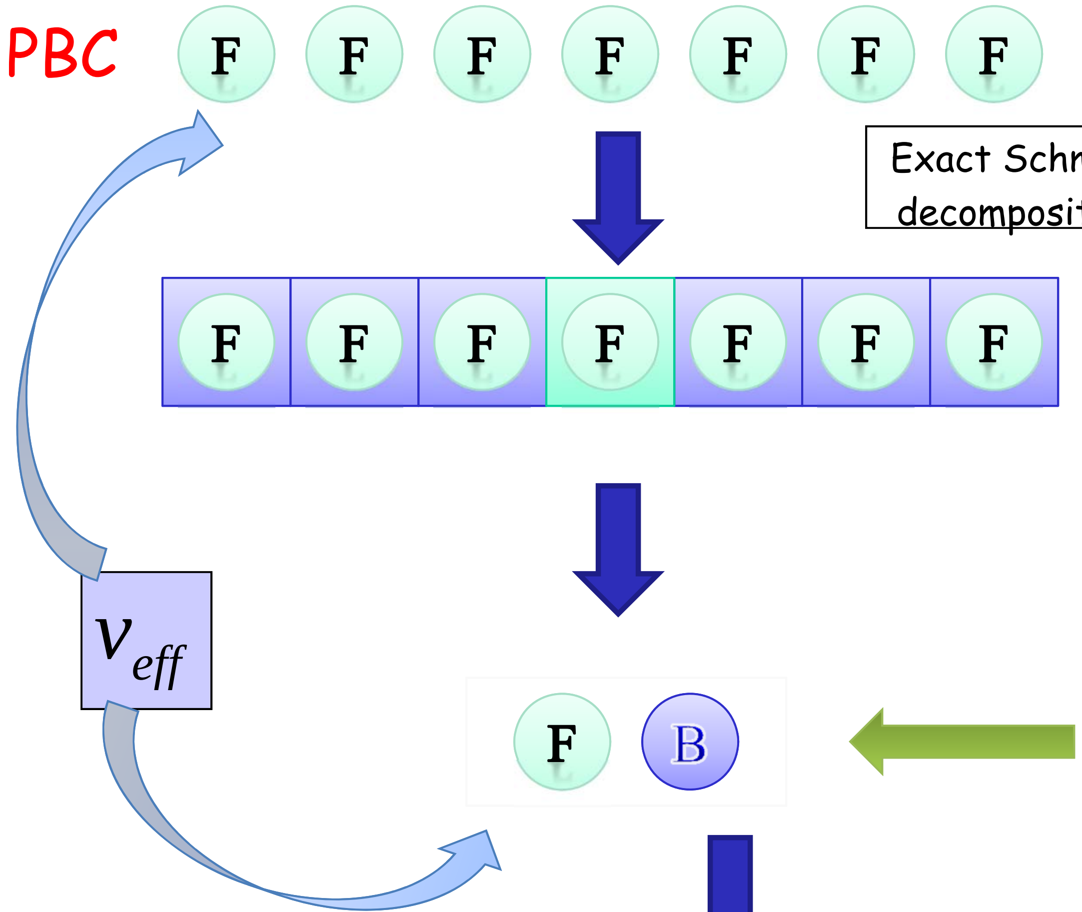
S_z-HF: **restore m=0**

Cluster mean field converges slowly to the exact result
but very rapidly with added **SB&R**.
Size of system is 4 plaquettes; for small size, **SB&R** overcorrelates.

quantum embedding

Density Matrix Embedding Theory

G. Knizia, G. K.-L. Chan, PRL **109**, 184604 (2012) & JCTC **9**, 1429 (2013)



Exact Schmidt decomposition →

Fragment

Bath

$$|\Psi\rangle = \sum \lambda_i |\alpha_i\rangle|\beta_i\rangle$$

Embedding Approximation:

$|\Psi\rangle =$ Slater Determinant

- Algebraic construction
- Clear definition of bath
- Single particle basis

Impurity Problem

- Small Hilbert space
- Accurate impurity solver possible
- Even if not size extensive!

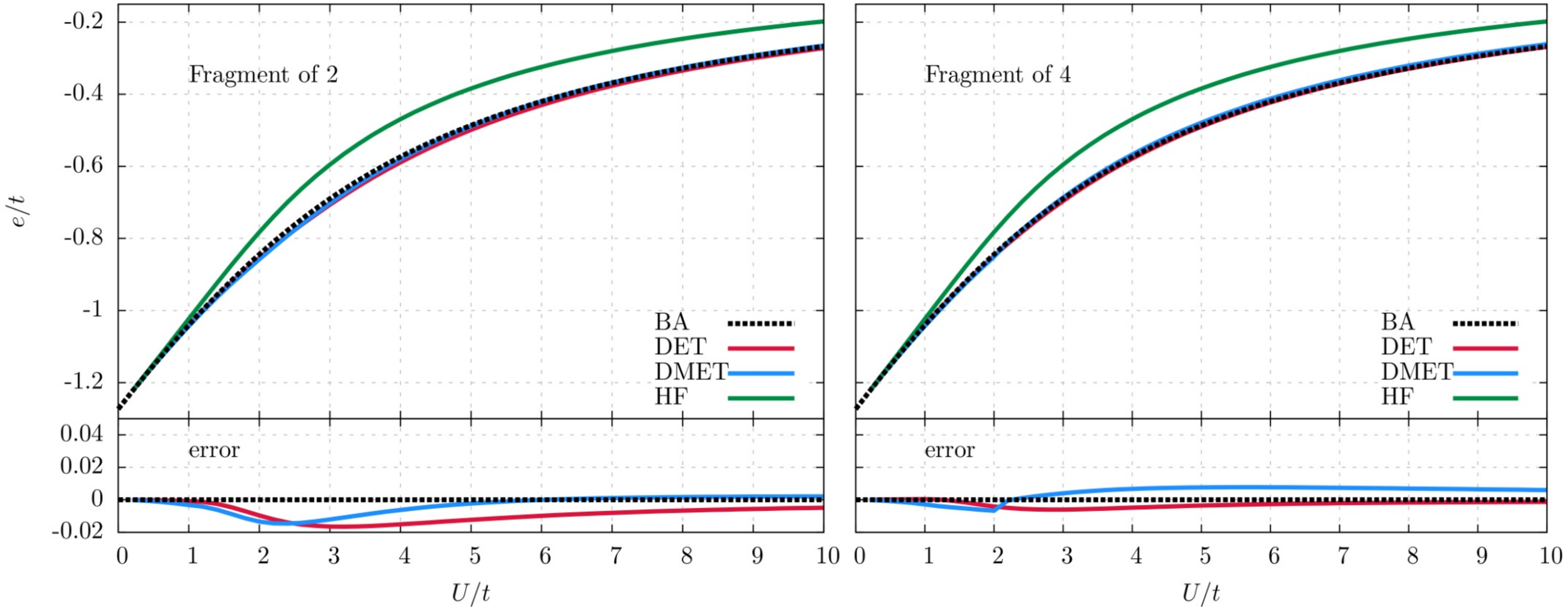
Match γ^{H} with $\gamma^{H_{imp}}$

Full (DMET) or diagonals (DET)

$$H_{imp} = \sum_{ijkl} |\alpha_i\rangle |\beta_j\rangle\langle\beta_j| \langle\alpha_i| H |\alpha_k\rangle |\beta_l\rangle\langle\alpha_k| \langle\beta_l|$$

Bulik, Scuseria, Dukelsky, *Phys. Rev.* **B 89**, 035140 (2014)

1D Hubbard: energy per site

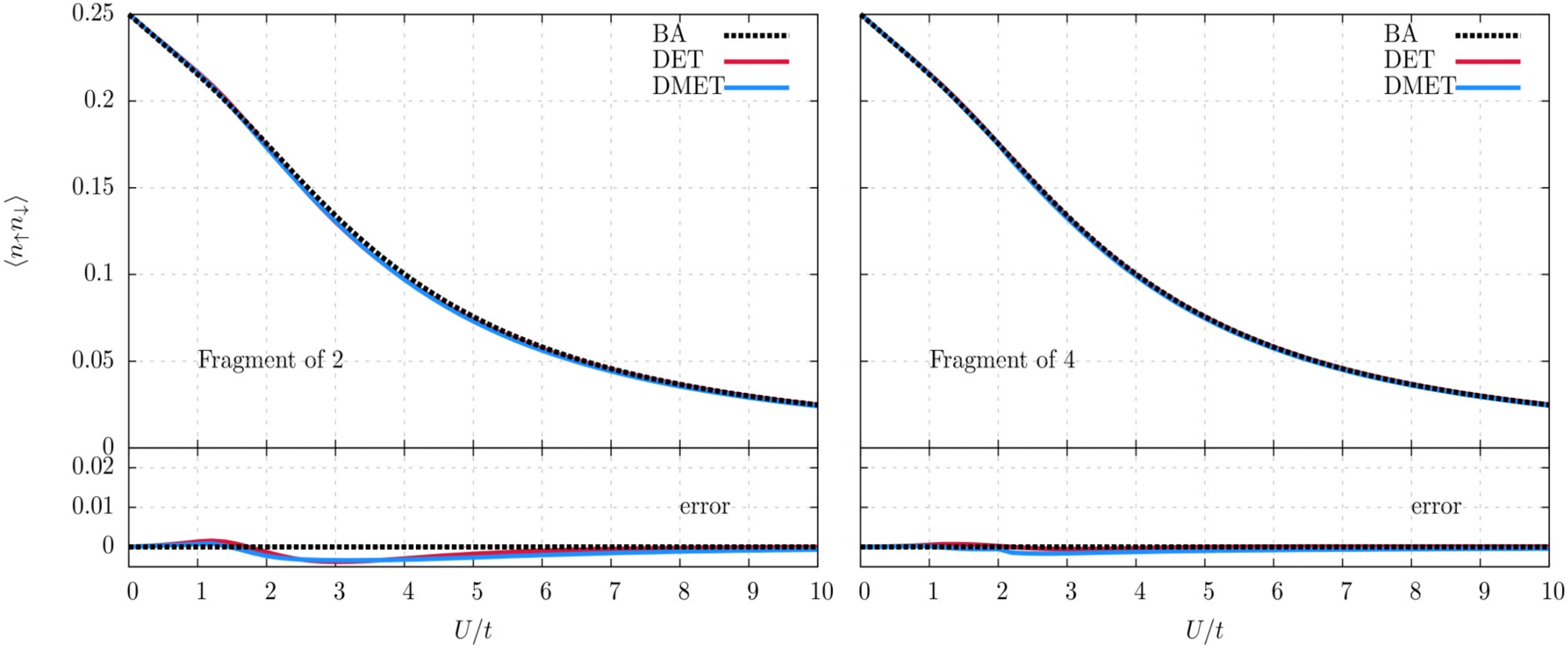


400 sites at half-filling => thermodynamic limit

BA = Bethe Ansatz (exact).

Impurity solver is **FCI**.

1D Hubbard: double occupancy

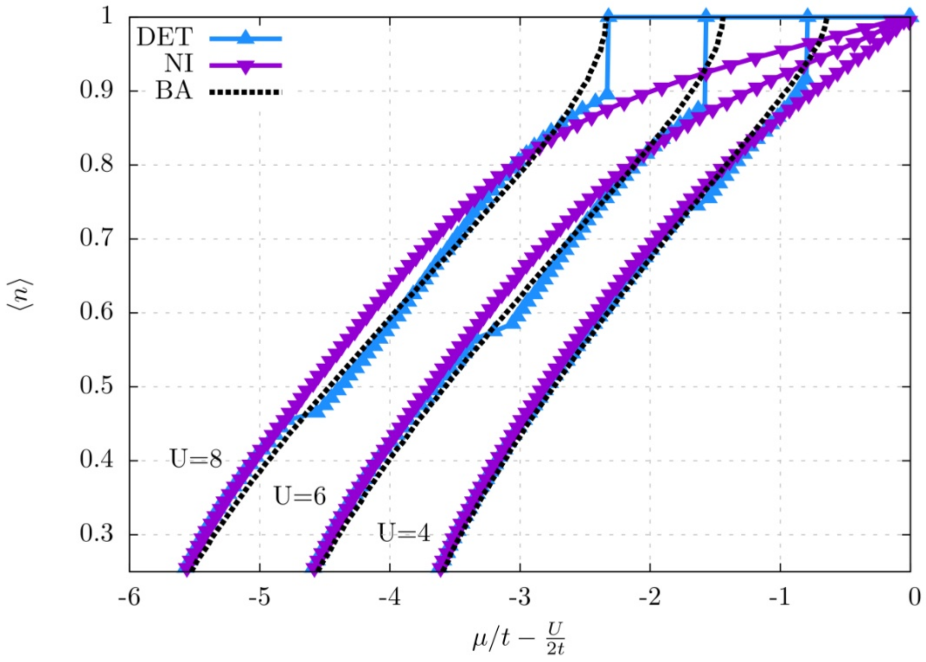


400 sites at half-filling, **BA** = Bethe Ansatz (exact)

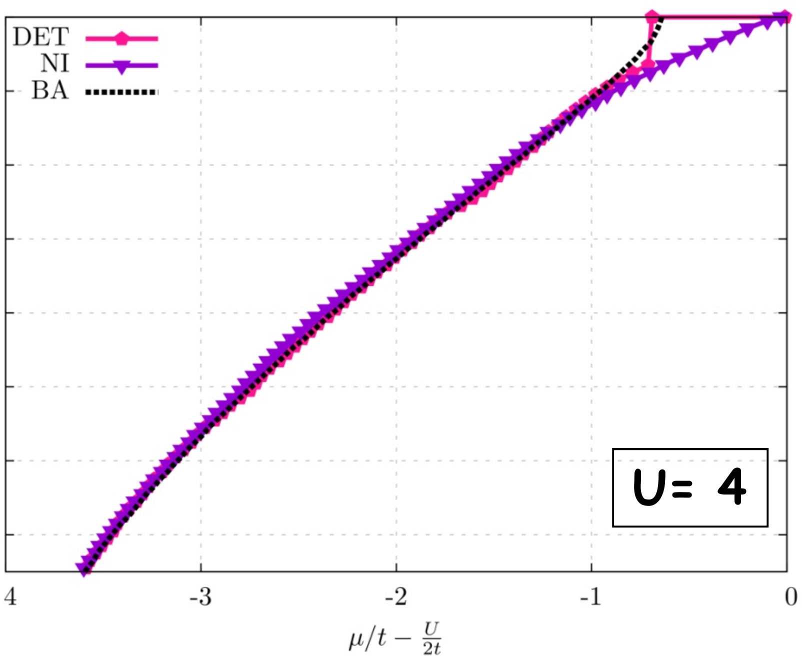
$\langle n_\uparrow n_\downarrow \rangle \rightarrow 0$ for large **U**: signature of Mott transition

1D Hubbard: metal-insulator transition
Density vs. chemical potential

Fragment of **2** sites



Fragment of **4** sites



400 sites at half-filling, **BA** = Bethe Ansatz (exact)
Impurity solver is **FCI**.

ab initio PBC implementation

I. W. Bulik and G. E. Scuseria, *J. Chem. Phys.* **141**, 054113 (2014).

1D polymers

2D boron nitride

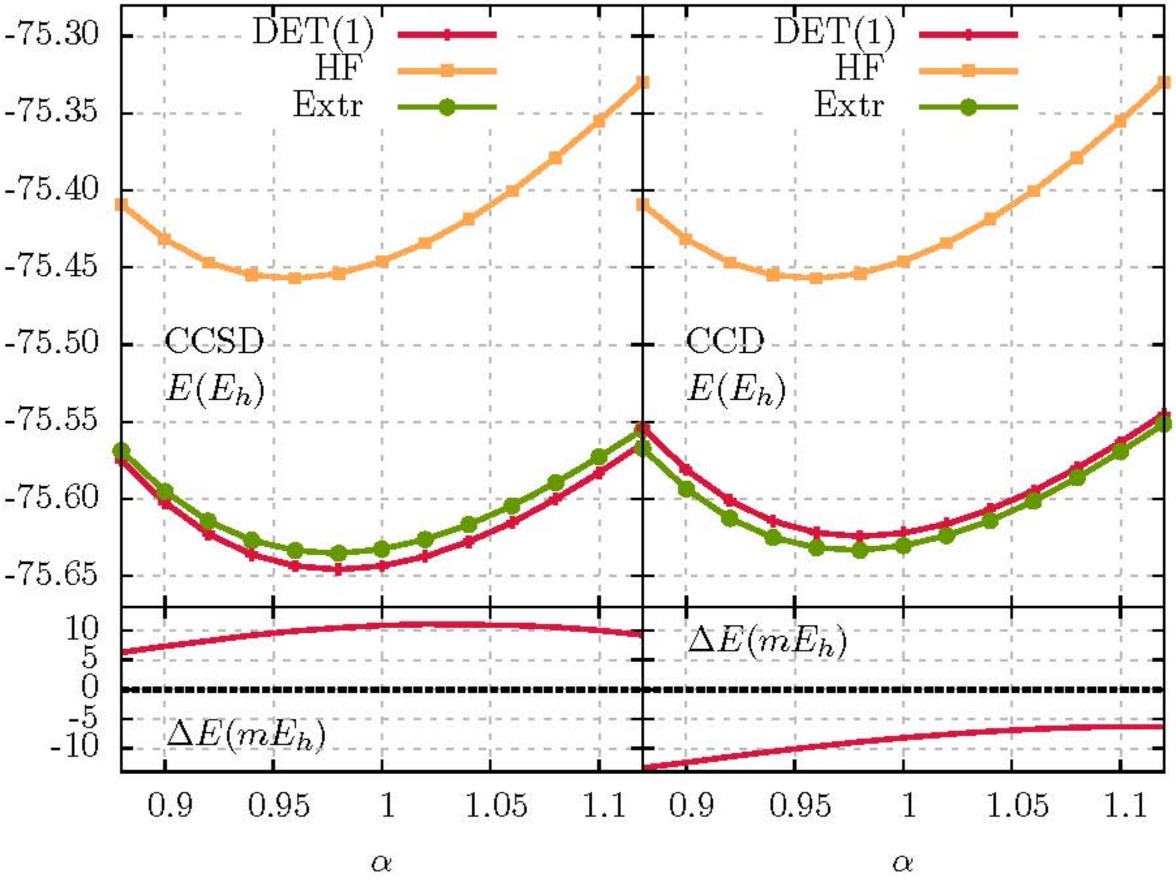
3D diamond

sto-3g & 6-31g bases

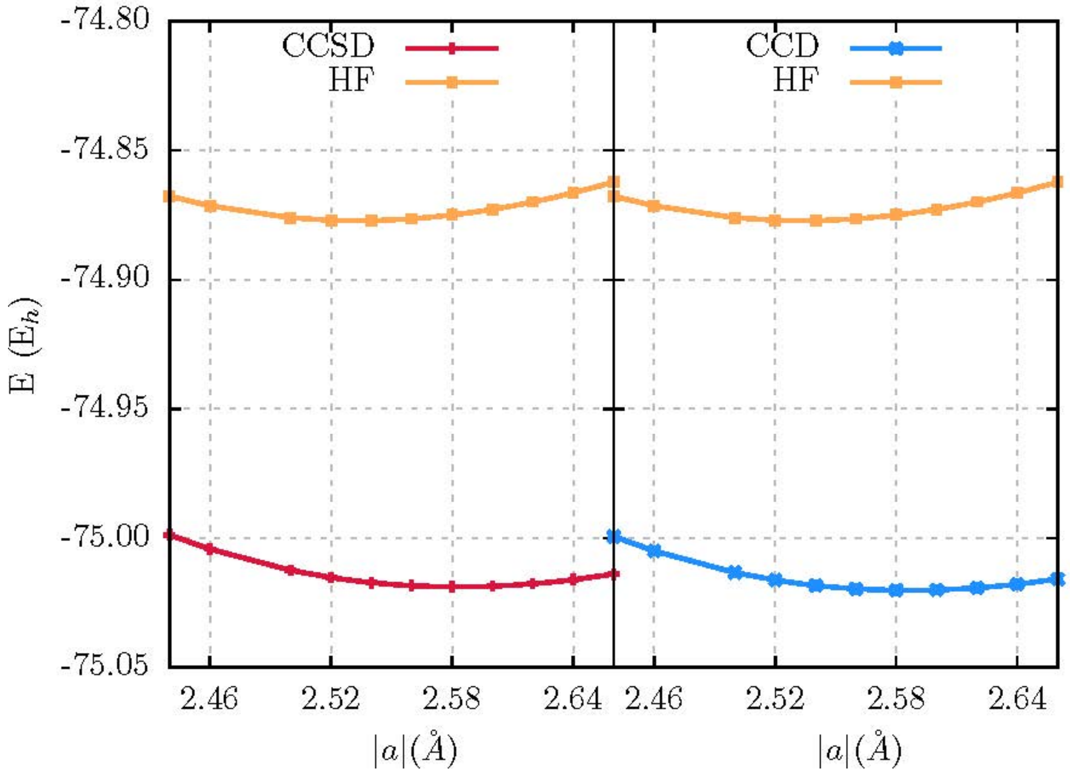
ccd & ccsd

Polyyne 6-31g

$(-C{\equiv}C-)_n$



Diamond sto-3g



Summary

- **Pair coupled cluster** theory for **strong** correlation.
- **Similarity transformation** theory **(generalized CC)** for **weak** correlation.
- **Cluster mean-field** theory & beyond.
- **Quantum embedding** for infinite systems.

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