New vistas on strong correlation from symmetry projection

Gustavo E. Scuseria

FAESM 2016, Hefei, 14-18 June 2016

Weak versus strong correlation: focus on pair-pair correlations

- **Weak** correlation:
  - The **independent** e^- picture is a good approximation.
  - A **mean-field** approach yields a good starting point.
  - Electrons **pairs** can be localized or delocalized.
  - But correlations between pairs are **weak**.

- **Strong** correlation:
  - Kinetic energy and Coulomb repulsion compete.
  - Degeneracy (or near-degeneracy) is rampant.
  - Electrons display **collective** behavior.
  - Correlations between pairs are **strong**.
  - **Equal** state occupation (large entanglement entropy)

Weak correlation paradigm

in quantum chemistry:

single reference

coupled cluster theory

CC theory

- **Coupled Cluster** theory is based on **particle-hole excitations**, **singles + doubles + triples +…** out of a reference det **|0>**

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

$$\left|\Psi\right\rangle = e^T \left|0\right\rangle \qquad He^T \left|0\right\rangle = Ee^T \left|0\right\rangle$$

i,j : occ; ***a,b***: unocc in reference det **|0>**

- Hamiltonian is similarity transformed and cluster correlation amplitudes are determined by left projection
- Let's consider $T_1 = 0$ (Brueckner orbitals) for simplicity

$$\overline{H} = e^{-T} H e^T; \quad \overline{H}\left|0\right\rangle = E\left|0\right\rangle; \quad E = \left\langle 0 \right| \overline{H} \left| 0 \right\rangle; \quad 0 = \left\langle 2 \right| \overline{H} \left| 0 \right\rangle$$

- ***CC*** energy is linear in T_2
- Doubles residual is quadratic in T_2 and linear in T_3 and T_4
- ***If we were given*** T_3 and T_4 ***we could have an exact CCD theory***

Desiderata

- We want good quantum numbers, so we will do a symmetry adapted theory.
- We want a T_2 **only** theory to keep cost down.
- We want a similarity transformation theory (canonical transformation) to remain size extensive.
- **CCSD(T)** is the "**gold standard**" for **weak correlation where** $T_4 \approx 0$ **and quadruples** $C_4 \approx \frac{1}{2}(T_2)^2$ **but** for **strongly correlated** systems where collective excitations become important, T_4 **becomes large** & **single-reference CC falls dead**
- We will challenge the notion that **EXP** is the best option in a T_2 **only** theory when **strongly** correlated.
- We will model T_4 from T_2 using **symmetry collective states**

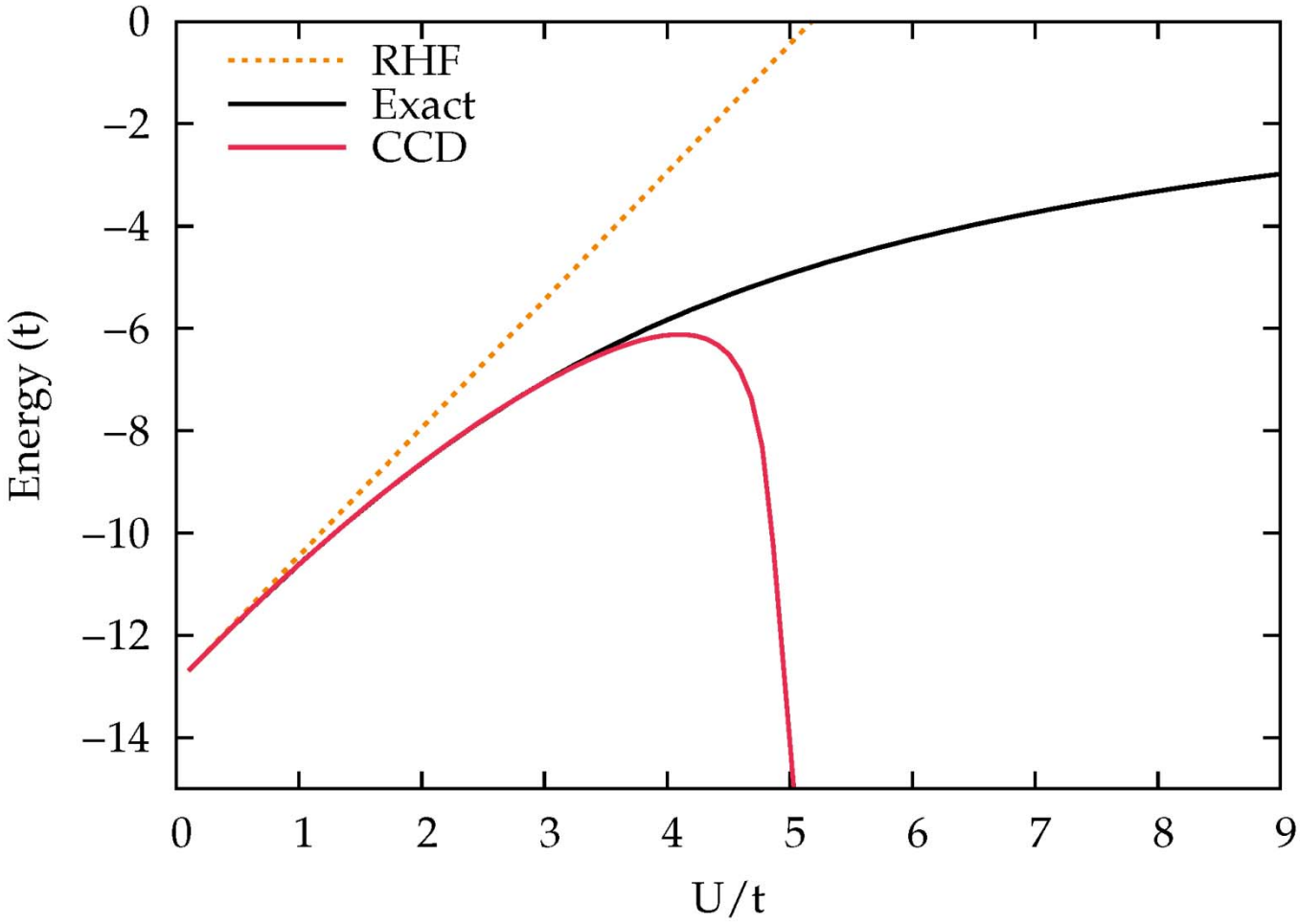
Hubbard model

$$H = -t \sum_{<p,q>\sigma} c^{\dagger}_{p\sigma} c_{q\sigma} + U \sum_{p} n_{p\uparrow} n_{p\downarrow}, \qquad n_{p\sigma} = c^{\dagger}_{p\sigma} c_{p\sigma}$$

- **U = 0** => **RHF** is exact
- **U/t small** => **weakly** correlated
- **U/t large** => **strongly** correlated
- Exact solution known in **1D** => Bethe ansatz
- **In repulsive model (U>0)**, **RHF** spontaneously breaks **spin** symmetry but does not break **number** symmetry
- Model has a local interaction but yields long-range entanglement for large **U**

CC catastrophic failure

1D Hubbard ring (**PBC**); **10** sites; half-filling.
As **U/t** increases, the system gets strongly correlated.



$T_1 = 0$
by symmetry

CCDT, CCDTQ… all fail similarly
Unrestricted CC is fine but we lose good quantum numbers

Outline

- Understanding why symmetry adapted ***CC*** theory fails under **strong correlation**

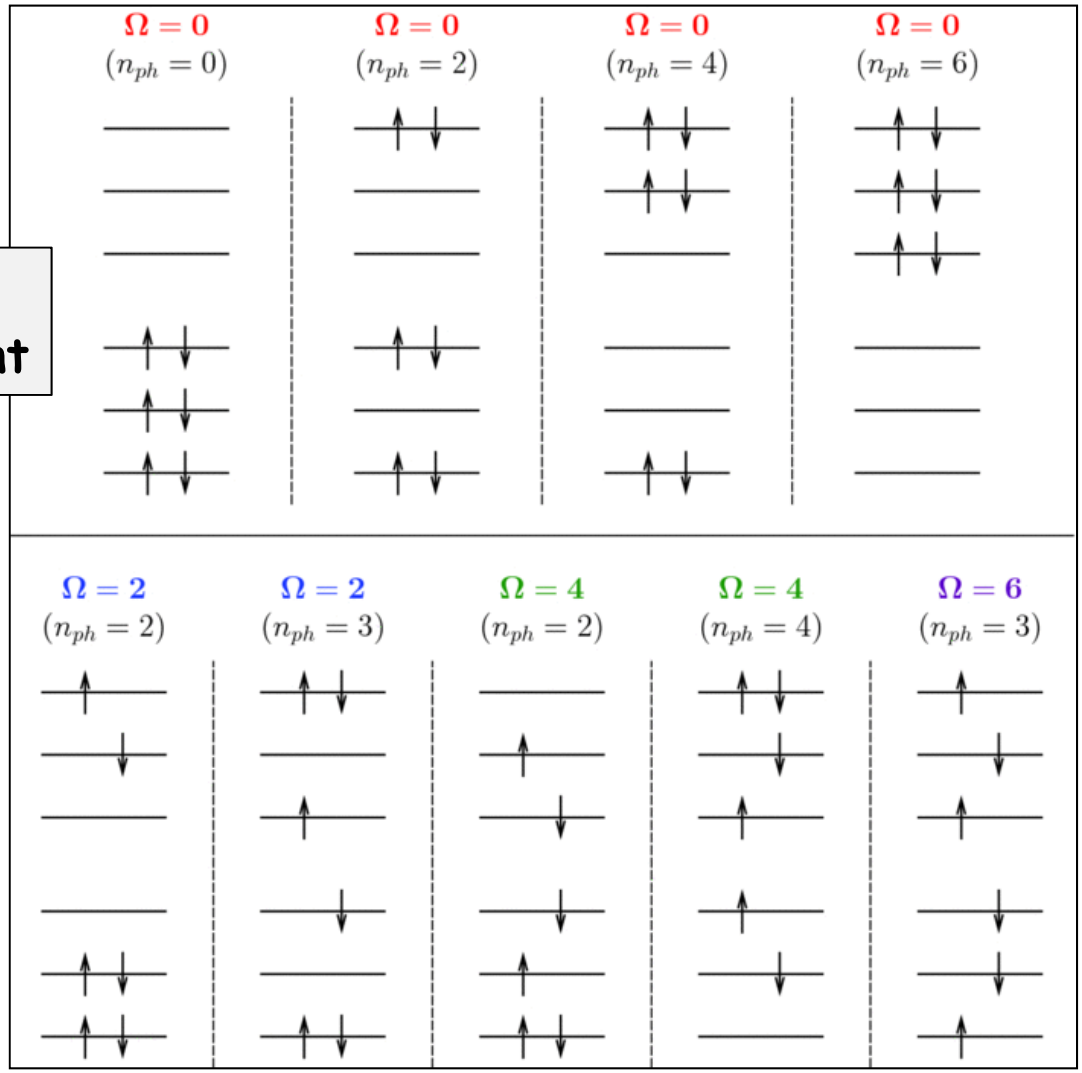
- Understanding the crucial role of collective states arising from **symmetry degeneracies** which cannot be neglected

- **Marrying *CC*** theory with symmetry projection: similarity transformation theory with non-exponential correlator (**PoST**)

strong correlation and pair excitations

Seniority (Ω) vs. ph excitations

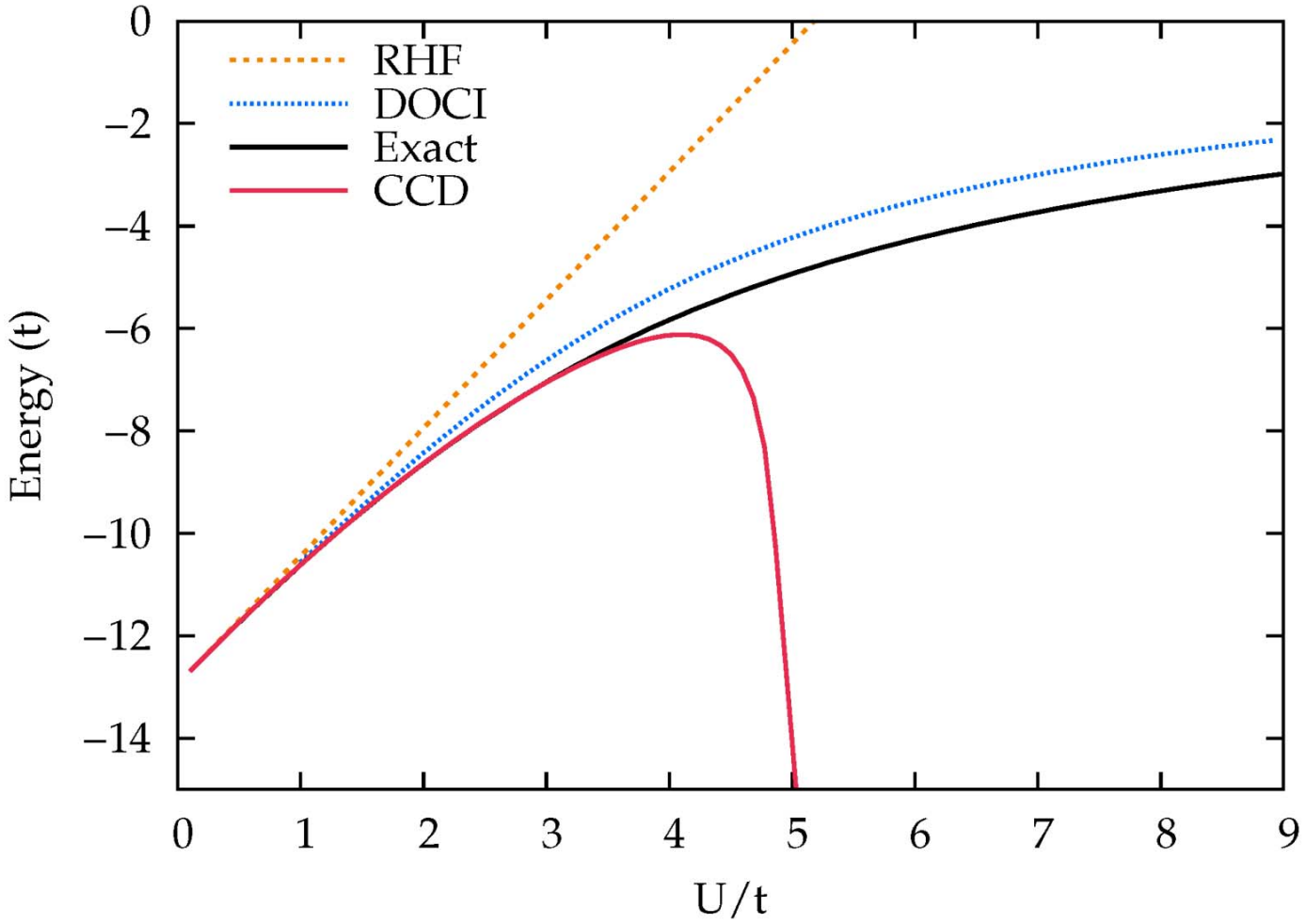
reference determinant



Ω is the number of **unpaired** electrons

L. Bytautas, T. M. Henderson, C. A. Jimenez-Hoyos, J. K. Ellis, and G. E. Scuseria, *J. Chem. Phys.* **135**, 044119 (2011)

DOCI : seniority zero full CI



Good news: pair excitations to all orders do not break down

Bad news: **DOCI** has combinatorial cost -> doable only for small systems

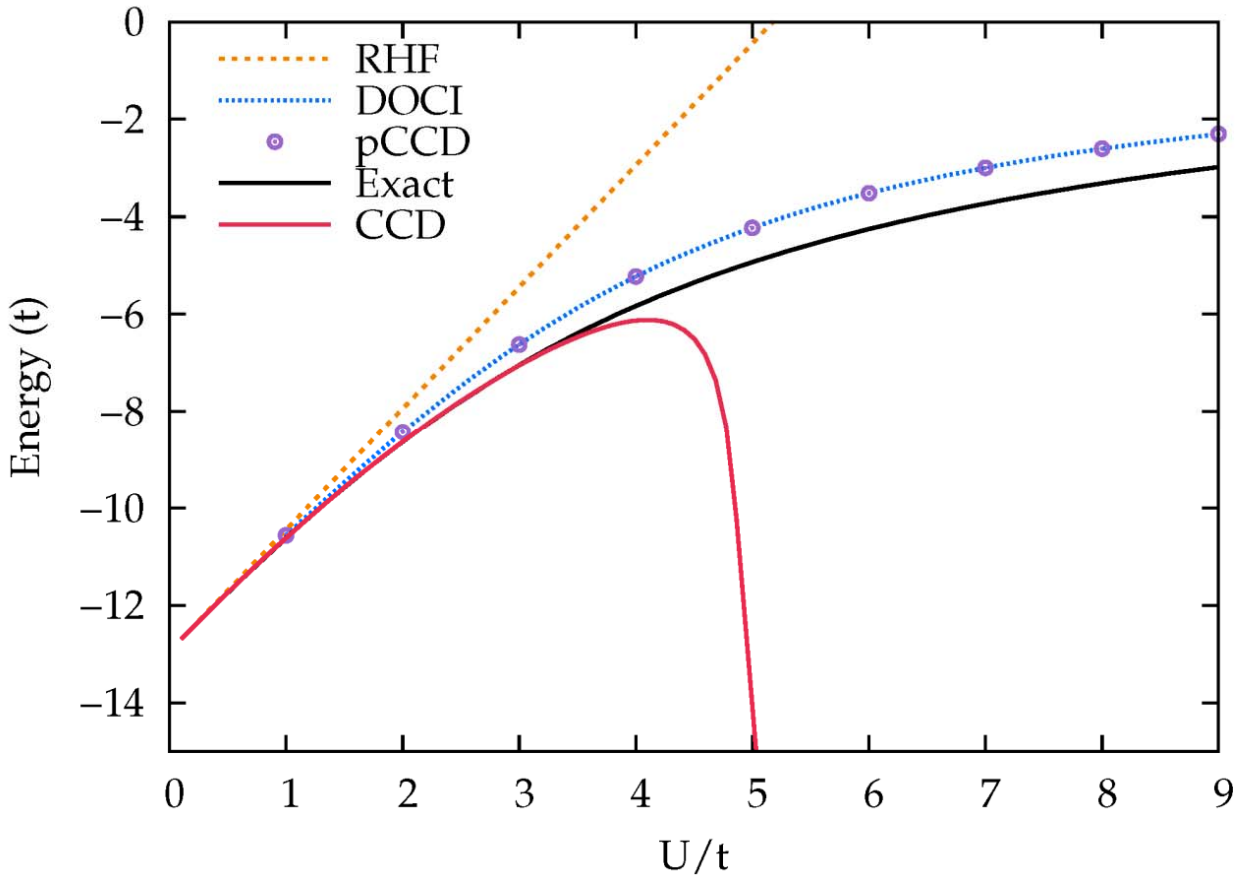
pair coupled cluster theory

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

- Matches **DOCI** for **repulsive** interactions
- **Mean-field** $O(N^3)$ computational cost
- It does not fail in the strong correlation regime

pCCD describes strong correlation

1D Hubbard ring; 10 sites; half-filling



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

pair CCD

- **CCD** theory with a **diagonal** **singlet-paired** excitation operator

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

- A **simpler** version of **CCD** with only **O(N²)** amplitudes

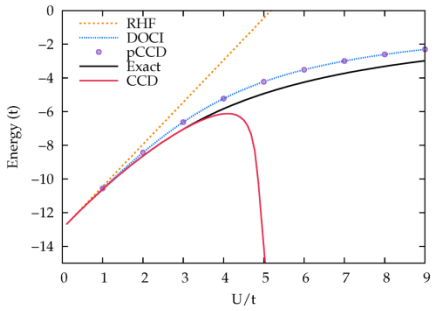
- **Bad news:**

  (1) **Not** a good starting point for breaking pairs

  (2) It does not work for strongly correlated **attractive** systems

  WHY?

Broken-pair correlations



frozen-pair (fp) CCSD approach:

- Do **pCCD** with optimized orbitals (**oo-pCCD**)
- Freeze the pair amplitudes
- Solve for all other **CCSD** amplitudes.

$$\exp(T_1 + T_2) = \exp[T_1 + T_2(\,pairs) + T_2(broken\ \ pairs)]$$

$$T_1 : changes\ seniority\ by\ 2$$

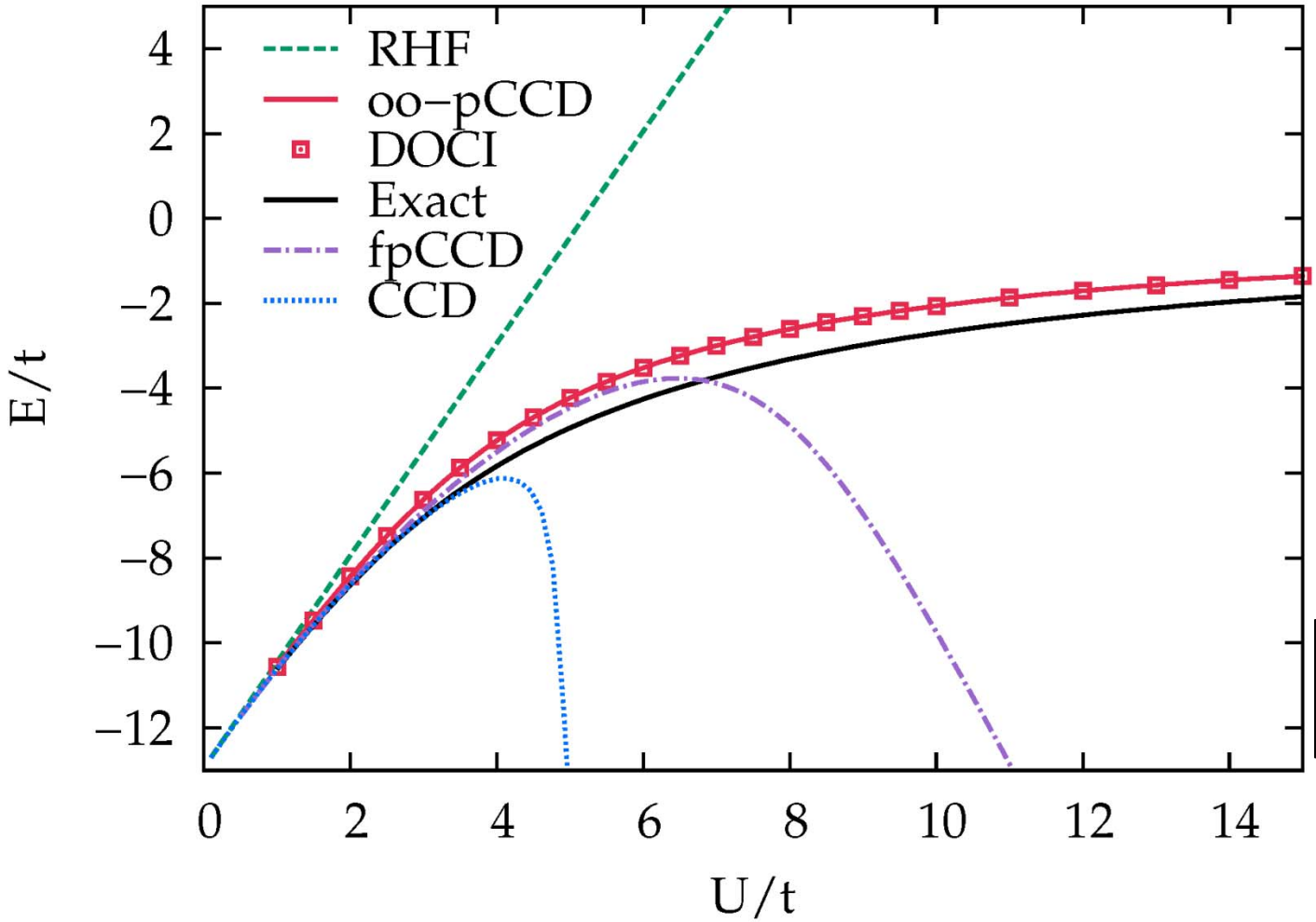
$$T_2(\,pairs) : preserves\ seniority$$

$$T_2(broken\ \ pairs) : changes\ seniority\ by\ 2\ or\ 4$$

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



$T_1 = 0$ by symmetry

fpCCD breaks down in the strongly correlated regime

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

Why is pair-CCD not a good starting point for breaking pairs?

Insights from Attractive Pairing (reduced BCS Hamiltonian)

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

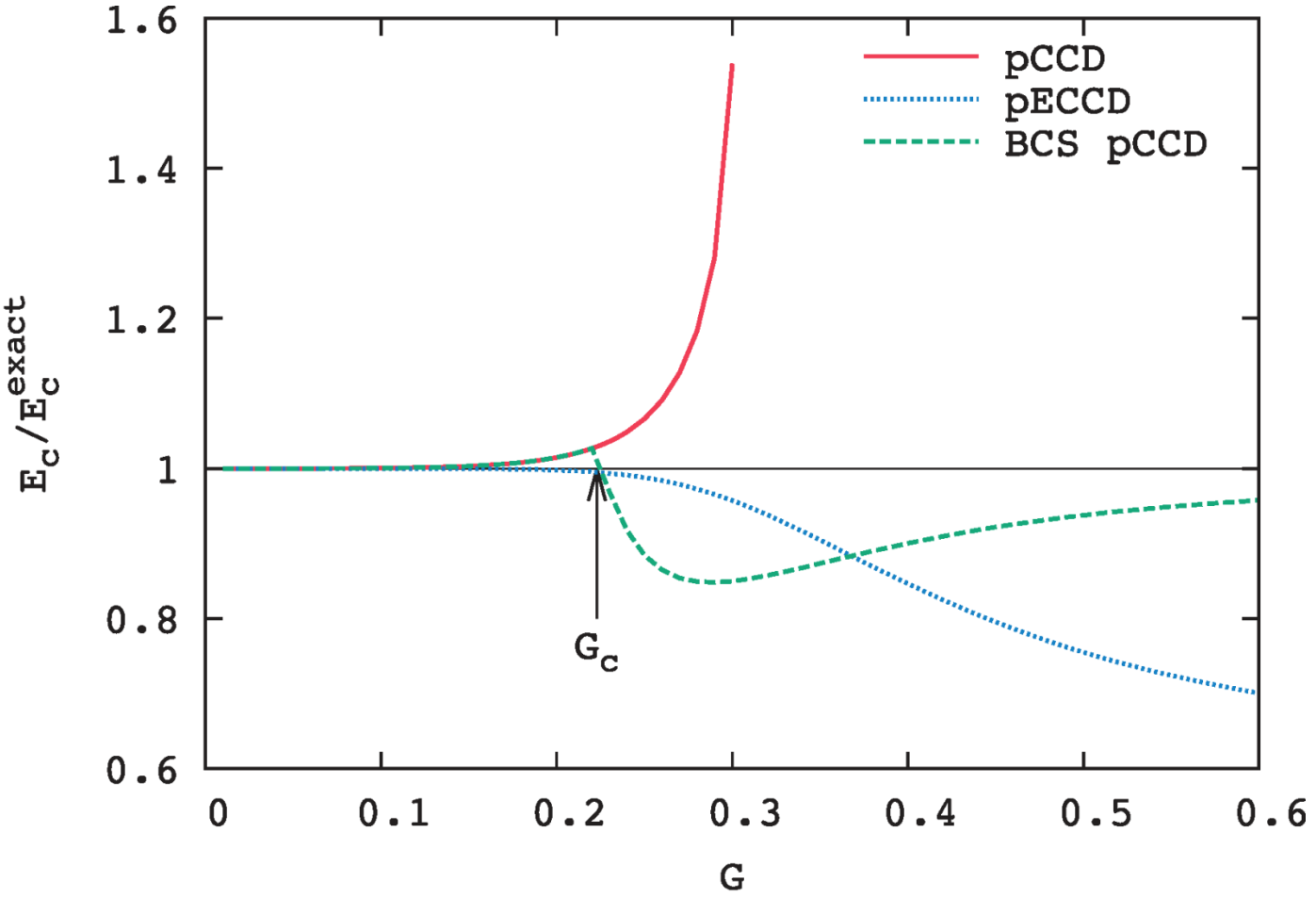
$$P_p^\dagger = c_{p\uparrow}^\dagger c_{p\downarrow}^\dagger, \quad N_p = c_{p\uparrow}^\dagger c_{p\uparrow} + c_{p\downarrow}^\dagger c_{p\downarrow}$$

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

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

- Exactly solvable model by Bethe ansatz (Richardson, 1960s)
- Eigenfunctions are antisymmetrized products of geminals
- In weakly correlated limit, geminals are all different => **pCCD**
- In strongly correlated limit, geminals are all the same => **AGP/PBCS**

Attractive Pairing



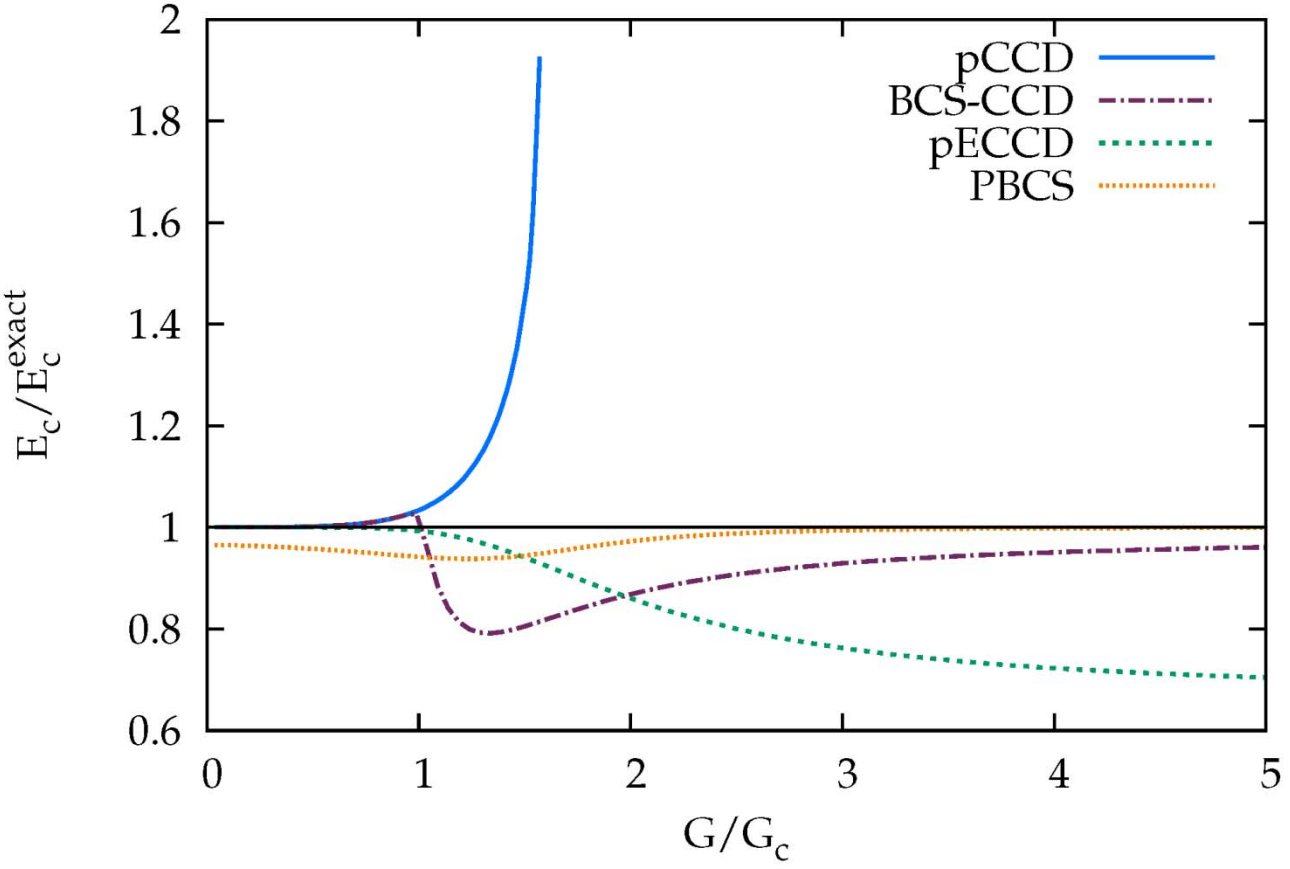
40 pairs
½ filling

pCCD fails catastrophically past the number symmetry breaking point.
pCCD works well when pairs repel rather than attract (rep. Hub 1D).

T. M. Henderson, G. E. Scuseria, J. Dukelsky, A. Signoracci, and T. Duguet, *Phys. Rev.* **C 89**, 054305 (2014).

T. M. Henderson, I. W. Bulik, and G. E. Scuseria, *J. Chem. Phys.* **142**, 214116 (2015).

PBCS works well for large attractive G



- **PBCS** = **number projected BCS** (condensate of fermion pairs) does not work well for weak correlation.
- **CCD** is **the** theory of weak correlation

Insights from symmetry breaking & restoration

Symmetries, degeneracies & strong correlation

- **Symmetry** implies **degeneracy:**

  if $H\,g = g\,H$ (where g is a symmetry)

  then $H\,g\Psi = g\,H\Psi = g\,E\Psi = E\,g\Psi$

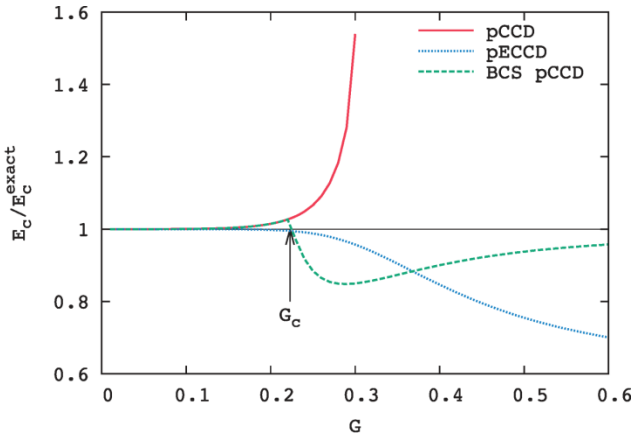
  Ψ and $g\Psi$ have the same energy E

- **Degeneracy** leads to **strong correlation**

Dealing with strong correlation cheaply

Unrestricted formalism with **broken-symmetry orbitals** yields some **strong correlation** cheaply.

But symmetry breaking is unphysical in finite systems. Symmetries should be restored.



Symmetry breaking & restoration

- Spontaneous **s**ymmetry **b**reaking in **RHF** flags the importance of degeneracies.

- **When symmetries break, we can restore them by projection.**

- **It is much better to** break symmetries and then restore them self-consistently : **$E \sim \langle 0| P^{\dagger} H P |0\rangle$ and $\delta E=0$** where **|0>** is optimized.

- Equivalent to ***CI*** between non-orthogonal determinants but done through integration of symmetry coherent states (Lie group).

- Our work (2011-2015): we **deliberately** break and restore:
  - **Continuous**: **Number U(1)** and **Spin** (S^2 and S_z) **SU(2)**
  - **Discrete**: **Complex Conjugation** (**K**), **Point Group** (**PG**)
  - **Discrete in lattices**: **Linear Momentum** (**LM**), **Space Group** (**SG=LM+PG**)

Spin Projection

Lowdin's approach (1955): a multi-body projection operator that leads to a complicated set of equations

$$\hat{P}^s = \prod_{l \neq s} \frac{\hat{S}^2 - l(l+1)}{s(s+1) - l(l+1)}$$

Alternative: Rotational invariance in spin space

$$\hat{P}^s_{mm} = \frac{2s+1}{2} \int_0^\pi d\beta \sin\beta \; d^s_{mm}(\beta) \, e^{i\beta \hat{S}_y}$$

$$\hat{R}(\Omega) = e^{i\alpha \hat{S}_z} \; e^{i\beta \hat{S}_y} \; e^{i\gamma \hat{S}_z}$$

This leads to a simple set of equations at ~**HF** computational cost.

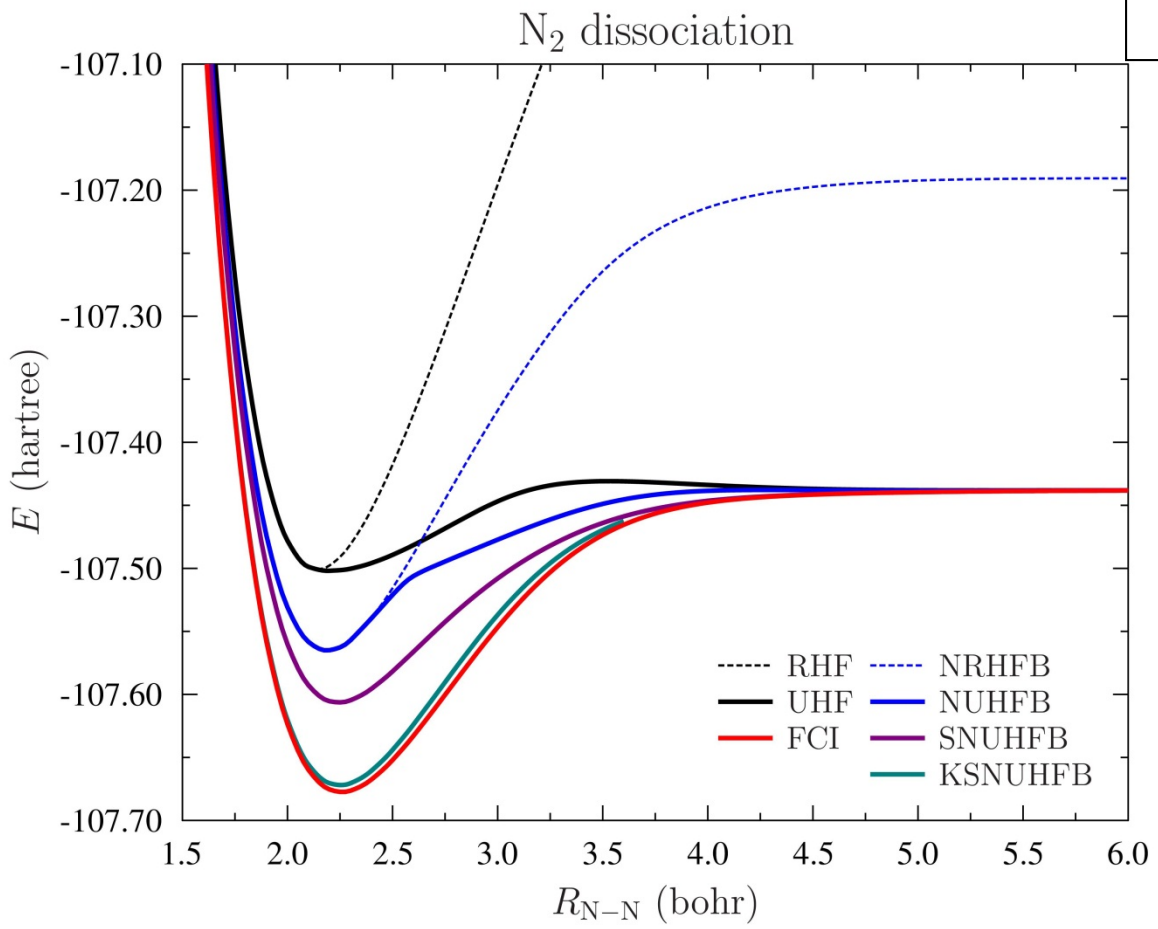
The language of **SB&R** is **generalized coherent states**, non-orthogonal states and collective excitations.

Number Projection :

$$\hat{P}_N = \frac{1}{2\pi} \int_0^{2\pi} d\varphi \; e^{i\varphi(\hat{N} - n)}$$

N_2: triple-bond dissociation

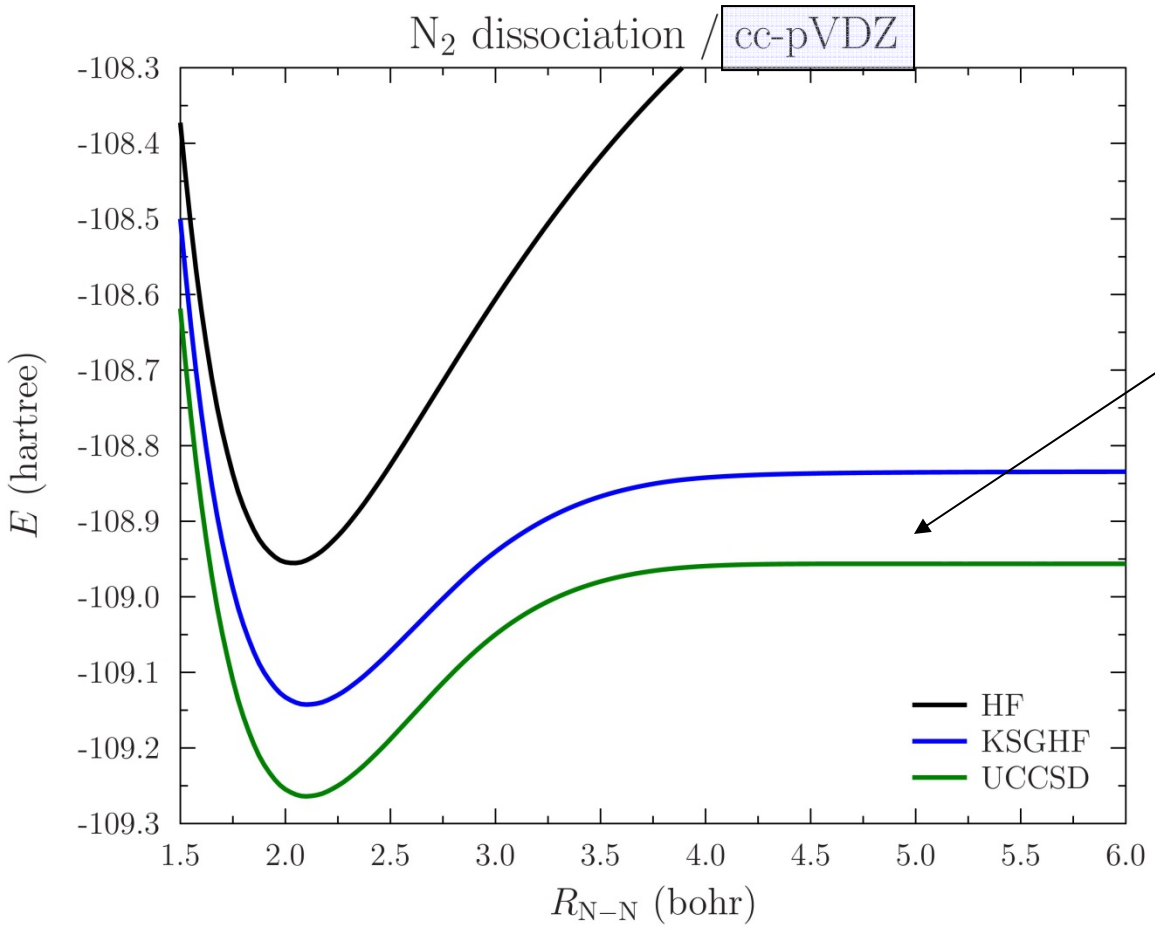
min basis



Break all symmetries & restore them: **KSNUHFB** ~ **FCI** quality

Complex conjugation (**K**), spin (**S**), and number (**N**) broken & restored

N_2: triple-bond dissociation



Residual correlations are large

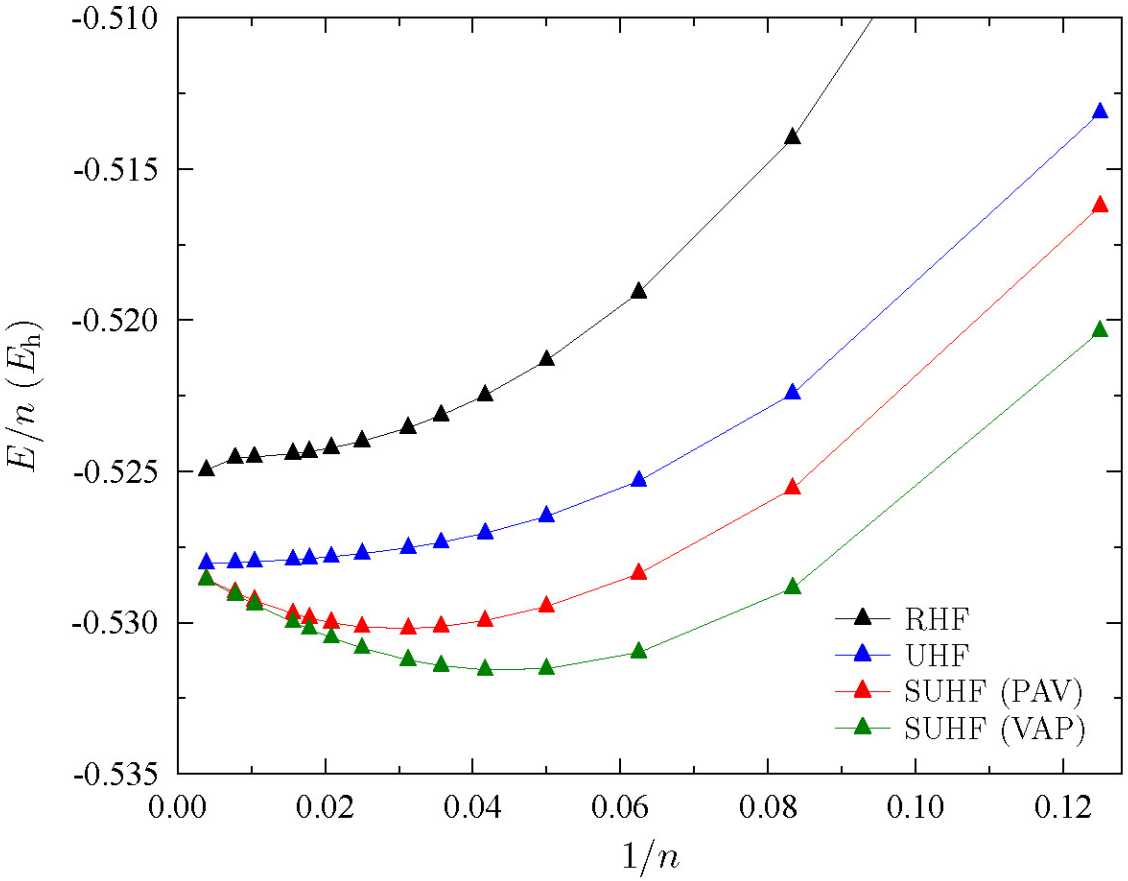
UCCSD: right energy but wrong Ψ

RCCSD (not shown) is not good

Away from minimum bases, **weak residual** correlations appear.
It would be great if we could **marry SB&R w/ CC theory**.

SB&R problem: not size extensive

Equidistant H atom rings @ 1.80 Bohr with minimum basis



Spin projection (**SUHF**) yields **zero** correlation energy per electron in infinite systems

How can we marry SB&R with CC theory?

Two dissimilar theories:

- **CC** is not variational and size-extensive.
- **PBCS/PHF** is variational and size intensive.
- For the attractive pairing Hamiltonian these two theories are exact on opposite limits.
- Can we merge them on a common ground?

PBCS and pair-CCD

- The broken symmetry **BCS** state can be obtained by a qpThouless:

$$\left|BCS\right\rangle \approx \exp(\sum z_{pq}\beta_p^\dagger\beta_q^\dagger)\left|\phi\right\rangle$$

- Written in the **particle-hole** basis **BCS** becomes:

$$\left|BCS\right\rangle \approx \exp(\sum x_a P_a^\dagger + y_i P_i)\left|RHF\right\rangle \approx \exp(\sum x_a P_a^\dagger)\exp(\sum y_i P_i)\left|RHF\right\rangle$$

- The **projected state** is the diagonal term:

$$\left|PBCS\right\rangle \approx \sum_n \frac{1}{n!^2}\left(\sum_{ia} t_i^a P_a^\dagger P_i\right)^n \left|RHF\right\rangle$$

- And suggests an interpolating ansatz of the form:

$$\left|PoST\right\rangle \approx \sum_n \frac{1}{n!^\alpha}\left(\sum_{ia} t_i^a P_a^\dagger P_i\right)^n \left|RHF\right\rangle$$

- **pair-CCD** is α=1 and **PBCS** is α=2 (**Bessel** parametrization of wave op.)
- Similar arguments can be made for spin projection

PoST theory

- **Polynomial Similarity Transformation** uses a non-exponential correlator based on **doubles only**

$$F(T) = I + T + aT^2 + \ldots \quad \left(a = 2^{-\alpha}\right), \quad T = \sum t_{ij}^{ab} c_a^\dagger c_b^\dagger c_i c_j$$

- Hamiltonian is similarity transformed and correlation amplitudes are determined by left projection (**CC**-like)

$$\overline{H} = F^{-1}(T) H F(T), \quad E = \left\langle 0 \middle| \overline{H} \middle| 0 \right\rangle, \quad 0 = \left\langle 2 \middle| \overline{H} \middle| 0 \right\rangle$$

- α is determined via variance minimization of quadruples residual
- Because **F(T)** is not **exp(T)**, this theory contains unlinked terms

$$\overline{H} = H + [H,T] + (1-a)[[H,T],T] + (2a-1)T[H,T]$$

- Renormalization of 2nd commutator coefficients and unlinked terms take care of symmetry collective states built out of **RHF** as **ph** excitations.

PoST theory in a nutshell

PHYSICAL REVIEW B **93**, 125124 (2016)

Polynomial similarity transformation theory: A smooth interpolation between coupled cluster doubles and projected BCS applied to the reduced BCS Hamiltonian

Matthias Degroote
Department of Chemistry, Rice University, Houston, Texas 77005-1892, USA

Thomas M. Henderson
Department of Chemistry and Department of Physics and Astronomy, Rice University, Houston, Texas 77005-1892, USA

Jinmo Zhao
Department of Chemistry, Rice University, Houston, Texas 77005-1892, USA

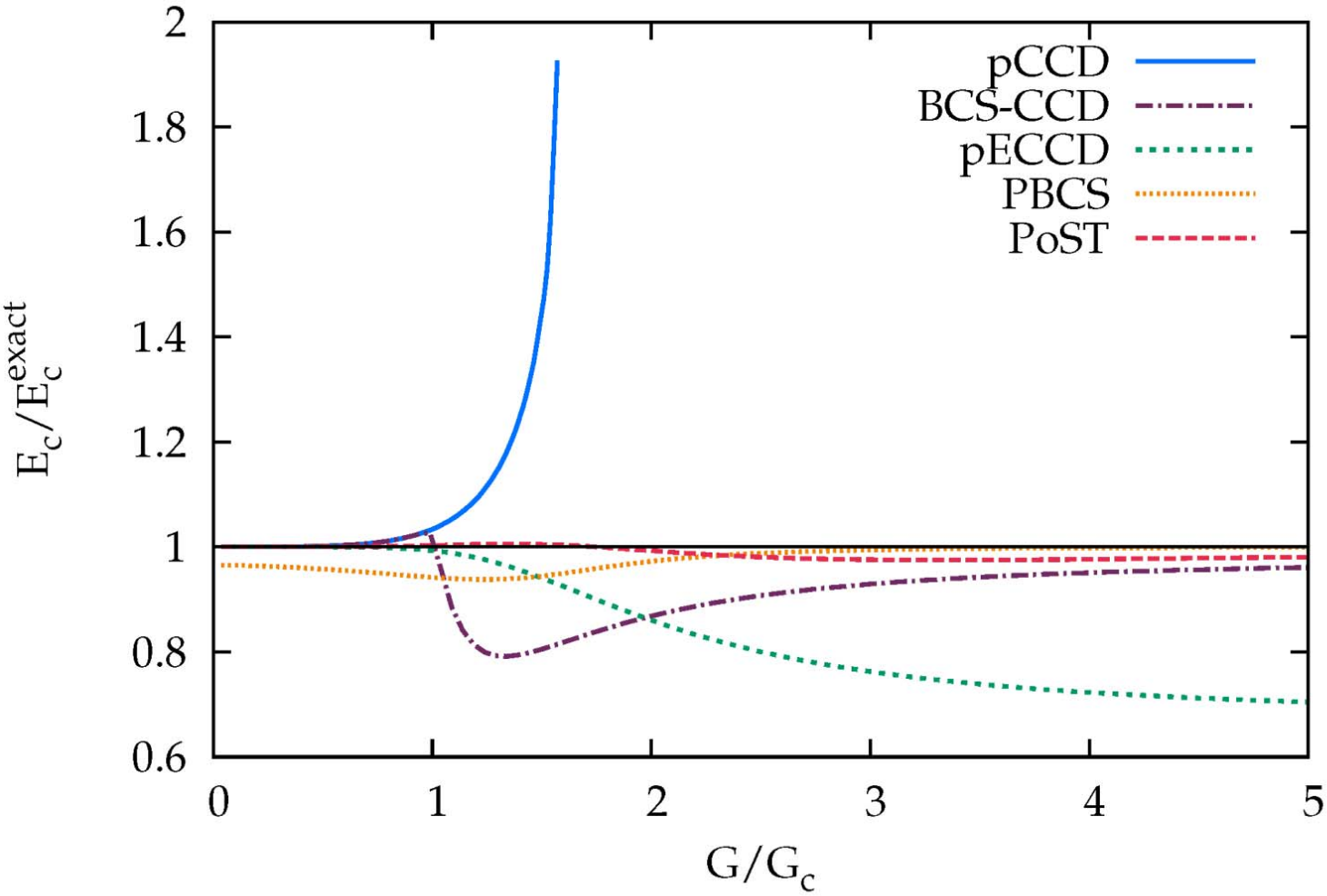
Jorge Dukelsky
Instituto de Estructura de la Materia, CSIC, Serrano 123, E-28006 Madrid, Spain

Gustavo E. Scuseria
Department of Chemistry and Department of Physics and Astronomy, Rice University, Houston, Texas 77005-1892, USA
(Received 18 December 2015; revised manuscript received 26 February 2016; published 14 March 2016)

We present a similarity transformation theory based on a polynomial form of a particle-hole pair excitation operator. In the weakly correlated limit, this polynomial becomes an exponential, leading to coupled cluster doubles. In the opposite strongly correlated limit, the polynomial becomes an extended Bessel expansion and yields the projected BCS wave function. In between, we interpolate using a single parameter. The effective Hamiltonian is non-Hermitian and this polynomial similarity transformation theory follows the philosophy of traditional coupled cluster, left projecting the transformed Hamiltonian onto subspaces of the Hilbert space in which the wave function variance is forced to be zero. Similarly, the interpolation parameter is obtained through minimizing the next residual in the projective hierarchy. We rationalize and demonstrate how and why coupled cluster doubles is ill suited to the strongly correlated limit, whereas the Bessel expansion remains well behaved. The model provides accurate wave functions with energy errors that in its best variant are smaller than 1% across all interaction strengths. The numerical cost is polynomial in system size and the theory can be straightforwardly applied to any realistic Hamiltonian.

Interpolation between **CCD** and **SB&R** in the **CC** framework

Attractive Pairing



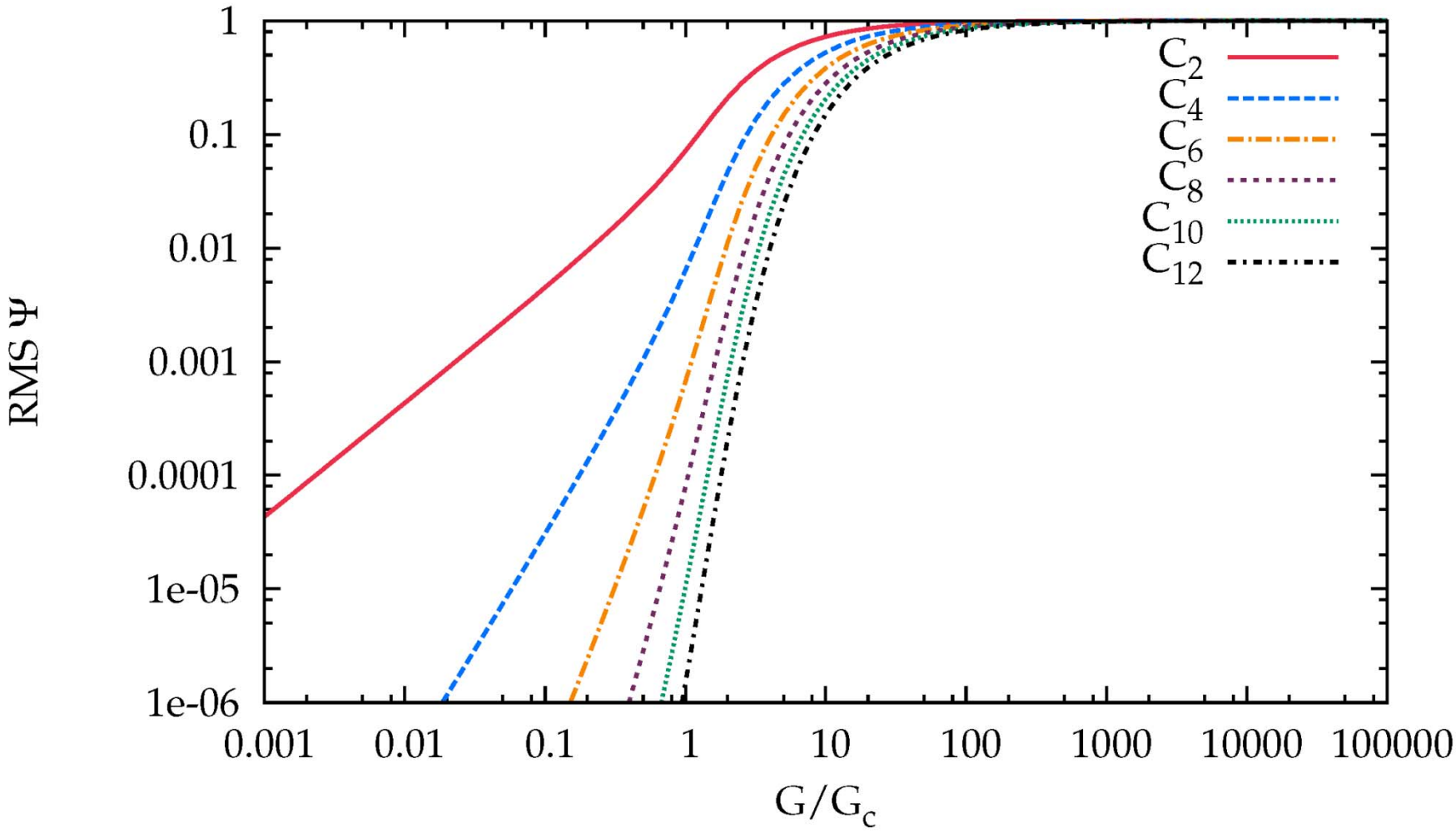
16 sites
half-filled

PoST energy error is ~1%; wavefunction is very accurate

(α is determined via variance minimization of quadruples residuals)

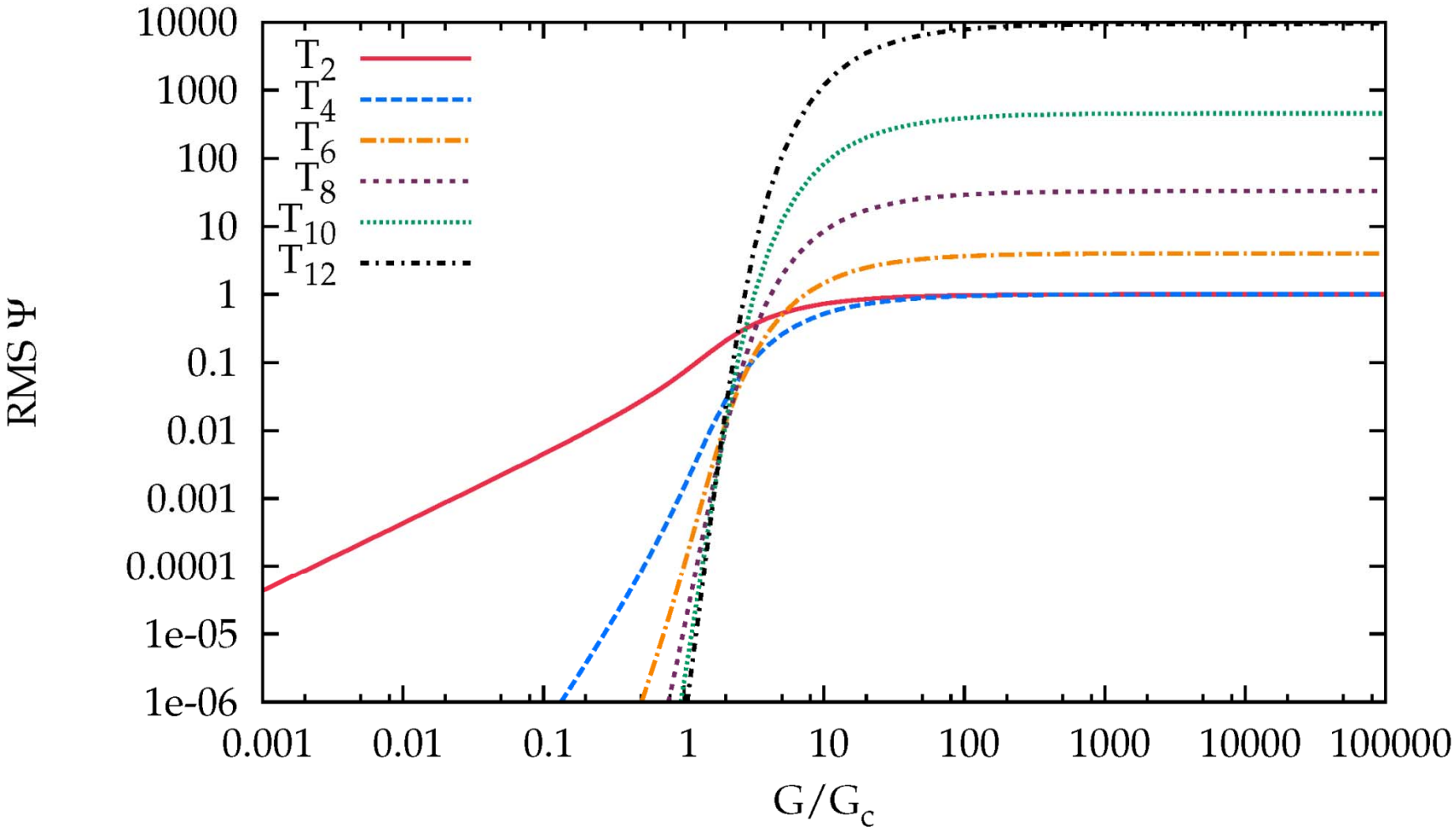
Why does CCD fail?

Full CI amplitudes



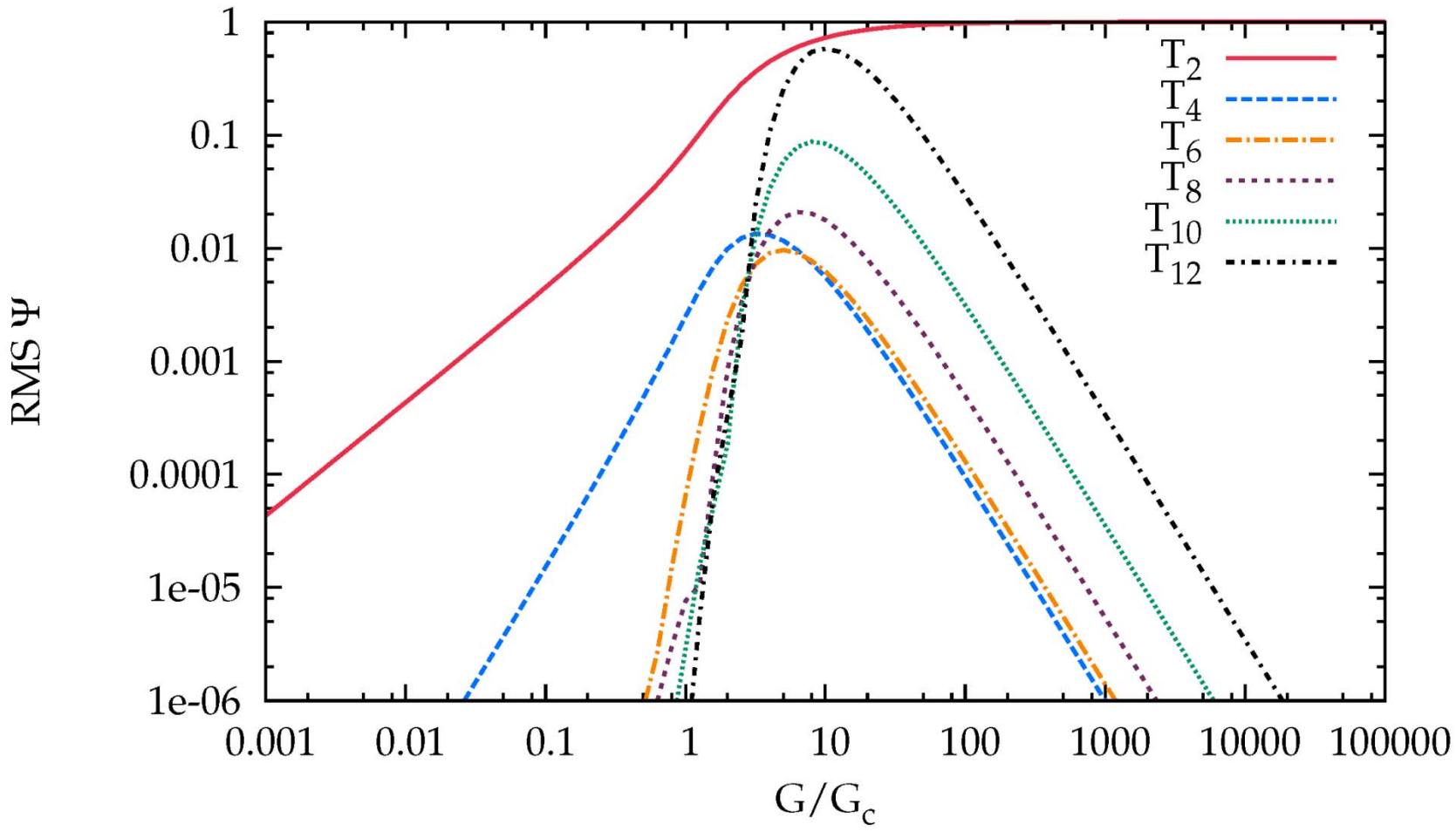
In strongly correlated limit, all determinants have weight equal to 1 because of intermediate normalization

Full CC reverse-engineered from FCI



Full-*CC* is numerically ill-posed in the strongly correlated limit.
No natural truncation.

Bessel (PBCS) parametrization

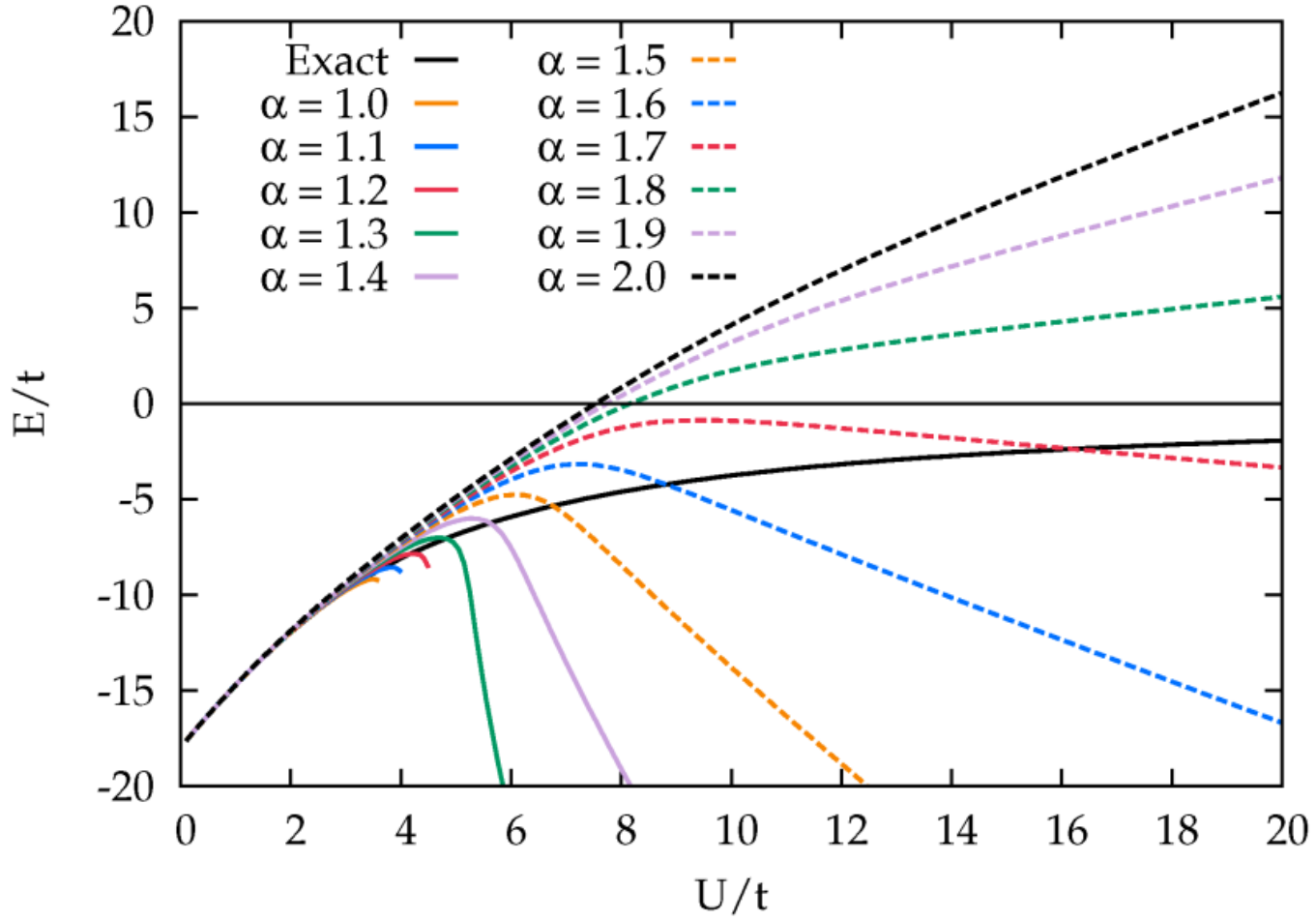


Bessel is fine and does for strong correlation
what **CCD** does for weak correlation

How does PoST perform for strongly correlated repulsive Hubbard?

(Hamiltonian breaks seniority)

Hubbard 1D

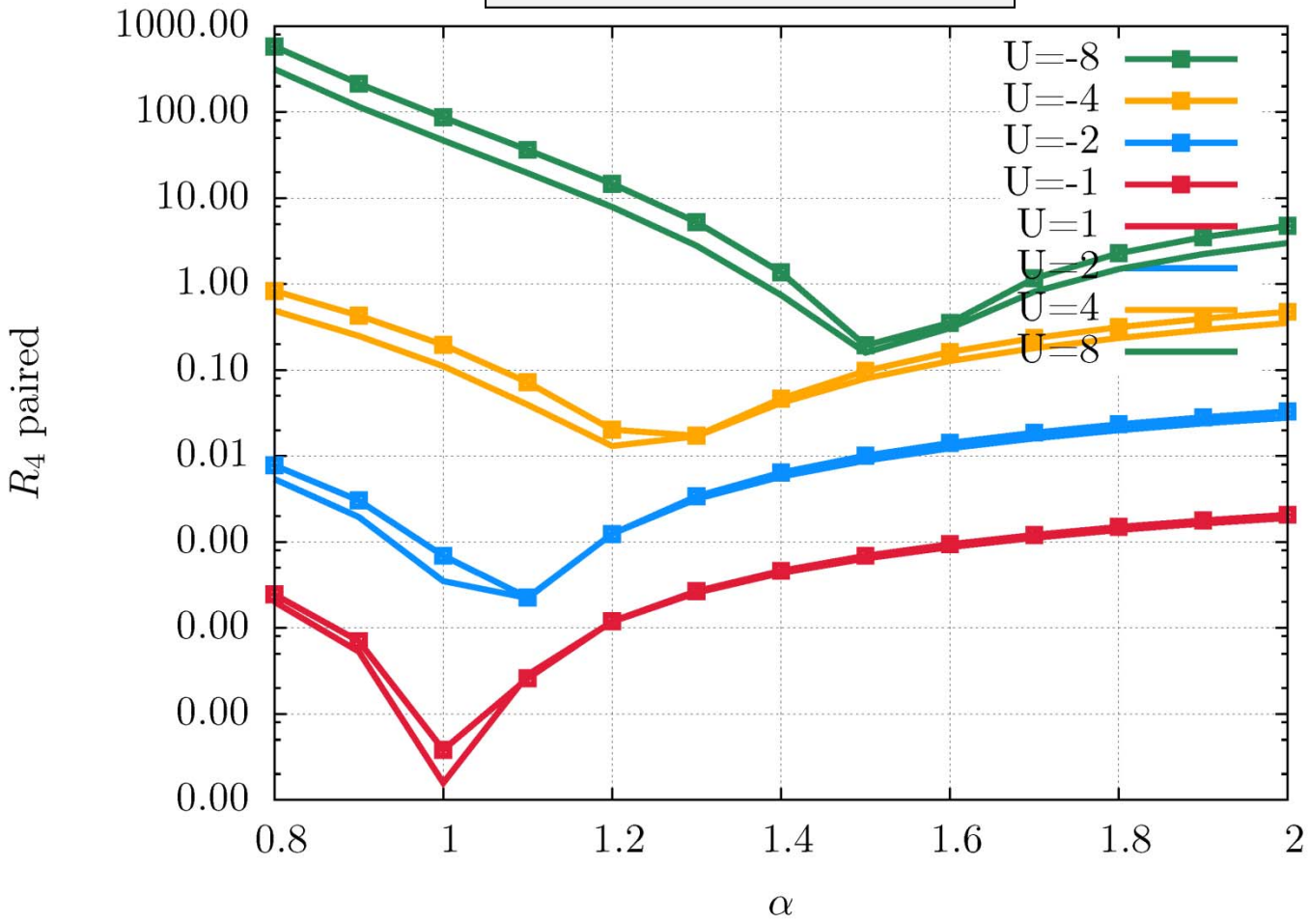


16 sites, half-filled:
PoST curves cross the exact energy only once

Optimum α by residual minimization

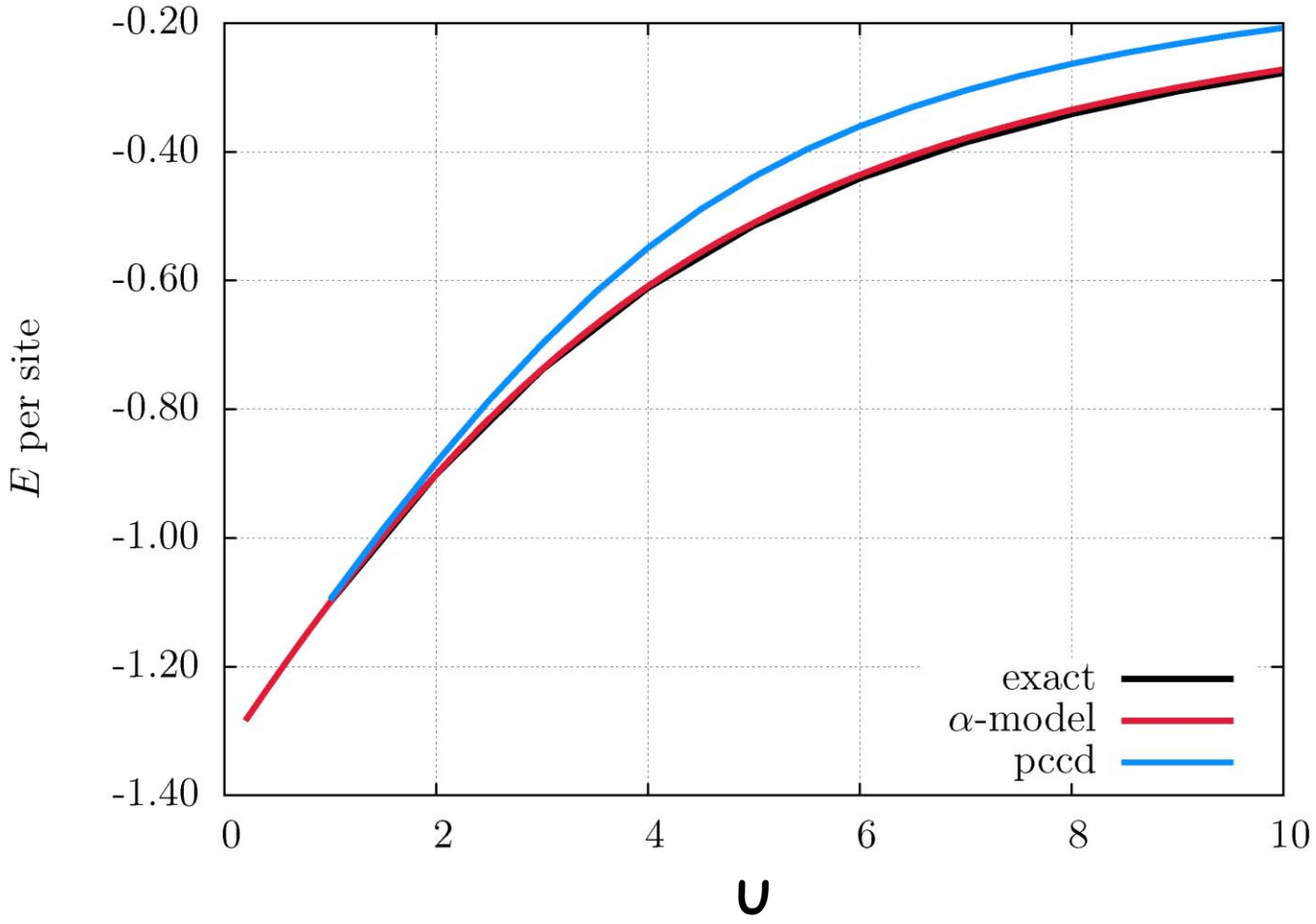
Hubbard **1D**, 16 sites, half-filled, repulsive & attractive

$$\alpha = \arg\min \left\langle 4 \mid \overline{H} \mid 0 \right\rangle^2$$



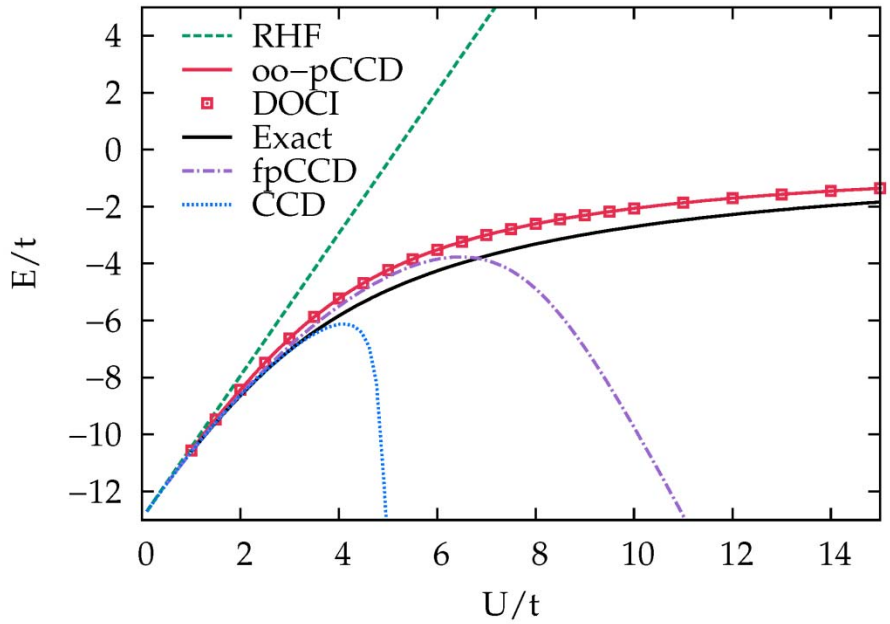
SO(4) symmetry: **ph** transformation maps **H**(-U) onto **H**(+U) @ ½ filling

Energy with optimum α



Hubbard **1D**, 16 sites, half-filled.
PoST: High quality results. No breakdown.

CCD catastrophic failure



- **fpCCD**: onset of catastrophe is at **U** much larger than **CCD** but **fpCCD** fails too.
- This means that **pCCD** is not a good starting point for breaking pairs. **Why?**
- Let's reverse engineer **FCI** and look at the exact **pair** amplitudes.
- They are not close to **pCCD**; they are rather similar to those in **PoST**, which contain a good dose of **PBCS**.
- **Conjecture**: in a **strongly** correlated **repulsive H**, **ph** excitations that break pairs renormalize the bare **repulsive pairing** interaction and develop **attractive channels**, thus **pCCD/CCD** fails and **PoST** is needed.

Conclusions

- **Symmetry** implies degeneracy and degeneracy implies **strong correlation.**

- **Strong correlation** from **symmetry degeneracies** implies factorization of connected high excitations: T_4, T_6,... dominated by disconnected terms that are not described by a T_2 exponential

- We are incorporating these factorizations into the **CCD** formalism:

$$F_N(T_2) = 1 + T_2 + \tfrac{1}{4}(T_2)^2 + \ldots \quad \text{(number projection)}$$
$$F_S(T_2) = 1 + T_2 + 3/10\,(T_2)^2 + \ldots \quad \text{(spin projection)}$$
$$EXP(T_2) = 1 + T_2 + \tfrac{1}{2}(T_2)^2 + \ldots \quad \text{(dynamical corr.)}$$

Acknowledgments

PoST team: Dr. Tom Henderson, Dr. Matthias Degroote, Dr. Matthew Hermes, Ethan Qiu, Jinmo Zhao, John Gomez; collaborator: Jorge Dukelsky

$ DOE, NSF, Welch, Gaussian