Symmetry, degeneracy and strong correlation

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RICE
Unconventional Wisdom

ESNT workshop on many-body perturbation theories in modern quantum chemistry and nuclear physics
CEA Saclay, 26-30 March 2018

Outline

- Not a talk about perturbation theory
- Failure of the coupled cluster paradigm
- Understanding the role of symmetry
- Designing solutions based on symmetry restoration

- Alternatives to the exponential ansatz
- Polynomials of excitations that represent **PHF**
- Polynomial Product States
- Symmetry-projected **UCCSD**
- **CCSD** on **PHF**

Why is symmetry important ?

- **Symmetry implies** <u>**degeneracy**</u> **and** <u>**factorization**</u>

- Simplest example: **Hydrogen atom spherical symmetry**

$$\Psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\varphi), \quad E = E(n), \quad 2n^2 \ degenerate\ states$$

- **Symmetry degeneracy** becomes "**strong correlation**" only when near the Fermi energy; this is flagged by **SSB** (e.g., **UHF** atoms down the periodic table)
- Exploiting **factorization** in electronic structure theory due to symmetry degeneracies (spin, number, point group, etc.) is far from trivial
- This is what we are doing by merging coupled cluster theory with symmetry breaking and restoration ideas
- <u>**This talk**</u>: progress report on several fronts

Weak vs Strong Correlation

- **Weak correlation** : $|H_1| >> |H_2|$ (in a loose sense)
  - The **mean-field Restricted Hartree-Fock (RHF)** picture in the symmetry adapted basis is qualitatively correct.
  - Perturbation theory works (Taylor expansion of the wavefunction).
- **Strong correlation** : $|H_1| << |H_2|$
  - Physics is determined by the interaction, not the mean-field.
  - **RHF** is bad. Symmetries break spontaneously in **HF**.
  - No good perturbation expansion in **R** basis. Degeneracy rules.
  - **Collective** behavior becomes important !
  - Range of weak & strong correlations are different
  - In quantum chemistry, the Coulombic repulsive **H** cannot break **number symmetry** in mean-field; it does break **spin symmetry**

An important remark on HF symmetry breaking

- Stationarity of the **HF** does not imply a local minimum
- The **diagonal** of the number conserving (ph-ph) **HF** **instability hessian** is instructive:

$$M^{t}_{ai,ai} = \varepsilon_a - \varepsilon_i - J_{ai} - K_{ai}$$
$$M^{c}_{ai,ai} = \varepsilon_a - \varepsilon_i - J_{ai} + K_{ai}$$
$$M^{s}_{ai,ai} = \varepsilon_a - \varepsilon_i - J_{ai} + 3K_{ai}$$

$$J_{ai} > 0$$
$$K_{ai} > 0$$
$$J_{ai} > K_{ai}$$

$$i : occ$$
$$a : unocc$$

- For the hessian to have a negative eigenvalue, a negative diagonal element is **sufficient** (but not necessary)
- Symmetry breaking can occur with large gaps if **J** and **K** are even larger -> **strong correlation**
- **Good example**: fullerenes and particularly C_{60}

Weak Correlation Paradigm: Coupled Cluster Theory

CC works very well in weakly correlated situations where symmetries do not break and (symmetry adapted) **Restricted Hartree-Fock** (RHF) is a good approximation

Achieving Chemical Accuracy with Coupled-Cluster Theory

Timothy J. Lee
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and

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August-1994

Abstract

Due to formal and computational advances in coupled-cluster theory over the past few years, it is now possible to obtain very accurate molecular geometries, vibrational frequencies, heats of formation, binding energies, and vertical electronic excitation energies. For example, based on statistical analyses of a large number of calculations, it is shown that the CCSD(T)/*spdfg* level of theory gives r_{XH}, r_{XY} (double bonds), and r_{XY} (triple bonds) with an average error of 0.0010, 0.0020, and 0.0026 Å, respectively, with the theoretical bond distances usually too long relative to experiment. This level of theory yields bond angle predictions that are too small by 0.21 degrees on average. Fundamental vibrational frequencies predicted at the CCSD(T)/*spdfg* level of theory are accurate to better than 8.0 cm^{-1} on average,

Sometimes referred to as the "**gold standard**"

Coupled Cluster theory

- **Coupled Cluster** theory is based on an **exponential** ansatz of **particle-hole excitations** ***T*** out of a reference determinant **|0>**

$$\left|\Psi\right\rangle = e^{T}\left|0\right\rangle, \qquad He^{T}\left|0\right\rangle = Ee^{T}\left|0\right\rangle, \qquad T = T_1 + T_2 + T_3 + T_4 + \ldots$$

- ***CC*** reparametrizes the **exact solution (FCI)** via an **exponential**

$$\left|FCI\right\rangle = (1 + C_1 + C_2 + C_3 + C_4 + \ldots)\left|0\right\rangle = e^{T_1+T_2+T_3+T_4+\ldots}\left|0\right\rangle$$

$$C_1 = T_1, \quad C_2 = T_2 + \frac{1}{2!}T_1^2, \quad C_3 = \cancel{T_3} + T_2T_1 + \frac{1}{3!}T_1^3$$

$$C_4 = \cancel{T_4} + \cancel{T_3T_1} + \frac{1}{2}T_2^2 + \frac{1}{2}T_2T_1^2 + \frac{1}{4!}T_1^4$$

- The **Hamiltonian** is similarity transformed: $\overline{H} = e^{-T} H\, e^{T}$
- ***CC*** yields a set of nonlinear algebraic equations: $R_n = \left\langle n\middle|\overline{H}\middle|0\right\rangle = 0$
- To decouple the equations, one neglects high-order **connected** excitations T_{n+1} and T_{n+2} in R_n (T_3 and T_4 in **CCSD**)
- Truncated ***CC*** retains **disconnected** higher order excitations.

Coupled Cluster theory

- By retaining disconnected terms, the ***CC*** ansatz yields size extensivity, adding terms absent in **CI** via **exponential factorization**

- ***CC*** computational cost is **polynomial** as a function of size

- By increasing **n** in T_n , ***CC*** yields a series of approximations that **eventually** gets the right answer for the right reason

- We must truncate T_n to avoid combinatorial cost and decouple the ***CC*** algebraic equations

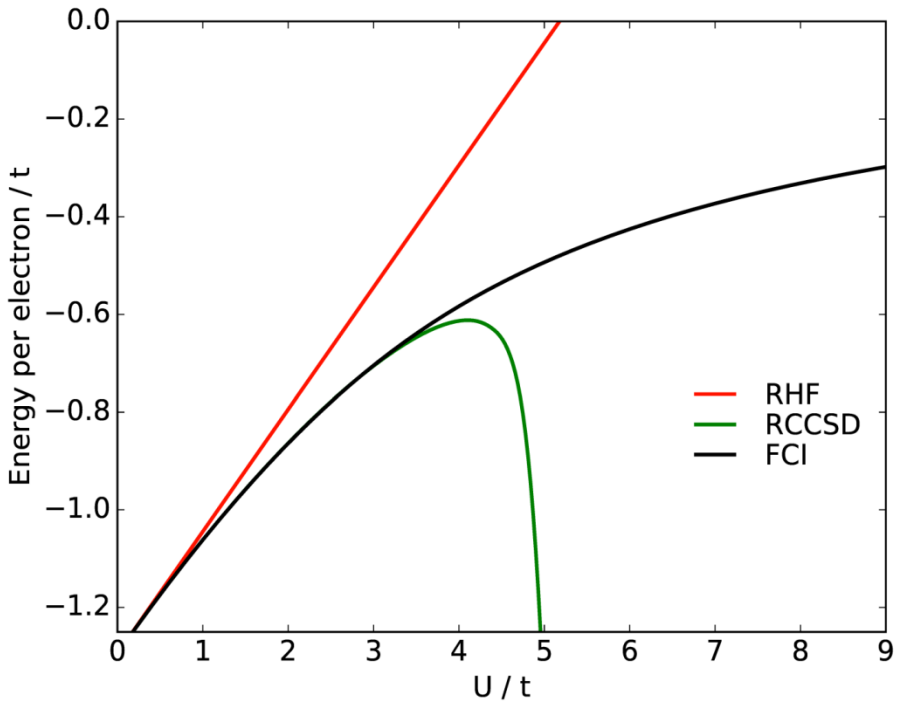
- Truncated ***CC*** is **not** variational

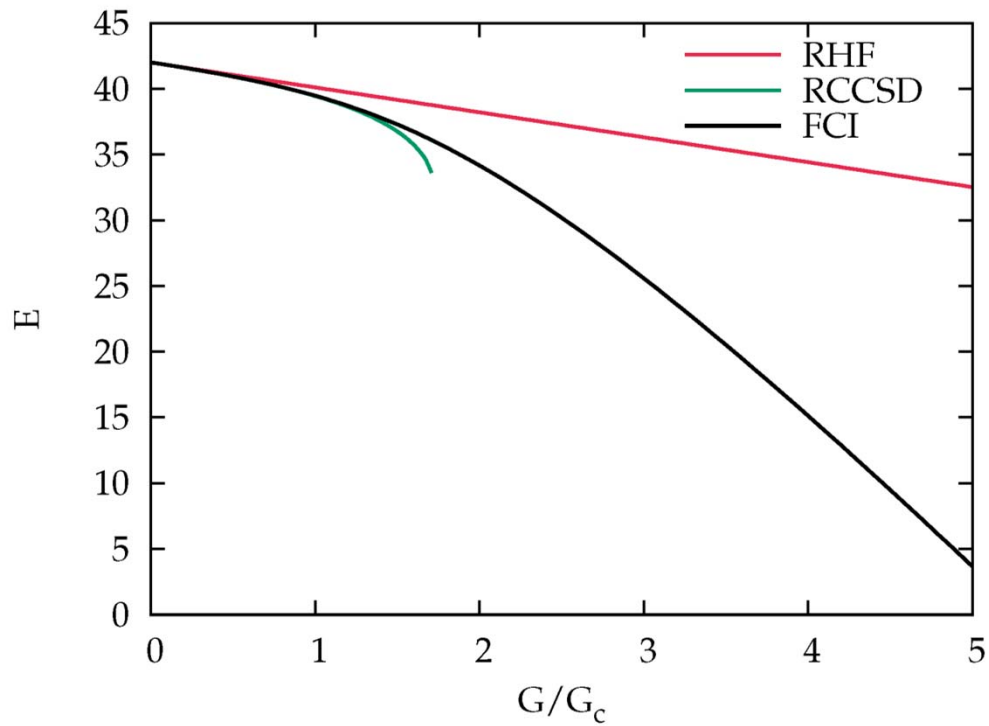
An incredibly successful theory but…

RCC catastrophic failure

1D Hubbard ring
10 fermions on 10 sites
Large U/t → strongly correlated

Attractive pairing (reduced BCS)
6 pairs on 12 sites
Large G/G_c → strongly correlated



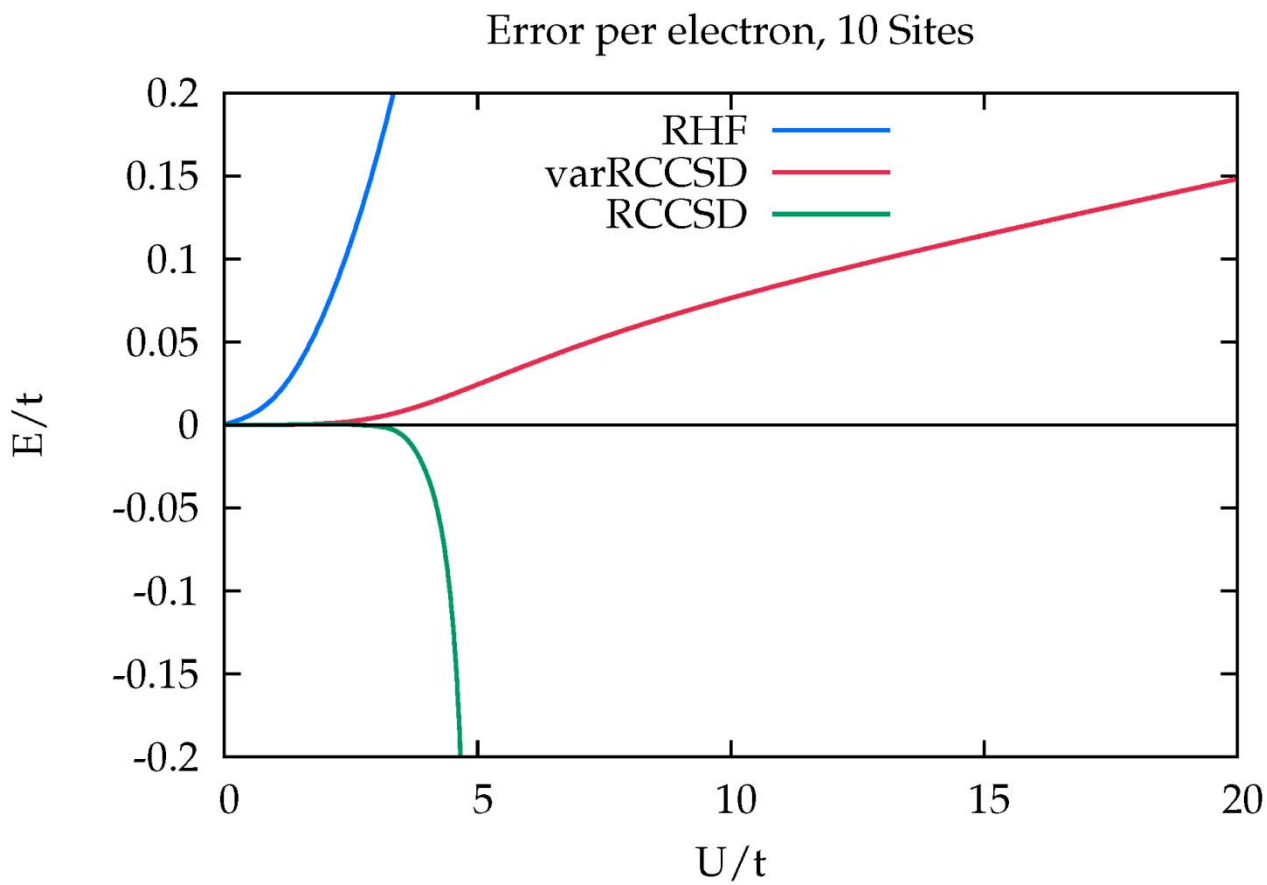


RCCSDT, RCCSDTQ… all fail similarly, except for **full CC.**

Variational RCCSD undercorrelates (**next slide; combinatorial cost !)**

Variational RCCSD

10x1 Hubbard chain; 10 electrons
Error per electron respect to FCI



RHF basis

Variational RCCSD undercorrelates badly.
The ***CC*** ansatz (traditional or variational) is not accurate in the strongly correlated regime.

The problem is to know what the problem is

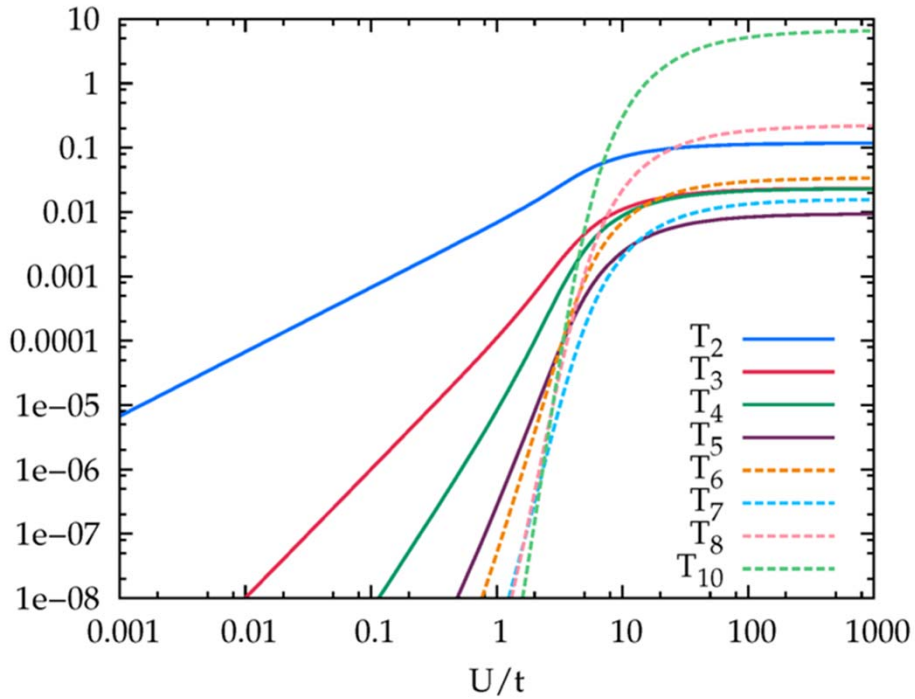
Albert Einstein

The hard part of solving a problem
is identifying the problem itself

Why does coupled cluster fail under strong correlation ?

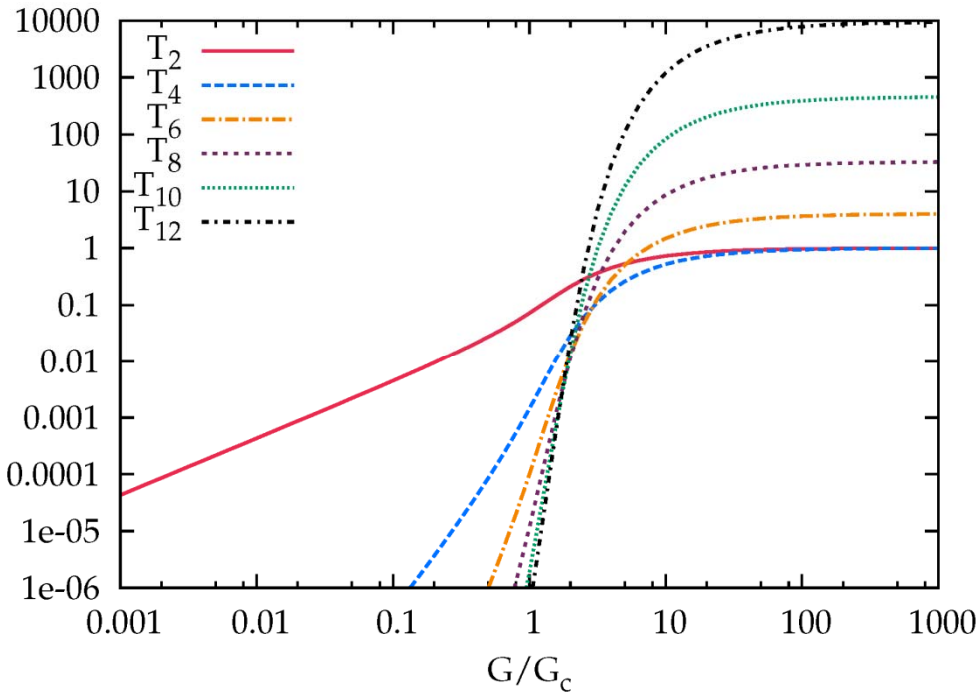
RCC reverse-engineered from FCI

10x1 Hubbard ring; 10 electrons



RHF orbitals, T_1 = T_9 = 0 by symmetry

Attractive pairing; N = 12 electrons



RHF orbitals, T_{odd} = 0 by symmetry

In the **strongly correlated limit**, **RCC** has **no natural truncation.**
Note huge size of $T_{n>2}$. **RCCD assumes $T_{n>2} \approx 0$**

All is well with the **FCI** coefficients !

Why does coupled cluster fail under SC ?

Because decoupling does not work if neglected $\mathbf{T_n}$ are large

Why are the T_n large ?

Because **exp[**truncated**(T)]** is a poor approximation to **FCI**

- Given that the **FCI** coefficients are always small, could there be a better polynomial of excitations ?

$$\begin{aligned}\left|FCI\right\rangle &= (1+C_1+C_2+C_3+C_4+\ldots)\left|0\right\rangle = F(K_1,K_2,K_3,K_4,\ldots)\cdot\left|0\right\rangle \\ &= (1+K_1+K_2+K_3+K_4+a_1K_1^2+a_2K_2^2+b_2K_3^2+K_2K_3+\ldots)\cdot\left|0\right\rangle\end{aligned}$$

$$C_4 = \cancel{K_4} + \cancel{K_3K_1} + a_2K_2^2 + a_1K_2K_1^2 + a_1^2K_1^4$$

Where could F come from?

- **Symmetry collective states** because :
- Broken symmetry **UCCSD** energy is fine
- Strong correlation => symmetry breaking and degeneracy
- Projected **HF** is exact in **SC** limit of these model **H**

Why is symmetry important?

- **Symmetry implies degeneracy and factorization**
- Exploiting **factorization** from symmetry (spin, number, point group, etc.) in electronic structure is non trivial
- This is what we are doing via **collective states**
- In the language of **p-h excitations**, we have discovered **polynomials associated with symmetry projection**

Reduced BCS Hamiltonian

$$H = \sum_p \varepsilon_p N_p - G \sum_{pq} P_p^\dagger P_q, \qquad P_p^\dagger = c_{p\uparrow}^\dagger c_{p\downarrow}^\dagger, \quad N_p = c_{p\uparrow}^\dagger c_{p\uparrow} + c_{p\downarrow}^\dagger c_{p\downarrow}$$

- In large **G** limit, **PBCS** is exact
- Full **CC** is of course exact but truncated **CCD** blows up
- The **FCI** eigenfunction can be rewritten as a non-exp polynomial of **only** doubles, with factorized amplitudes

$$\left|FCI\right\rangle = \exp\left(T_2 + T_4 + T_6 + T_8 + T_{10} + \ldots\right)\left|RHF\right\rangle = F(T_2)\left|RHF\right\rangle = \left|PBCS\right\rangle$$

$$\left|PBCS\right\rangle = \widehat{P_N}\left|BCS\right\rangle = \widehat{P_N}\exp Q_1\left|RHF\right\rangle = \widehat{P_N}\exp\left(\sum_a x^a P_a^\dagger\right)\exp\left(\sum_i x_i P_i\right)\left|RHF\right\rangle$$

$$= \widehat{P_N}(1 + \sum_i x_i P_i + \frac{1}{2}\sum_{ij} x_i x_j P_i P_j + \ldots)(1 + \sum_a x^a P_a^\dagger + \frac{1}{2}\sum_a x^a x^b P_a^\dagger P_b^\dagger + \ldots)\left|0\right\rangle$$

$$= \left(1 + T_2 + \frac{1}{4}T_2^2 + \ldots\right)\left|0\right\rangle = F(T_2)\left|RHF\right\rangle, \qquad T_2 = \sum_{ia} x_i x^a P_a^\dagger P_i$$

M. Degroote, T. M. Henderson, J. Zhao, J. Dukelsky, and G. E. Scuseria, *Phys. Rev.* **B 93**,125124 (2016)

Spin S^2 symmetry factorization

$$|SUHF\rangle = \widehat{P_S}\,|\phi\rangle = \widehat{P_S}\,e^{Q_{1S}}\,|0\rangle = F_S\,|0\rangle = (1 + K_{2S} + \frac{3}{10}K_{2S}^2 + \ldots)|0\rangle$$

$$Q_{1S} = \sum_{ia} q_i^a \left(c_{a\uparrow}^\dagger c_{i\uparrow} - c_{a\downarrow}^\dagger c_{i\downarrow}\right), \qquad K_{2S} = -\frac{1}{6}\sum_{ijab}\left(q_i^a q_j^b + 2q_i^b q_j^a\right)E_a^i E_b^j$$

$$E_a^i = c_{a\uparrow}^\dagger c_{i\uparrow} + c_{a\downarrow}^\dagger c_{i\downarrow}$$

|ϕ> is **broken symmetry**, **|0>** is **symmetry adapted**

Q_{1S} breaks spin symmetry and transforms **RHF** into **UHF**

Symmetry projection is here done **analytically**

K_{2S} factorizes. E_a^i are symmetry adapted (totally symmetric)

SUHF has $a_2 = 3/10$, **PBCS** has $a_2 = \frac{1}{4}$, **CC** has $a_2 = \frac{1}{2}$ (fails under **SC**)

The change in a_2 with interaction regime is a **renormalization effect.**

These results can be used to **merge CC** with **Projected HF**

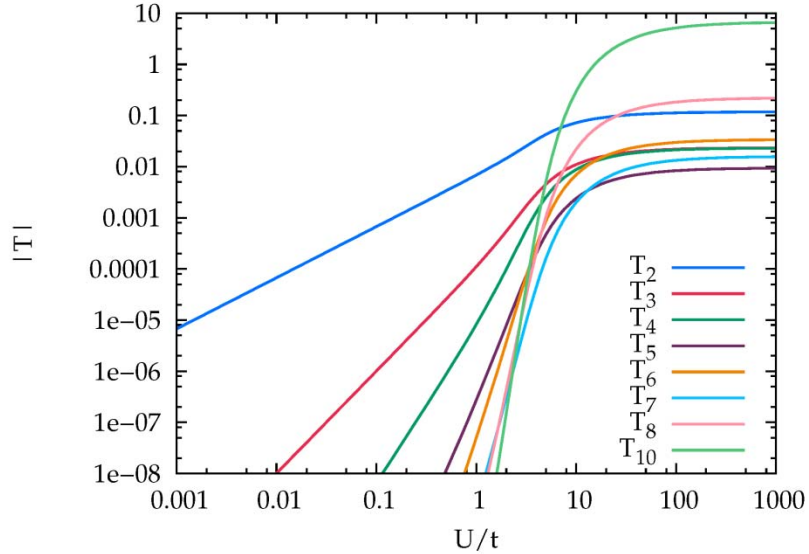
M. Degroote, T. M. Henderson, J. Zhao, J. Dukelsky, and G. E. Scuseria, *Phys. Rev.* **B 93**,125124 (2016).

Y. Qiu, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys.* **146** , 184105 (2017).

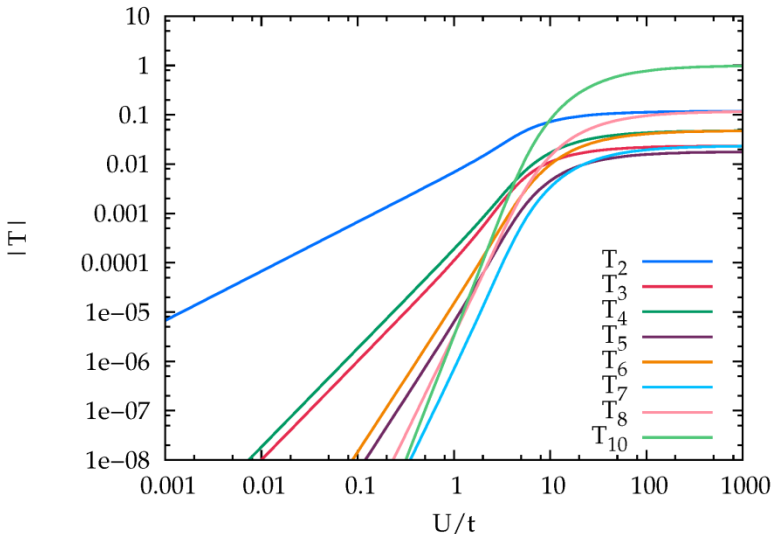
T. M. Henderson and G. E. Scuseria, *Phys. Rev.* **A 96** , 022506 (2017).

Hubbard 10x1 ½ filled

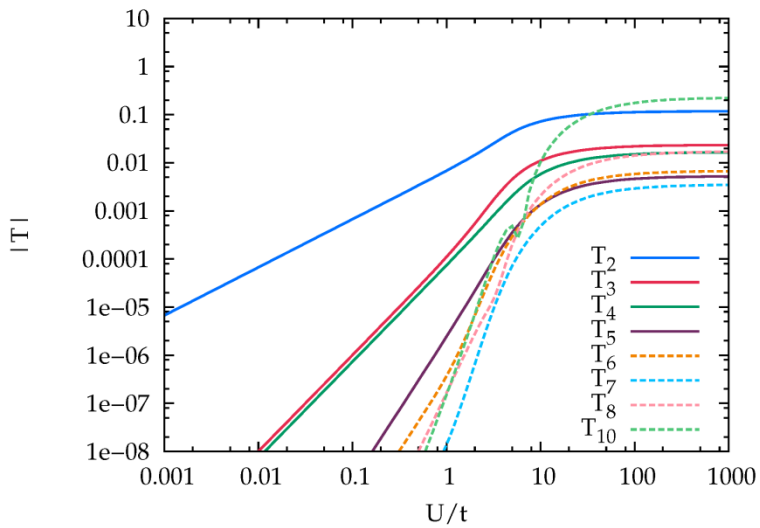
FCC



FCI



SUHF (≠ FCI)



Spin Polynomial Similarity Transformation

- **SPoST** is an **interpolation** between **CCSD** and **SUHF**

$$F(T_2) = 1 + T_2 + a_2 T_2^{\,2} + a_3 T_2^{\,3} + \ldots$$

- Hamiltonian is similarity transformed $\overline{H} = F^{-1}(T_2) H\, F(T_2)$

- a_2 and T_2 are optimized using **CC**-like equations

Attenuated Coupled Cluster Theory

- **aCCSD** identifies collective mode(s) by diagonalizing $T_2 = K_2 + S_2$
- The largest eigenvalue mode (K_2) is treated with the symmetry polynomial $F(K_2)$ while the rest of the modes uses **exp**(S_2)

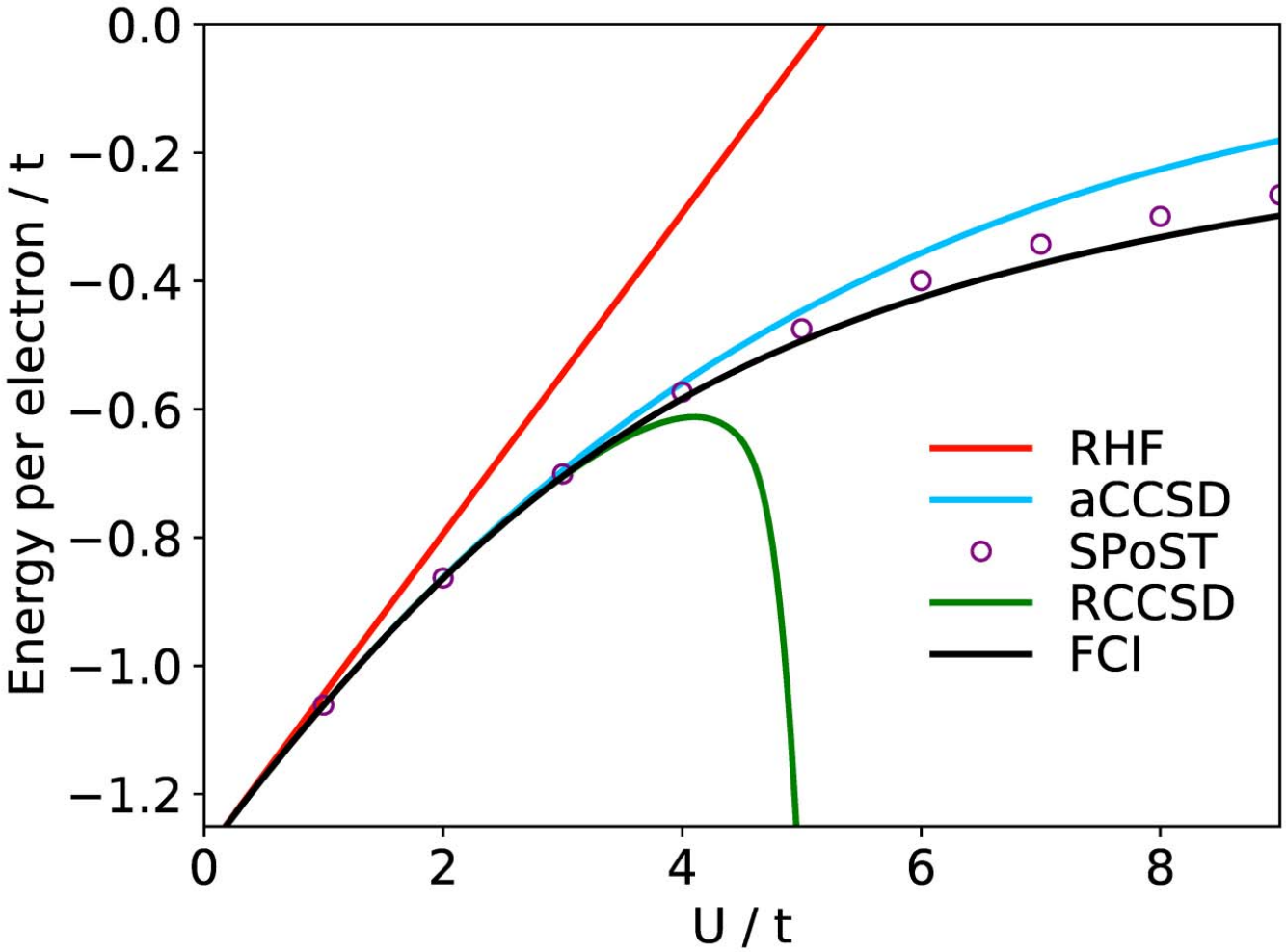
$$\overline{H} = e^{-S_2} F^{-1}(K_2) H\, F(K_2)\, e^{S_2}$$

J. A. Gomez, M. Degroote, J. Zhao, Y. Qiu, and G. E. Scuseria, *Phys. Chem. Chem. Phys.* **19**, 22385 (2017).

J. A. Gomez, T. M. Henderson, and G. E. Scuseria, *Mol. Phys.* **115**, 2673 (2017).

Merging spin collective states with CCSD

10x1 Hubbard ring; 10 electrons



Proof of Principle: **aCCSD** and **SPoST** are qualitatively correct (and symmetry adapted)

Polynomial Product States

- Consider an ansatz composed of products of polynomials of particle-hole excitations that preserve (**T**) or break (**Q**) symmetries
- Symmetry-project broken-symmetry terms

$$\hat{P}(e^{Q_1+Q_2+\dots}) = F(K) = I + K + a_2 K^2 + a_3 K^3 + \dots$$

- Similarity-transform

$$\overline{H} = F^{-1}(K) e^{-T} H e^{T} F(K)$$

- Solve via ***CC*-like** equations

$$E = \langle 0 | \overline{H} | 0 \rangle, \quad 0 = \langle n | \overline{H} | 0 \rangle$$

- More general than **attenuated *CC*** or **PoST**

The thermodynamic limit

- **PPS** are size extensive and different from ***CC***
- In **TDL** only linked diagrams (***CC***) survive but the ***CC*** weight gets renormalized by **F(K)**
- **PPS** carry "rank-**n** extensivity" associated with the '**n**' in $\mathbf{Q_n}$

Take II: broken symmetry

- **Smoking gun:**

  If we allow spin symmetry to break (**RHF** → **UHF**) the **UHF** energy is fine and even better at the **UCC** level .

- But the wave function has wrong quantum numbers !

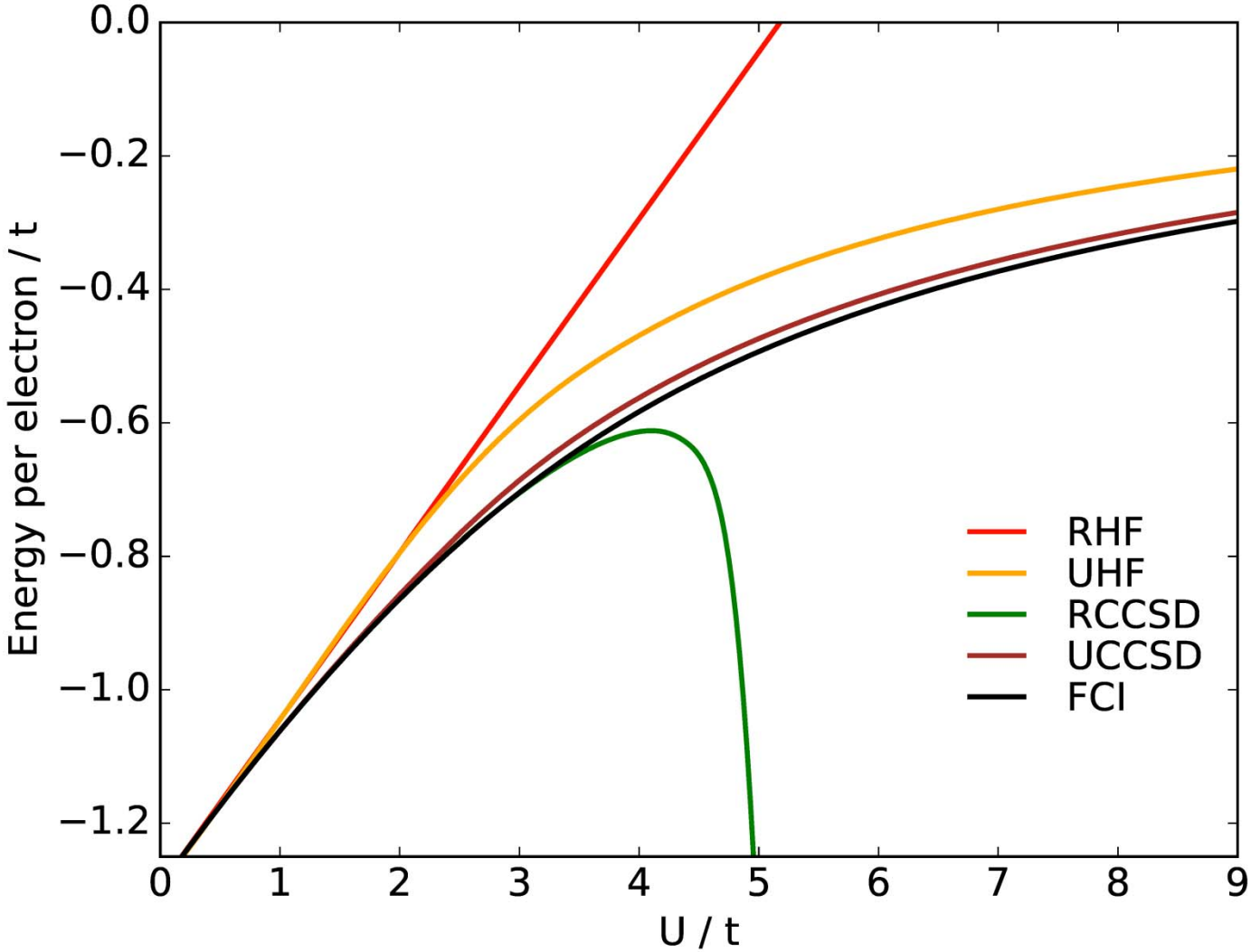
- **Symmetry dilemma:**

  Symmetries can be broken to improve the energy but the road to eigenfunctions can be full of obstacles

- Close connection among symmetry breaking, degeneracy & strong correlation

- Let's see what happens in the broken symmetry basis

Broken spin symmetry picture



UHF and UCCSD energies are fine but we lose good quantum numbers

Inspection of U_3, U_4, etc., shows that they are small

S^2 projection: SUHF

- Spin restoration is done imposing rotational invariance in spin space using a projection operator $\hat{P}$ acting over broken symmetry determinants $e^{i\beta\hat{S}_y}\left|\phi\right\rangle$

$$\left|SUHF\right\rangle = \hat{P}\left|\phi\right\rangle = \int_0^{\pi} d\beta \sin\beta \;\; e^{i\beta\hat{S}_y}\left|\phi\right\rangle$$

- This leads to numerical integration with ~ **HF** computational cost

- **SUHF** → **non-orthogonal** determinants in the **broken symmetry** basis → **collective** excitations in **symmetry adapted** basis.

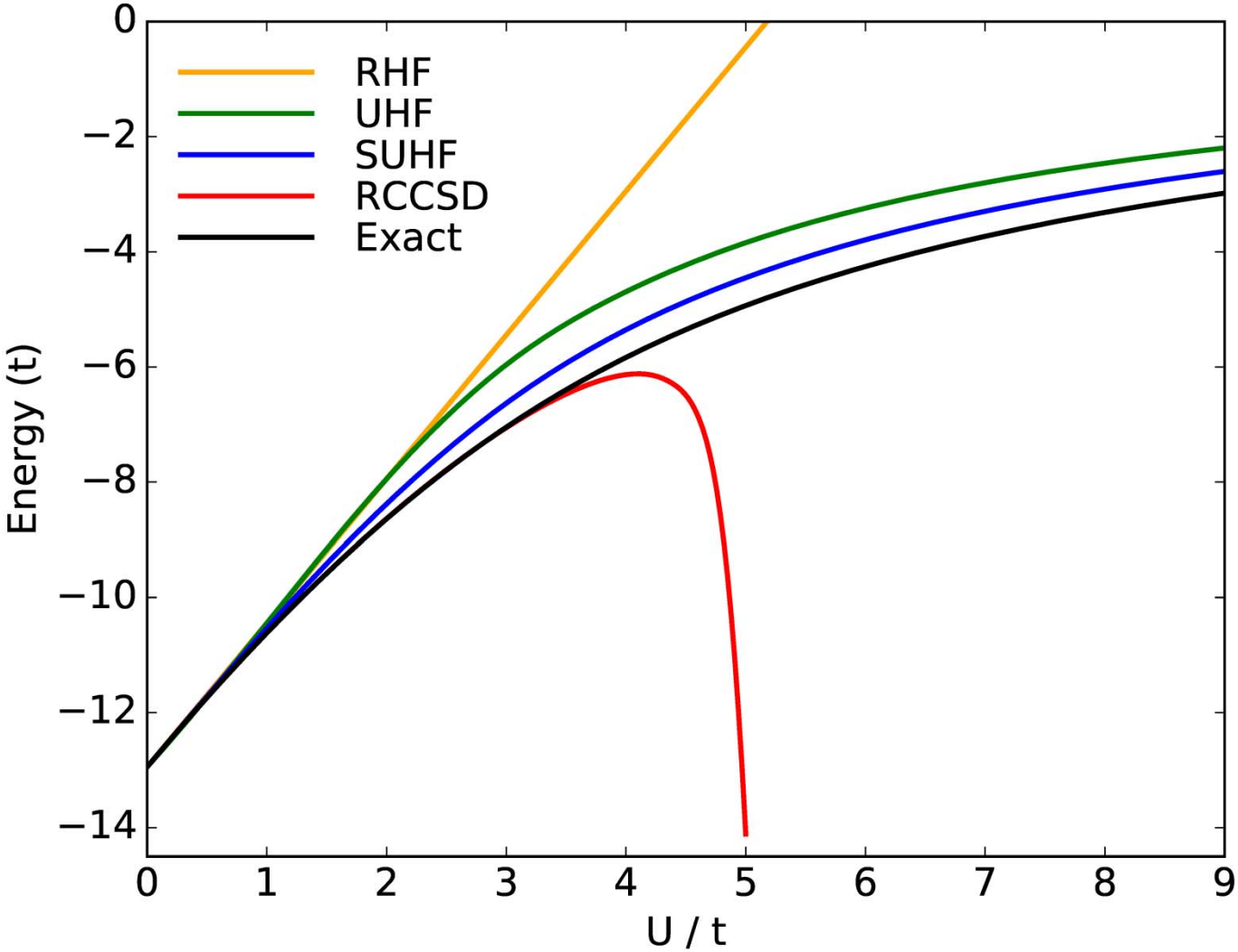
$$\left\langle\phi\right| e^{i\beta\hat{S}_y}\left|\phi\right\rangle = \left\langle\phi\,|\,\beta\right\rangle \neq 0$$

- Spin projection has a long history (Löwdin **1955**) but never took off
- Our work on symmetry breaking and restoration :
  - **Number** and **Spin** (both $\mathbf{S^2}$ and $\mathbf{S_z}$) (continuous)
  - **Complex Conjugation** and **Point Group** (discrete)
  - **Linear Momentum** and **Space Group** in periodic systems

J. Chem. Phys. **135**, 124108 (2011), *J. Chem. Phys.* **136**, 164109 (2012), *J. Chem. Phys.* **139**, 204102 (2013).

S^2 projection: SUHF

10x1 Hubbard ring; **10** electrons



SUHF is a spin eigenfunction (like **RCCSD**) but does not fail

Spin Projected UCCSD

$$H\,\hat{P}e^{U_1+U_2}\left|\phi\right\rangle = E\,\hat{P}e^{U_1+U_2}\left|\phi\right\rangle$$

$$\hat{P} = \int_0^{\pi} d\beta \sin\beta \quad e^{i\beta\hat{S}_y}$$

The merge seems simple but there is a fundamental **language barrier**:

- ***CC*** is built from **orthogonal** p-h excitations
- Symmetry projection uses **non-orthogonal** determinants

Main result of our work: **disentangled cluster formalism**

$$e^{i\beta\hat{S}_y}e^{U_1+U_2}\left|\phi\right\rangle = e^{W_0(\beta)}\,e^{W_1(\beta)+W_2(\beta)+W_3(\beta)+\ldots}\left|\phi\right\rangle$$

$W_0(\beta)$ is a constant. The $W_n(\beta)$ are **purely excitation** operators.

They restore symmetry.

They afford truncation in the spirit of ***UCC*** theory.

At $\beta = 0 \quad \Rightarrow \quad W_1(0) = U_1, \quad W_2(0) = U_2, \quad W_{n>2}(0) = 0$

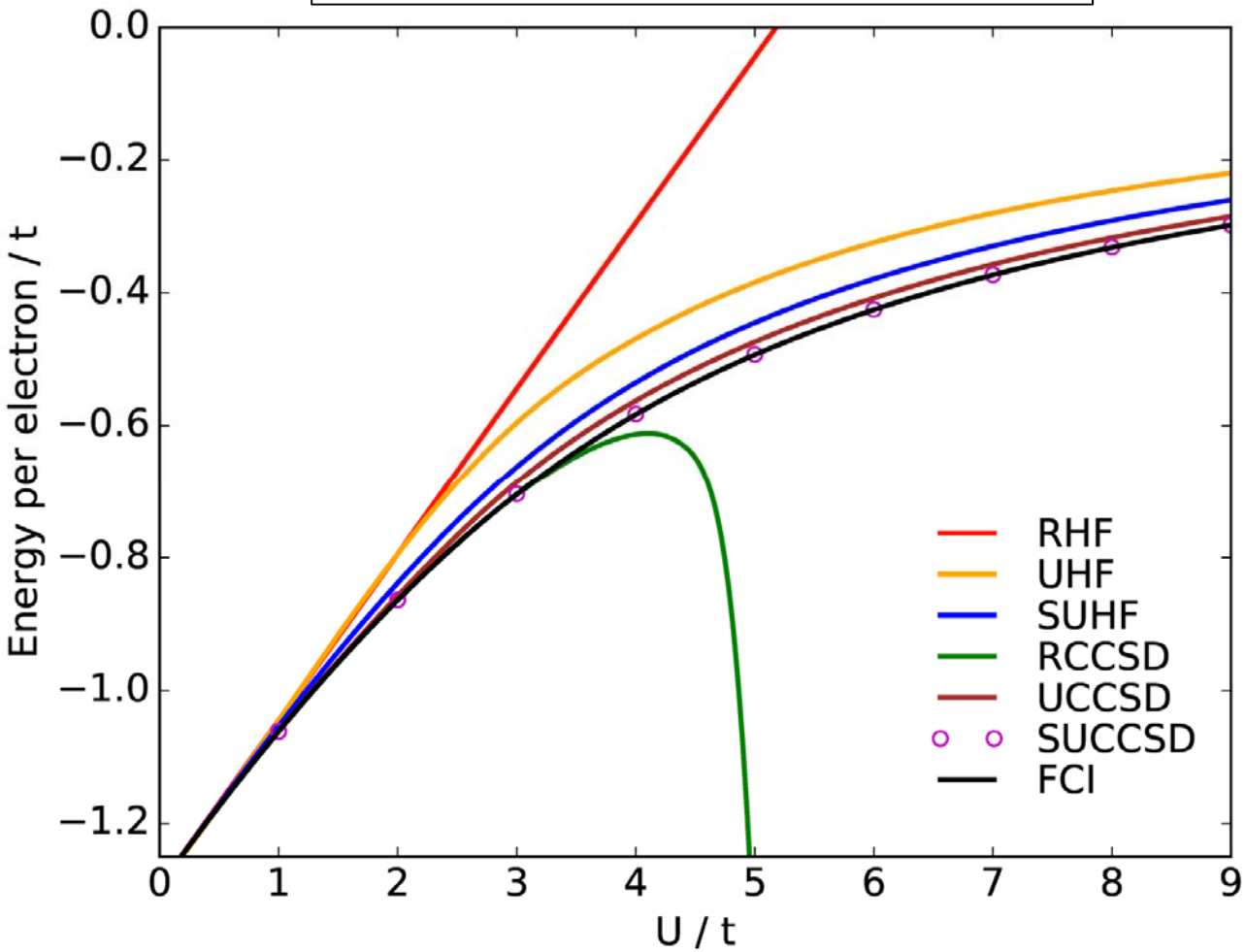
$W_n(\beta)$ are obtained solving differential equations in su(2)

T. Duguet, *J. Phys. G* **42**, 025107 (2015)

Y. Qiu, T. M. Henderson, J. Zhao & G. E. Scuseria, *J. Chem. Phys.* **147**, 064111 (2017)

Spin Projected UCCSD

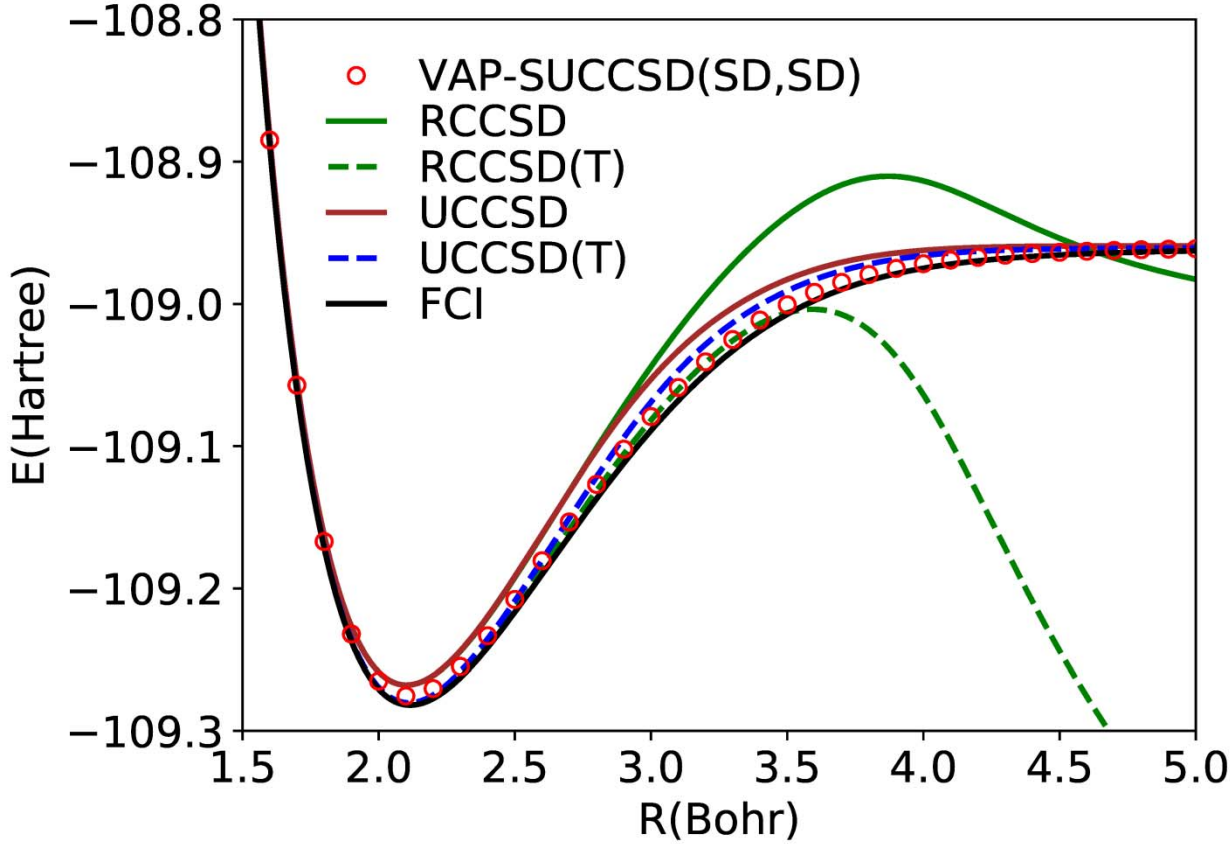
10x1 Hubbard ring; **10** electrons



SUCCSD is a spin eigenfunction and very close to **FCI**

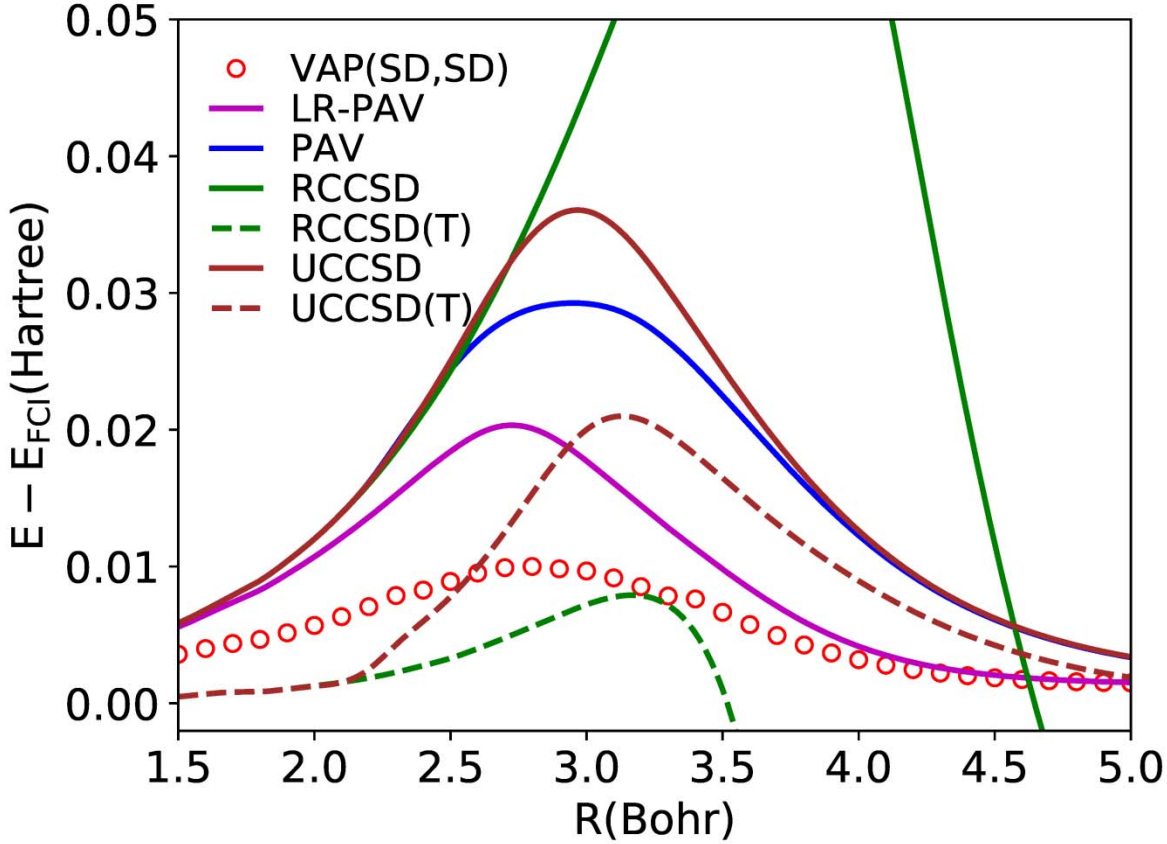
Y. Qiu, T. M. Henderson, J. Zhao & G. E Scuseria, *J. Chem. Phys.* **147**, 064111 (2017)

N_2 dissociation cc-pvdz



Y. Qiu, T. M. Henderson & GES, work in progress

N_2 dissociation cc-pvdz



Y. Qiu, T. M. Henderson & GES, work in progress

Take III: CCSD on PHF

$$E = \frac{\langle SUHF | (1+Z) e^{-T} H e^{T} | SUHF \rangle}{\langle PHF | PHF \rangle}$$

$$0 = \langle SUHF | \hat{T}^{\dagger} e^{-T} (H - E) e^{T} | SUHF \rangle$$

$$| SUHF \rangle = \hat{P} | \phi \rangle = \int_0^{\pi} d\beta \sin\beta \;\; e^{i\beta \hat{S}_y} | \phi \rangle$$

- **SUHF** is done variationally and **CCSD** non-variationally
- Conceptually the simplest model but **SUHF 6-rdm** is scary!
- Requires grid integration over rotated states
- Not implemented until recently, after ***drudge*** was born

CCSD on PHF
by *drudge**

When robots do the algebra and write the code, the **6-rdm** is no longer intimidating.

Algebraic manipulators can be instrumental in implementing algebraic involved theories.

* Jinmo Zhao & GES
(unpublished)

CCSD on PHF

Resulting residual:

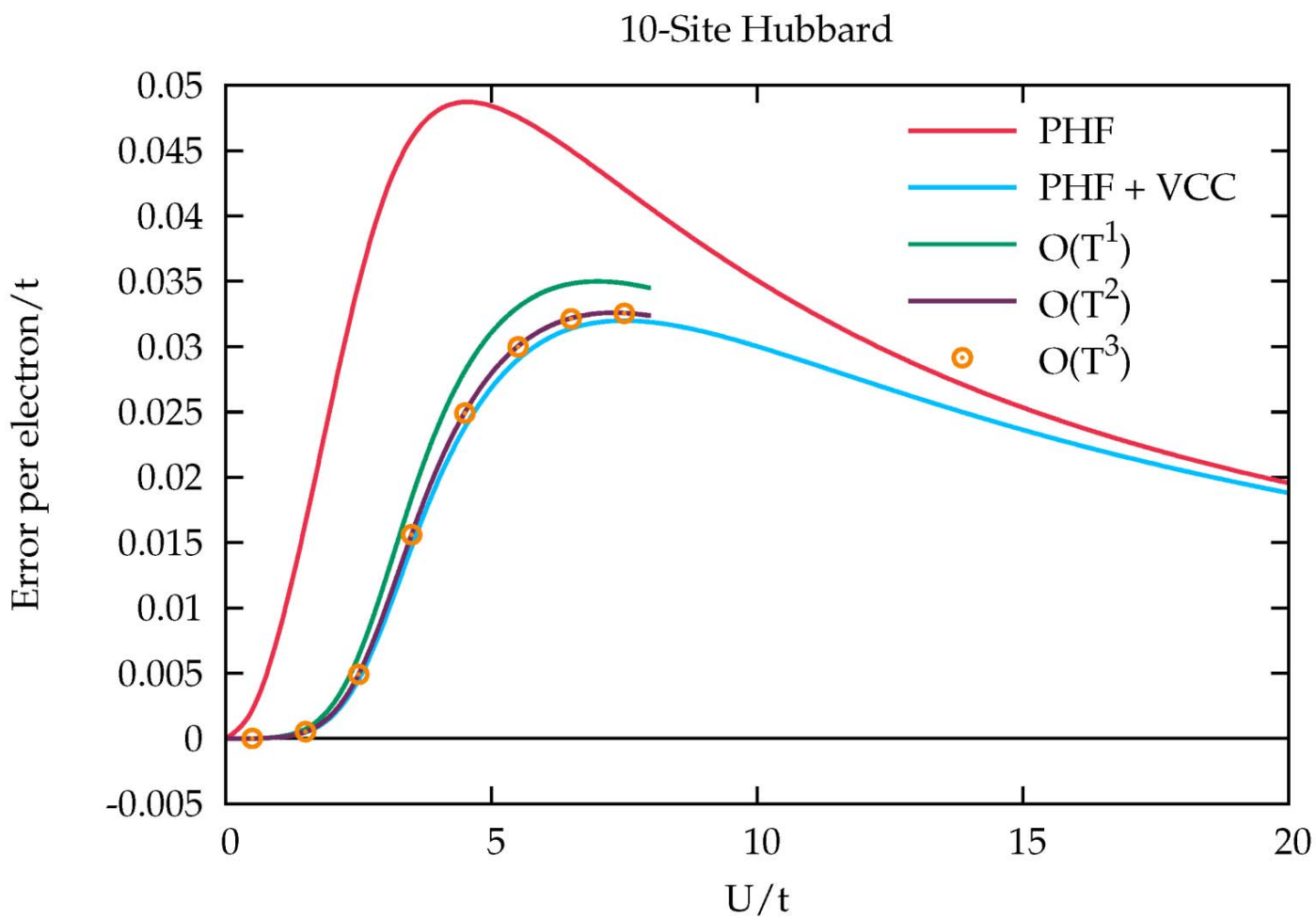
$$
\begin{aligned}
R_{ij}^{ab} \approx n_i\, n_j\, \bar{n}_a\, \bar{n}_b \Big\{ & \bar{v}_{ij}^{ab} + f_c^b\, t_{ij}^{ac} + f_c^a\, t_{ij}^{cb} - f_i^k\, t_{kj}^{ab} - f_j^k\, t_{ik}^{ab} \\
& + \frac{1}{2}\, (1 - n_c - n_d)\, \bar{v}_{cd}^{ab}\, t_{ij}^{cd} - \frac{1}{2}\, (1 - n_k - n_l)\, \bar{v}_{ij}^{kl}\, t_{kl}^{ab} \\
& + \frac{1}{4}\, [-1 + n_k + n_l + (n_c + n_d)\, (1 + n_k + n_l)]\, \bar{v}_{cd}^{kl}\, t_{kl}^{ab}\, t_{ij}^{cd} \\
& - \frac{1}{2}\, [n_d\, (1 - n_k - n_l) + n_k\, n_l]\, \bar{v}_{cd}^{kl}\, \left(t_{kl}^{bd}\, t_{ij}^{ac} + t_{kl}^{ad}\, t_{ij}^{cb}\right) \\
& - \frac{1}{2}\, [n_l\, (1 - n_c - n_d) + n_c\, n_d]\, \bar{v}_{cd}^{kl}\, \left(t_{jl}^{cd}\, t_{ik}^{ab} + t_{il}^{cd}\, t_{kj}^{ab}\right) \\
& + \mathcal{P}_{ij}\, \mathcal{P}_{ab}\, (n_k - n_c)\, \bar{v}_{jc}^{bk}\, t_{ik}^{ac} \\
& + (n_k - n_c)\, (n_l - n_d)\, \bar{v}_{cd}^{kl}\, \left(t_{ik}^{ac}\, t_{lj}^{db} - t_{ik}^{cb}\, t_{lj}^{ad}\right) \Big\}
\end{aligned}
$$

cf. spin-orbital **CCD** equations in JCP **139**, 104113 (2013)
(three quadratic channels: ladders, rings & xrings)

Two interesting limits: $\mathbf{n_{occ} = 1}$, $\mathbf{n_{unocc} = 0}$ (**RCCSD**),
$\mathbf{n_{occ} = n_{unocc} = \frac{1}{2}}$ (maximum entanglement)

CCSD on PHF

PHF = S^2 projected UHF = SUHF

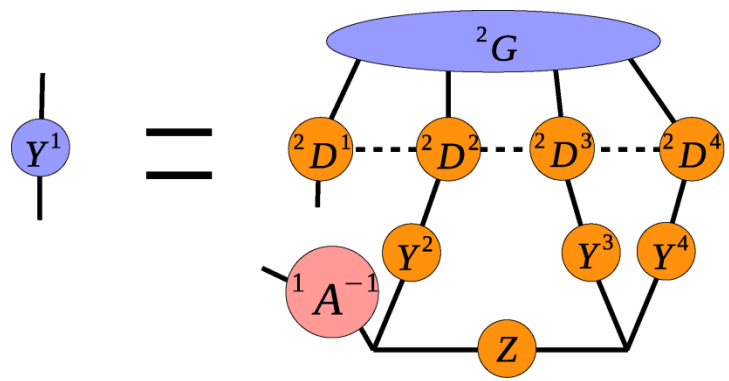


Similarity transformed CCSD on PHF with N^6 cost accurately reproduces the PHF+VCCD variational model

T. M. Henderson & GES, work in progress

Tensor Decomposition

- Using tensor hypercontraction and canonical polyadic decomposition, we break down both the interaction **(V)** and **CCSD** amplitudes **(T)** into matrices
- We next demand energy stationarity with respect to **T** decomposition factors :



- Solving for the factors above yields an **O(N^4)** procedure with sub-millihartree accuracy

Details: Tensor-structured coupled cluster theory, R. Schutski, J. Zhao, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys.* **147**, 184113 (2017).

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