Merging Symmetry Restoration and Coupled Cluster Theories

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Theory and applications of RPA-and-beyond methods in physics and chemistry
Paris, UPMC Jussieu, 2-4 May 2017

Outline

- Successes & failures of
  - **Coupled Cluster** (CC) theory
  - **Symmetry breaking & restoration (SB&R)**
- Their merger
  - Using a **symmetry adapted** reference
  - Using a **symmetry broken** reference
- A few benchmark results

Weak correlation paradigm

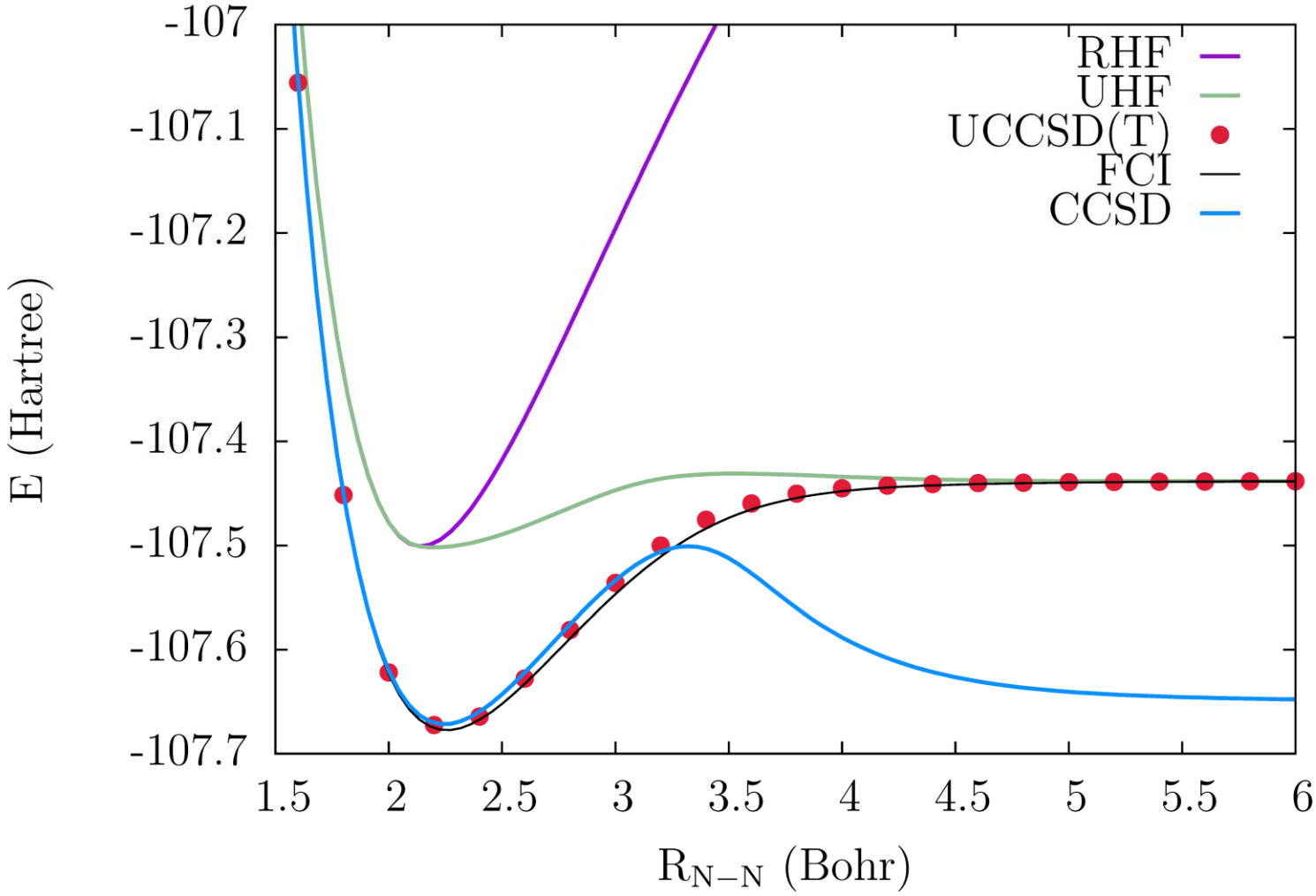
in quantum chemistry :

single reference

coupled cluster theory

an incredibly successful theory but…

N_2 dissociation



min basis:
strong correlation dominates at dissociation

CCSD has an unphysical bump
UCCSD(T) : right energy but wrong wavefunction

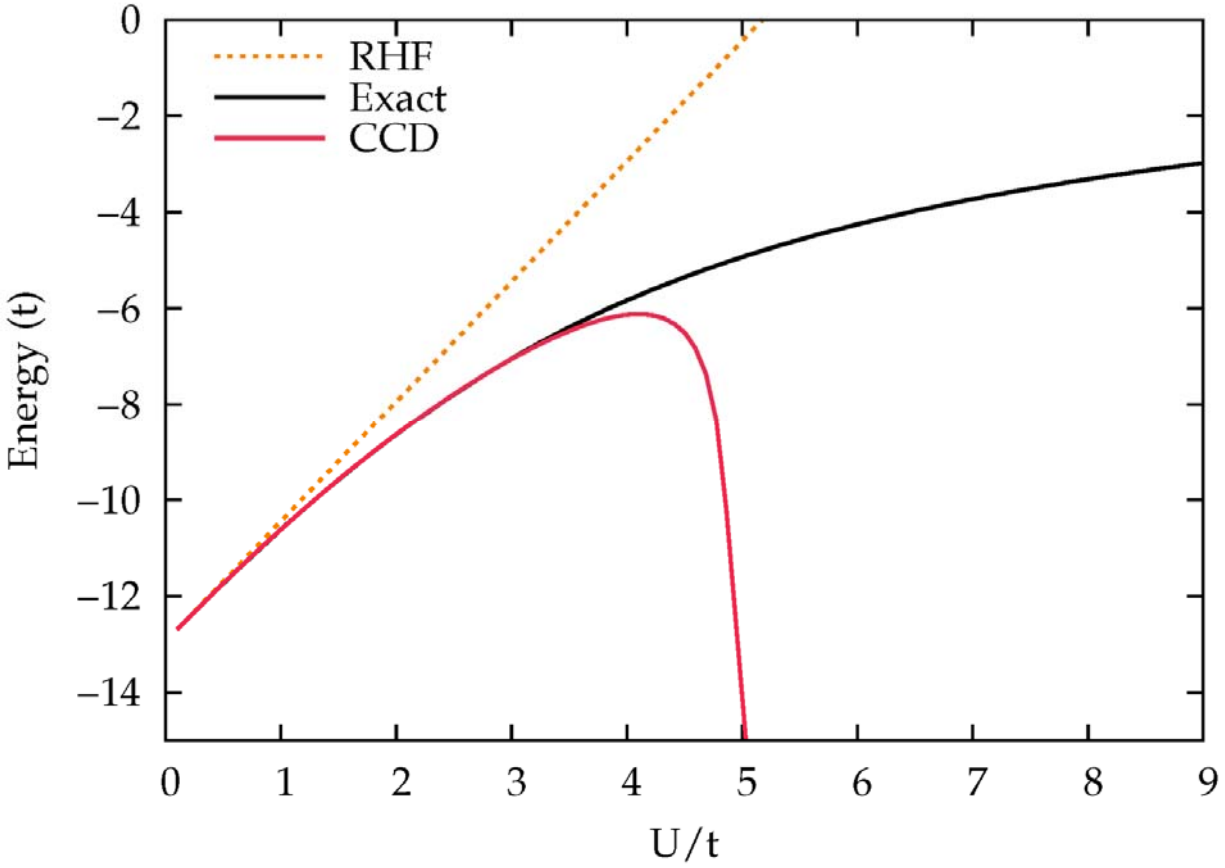
Repulsive Hubbard model

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

- U = 0 => **RHF** is exact
- U small => **weakly** correlated
- U large => **strongly** correlated
- Exact solution is known in **1D**
- Model has a **local interaction** but at large U yields **huge degeneracy** and **collective excitations**

CC catastrophic failure

10x1 Hubbard ring (**PBC**); **10** sites; half-filling
As **U/t** increases, the system gets **strongly correlated**

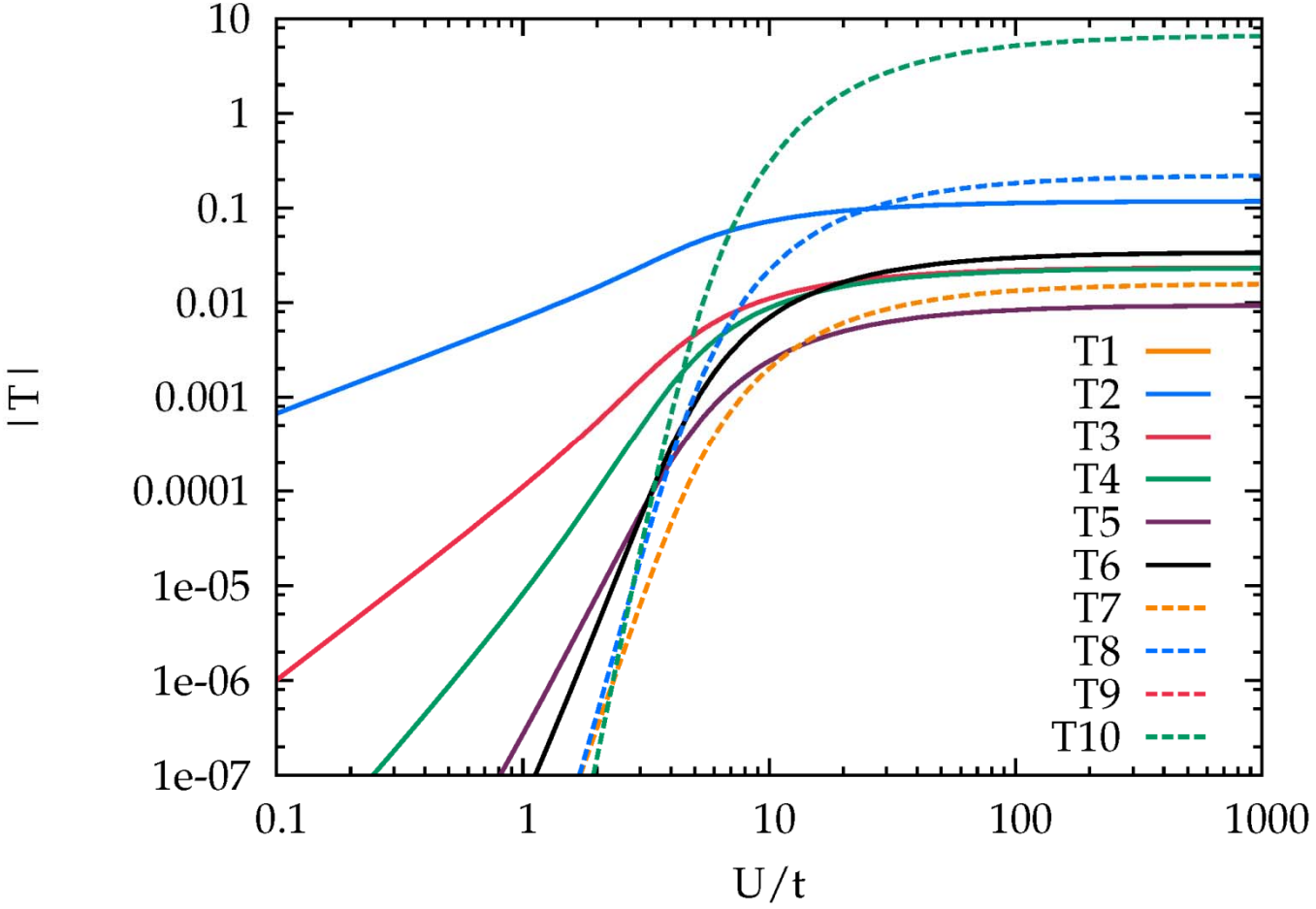


$T_1 = 0$
by symmetry

CCDT, CCDTQ… all fail similarly, except for **full CC**
UCCSD is fine but we lose good quantum numbers
Variational CCD (not shown) undercorrelates

Full CC reverse-engineered from FCI

10x1 Hubbard ring; 10 electrons ; **RHF** (plane wave) basis



$T_1 = T_9 = 0$ by symmetry

In the **large U limit** (strongly correlated), **full-CC** has **no natural truncation.**
Note how large are T_3 & T_4; CCSD assumes $T_3 \sim T_4 \sim 0$

Weak & strong correlation

- **Weak** correlation: $|H_1| >> |H_2|$, **RHF** is stable, symmetries do not break, **PT** works and ***CC*** is king

- **Strong** correlation: $|H_1| << |H_2|$, **RHF** is unstable, symmetries break spontaneously, ***CC*** fails and **PHF** is important

- **Symmetry implies degeneracy and degeneracy near the ground state implies strong correlation that can be spotted by spontaneous symmetry breaking of the RHF solution, a symmetry dilemma**

RHF instabilities

- The **diagonal** of the hessian matrix is very instructive:

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

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

- For the hessian to have a negative eigenvalue, a negative diagonal element is **sufficient** but not **necessary**.
- Under orbital near-degeneracy (small HOMO-LUMO gap), the triplet instability occurs first.
- Yet, strong correlation can occur with very large gaps.
- Best example: fullerenes and particularly C_{60}

Symmetry Breaking & Restoration

- When symmetries break, we can **restore them by projection: $P\,|\Phi\rangle$**
- We can also do **variation after projection**:
  Optimize $|\Phi\rangle$ to minimize $E \sim \langle\Phi|\, P^\dagger H P\, |\Phi\rangle$ with $\delta E = 0$
  (**deliberate** symmetry breaking and restoration)
- P is an integral operator that is discretized over a grid (next slide)
- Equivalent to **CI** between non-orthogonal determinants with known **CI** coefficients: only the orbitals need to be optimized
- Our work (**2011-2015**):
  - **Number** (**N**), **Spin** (**S^2** and **S_z**)
  - **Complex Conjugation** (**K**), **Point Group** (**PG**)
  - **Under PBC: Linear Momentum** (**LM**), **Space Group** (**SG=LM+PG**)

S^2 spin projection: SUHF

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

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

One can simply impose rotational invariance in spin space

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

J. Chem. Phys. **136**, 164109 (2012)

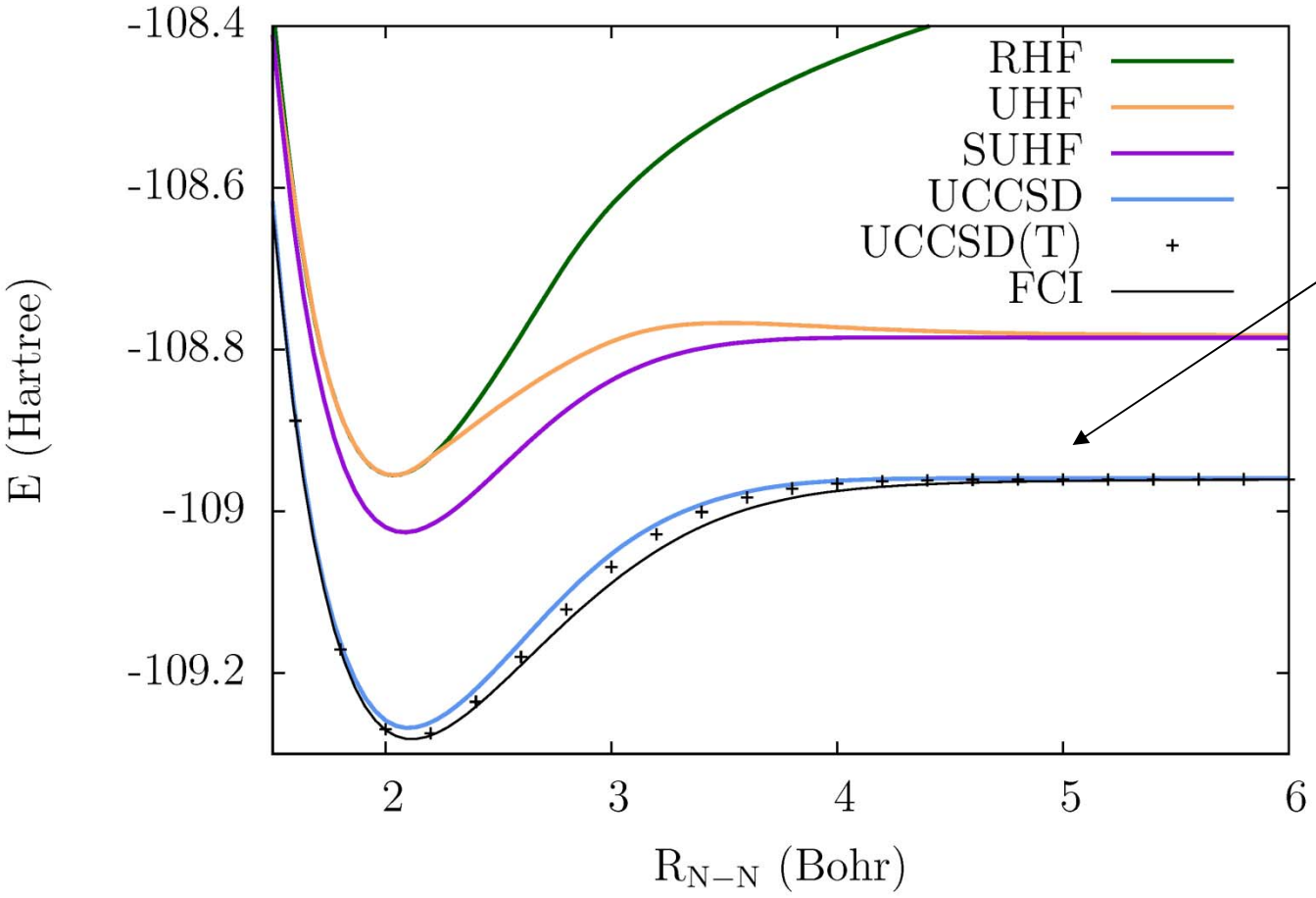
This leads to simple equations with ~ **HF x N_g** computational cost

$$|SUHF\rangle = \hat{P}|\phi\rangle = \int_0^{\pi} d\beta \sin\beta \; e^{i\beta \hat{S}_y} |\phi\rangle, \qquad \langle\phi| e^{i\beta \hat{S}_y} |\phi\rangle \neq 0$$

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

N_2 dissociation

cc-pvDZ basis : weak correlation is important everywhere



Residual weak correlations are large

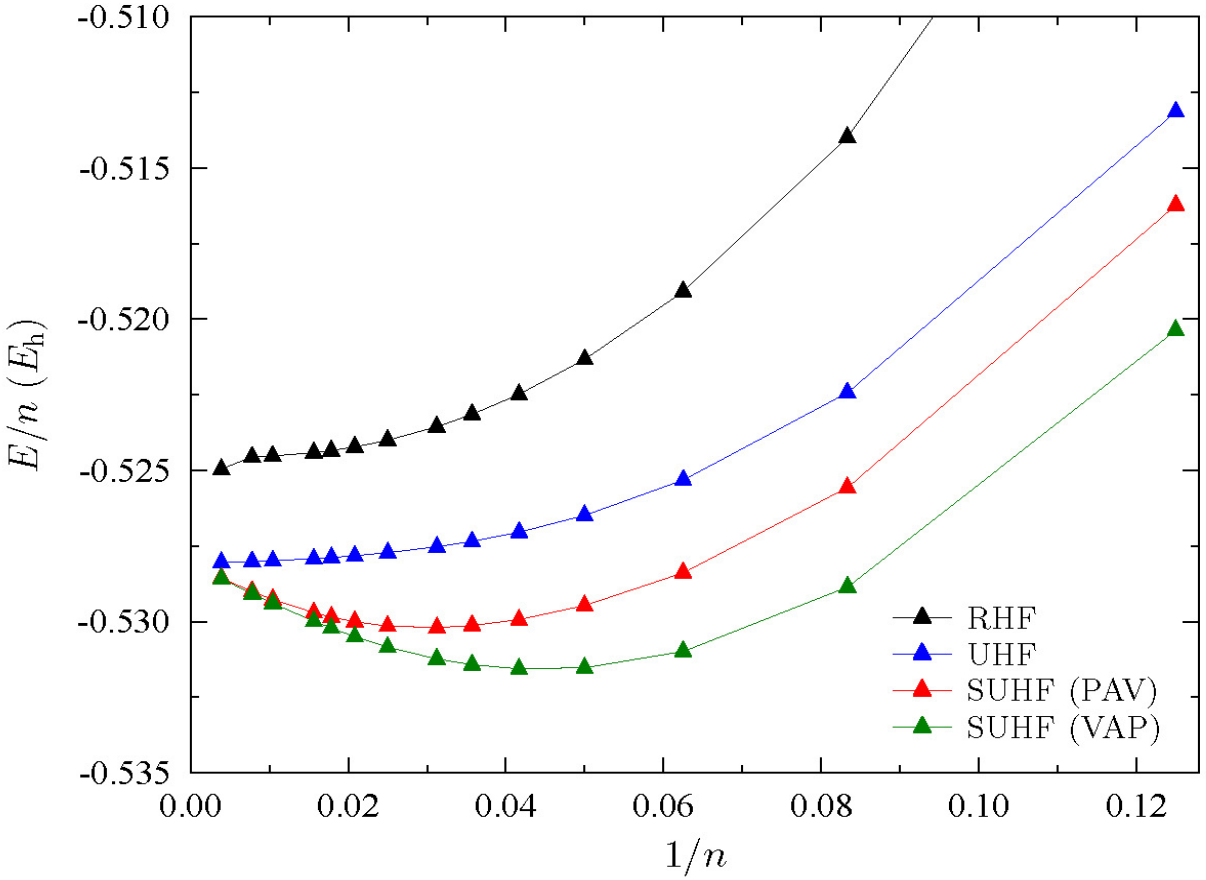
UCCSD(T) right energy but wrong Ψ

RCCSD (not shown) is not good

SUHF includes all **strong/static** but very little **weak/dynamic** correlation

Another problem: SUHF size extensivity

Rings of equidistant **H** atoms @ 1.80 Bohr with minimum basis



SUHF yields **zero** correlation energy **per electron** with respect to **UHF** in infinite systems

PHF and CC

Merging PHF with CC is challenging because they are dissimilar theories !

- **CC** is **not variational** but **size-extensive**
  It uses **ph** excitations and **orthogonal** determinants

- **PHF** is **variational**; size extensive component is **UHF**
  It uses rotations and **non-orthogonal** determinants

- We are pursuing two mergers:
  - Express **PHF** in terms of **ph** excitations of **RHF** and do **PHF** together with **RCCSD**
  - Work in the unrestricted basis (**UCCSD**) and then project

PHF + CC

- **CC** is based on a similarity transformation that **does not change** the Hamiltonian spectrum
- H_{eff} = **exp(-T) H exp(T)** truncates at 4^{th} commutator (6-b)
- **CCSD** is exact if given the exact T_3 and T_4

- **Symmetry adapted reference model**

  Bad news: T_3 and T_4 are large and cannot be neglected

  Good news: T_3 and T_4 factorize from one-body amplitudes and we **now** understand their structure

- **Broken symmetry reference model**

  Good news: U_3 and U_4 are small and can be neglected

  Bad news: We lose good quantum numbers and restoring symmetries is complicated

SUHF as a ph excitation ansatz

- **UHF** can be obtained from a **Thouless** rotation:

$$\left|UHF\right\rangle = e^{T_1+U_1^0}\left|RHF\right\rangle$$

- T_1 is the totally symmetric component (**s=0,m=0**) of singles
- U_1 is the **(s=1,m=0)** component that breaks S^2

$$T_1 = \sum t_i^a \left(c_{a\uparrow}^\dagger c_{i\uparrow} + c_{a\downarrow}^\dagger c_{i\downarrow}\right) = \sum t_i^a E_a^i, \quad U_1^0 = \sum u_i^a \left(c_{a\uparrow}^\dagger c_{i\uparrow} - c_{a\downarrow}^\dagger c_{i\downarrow}\right)$$

- The **projected spin state** is:

$$\left|SUHF\right\rangle = e^{T_1}\hat{P}(e^{U_1})\left|RHF\right\rangle = e^{T_1}F(K_2)\left|RHF\right\rangle$$

- The polynomial **F(K$_2$)** contains only even powers of **U$_1$**

$$F(K_2) = I + K_2 + \frac{3}{10}K_2^{\,2} + \frac{3}{70}K_2^{\,3} + \frac{1}{280}K_2^{\,4} + \ldots = \frac{\sinh\sqrt{6K_2}}{\sqrt{6K_2}}$$

$$K_2 = \frac{1}{2}\hat{P}\left(U_1^0 U_1^0\right) = -\frac{1}{6}\sum (u_i^a u_j^b + 2u_i^b u_j^a) E_a^i E_b^j$$

Y. Qiu, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys.* **145**, 111102 (2016)

Similar idea for Number projection yields a Bessel polynomial of ph excitations:
Phys. Rev. **B 93**, 125124 (2016)

SUHF + CCSD

- Proof of principle results can be obtained for the joint **SUHF + CCSD** ansatz on small systems using a **variational** representation of both components:

$$E = \frac{\left\langle RHF \left| F(K_2^\dagger) e^{T_1^\dagger + T_2^\dagger} H e^{T_1 + T_2} F(K_2) \right| RHF \right\rangle}{\left\langle RHF \left| F(K_2^\dagger) e^{T_1^\dagger + T_2^\dagger} e^{T_1 + T_2} F(K_2) \right| RHF \right\rangle}$$

- Think of **$F(K_2)$ |RHF>** as a multireference for **CCSD**
- Two examples:

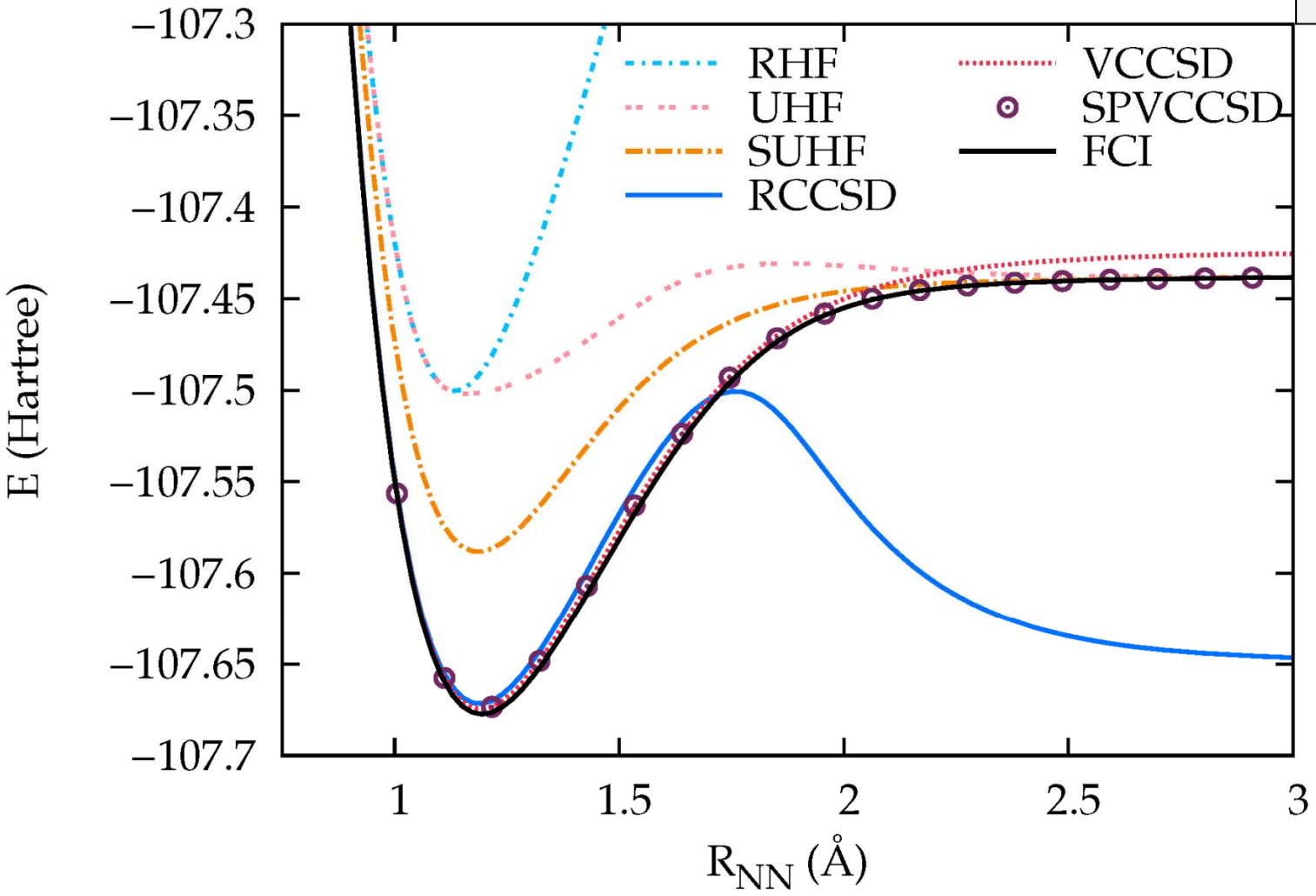
  N_2 dissociation in a minimum basis

  10x1 Hubbard at half-filling

- Projected Hartree Fock Theory as a Polynomial Similarity Transformation Theory of Single Excitations, Y. Qiu, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys.* **145**, 111102 (2016).
- Projected Hartree-Fock as a polynomial of particle-hole excitations and its combination with variational coupled cluster theory, Y. Qiu, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys. in press.*

N_2 dissociation

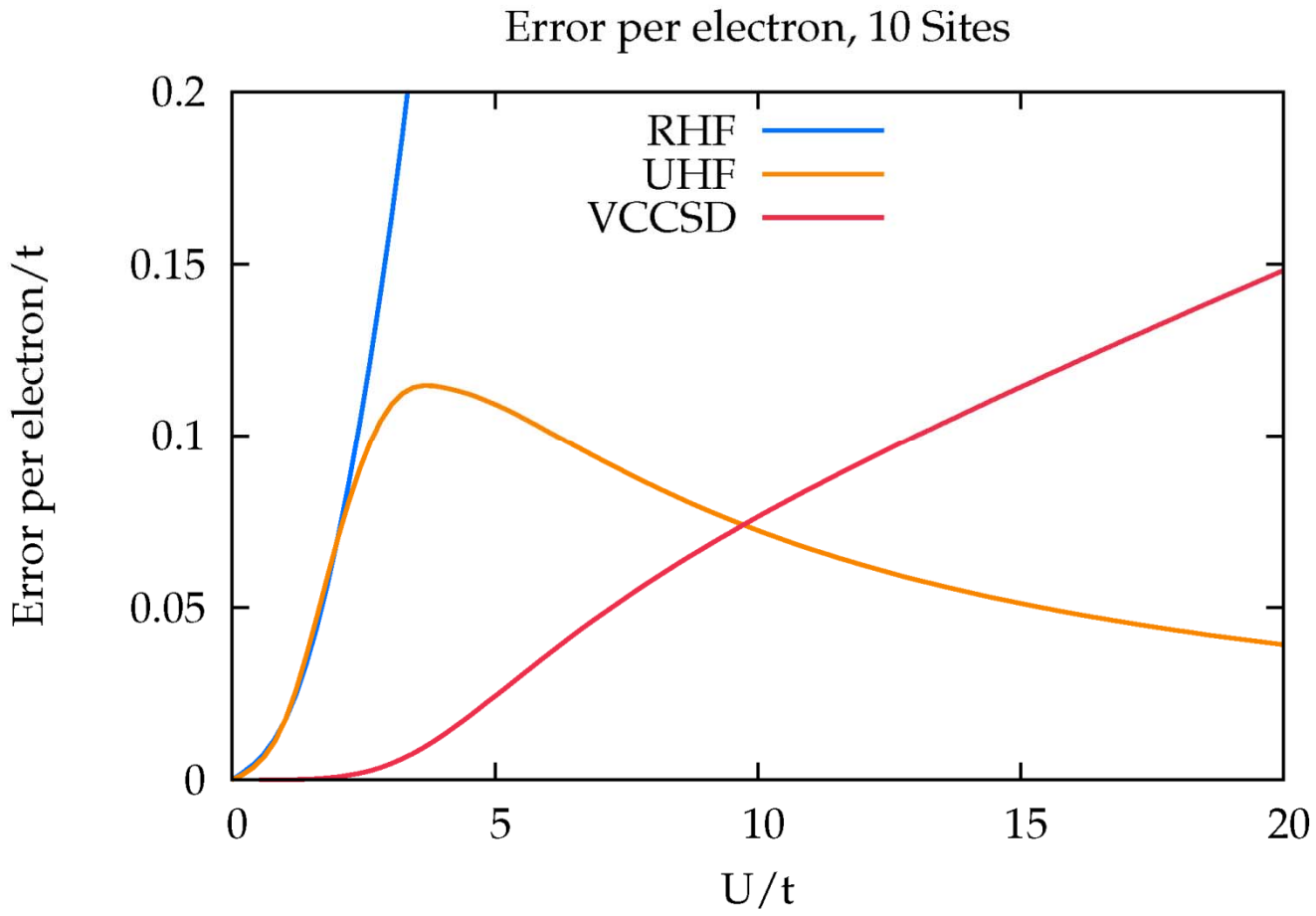
min basis



VCCSD does not get the right answer at dissociation
SPVCCSD = **SUHF+VCCSD** is very accurate everywhere

VCCSD

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

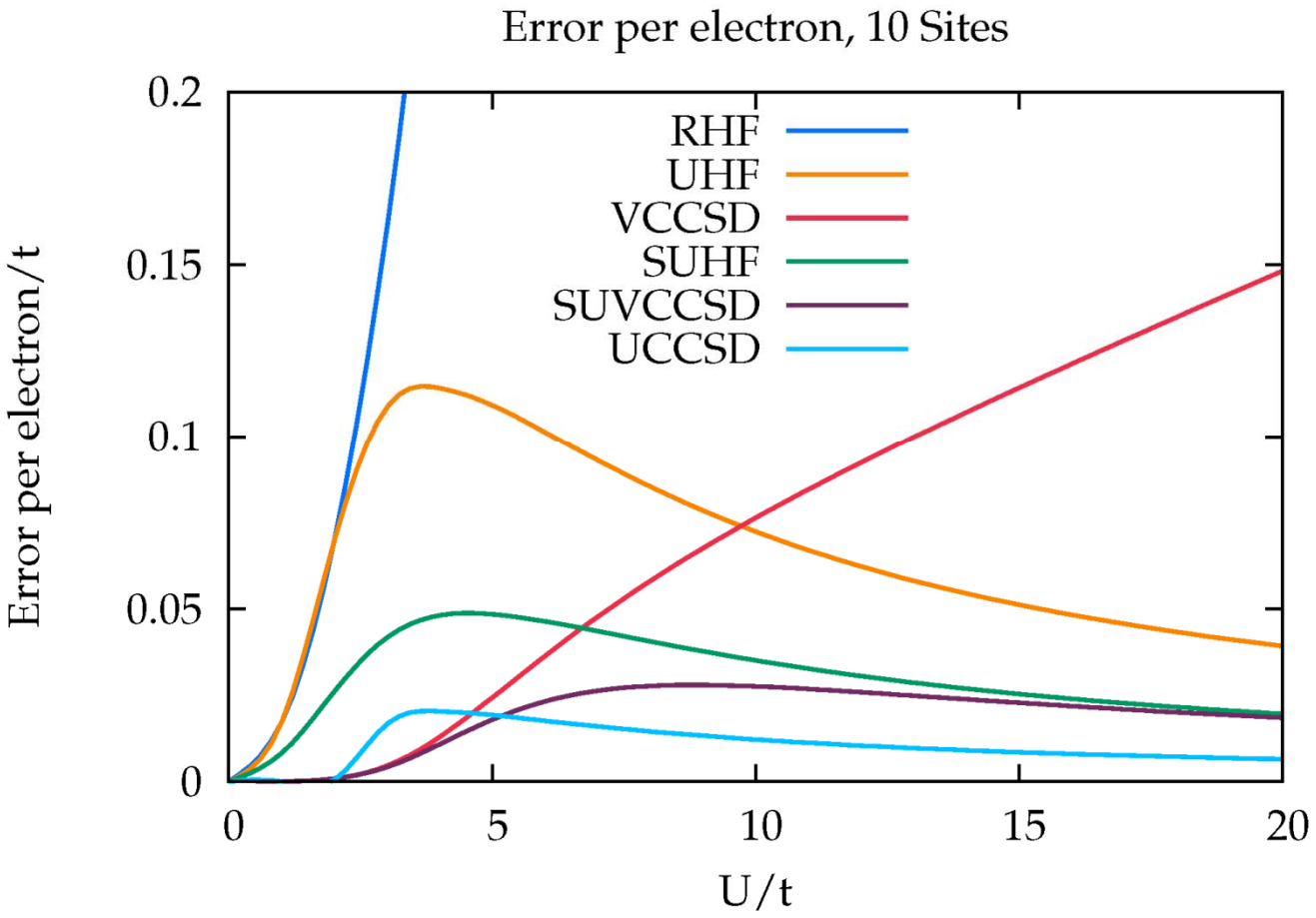


RHF basis

VCCSD undercorrelates badly.
exp(T_2) misses important **high-order symmetry collective** excitations

SUHF + VCCSD

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



RHF basis

UCCSD has better energy than **SUHF+VCCSD**

SGHF as a ph excitation ansatz

- **GHF** (broken S^2 and S_z) can be obtained by a **Thouless** rotation:

$$\left|GHF\right\rangle = e^{T_1+U_1^0+U_1^1+U_1^{-1}}\left|RHF\right\rangle$$

T_1 is the totally symmetric component (**s=0,m=0**) of singles
U_1^0 is the **(s=1,m=0)** component that breaks S^2
U_1^1 is the **(s=1,m=1)** component that breaks S_z by $\Delta m=+1$
U_1^{-1} is the **(s=1,m=-1)** component that breaks S_z by $\Delta m=-1$

$$T_1 = \sum t_i^a \left(c_{a\uparrow}^\dagger c_{i\uparrow} + c_{a\downarrow}^\dagger c_{i\downarrow}\right), \qquad U_1^1 = \sum v_i^a c_{a\uparrow}^\dagger c_{i\downarrow}$$

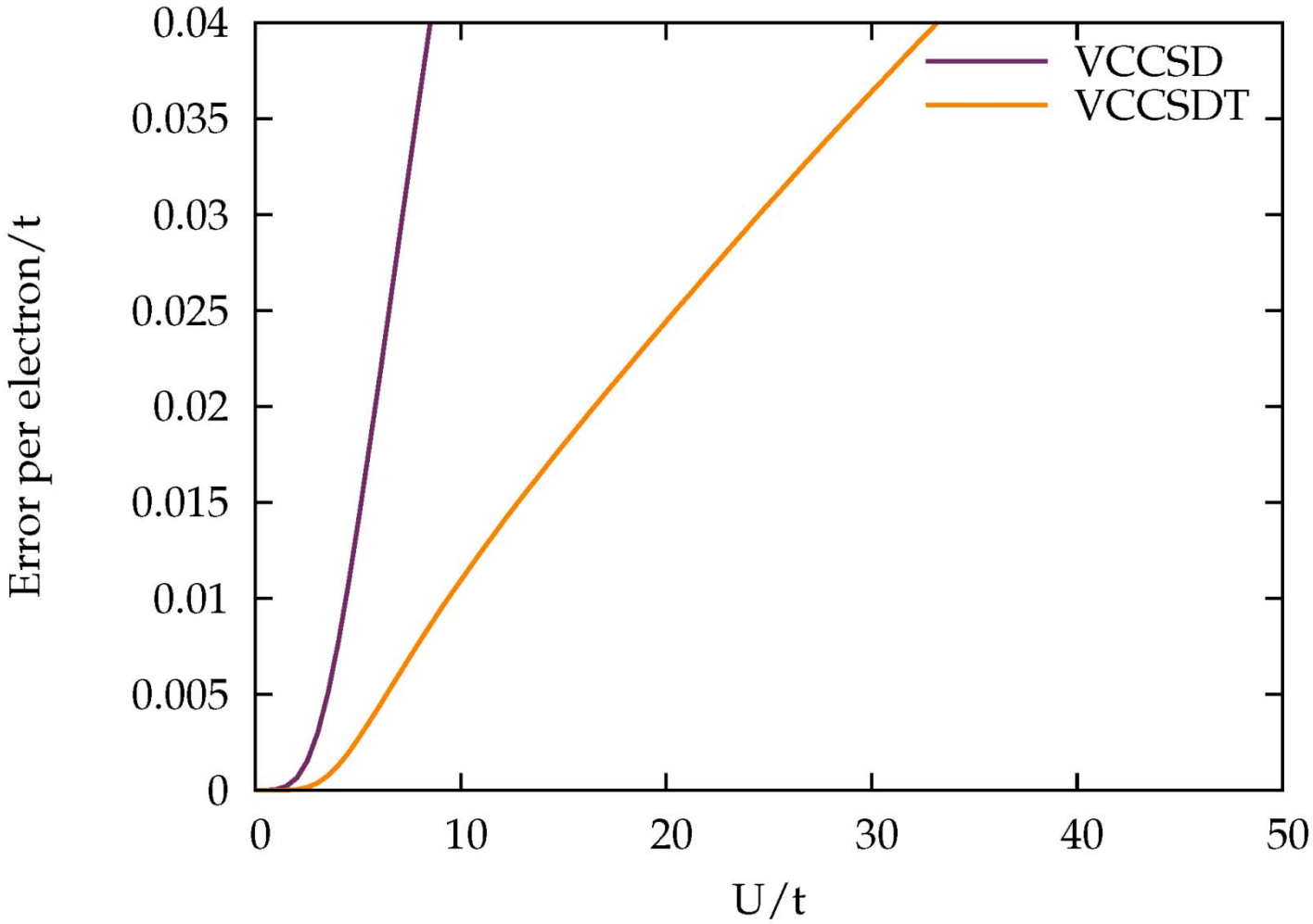
$$U_1^0 = \sum u_i^a \left(c_{a\uparrow}^\dagger c_{i\uparrow} - c_{a\downarrow}^\dagger c_{i\downarrow}\right), \qquad U_1^{-1} = \sum w_i^a c_{a\downarrow}^\dagger c_{i\uparrow}$$

- The **projected spin state** is:

$$\left|SGHF\right\rangle = e^{T_1}\hat{P}(e^{U_1^0+U_1^1+U_1^{-1}})\left|RHF\right\rangle = e^{T_1}G(K_2,K_3,K_4)\left|RHF\right\rangle$$

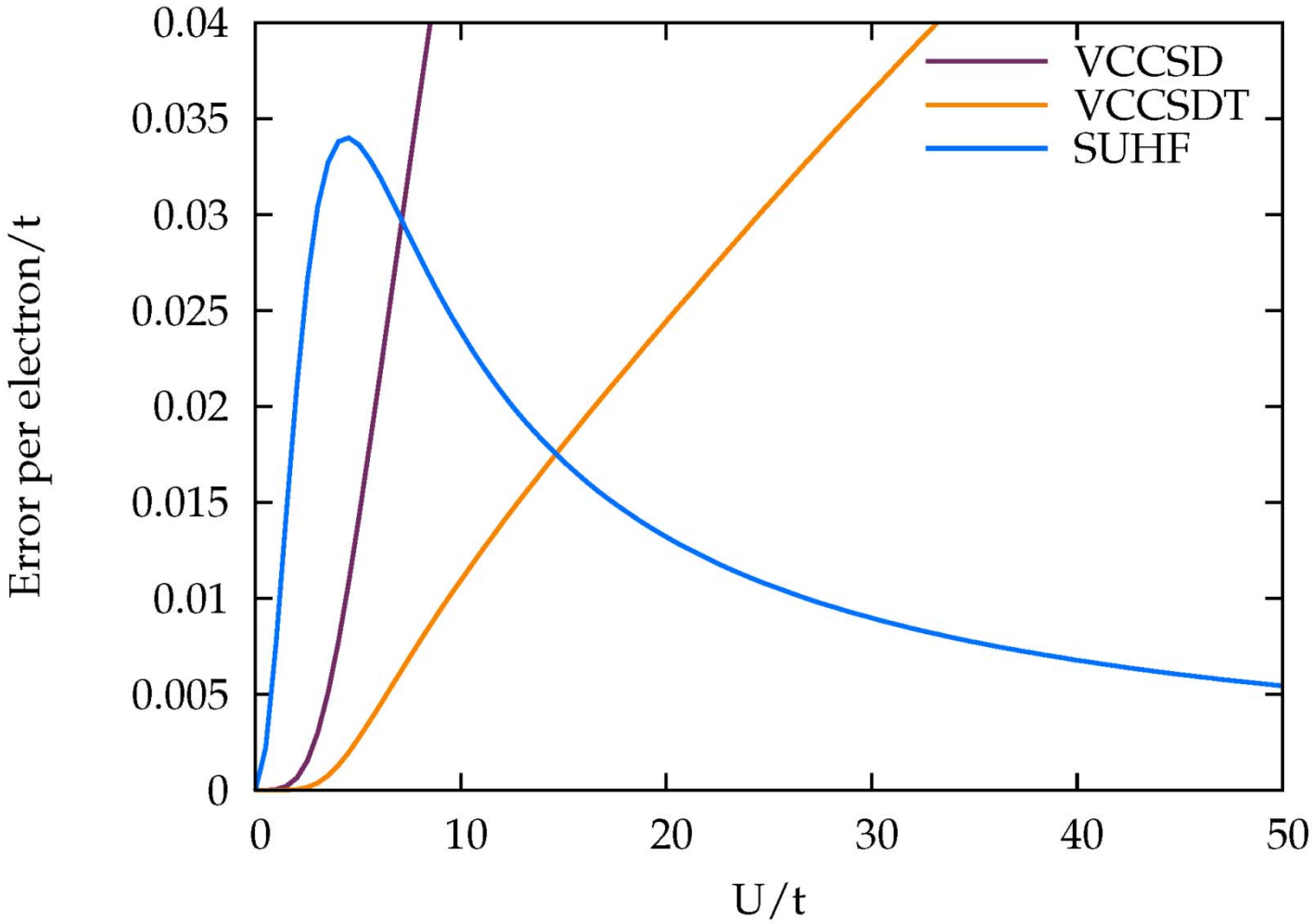
T. M. Henderson & G. E. Scuseria, in preparation.

Error per electron

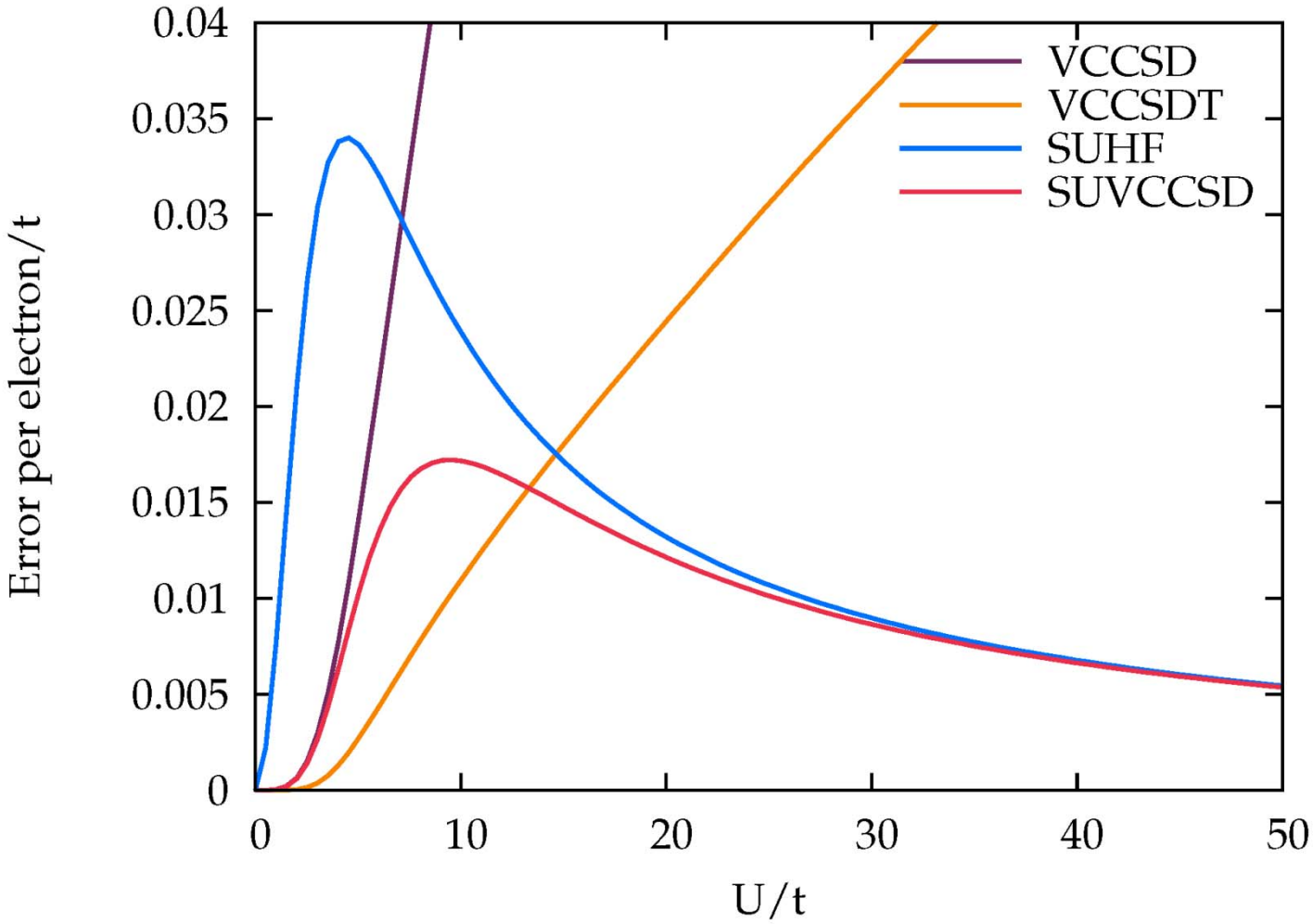


VCCSD & VCCSDT undercorrelate.
High-order collective excitations are important and **exp(T_2+T_3)** misses them !

Error per electron



Error per electron



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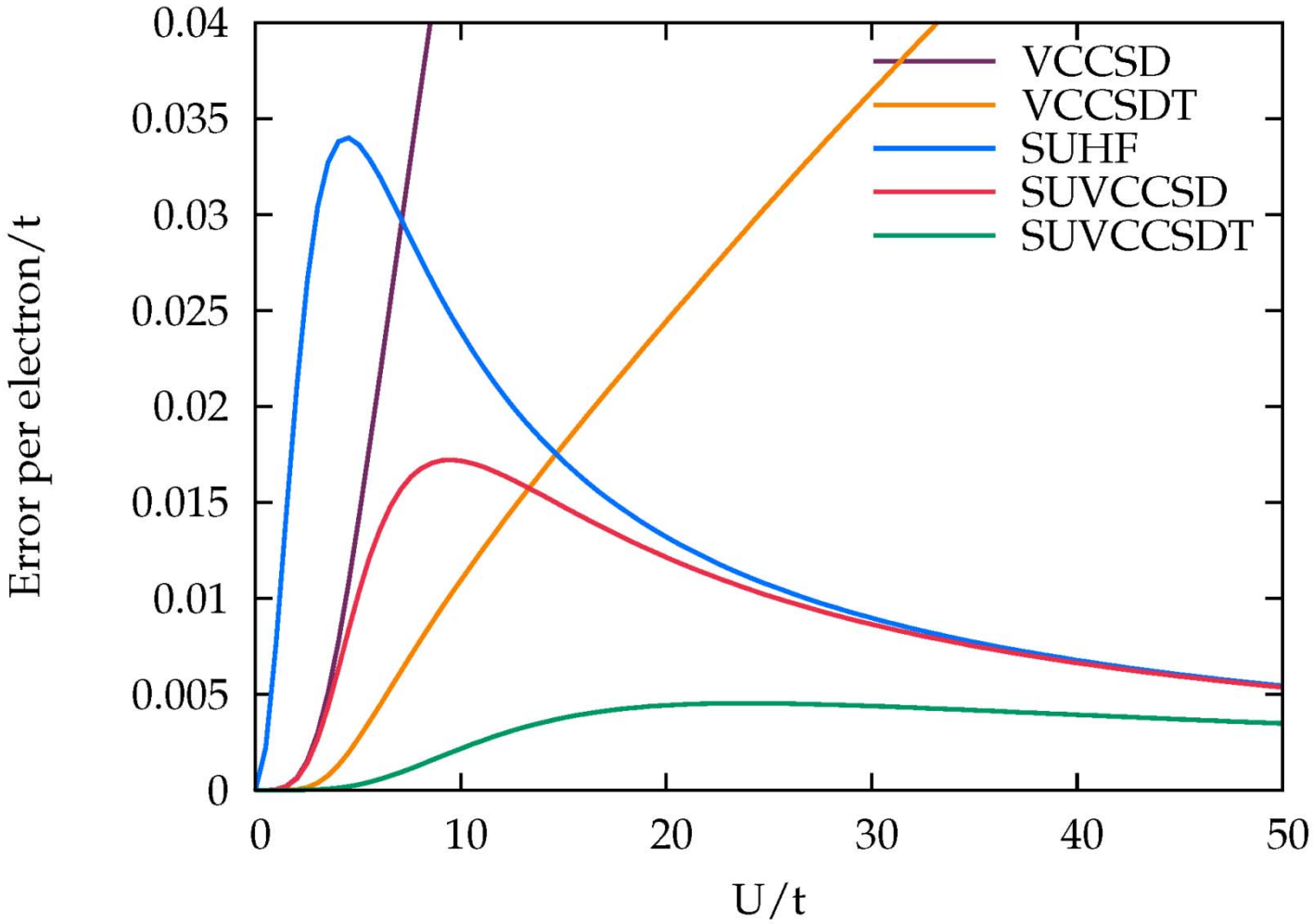
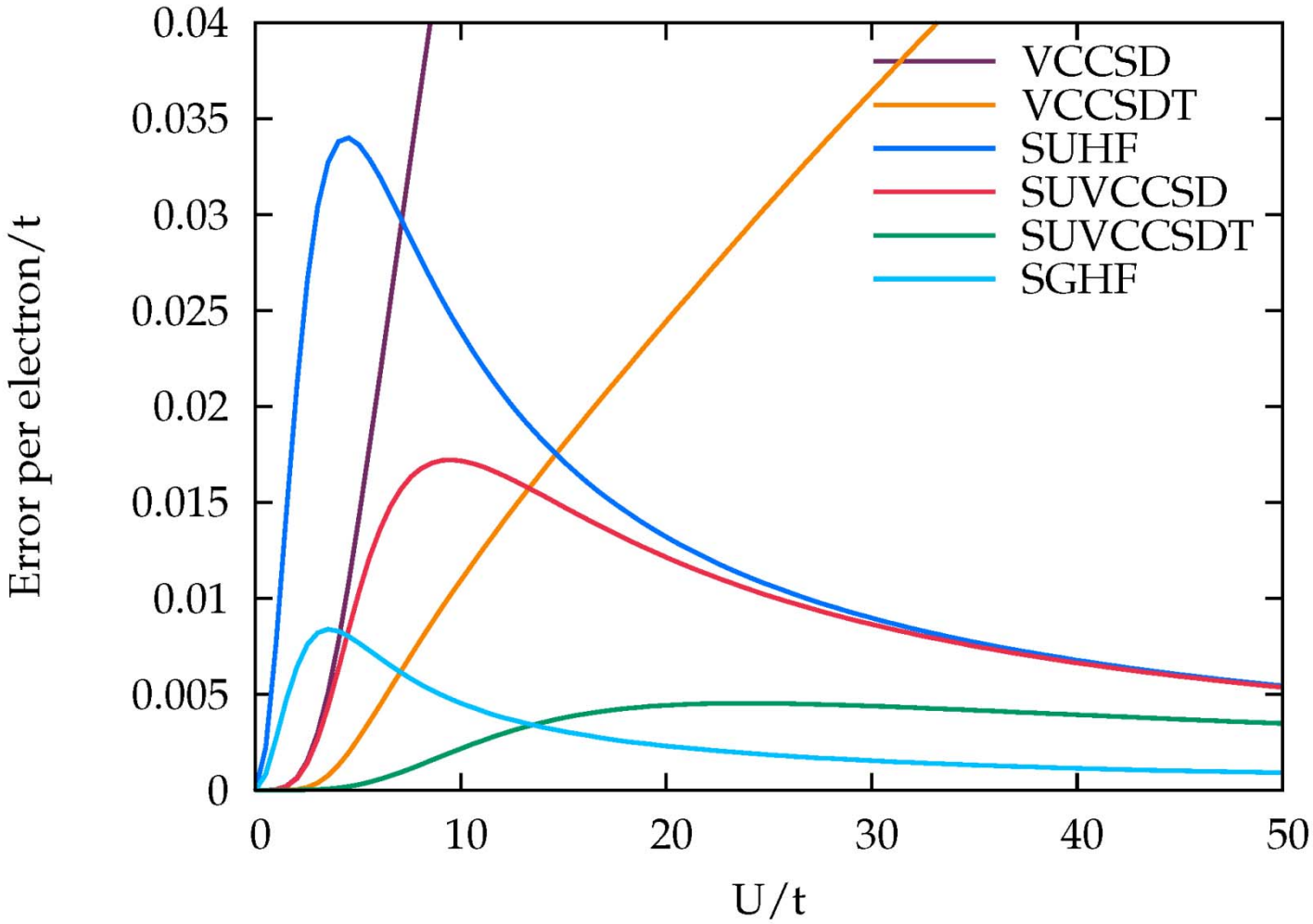


Error per electron



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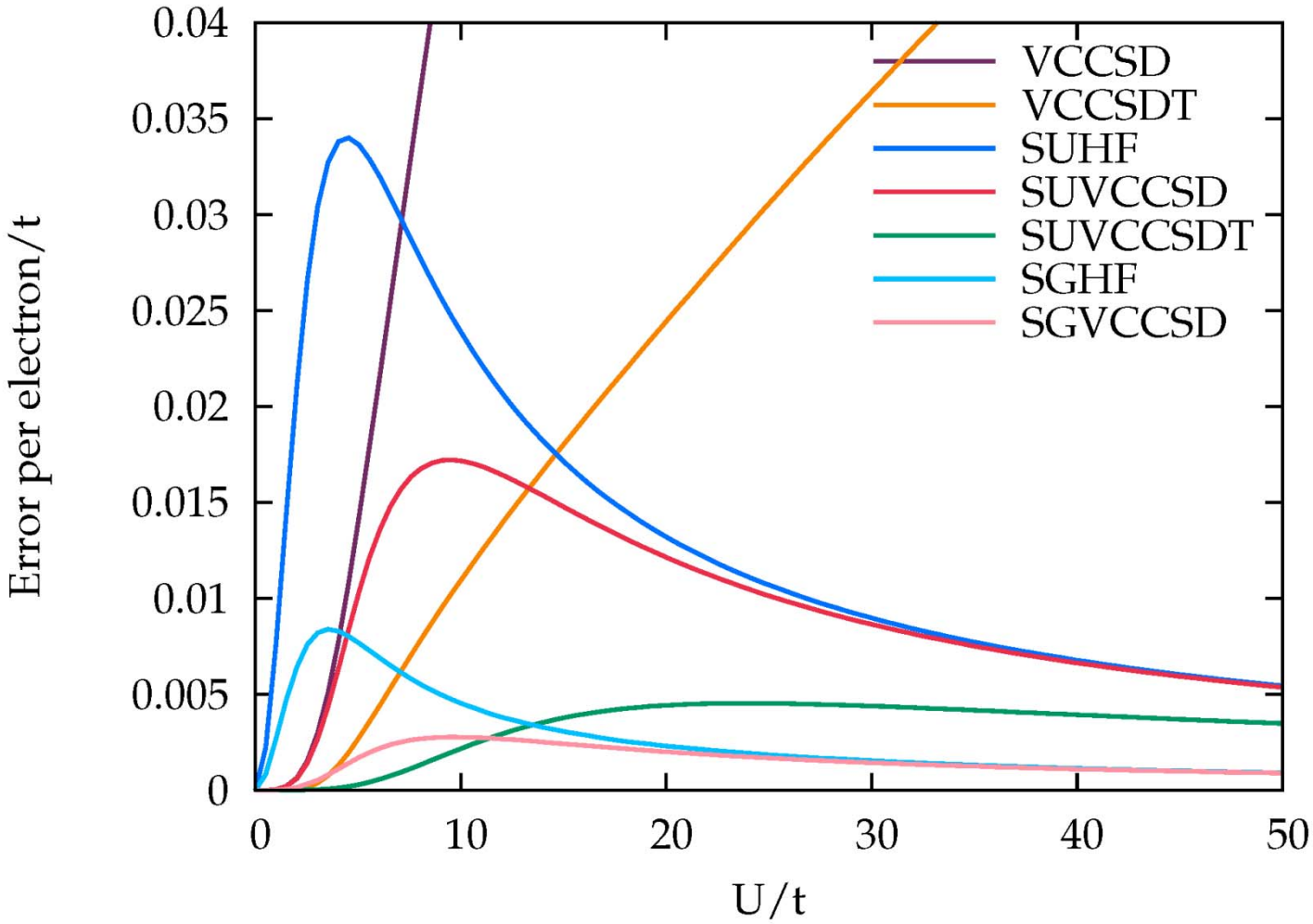
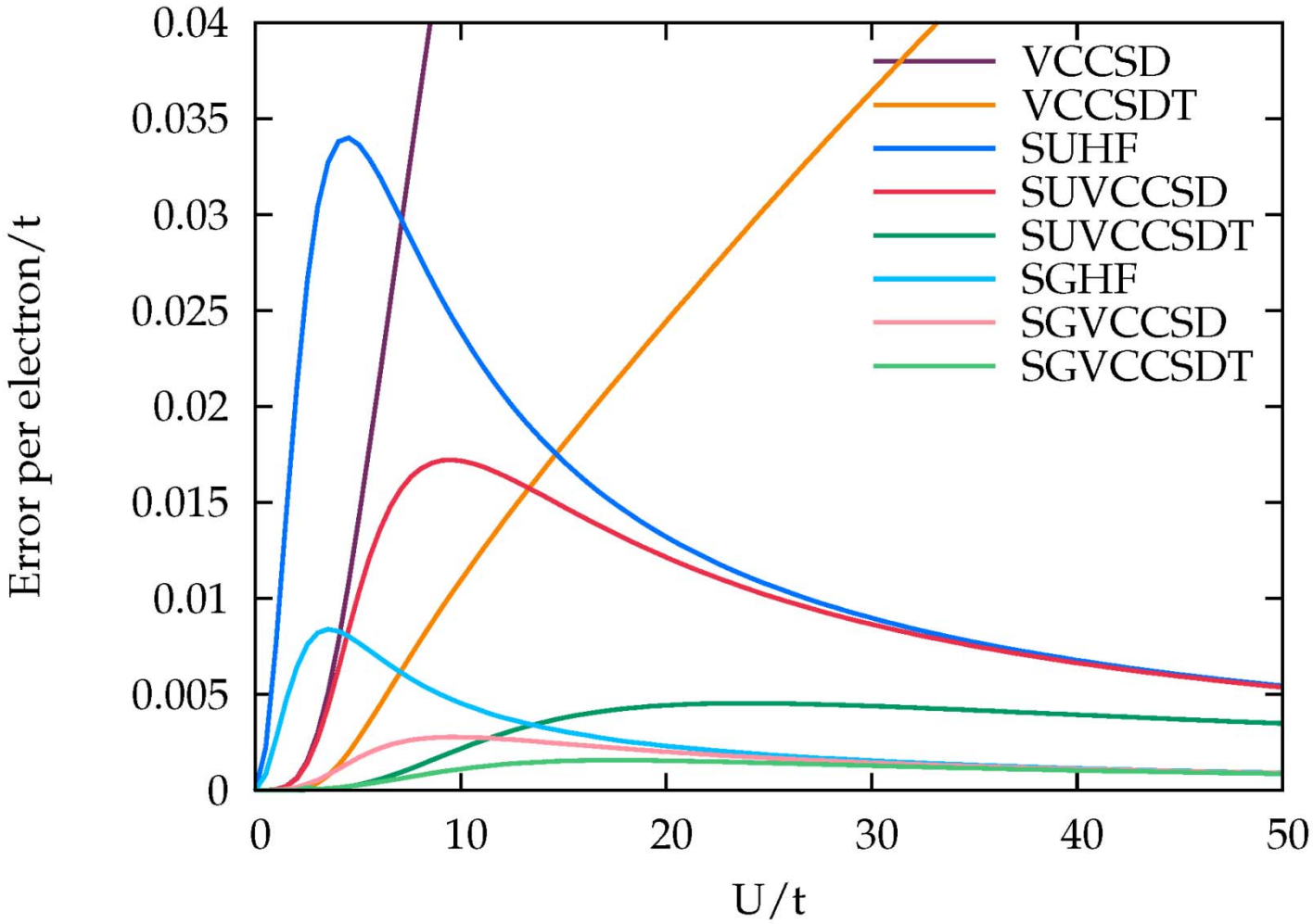


Error per electron



Proof of principle results. Combinatorial cost. Not practical. Similarity transformed version in progress.

Projected UCCSD

$$E = \frac{\langle UHF | (I + Z_1 + Z_2) e^{-U_1 - U_2} H \hat{P} e^{U_1 + U_2} | UHF \rangle}{\langle UHF | (I + Z_1 + Z_2) e^{-U_1 - U_2} \hat{P} e^{U_1 + U_2} | UHF \rangle}$$

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

S² projection

Main result of this work:

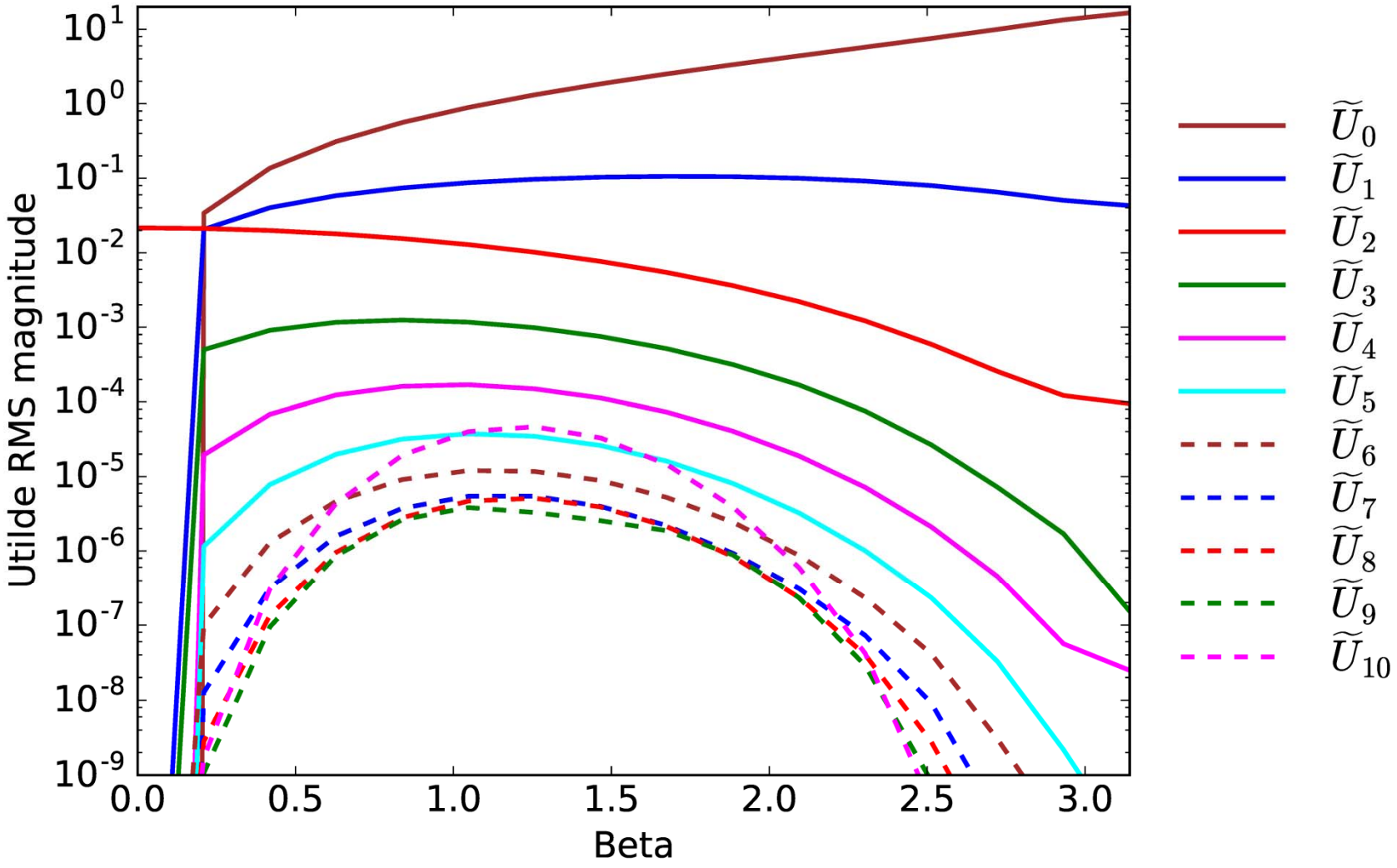
$$e^{i\beta \hat{S}_y} e^{U_1 + U_2} = e^{\tilde{U}_0(\beta)} e^{\tilde{U}_1(\beta) + \tilde{U}_2(\beta) + \tilde{U}_3(\beta) + \tilde{U}_4(\beta) + \ldots}$$

disconnected terms cancel out.

The $\tilde{U}_n(\beta)$ afford truncation in the spirit of **CC** theory

Ethan Qiu, Tom Henderson & GES, in preparation

Projected UCCSD



10x1 Hubbard $\frac{1}{2}$ filling U=10

Projected UCCSD

$$E = \frac{\langle UHF | (I + Z_1 + Z_2) e^{-U_1 - U_2} H \hat{P} e^{U_1 + U_2} | UHF \rangle}{\langle UHF | (I + Z_1 + Z_2) e^{-U_1 - U_2} \hat{P} e^{U_1 + U_2} | UHF \rangle}$$

Three models:

(1) **PAV** : **Z=0** and U_1/U_2 from **UCCSD**

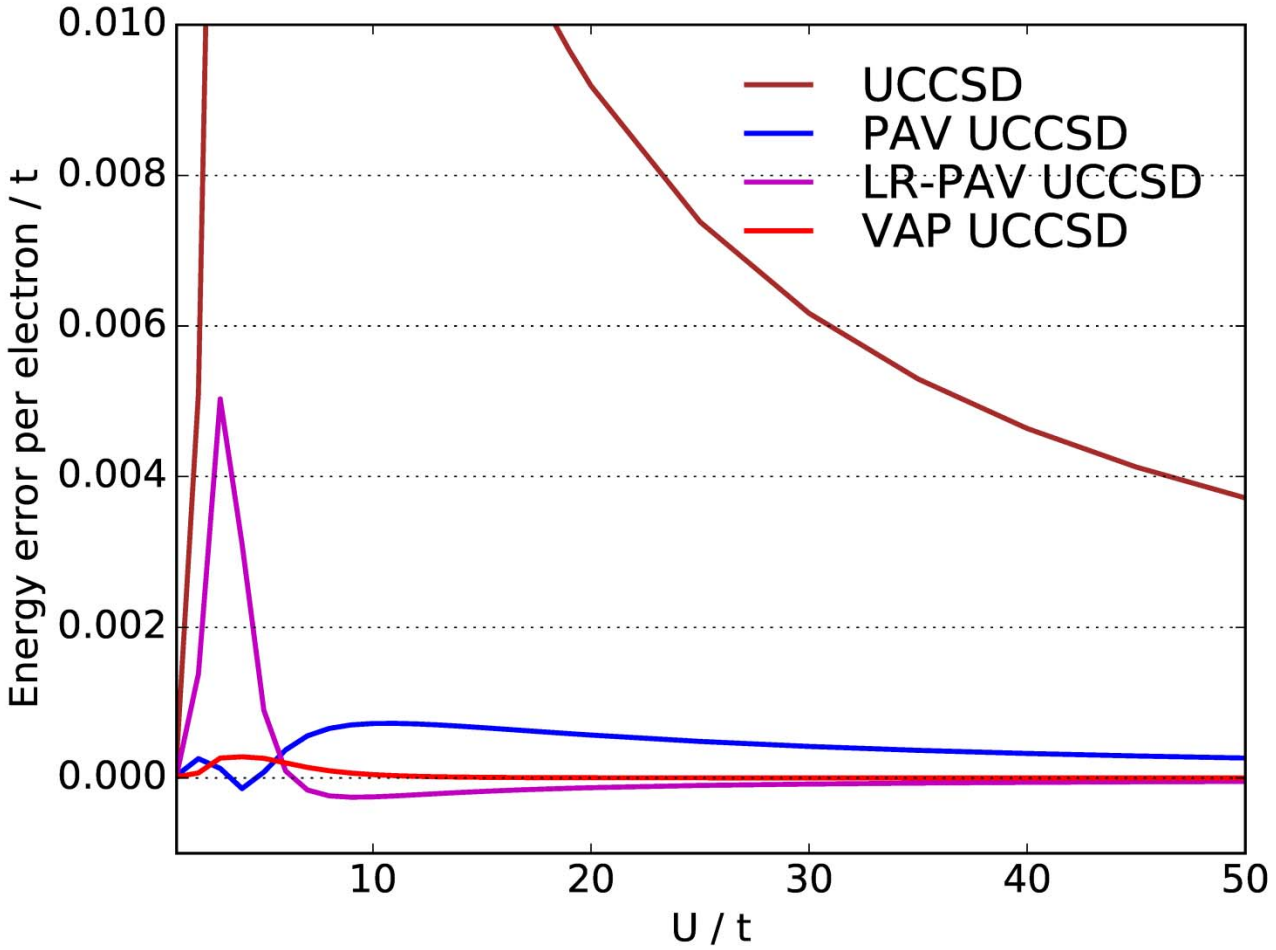
(2) **LR-PAV**: solve for **Z≠0** and U_1/U_2 from **UCCSD**

(3) **VAP**: re-optimize U_1/U_2 in the presence of $\hat{P}$

$$\frac{\partial E}{\partial z_a^i} = \left\langle \begin{matrix} a \\ i \end{matrix} \middle| e^{-U_1 - U_2} H \hat{P} e^{U_1 + U_2} \middle| UHF \right\rangle - E \left\langle \begin{matrix} a \\ i \end{matrix} \middle| e^{-U_1 - U_2} \hat{P} e^{U_1 + U_2} \middle| UHF \right\rangle = 0$$

$$\frac{\partial E}{\partial z_{ab}^{ij}} = \left\langle \begin{matrix} ab \\ ij \end{matrix} \middle| e^{-U_1 - U_2} H \hat{P} e^{U_1 + U_2} \middle| UHF \right\rangle - E \left\langle \begin{matrix} ab \\ ij \end{matrix} \middle| e^{-U_1 - U_2} \hat{P} e^{U_1 + U_2} \middle| UHF \right\rangle = 0$$

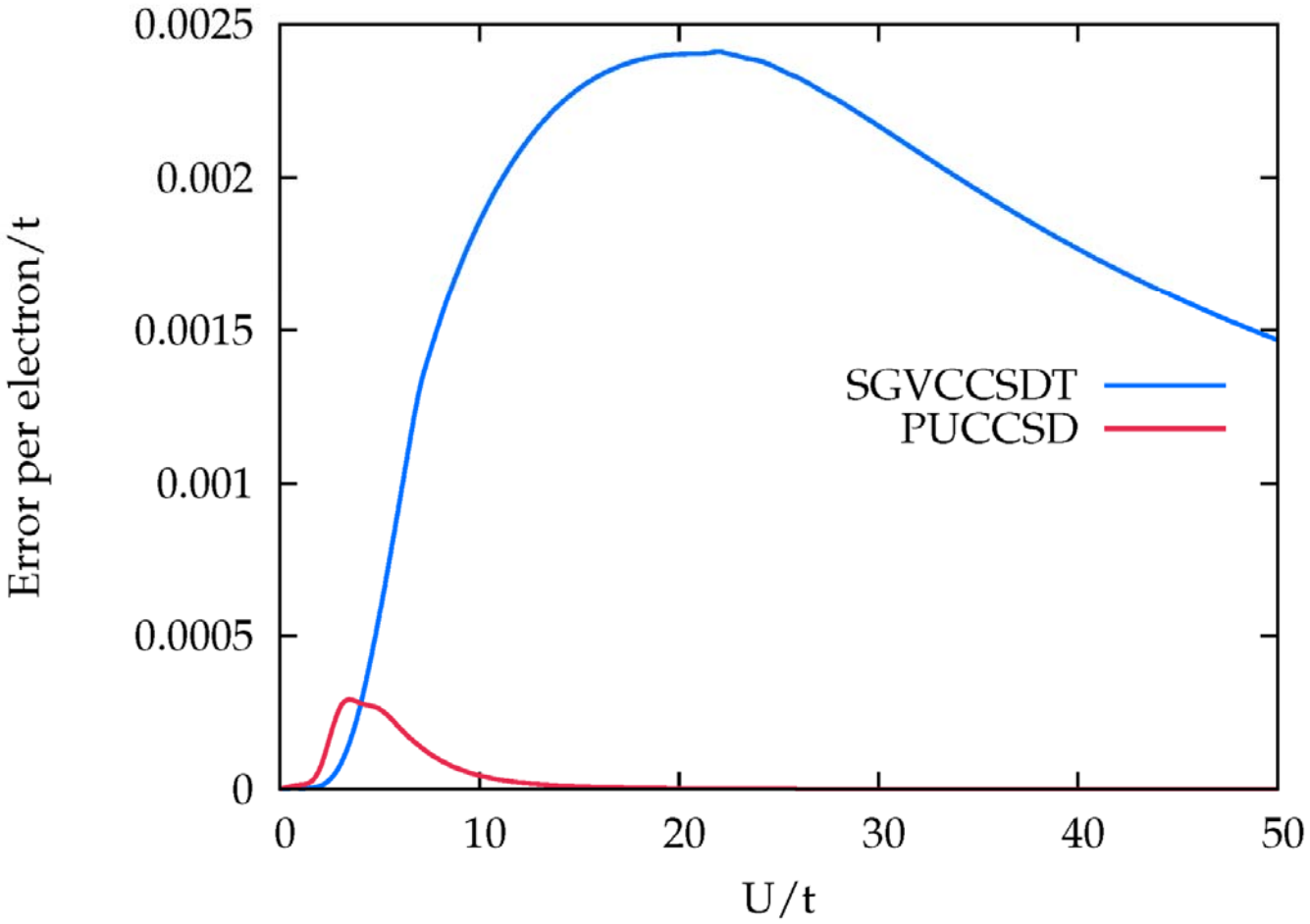
S^2 projected UCCSD



10×1

All calculations use the **SUHF** optimized determinant (so that there is a broken symmetry reference even when spin does not break spontaneously)

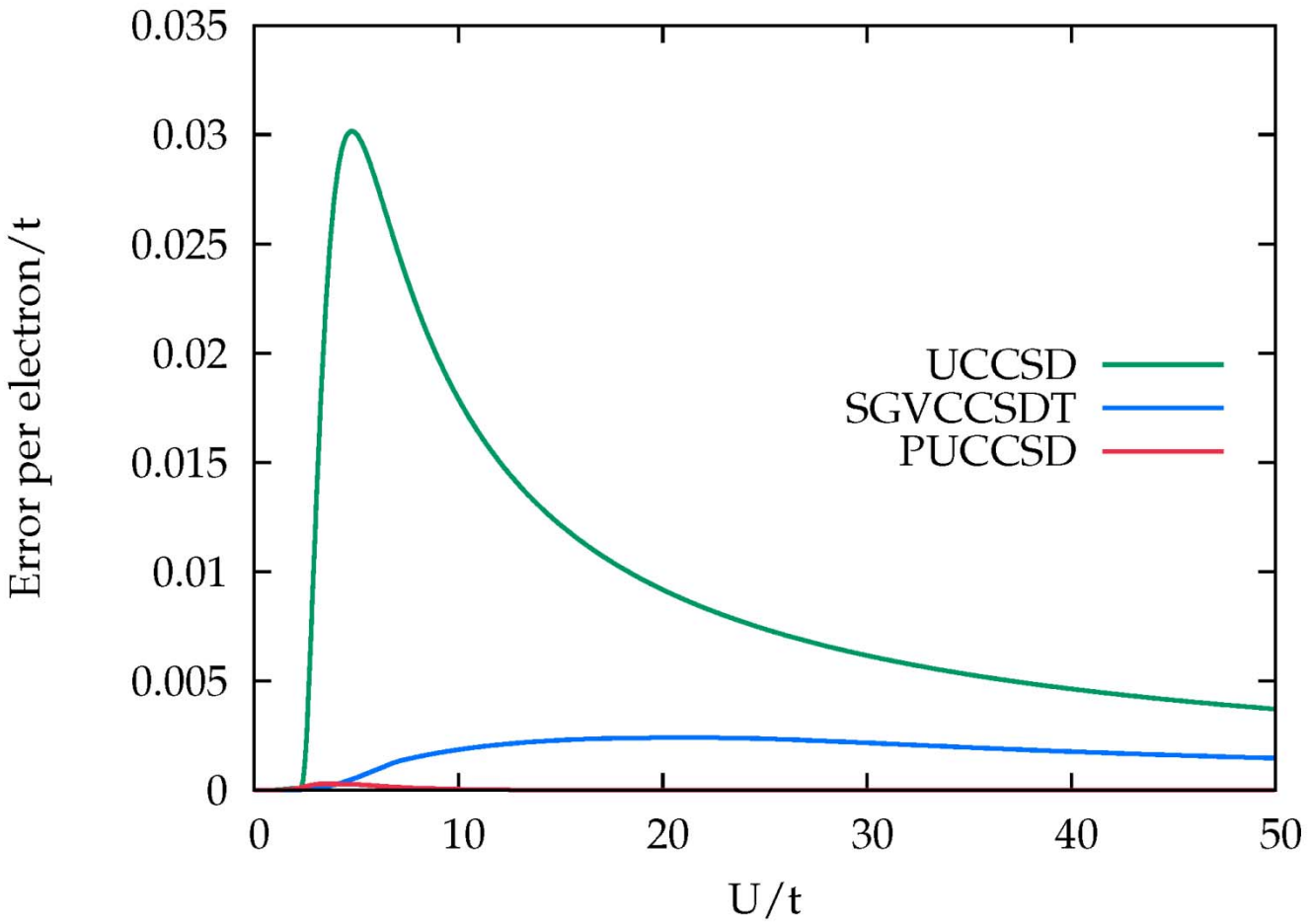
Comparing our best models so far



10×1

There is a small advantage of **symmetry adapted** methods in the recoupling region which may be relevant for molecules

And for a bit of perspective…



10×1

Conclusion

Symmetry breaking and restoration methods combined with coupled cluster theory look very promising

Related work on PHF+CC

Merging symmetry projection methods with coupled cluster theory:
Lessons from the **Lipkin model Hamiltonian**,
J. M. Wahlen-Strothman, T. M. Henderson, M. R. Hermes,
M. Degroote, Y. Qiu, J. Zhao, J. Dukelsky, and G. E. Scuseria,
J. Chem. Phys. **146**, 054110 (2017),
https://arxiv.org/abs/1611.06273

Combining symmetry collective states with coupled cluster theory:
Lessons from the **Agassi model Hamiltonian**,
M. R. Hermes, J. Dukelsky, and G. E. Scuseria,
https://arxiv.org/abs/1703.02123

MOLECULAR PHYSICS, 2017
https://doi.org/10.1080/00268976.2017.1302610

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SPECIAL ISSUE IN HONOUR OF DEBASHIS MUKHERJEE

Attenuated coupled cluster: a heuristic polynomial similarity transformation incorporating spin symmetry projection into traditional coupled cluster theory

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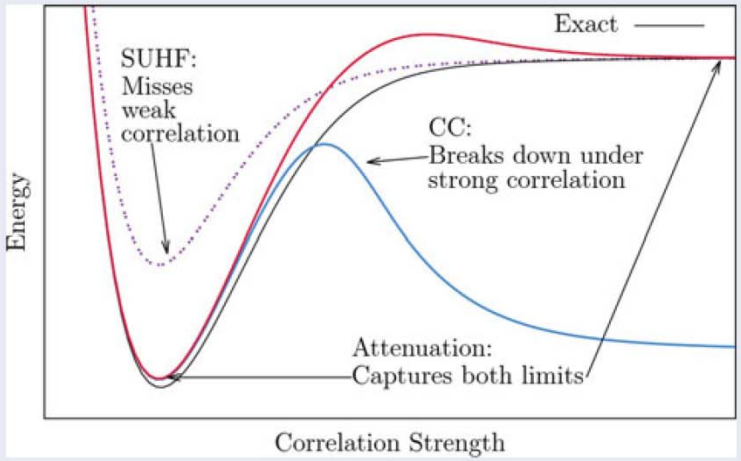
ABSTRACT

In electronic structure theory, restricted single-reference coupled cluster (CC) captures weak correlation but fails catastrophically under strong correlation. Spin-projected unrestricted Hartree-Fock (SUHF), on the other hand, misses weak correlation but captures a large portion of strong correlation. The theoretical description of many important processes, e.g. molecular dissociation, requires a method capable of accurately capturing both weak and strong correlation simultaneously, and would likely benefit from a combined CC-SUHF approach. Based on what we have recently learned about SUHF written as particle-hole excitations out of a symmetry-adapted reference determinant, we here propose a heuristic CC doubles model to attenuate the dominant spin collective channel of the quadratic terms in the CC equations. Proof of principle results presented here are encouraging and point to several paths forward for improving the method further.



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KEYWORDS
Coupled cluster theory; spin symmetry projection; strong correlation; molecular dissociation; Hubbard Hamiltonian

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