

TOWARD EXACT QUANTUM CHEMISTRY: HIGH-LEVEL COUPLED-CLUSTER ENERGETICS BY MONTE CARLO SAMPLING AND MOMENT EXPANSIONS

Piotr Piecuch, J. Emiliano Deustua, and Jun Shen

Department of Chemistry and Department of Physics & Astronomy, Michigan State University, East Lansing, Michigan 48824



U.S. DEPARTMENT OF
ENERGY

Office of
Science

Office of Basic Energy Sciences
Chemical Sciences, Geosciences
& Biosciences Division



**The Annual Workshop on Recent Developments
in Electronic Structure Methods (ES18) and Penn Conference in Theoretical
Chemistry (PCTC18), Philadelphia, Pennsylvania, U.S.A., June 10-14, 2018**

**MANY THANKS TO PROFESSORS ANDREW RAPPE
AND JOSEPH SUBOTNIK FOR INVITATION**

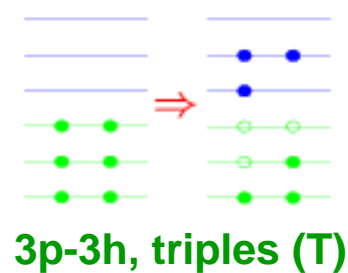
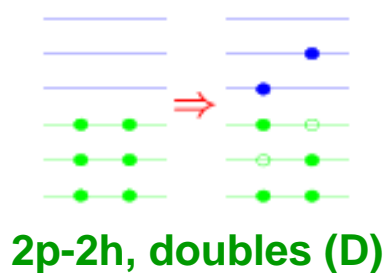
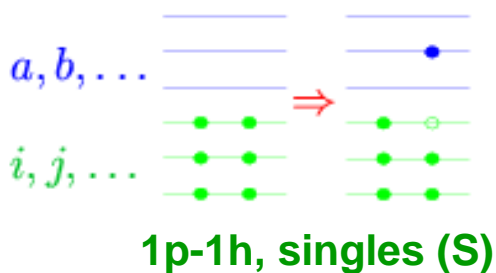


SINGLE-REFERENCE COUPLED-CLUSTER (CC) THEORY

(F. Coester, 1958; F. Coester and H. Kümmel, 1960; J. Čížek, 1966,1969; J. Čížek and J. Paldus, 1971)

$$|\Psi\rangle = e^{T^{(A)}} |\Phi\rangle, \quad T^{(A)} = \sum_{k=1}^{m_A} T_k$$

$$T_1|\Phi\rangle = \sum_i t_a^i |\Phi_i^a\rangle, \quad T_2\Phi = \sum_{\substack{i > j \\ a > b}} t_{ab}^{ij} |\Phi_{ij}^{ab}\rangle, \quad T_3\Phi = \sum_{\substack{i > j > k \\ a > b > c}} t_{abc}^{ijk} |\Phi_{ijk}^{abc}\rangle, \quad \text{etc.}$$



SINGLE-REFERENCE COUPLED-CLUSTER (CC) THEORY

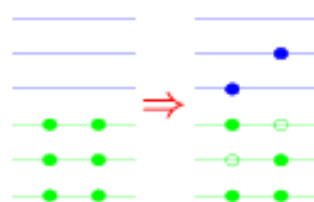
(F. Coester, 1958; F. Coester and H. Kümmel, 1960; J. Čížek, 1966,1969; J. Čížek and J. Paldus, 1971)

$$|\Psi\rangle = e^{T^{(A)}} |\Phi\rangle, \quad T^{(A)} = \sum_{k=1}^{m_A} T_k$$

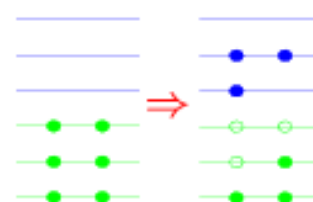
$$T_1|\Phi\rangle = \sum_i t_a^i |\Phi_i^a\rangle, \quad T_2\Phi = \sum_{\substack{i > j \\ a > b}} t_{ab}^{ij} |\Phi_{ij}^{ab}\rangle, \quad T_3\Phi = \sum_{\substack{i > j > k \\ a > b > c}} t_{abc}^{ijk} |\Phi_{ijk}^{abc}\rangle, \quad \text{etc.}$$



1p-1h, singles (S)



2p-2h, doubles (D)



3p-3h, triples (T)

$m_A = N \Rightarrow$ exact theory (full CI), $m_A < N \Rightarrow$ approximations

$$m_A = 2$$

$$T = T_1 + T_2$$

CCSD

$$n_o^2 n_u^4 (n_o^2 n_u^2) \leftarrow \text{iterative } N^6$$

$$m_A = 3$$

$$T = T_1 + T_2 + T_3$$

CCSDT

$$n_o^3 n_u^5 (n_o^3 n_u^3) \leftarrow \text{iterative } N^8$$

$$m_A = 4$$

$$T = T_1 + T_2 + T_3 + T_4$$

CCSDTQ

$$n_o^4 n_u^6 (n_o^4 n_u^4) \leftarrow \text{iterative } N^{10}$$

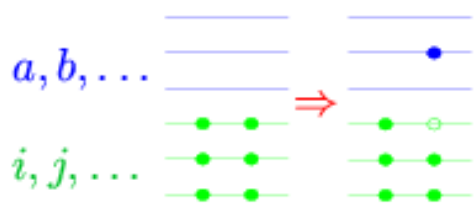
CPU time
scaling with the
system size

SINGLE-REFERENCE COUPLED-CLUSTER (CC) THEORY

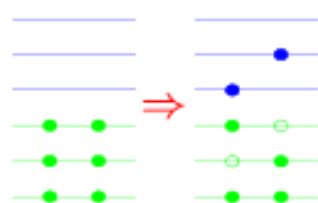
(F. Coester, 1958; F. Coester and H. Kümmel, 1960; J. Čížek, 1966,1969; J. Čížek and J. Paldus, 1971)

$$|\Psi\rangle = e^{T^{(A)}} |\Phi\rangle, \quad T^{(A)} = \sum_{k=1}^{m_A} T_k$$

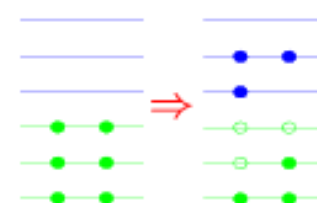
$$T_1|\Phi\rangle = \sum_i t_a^i |\Phi_i^a\rangle, \quad T_2\Phi = \sum_{\substack{i > j \\ a > b}} t_{ab}^{ij} |\Phi_{ij}^{ab}\rangle, \quad T_3\Phi = \sum_{\substack{i > j > k \\ a > b > c}} t_{abc}^{ijk} |\Phi_{ijk}^{abc}\rangle, \quad \text{etc.}$$



1p-1h, singles (S)



2p-2h, doubles (D)



3p-3h, triples (T)

$m_A = N \Rightarrow$ exact theory (full CI), $m_A < N \Rightarrow$ approximations

$m_A = 2$	$T = T_1 + T_2$	CCSD	$n_o^2 n_u^4 (n_o^2 n_u^2)$	← iterative N^6
$m_A = 3$	$T = T_1 + T_2 + T_3$	CCSDT	$n_o^3 n_u^5 (n_o^3 n_u^3)$	← iterative N^8
$m_A = 4$	$T = T_1 + T_2 + T_3 + T_4$	CCSDTQ	$n_o^4 n_u^6 (n_o^4 n_u^4)$	← iterative N^{10}

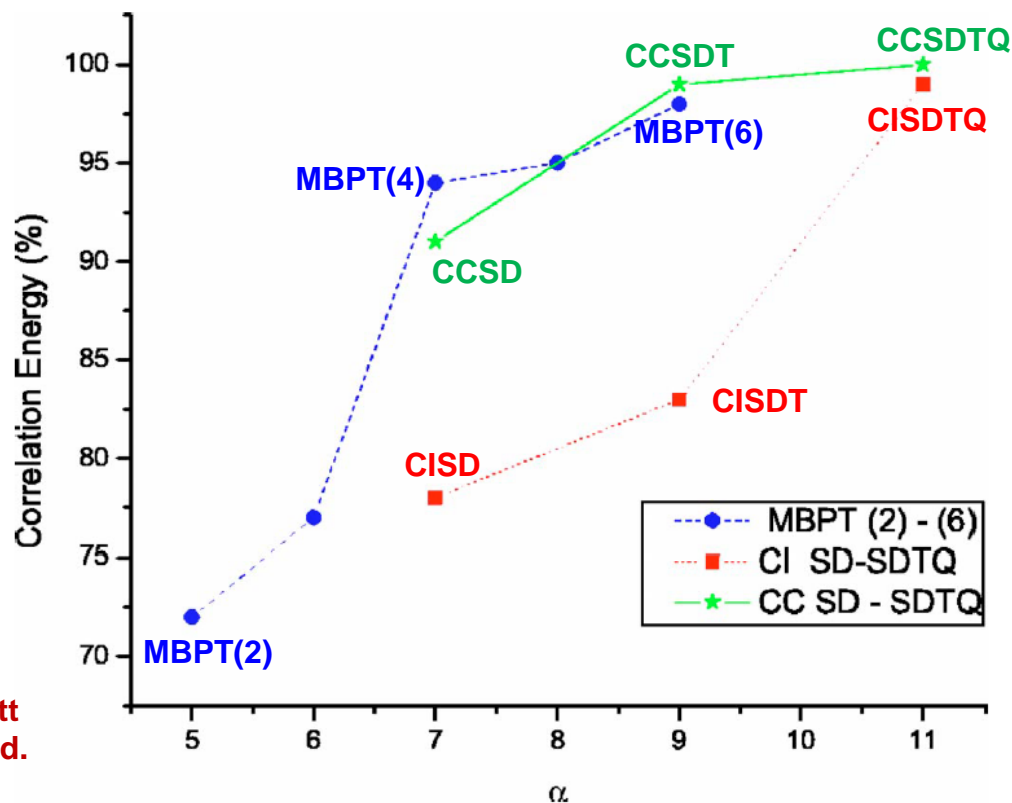
CPU time scaling with the system size

$$\langle \Phi_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k} | \left(H_N e^{T^{(A)}} \right)_C |\Phi\rangle = 0, \quad k = 1 \dots, m_A$$

$$E_0 = \langle \Phi | H | \Phi \rangle + \langle \Phi | \left(H_N e^{T^{(A)}} \right)_C |\Phi\rangle = \langle \Phi | H | \Phi \rangle + \langle \Phi | [H_N (T_1 + T_2 + \frac{1}{2} T_1^2)]_C |\Phi\rangle$$

ARGUMENTS IN FAVOR OF THE CC THEORY

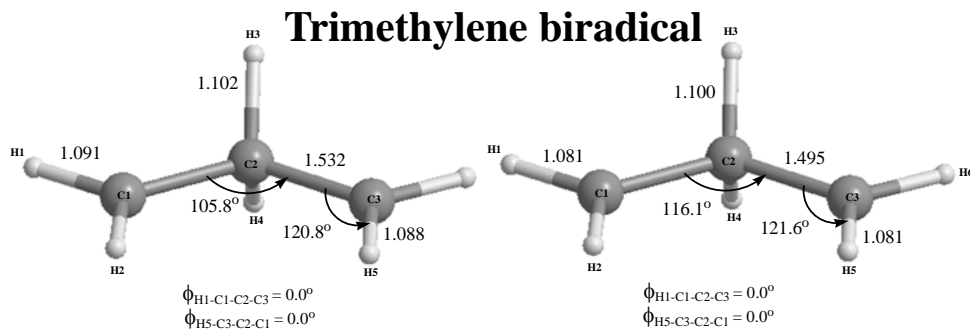
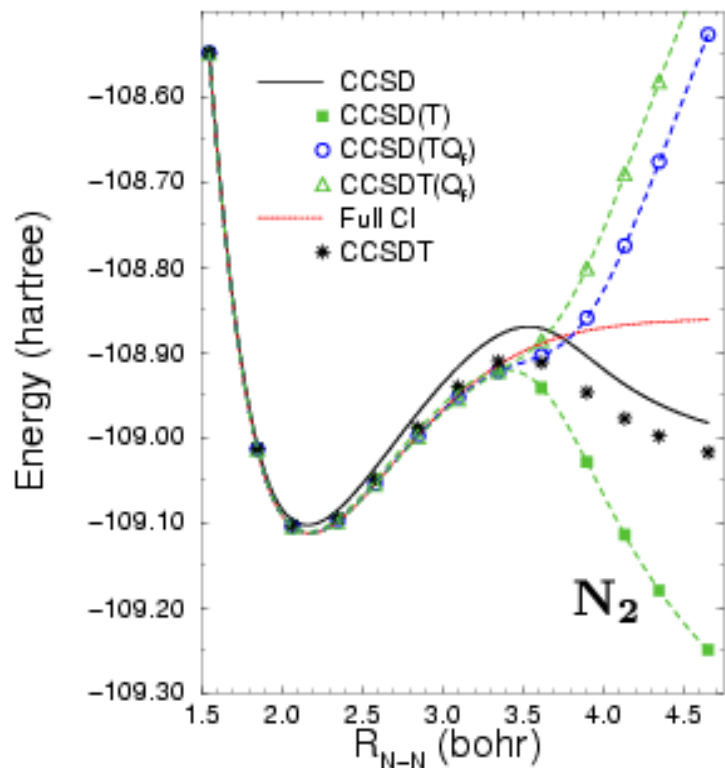
- ❑ Size-extensivity of the resulting approximations (no loss of accuracy occurs when the system is made larger)
- ❑ Separability or size consistency if the reference state separates correctly
- ❑ Fastest convergence toward the exact, full CI, limit



Taken from R.J. Bartlett
and M. Musiał, Rev. Mod.
Phys., 2007

KEY CHALLENGE: How to incorporate T_n and R_n components with $n > 2$, needed to achieve a quantitative description, without running into prohibitive computational costs of CCSDT, CCSDTQ, and similar schemes?

TRADITIONAL SOLUTION: Noniterative corrections of the CCSD(T) type, iterative CCSDT- n and similar approximations, and their linear-response CCSDR3, CC3, etc. counterparts (replace iterative N^8 and N^{10} steps of CCSDT and CCSDTQ by iterative N^6 plus noniterative N^7 or N^9 , or iterative N^7 or N^9 operations)



CCSD(T)		MRCI	
Vib mode	[1/cm]	Vib mode	[1/cm]
1	411.2i	1	139.2i
2	157.1i	2	61.1
3	168.1	3	277.9
4	237.6	4	361.3
5	336.6	5	372.5
...
% Av Err	89.3		
		CASSCF:	330.0i, 314.5i
		MCQDPT2:	131.7i

BETTER SOLUTION: MOMENT ENERGY EXPANSIONS

[original ideas: K. Kowalski and P. Piecuch, 2000 (ground states); 2001 (excited states)]

Instead of conventional $E_0 = \langle \Phi | H e^{T_1+T_2+\dots+T_N} | \Phi \rangle$, use

BETTER SOLUTION: MOMENT ENERGY EXPANSIONS

[original ideas: K. Kowalski and P. Piecuch, 2000 (ground states); 2001 (excited states)]

Instead of conventional $E_0 = \langle \Phi | H e^{T_1+T_2+\dots+T_N} | \Phi \rangle$, use

$$\Lambda[\Psi] = \frac{\langle \Psi | H e^{T^{(A)}} | \Phi \rangle}{\langle \Psi | e^{T^{(A)}} | \Phi \rangle}$$



MMCC functional

(K.Kowalski and P. Piecuch, 2000)

$$(T^{(A)} = T_1 + \dots + T_{m_A})$$

BETTER SOLUTION: MOMENT ENERGY EXPANSIONS

[original ideas: K. Kowalski and P. Piecuch, 2000 (ground states); 2001 (excited states)]

Instead of conventional $E_0 = \langle \Phi | H e^{T_1+T_2+\dots+T_N} | \Phi \rangle$, use

$$\Lambda[\Psi] = \frac{\langle \Psi | H e^{T^{(A)}} | \Phi \rangle}{\langle \Psi | e^{T^{(A)}} | \Phi \rangle}$$

← **MMCC functional**

(K.Kowalski and P. Piecuch, 2000)

$$(T^{(A)} = T_1 + \dots + T_{m_A})$$

$$\Lambda[\Psi_0] = E_0$$

← **exact, independent of
truncation m_A defining $T^{(A)}$**

BETTER SOLUTION: MOMENT ENERGY EXPANSIONS

[original ideas: K. Kowalski and P. Piecuch, 2000 (ground states); 2001 (excited states)]

Instead of conventional $E_0 = \langle \Phi | H e^{T_1+T_2+\dots+T_N} | \Phi \rangle$, use

$$\Lambda[\Psi] = \frac{\langle \Psi | H e^{T^{(A)}} | \Phi \rangle}{\langle \Psi | e^{T^{(A)}} | \Phi \rangle} \longleftarrow \text{MMCC functional}$$

(K.Kowalski and P. Piecuch, 2000)

$$(T^{(A)} = T_1 + \dots + T_{m_A})$$

$$\Lambda[\Psi_0] = E_0 \longleftarrow \text{exact, independent of truncation } m_A \text{ defining } T^{(A)}$$

$$E_0 = \frac{\langle \Psi_0 | H e^{T^{(A)}} | \Phi \rangle}{\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle}$$

BETTER SOLUTION: MOMENT ENERGY EXPANSIONS

[original ideas: K. Kowalski and P. Piecuch, 2000 (ground states); 2001 (excited states)]

Instead of conventional $E_0 = \langle \Phi | H e^{T_1+T_2+\dots+T_N} | \Phi \rangle$, use

$$\Lambda[\Psi] = \frac{\langle \Psi | H e^{T^{(A)}} | \Phi \rangle}{\langle \Psi | e^{T^{(A)}} | \Phi \rangle} \longleftarrow \text{MMCC functional}$$

(K.Kowalski and P. Piecuch, 2000)

$$(T^{(A)} = T_1 + \dots + T_{m_A})$$

$$\Lambda[\Psi_0] = E_0 \longleftarrow \text{exact, independent of truncation } m_A \text{ defining } T^{(A)}$$

$$E_0 = \frac{\langle \Psi_0 | e^{T^{(A)}} e^{-T^{(A)}} H e^{T^{(A)}} | \Phi \rangle}{\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle} = \frac{\langle \Psi_0 | e^{T^{(A)}} (e^{-T^{(A)}} H e^{T^{(A)}}) | \Phi \rangle}{\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle}$$

BETTER SOLUTION: MOMENT ENERGY EXPANSIONS

[original ideas: K. Kowalski and P. Piecuch, 2000 (ground states); 2001 (excited states)]

Instead of conventional $E_0 = \langle \Phi | H e^{T_1+T_2+\dots+T_N} | \Phi \rangle$, use

$$\Lambda[\Psi] = \frac{\langle \Psi | H e^{T^{(A)}} | \Phi \rangle}{\langle \Psi | e^{T^{(A)}} | \Phi \rangle}$$

← **MMCC functional**

(K.Kowalski and P. Piecuch, 2000)

$$(T^{(A)} = T_1 + \dots + T_{m_A})$$

$$\Lambda[\Psi_0] = E_0$$

← **exact, independent of truncation m_A defining $T^{(A)}$**

$$E_0 = \frac{\langle \Psi_0 | e^{T^{(A)}} e^{-T^{(A)}} H e^{T^{(A)}} | \Phi \rangle}{\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle} = \frac{\langle \Psi_0 | e^{T^{(A)}} (e^{-T^{(A)}} H e^{T^{(A)}}) | \Phi \rangle}{\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle}$$

$$E_0 = \frac{\langle \Psi_0 | e^{T^{(A)}} (H e^{T^{(A)}})_c | \Phi \rangle}{\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle}$$

BETTER SOLUTION: MOMENT ENERGY EXPANSIONS

[original ideas: K. Kowalski and P. Piecuch, 2000 (ground states); 2001 (excited states)]

Instead of conventional $E_0 = \langle \Phi | H e^{T_1+T_2+\dots+T_N} | \Phi \rangle$, use

$$\Lambda[\Psi] = \frac{\langle \Psi | H e^{T^{(A)}} | \Phi \rangle}{\langle \Psi | e^{T^{(A)}} | \Phi \rangle}$$

← **MMCC functional**

(K.Kowalski and P. Piecuch, 2000)

$$(T^{(A)} = T_1 + \dots + T_{m_A})$$

$$\Lambda[\Psi_0] = E_0$$

← **exact, independent of truncation m_A defining $T^{(A)}$**

$$E_0 = \frac{\langle \Psi_0 | e^{T^{(A)}} e^{-T^{(A)}} H e^{T^{(A)}} | \Phi \rangle}{\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle} = \frac{\langle \Psi_0 | e^{T^{(A)}} (e^{-T^{(A)}} H e^{T^{(A)}}) | \Phi \rangle}{\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle}$$

$$|\Phi\rangle\langle\Phi| + \sum_{n=1}^N \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} |\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle \langle\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}|$$

$$\langle\Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | (H e^{T^{(A)}})_C | \Phi \rangle$$

$$= \mathfrak{M}_{0, a_1, \dots, a_n}^{i_1, \dots, i_n}(m_A)$$

$$E_0 = \frac{\langle \Psi_0 | e^{T^{(A)}} (H e^{T^{(A)}})_C | \Phi \rangle}{\langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle} = E_0^{(A)} + \delta_0^{(A)}$$

(moments of CC equations)

BIORTHOGONAL MOMENT EXPANSIONS

(the ground-state problem: P. Piecuch and M. Włoch, 2005; excited states: P. Piecuch et al., 2006)

BIORTHOGONAL MOMENT EXPANSIONS

(the ground-state problem: P. Piecuch and M. Włoch, 2005; excited states: P. Piecuch et al., 2006)

Instead of

$$|\Phi\rangle\langle\Phi| + \sum_{n=1}^N \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} |\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle\langle\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}|$$

$$E_0 = \Lambda[\Psi_0] = \frac{\langle\Psi_0|He^{T^{(A)}}|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle} = \frac{\langle\Psi_0|e^{T^{(A)}}\downarrow(He^{T^{(A)}})_C|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle}$$

BIORTHOGONAL MOMENT EXPANSIONS

(the ground-state problem: P. Piecuch and M. Włoch, 2005; excited states: P. Piecuch et al., 2006)

Instead of

$$|\Phi\rangle\langle\Phi| + \sum_{n=1}^N \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} |\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle\langle\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}|$$

$$E_0 = \Lambda[\Psi_0] = \frac{\langle\Psi_0|He^{T^{(A)}}|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle} = \frac{\langle\Psi_0|e^{T^{(A)}}\downarrow(He^{T^{(A)}})_C|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle}$$

before exploiting the resolution of identity, introduce the ansatz:

$$\langle\Psi_0| = \langle\Phi|L_0e^{-T^{(A)}}, \quad L_0 = \sum_{n=0}^N L_{0,n}, \quad \langle\Phi|L_0|\Phi\rangle = 1$$

BIORTHOGONAL MOMENT EXPANSIONS

(the ground-state problem: P. Piecuch and M. Włoch, 2005; excited states: P. Piecuch et al., 2006)

Instead of

$$|\Phi\rangle\langle\Phi| + \sum_{n=1}^N \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} |\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle\langle\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}|$$

$$E_0 = \Lambda[\Psi_0] = \frac{\langle\Psi_0|He^{T^{(A)}}|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle} = \frac{\langle\Psi_0|e^{T^{(A)}}\downarrow(He^{T^{(A)}})_C|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle}$$

before exploiting the resolution of identity, introduce the ansatz:

$$\langle\Psi_0| = \langle\Phi|L_0e^{-T^{(A)}}, \quad L_0 = \sum_{n=0}^N L_{0,n}, \quad \langle\Phi|L_0|\Phi\rangle = 1$$

$$E_0 = \frac{\langle\Phi|L_0e^{-T^{(A)}}e^{T^{(A)}}(He^{T^{(A)}})_C|\Phi\rangle}{\langle\Phi|L_0e^{-T^{(A)}}e^{T^{(A)}}|\Phi\rangle}$$

BIORTHOGONAL MOMENT EXPANSIONS

(the ground-state problem: P. Piecuch and M. Włoch, 2005; excited states: P. Piecuch et al., 2006)

Instead of

$$|\Phi\rangle\langle\Phi| + \sum_{n=1}^N \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} |\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle \langle\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}|$$

$$E_0 = \Lambda[\Psi_0] = \frac{\langle\Psi_0|He^{T^{(A)}}|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle} = \frac{\langle\Psi_0|e^{T^{(A)}}\downarrow(He^{T^{(A)}})_C|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle}$$

before exploiting the resolution of identity, introduce the ansatz:

$$\langle\Psi_0| = \langle\Phi|L_0e^{-T^{(A)}}, \quad L_0 = \sum_{n=0}^N L_{0,n}, \quad \langle\Phi|L_0|\Phi\rangle = 1$$

$$E_0 = \frac{\langle\Phi|L_0e^{-T^{(A)}}e^{T^{(A)}}(He^{T^{(A)}})_C|\Phi\rangle}{\langle\Phi|L_0e^{-T^{(A)}}e^{T^{(A)}}|\Phi\rangle}$$

BIORTHOGONAL MOMENT EXPANSIONS

(the ground-state problem: P. Piecuch and M. Włoch, 2005; excited states: P. Piecuch et al., 2006)

Instead of

$$|\Phi\rangle\langle\Phi| + \sum_{n=1}^N \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} |\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle\langle\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}|$$

$$E_0 = \Lambda[\Psi_0] = \frac{\langle\Psi_0|He^{T^{(A)}}|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle} = \frac{\langle\Psi_0|e^{T^{(A)}}\downarrow(He^{T^{(A)}})_C|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle}$$

before exploiting the resolution of identity, introduce the ansatz:

$$\langle\Psi_0| = \langle\Phi|L_0e^{-T^{(A)}}, \quad L_0 = \sum_{n=0}^N L_{0,n}, \quad \langle\Phi|L_0|\Phi\rangle = 1$$

$$E_0 = \frac{\langle\Phi|L_0e^{-T^{(A)}}e^{T^{(A)}}(He^{T^{(A)}})_C|\Phi\rangle}{\langle\Phi|L_0e^{-T^{(A)}}e^{T^{(A)}}|\Phi\rangle} = \langle\Phi|L_0(He^{T^{(A)}})_C|\Phi\rangle \leftarrow \text{exact, independent of truncation } m_A \text{ defining } T^{(A)}$$

BIORTHOGONAL MOMENT EXPANSIONS

(the ground-state problem: P. Piecuch and M. Włoch, 2005; excited states: P. Piecuch et al., 2006)

Instead of

$$|\Phi\rangle\langle\Phi| + \sum_{n=1}^N \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} |\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle \langle\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}|$$

$$E_0 = \Lambda[\Psi_0] = \frac{\langle\Psi_0|He^{T^{(A)}}|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle} = \frac{\langle\Psi_0|e^{T^{(A)}}\downarrow(He^{T^{(A)}})_C|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle}$$

before exploiting the resolution of identity, introduce the ansatz:

$$\langle\Psi_0| = \langle\Phi|L_0e^{-T^{(A)}}, \quad L_0 = \sum_{n=0}^N L_{0,n}, \quad \langle\Phi|L_0|\Phi\rangle = 1$$

$$E_0 = \frac{\langle\Phi|L_0\circlearrowleft e^{-T^{(A)}}\circlearrowright e^{T^{(A)}}(He^{T^{(A)}})_C|\Phi\rangle}{\langle\Phi|L_0\circlearrowleft e^{-T^{(A)}}\circlearrowright e^{T^{(A)}}|\Phi\rangle} = \langle\Phi|L_0\uparrow(He^{T^{(A)}})_C|\Phi\rangle \leftarrow \text{exact, independent of truncation } m_A \text{ defining } T^{(A)}$$

$$|\Phi\rangle\langle\Phi| + \sum_{n=1}^N \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} |\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle \langle\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}|$$

BIORTHOGONAL MOMENT EXPANSIONS

(the ground-state problem: P. Piecuch and M. Włoch, 2005; excited states: P. Piecuch et al., 2006)

Instead of

$$|\Phi\rangle\langle\Phi| + \sum_{n=1}^N \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} |\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle\langle\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}|$$

$$E_0 = \Lambda[\Psi_0] = \frac{\langle\Psi_0|He^{T^{(A)}}|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle} = \frac{\langle\Psi_0|e^{T^{(A)}}\downarrow(He^{T^{(A)}})_C|\Phi\rangle}{\langle\Psi_0|e^{T^{(A)}}|\Phi\rangle}$$

before exploiting the resolution of identity, introduce the ansatz:

$$\langle\Psi_0| = \langle\Phi|L_0e^{-T^{(A)}}, \quad L_0 = \sum_{n=0}^N L_{0,n}, \quad \langle\Phi|L_0|\Phi\rangle = 1$$

$$E_0 = \frac{\langle\Phi|L_0\circlearrowleft e^{-T^{(A)}}\circlearrowright e^{T^{(A)}}(He^{T^{(A)}})_C|\Phi\rangle}{\langle\Phi|L_0\circlearrowleft e^{-T^{(A)}}\circlearrowright e^{T^{(A)}}|\Phi\rangle} = \langle\Phi|L_0\uparrow(He^{T^{(A)}})_C|\Phi\rangle \leftarrow \text{exact, independent of truncation } m_A \text{ defining } T^{(A)}$$

BIORTHOGONAL MMCC EXPANSION

$$|\Phi\rangle\langle\Phi| + \sum_{n=1}^N \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} |\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle\langle\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}|$$

$$\delta_0^{(A)} \equiv E_0 - E_0^{(A)} = \sum_{n=m_A+1}^{N_{0,A}} \langle\Phi|L_{0,n}M_{0,n}(m_A)|\Phi\rangle = \sum_{n=m_A+1}^{N_{0,A}} \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} \rho_{0,i_1 \dots i_n}^{a_1 \dots a_n} \mathfrak{M}_{0,a_1 \dots a_n}^{i_1 \dots i_n}(m_A)$$

Example: CR-CC(2,3), robust noniterative triples correction to CCSD

iterative $n_o^2 n_u^4 (N^6)$ + noniterative $n_o^3 n_u^4 (N^7)$; CCTYP=CR-CCL in GAMESS

$$E_0^{(\text{CR-CC}(2,3))} = E_0^{(\text{CCSD})} + \delta_0(2,3), \quad \delta_0(2,3) = \sum_{i<j<k, a<b<c} \ell_{0,ijk}^{abc}(2) \mathfrak{M}_{0,abc}^{ijk}(2)$$

$$\mathfrak{M}_{0,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi \rangle, \quad \bar{H}^{(\text{CCSD})} = e^{-T_1 - T_2} H e^{T_1 + T_2} = (H e^{T_1 + T_2})_C$$

$$\ell_{0,ijk}^{abc}(2) = \langle \Phi | L_0^{(\text{CCSD})} \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle / D_{0,abc}^{ijk}(2), \quad D_{0,abc}^{ijk}(2) = E_0^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle$$

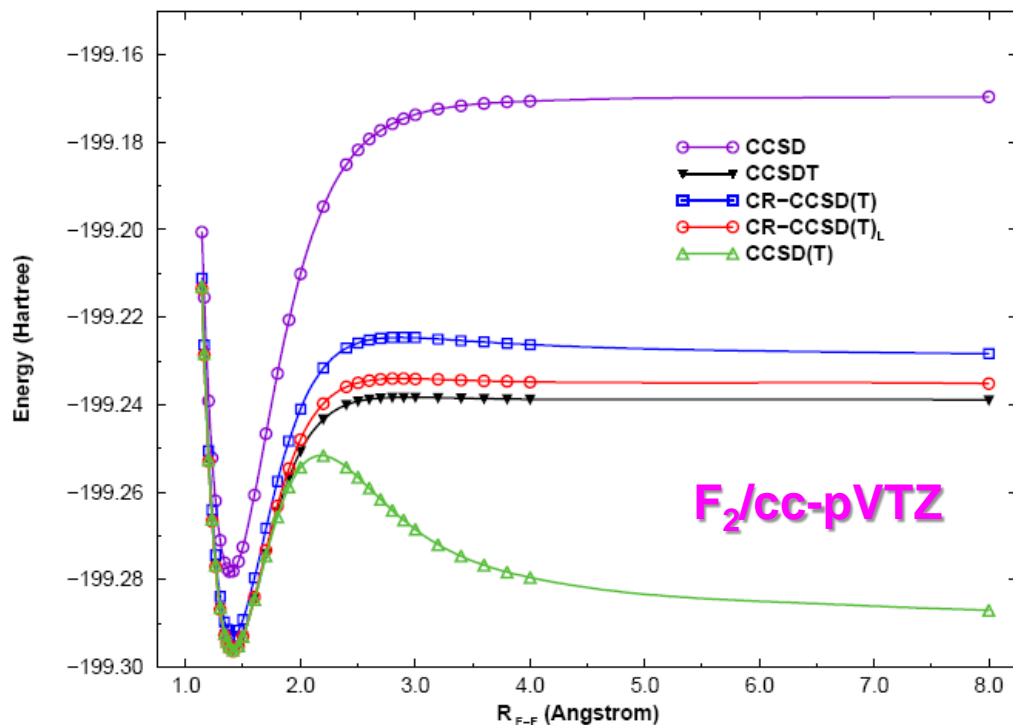
Example: CR-CC(2,3), robust noniterative triples correction to CCSD

iterative $n_o^2 n_u^4 (N^6)$ + noniterative $n_o^3 n_u^4 (N^7)$; CCTYP=CR-CCL in GAMESS

$$E_0^{(\text{CR-CC}(2,3))} = E_0^{(\text{CCSD})} + \delta_0(2,3), \quad \delta_0(2,3) = \sum_{i < j < k, a < b < c} \rho_{0,ijk}^{abc}(2) \mathfrak{M}_{0,abc}^{ijk}(2)$$

$$\mathfrak{M}_{0,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi \rangle, \quad \bar{H}^{(\text{CCSD})} = e^{-T_1 - T_2} H e^{T_1 + T_2} = (H e^{T_1 + T_2})_C$$

$$\rho_{0,ijk}^{abc}(2) = \langle \Phi | L_0^{(\text{CCSD})} \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle / D_{0,abc}^{ijk}(2), \quad D_{0,abc}^{ijk}(2) = E_0^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle$$



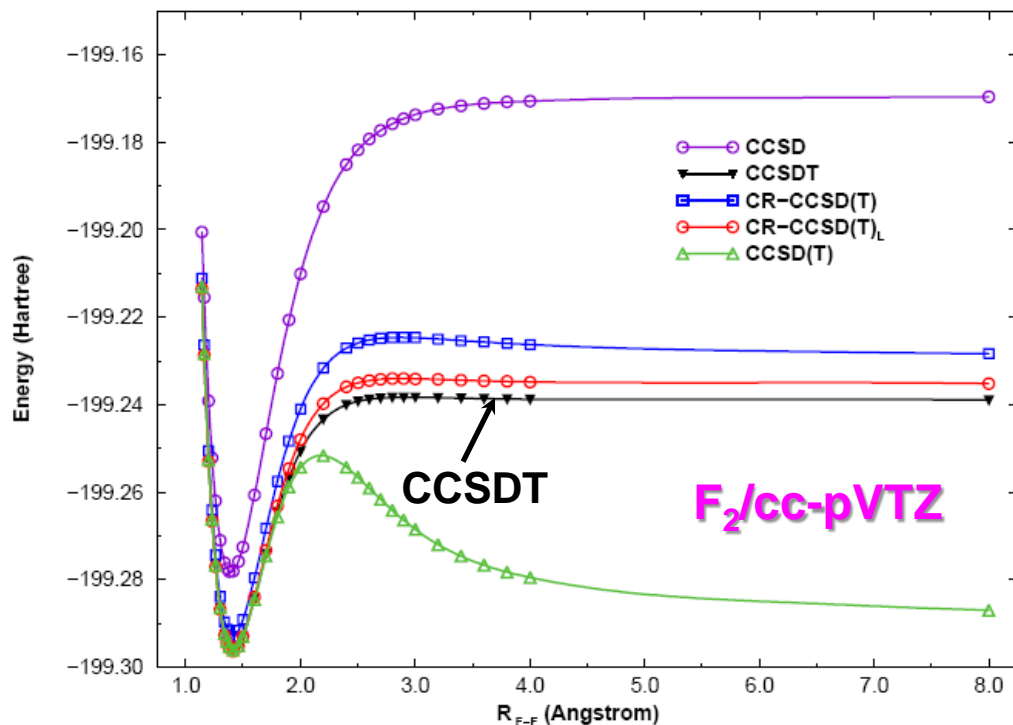
Example: CR-CC(2,3), robust noniterative triples correction to CCSD

iterative $n_o^2 n_u^4 (N^6)$ + noniterative $n_o^3 n_u^4 (N^7)$; CCTYP=CR-CCL in GAMESS

$$E_0^{(\text{CR-CC}(2,3))} = E_0^{(\text{CCSD})} + \delta_0(2,3), \quad \delta_0(2,3) = \sum_{i < j < k, a < b < c} \rho_{0,ijk}^{abc}(2) \mathfrak{M}_{0,abc}^{ijk}(2)$$

$$\mathfrak{M}_{0,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi \rangle, \quad \bar{H}^{(\text{CCSD})} = e^{-T_1 - T_2} H e^{T_1 + T_2} = (H e^{T_1 + T_2})_C$$

$$\rho_{0,ijk}^{abc}(2) = \langle \Phi | L_0^{(\text{CCSD})} \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle / D_{0,abc}^{ijk}(2), \quad D_{0,abc}^{ijk}(2) = E_0^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle$$



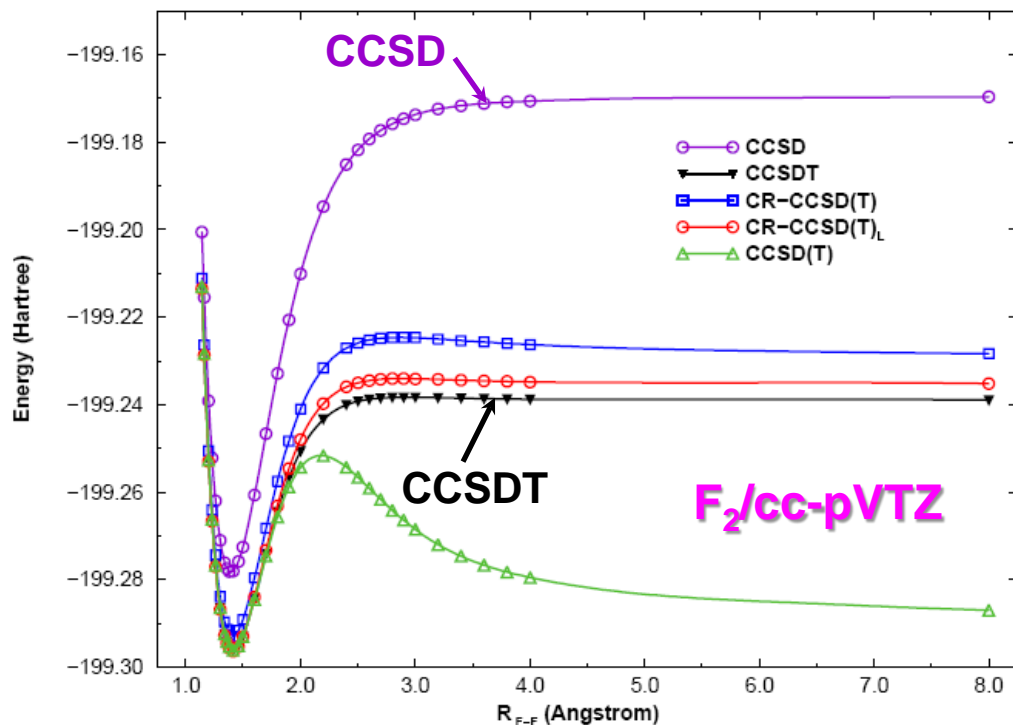
Example: CR-CC(2,3), robust noniterative triples correction to CCSD

iterative $n_o^2 n_u^4 (N^6)$ + noniterative $n_o^3 n_u^4 (N^7)$; CCTYP=CR-CCL in GAMESS

$$E_0^{(\text{CR-CC}(2,3))} = E_0^{(\text{CCSD})} + \delta_0(2,3), \quad \delta_0(2,3) = \sum_{i < j < k, a < b < c} \rho_{0,ijk}^{abc}(2) \mathfrak{M}_{0,abc}^{ijk}(2)$$

$$\mathfrak{M}_{0,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi \rangle, \quad \bar{H}^{(\text{CCSD})} = e^{-T_1 - T_2} H e^{T_1 + T_2} = (H e^{T_1 + T_2})_C$$

$$\rho_{0,ijk}^{abc}(2) = \langle \Phi | L_0^{(\text{CCSD})} \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle / D_{0,abc}^{ijk}(2), \quad D_{0,abc}^{ijk}(2) = E_0^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle$$



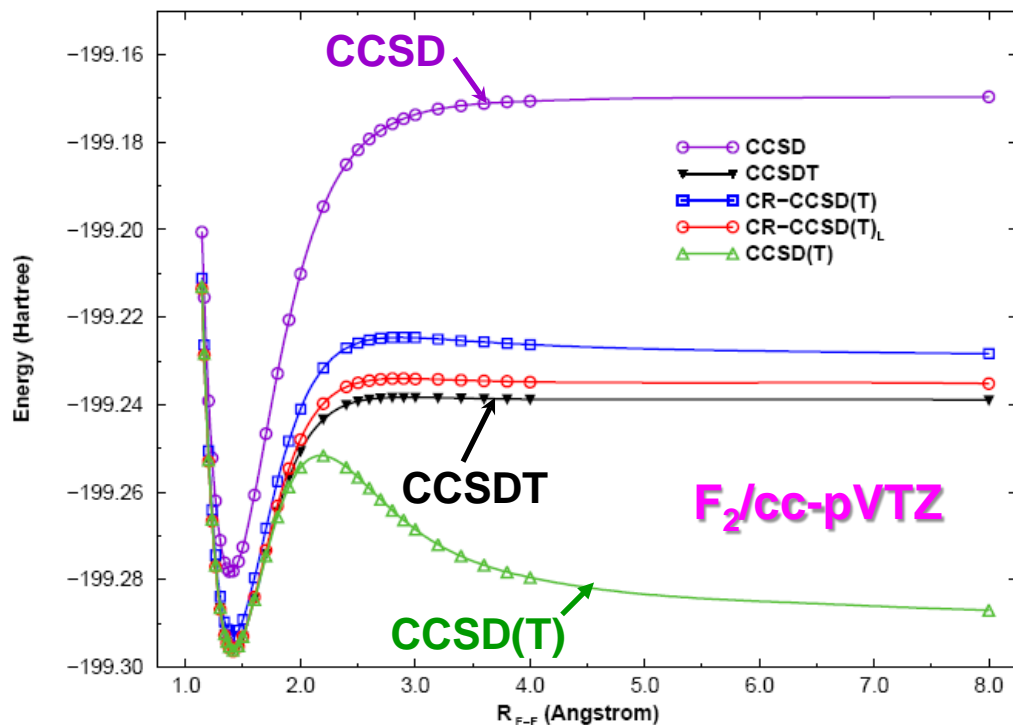
Example: CR-CC(2,3), robust noniterative triples correction to CCSD

iterative $n_o^2 n_u^4 (N^6)$ + noniterative $n_o^3 n_u^4 (N^7)$; CCTYP=CR-CCL in GAMESS

$$E_0^{(\text{CR-CC}(2,3))} = E_0^{(\text{CCSD})} + \delta_0(2,3), \quad \delta_0(2,3) = \sum_{i < j < k, a < b < c} \rho_{0,ijk}^{abc}(2) \mathfrak{M}_{0,abc}^{ijk}(2)$$

$$\mathfrak{M}_{0,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi \rangle, \quad \bar{H}^{(\text{CCSD})} = e^{-T_1 - T_2} H e^{T_1 + T_2} = (H e^{T_1 + T_2})_C$$

$$\rho_{0,ijk}^{abc}(2) = \langle \Phi | L_0^{(\text{CCSD})} \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle / D_{0,abc}^{ijk}(2), \quad D_{0,abc}^{ijk}(2) = E_0^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle$$



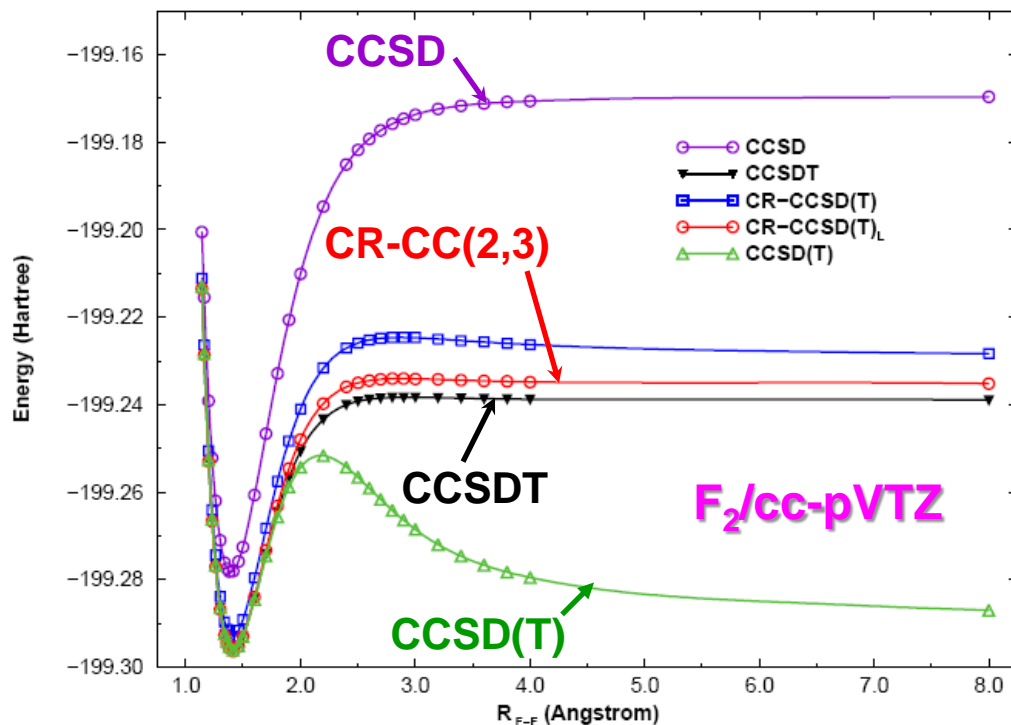
Example: CR-CC(2,3), robust noniterative triples correction to CCSD

iterative $n_o^2 n_u^4 (N^6)$ + noniterative $n_o^3 n_u^4 (N^7)$; CCTYP=CR-CCL in GAMESS

$$E_0^{(\text{CR-CC}(2,3))} = E_0^{(\text{CCSD})} + \delta_0(2,3), \quad \delta_0(2,3) = \sum_{i < j < k, a < b < c} \rho_{0,ijk}^{abc}(2) \mathfrak{M}_{0,abc}^{ijk}(2)$$

$$\mathfrak{M}_{0,abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi \rangle, \quad \bar{H}^{(\text{CCSD})} = e^{-T_1 - T_2} H e^{T_1 + T_2} = (H e^{T_1 + T_2})_C$$

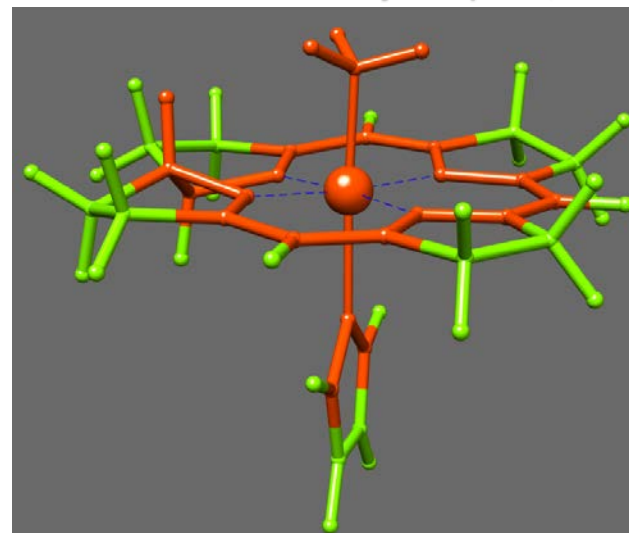
$$\rho_{0,ijk}^{abc}(2) = \langle \Phi | L_0^{(\text{CCSD})} \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle / D_{0,abc}^{ijk}(2), \quad D_{0,abc}^{ijk}(2) = E_0^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle$$



Functional	BDE (with ZPE), kcal/mol, 6-31G(d) / 6- 311++G(d,p)
BHandHLYP (50% HF)	1.2 / -2.2
MPW1K (42.8 % HF)	8.9 / 6.0
M06-2X (54 % HF)	13.5 / 9.2
MPW1PW91 (25 % HF)	18.1 / 16.1
B3LYP (20 % HF)	17.8 / 15.9
B3LYP+D3 (20 % HF)	21.2 / 24.7
M06 (27 % HF)	27.4 / 26.2
TPSSh (10 % HF)	24.5 / 23.0
ω B97X-D (22 % HF)	26.8 / 24.8
BLYP	25.7 / 24.8
TPSS	29.1 / 28.1
MPWPW91	30.3 / 29.7
M06-L	31.3 / 29.8
BP86	30.6 / 30.0
BP86+D3	35.2 / 39.7
B97-D	35.1 / 34.8
CIM-CR-CC(2,3)/CCSD	39.8 / 37.8
Experiment	37 \pm 3, 36 \pm 4

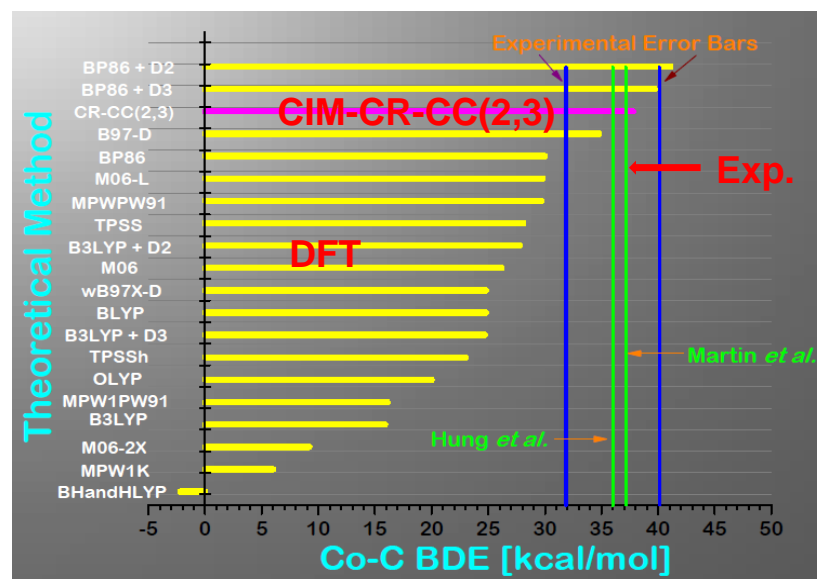
LARGE SYSTEMS (LOCAL CC): CIM-CR-CC(2,3) STUDY OF Co-C BOND DISSOCIATION IN METHYLCOBALAMIN

[P.M. Kozłowski, M. Kumar, P. Piecuch, W. Li, N.P. Bauman, J.A. Hansen, P. Lodowski, and M. Jaworska, *J. Chem. Theory Comput.* 8, 1870 (2012)]



[In GAMESS:
CIMTYP =
GSECIM]

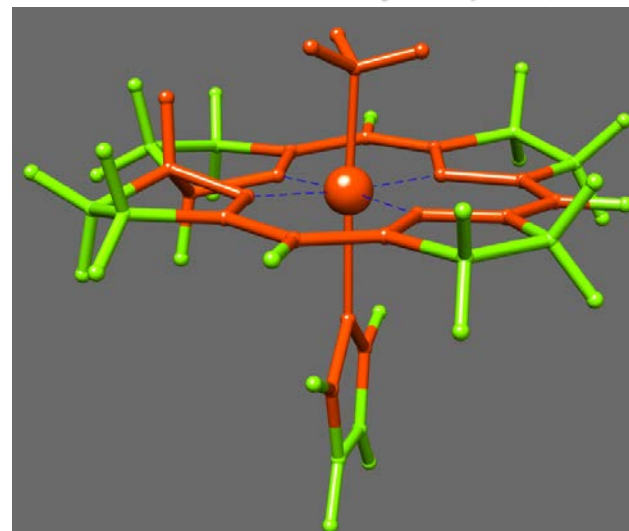
Structural
model: 58
atoms; 234
electrons.



Functional	BDE (with ZPE), kcal/mol, 6-31G(d) / 6- 311++G(d,p)
BHandHLYP (50% HF)	1.2 / -2.2
MPW1K (42.8 % HF)	8.9 / 6.0
M06-2X (54 % HF)	13.5 / 9.2
MPW1PW91 (25 % HF)	18.1 / 16.1
B3LYP (20 % HF)	17.8 / 15.9
B3LYP+D3 (20 % HF)	21.2 / 24.7
M06 (27 % HF)	27.4 / 26.2
TPSSh (10 % HF)	24.5 / 23.0
ω B97X-D (22 % HF)	26.8 / 24.8
BLYP	25.7 / 24.8
TPSS	29.1 / 28.1
MPWPW91	30.3 / 29.7
M06-L	31.3 / 29.8
BP86	30.6 / 30.0
BP86+D3	35.2 / 39.7
B97-D	35.1 / 34.8
CIM-CR-CC(2,3)/CCSD	39.8 / 37.8
Experiment	37 \pm 3, 36 \pm 4
CASSCF(11,10), CASPT2(11,10)	15.1, 53.8

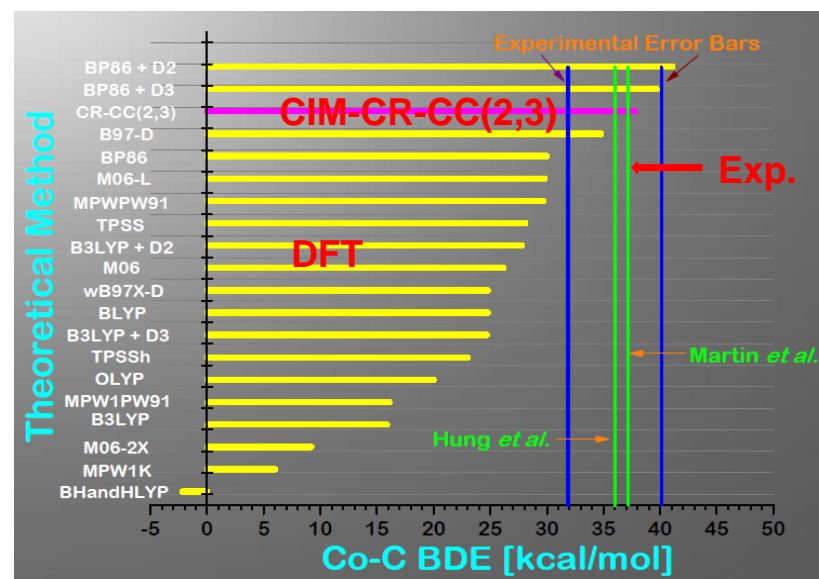
LARGE SYSTEMS (LOCAL CC): CIM-CR-CC(2,3) STUDY OF Co-C BOND DISSOCIATION IN METHYLCOBALAMIN

[P.M. Kozłowski, M. Kumar, P. Piecuch, W. Li, N.P. Bauman, J.A. Hansen, P. Lodowski, and M. Jaworska, *J. Chem. Theory Comput.* 8, 1870 (2012)]

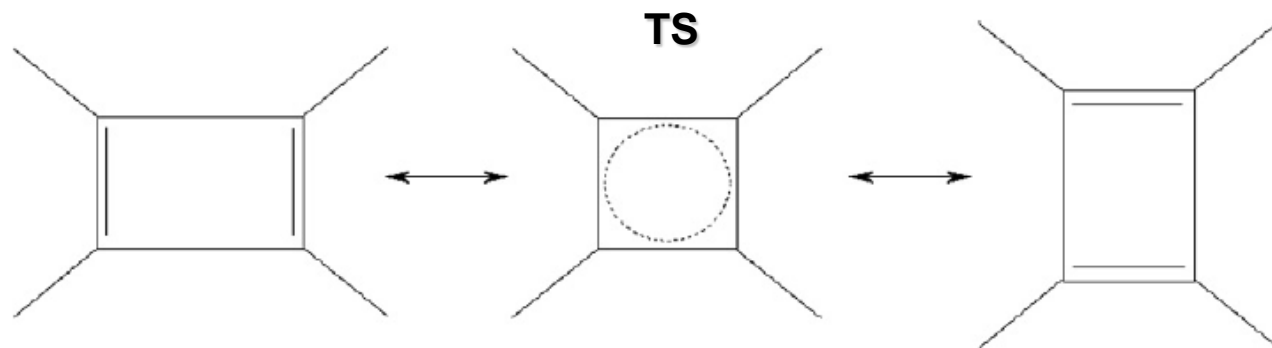


[In GAMESS:
CIMTYP =
GSECIM]

Structural
model: 58
atoms; 234
electrons.



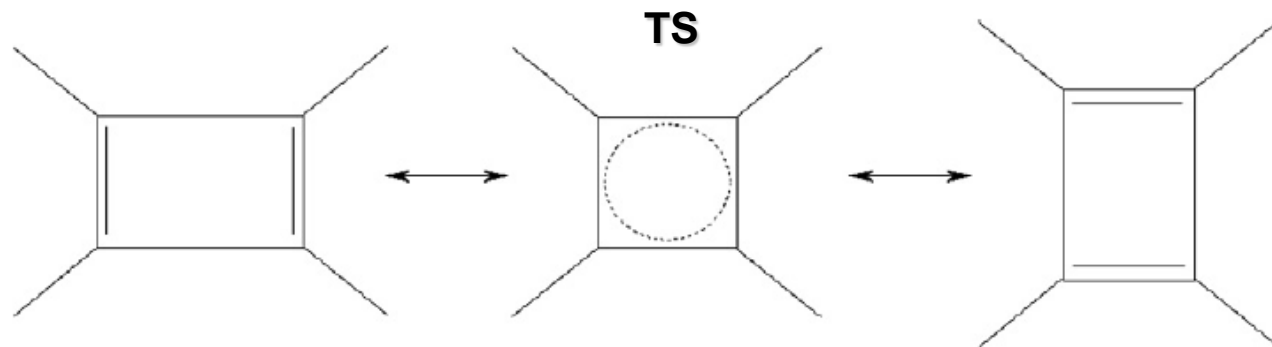
AUTOMERIZATION OF CYCLOBUTADIENE



Various CC energies (in millihartree) relative to full CCSDT (in hartree),
cc-pVDZ basis set

	Reactant	TS	Barrier Height (kcal/mol)
CCSD	26.827	47.979	20.9
CCSD(T)	1.123	14.198	15.8
CR-CC(2,3)	0.848	14.636	16.3
CCSDT	-154.244157	-154.232002	7.6

AUTOMERIZATION OF CYCLOBUTADIENE



Various CC energies (in millihartree) relative to full CCSDT (in hartree), cc-pVDZ basis set

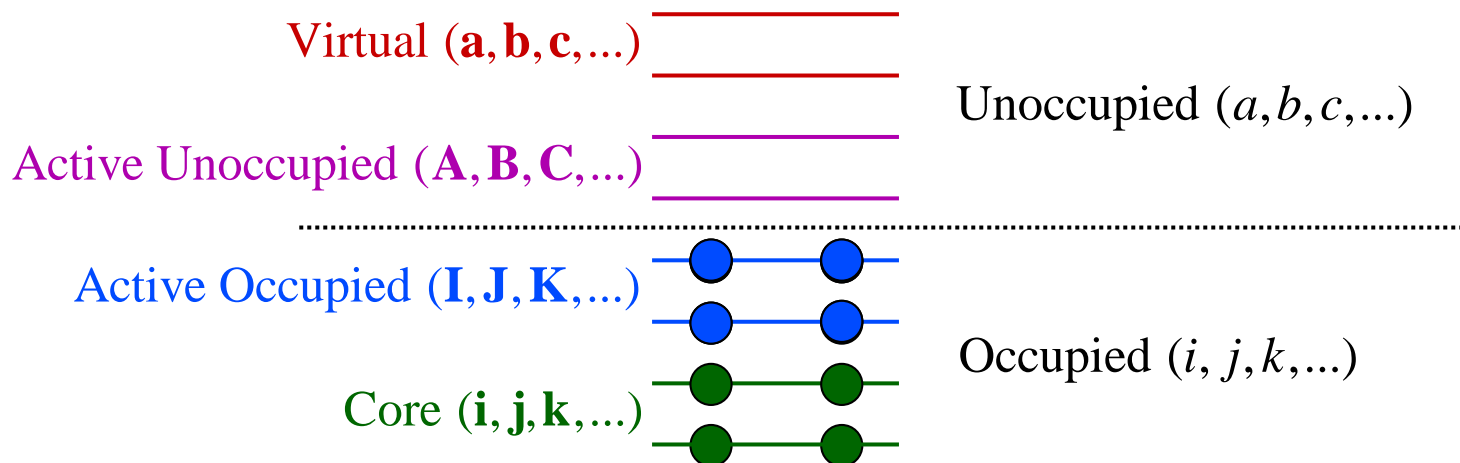
	Reactant	TS	Barrier Height (kcal/mol)
CCSD	26.827	47.979	20.9
CCSD(T)	1.123	14.198	15.8
CR-CC(2,3)	0.848	14.636	16.3
CCSDT	-154.244157	-154.232002	7.6

T_1 and T_2
decoupled from T_3



CAPTURING THE COUPLING OF LOWER- AND HIGHER-ORDER CLUSTERS: ACTIVE-SPACE CC APPROACHES (CCSDt, CCSDtq, etc.)

[Key concepts: Oliphant and Adamowicz, 1991; Piecuch, Oliphant, and Adamowicz, 1993; Piecuch and Adamowicz, 1994; Piecuch, Kucharski, and Bartlett, 1999; Kowalski and Piecuch, 2000-2001; Gour, Piecuch, and Włoch, 2005-2006; Shen, Ajala, and Piecuch, 2013-2017; cf., also, CASCC work by Adamowicz et al.]



$$T^{(\text{CCSDt})} = T_1 + T_2 + t_3, \quad T^{(\text{CCSDtq})} = T_1 + T_2 + t_3 + t_4, \quad \text{etc.}$$

$$t_3 = \sum_{\substack{I>J>K \\ a>b>C}} t_{abC}^{Ijk} E_{Ijk}^{abC}, \quad t_4 = \sum_{\substack{I>J>K>L \\ a>b>C>D}} t_{abCD}^{IJKL} E_{IJKL}^{abCD}$$

Method

CCSDt/EOMCCSDt

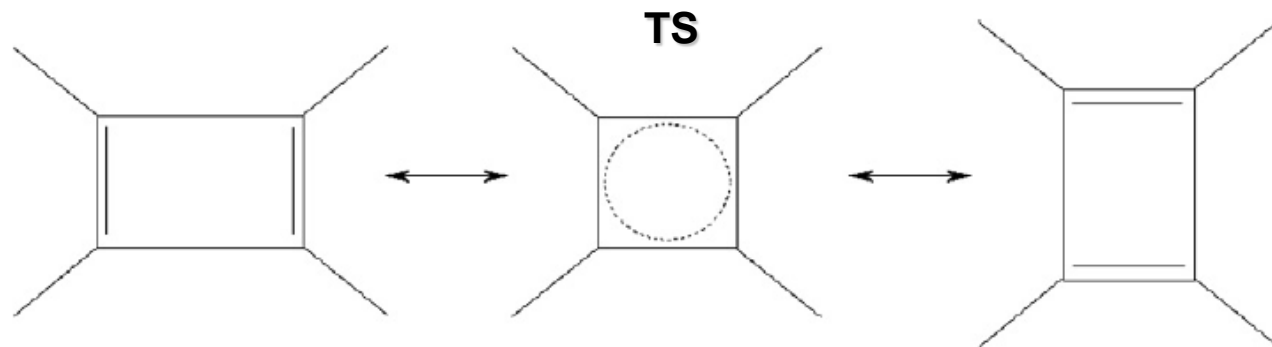
CCSDtq/EOMCCSDtq

CPU Time Scaling

$$N_o N_u n_o^2 n_u^4$$

$$N_o^2 N_u^2 n_o^2 n_u^4$$

AUTOMERIZATION OF CYCLOBUTADIENE



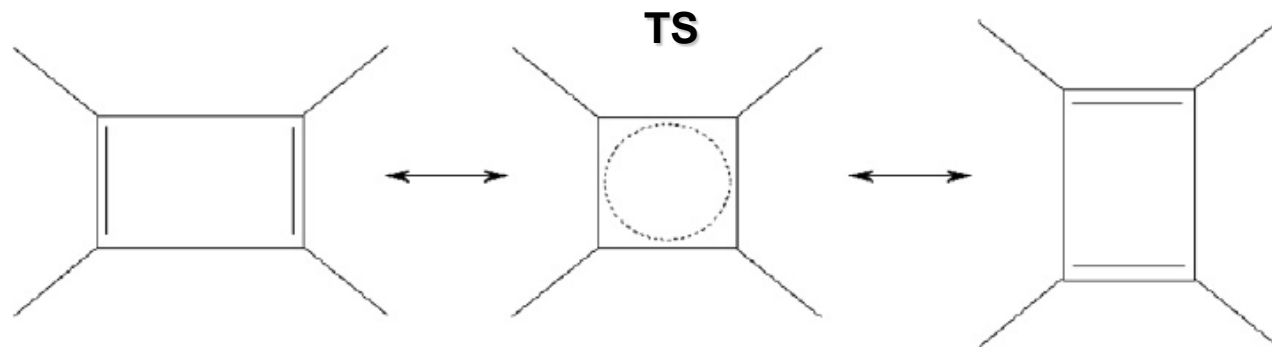
Various CC energies (in millihartree) relative to full CCSDT (in hartree), cc-pVDZ basis set

	Reactant	TS	Barrier Height (kcal/mol)
CCSD	26.827	47.979	20.9
CCSD(T)	1.123	14.198	15.8
CR-CC(2,3)	0.848	14.636	16.3
CCSDt	20.786	20.274	7.3
CCSDT	-154.244157	-154.232002	7.6

T_1 and T_2
decoupled from T_3



AUTOMERIZATION OF CYCLOBUTADIENE



Various CC energies (in millihartree) relative to full CCSDT (in hartree), cc-pVDZ basis set

	Reactant	TS	Barrier Height (kcal/mol)
CCSD	26.827	47.979	20.9
CCSD(T)	1.123	14.198	15.8
CR-CC(2,3)	0.848	14.636	16.3
CCSDt	20.786	20.274	7.3
CCSDT	-154.244157	-154.232002	7.6

T_1 and T_2
decoupled from T_3



t_3 misses some
dynamical
correlations

BEST SOLUTION: CC(P;Q) MOMENT EXPANSIONS

[J. Shen and P. Piecuch, Chem. Phys., 2012; J. Chem. Phys., 2012; J. Chem. Theory Comput., 2012]

$$E_{\mu}^{(P+Q)} = E_{\mu}^{(P)} + \delta_{\mu}(P;Q)$$

BEST SOLUTION: CC(P ; Q) MOMENT EXPANSIONS

[J. Shen and P. Piecuch, Chem. Phys., 2012; J. Chem. Phys., 2012; J. Chem. Theory Comput., 2012]

$$E_{\mu}^{(P+Q)} = E_{\mu}^{(P)} + \delta_{\mu}(P; Q)$$

CC ($\mu = 0$) or EOMCC ($\mu > 0$)
energy obtained in the P space $\mathcal{H}^{(P)}$

BEST SOLUTION: CC($P;Q$) MOMENT EXPANSIONS

[J. Shen and P. Piecuch, Chem. Phys., 2012; J. Chem. Phys., 2012; J. Chem. Theory Comput., 2012]

$$E_{\mu}^{(P+Q)} = E_{\mu}^{(P)} + \delta_{\mu}(P;Q)$$

CC ($\mu = 0$) or EOMCC ($\mu > 0$)
energy obtained in the P space $\mathcal{K}^{(P)}$

Correction due to correlation effects
captured by the Q space $\mathcal{K}^{(Q)}$

BEST SOLUTION: CC(P;Q) MOMENT EXPANSIONS

[J. Shen and P. Piecuch, Chem. Phys., 2012; J. Chem. Phys., 2012; J. Chem. Theory Comput., 2012]

$$E_{\mu}^{(P+Q)} = E_{\mu}^{(P)} + \delta_{\mu}(P;Q)$$

CC ($\mu = 0$) or EOMCC ($\mu > 0$)
energy obtained in the P space $\mathcal{H}^{(P)}$

Correction due to correlation effects
captured by the Q space $\mathcal{H}^{(Q)}$

$$E_{\mu}^{(P+Q)} \equiv E_{\mu}^{(P)} + \delta_{\mu}(P;Q), \quad \delta_{\mu}(P;Q) = \sum_{\substack{|\Phi_K\rangle \in \mathcal{H}^{(Q)} \\ \text{rank}(|\Phi_K\rangle) \leq \min(N_{\mu}^{(P)}, \Xi^{(Q)})}} \ell_{\mu,K}(P) \mathfrak{M}_{\mu,K}(P)$$

$$\mathfrak{M}_{\mu,K}(P) = \langle \Phi_K | (\bar{H}^{(P)} R_{\mu}^{(P)}) | \Phi \rangle, \quad \bar{H}^{(P)} = e^{-T^{(P)}} H e^{T^{(P)}} = (H e^{T^{(P)}})_C$$

$$\ell_{\mu,K}(P) = \langle \Phi | L_{\mu}^{(P)} \bar{H}^{(P)} | \Phi_K \rangle / D_{\mu,K}(P), \quad D_{\mu,K}(P) = E_{\mu}^{(P)} - \langle \Phi_K | \bar{H}^{(P)} | \Phi_K \rangle$$

BEST SOLUTION: CC(P;Q) MOMENT EXPANSIONS

[J. Shen and P. Piecuch, Chem. Phys., 2012; J. Chem. Phys., 2012; J. Chem. Theory Comput., 2012]

$$E_{\mu}^{(P+Q)} = E_{\mu}^{(P)} + \delta_{\mu}(P;Q)$$

CC ($\mu = 0$) or EOMCC ($\mu > 0$)
energy obtained in the P space $\mathcal{H}^{(P)}$

Correction due to correlation effects
captured by the Q space $\mathcal{H}^{(Q)}$

$$E_{\mu}^{(P+Q)} \equiv E_{\mu}^{(P)} + \delta_{\mu}(P;Q), \quad \delta_{\mu}(P;Q) = \sum_{\substack{|\Phi_K\rangle \in \mathcal{H}^{(Q)} \\ \text{rank}(|\Phi_K\rangle) \leq \min(N_{\mu}^{(P)}, \Xi^{(Q)})}} \ell_{\mu,K}(P) \mathfrak{M}_{\mu,K}(P)$$

moments of CC/EOMCC equations

$$\mathfrak{M}_{\mu,K}(P) = \langle \Phi_K | (\bar{H}^{(P)} R_{\mu}^{(P)}) | \Phi \rangle, \quad \bar{H}^{(P)} = e^{-T^{(P)}} H e^{T^{(P)}} = (H e^{T^{(P)}})_C$$

$$\ell_{\mu,K}(P) = \langle \Phi | L_{\mu}^{(P)} \bar{H}^{(P)} | \Phi_K \rangle / D_{\mu,K}(P), \quad D_{\mu,K}(P) = E_{\mu}^{(P)} - \langle \Phi_K | \bar{H}^{(P)} | \Phi_K \rangle$$

BEST SOLUTION: CC($P;Q$) MOMENT EXPANSIONS

[J. Shen and P. Piecuch, Chem. Phys., 2012; J. Chem. Phys., 2012; J. Chem. Theory Comput., 2012]

$$E_{\mu}^{(P+Q)} = E_{\mu}^{(P)} + \delta_{\mu}(P;Q)$$

CC ($\mu = 0$) or EOMCC ($\mu > 0$)
energy obtained in the P space $\mathcal{K}^{(P)}$

Correction due to correlation effects
captured by the Q space $\mathcal{K}^{(Q)}$

BEST SOLUTION: CC(P;Q) MOMENT EXPANSIONS

[J. Shen and P. Piecuch, Chem. Phys., 2012; J. Chem. Phys., 2012; J. Chem. Theory Comput., 2012]

$$E_{\mu}^{(P+Q)} = E_{\mu}^{(P)} + \delta_{\mu}(P;Q)$$

CC ($\mu = 0$) or EOMCC ($\mu > 0$)
energy obtained in the P space $\mathcal{K}^{(P)}$

Correction due to correlation effects
captured by the Q space $\mathcal{K}^{(Q)}$

Examples:

- P space: singly and doubly excited determinants (CCSD)
- Q space: triply excited determinants

CR-CC(2,3)

BEST SOLUTION: CC(P ; Q) MOMENT EXPANSIONS

[J. Shen and P. Piecuch, Chem. Phys., 2012; J. Chem. Phys., 2012; J. Chem. Theory Comput., 2012]

$$E_{\mu}^{(P+Q)} = E_{\mu}^{(P)} + \delta_{\mu}(P; Q)$$

CC ($\mu = 0$) or EOMCC ($\mu > 0$)
energy obtained in the P space $\mathcal{K}^{(P)}$

Correction due to correlation effects
captured by the Q space $\mathcal{K}^{(Q)}$

Examples:

- P space: singly and doubly excited determinants (CCSD)
- Q space: triply excited determinants

CR-CC(2,3)

- P space: singly and doubly excited determinants (CCSD)
- Q space: triply and quadruply excited determinants

CR-CC(2,4)

BEST SOLUTION: CC(P;Q) MOMENT EXPANSIONS

[J. Shen and P. Piecuch, Chem. Phys., 2012; J. Chem. Phys., 2012; J. Chem. Theory Comput., 2012]

$$E_{\mu}^{(P+Q)} = E_{\mu}^{(P)} + \delta_{\mu}(P;Q)$$

CC ($\mu = 0$) or EOMCC ($\mu > 0$)
energy obtained in the P space $\mathcal{K}^{(P)}$

Correction due to correlation effects
captured by the Q space $\mathcal{K}^{(Q)}$

Examples:

- P space: singles, doubles, and a subset of triples defined via active orbitals, as in CCSDt
- Q space: remaining triples not captured by CCSDt

CC(t;3)

BEST SOLUTION: CC(P;Q) MOMENT EXPANSIONS

[J. Shen and P. Piecuch, Chem. Phys., 2012; J. Chem. Phys., 2012; J. Chem. Theory Comput., 2012]

$$E_{\mu}^{(P+Q)} = E_{\mu}^{(P)} + \delta_{\mu}(P;Q)$$

CC ($\mu = 0$) or EOMCC ($\mu > 0$)
energy obtained in the P space $\mathcal{K}^{(P)}$

Correction due to correlation effects
captured by the Q space $\mathcal{K}^{(Q)}$

Examples:

- P space: singles, doubles, and a subset of triples defined via active orbitals, as in CCSDt
- Q space: remaining triples not captured by CCSDt

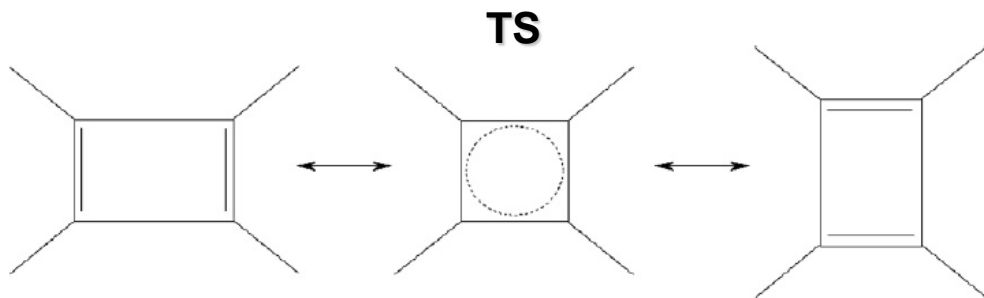
CC(t;3)

- P space: singles, doubles, and a subset of triples and quadruples defined via active orbitals, as in CCSDtq
- Q space: remaining triples and quadruples not captured by CCSDtq

CC(t,q;3,4)

AUTOMERIZATION OF CYCLOBUTADIENE

[J. Shen and P. Piecuch, *J. Chem. Phys.* 136, 144104 (2012)]



Various CC energies (in millihartree) relative to full CCSDT (in hartree), cc-pVDZ

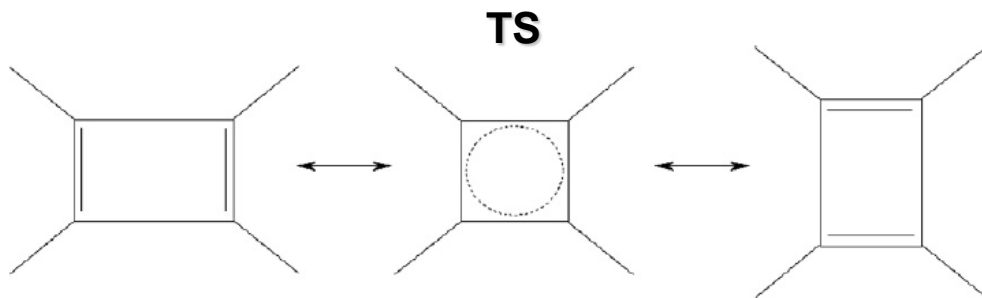
	Reactant	TS
CCSDT	-154.244157	-154.232002
CCSD	26.827	47.979
CCSD(T)	1.123	14.198
CR-CC(2,3)	0.848	14.636
CCSDt(I)	20.786	20.274
CCSD(T)-h(I)	-0.371	-4.548
CC(t;3)(I)	-0.137	0.071

Barrier heights (in kcal/mol) →

Method	cc-pVDZ	cc-pVTZ
CCSD	20.9	22.6
CCSD(T)	15.8	18.1
CR-CC(2,3)	16.3	18.6
CCSDt(I)	7.3	9.5
CCSD(T)-h(I)	5.0	6.8
CC(t;3)(I)	7.8	10.0
→ CCSDT	7.6	10.6
ΔCCSD(T) ^a	16.8	19.2
TCCSD ^a	9.4	12.9
TCCSD(T) ^a	4.6	7.0
CAS-BCCC4 ^b	7.6	8.7
CASPT2 ^b	3.4	3.8
SUCCSD ^c	7.0	8.7
MkCCSD ^c	7.8	9.6
RMRCCSD ^c	10.4	13.0
SUCCSD(T) ^c	4.8	5.9
RMRCCSD(T) ^c	7.2	9.5
SUCCSD/mcscf ^c	7.2	8.9
MkCCSD/mcscf ^c	7.9	9.7
RMRCCSD/mcscf ^c	9.5	11.4
SUCCSD(T)/mcscf ^c	5.7	7.2
RMRCCSD(T)/mcscf ^c	5.9	7.5
2D-MRCCSD(T) ^d	6.6	
BWCCSD(a.c.) ^e	6.5	7.6
BWCCSD(i.c.) ^e	6.2	7.4
BWCCSD(T)(a.c.) ^e	6.1	7.0
BWCCSD(T)(i.c.) ^e	5.7	6.8
MkCCSD ^e	7.8	9.1
MkCCSD(T) ^e	7.8	8.9
AQCC/SS-CASSCF ^f	7.7	8.9
AQCC/SA-2-CASSCF ^f	7.3	8.4
DIP-EOM-CCSD ^a	8.3	10.7
SS-EOM-CCSD[+2] ^g	8.3	9.5
Experimental range ^h		1.6-10
ΔZPVE ⁱ		-2.5

AUTOMERIZATION OF CYCLOBUTADIENE

[J. Shen and P. Piecuch, *J. Chem. Phys.* 136, 144104 (2012)]



Various CC energies (in millihartree) relative to full CCSDT (in hartree), cc-pVDZ

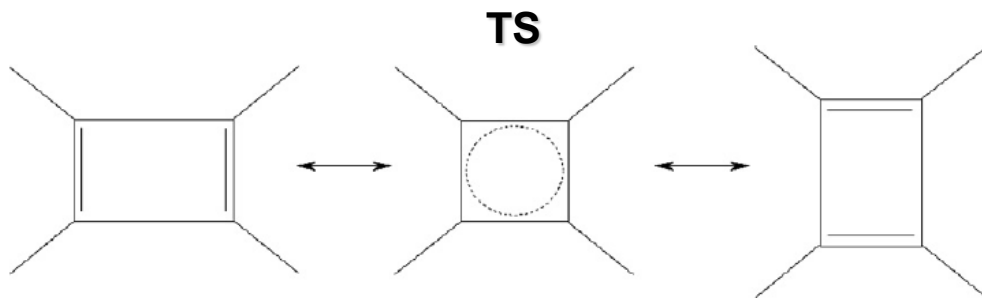
	Reactant	TS
CCSDT	-154.244157	-154.232002
CCSD	26.827	47.979
CCSD(T)	1.123	14.198
CR-CC(2,3)	0.848	14.636
CCSDt(I)	20.786	20.274
CCSD(T)-h(I)	-0.371	-4.548
CC(t;3)(I)	-0.137	0.071

Barrier heights (in kcal/mol) →

Method	cc-pVDZ	cc-pVTZ
CCSD	20.9	22.6
CCSD(T)	15.8	18.1
CR-CC(2,3)	16.3	18.6
CCSDt(I)	7.3	9.5
CCSD(T)-h(I)	5.0	6.8
CC(t;3)(I)	7.8	10.0
CCSDT	7.6	10.6
ΔCCSD(T) ^a	16.8	19.2
TCCSD ^a	9.4	12.9
TCCSD(T) ^a	4.6	7.0
CAS-BCCC4 ^b	7.6	8.7
CASPT2 ^b	3.4	3.8
SUCCSD ^c	7.0	8.7
MkCCSD ^c	7.8	9.6
RMRCCSD ^c	10.4	13.0
SUCCSD(T) ^c	4.8	5.9
RMRCCSD(T) ^c	7.2	9.5
SUCCSD/mcscf ^c	7.2	8.9
MkCCSD/mcscf ^c	7.9	9.7
RMRCCSD/mcscf ^c	9.5	11.4
SUCCSD(T)/mcscf ^c	5.7	7.2
RMRCCSD(T)/mcscf ^c	5.9	7.5
2D-MRCCSD(T) ^d	6.6	
BWCCSD(a.c.) ^e	6.5	7.6
BWCCSD(i.c.) ^e	6.2	7.4
BWCCSD(T)(a.c.) ^e	6.1	7.0
BWCCSD(T)(i.c.) ^e	5.7	6.8
MkCCSD ^e	7.8	9.1
MkCCSD(T) ^e	7.8	8.9
AQCC/SS-CASSCF ^f	7.7	8.9
AQCC/SA-2-CASSCF ^f	7.3	8.4
DIP-EOM-CCSD ^a	8.3	10.7
SS-EOM-CCSD[+2] ^g	8.3	9.5
Experimental range ^h		1.6-10
ΔZPVE ⁱ		-2.5

AUTOMERIZATION OF CYCLOBUTADIENE

[J. Shen and P. Piecuch, *J. Chem. Phys.* 136, 144104 (2012)]



Various CC energies (in millihartree) relative to full CCSDT (in hartree), cc-pVDZ

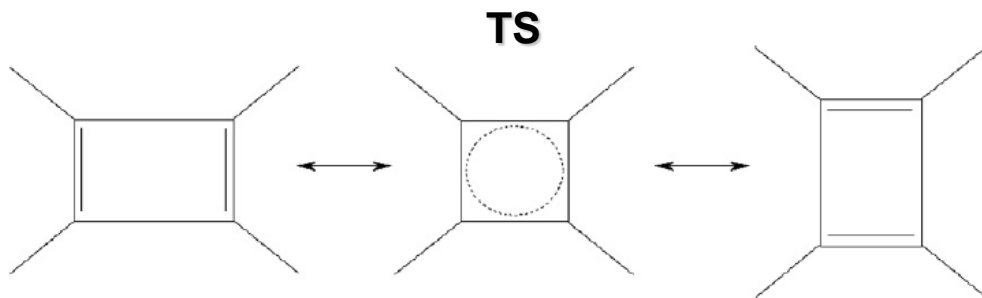
	Reactant	TS
CCSDT	-154.244157	-154.232002
CCSD	26.827	47.979
CCSD(T)	1.123	14.198
CR-CC(2,3)	0.848	14.636
CCSDt(I)	20.786	20.274
CCSD(T)-h(I)	-0.371	-4.548
CC(t;3)(I)	-0.137	0.071

Barrier heights (in kcal/mol) →

Method	cc-pVDZ	cc-pVTZ
CCSD	20.9	22.6
CCSD(T)	15.8	18.1
CR-CC(2,3)	16.3	18.6
CCSDt(I)	7.3	9.5
CCSD(T)-h(I)	5.0	6.8
CC(t;3)(I)	7.8	10.0
CCSDT	7.6	10.6
ΔCCSD(T) ^a	16.8	19.2
TCCSD ^a	9.4	12.9
TCCSD(T) ^a	4.6	7.0
CAS-BCCC4 ^b	7.6	8.7
CASPT2 ^b	3.4	3.8
SUCCSD ^c	7.0	8.7
MkCCSD ^c	7.8	9.6
RMRCCSD ^c	10.4	13.0
SUCCSD(T) ^c	4.8	5.9
RMRCCSD(T) ^c	7.2	9.5
SUCCSD/mcscf ^c	7.2	8.9
MkCCSD/mcscf ^c	7.9	9.7
RMRCCSD/mcscf ^c	9.5	11.4
SUCCSD(T)/mcscf ^c	5.7	7.2
RMRCCSD(T)/mcscf ^c	5.9	7.5
2D-MRCCSD(T) ^d	6.6	
BWCCSD(a.c.) ^e	6.5	7.6
BWCCSD(i.c.) ^e	6.2	7.4
BWCCSD(T)(a.c.) ^e	6.1	7.0
BWCCSD(T)(i.c.) ^e	5.7	6.8
MkCCSD ^e	7.8	9.1
MkCCSD(T) ^e	7.8	8.9
AQCC/SS-CASSCF ^f	7.7	8.9
AQCC/SA-2-CASSCF ^f	7.3	8.4
DIP-EOM-CCSD ^a	8.3	10.7
SS-EOM-CCSD[+2] ^g	8.3	9.5
Experimental range ^h	1.6-10	
ΔZPVE ⁱ	-2.5	

AUTOMERIZATION OF CYCLOBUTADIENE

[J. Shen and P. Piecuch, *J. Chem. Phys.* 136, 144104 (2012)]



Various CC energies (in millihartree) relative to full CCSDT (in hartree), cc-pVDZ

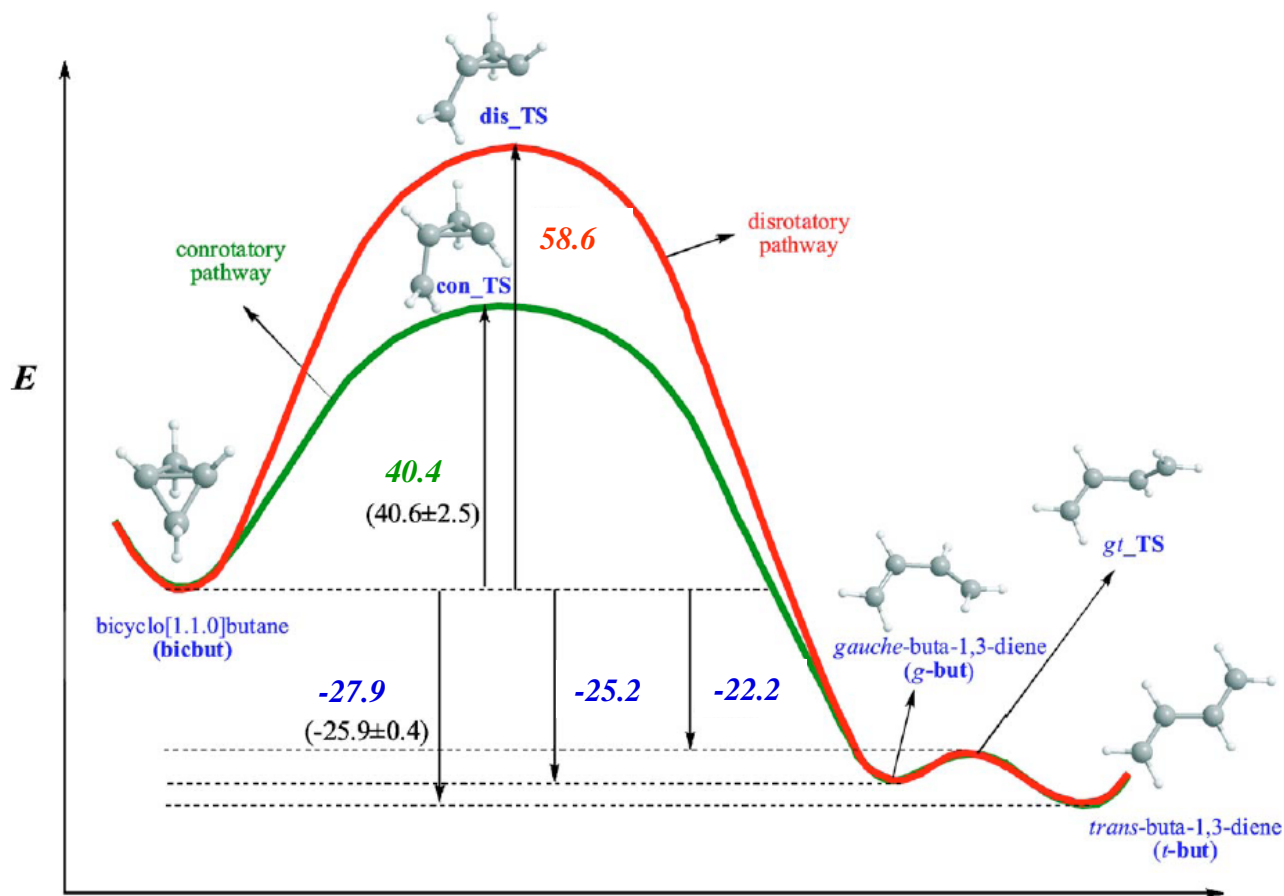
	Reactant	TS
CCSDT	-154.244157	-154.232002
CCSD	26.827	47.979
CCSD(T)	1.123	14.198
CR-CC(2,3)	0.848	14.636
CCSDt(I)	20.786	20.274
CCSD(T)-h(I)	-0.371	-4.548
CC(t;3)(I)	-0.137	0.071

Barrier heights (in kcal/mol) →

Method	cc-pVDZ	cc-pVTZ
CCSD	20.9	22.6
CCSD(T)	15.8	18.1
CR-CC(2,3)	16.3	18.6
CCSDt(I)	7.3	9.5
CCSD(T)-h(I)	5.0	6.8
CC(t;3)(I)	7.8	10.0
CCSDT	7.6	10.6
ACCSD(T) ^a	16.8	19.2
TCCSD ^a	9.4	12.9
TCCSD(T) ^a	4.6	7.0
CAS-BCCC4 ^b	7.6	8.7
CASPT2 ^b	3.4	3.8
SUCCSD ^c	7.0	8.7
MkCCSD ^c	7.8	9.6
RMRCCSD ^c	10.4	13.0
SUCCSD(T) ^c	4.8	5.9
RMRCCSD(T) ^c	7.2	9.5
SUCCSD/mcscf ^c	7.2	8.9
MkCCSD/mcscf ^c	7.9	9.7
RMRCCSD/mcscf ^c	9.5	11.4
SUCCSD(T)/mcscf ^c	5.7	7.2
RMRCCSD(T)/mcscf ^c	5.9	7.5
2D-MRCCSD(T) ^d	6.6	
BWCCSD(a.c.) ^e	6.5	7.6
BWCCSD(i.c.) ^e	6.2	7.4
BWCCSD(T)(a.c.) ^e	6.1	7.0
BWCCSD(T)(i.c.) ^e	5.7	6.8
MkCCSD ^e	7.8	9.1
MkCCSD(T) ^e	7.8	8.9
AQCC/SS-CASSCF ^f	7.7	8.9
AQCC/SA-2-CASSCF ^f	7.3	8.4
DIP-EOM-CCSD ^a	8.3	10.7
SS-EOM-CCSD[+2] ^g	8.3	9.5
Experimental range ^h	1.6-10	
ΔZPVE ⁱ	-2.5	

The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]butane to Butadiene (enthalpies at 0 K in kcal/mol)

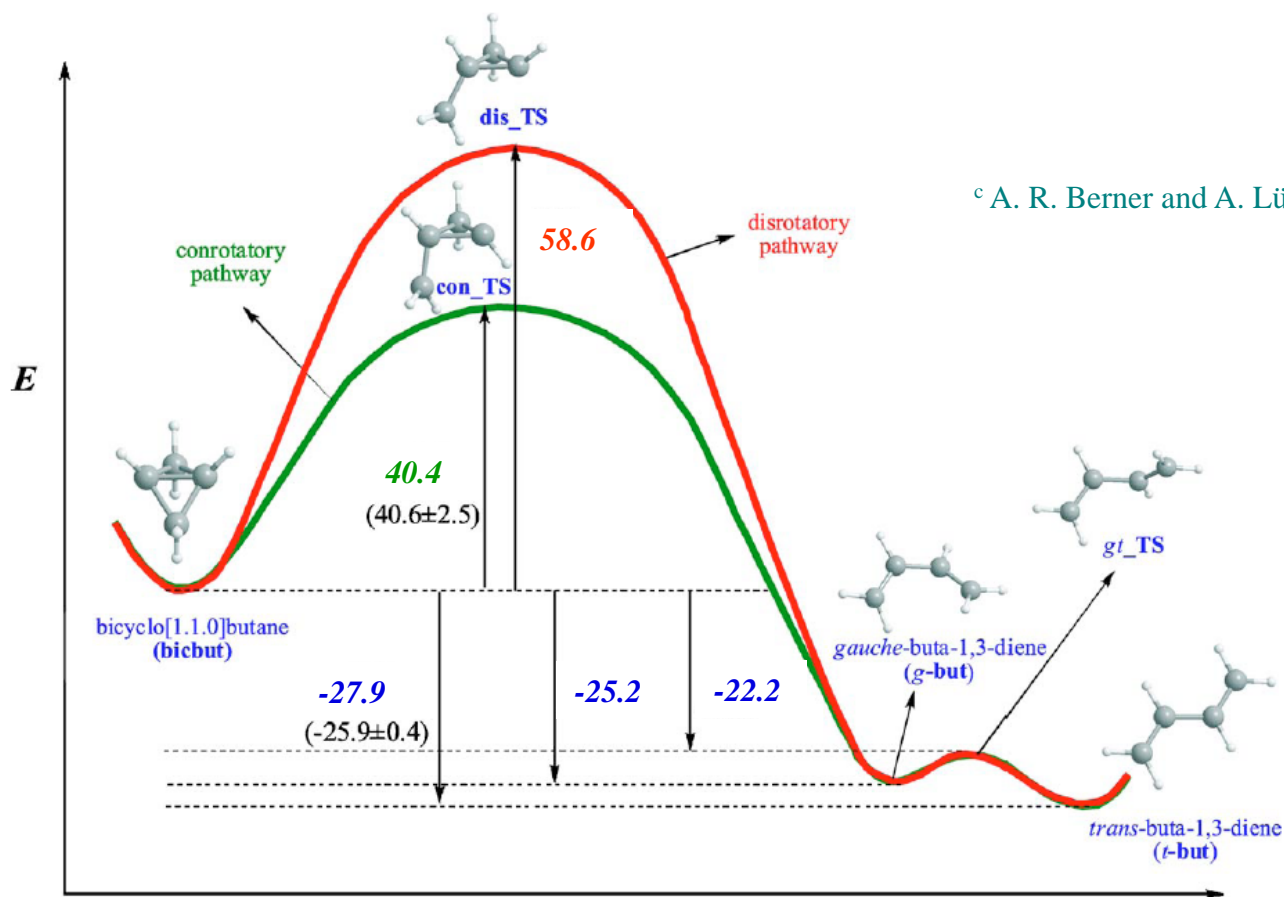
	con_TS	dis_TS	g-but	gt_TS	t-but
--	--------	--------	-------	-------	-------



The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]butane to Butadiene (enthalpies at 0 K in kcal/mol)

	con_TS	dis_TS	g-but	gt_TS	t-but
--	--------	--------	-------	-------	-------

OMR3-DMC ^c	40.4(5)	58.6(5)	-25.2(5)	-22.2(5)	-27.9(5)
-----------------------	---------	---------	----------	----------	----------



^c A. R. Berner and A. Lüchow, *J. Phys. Chem. A* **114**, 13222 (2010)

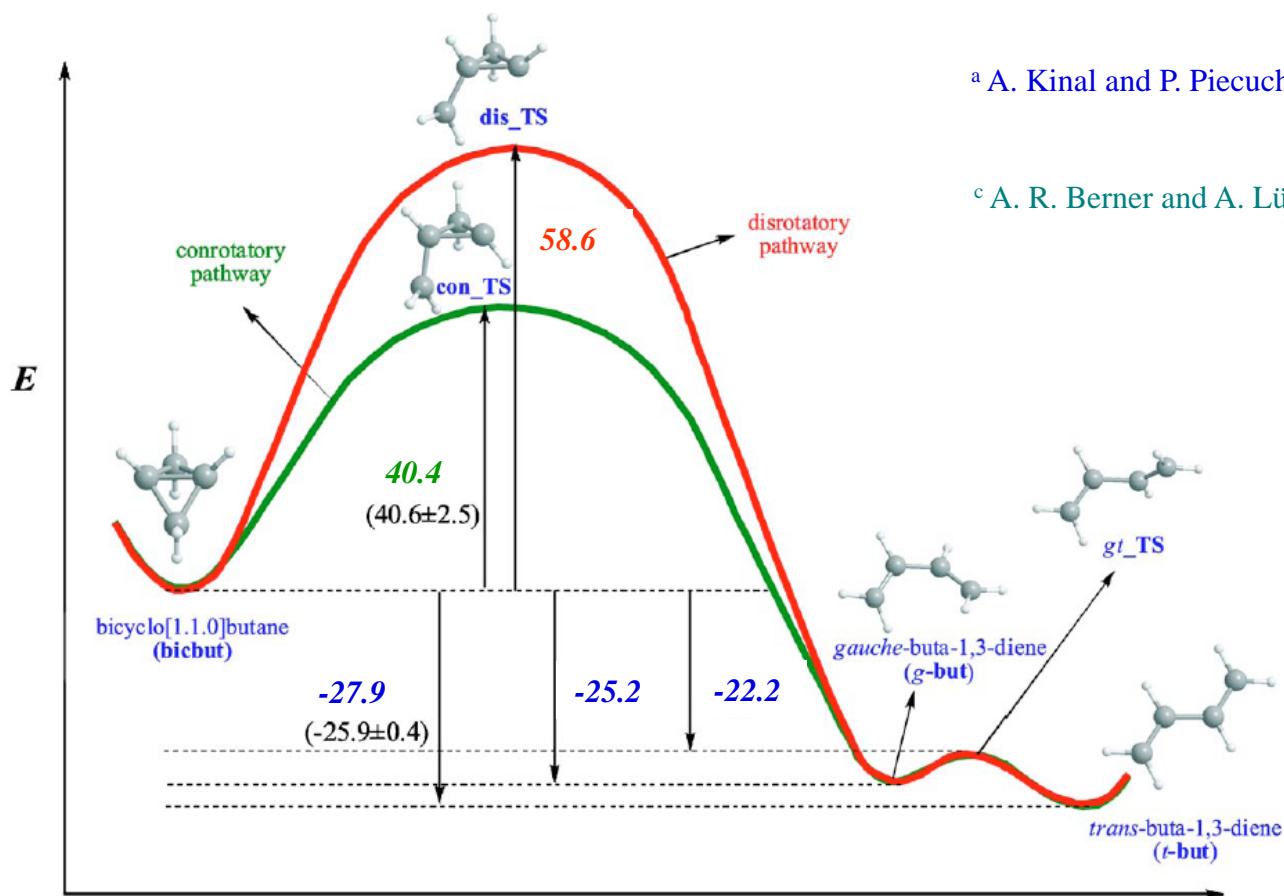
The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]butane to Butadiene (enthalpies at 0 K in kcal/mol)

	con_TS	dis_TS	g-but	gt_TS	t-but
CCSD(T) ^a	40.4	21.8	-25.1	-22.3	-28.0

OMR3-DMC ^c	40.4(5)	58.6(5)	-25.2(5)	-22.2(5)	-27.9(5)
-----------------------	---------	---------	----------	----------	----------

^a A. Kinal and P. Piecuch, *J. Phys. Chem. A* **111**, 734 (2007)

^c A. R. Berner and A. Lüchow, *J. Phys. Chem. A* **114**, 13222 (2010)



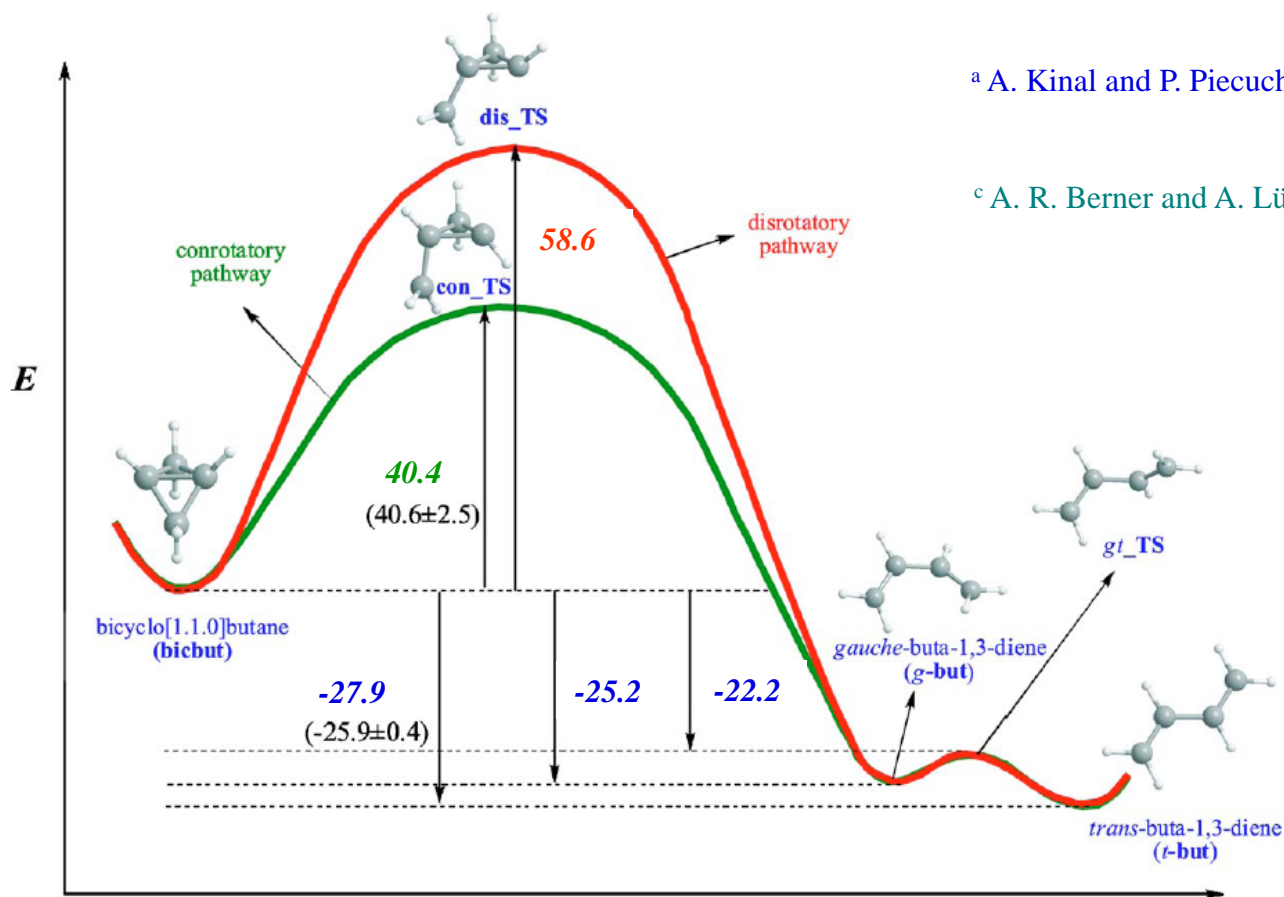
The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]butane to Butadiene (enthalpies at 0 K in kcal/mol)

	con_TS	dis_TS	g-but	gt_TS	t-but
CCSD(T) ^a	40.4	21.8	-25.1	-22.3	-28.0
CR-CC(2,3) ^a	41.1	66.1	-24.9	-22.1	-27.9

OMR3-DMC ^c	40.4(5)	58.6(5)	-25.2(5)	-22.2(5)	-27.9(5)
-----------------------	---------	---------	----------	----------	----------

^a A. Kinal and P. Piecuch, *J. Phys. Chem. A* **111**, 734 (2007)

^c A. R. Berner and A. Lüchow, *J. Phys. Chem. A* **114**, 13222 (2010)



The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]butane to Butadiene (enthalpies at 0 K in kcal/mol)

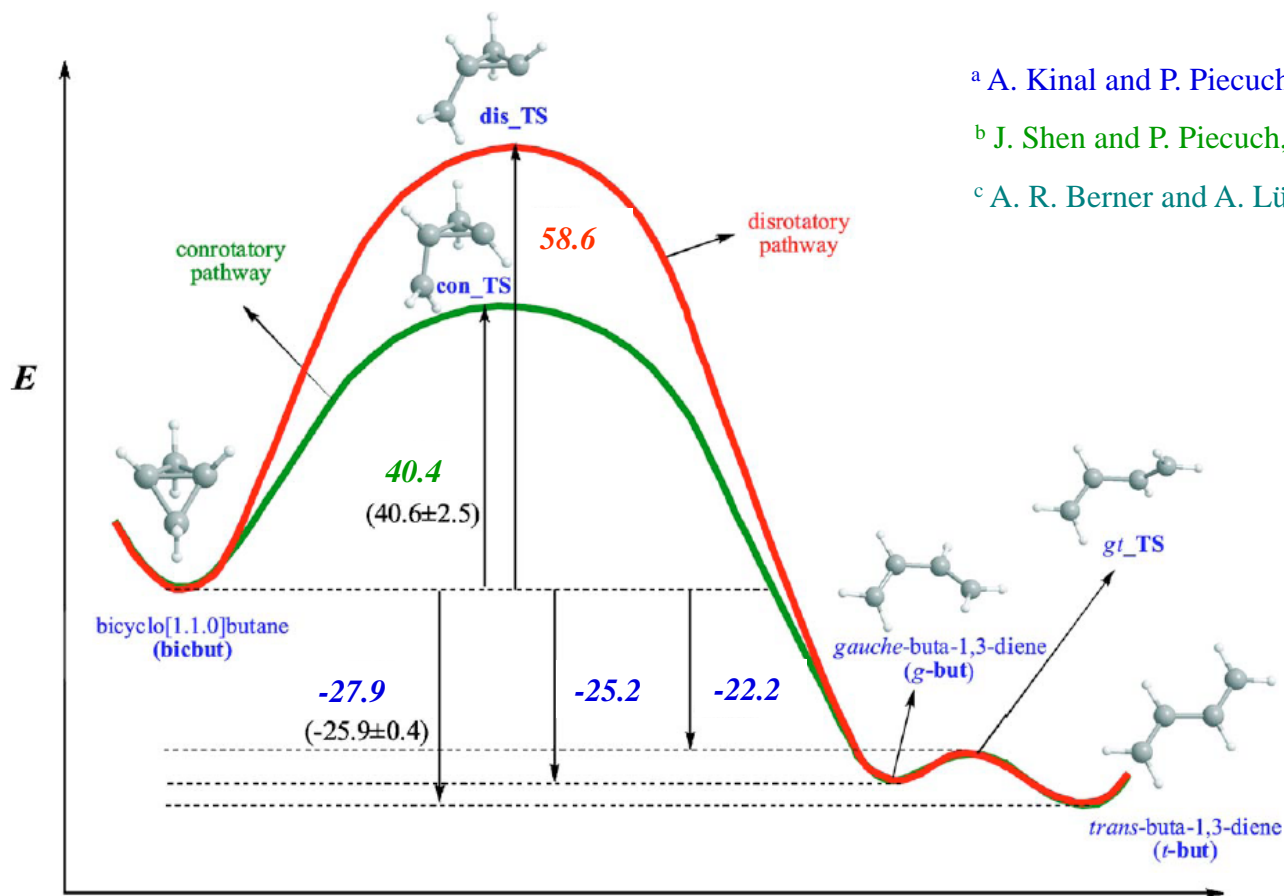
	con_TS	dis_TS	g-but	gt_TS	t-but
CCSD(T) ^a	40.4	21.8	-25.1	-22.3	-28.0
CR-CC(2,3) ^a	41.1	66.1	-24.9	-22.1	-27.9
CCSDt ^b	40.1	59.0	-27.2	-25.3	-31.1

OMR3-DMC ^c	40.4(5)	58.6(5)	-25.2(5)	-22.2(5)	-27.9(5)
-----------------------	---------	---------	----------	----------	----------

^a A. Kinal and P. Piecuch, *J. Phys. Chem. A* **111**, 734 (2007)

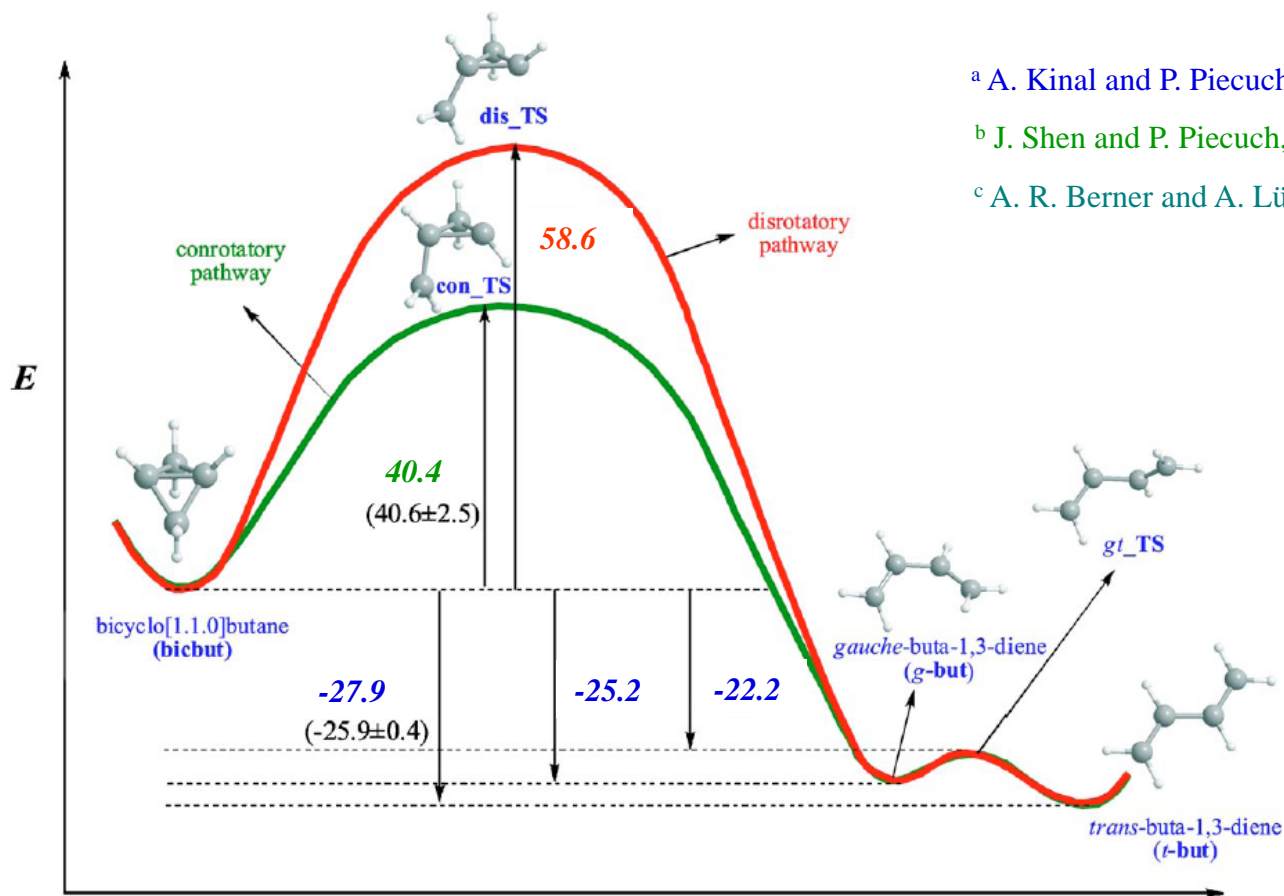
^b J. Shen and P. Piecuch, *J. Chem. Phys.* **136**, 144104 (2012)

^c A. R. Berner and A. Lüchow, *J. Phys. Chem. A* **114**, 13222 (2010)



The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]butane to Butadiene (enthalpies at 0 K in kcal/mol)

	con_TS	dis_TS	g-but	gt_TS	t-but
CCSD(T) ^a	40.4	21.8	-25.1	-22.3	-28.0
CR-CC(2,3) ^a	41.1	66.1	-24.9	-22.1	-27.9
CCSDt ^b	40.1	59.0	-27.2	-25.3	-31.1
CC(t;3) ^b	40.2	60.1	-25.3	-22.6	-28.3
OMR3-DMC ^c	40.4(5)	58.6(5)	-25.2(5)	-22.2(5)	-27.9(5)



^a A. Kinal and P. Piecuch, *J. Phys. Chem. A* **111**, 734 (2007)

^b J. Shen and P. Piecuch, *J. Chem. Phys.* **136**, 144104 (2012)

^c A. R. Berner and A. Lüchow, *J. Phys. Chem. A* **114**, 13222 (2010)

The $CC(t;3)$, $CC(t,q;3)$, $CC(t,q;3,4)$, etc. hierarchy works well, but it requires choosing user- and system-dependent active orbitals to select the dominant T_n and R_n components with $n > 2$ prior to the determination of $CC(P;Q)$ corrections, i.e., it is not a black-box methodology.

The $CC(t;3)$, $CC(t,q;3)$, $CC(t,q;3,4)$, etc. hierarchy works well, but it requires choosing user- and system-dependent active orbitals to select the dominant T_n and R_n components with $n > 2$ prior to the determination of $CC(P;Q)$ corrections, i.e., it is not a black-box methodology.

QUESTIONS:

The $CC(t;3)$, $CC(t,q;3)$, $CC(t,q;3,4)$, etc. hierarchy works well, but it requires choosing user- and system-dependent active orbitals to select the dominant T_n and R_n components with $n > 2$ prior to the determination of $CC(P;Q)$ corrections, i.e., it is not a black-box methodology.

QUESTIONS:

- ❖ Is there an automated way of determining P spaces reflecting on the nature of states being calculated, while using corrections $\delta_\mu(P;Q)$ to capture the remaining correlations of interest?

The $CC(t;3)$, $CC(t,q;3)$, $CC(t,q;3,4)$, etc. hierarchy works well, but it requires choosing user- and system-dependent active orbitals to select the dominant T_n and R_n components with $n > 2$ prior to the determination of $CC(P;Q)$ corrections, i.e., it is not a black-box methodology.

QUESTIONS:

- ❖ Is there an automated way of determining P spaces reflecting on the nature of states being calculated, while using corrections $\delta_\mu(P;Q)$ to capture the remaining correlations of interest?
- ❖ Can this be done such that the resulting electronic energies rapidly converge to their high-level (CCSDT, CCSDTQ, etc.) parents, even when higher-than-two-body clusters become large, at the small fraction of the computational effort and with an ease of a black-box computation?

The $CC(t;3)$, $CC(t,q;3)$, $CC(t,q;3,4)$, etc. hierarchy works well, but it requires choosing user- and system-dependent active orbitals to select the dominant T_n and R_n components with $n > 2$ prior to the determination of $CC(P;Q)$ corrections, i.e., it is not a black-box methodology.

QUESTIONS:

- ❖ Is there an automated way of determining P spaces reflecting on the nature of states being calculated, while using corrections $\delta_\mu(P;Q)$ to capture the remaining correlations of interest?
- ❖ Can this be done such that the resulting electronic energies rapidly converge to their high-level (CCSDT, CCSDTQ, etc.) parents, even when higher-than-two-body clusters become large, at the small fraction of the computational effort and with an ease of a black-box computation?

Both questions have positive answers if we fuse

DETERMINISTIC $CC(P;Q)$ METHODOLOGY

with

STOCHASTIC CI AND CC MONTE CARLO.

[J.E. Deustua, J. Shen, and P. Piecuch, Phys. Rev. Lett. 119, 223003 (2017)]

CI QUANTUM MONTE CARLO (CIQMC)

THE JOURNAL OF CHEMICAL PHYSICS **131**, 054106 (2009)

Fermion Monte Carlo without fixed nodes: A game of life, death, and annihilation in Slater determinant space

George H. Booth,¹ Alex J. W. Thom,^{1,2} and Ali Alavi^{1,a)}

¹*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

²*Department of Chemistry, University of California Berkeley, Berkeley, California 94720, USA*

(Received 15 May 2009; accepted 13 July 2009; published online 4 August 2009)

CC MONTE CARLO (CCMC)

PRL **105**, 263004 (2010)

PHYSICAL REVIEW LETTERS

week ending
31 DECEMBER 2010

Stochastic Coupled Cluster Theory

Alex J. W. Thom*

*Department of Chemistry, Imperial College London, London SW7 2AZ, United Kingdom and
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

(Received 14 September 2010; published 28 December 2010)

CIQMC (FCIQMC, CISDT-MC, CISDTQ-MC, etc.)

$$\lim_{\tau \rightarrow \infty} |\Psi(\tau)\rangle = \lim_{\tau \rightarrow \infty} e^{-(H-S)\tau} |\Phi_0\rangle = \begin{cases} c_0 |\Psi_0\rangle & \text{for } S = E_0 \\ \infty & \text{for } S > E_0 \\ 0 & \text{for } S < E_0 \end{cases}$$

$$|\Psi(\tau)\rangle = c_0(\tau) |\Phi_0\rangle + \sum_K c_K(\tau) |\Phi_K\rangle$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S)c_K(\tau) - \sum_{L(\neq K)} H_{KL}c_L(\tau)$$

If $S \rightarrow E_0$, $\lim_{\tau \rightarrow \infty} \frac{\partial c_K(\tau)}{\partial \tau} = 0$ and we obtain $\sum_L H_{KL}c_L(\infty) = E_0c_K(\infty)$

CIQMC (FCIQMC, CISDT-MC, CISDTQ-MC, etc.)

WALKER POPULATION DYNAMICS

$$c_K(\tau) \sim N_K = \sum_{\alpha} s_{\alpha} \delta_{K, K_{\alpha}}, \quad s_{\alpha} = \pm 1$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S)c_K(\tau) - \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

birth and death



spawning



$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau) \quad c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

1. Place a certain number of walkers on a reference determinant (or determinants) and set S at some value above E_0 .

2. In every time step, attempt

- i. spawning: spawn walkers at different determinants.
- ii. birth or death: create or destroy walkers at a given determinant.
- iii. annihilation: eliminate pairs of oppositely signed walkers at a given determinant.

3. Once a critical (or sufficiently large) number of walkers is reached, start applying energy shifts in S to stabilize walker population and reach convergence.

CIQMC (FCIQMC, CISDT-MC, CISDTQ-MC, etc.)

WALKER POPULATION DYNAMICS

$$c_K(\tau) \sim N_K = \sum_{\alpha} s_{\alpha} \delta_{K, K_{\alpha}}, \quad s_{\alpha} = \pm 1$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S)c_K(\tau) - \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

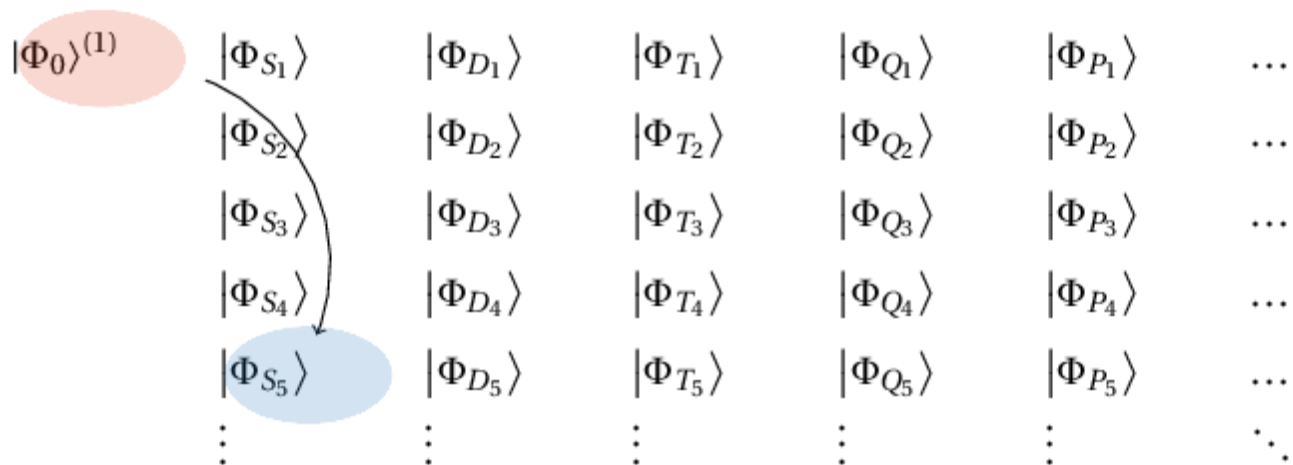
birth and death



spawning



$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau) \quad c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL} c_L(\tau)$$



CIQMC (FCIQMC, CISDT-MC, CISDTQ-MC, etc.)

WALKER POPULATION DYNAMICS

$$c_K(\tau) \sim N_K = \sum_{\alpha} s_{\alpha} \delta_{K, K_{\alpha}}, \quad s_{\alpha} = \pm 1$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S)c_K(\tau) - \sum_{L(\neq K)} H_{KL}c_L(\tau)$$

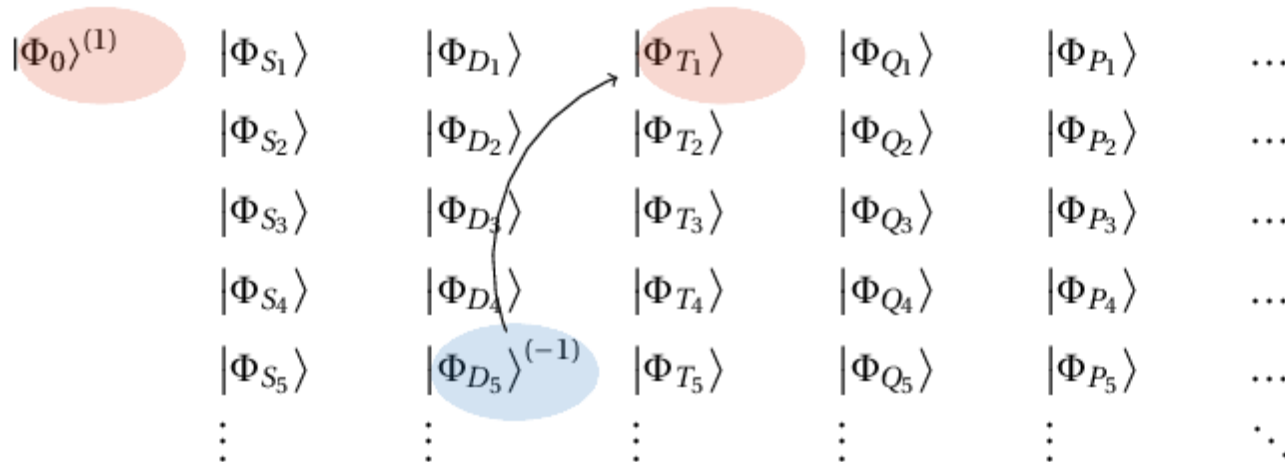
birth and death



spawning



$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau) \quad c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL}c_L(\tau)$$



CIQMC (FCIQMC, CISDT-MC, CISDTQ-MC, etc.)

WALKER POPULATION DYNAMICS

$$c_K(\tau) \sim N_K = \sum_{\alpha} s_{\alpha} \delta_{K, K_{\alpha}}, \quad s_{\alpha} = \pm 1$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S)c_K(\tau) - \sum_{L(\neq K)} H_{KL}c_L(\tau)$$

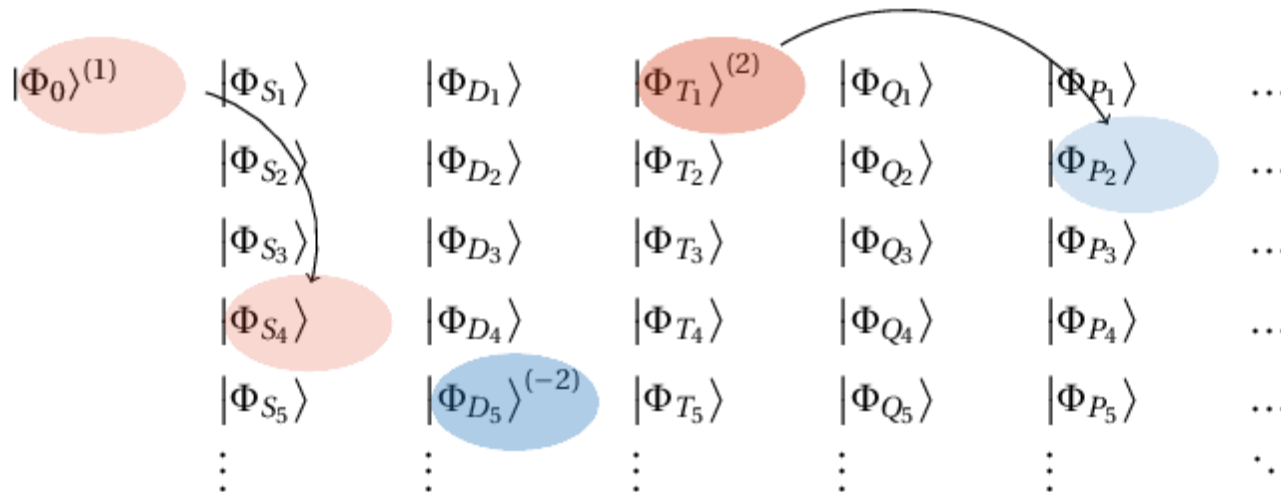
birth and death



spawning



$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau) \quad c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL}c_L(\tau)$$



CIQMC (FCIQMC, CISDT-MC, CISDTQ-MC, etc.)

WALKER POPULATION DYNAMICS

$$c_K(\tau) \sim N_K = \sum_{\alpha} s_{\alpha} \delta_{K, K_{\alpha}}, \quad s_{\alpha} = \pm 1$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S)c_K(\tau) - \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

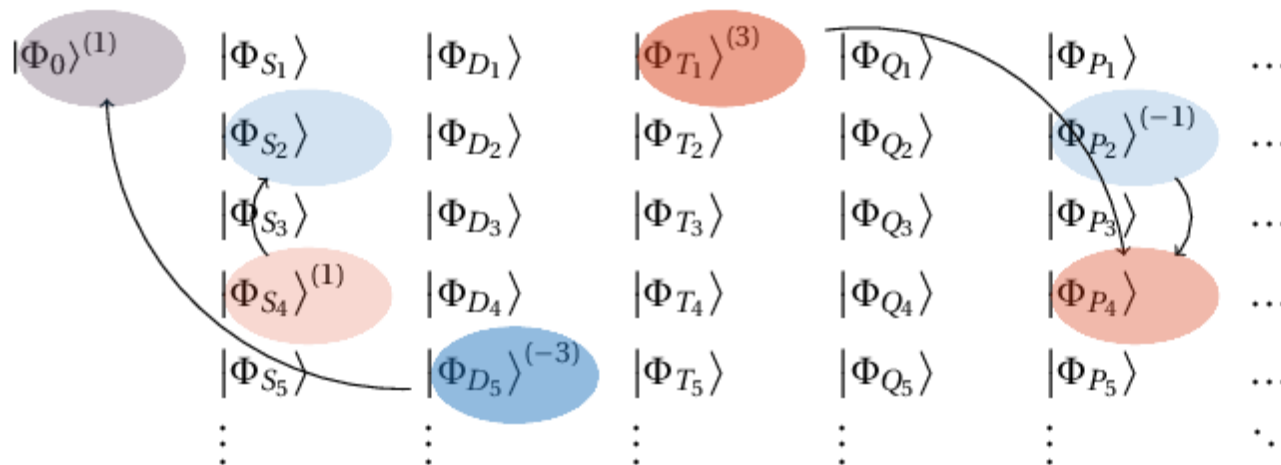
birth and death



spawning



$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau) \quad c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL} c_L(\tau)$$



CIQMC (FCIQMC, CISDT-MC, CISDTQ-MC, etc.)

WALKER POPULATION DYNAMICS

$$c_K(\tau) \sim N_K = \sum_{\alpha} s_{\alpha} \delta_{K, K_{\alpha}}, \quad s_{\alpha} = \pm 1$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S)c_K(\tau) - \sum_{L(\neq K)} H_{KL}c_L(\tau)$$

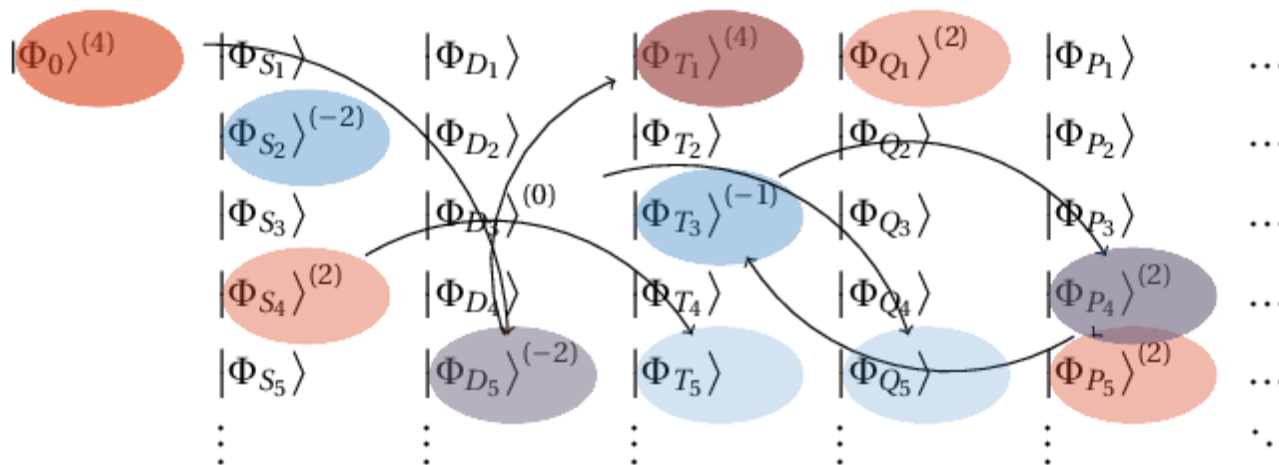
birth and death



spawning



$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau) \quad c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL}c_L(\tau)$$



CIQMC (FCIQMC, CISDT-MC, CISDTQ-MC, etc.)

WALKER POPULATION DYNAMICS

$$c_K(\tau) \sim N_K = \sum_{\alpha} s_{\alpha} \delta_{K, K_{\alpha}}, \quad s_{\alpha} = \pm 1$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S)c_K(\tau) - \sum_{L(\neq K)} H_{KL}c_L(\tau)$$

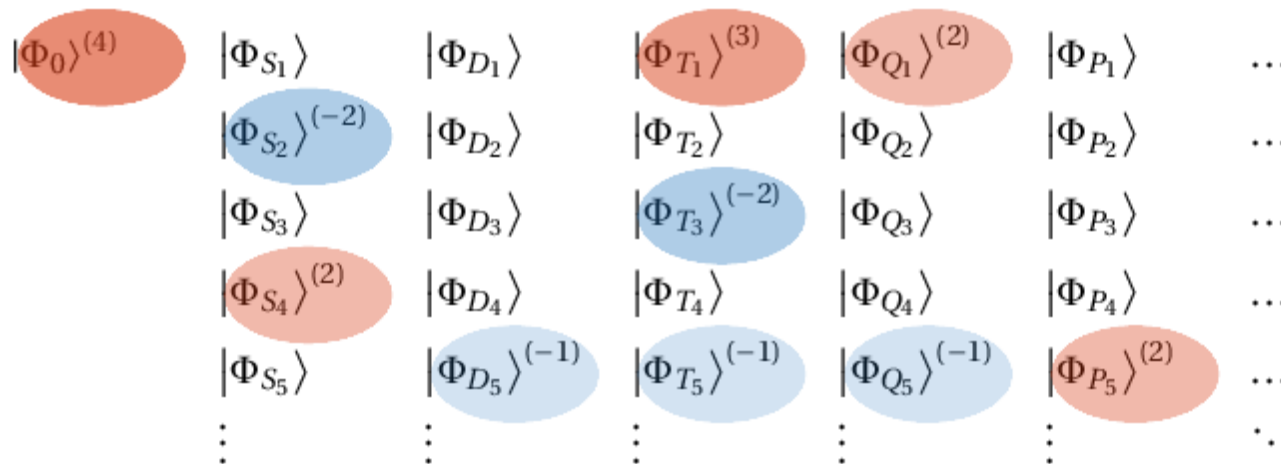
birth and death



spawning



$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau) \quad c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL}c_L(\tau)$$



CIQMC (FCIQMC, CISDT-MC, CISDTQ-MC, etc.)

WALKER POPULATION DYNAMICS

$$c_K(\tau) \sim N_K = \sum_{\alpha} s_{\alpha} \delta_{K, K_{\alpha}}, \quad s_{\alpha} = \pm 1$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S)c_K(\tau) - \sum_{L(\neq K)} H_{KL}c_L(\tau)$$

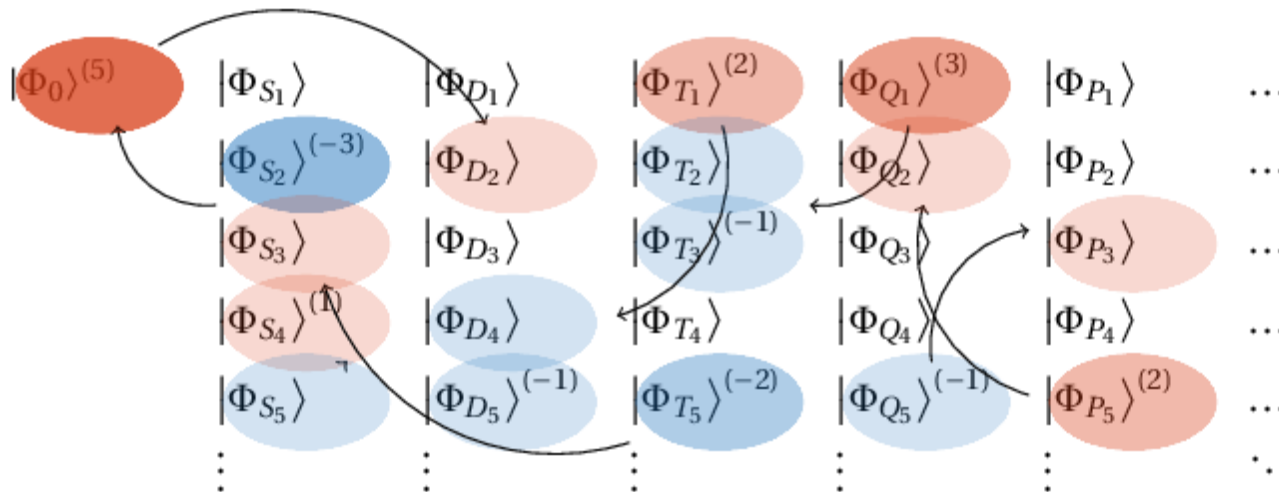
birth and death



spawning



$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau) \quad c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL}c_L(\tau)$$



CIQMC (FCIQMC, CISDT-MC, CISDTQ-MC, etc.)

WALKER POPULATION DYNAMICS

$$c_K(\tau) \sim N_K = \sum_{\alpha} s_{\alpha} \delta_{K, K_{\alpha}}, \quad s_{\alpha} = \pm 1$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S)c_K(\tau) - \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

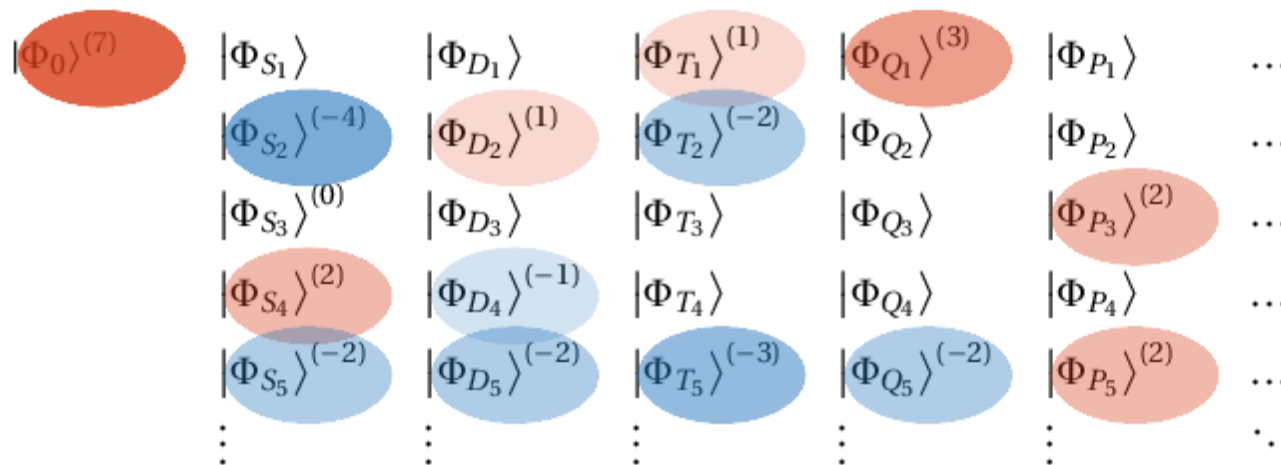
birth and death



spawning



$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau) \quad c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL} c_L(\tau)$$



CIQMC (FCIQMC, CISDT-MC, CISDTQ-MC, etc.)

WALKER POPULATION DYNAMICS

$$c_K(\tau) \sim N_K = \sum_{\alpha} s_{\alpha} \delta_{K, K_{\alpha}}, \quad s_{\alpha} = \pm 1$$

$$\frac{\partial c_K(\tau)}{\partial \tau} = -(H_{KK} - S)c_K(\tau) - \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

birth and death



spawning



$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau) \quad c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

CCMC (CCSDT-MC, CCSDTQ-MC, etc.)

In CCMC, instead of sampling determinants by walkers, one samples the space of excitation amplitudes (amplitudes of “excitors”) by excitor particles (“excips”).

To accelerate convergence, one can use the **initiator CIQMC (*i*-CIQMC)** and **CCMC (*i*-CCMC)** approaches, where only those determinants or excitors that acquire a walker/excipient population exceeding a preset value n_a are allowed to spawn new walkers onto empty determinants/exciters. One can start *i*-CIQMC and *i*-CCMC simulations by placing a certain, sufficiently large, number of walkers/excipients on the reference determinant (in our case, the RHF state).

THE JOURNAL OF CHEMICAL PHYSICS **132**, 041103 (2010)

Communications: Survival of the fittest: Accelerating convergence in full configuration-interaction quantum Monte Carlo

Deidre Cleland, George H. Booth, and Ali Alavi^{a)}

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

(Received 11 December 2009; accepted 11 January 2010; published online 28 January 2010)

THE JOURNAL OF CHEMICAL PHYSICS **144**, 084108 (2016)



Developments in stochastic coupled cluster theory: The initiator approximation and application to the uniform electron gas

James S. Spencer¹ and Alex J. W. Thom^{2,a)}

¹*Department of Physics and Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom*

²*University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom and Department of Chemistry, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom*

(Received 17 November 2015; accepted 4 February 2016; published online 24 February 2016)

Developing a Stochastic CC($P; Q$) Approach

Developing a Stochastic CC($P; Q$) Approach

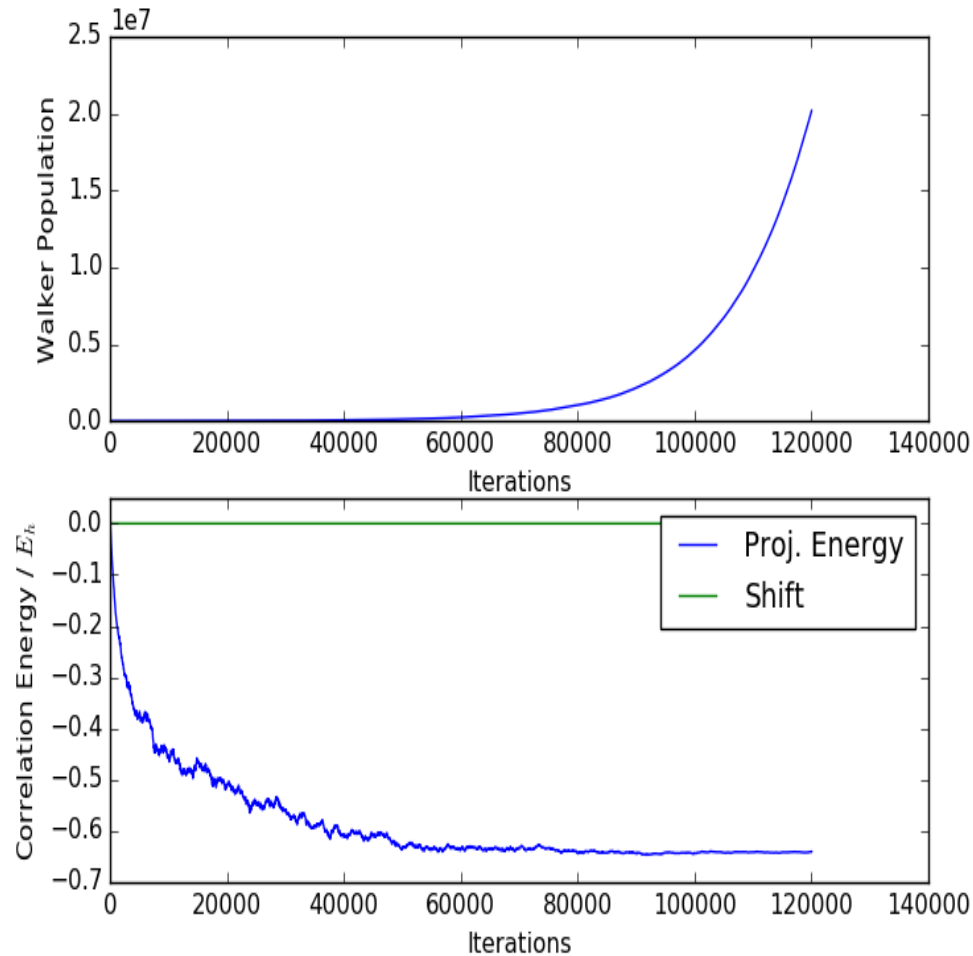
1. Start a CIQMC (e.g., i -CIQMC) or CCMC (e.g., i -CCMC) propagation by placing a certain number of walkers or excips on the reference determinant.

Developing a Stochastic CC(P ; Q) Approach

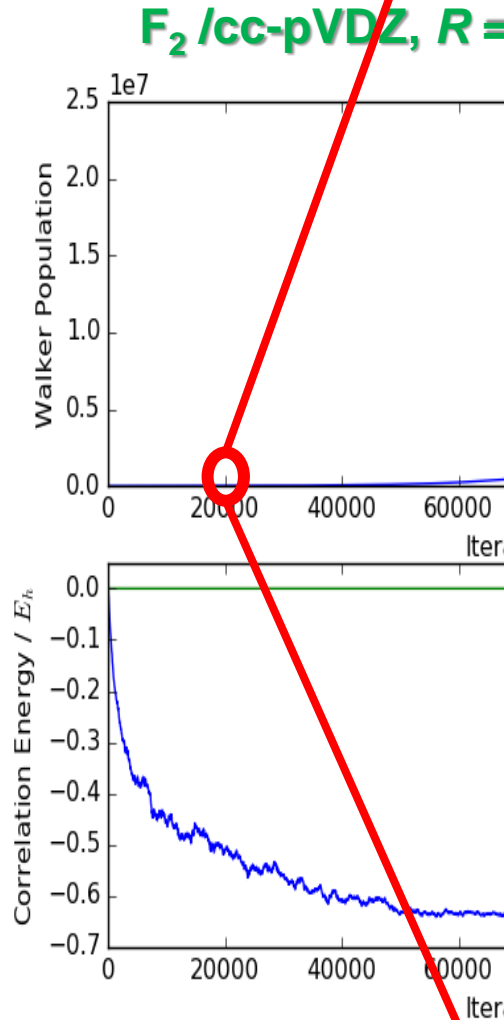
1. Start a CIQMC (e.g., i -CIQMC) or CCMC (e.g., i -CCMC) propagation by placing a certain number of walkers or excips on the reference determinant.
2. Extract a list of the most important determinants or cluster amplitude types relevant to the CC theory of interest (triples for CCSDT; triples and quadruples for CCSDTQ, etc.) from the CIQMC or CCMC propagation at a given time τ to define the P space for CC(P) calculations as follows:
 - if the target approach is CCSDT, the P space is defined as all singles, all doubles, and a subset of triples having at least n_p (e.g., one) positive or negative walkers/excips on them.
 - if the target approach is CCSDTQ, the P space is defined as all singles, all doubles, and a subset of triples and quadruples having at least n_p (e.g., one) positive or negative walkers/excips on them, etc.

Developing a Stochastic CC(P ; Q) Approach

F_2 /cc-pVDZ, $R = 2 R_e$, i -FCIQMC

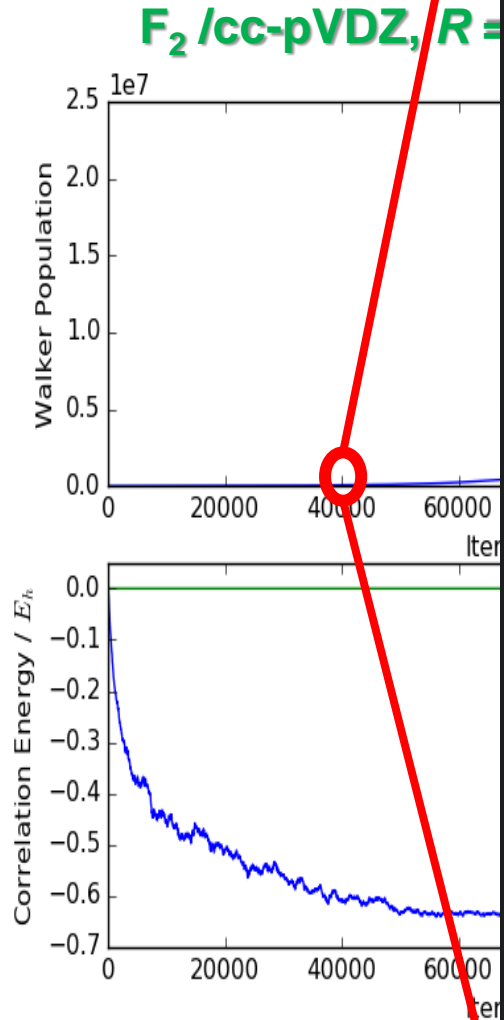


Developing a Stochastic



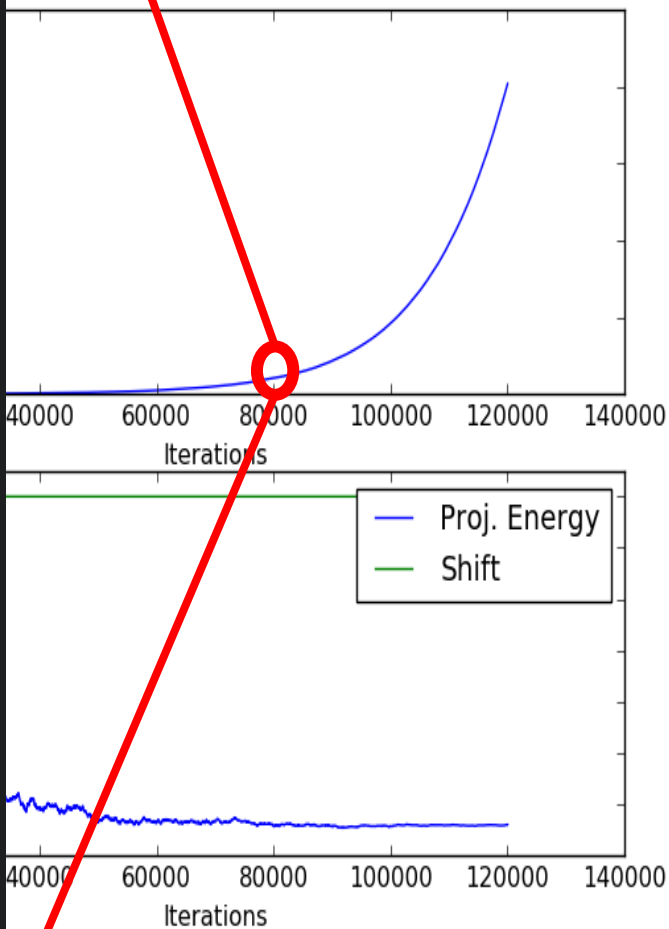
```
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
2 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
3 -10 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
4 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
5 4 5 6 7 8 9 10 11 12 13 14 15 16 17
6 6 -1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
7 8 -3 4 5 6 7 8 9 10 11 12 13 14 15 16
8 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
9 10 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
11 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
12 -1 2 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
13 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
14 -2 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
15 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
16 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
17 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
18 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
19 -2 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
20 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
21 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
22 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
23 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
24 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
25 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
26 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
27 -6 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
28 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
29 2 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
30 -1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
31 -1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
32 -1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
33 -2 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
34 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
35 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
36 -8 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
37 -2 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
38 2 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
39 2 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
40 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
41 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
42 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
43 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
44 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
45 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
46 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
47 -4 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
48 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
49 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
50 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
51 8 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
52 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
53 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
54 -1 3 4 5 6 7 8 9 10 11 12 13 14 15 16
55 -1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
56 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
57 -2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
58 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
59 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
60 -2 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
61 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
62 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
63 -2 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
64 -5 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
65 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
66 -3 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
67 -1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
68 2 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
69 2 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
70 1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
71 1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
72 1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
73 1 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
```

Developing a Stochastic



Stochastic CC(P;Q) Approach

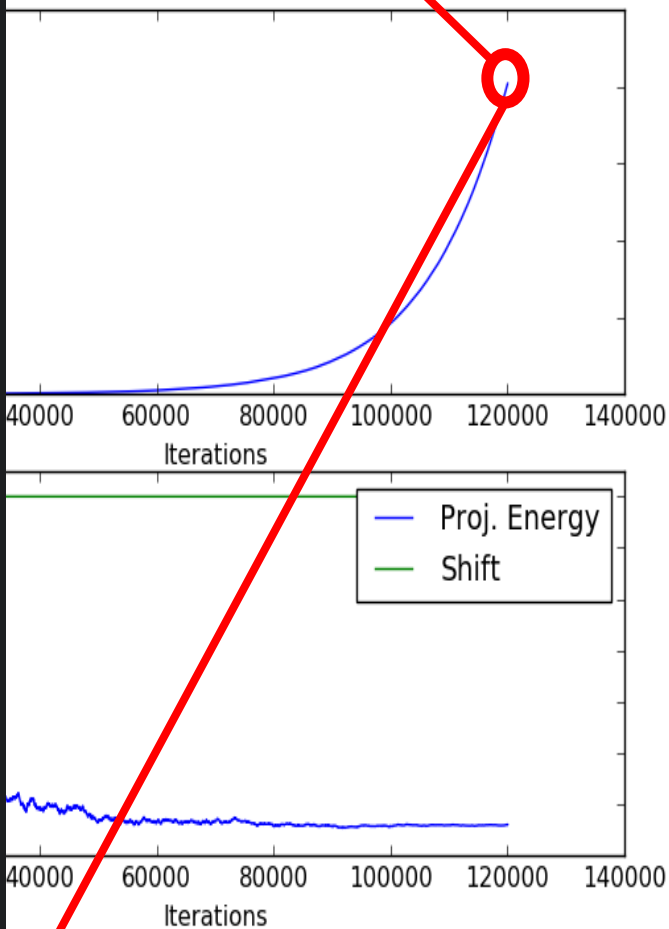
VDZ, $R = 2 R_e$, i -FCIQMC



David P. Piecuch, Phys. Rev. Lett. 119, 223003 (2017)]

Stochastic CC(P;Q) Approach

VDZ, $R = 2 R_e$, FCIQMC



Developing a Stochastic CC(P ; Q) Approach

1. Start a CIQMC (e.g., i -CIQMC) or CCMC (e.g., i -CCMC) propagation by placing a certain number of walkers or excips on the reference determinant.
2. Extract a list of the most important determinants or cluster amplitude types relevant to the CC theory of interest (triples for CCSDT; triples and quadruples for CCSDTQ, etc.) from the CIQMC or CCMC propagation at a given time τ to define the P space for CC(P) calculations as follows:
 - if the target approach is CCSDT, the P space is defined as all singles, all doubles, and a subset of triples having at least n_p (e.g., one) positive or negative walkers/excips on them.
 - if the target approach is CCSDTQ, the P space is defined as all singles, all doubles, and a subset of triples and quadruples having at least n_p (e.g., one) positive or negative walkers/excips on them, etc.

Developing a Stochastic CC(P ; Q) Approach

1. Start a CIQMC (e.g., i -CIQMC) or CCMC (e.g., i -CCMC) propagation by placing a certain number of walkers or excips on the reference determinant.

2. Extract a list of the most important determinants or cluster amplitude types relevant to the CC theory of interest (triples for CCSDT; triples and quadruples for CCSDTQ, etc.) from the CIQMC or CCMC propagation at a given time τ to define the P space for CC(P) calculations as follows:

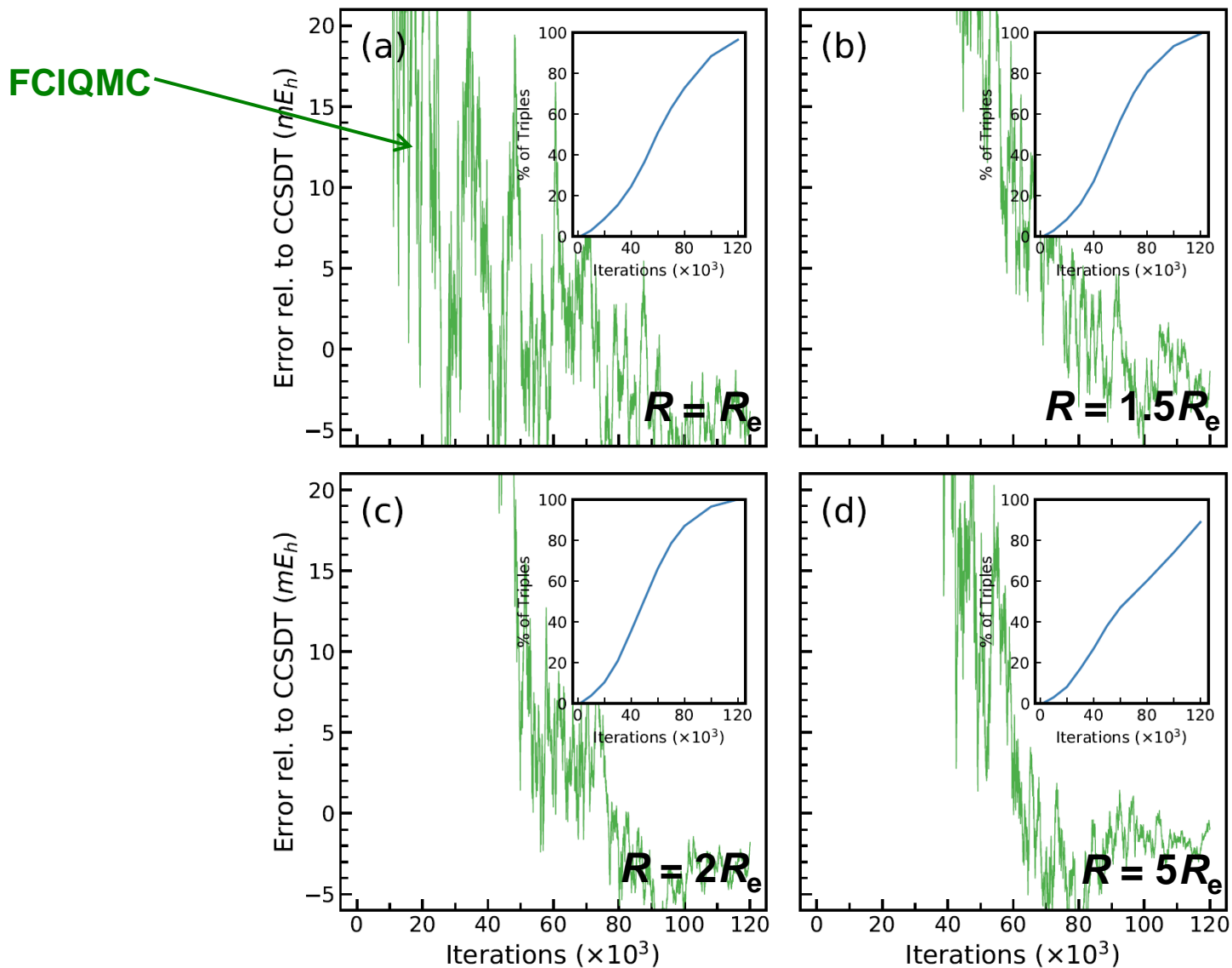
- if the target approach is CCSDT, the P space is defined as all singles, all doubles, and a subset of triples having at least n_p (e.g., one) positive or negative walkers/excips on them.
- if the target approach is CCSDTQ, the P space is defined as all singles, all doubles, and a subset of triples and quadruples having at least n_p (e.g., one) positive or negative walkers/excips on them, etc.

3. Solve the CC(P) equations.

- if the target approach is CCSDT, use $T^{(P)} = T_1 + T_2 + T_3^{(MC)}$
- if the target approach is CCSDTQ, use $T^{(P)} = T_1 + T_2 + T_3^{(MC)} + T_4^{(MC)}$
etc.

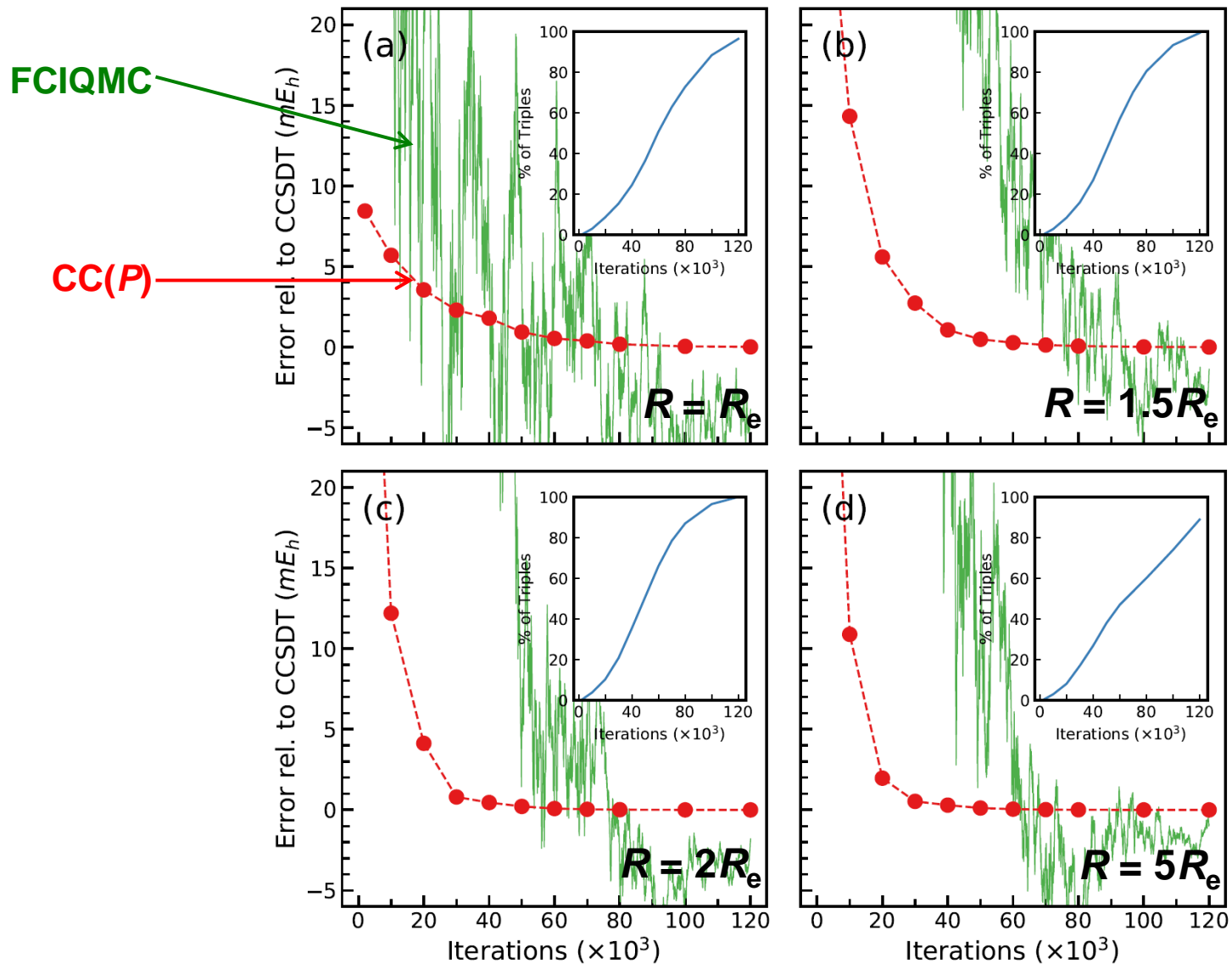
RECOVERING CCSDT ENERGISTICS FOR $F_2/cc\text{-pVDZ}$

MONTE CARLO APPROACH = i -FCIQMC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)



RECOVERING CCSDT ENERGETICS FOR $F_2/cc\text{-pVDZ}$

MONTE CARLO APPROACH = i -FCIQMC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)



Developing a Stochastic CC(P ; Q) Approach

1. Start a CIQMC (e.g., i -CIQMC) or CCMC (e.g., i -CCMC) propagation by placing a certain number of walkers or excips on the reference determinant.

2. Extract a list of the most important determinants or cluster amplitude types relevant to the CC theory of interest (triples for CCSDT; triples and quadruples for CCSDTQ, etc.) from the CIQMC or CCMC propagation at a given time τ to define the P space for CC(P) calculations as follows:

- if the target approach is CCSDT, the P space is defined as all singles, all doubles, and a subset of triples having at least n_p (e.g., one) positive or negative walkers/excips on them.
- if the target approach is CCSDTQ, the P space is defined as all singles, all doubles, and a subset of triples and quadruples having at least n_p (e.g., one) positive or negative walkers/excips on them, etc.

3. Solve the CC(P) equations.

- if the target approach is CCSDT, use $T^{(P)} = T_1 + T_2 + T_3^{(MC)}$
- if the target approach is CCSDTQ, use $T^{(P)} = T_1 + T_2 + T_3^{(MC)} + T_4^{(MC)}$
etc.

Developing a Stochastic CC(P ; Q) Approach

1. Start a CIQMC (e.g., i -CIQMC) or CCMC (e.g., i -CCMC) propagation by placing a certain number of walkers or excips on the reference determinant.

2. Extract a list of the most important determinants or cluster amplitude types relevant to the CC theory of interest (triples for CCSDT; triples and quadruples for CCSDTQ, etc.) from the CIQMC or CCMC propagation at a given time τ to define the P space for CC(P) calculations as follows:

- if the target approach is CCSDT, the P space is defined as all singles, all doubles, and a subset of triples having at least n_p (e.g., one) positive or negative walkers/excips on them.
- if the target approach is CCSDTQ, the P space is defined as all singles, all doubles, and a subset of triples and quadruples having at least n_p (e.g., one) positive or negative walkers/excips on them, etc.

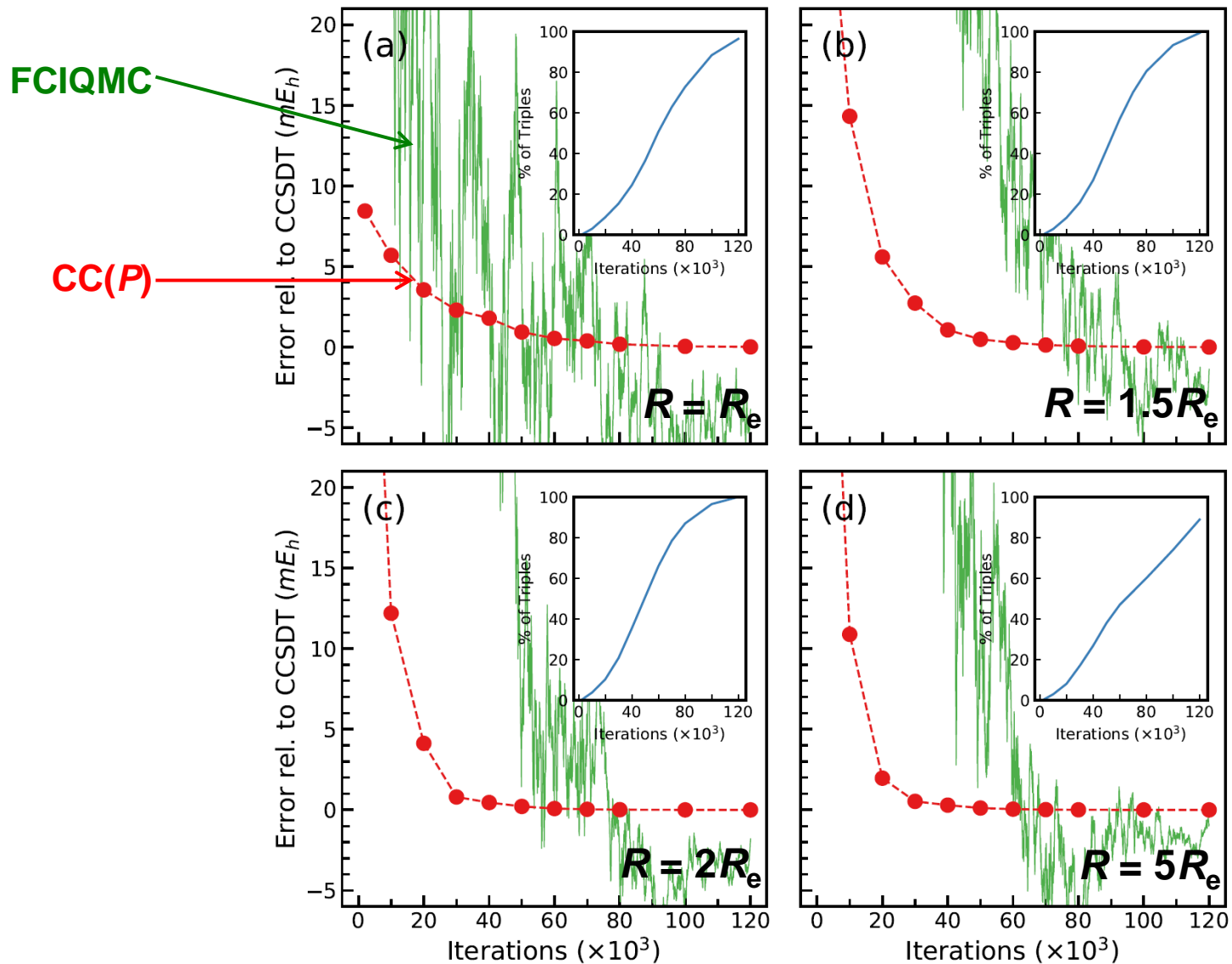
3. Solve the CC(P) equations.

- if the target approach is CCSDT, use $T^{(P)} = T_1 + T_2 + T_3^{(MC)}$
- if the target approach is CCSDTQ, use $T^{(P)} = T_1 + T_2 + T_3^{(MC)} + T_4^{(MC)}$
etc.

4. Correct the CC(P) energy for the remaining triples (if the target approach is CCSDT), triples and quadruples (if the target approach is CCSDTQ), etc. using the non-iterative CC(P ; Q) correction $\delta(P; Q)$.

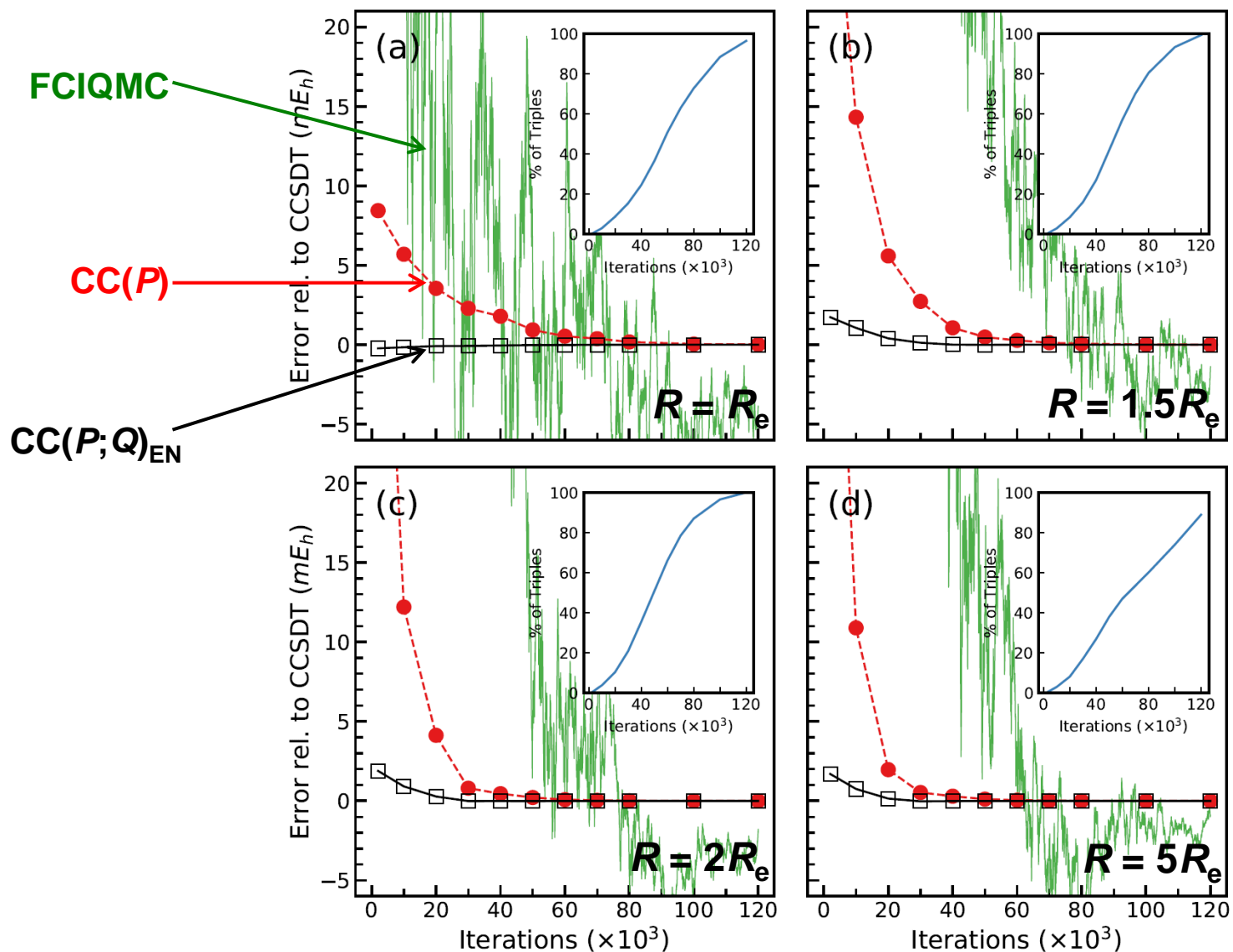
RECOVERING CCSDT ENERGETICS FOR $F_2/cc\text{-pVDZ}$

MONTE CARLO APPROACH = i -FCIQMC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)



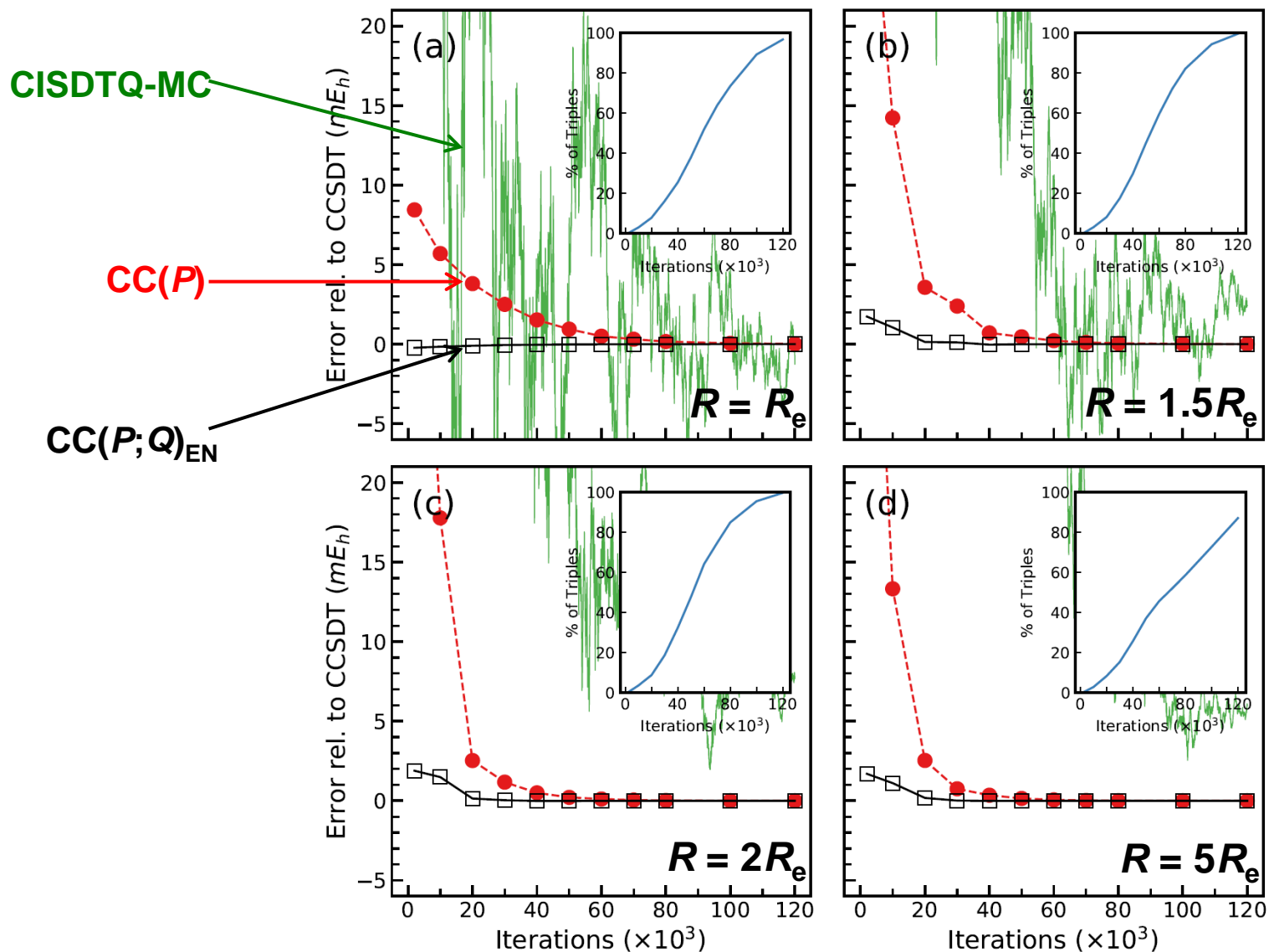
RECOVERING CCSDT ENERGISTICS FOR $F_2/cc\text{-pVDZ}$

MONTE CARLO APPROACH = i -FCIQMC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)



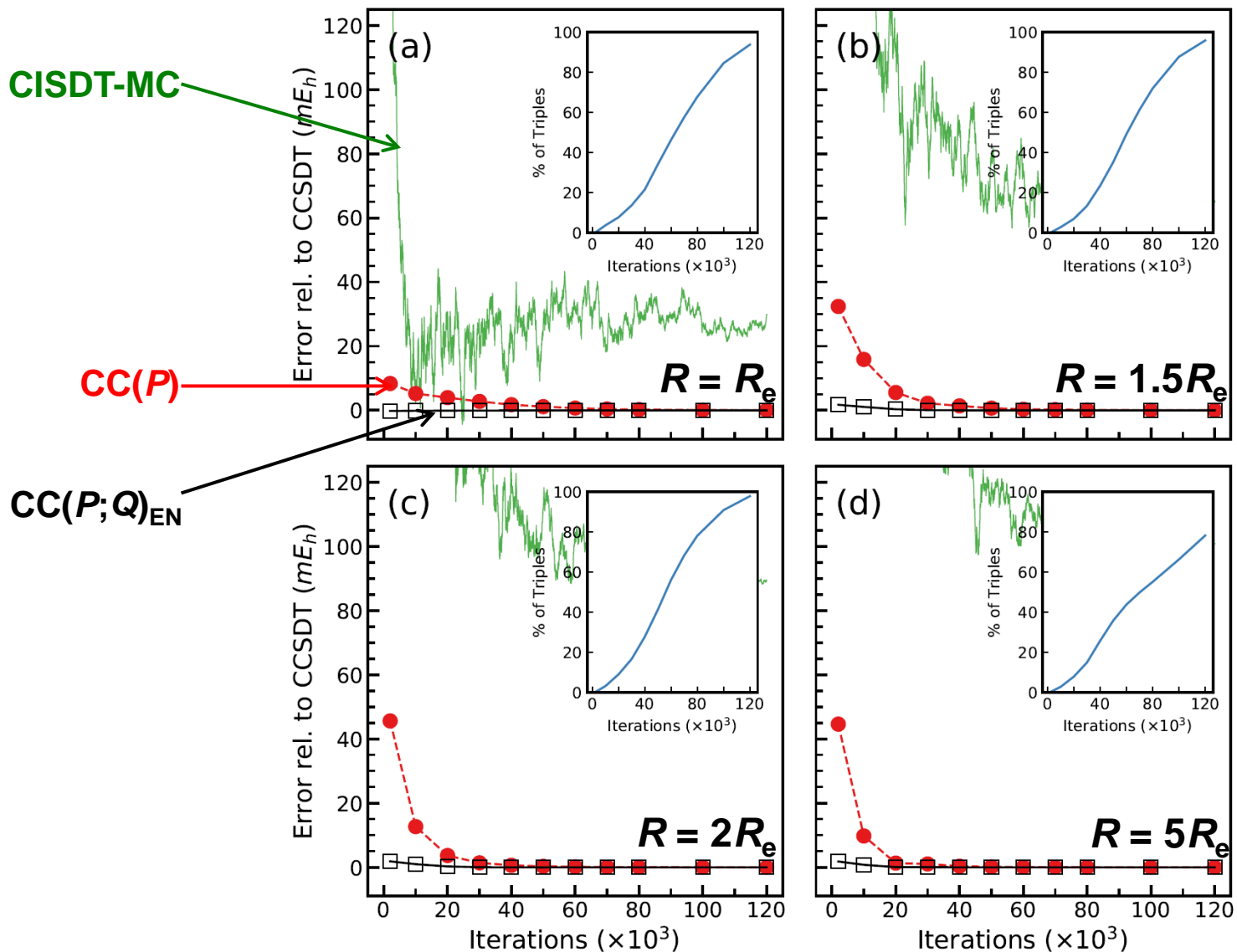
RECOVERING CCSDT ENERGETICS FOR $F_2/cc\text{-pVDZ}$

MONTE CARLO APPROACH = $i\text{-CCSDTQ-MC}$ ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)



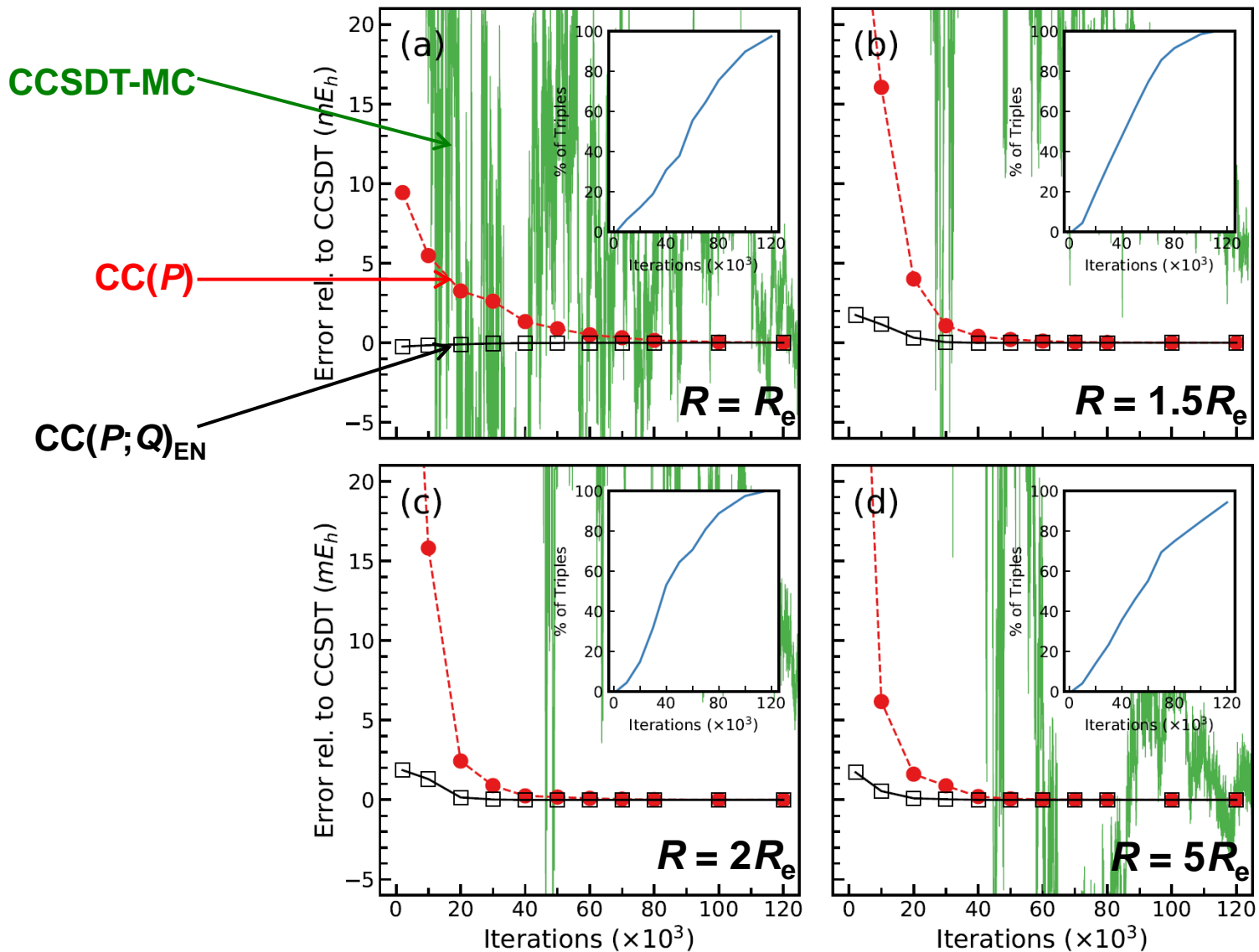
RECOVERING CCSDT ENERGISTICS FOR $F_2/cc\text{-pVDZ}$

MONTE CARLO APPROACH = \hat{i} -CCSDT-MC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)



RECOVERING CCSDT ENERGISTICS FOR $F_2/cc\text{-pVDZ}$

MONTE CARLO APPROACH = i -CCSDT-MC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)



RECOVERING CCSDT ENERGISTICS FOR $F_2/cc\text{-pVDZ}$
MONTE CARLO APPROACH = i -FCIQMC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)

$$R = 2 R_e$$

Errors relative to CCSDT

MC Iter.	% of Triples in P space	CC(P) (mE_h)	CC($P;Q$) _{MP} (mE_h)	CC($P;Q$) _{EN} (mE_h)	Wall Time (s)		
					MC	CC($P;Q$)	Total
0	0	45.638 CCSD	6.357 CCSD(2) _T	1.862 CR-CC(2,3)	0	2	2
10,000	4	12.199	1.887	0.915	3	2	5
20,000	10	4.127	0.596	0.279	10	5	15
30,000	21	0.802	0.067	-0.009	28	13	41
40,000	35	0.456	0.036	-0.007	66	31	97
∞	100	-199.058201 E_h			208		

Errors relative to CCSDT

CCSD: 45.638 mE_h

CCSD(T): -23.596 mE_h

RECOVERING CCSDT ENERGISTICS FOR $F_2/cc\text{-pVDZ}$
MONTE CARLO APPROACH = i -CCSDT-MC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)

$$R = 2 R_e$$

Errors relative to CCSDT

MC Iter.	% of Triples in P space	CC(P) (mE_h)	CC($P;Q$) _{MP} (mE_h)	CC($P;Q$) _{EN} (mE_h)	Wall Time (s)		
					MC	CC($P;Q$)	Total
0	0	45.638 CCSD	6.357 CCSD(2) _T	1.862 CR-CC(2,3)	0	2	2
10,000	3	12.687	2.069	0.978	3	2	5
20,000	9	3.672	0.583	0.280	9	3	12
30,000	17	1.393	0.154	0.030	17	8	25
40,000	28	0.627	0.053	-0.005	32	16	48
∞	100	-199.058201 E_h			208		

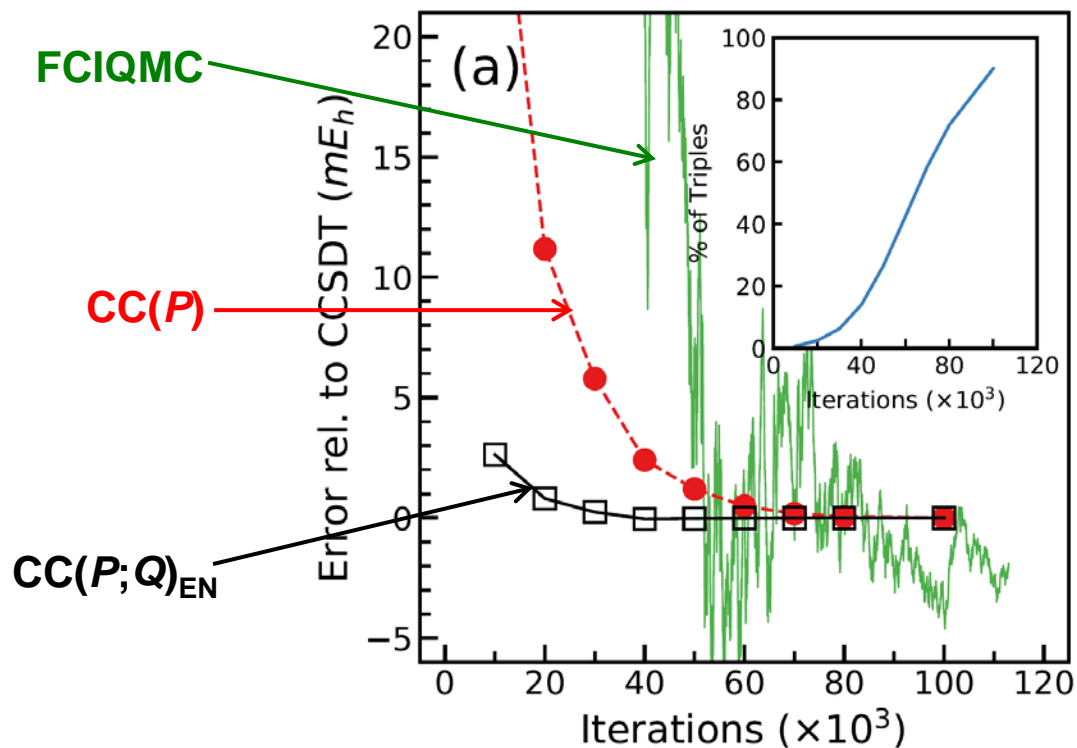
Errors relative to CCSDT

CCSD: 45.638 mE_h

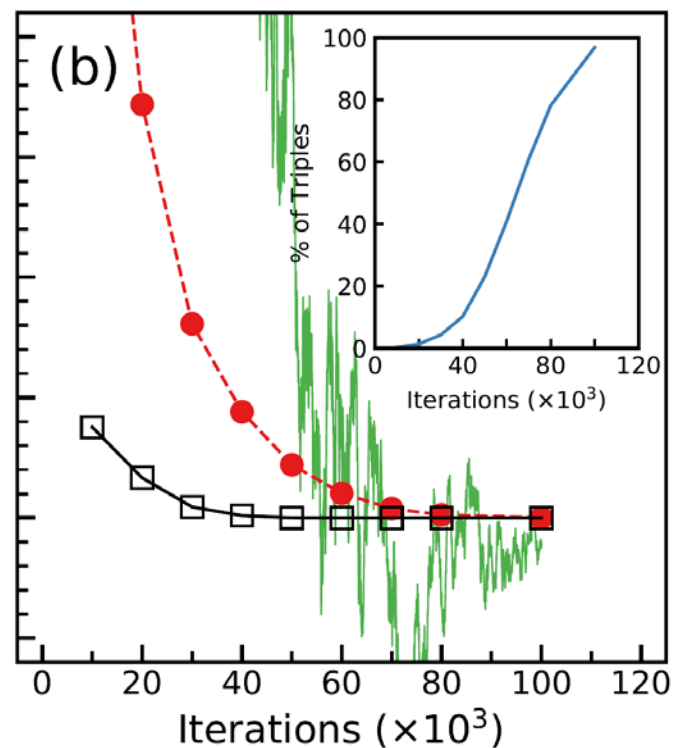
CCSD(T): -23.596 mE_h

RECOVERING CCSDT ENERGETICS FOR LARGER BASIS SETS

MONTE CARLO APPROACH = i -FCIQMC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)



$F_2/cc-pVTZ$, $R = 2R_e$



$F_2/aug-cc-pVTZ$, $R = 2R_e$

RECOVERING CCSDT ENERGETICS FOR F_2 /aug-cc-pVTZ
MONTE CARLO APPROACH = \hat{i} -FCIQMC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)

$$R = 2 R_e$$

Errors relative to CCSDT

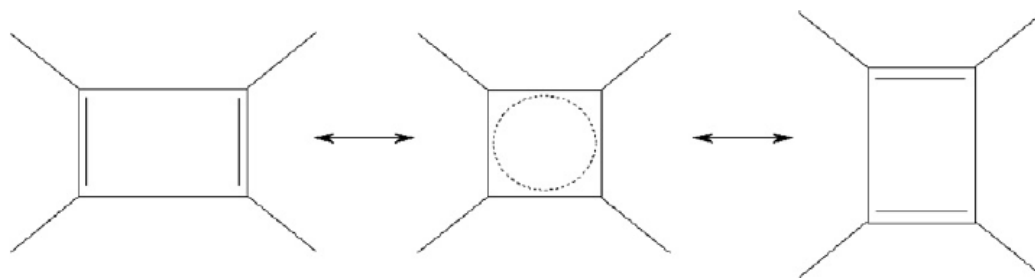
MC Iter.	% of Triples in P space	CC(P) (mE_h)	CC($P;Q$) _{MP} (mE_h)	CC($P;Q$) _{EN} (mE_h)	Speedup rel. to CCSDT
0	0	65.036 CCSD	9.808 CCSD(2) _T	5.595 CR-CC(2,3)	~300
30,000	4	8.065	0.858	0.454	90
40,000	10	4.408	0.330	0.093	30
50,000	23	2.208	0.125	0.002	10
∞	100	-199.253022 E_h			1

Errors relative to CCSDT

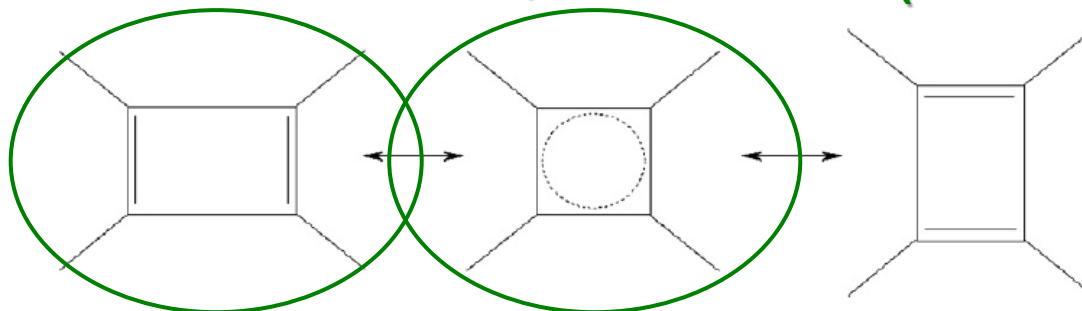
CCSD: 65.036 mE_h

CCSD(T): -27.209 mE_h

**RECOVERING CCSDT ENERGISTICS FOR
AUTOMERIZATION OF CYCLOBUTADIENE/cc-pVDZ
MONTE CARLO APPROACH = *i*-FCIQMC/*i*-CISDT-MC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)**



**RECOVERING CCSDT ENERGIES FOR
AUTOMERIZATION OF CYCLOBUTADIENE/cc-pVDZ
MONTE CARLO APPROACH = *i*-FCIQMC/*i*-CISDT-MC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)**



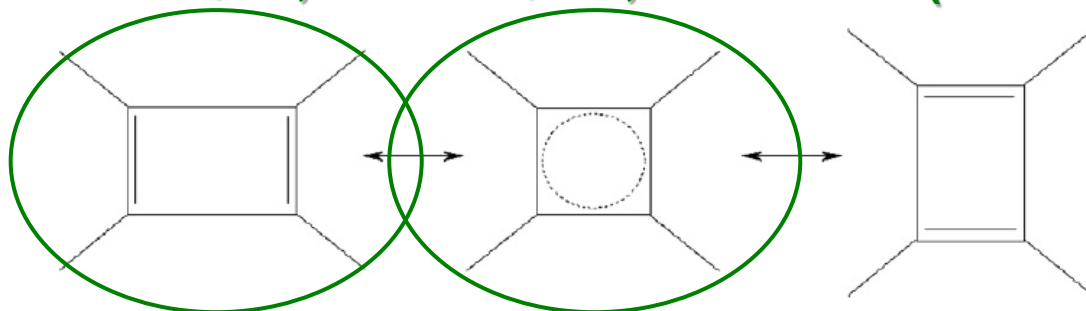
Errors relative to CCSDT

MC Iter.	% of Triples in <i>P</i> space	CC(<i>P</i> ; <i>Q</i>) _{MP} (kcal/mol)	CC(<i>P</i> ; <i>Q</i>) _{EN} (kcal/mol)	Total Wall Time (hrs)		
				MC	CC(<i>P</i> ; <i>Q</i>)	Total
0	0/0	9.6 CCSD(2) _T	8.7 CR-CC(2,3)	0/0	0.4/0.4	0.4/0.4
40,000	15-22/14-18	1.5/3.5	1.7/3.5	1.0/0.3	1.9/1.4	2.9/1.7
50,000	31-41/26-34	0.5/1.1	0.6/1.2	3.1/0.7	5.9/4.3	9.0/5.0
60,000	51-61/43-51	0.0/0.8	0.1/0.9	11.6/1.4	13.6/9.8	25.2/11.2
∞	100	7.6 kcal/mol		41.05		

Errors relative to CCSDT
 CCSD: 13.3 kcal/mol
 CCSD(T): 8.2 kcal/mol

RECOVERING CCSDT ENERGISTICS FOR AUTOMERIZATION OF CYCLOBUTADIENE/cc-pVDZ

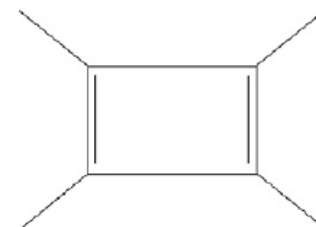
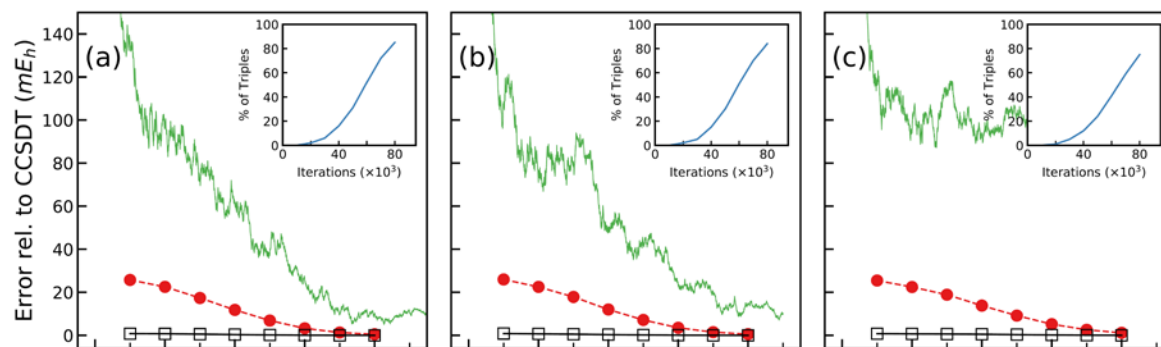
MC APPROACH = *i*-FCIQMC, *i*-CISDTQ-MC, *i*-CISDT-MC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)



MC = FCIQMC

MC = CISDTQ-MC

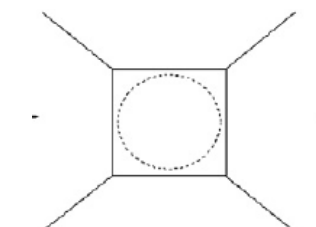
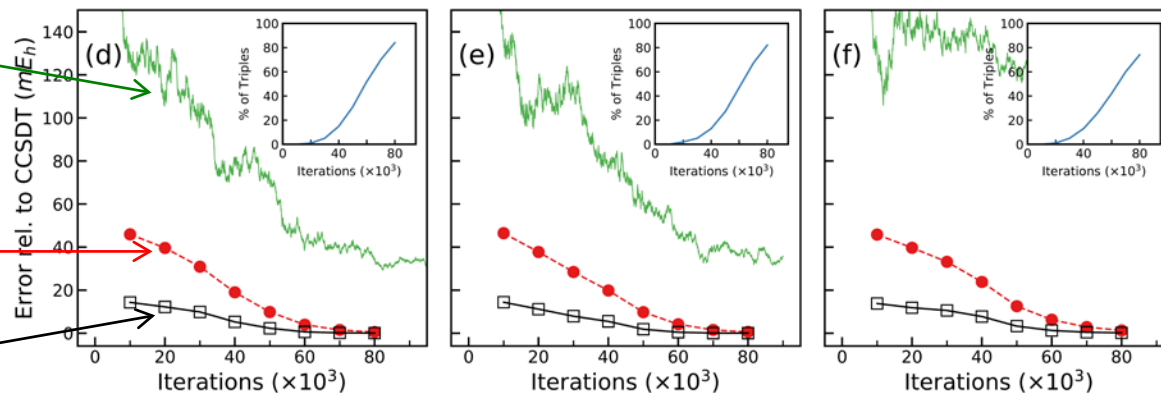
MC = CISDT-MC



MC

CC(P)

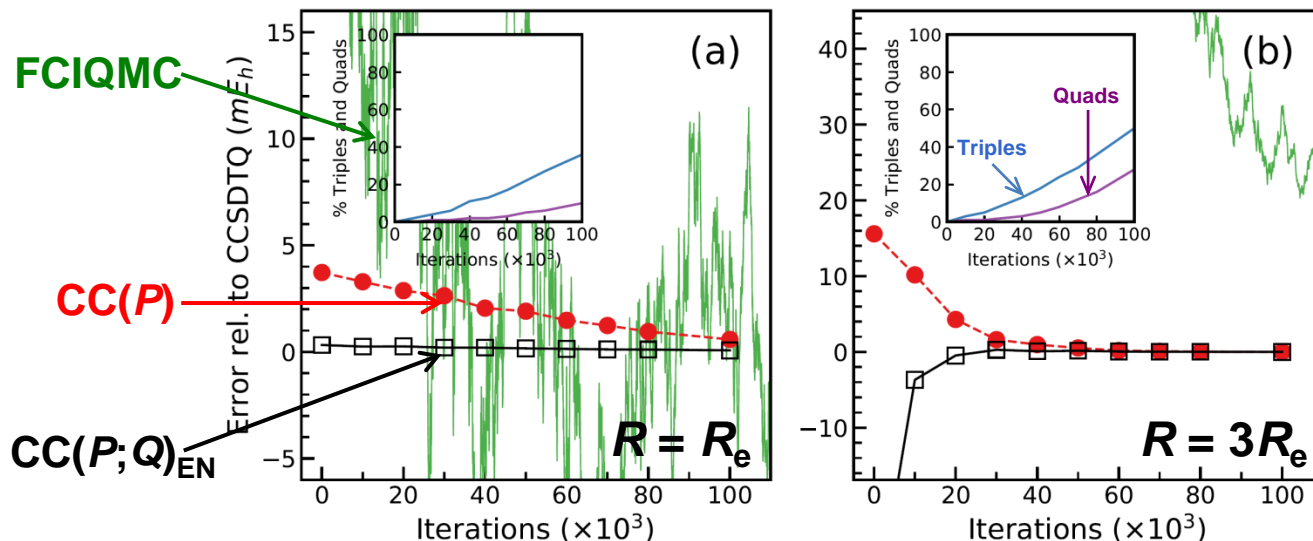
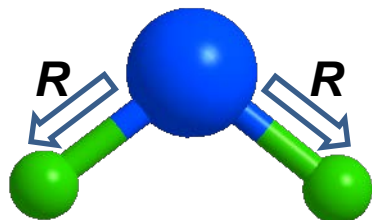
CC(P;Q)_{EN}



RECOVERING CCSDTQ ENERGETICS FOR H₂O/cc-pVDZ

MONTE CARLO APPROACH = *i*-FCIQMC ($\Delta\tau = 0.0001$ a.u., $n_a = 3$)

J.E. Deustua, J. Shen, and P. Piecuch, in preparation



$$R = 3R_e$$

Errors relative to CCSDTQ

MC Iter.	% of Triples/Quads	CC(P) (mE _h)	CC(P;Q) _{MP} (mE _h)	CC(P;Q) _{EN} (mE _h)
0	0/0	15.582 CCSD	-28.302 CCSD(2) _T	-35.823 CR-CC(2,3)
10,000	3/1	10.165	-2.198	-3.682
20,000	5/1	4.282	-0.091	-0.469
40,000	13/3	0.969	0.170	0.085
80,000	36/16	0.030	0.015	0.013
∞	100/100		-75.916679 E _h	

Errors relative to FCI:

CCSD	45.638 mE _h	CCSDT	-40.126 mE _h
CCSD(T)	-23.596 mE _h	CCSDTQ	-4.733 mE _h

SUMMARY

SUMMARY

- By combining the stochastic CIQMC and CCMC methodologies with the deterministic CC($P;Q$) framework one can recover high-level CC energetics based on the information extracted from the early stages of CIQMC or CCMC propagations, even when electronic quasi-degeneracies and higher-than-pair clusters become substantial.

SUMMARY

- By combining the stochastic CIQMC and CCMC methodologies with the deterministic $CC(P;Q)$ framework one can recover high-level CC energetics based on the information extracted from the early stages of CIQMC or CCMC propagations, even when electronic quasi-degeneracies and higher-than-pair clusters become substantial.
- Paraphrasing the title of the original FCIQMC paper,

THE JOURNAL OF CHEMICAL PHYSICS 131, 054106 (2009)

Fermion Monte Carlo without fixed nodes: A game of life, death, and annihilation in Slater determinant space

George H. Booth,¹ Alex J. W. Thom,^{1,2} and Ali Alavi^{1,a)}

¹*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

²*Department of Chemistry, University of California Berkeley, Berkeley, California 94720, USA*

(Received 15 May 2009; accepted 13 July 2009; published online 4 August 2009)

the stochastic $CC(P;Q)$ formalism is a “game of life, death, and annihilation,” but based on our results one may avoid playing much of it and yet know the outcome.

Citing the referee, who reviewed our paper submitted to *Physical Review Letters*:

“This is the first work that I’ve seen where stochastic methods are used to determine what is important, and then deterministic methods are used to solve for the amplitudes of what is important. In this sense, the method is completely original and **OPENS A FULL NEW RESEARCH PARADIGM**. Just because of this, I think it should be published in PRL.”



THANK YOU

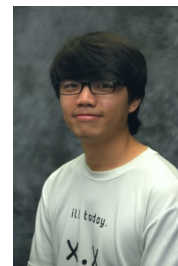


Emiliano Deustua
(2014-present)

Ilias Magoulas
(2015-present)

Dr. Jun Shen
(2010-present)

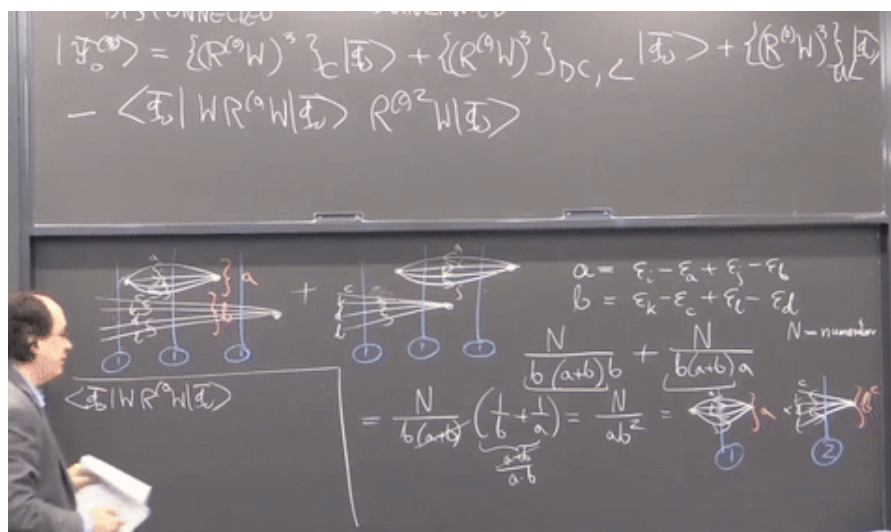
Stephen Yuwono
(2017-present)



“Algebraic and Diagrammatic Methods for Many-Fermion Systems”

<https://pages.wustl.edu/ppiecuch/course-videos>

Search for Chem 580 in YouTube



Search for
Chem 580

