PERTURBATIVE CORRECTIONS TO NON-PERTURBATIVE METHODS

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Workshop of the *Espace de Structure et de Réactions Nucléaires Théorique* on "Many-Body Perturbation Theories in Modern Quantum Chemistry and Nuclear Physics", March 26-30, 2018, CEA Saclay, Gif-sur-Yvette, France

MANY THANKS TO ALEXANDER TICHAI, EMMANUEL GINER, AND THOMAS DUGUET FOR THE INVITATION

HIGH-LEVEL COUPLED-CLUSTER ENERGETICS BY MONTE CARLO SAMPLING AND MOMENT EXPANSIONS

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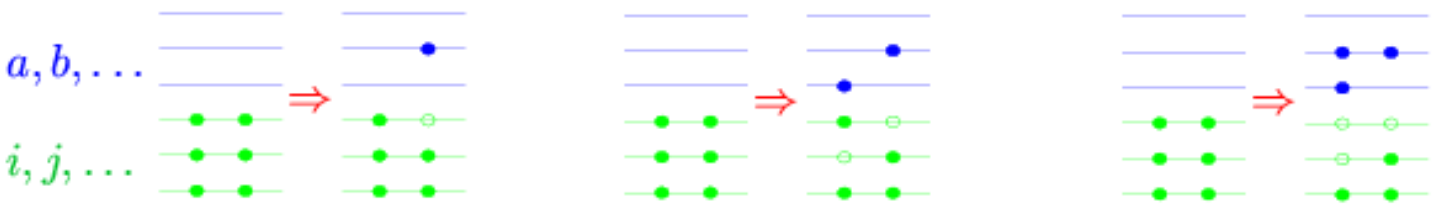
SINGLE-REFERENCE COUPLED-CLUSTER (CC) THEORY

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

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

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



1p-1h, singles (S) 2p-2h, doubles (D) 3p-3h, triples (T)

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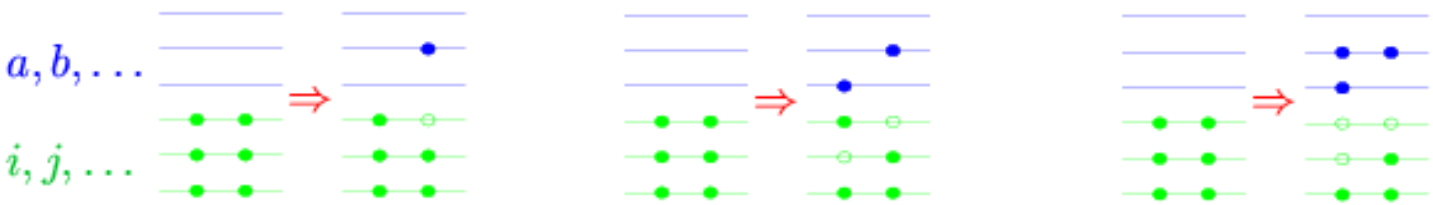

1p-1h, singles (S) **2p-2h, doubles (D)** **3p-3h, triples (T)**

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

				CPU time scaling with the system size
$m_A = 2$	$T = T_1 + T_2$	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}

Standard CC Equations

(J. Čížek, 1966)

We do not minimize

$$E[\Psi] = \langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle = \langle\Phi|(e^{T^\dagger} H e^T)_C|\Phi\rangle,$$

which is a nonterminating series in T. We transform and project the Schrödinger equation.

$$H\, e^T|\Phi\rangle = E_0\, e^T|\Phi\rangle$$

$$e^{-T} H e^T|\Phi\rangle = E_0\, e^{-T} e^T|\Phi\rangle = E_0\,|\Phi\rangle$$

$$\bar{H}\,|\Phi\rangle = E_0\,|\Phi\rangle, \quad \bar{H} = e^{-T} H e^T = (H e^T)_C$$

$\bar{H}$ is a finite series in T; for pairwise interactions,

$$\bar{H} = H + [H,T] + \tfrac{1}{2}[[H,T],T]] + \tfrac{1}{6}[[[H,T],T],T] + \tfrac{1}{24}[[[[H,T],T],T],T]$$

kp-kh $\longrightarrow$ $\langle\Phi^{a_1 a_2 \ldots a_k}_{i_1 i_2 \ldots i_k}|\left(H_N e^{T^{(A)}}\right)_C|\Phi\rangle = 0, \quad k = 1 \ldots, m_A$

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

ARGUMENTS IN FAVOR OF THE CC THEORY

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Linked cluster (diagram) theorem (Brueckner, 1955; Goldstone, 1957)

MBPT

$$\begin{aligned}\Psi^{(k)} &= (R_0W)^k\Phi_0 + \text{renormalization terms} \\ &= \left[(R_0W)^k\right]_{\text{linked}}\Phi_0\,, \quad (k=1,2,\ldots),\end{aligned}$$

$$\begin{aligned}\Delta E^{(k+1)} &= \langle\Phi_0|W(R_0W)^k|\Phi_0\rangle + \text{renormalization terms} \\ &= \langle\Phi_0|\left[W(R_0W)^k\right]_{\text{connected}}|\Phi_0\rangle\,, \quad (k=1,2,\ldots).\end{aligned}$$

Connected cluster theorem (Hubbard, 1957; Hugenholtz, 1957)

$$\Psi = e^T\Phi, \quad T = \sum_{k=1}^{\infty}\sum_{C}\{(R_0W)^k\}_C$$

$C \Leftrightarrow$ connected diagrams (including EPV terms)

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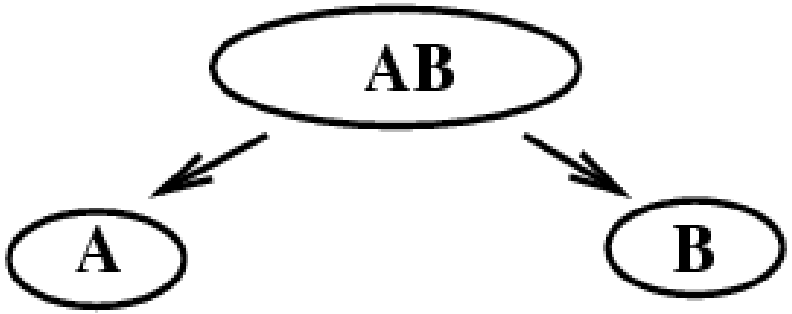

$$H_{\mathrm{AB}} \rightarrow H_A + H_B$$

$$T = T_{\mathrm{AB}} \longrightarrow T_{\mathrm{A}} + T_{\mathrm{B}}, \quad [T_{\mathrm{A}}, T_{\mathrm{B}}] = 0$$

$$e^{T_{\mathrm{AB}}} = e^{T_{\mathrm{A}}} e^{T_{\mathrm{B}}}$$

$$|\Psi_{\mathrm{AB}}\rangle = e^{T_{\mathrm{AB}}}|\Phi_{\mathrm{AB}}\rangle = e^{T_{\mathrm{A}}}|\Phi_{\mathrm{A}}\rangle e^{T_{\mathrm{B}}}|\Phi_{\mathrm{B}}\rangle = |\Psi_{\mathrm{A}}\rangle|\Psi_{\mathrm{B}}\rangle$$

$$E_{\mathrm{AB}} = \langle\Phi_{\mathrm{AB}}|H_{\mathrm{AB}}|\Psi_{\mathrm{AB}}\rangle = \langle\Phi_{\mathrm{A}}|H_{\mathrm{A}}|\Psi_{\mathrm{A}}\rangle\langle\Phi_{\mathrm{B}}|\Psi_{\mathrm{B}}\rangle + \langle\Phi_{\mathrm{B}}|H_{\mathrm{B}}|\Psi_{\mathrm{B}}\rangle\langle\Phi_{\mathrm{A}}|\Psi_{\mathrm{A}}\rangle = E_{\mathrm{A}} + E_{\mathrm{B}}$$

ARGUMENTS IN FAVOR OF THE CC THEORY

- **Size-extensivity of the resulting approximations (no loss of accuracy occurs when the system is made larger)**
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- **Fastest convergence toward the exact, full CI, limit**

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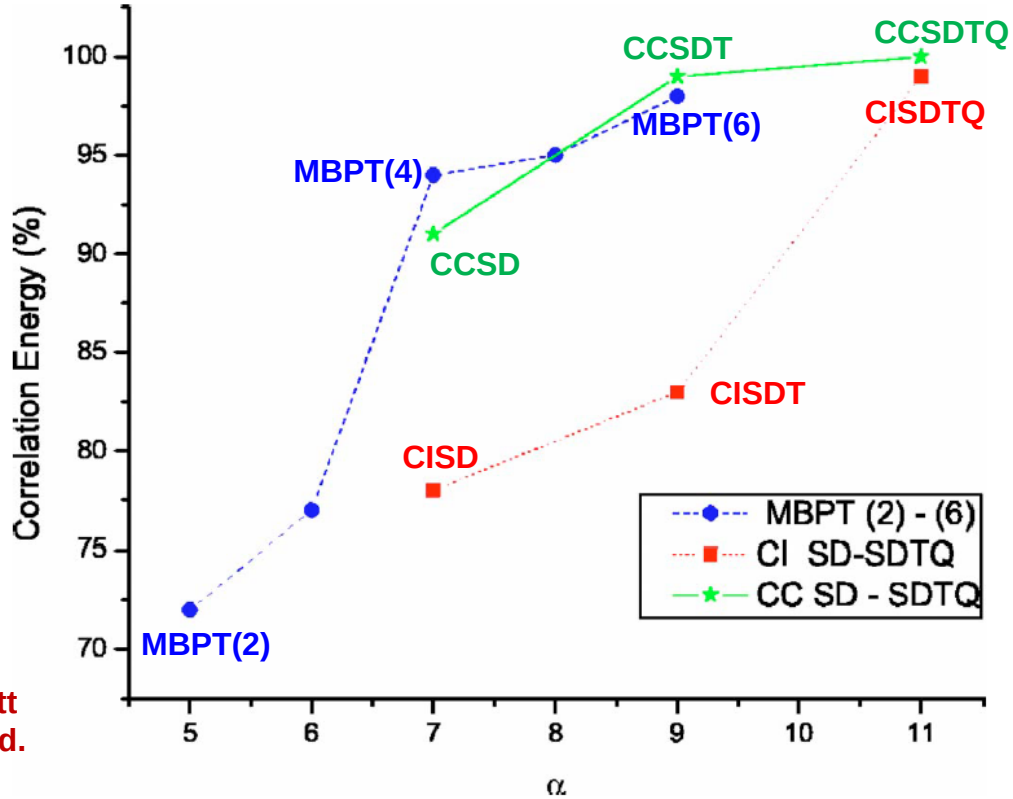
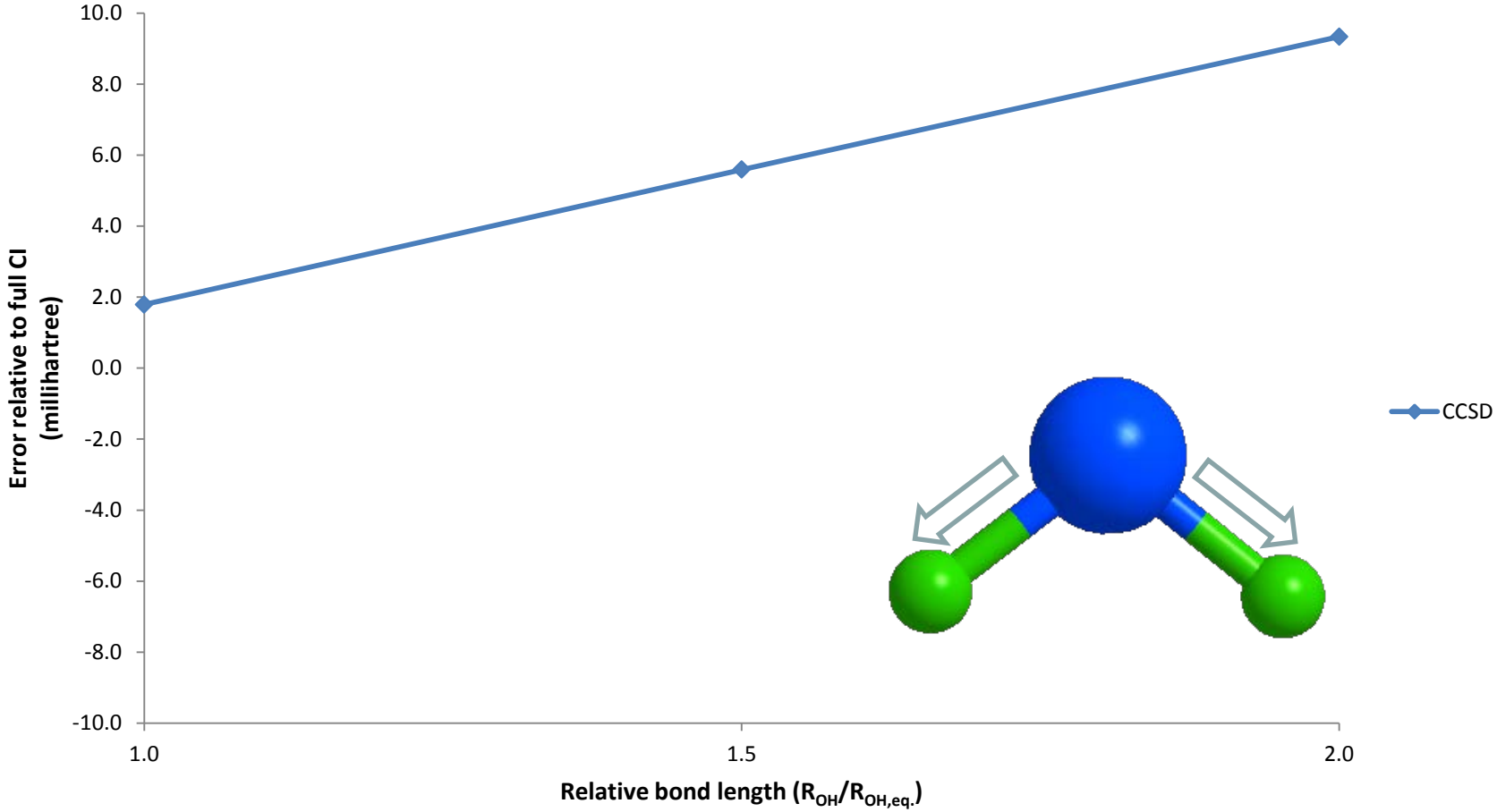


Taken from R.J. Bartlett and M. Musiał, Rev. Mod. Phys., 2007

ARGUMENTS IN FAVOR OF THE CC THEORY

H_2O



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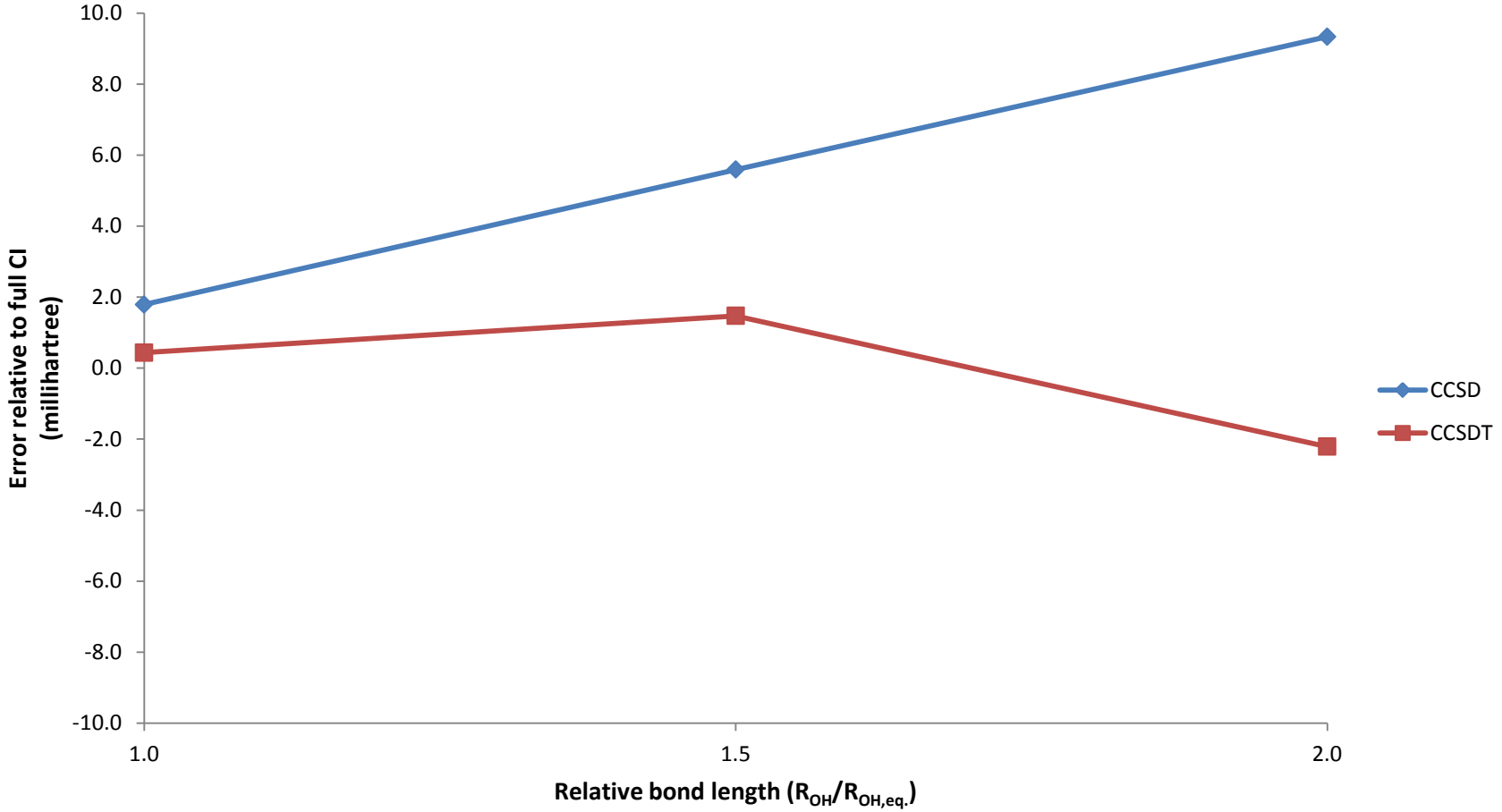

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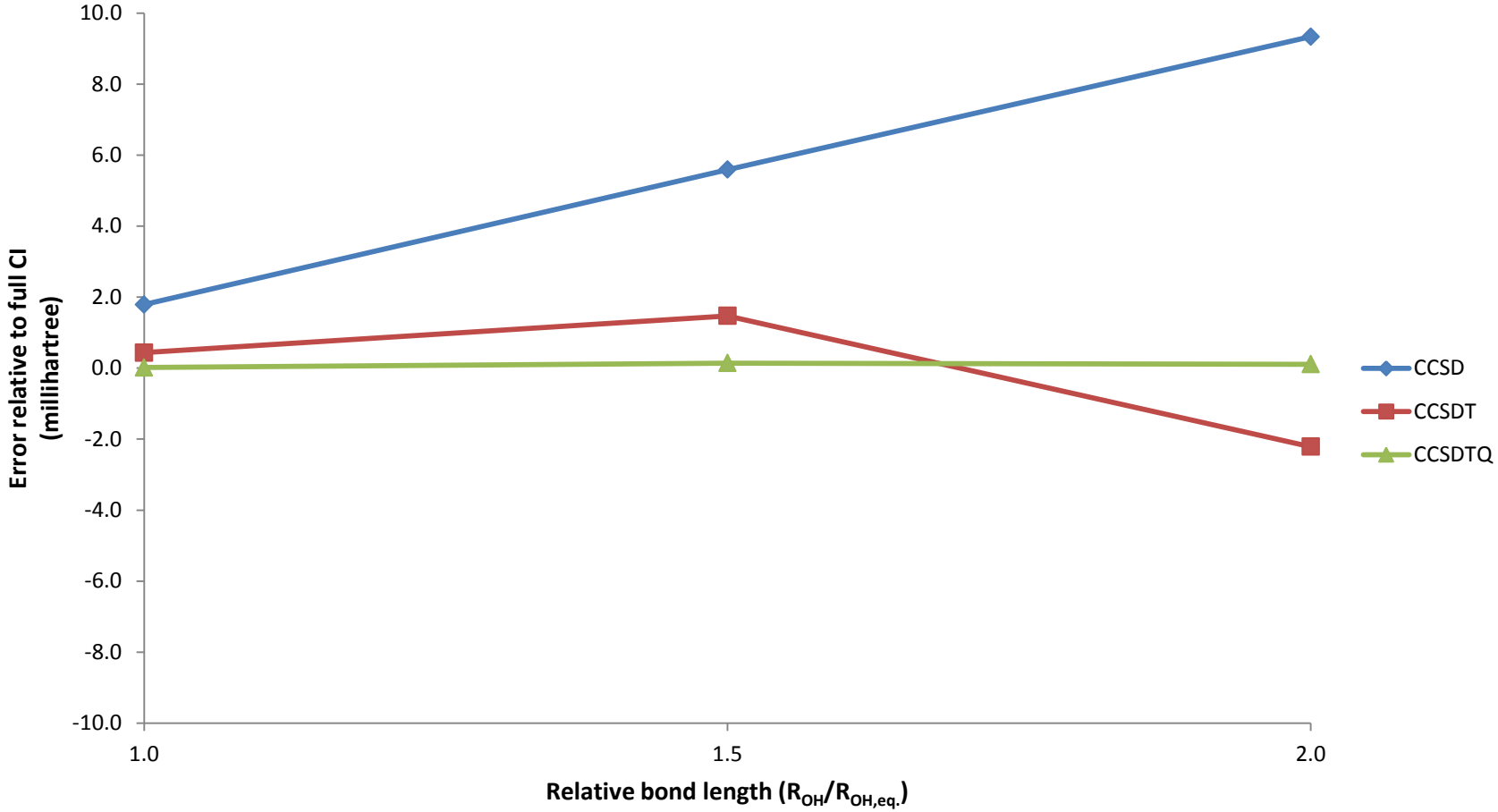

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$$|\Psi\rangle = \underbrace{(1 + C_1 + C_2 + \cdots)|\Phi\rangle}_{\textit{CI expansion}} = \underbrace{e^{T_1+T_2+\cdots}|\Phi\rangle}_{\textit{CC expansion}}$$

$$T = \ln(1 + C) = \sum_{k=1}^{N} \frac{(-1)^{k-1}}{k} C^k$$

CIS = CI(1p-1h) →

CISD = CI(2p-2h) →

CISDT = CI(3p-3h) →

CISDTQ = CI(4p-4h) →

$$C_1 = T_1$$

$$C_2 = T_2 + \tfrac{1}{2}(T_1)^2$$

$$C_3 = T_3 + T_1 T_2 + \tfrac{1}{6}(T_1)^3$$

$$C_4 = T_4 + \tfrac{1}{2}(T_2)^2 + T_1 T_3 + \tfrac{1}{2}(T_1)^2 T_2 + \tfrac{1}{24}(T_1)^4, \text{ etc.}$$

→ CCSDT

$$T_4 \ll \tfrac{1}{2} T_2^2$$

EXCITED STATES: EQUATION-OF-MOTION CC (EOMCC) THEORY, SYMMETRY-ADAPTED-CLUSTER CONFIGURATION INTERACTION APPROACH (SAC-CI), AND RESPONSE CC METHODS

(H. Monkhorst, 1977; D. Mukherjee and P.K. Mukherjee, 1979; H. Nakatsuji and K. Hirao, 1978; K. Emrich, 1981; M. Takahashi and J. Paldus; 1986; J. Geertsen, M. Rittby, and R.J. Bartlett, 1989)

$$|\Psi_K\rangle = R_K|\Psi_0\rangle, \qquad |\Psi_0\rangle = e^T|\Phi\rangle$$

$$T = T_1 + T_2 + \cdots, \quad R_K = R_{K,0} + R_{K,\text{open}}, \quad R_{K,\text{open}} = R_{K,1} + R_{K,2} + \cdots$$

Example: EOMCC

(K. Emrich, 1981; J. Geertsen, M. Rittby, and R.J. Bartlett, 1989; J.F. Stanton and R.J. Bartlett, 1993)

In the exact theory,

$$(\bar{H}_{N,\text{open}} R_{K,\text{open}})_C|\Phi\rangle = \omega_K R_K|\Phi\rangle \text{ or } [\bar{H}_{N,\text{open}}, R_{K,\text{open}}]|\Phi\rangle = \omega_K R_K$$

$$\bar{H}_N = e^{-T} H_N e^T = (H_N e^T)_C, \quad \omega_K = E_K - E_0, \quad R_{K,\text{open}} = R_K - R_{K,0}.$$

In approximate methods,

$$T \simeq T^{(A)} = \sum_{n=1}^{m_A} T_n, \quad R_K \simeq R_K^{(A)} = \sum_{n=0}^{m_A} R_{K,n} \quad (m_A < N)$$

Basic approximation: EOMCCSD

$$m_A = 2 : T = T_1 + T_2$$

$$R_K = R_{K,0} + R_{K,1} + R_{K,2}$$

$$\bar{\mathbf{H}}^{\text{CCSD}} = \begin{pmatrix} \bar{\mathbf{H}}_{\mathbf{SS}} & \bar{\mathbf{H}}_{\mathbf{SD}} \\ \bar{\mathbf{H}}_{\mathbf{DS}} & \bar{\mathbf{H}}_{\mathbf{DD}} \end{pmatrix}$$

Higher-order methods: EOMCCSDT, EOMCCSDTQ, etc.

Vertical excitation energies of C_2 (in eV) [K. Kowalski and P. Piecuch, 2002; S. Hirata, 2004]

State	Full CI[a]	EOM-CCSD[b]	EOM-CCSDT[c]	EOM-CCSDTQ[d]
$^1\Pi_u$	1.385	+0.090	+0.034	+0.001
$^1\Delta_g$	2.293	+2.054	+0.407	+0.024
$^1\Sigma_u^+$	5.602	+0.197	+0.113	+0.013
$^1\Pi_g$	4.494	+1.708	+0.088	−0.007

errors relative to full CI (eV)

Adiabatic excitation energies of the CH radical (in eV) [S. Hirata, 2004]

State	EOMCCSD	EOMCCSDT	EOMCCSDTQ	Experiment
a $^4\Sigma^-$	0.95	0.66	0.65	0.74
A $^2\Delta$	3.33	3.02	3.00	2.88
B $^2\Sigma^-$	4.41	3.27	3.27	3.23
C $^2\Sigma^+$	5.29	4.07	4.04	3.94

> 1 eV errors

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?

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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)

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- **Iterative perturbative methods: CCSDT-n, CCSDTQ-n, etc.**

  Example: CCSDT-1 equations – $n_o^3 n_u^4$ $(\mathcal{N}^7)$

$$\langle \Phi_i^a | [H_N(1 + T_1 + T_2 + \tfrac{1}{2}T_1^2 + T_3^{[2]} + T_1T_2 + \tfrac{1}{6}T_1^3)]_C | \Phi \rangle = 0$$

$$\langle \Phi_{ij}^{ab} | [H_N(1 + T_1 + T_2 + \tfrac{1}{2}T_1^2 + T_3^{[2]} + T_1T_2 + \tfrac{1}{6}T_1^3 + \tfrac{1}{2}T_2^2 + \tfrac{1}{2}T_1^2T_2 + \tfrac{1}{24}T_1^4)]_C | \Phi \rangle = 0$$

$$T_3^{[2]} | \Phi \rangle = R_0^{(3)} (V_N T_2)_C | \Phi \rangle$$

- **Non-iterative perturbative methods: CCSD(T), CCSD(TQ$_f$), CCSDT(Q$_f$), etc.**

  Example: CCSD(T) method – **iterative** $n_o^2 n_u^4$ $(\mathcal{N}^6)$ **plus non-iterative** $n_o^3 n_u^4$ $(\mathcal{N}^7)$

$$E_0^{(\mathrm{CCSD(T)})} = E_0^{(\mathrm{CCSD})} + E^{(\mathrm{T})}$$

$$E^{(\mathrm{T})} = \langle \Phi | (T_3^{[2]} + Z_3)^\dagger (V_N T_2)_C | \Phi \rangle$$

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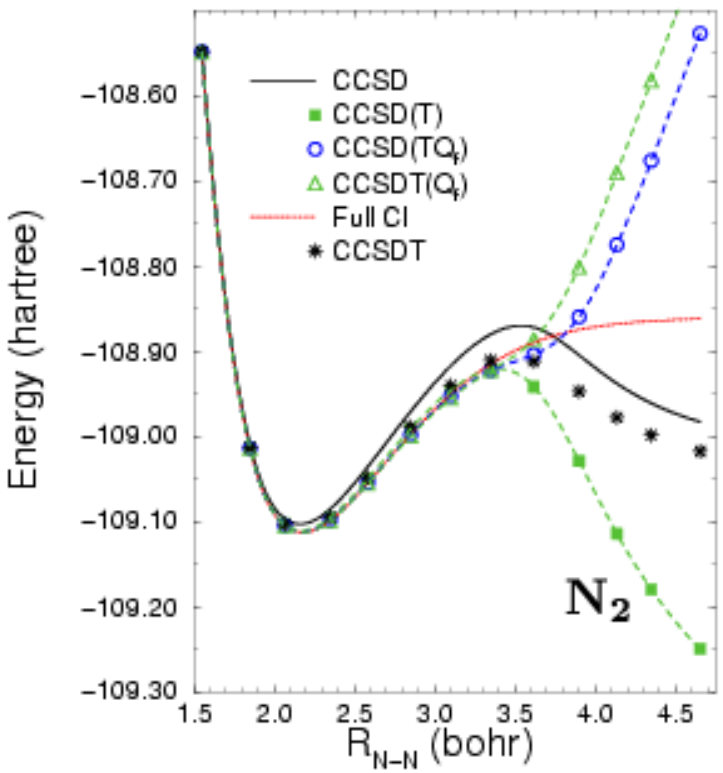

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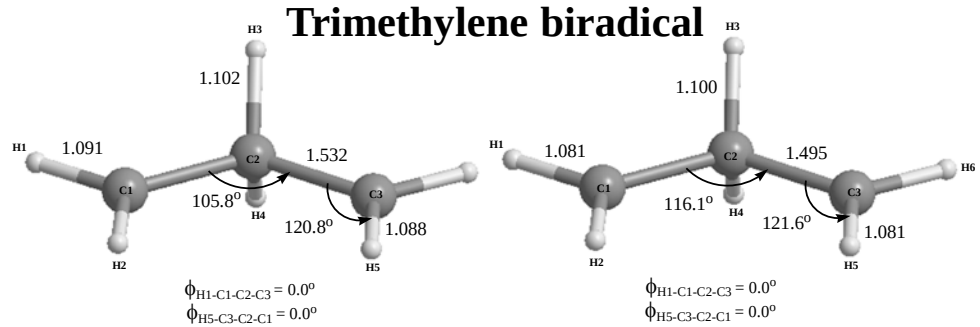

	CCSD(T)		MRCI
Vib mode	*[1/cm]*	*Vib mode*	*[1/cm]*
1	411.2i	1	139.2i
2	157.1i	2	61.1
3	168.1	3	277.9
4	237.6	4	361.3
5	336.6	5	372.5
…	…	…	
%Av Err	89.3		

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 $E_0 = \left\langle \Phi \middle| H \; e^{T_1 + T_2 + \cdots + T_N} \middle| \Phi \right\rangle$**, use**

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

MMCC functional

(K.Kowalski and P. Piecuch, 2000)

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

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$$\boxed{|\Phi\rangle\langle\Phi| + \sum_{n=1}^{N} \sum_{i_1<\cdots<i_n, a_1<\cdots<a_n} \left| \Phi_{i_1\ldots i_n}^{a_1\ldots a_n} \right\rangle \left\langle \Phi_{i_1\ldots i_n}^{a_1\ldots a_n} \right|}$$

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

$$\left\langle \Phi_{i_1\ldots i_n}^{a_1\ldots a_n} \middle| (H e^{T^{(A)}})_C \middle| \Phi \right\rangle = \mathfrak{W}_{0,a_1,\ldots,a_n}^{i_1,\ldots i_n}(m_A)$$

(moments of CC equations)

BIORTHOGONAL MOMENT EXPANSIONS

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

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Instead of

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

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before exploiting the resolution of identity, introduce the ansatz:

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

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

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

$$\boxed{\left|\Phi\right\rangle\left\langle\Phi\right| + \sum_{n=1}^{N} \sum_{i_1<\cdots<i_n,\, a_1<\cdots<a_n} \left|\Phi_{i_1\ldots i_n}^{a_1\ldots a_n}\right\rangle\left\langle\Phi_{i_1\ldots i_n}^{a_1\ldots a_n}\right|}$$

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

BIORTHOGONAL MMCC EXPANSION

$$\boxed{\left|\Phi\right\rangle\left\langle\Phi\right| + \sum_{n=1}^{N} \sum_{i_1<\cdots<i_n,\, a_1<\cdots<a_n} \left|\Phi_{i_1\ldots i_n}^{a_1\ldots a_n}\right\rangle\left\langle\Phi_{i_1\ldots i_n}^{a_1\ldots a_n}\right|}$$

$$\boxed{\delta_0^{(A)} \equiv E_0 - E_0^{(A)} = \sum_{n=m_A+1}^{N_{0,A}} \left\langle\Phi\left|L_{0,n} M_{0,n}(m_A)\right|\Phi\right\rangle = \sum_{n=m_A+1}^{N_{0,A}} \sum_{i_1<\cdots<i_n,\, a_1<\cdots<a_n} \ell_{0,i_1,\ldots,i_n}^{a_1,\ldots,a_n} \mathfrak{W}_{0,a_1,\ldots,a_n}^{i_1,\ldots i_n}(m_A)}$$

MOMENT ENERGY EXPANSIONS FOR GROUND AND EXCITED STATES

$$E_\mu = \langle \Psi_\mu | H R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle$$

$$\delta_\mu^{(A)} \equiv E_\mu - E_\mu^{(A)}$$

MOMENT ENERGY EXPANSIONS FOR GROUND AND EXCITED STATES

$$E_\mu = \langle \Psi_\mu | H R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle \qquad \delta_\mu^{(A)} \equiv E_\mu - E_\mu^{(A)}$$

$$\boxed{\delta_\mu^{(A)} = \sum_{n=m_A+1}^{N} \sum_{k=m_A+1}^{n} \langle \Psi_\mu | C_{n-k}(m_A)\, M_{\mu,k}(m_A) | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle}$$

$$M_{\mu,n}(m_A) = \sum_{\substack{i_1 < \cdots < i_n \\ a_1 < \cdots < a_n}} \mathfrak{M}_{\mu,a_1 \ldots a_n}^{i_1 \ldots i_n}(m_A)\, a^{a_1} \cdots a^{a_n} a_{i_n} \cdots a_{i_1}$$

CR-CCSD(T), CR-CCSD(TQ), CR-EOMCCSD(T), etc.

$$\mathfrak{M}_{\mu,a_1 \ldots a_n}^{i_1 \ldots i_n}(m_A) = \langle \Phi_{i_1 \ldots i_n}^{a_1 \ldots a_n} | (\bar{H}^{(A)} R_\mu^{(A)}) | \Phi \rangle$$

MOMENT ENERGY EXPANSIONS FOR GROUND AND EXCITED STATES

$$E_\mu = \langle \Psi_\mu | H R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle \qquad \delta_\mu^{(A)} \equiv E_\mu - E_\mu^{(A)}$$

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$$\mathfrak{M}_{\mu,a_1 \ldots a_n}^{i_1 \ldots i_n}(m_A) = \langle \Phi_{i_1 \ldots i_n}^{a_1 \ldots a_n} | (\bar{H}^{(A)} R_\mu^{(A)}) | \Phi \rangle$$

CR-CCSD(T), CR-CCSD(TQ), CR-EOMCCSD(T), etc.

CR-CC(2,3), CR-CC(2,4), CR-EOMCC(2,3), etc.

$$\langle \Psi_\mu | = \langle \Phi | \mathscr{L}_\mu\, e^{-T^{(A)}}$$

$$\delta_\mu^{(A)} = \sum_{n=m_A+1}^{N_{A,\mu}} \langle \Phi | \mathscr{L}_{\mu,n}\, M_{\mu,n}(m_A) | \Phi \rangle = \sum_{n=m_A+1}^{N_{A,\mu}} \sum_{\substack{i_1 < \cdots < i_n \\ a_1 < \cdots < a_n}} \ell_{\mu,i_1 \ldots i_n}^{a_1 \ldots a_n}\, \mathfrak{M}_{\mu,a_1 \ldots a_n}^{i_1 \ldots i_n}(m_A)$$

MOMENT ENERGY EXPANSIONS FOR GROUND AND EXCITED STATES

$$E_\mu = \langle \Psi_\mu | H R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle \qquad \delta_\mu^{(A)} \equiv E_\mu - E_\mu^{(A)}$$

$$\delta_\mu^{(A)} = \sum_{n=m_A+1}^{N} \sum_{k=m_A+1}^{n} \langle \Psi_\mu | C_{n-k}(m_A)\, \underline{M_{\mu,k}(m_A)} | \Phi \rangle / \langle \Psi_\mu | R_\mu^{(A)} e^{T^{(A)}} | \Phi \rangle$$

$$M_{\mu,n}(m_A) = \sum_{\substack{i_1 < \cdots < i_n \\ a_1 < \cdots < a_n}} \underline{\mathfrak{M}_{\mu,a_1\ldots a_n}^{i_1\ldots i_n}(m_A)}\, a^{a_1} \cdots a^{a_n} a_{i_n} \cdots a_{i_1}$$

CR-CCSD(T), CR-CCSD(TQ), CR-EOMCCSD(T), etc.

$$\mathfrak{M}_{\mu,a_1\ldots a_n}^{i_1\ldots i_n}(m_A) = \langle \Phi_{i_1\ldots i_n}^{a_1\ldots a_n} | (\bar{H}^{(A)} R_\mu^{(A)}) | \Phi \rangle$$

CR-CC(2,3), CR-CC(2,4), CR-EOMCC(2,3), etc.

$$\langle \Psi_\mu | = \langle \Phi | \mathscr{L}_\mu\, e^{-T^{(A)}}$$

$$\delta_\mu^{(A)} = \sum_{n=m_A+1}^{N_{A,\mu}} \langle \Phi | \mathscr{L}_{\mu,n}\, M_{\mu,n}(m_A) | \Phi \rangle = \sum_{n=m_A+1}^{N_{A,\mu}} \sum_{\substack{i_1 < \cdots < i_n \\ a_1 < \cdots < a_n}} \ell_{\mu,i_1\ldots i_n}^{a_1\ldots a_n}\, \underline{\mathfrak{M}_{\mu,a_1\ldots a_n}^{i_1\ldots i_n}(m_A)}$$

BIORTHOGONAL MOMENT EXPANSIONS: CR-CC(m_A,m_B) HIERARCHY

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

$$\delta_\mu(m_A, m_B) = \sum_{n=m_A+1}^{m_B} \sum_{\substack{i_1<\cdots<i_n \\ a_1<\cdots<a_n}} \ell^{a_1,\ldots,a_n}_{\mu,i_1,\ldots,i_n} \mathfrak{W}^{i_1,\ldots i_n}_{\mu,a_1,\ldots,a_n}(m_A)$$

$$\delta_\mu(2,3) = \sum_{\substack{i<j<k \\ a<b<c}} \ell^{abc}_{\mu,ijk}(2)\mathfrak{W}^{ijk}_{\mu,abc}(2)$$

CR-CC(2,3)
CR-EOMCC(2,3)

$$\delta_\mu(2,4) = \sum_{\substack{i<j<k \\ a<b<c}} \ell^{abc}_{\mu,ijk}(2)\mathfrak{W}^{ijk}_{\mu,abc}(2) + \sum_{\substack{i<j<k<l \\ a<b<c<d}} \ell^{abcd}_{\mu,ijkl}(2)\mathfrak{W}^{ijkl}_{\mu,abcd}(2)$$

CR-CC(2,4)
CR-EOMCC(2,4)

$$\delta_\mu(3,4) = \sum_{\substack{i<j<k<l \\ a<b<c<d}} \ell^{abcd}_{\mu,ijkl}(3)\mathfrak{W}^{ijkl}_{\mu,abcd}(3)$$

CR-CC(3,4)
CR-EOMCC(3,4)

Example: CR-CC(2,3), T_3 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

$$\boxed{E_0(2,3) = E_0^{(\mathrm{CCSD})} + \left\langle \Phi \middle| L_3 M_3(2) \middle| \Phi \right\rangle = E_0^{(\mathrm{CCSD})} + \sum_{i_1<j<k,a<b<c} \ell_{abc}^{ijk} M_{ijk}^{abc}(2)} \leftarrow \left\langle \Phi_{ijk}^{abc} \middle| \left(H_N e^{T_1+T_2} \right)_C \middle| \Phi \right\rangle$$

Example: CR-CC(2,3), T_3 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

$$\boxed{E_0(2,3) = E_0^{(\mathrm{CCSD})} + \langle \Phi | L_3 M_3(2) | \Phi \rangle = E_0^{(\mathrm{CCSD})} + \sum_{i_1<j<k,a<b<c} \ell_{abc}^{ijk} M_{ijk}^{abc}(2)} \leftarrow \langle \Phi_{ijk}^{abc} | \left(H_N e^{T_1+T_2}\right)_C | \Phi \rangle$$

$$\langle \Phi | L \overline{H}^{(CCSD)} = E_0 \langle \Phi | L, \quad \overline{H}^{(CCSD)} = e^{-T_1-T_2} H e^{T_1+T_2} = (H e^{T_1+T_2})_C$$

$$\langle \Phi | L \overline{H}^{(CCSD)} | \Phi_{ijk}^{abc} \rangle = E_0 \ell_{abc}^{ijk}, \quad L \approx L_0^{(CCSD)} + L_3, \quad E_0 \approx E_0^{(CCSD)}$$

$$\langle \Phi | L_0^{(CCSD)} \overline{H}^{(CCSD)} | \Phi_{ijk}^{abc} \rangle + \sum_{l<m<n,d<e<f} \langle \Phi_{lmn}^{def} | \overline{H}^{(CCSD)} | \Phi_{ijk}^{abc} \rangle \ell_{def}^{lmn} = E_0^{(CCSD)} \ell_{abc}^{ijk}$$

$$\ell_{abc}^{ijk} = \langle \Phi | L_0^{(CCSD)} \overline{H}^{(CCSD)} | \Phi_{ijk}^{abc} \rangle / (E_0^{(CCSD)} - \langle \Phi_{ijk}^{abc} | \overline{H}^{(CCSD)} | \Phi_{ijk}^{abc} \rangle)$$

Example: CR-CC(2,3), T_3 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

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$$\ell_{abc}^{ijk} = \langle \Phi | L_0^{(CCSD)} \overline{H}^{(CCSD)} | \Phi_{ijk}^{abc} \rangle / (E_0^{(CCSD)} - \langle \Phi_{ijk}^{abc} | \overline{H}^{(CCSD)} | \Phi_{ijk}^{abc} \rangle)$$

CR-CC(2,3)

S.A. Kucharski and R.J. Bartlett; A.G. Taube and R.J. Bartlett; J.F. Stanton and T.D. Crawford

K. Kowalski and P. Piecuch

$CCSD(2)_T$=CR-CC(2,3),A or B; $CCSD(T)_\Lambda$; R-CCSD(T), CR-CCSD(T), LR-CCSD(T)

S.R. Gwaltney and M. Head-Gordon; S. Hirata et al.

CCSD(T)

K. Raghavachari, G.W. Trucks, J.A. Pople, and M. Head-Gordon

CCSD[T]

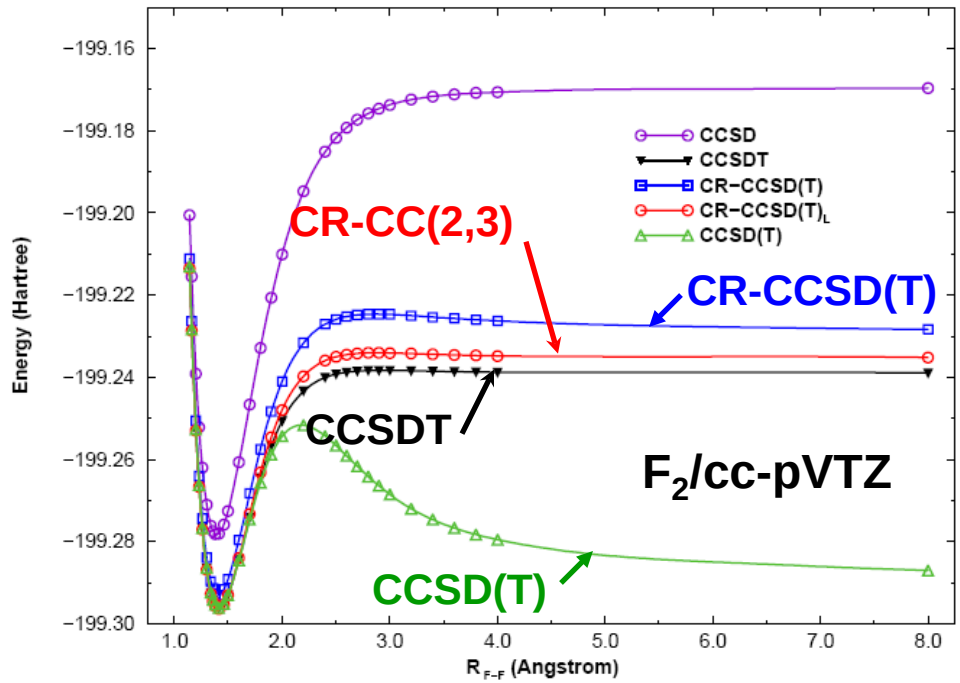
M. Urban, J. Noga, S.J. Cole, and R.J. Bartlett

CR-CC(2,3) [in GAMESS: CCTYP = CR-CCL]: the most accurate non-iterative triples correction to CCSD. Example: potential energy curve of OH^-.

	$R_{O\text{-}H}$												
Method	0.77	0.87	0.92	0.96966[b]	1.02	1.07	1.27	1.50	1.75	2.00	2.25	2.50	3.00
Full CI	-75.468511	-75.518758	-75.528442	-75.531783	-75.530756	-75.526756	-75.497668	-75.461721	-75.430711	-75.408175	-75.392615	-75.382311	-75.371727
CCSD	2.087	2.356	2.524	2.714	2.931	3.172	4.424	6.508	9.487	12.958	16.674	20.410	26.865
CCSDT	0.464	0.530	0.562	0.594	0.624	0.652	0.735	0.779	0.826	0.927	1.103	1.341	1.840
CCSD(T)	0.554	0.629	0.669	0.710	0.752	0.794	0.938	0.931	0.278	-2.025	-7.905	-21.201	-108.982
CCSD(2)$_T$	0.660	0.764	0.822	0.885	0.953	1.026	1.376	1.929	2.733	3.672	4.611	5.391	5.827
CR-CCSD(T)$_{\mathscr{L}}$	0.338	0.398	0.425	0.446	0.464	0.479	0.501	0.458	0.435	0.618	0.955	1.179	0.701

CR-CC(2,3)

Another example …



CR-CC(2,3) ⟹ CCSD(T)

$$E_0(2,3) = E_0^{(\mathrm{CCSD})} + \sum_{i_1<j<k,\,a<b<c} \ell_{abc}^{ijk} M_{ijk}^{abc}(2)$$

CR-CC(2,3) ⟹ CCSD(T)

$$\boxed{E_0(2,3) = E_0^{(\mathrm{CCSD})} + \sum_{i_1<j<k,\,a<b<c} \ell_{abc}^{ijk} M_{ijk}^{abc}(2)}$$

$$M_{abc}^{ijk}(2) = \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(CCSD)} \middle| \Phi \right\rangle \Longrightarrow \left\langle \Phi_{ijk}^{abc} \middle| (V_N T_2)_C \middle| \Phi \right\rangle$$

CR-CC(2,3) ⟹ CCSD(T)

$$\boxed{E_0(2,3) = E_0^{(\mathrm{CCSD})} + \sum_{i_1<j<k,a<b<c} \ell_{abc}^{ijk} M_{ijk}^{abc}(2)}$$

$$M_{abc}^{ijk}(2) = \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(CCSD)} \middle| \Phi \right\rangle \Longrightarrow \left\langle \Phi_{ijk}^{abc} \middle| (V_N T_2)_C \middle| \Phi \right\rangle$$

(3) **(4)** **(2)**

$$\ell_{abc}^{ijk} = \left\langle \Phi \middle| [(L_1^{(CCSD)} \overline{H}_2^{(CCSD)})_{DC} + (L_2^{(CCSD)} \overline{H}_1^{(CCSD)})_{DC} + (L_2^{(CCSD)} \overline{H}_2^{(CCSD)})_C \middle| \Phi_{ijk}^{abc} \right\rangle / D_{abc}^{ijk}$$

CR-CC(2,3) ⟹ CCSD(T)

$$\boxed{E_0(2,3) = E_0^{(\mathrm{CCSD})} + \sum_{i_1<j<k,\,a<b<c} \ell_{abc}^{ijk} M_{ijk}^{abc}(2)}$$

$$M_{abc}^{ijk}(2) = \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(CCSD)} \middle| \Phi \right\rangle \Longrightarrow \left\langle \Phi_{ijk}^{abc} \middle| (V_N T_2)_C \middle| \Phi \right\rangle$$

$$\ell_{abc}^{ijk} = \left\langle \Phi \middle| [(\underbrace{L_1^{(CCSD)} \overline{H}_2^{(CCSD)}}_{(3)})_{DC} + \underbrace{\cancel{(L_2^{(CCSD)} \overline{H}_1^{(CCSD)})_{DC}}}_{(4)} + (\underbrace{L_2^{(CCSD)} \overline{H}_2^{(CCSD)}}_{(2)})_C \middle| \Phi_{ijk}^{abc} \right\rangle / D_{abc}^{ijk}$$

$$\Downarrow \qquad\qquad\qquad \Downarrow$$

$$(T_1^+ V_N)_{DC} \qquad\qquad\qquad (T_2^+ V_N)_C$$

CR-CC(2,3) ⟹ CCSD(T)

$$\boxed{E_0(2,3) = E_0^{(\mathrm{CCSD})} + \sum_{i_1<j<k,\,a<b<c} \ell_{abc}^{ijk} M_{ijk}^{abc}(2)}$$

$$M_{abc}^{ijk}(2) = \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(CCSD)} \middle| \Phi \right\rangle \Longrightarrow \left\langle \Phi_{ijk}^{abc} \middle| (V_N T_2)_C \middle| \Phi \right\rangle$$

$$\ell_{abc}^{ijk} = \left\langle \Phi \middle| [(\overset{(3)}{L_1^{(CCSD)} \overline{H}_2^{(CCSD)}})_{DC} + \cancel{(\overset{(4)}{L_2^{(CCSD)} \overline{H}_1^{(CCSD)}})_{DC}} + (\overset{(2)}{L_2^{(CCSD)} \overline{H}_2^{(CCSD)}})_C \middle| \Phi_{ijk}^{abc} \right\rangle / D_{abc}^{ijk}$$

$$\Downarrow \qquad\qquad\qquad\qquad \Downarrow$$

$$(T_1^+ V_N)_{DC} \qquad\qquad\qquad\qquad (T_2^+ V_N)_C$$

$$D_{abc}^{ijk} = E_0^{(CCSD)} - \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(CCSD)} \middle| \Phi_{ijk}^{abc} \right\rangle \Longrightarrow \varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c$$

CR-CC(2,3) ⟹ CCSD[T]=CCSD+T

$$\boxed{E_0(2,3) = E_0^{(\mathrm{CCSD})} + \sum_{i_1<j<k,\,a<b<c} \ell_{abc}^{ijk} M_{ijk}^{abc}(2)}$$

$$M_{abc}^{ijk}(2) = \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(CCSD)} \middle| \Phi \right\rangle \Longrightarrow \left\langle \Phi_{ijk}^{abc} \middle| (V_N T_2)_C \middle| \Phi \right\rangle$$

$$\ell_{abc}^{ijk} = \left\langle \Phi \middle| [\overset{(3)}{\cancel{(L_1^{(CCSD)} \overline{H}_2^{(CCSD)})_{DC}}} + \overset{(4)}{\cancel{(L_2^{(CCSD)} \overline{H}_1^{(CCSD)})_{DC}}} + \overset{(2)}{(L_2^{(CCSD)} \overline{H}_2^{(CCSD)})_C} \middle| \Phi_{ijk}^{abc} \right\rangle / D_{abc}^{ijk}$$

$$\Downarrow$$

$$(T_2^+ V_N)_C$$

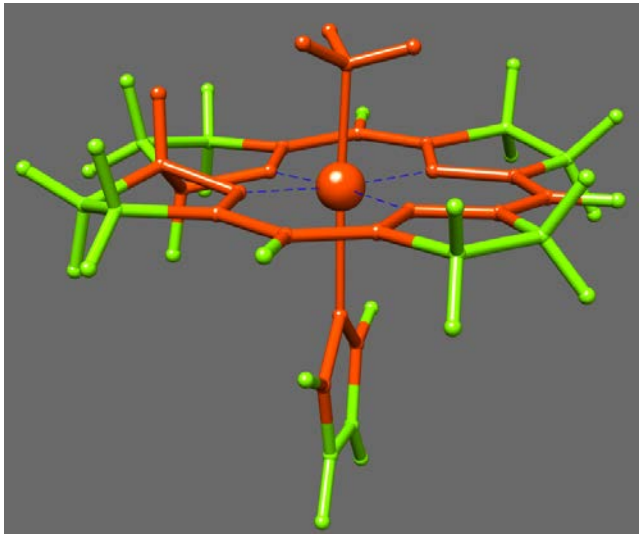
$$D_{abc}^{ijk} = E_0^{(CCSD)} - \left\langle \Phi_{ijk}^{abc} \middle| \overline{H}^{(CCSD)} \middle| \Phi_{ijk}^{abc} \right\rangle \Longrightarrow \varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c$$

LARGE SYSTEMS (LOCAL CC): CIM-CR-CC(2,3) STUDY OF Co-C BOND DISSOCIATON 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)]

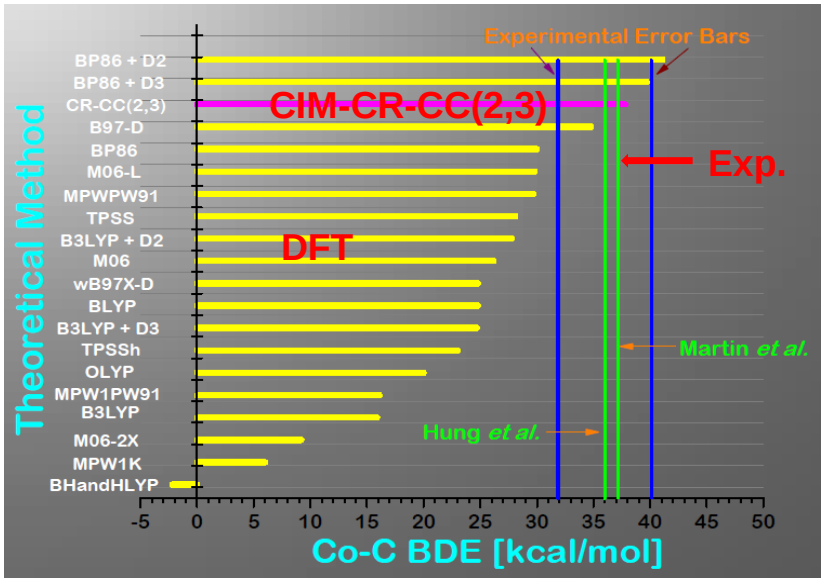
Functional	BDE (with ZPE), kcal/mol, 6-31G(d) / 6-311++G(d,p)
BHandHLYP (50% HF)	1.2 / -2.2
MPW1K (42.8 % HF)	8.9 / 6.0
M06-2X (54 % HF)	13.5 / 9.2
MPW1PW91 (25 % HF)	18.1 / 16.1
B3LYP (20 % HF)	17.8 / 15.9
B3LYP+D3 (20 % HF)	21.2 / 24.7
M06-HF (27 % HF)	27.4 / 26.2
TPSSh (10 % HF)	24.5 / 23.0
ωB97X-D (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 ± 3, 36 ± 4
CASSCF(11,10), CASPT2(11,10)	15.1, 53.8

DFT



[In GAMESS: CIMTYP = GSECIM]

Structural model: 58 atoms; 234 electrons.



ADIABATIC EXCITATIONS IN CH, CNC, C_2N (TRIPLES CORRECTIONS TO EOMCCSD)

[In GAMESS: CCTYP = CR-EOM, CR-EOML]

CH

[Piecuch, Gour, Włoch, IJQC (2009)]

State	Theory	E/Hartree	T_e/eV	REL
$B\ ^2\Sigma^-$	EOMCCSD	-38.228 924	4.241	1.79
	EOMCCSDT[b]	-38.267 435	3.273	
	EA-EOMCCSD(2p-1h)	-38.160 687	6.105	
	EA-EOMCCSD(3p-2h)	-38.262 600	3.377	
	EA-EOMCCSD(3p-2h){3}	-38.261 677	3.357	
	CR-EOMCCSD(T),ID[c]	-38.270 424	3.181	
	CR-EOMCC(2,3),A	-38.257 269	3.529	
	CR-EOMCC(2,3),B	-38.255 709	3.569	
	CR-EOMCC(2,3),C	-38.272 744	3.123	
	CR-EOMCC(2,3),D	-38.272 498	3.130	
	Experiment[d]		3.23	

State	Theory	E/Hartree	T_e/eV	REL
$C\ ^2\Sigma^+$	EOMCCSD	-38.194 213	5.185	1.87
	EOMCCSDT[b]	-38.238 031	4.073	
	EA-EOMCCSD(2p-1h)	-38.180 332	5.570	
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	EA-EOMCCSD(3p-2h){3}	-38.234 680	4.092	
	CR-EOMCCSD(T),ID[c]	-38.236 048	4.117	
	CR-EOMCC(2,3),A	-38.224 449	4.422	
	CR-EOMCC(2,3),B	-38.222 634	4.469	
	CR-EOMCC(2,3),C	-38.238 514	4.055	
	CR-EOMCC(2,3),D	-38.238 118	4.065	
	Experiment[e]		3.94	

ADIABATIC EXCITATIONS IN CH, CNC, C_2N (TRIPLES CORRECTIONS TO EOMCCSD)

[In GAMESS: CCTYP = CR-EOM, CR-EOML]

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ADIABATIC EXCITATIONS IN CH, CNC, C_2N (TRIPLES CORRECTIONS TO EOMCCSD)

[In GAMESS: CCTYP = CR-EOM, CR-EOML]

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ADIABATIC EXCITATIONS IN CH, CNC, C_2N (TRIPLES CORRECTIONS TO EOMCCSD)

[In GAMESS: CCTYP = CR-EOM, CR-EOML]

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ADIABATIC EXCITATIONS IN CH, CNC, C_2N (TRIPLES CORRECTIONS TO EOMCCSD)

[In GAMESS: CCTYP = CR-EOM, CR-EOML]

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[Piecuch, Gour, Włoch, IJQC (2009)]

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CNC, C_2N

[Piecuch, Gour, Włoch, IJQC (2009); Ehara, Gour, Piecuch, Mol. Phys. (2009); Hansen, Piecuch, Lutz, Gour, Phys. Scr. (2011)]

			EA-EOMCCSD					CR-EOMCC(2,3)				
Molecule	State	REL	(2p-1h)	(3p-2h)	(3p-2h){4}	EOMCCSD	CR-EOMCCSD(T),ID	A	B	C	D	Experiment[b]
CNC	$A\ ^2\Delta_u$	1.099	7.206	4.105	4.085	4.291	4.339	4.400	4.397	4.395	4.395	3.761
	$B\ ^2\Sigma_u^+$	1.979	7.639	4.718	4.704	7.123	4.675	5.432	5.595	4.582	4.599	4.315
C_2N	$A\ ^2\Delta$	1.090	6.190	3.055	3.028	3.191	3.344	3.377	3.368	3.389	3.388	2.636
	$B\ ^2\Sigma^-$	1.856	7.856	3.677	3.648	5.514	3.351	4.018	4.160	3.091	3.110	2.779
	$C\ ^2\Sigma^+$	1.897	6.722	3.809	3.788	6.358	4.023	4.741	4.901	3.799	3.824	3.306

ADIABATIC EXCITATIONS IN CH, CNC, C_2N (TRIPLES CORRECTIONS TO EOMCCSD)

[In GAMESS: CCTYP = CR-EOM, CR-EOML]

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[Piecuch, Gour, Włoch, IJQC (2009)]

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$C\ ^2\Sigma^+$	EOMCCSD (> 1 eV error)	-38.194 213	5.185	1.87
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CNC, C_2N

[Piecuch, Gour, Włoch, IJQC (2009); Ehara, Gour, Piecuch, Mol. Phys. (2009); Hansen, Piecuch, Lutz, Gour, Phys. Scr. (2011)]

			EA-EOMCCSD					CR-EOMCC(2,3)				
Molecule	State	REL	(2p-1h)	(3p-2h)	(3p-2h){4}	EOMCCSD	CR-EOMCCSD(T),ID	A	B	C	D	Experiment[b]
CNC	$A\ ^2\Delta_u$	1.099	7.206	4.105	4.085	4.291	4.339	4.400	4.397	4.395	4.395	3.761
	$B\ ^2\Sigma_u^+$	1.979	7.639	4.718	4.704	7.123	4.675	5.432	5.595	4.582	4.599	4.315
C_2N	$A\ ^2\Delta$	1.090	6.190	3.055	3.028	3.191	3.344	3.377	3.368	3.389	3.388	2.636
	$B\ ^2\Sigma^-$	1.856	7.856	3.677	3.648	5.514	3.351	4.018	4.160	3.091	3.110	2.779
	$C\ ^2\Sigma^+$	1.897	6.722	3.809	3.788	6.358	4.023	4.741	4.901	3.799	3.824	3.306

CR-CC and CR-EOMCC in nuclear structure …

VOLUME 92, NUMBER 13 PHYSICAL REVIEW LETTERS week ending 2 APRIL 2004

Coupled Cluster Calculations of Ground and Excited States of Nuclei

K. Kowalski,[1] D. J. Dean,[2] M. Hjorth-Jensen,[3] T. Papenbrock,[2,4] and P. Piecuch[1,5]

[1]*Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA*
[2]*Physics Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831, USA*
[3]*Department of Physics and Center of Mathematics for Applications, University of Oslo, N-0316 Oslo, Norway*
[4]*Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA*
[5]*Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824, USA*

(Received 29 October 2003; published 1 April 2004)

The standard and renormalized coupled cluster methods with singles, doubles, and noniterative triples and their generalizations to excited states, based on the equation of motion coupled cluster approach, are applied to the ^{4}He and ^{16}O nuclei. A comparison of coupled cluster results with the results of the exact diagonalization of the Hamiltonian in the same model space shows that the quantum chemistry inspired coupled cluster approximations provide an excellent description of ground and excited states of nuclei. The bulk of the correlation effects is obtained at the coupled cluster singles and doubles level. Triples, treated noniteratively, provide the virtually exact description.

CR-CC and CR-EOMCC in nuclear structure ...

TABLE I. The ground-state energies of ^{4}He calculated using the oscillator (Osc) and Hartree-Fock (HF) basis states. Units are MeV. The reference energies $\langle\Phi|H'|\Phi\rangle$ are -7.211 (Osc) and -10.520 (HF) MeV.

Method	Osc	HF
CCSD	-21.978	-21.385
CR-CCSD(T), a	-22.841	-22.395
CR-CCSD(T), $a/\Delta_0 = 1$	-23.524	-22.711
CR-CCSD(T), b	-22.396	-22.179
CR-CCSD(T), $b/\Delta_0 = 1$	-22.730	-22.428
CR-CCSD(T), c	-22.630	-22.450
CR-CCSD(T), $c/\Delta_0 = 1$	-23.149	-22.783
CISD	-20.175	-20.801
CISDT	-22.235	–
Exact	-23.484	-23.484

TABLE II. The excitation energies of ^{4}He calculated using the oscillator basis states (in MeV). The last column indicates the energy expectation for the center of mass mode.

State	EOMCCSD	CR-CCSD(T)[a]	CISD	Exact	$\langle\beta_{\rm c.m.}H_{\rm c.m.}\rangle$
$J=1$	11.791	12.044	17.515	11.465	8.2
$J=0$	21.203	21.489	24.969	21.569	0.8
$J=2$	22.435	22.650	24.966	22.697	14.3

[a]The difference of the CR-CCSC(T), c energy of the excited state and the CR-CCSD(T), b energy of the ground state.

CCSD, CR-CCSD(T), EOMCCSD, CR-EOMCCSD(T) vs truncated and full CI

PRL 94, 212501 (2005) PHYSICAL REVIEW LETTERS week ending 3 JUNE 2005

Ab-Initio Coupled-Cluster Study of ^{16}O

M. Włoch,[1] D. J. Dean,[2] J. R. Gour,[1] M. Hjorth-Jensen,[3] K. Kowalski,[1] T. Papenbrock,[2,4] and P. Piecuch[1]

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(Received 26 January 2005; published 3 June 2005)

We report converged results for the ground and excited states and matter density of ^{16}O using realistic two-body nucleon-nucleon interactions and coupled-cluster methods and algorithms developed in quantum chemistry. Most of the binding is obtained with the coupled-cluster singles and doubles approach. Additional binding due to three-body clusters (triples) is minimal. The coupled-cluster method with singles and doubles provides a good description of the matter density, charge radius, charge form factor, and excited states of a one-particle, one-hole nature, but it cannot describe the first-excited 0^+ state. Incorporation of triples has no effect on the latter finding.

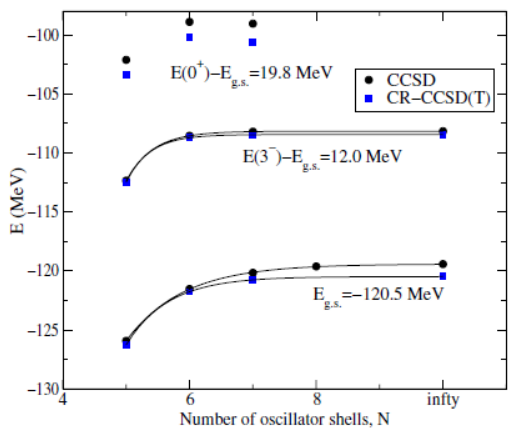

FIG. 1 (color online). The coupled-cluster energies of the ground-state (g.s.) and first-excited 3^- and 0^+ states as functions of the number of oscillator shells N obtained with the Idaho-A interaction.

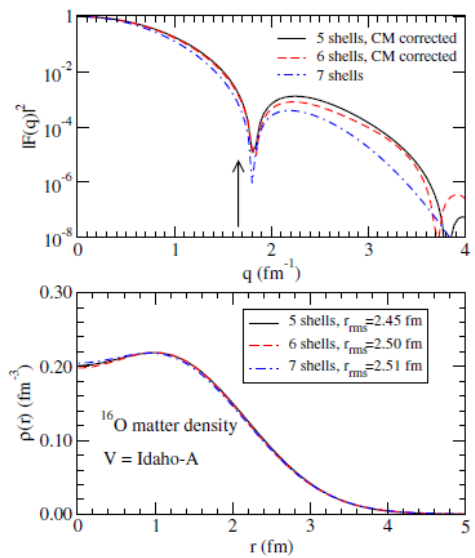

FIG. 2 (color online). Top panel: The charge form factor computed from the CCSD density matrix. Bottom panel: the matter density in ^{16}O. The results obtained with the Idaho-A interaction.

CCSD, CR-CCSD(T), EOMCCSD, CR-EOMCCSD(T), CCSD properties

Coupled-Cluster and Configuration-Interaction Calculations for Heavy Nuclei

M. Horoi,[1] J. R. Gour,[2] M. Włoch,[2] M. D. Lodriguito,[2] B. A. Brown,[3] and P. Piecuch[2,3]

[1]*Department of Physics, Central Michigan University, Mount Pleasant, Michigan 48859, USA*
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(Received 4 December 2006; published 13 March 2007)

We compare coupled-cluster (CC) and configuration-interaction (CI) results for ^{56}Ni obtained in the pf-shell basis, focusing on practical CC approximations that can be applied to systems with dozens or hundreds of correlated fermions. The weight of the reference state and the strength of correlation effects are controlled by the gap between the $f_{7/2}$ orbit and the $f_{5/2}$, $p_{3/2}$, $p_{1/2}$ orbits. Independent of the gap, the CC method with 1p-1h and 2p-2h clusters and a noniterative treatment of 3p-3h clusters is as accurate as the more demanding CI approach truncated at the 4p-4h level.

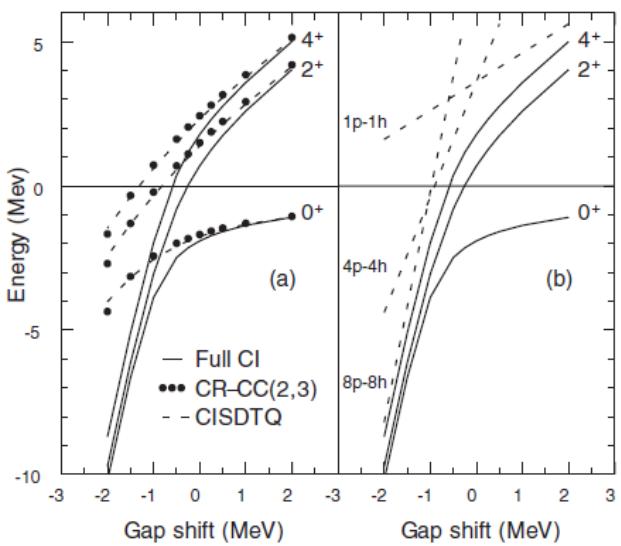

FIG. 1. (a) The full CI, CISDTQ, and CR-CC(2,3) energies of ^{56}Ni as functions of the shell-gap shift ΔG. (b) Comparison of full CI energies with the trends expected for the 1p-1h, 4p-4h, and 8p-8h configurations as functions of ΔG.

TABLE I. Energies (in MeV) of ^{56}Ni as functions of the shell-gap shift ΔG (also in MeV), relative to the reference energy $\langle\Phi_0|H|\Phi_0\rangle$. S_0 is defined as $|\langle\Phi_0|\Psi_0^{\text{Full-CI}}\rangle|$.

	ΔG	−2	−1	0	1	2
State	S_0	0.022	0.332	0.825	0.917	0.949
0^+	CCSD	−3.218	−2.048	−1.509	−1.202	−1.002
	CR-CC(2,3)	−4.355	−2.437	−1.686	−1.298	−1.060
	CR-CC(2,4)	−4.253	−2.415	−1.679	−1.295	−1.059
	CISD	−2.148	−1.652	−1.327	−1.104	−0.943
	CISDT	−2.706	−1.946	−1.488	−1.199	−1.004
	CISDTQ	−4.013	−2.548	−1.758	−1.334	−1.079
	Full CI	−10.198	−3.868	−1.909	−1.370	−1.091
	T2D	0.260	0.158	0.113	0.088	0.072
2^+	CCSD	−2.440	−0.065	1.595	2.983	4.241
	CR-CC(2,3)	−2.695	−0.218	1.496	2.915	4.192
	CR-CC(2,4)	−2.700	−0.222	1.493	2.913	4.190
	CISD	0.864	2.000	3.093	4.162	5.215
	CISDT	−1.227	0.359	1.771	3.066	4.283
	CISDTQ	−2.426	−0.335	1.378	2.833	4.137
	Full CI	−9.728	−3.054	0.689	2.594	4.027
	REL	1.309	1.178	1.114	1.080	1.060
4^+	CCSD	−1.373	0.910	2.551	3.942	5.211
	CR-CC(2,3)	−1.667	0.720	2.420	3.848	5.141
	CR-CC(2,4)	−1.626	0.736	2.428	3.852	5.144
	CISD	1.554	2.743	3.884	4.994	6.082
	CISDT	−0.271	1.301	2.713	4.017	5.248
	CISDTQ	−1.465	0.606	2.308	3.769	5.087
	Full CI	−8.700	−1.974	1.778	3.581	4.999
	REL	1.333	1.215	1.152	1.115	1.090

CR-CC(2,3), CR-EOMCC(2,3), CR-CC(2,4), CR-EOMCC(2,4) vs truncated and full CI

PHYSICAL REVIEW C **79**, 054325 (2009)

Ab initio coupled-cluster and configuration interaction calculations for ^{16}O using the V_{UCOM} interaction

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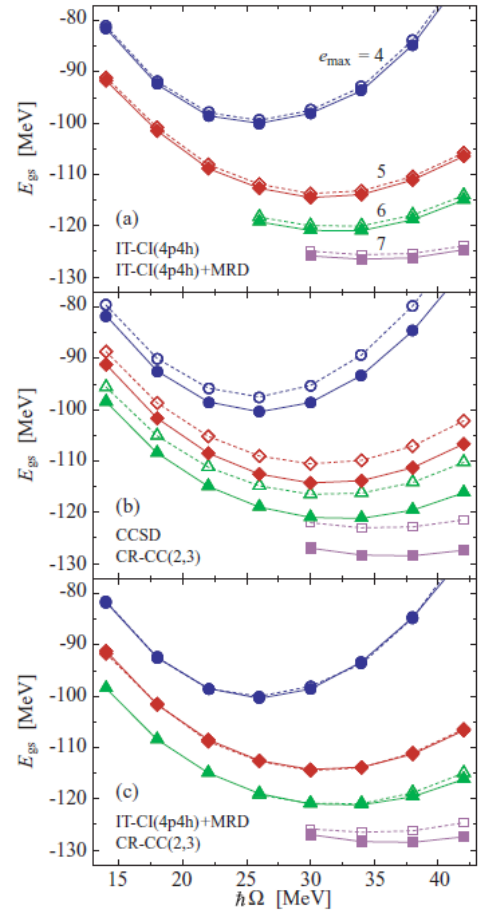
(Received 30 May 2008; revised manuscript received 7 November 2008; published 21 May 2009)

Using the ground-state energy of ^{16}O obtained with the realistic V_{UCOM} interaction as a test case, we present a comprehensive comparison of different configuration interaction (CI) and coupled-cluster (CC) methods, analyzing the intrinsic advantages and limitations of each of the approaches. In particular, we use the importance-truncated (IT) CI and no-core shell model (NCSM) schemes with up to 4-particle-4-hole (4p4h) excitations, with and without the Davidson extensivity corrections, as well as the size extensive CC methods with a complete treatment of one- and two-body clusters (CCSD) and a noniterative treatment of connected three-body clusters via the completely renormalized correction to the CCSD energy defining the CR-CC(2,3) approach, which are all capable of handling larger systems with dozens of explicitly correlated fermions. We discuss the impact of the center-of-mass contaminations, the choice of the single-particle basis, and size-extensivity on the resulting energies. When the IT-CI and IT-NCSM methods include the 4p4h excitations and when the CC calculations include the 1p1h, 2p2h, and 3p3h clusters, as in the CR-CC(2,3) approach, we observe an excellent agreement among the different methodologies, particularly when the Davidson extensivity corrections are added to the IT-CI energies and the effects of the connected three-body clusters are accounted for in the CC calculations. This shows that despite their individual limitations, the IT-CI, IT-NCSM, and CC methods can provide precise and consistent *ab initio* nuclear structure predictions. Furthermore, the IT-CI, IT-NCSM, and CC ground-state energy values obtained for ^{16}O are in reasonable agreement with the experimental value, providing further evidence that the V_{UCOM} two-body interaction may allow for a good description of binding energies for heavier nuclei and that all of the methods used in this study account for most of the relevant particle correlation effects.



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Center-of-mass problem in truncated configuration interaction and coupled-cluster calculations

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ABSTRACT

The problem of center-of-mass (CM) contaminations in *ab initio* nuclear structure calculations using configuration interaction (CI) and coupled-cluster (CC) approaches is analyzed. A rigorous and quantitative scheme for diagnosing the CM contamination of intrinsic observables is proposed and applied to ground-state calculations for ^{4}He and ^{16}O. The CI and CC calculations for ^{16}O based on model spaces defined via a truncation of the single-particle basis lead to sizable CM contaminations, while the importance-truncated no-core shell model based on the $N_{\max}\hbar\Omega$ space is virtually free of CM contaminations.

CR-CC(2,3) vs IT-CI(4p4h), center-of-mass problem in CC

PHYSICAL REVIEW C **88**, 054319 (2013)

Extension of coupled-cluster theory with a noniterative treatment of connected triply excited clusters to three-body Hamiltonians

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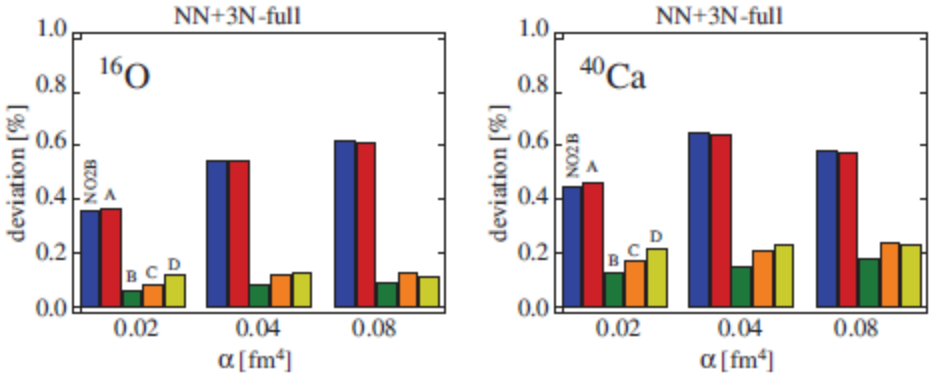
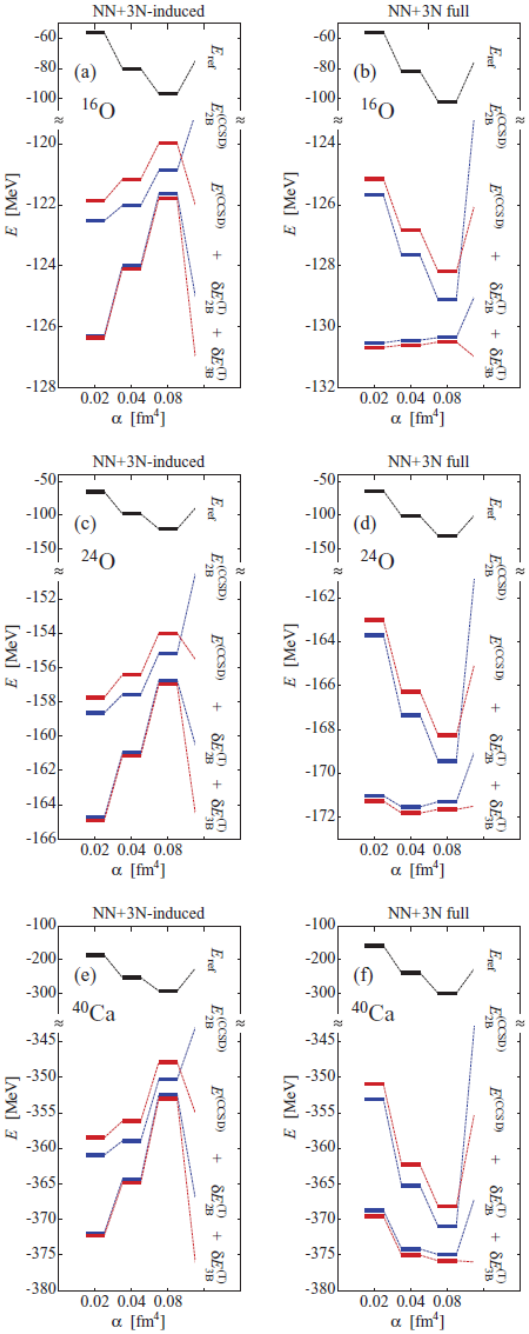
(Received 4 September 2013; published 20 November 2013)

We generalize the coupled-cluster (CC) approach with singles, doubles, and the noniterative treatment of triples termed ΛCCSD(T) to Hamiltonians containing three-body interactions. The resulting method and the underlying CC approach with singles and doubles only (CCSD) are applied to the medium-mass closed-shell nuclei ^{16}O, ^{24}O, and ^{40}Ca. By comparing the results of CCSD and ΛCCSD(T) calculations with explicit treatment of three-nucleon interactions to those obtained using an approximate treatment in which they are included effectively via the zero-, one-, and two-body components of the Hamiltonian in normal-ordered form, we quantify the contributions of the residual three-body interactions neglected in the approximate treatment. We find these residual normal-ordered three-body contributions negligible for the ΛCCSD(T) method, although they can become significant in the lower-level CCSD approach, particularly when the nucleon-nucleon interactions are soft.





CCSD plus a noniterative correction due to T_3 extracted from CR-CC(2,3) with NN+3N

Ab initio path to heavy nuclei: CCSD and CR-CC(2,3) results for the A = 16 – 132 nuclei

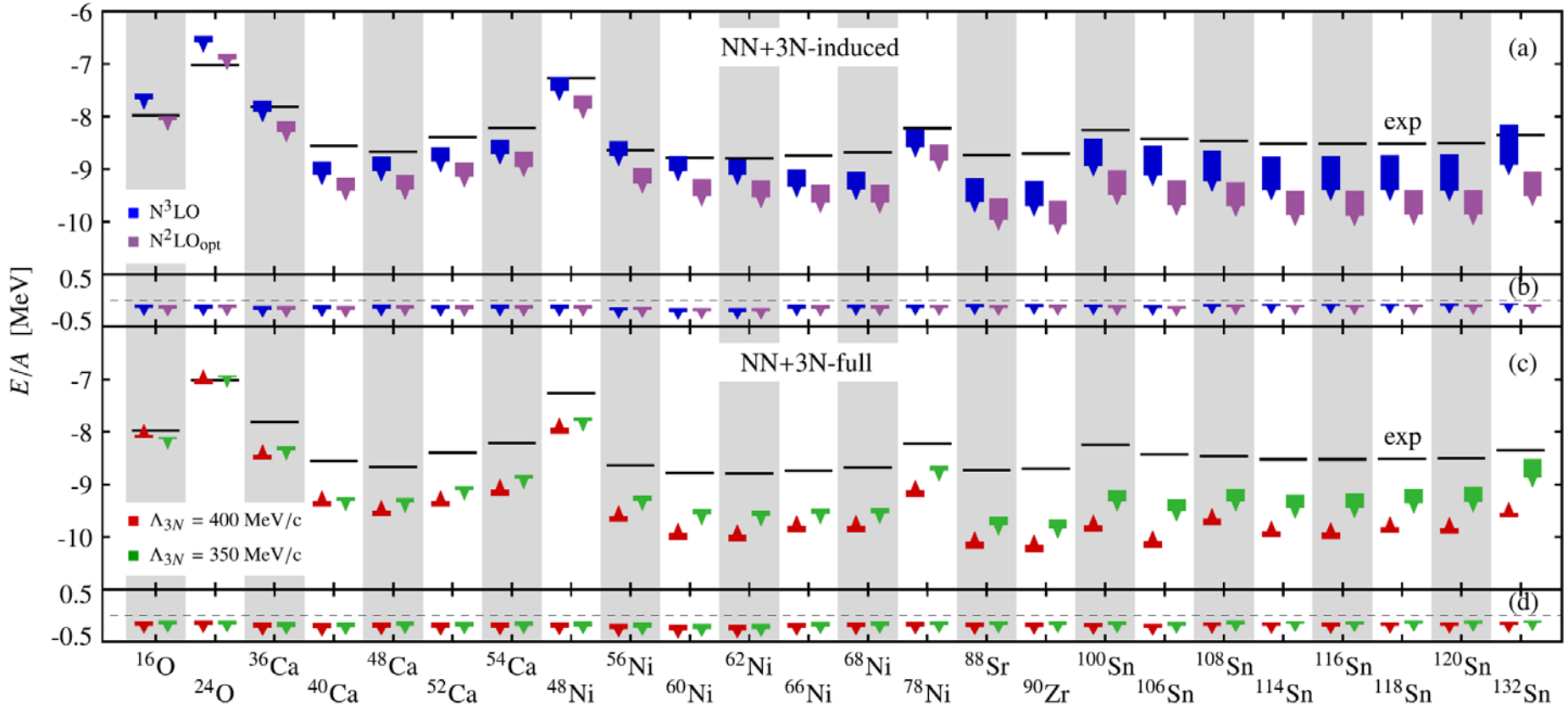
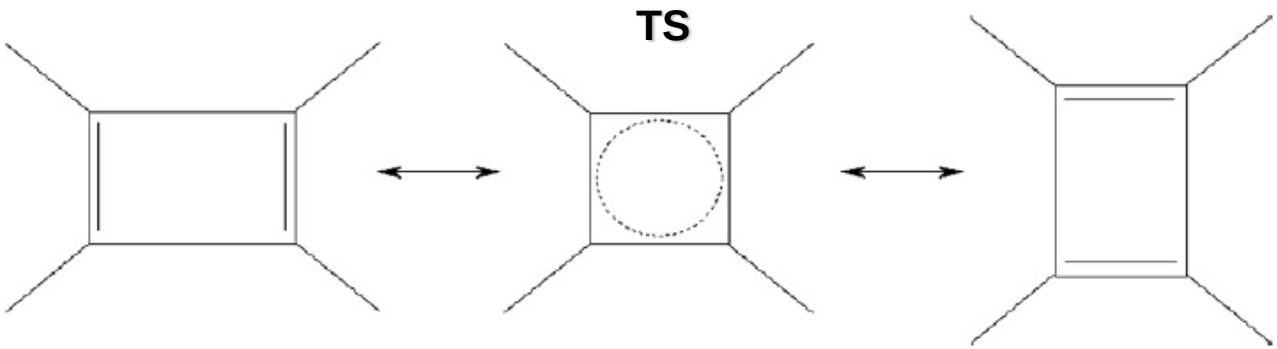


Fig. 5. (Color online.) Ground-state energies from CR-CC(2,3) for (a) the $NN+3N$-induced Hamiltonian starting from the N^{3}LO and N^{2}LO-optimized NN interaction and (c) the $NN+3N$-full Hamiltonian with $\Lambda_{3N}=400$ MeV/c and $\Lambda_{3N}=350$ MeV/c. The boxes represent the spread of the results from $\alpha=0.04$ fm^4 to $\alpha=0.08$ fm^4, and the tip points into the direction of smaller values of α. Also shown are the contributions of the CR-CC(2,3) triples correction to the (b) $NN+3N$-induced and (d) $NN+3N$-full results. All results employ $\hbar\Omega=24$ MeV and $3N$ interactions with $E_{3\,\max}=18$ in NO2B approximation and full inclusion of the $3N$ interaction in CCSD up to $E_{3\,\max}=12$. Black bars denote energies taken from [37,40].

AUTOMERIZATION OF CYCLOBUTADIENE

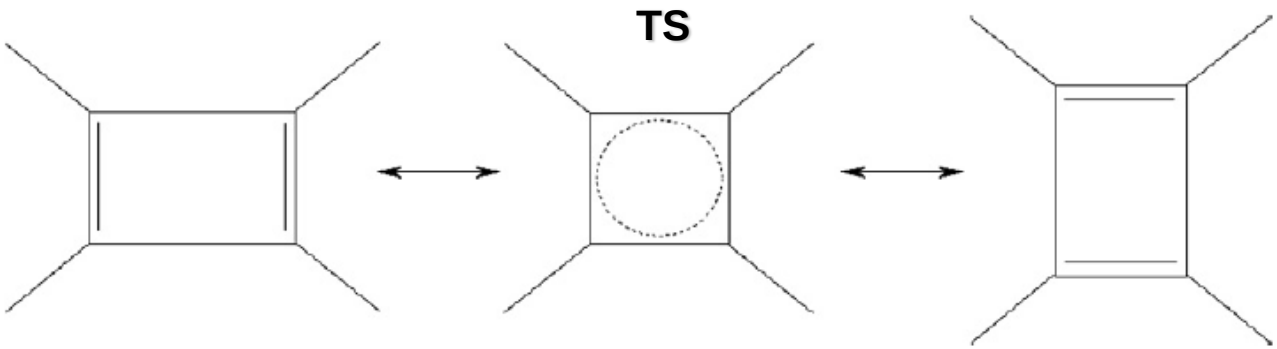


Various CC energies (in millihartree) relative to full CCSDT (in hartree), cc-pVDZ basis set

	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

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

AUTOMERIZATION OF CYCLOBUTADIENE



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

T_1 and T_2 decoupled from T_3

	Reactant	TS	Barrier Height (kcal/mol)
CCSD	26.827	47.979	20.9
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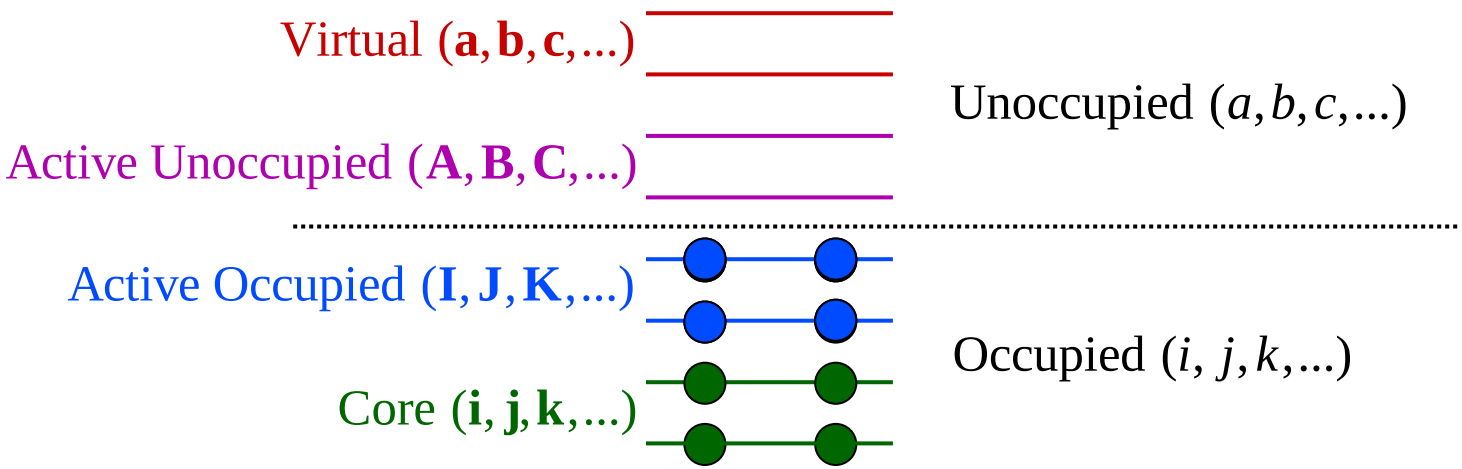
[J. Shen and P. Piecuch, J. Chem. Phys, 2012]

ALTERNATIVE SOLUTION: ACTIVE-SPACE CC/EOMCC APROACHES FOR CCSDt, CCSDtq, EOMCCSDt, 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 and Piecuch, 2013-2014; cf., also, CASCC work by Adamowicz et al.]



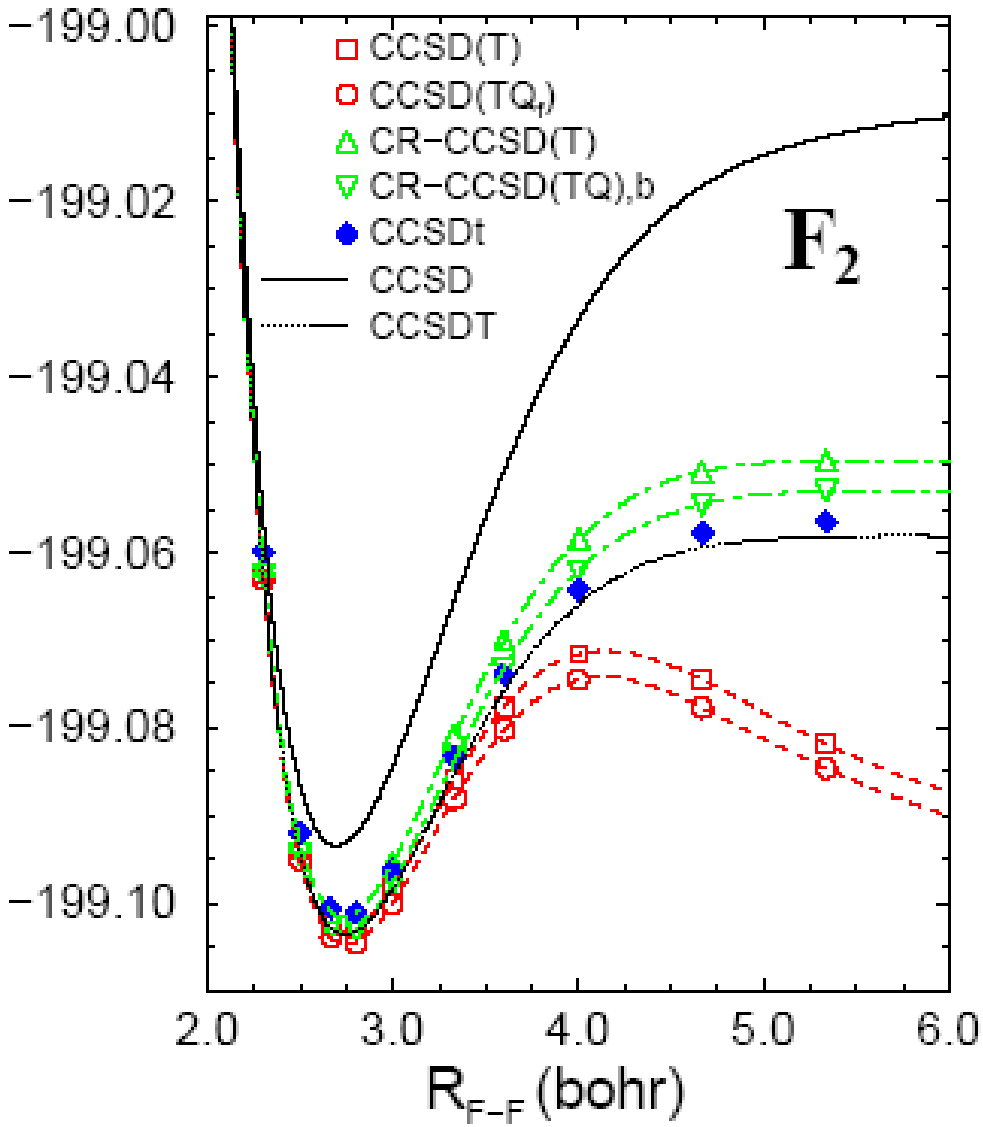
$$T^{(\mathrm{CCSDt})} = T_1 + T_2 + t_3, \quad T^{(\mathrm{CCSDtq})} = T_1 + T_2 + t_3 + t_4, \quad \text{etc.}$$

$$t_3 = \sum_{\substack{\mathbf{I}>j>k \\ a>b>\mathbf{C}}} t_{ab\mathbf{C}}^{\mathbf{I}jk} E_{\mathbf{I}jk}^{ab\mathbf{C}}, \qquad t_4 = \sum_{\substack{\mathbf{I}>\mathbf{J}>k>l \\ a>b>\mathbf{C}>\mathbf{D}}} t_{ab\mathbf{CD}}^{\mathbf{IJ}kl} E_{\mathbf{IJ}kl}^{ab\mathbf{CD}}$$

Method	**CPU Time Scaling**
CCSDt/EOMCCSDt	$N_o N_u n_o^2 n_u^4$
CCSDtq/EOMCCSDtq	$N_o^2 N_u^2 n_o^2 n_u^4$

EXAMPLE: Bond breaking in F_2

(K. Kowalski and P. Piecuch, Chem. Phys. Lett., 2001;
P. Piecuch et al., Chem. Phys. Lett., 2006)



EXAMPLE: Bond breaking in F_2

**(K. Kowalski and P. Piecuch, Chem. Phys. Lett., 2001;
P. Piecuch et al., Chem. Phys. Lett., 2006)**

Potential energy curves for F_2/cc-pVDZ. Differences with CCSDT (in millihartree)

Method	$0.75R_e$	R_e	$1.25R_e$	$1.5R_e$	$1.75R_e$	$2R_e$	$3R_e$	$5R_e$
CCSDT[a]	−198.922138	−199.102796	−199.085272	−199.065882	−199.059433	−199.058201	−199.058511	−199.058586
CCSD	4.504	9.485	19.917	32.424	41.184	45.638	49.425	49.816
CCSD(T)[a]	0.102	0.248	−0.503	−5.711	−15.133	−23.596	−35.700	−39.348
CR-CCSD(T)[a]	0.709	1.799	4.482	7.408	8.636	8.660	7.460	6.350
LR-CCSD(T)[b]	0.540	1.260	2.801	3.601	2.465	0.693	−2.859	−4.518
$CCSD(2)_T$[c]	0.460	1.398	3.698	5.984	6.637	6.357	4.976	3.895
CR-CC(2,3)	−0.289	−0.240	0.707	1.735	1.971	1.862	1.643	1.613
CCSDt[a]	2.677	2.297	1.907	1.720	1.730	1.789	1.889	1.891

EXAMPLE: Bond breaking in F_2

**(K. Kowalski and P. Piecuch, Chem. Phys. Lett., 2001;
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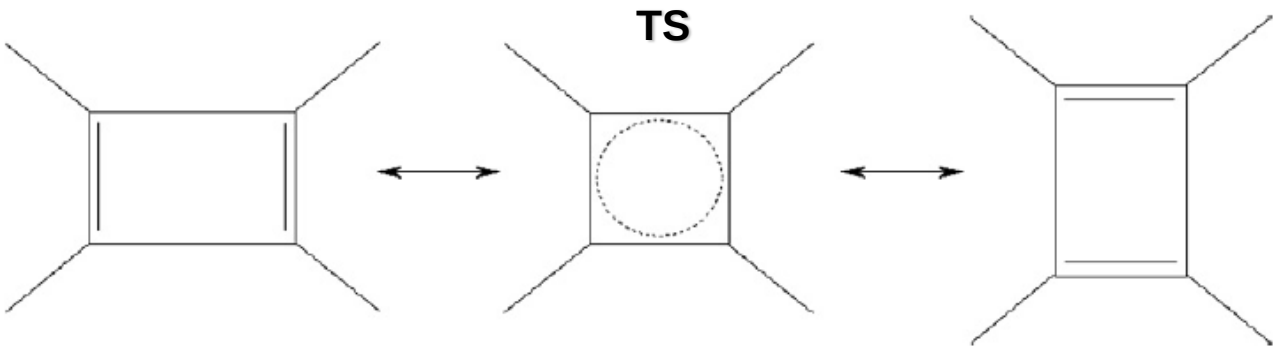
CCSDT[a]	−198.922138	−199.102796	−199.085272	−199.065882	−199.059433	−199.058201	−199.058511	−199.058586	
CCSD	4.504	9.485	19.917	32.424	41.184	45.638	49.425	49.816	45.312
CCSD(T)[a]	0.102	0.248	−0.503	−5.711	−15.133	−23.596	−35.700	−39.348	39.596
CR-CCSD(T)[a]	0.709	1.799	4.482	7.408	8.636	8.660	7.460	6.350	7.951
LR-CCSD(T)[b]	0.540	1.260	2.801	3.601	2.465	0.693	−2.859	−4.518	8.119
$CCSD(2)_T$[c]	0.460	1.398	3.698	5.984	6.637	6.357	4.976	3.895	6.177
CR-CC(2,3)	−0.289	−0.240	0.707	1.735	1.971	1.862	1.643	1.613	2.260
CCSDt[a]	2.677	2.297	1.907	1.720	1.730	1.789	1.889	1.891	0.957

AUTOMERIZATION OF CYCLOBUTADIENE



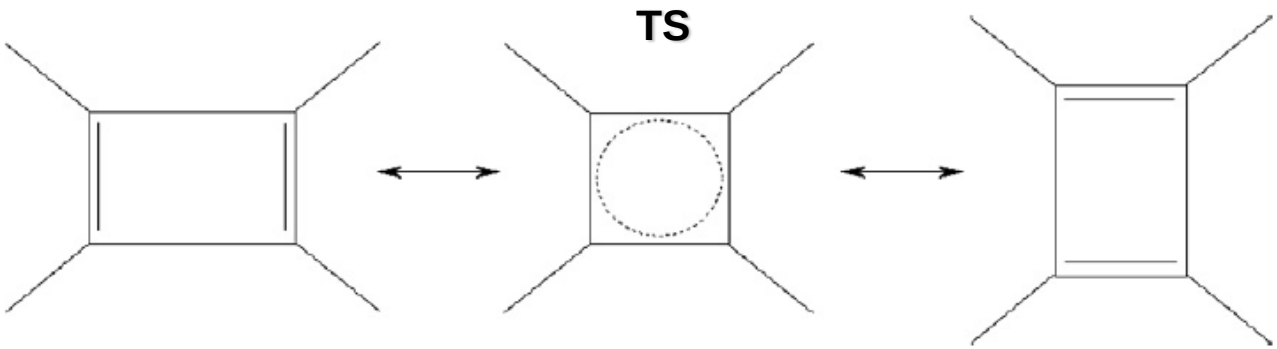
Various CC energies (in millihartree) relative to full CCSDT (in hartree), cc-pVDZ basis set

T_1 and T_2 decoupled from T_3

	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

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

AUTOMERIZATION OF CYCLOBUTADIENE



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T_1 and T_2 decoupled from T_3

t_3 misses some dynamical correlations

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

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

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

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

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

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moments of CC/EOMCC equations

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

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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)

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CC(t;3)

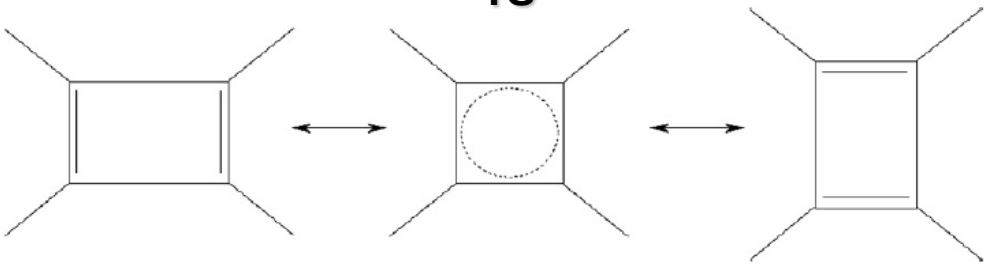
- P space: singles, doubles, and a subset of triples and quadruples defined via active orbitals, as in CCSDtq
- Q space: remaining triples and quadruples not captured by CCSDtq

CC(t,q;3,4)

AUTOMERIZATION OF CYCLOBUTADIENE

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

TS



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	Reactant	TS
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CCSD	26.827	47.979
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CCSDt(I)	20.786	20.274
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CC(t;3)(I)	-0.137	0.071

Barrier heights (in kcal/mol) →

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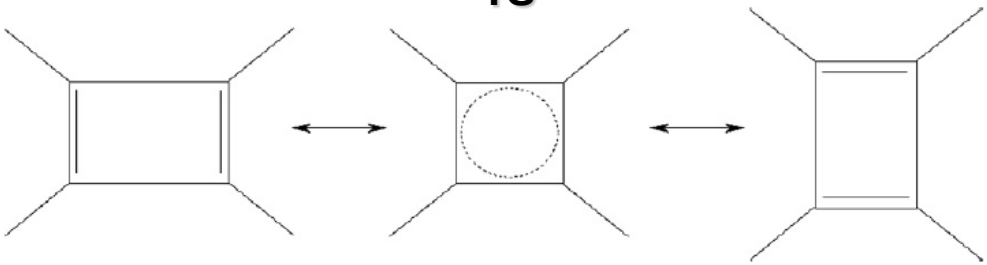

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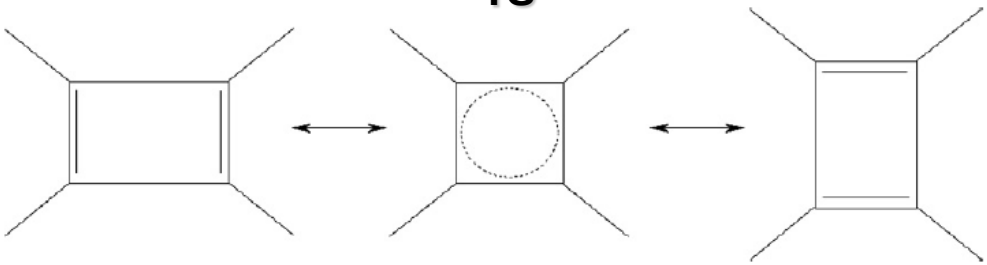

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[J. Shen and P. Piecuch, *J. Chem. Phys*. 136, 144104 (2012)]

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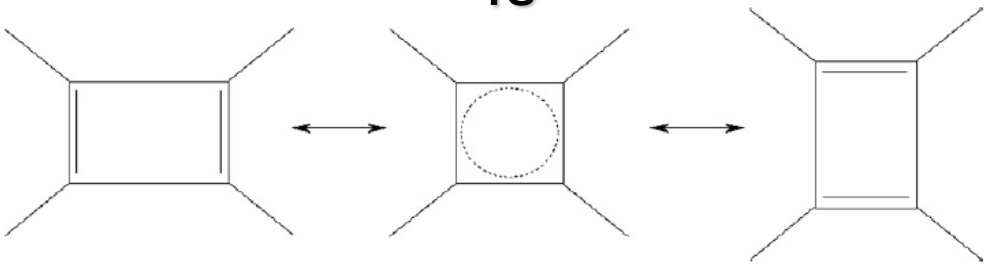

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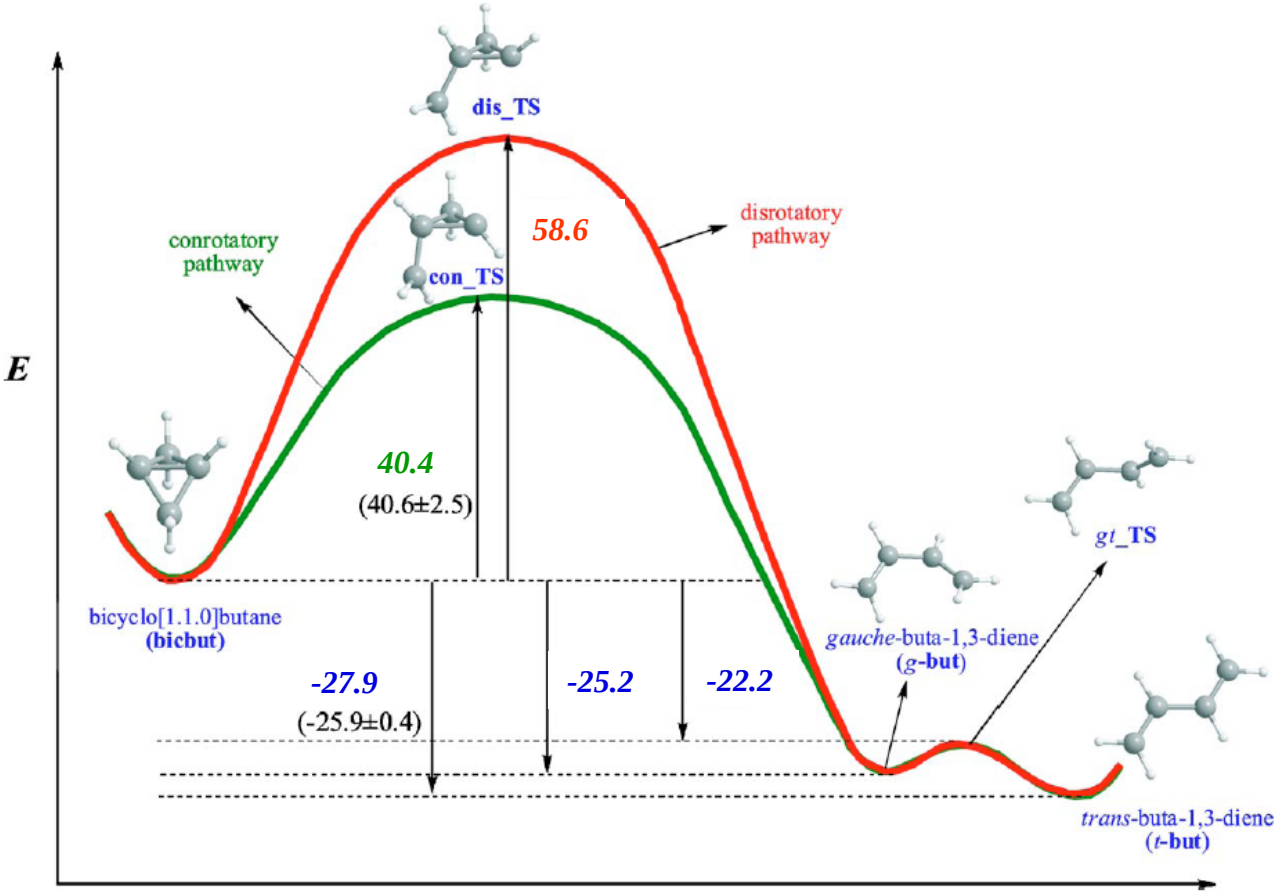
The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]-butane to Butadiene (enthalpies at 0 K in kcal/mol)

	con_TS	dis_TS	g-but	gt_TS	t-but



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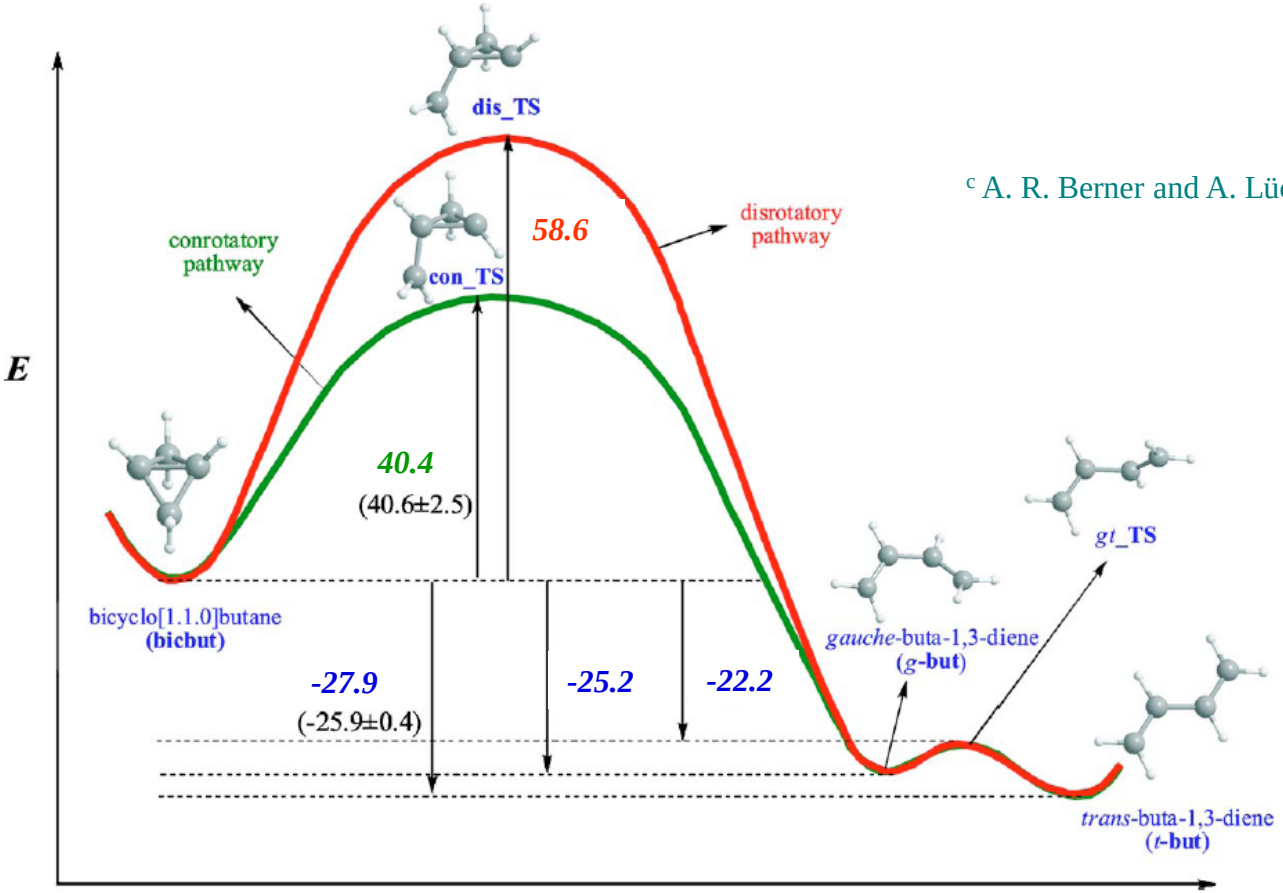

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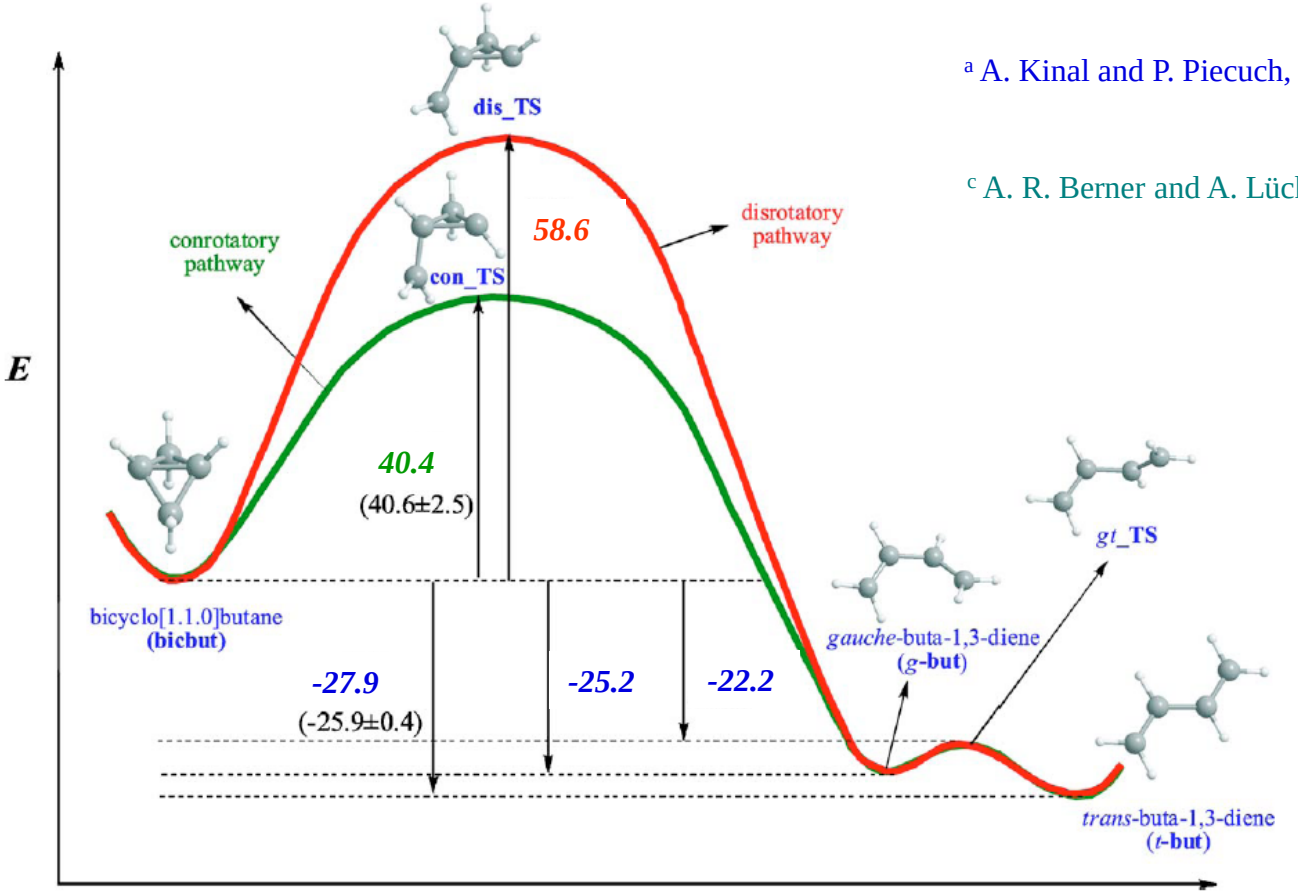

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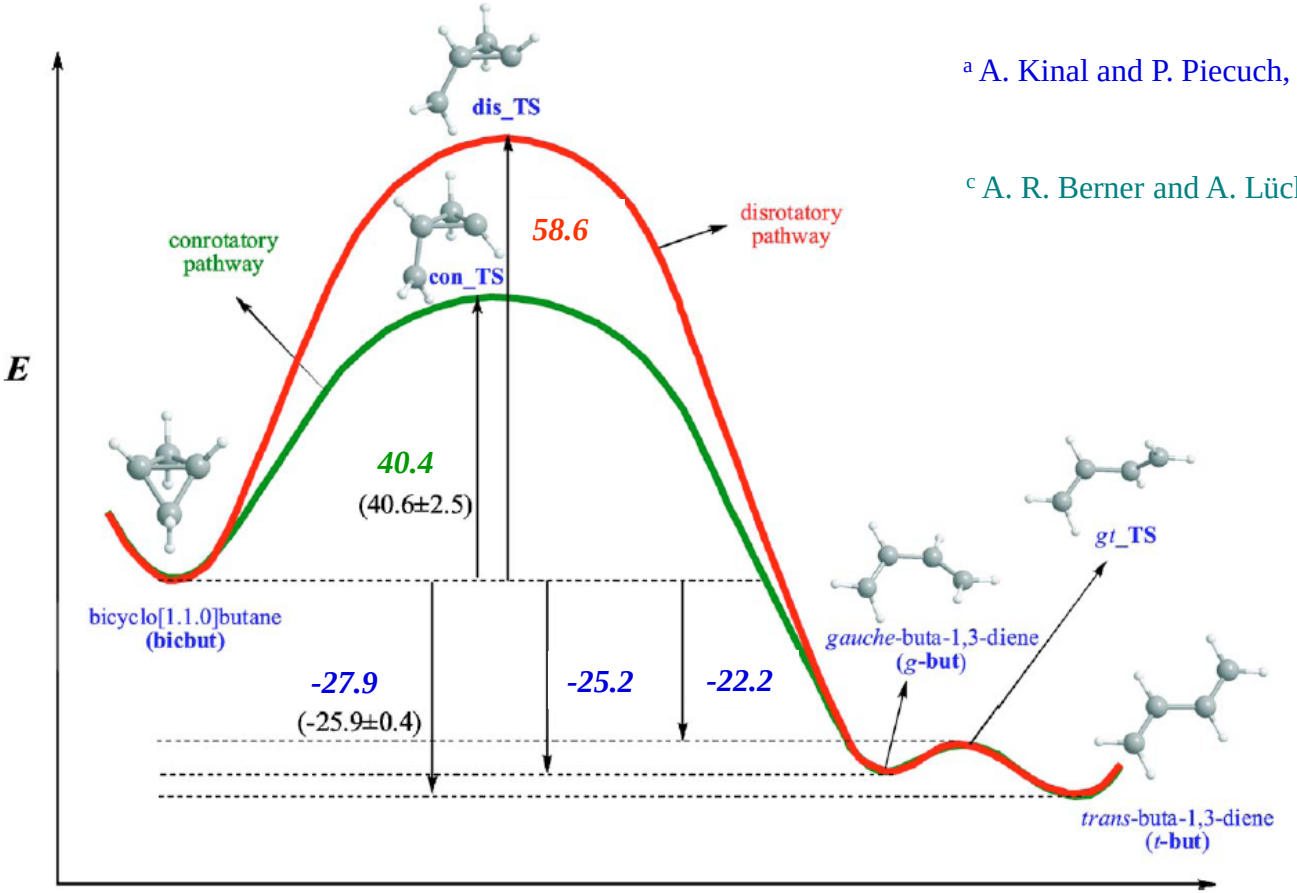

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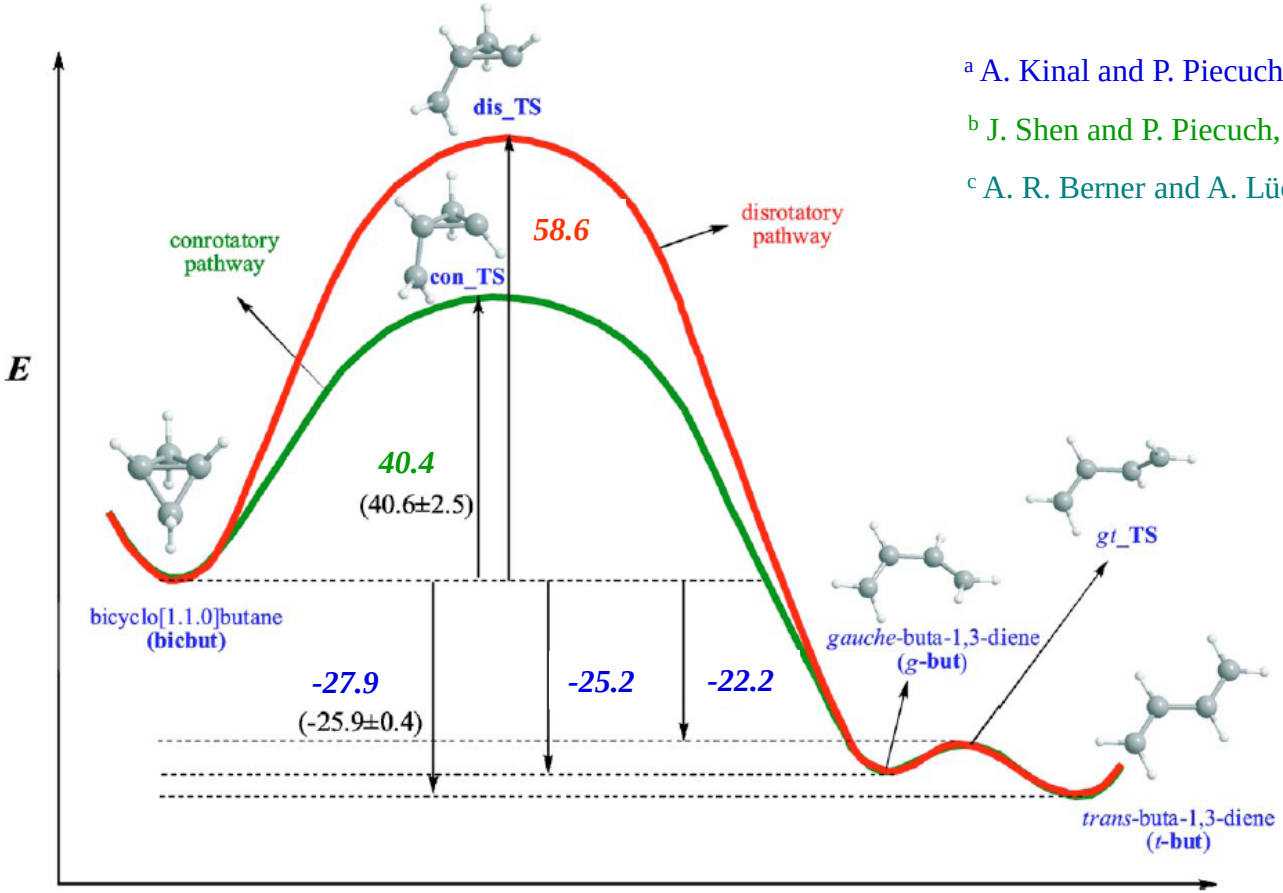

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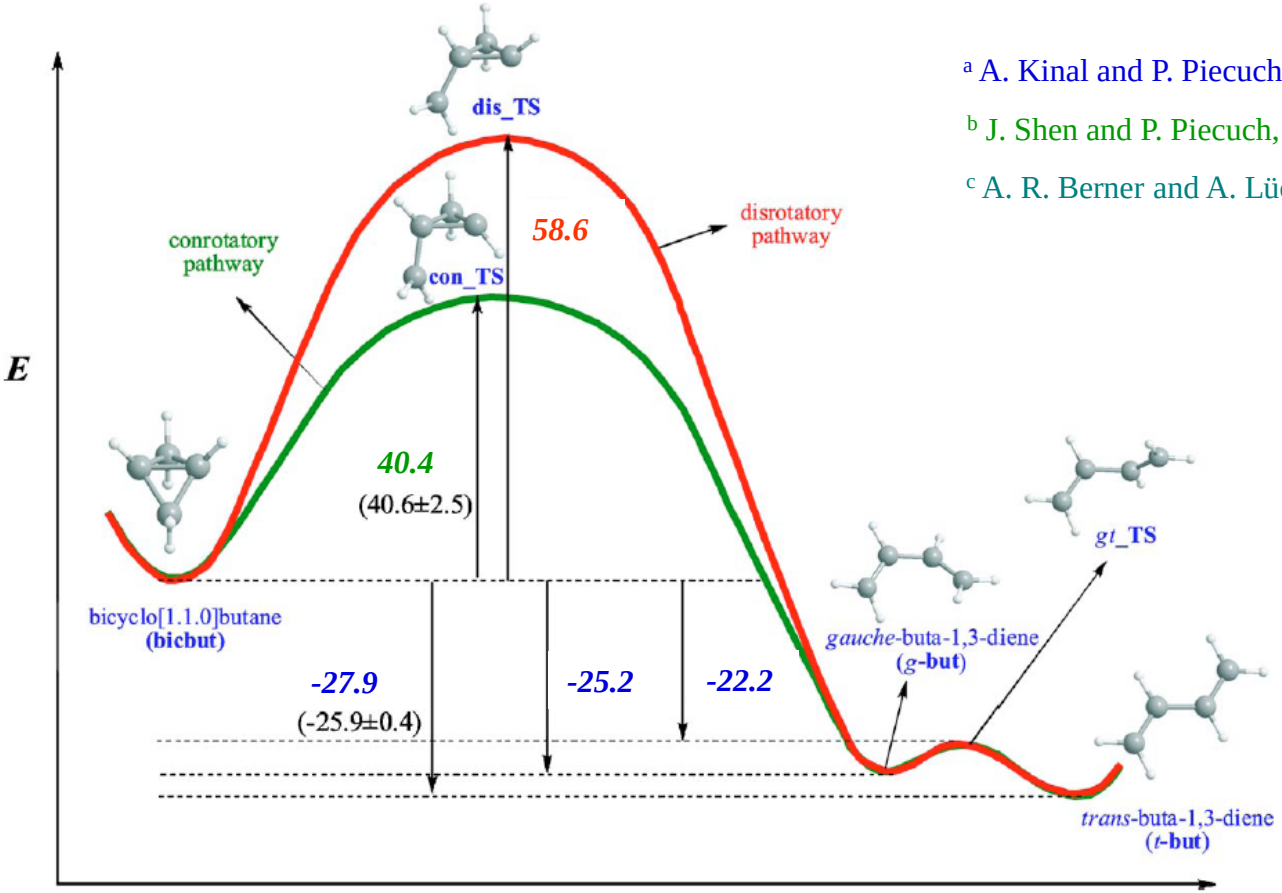

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The CC(t;3), CC(t,q;3), CC(t,q;3,4), etc. hierarchy works well, but it requires choosing <u>user- and system-dependent</u> active orbitals to select the dominant T_n and R_n components with $n > 2$ prior to the determination of CC(P;Q) corrections,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

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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)]

Jorge Emiliano Deustua

Dr. Jun Shen

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)]
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CC MONTE CARLO (CCMC)

PRL **105,** 263004 (2010) PHYSICAL REVIEW LETTERS week ending 31 DECEMBER 2010

Stochastic Coupled Cluster Theory

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(Received 14 September 2010; published 28 December 2010)

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

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

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

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

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

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WALKER POPULATION DYNAMICS

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

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birth and death

spawning

$$c_K(\tau + \Delta\tau) = [1 - (H_{KK} - S)\Delta\tau]c_K(\tau)$$

$$c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

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.

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 & |\Phi_{S_2}\rangle & |\Phi_{D_2}\rangle & |\Phi_{T_2}\rangle & |\Phi_{Q_2}\rangle & |\Phi_{P_2}\rangle & \cdots \\
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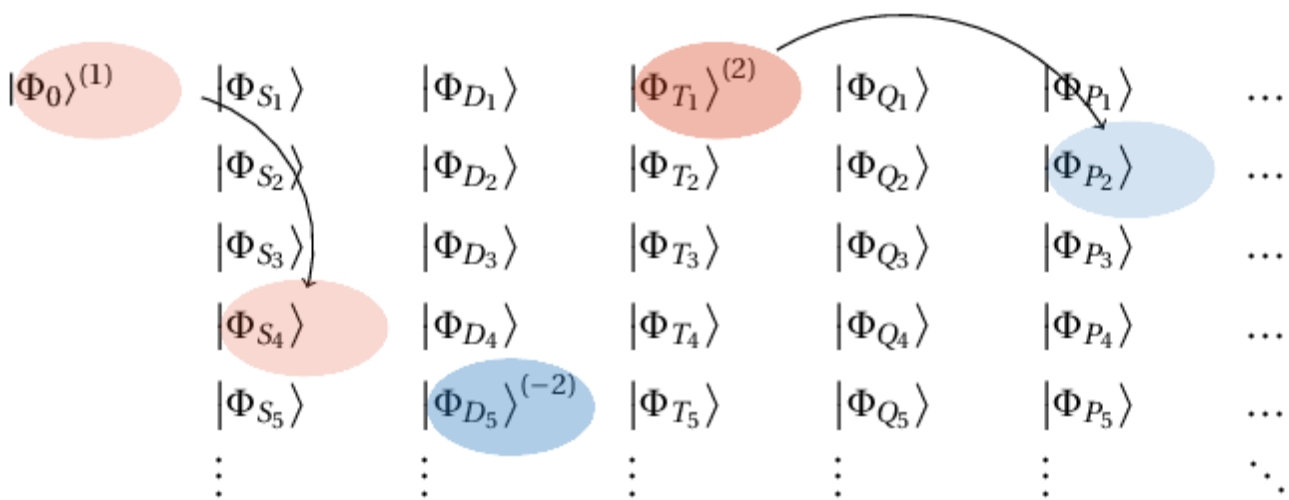

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$$c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

$\lvert\Phi_0\rangle^{(1)}$	$\lvert\Phi_{S_1}\rangle$	$\lvert\Phi_{D_1}\rangle$	$\lvert\Phi_{T_1}\rangle^{(2)}$	$\lvert\Phi_{Q_1}\rangle$	$\lvert\Phi_{P_1}\rangle$	$\cdots$
	$\lvert\Phi_{S_2}\rangle$	$\lvert\Phi_{D_2}\rangle$	$\lvert\Phi_{T_2}\rangle$	$\lvert\Phi_{Q_2}\rangle$	$\lvert\Phi_{P_2}\rangle^{(-1)}$	$\cdots$
	$\lvert\Phi_{S_3}\rangle$	$\lvert\Phi_{D_3}\rangle$	$\lvert\Phi_{T_3}\rangle$	$\lvert\Phi_{Q_3}\rangle$	$\lvert\Phi_{P_3}\rangle$	$\cdots$
	$\lvert\Phi_{S_4}\rangle^{(1)}$	$\lvert\Phi_{D_4}\rangle$	$\lvert\Phi_{T_4}\rangle$	$\lvert\Phi_{Q_4}\rangle$	$\lvert\Phi_{P_4}\rangle$	$\cdots$
	$\lvert\Phi_{S_5}\rangle$	$\lvert\Phi_{D_5}\rangle^{(-2)}$	$\lvert\Phi_{T_5}\rangle$	$\lvert\Phi_{Q_5}\rangle$	$\lvert\Phi_{P_5}\rangle$	$\cdots$
	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$

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

WALKER POPULATION DYNAMICS

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birth and death

spawning

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	$\lvert\Phi_{S_2}\rangle$	$\lvert\Phi_{D_2}\rangle$	$\lvert\Phi_{T_2}\rangle$	$\lvert\Phi_{Q_2}\rangle$	$\lvert\Phi_{P_2}\rangle^{(-1)}$	$\cdots$
	$\lvert\Phi_{S_3}\rangle$	$\lvert\Phi_{D_3}\rangle$	$\lvert\Phi_{T_3}\rangle$	$\lvert\Phi_{Q_3}\rangle$	$\lvert\Phi_{P_3}\rangle$	$\cdots$
	$\lvert\Phi_{S_4}\rangle^{(1)}$	$\lvert\Phi_{D_4}\rangle$	$\lvert\Phi_{T_4}\rangle$	$\lvert\Phi_{Q_4}\rangle$	$\lvert\Phi_{P_4}\rangle$	$\cdots$
	$\lvert\Phi_{S_5}\rangle$	$\lvert\Phi_{D_5}\rangle^{(-3)}$	$\lvert\Phi_{T_5}\rangle$	$\lvert\Phi_{Q_5}\rangle$	$\lvert\Phi_{P_5}\rangle$	$\cdots$
	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$

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$\lvert\Phi_0\rangle^{(1)}$	$\lvert\Phi_{S_1}\rangle$	$\lvert\Phi_{D_1}\rangle$	$\lvert\Phi_{T_1}\rangle^{(3)}$	$\lvert\Phi_{Q_1}\rangle$	$\lvert\Phi_{P_1}\rangle$	$\cdots$
	$\lvert\Phi_{S_2}\rangle^{(-1)}$	$\lvert\Phi_{D_2}\rangle$	$\lvert\Phi_{T_2}\rangle$	$\lvert\Phi_{Q_2}\rangle$	$\lvert\Phi_{P_2}\rangle^{(-1)}$	$\cdots$
	$\lvert\Phi_{S_3}\rangle$	$\lvert\Phi_{D_3}\rangle$	$\lvert\Phi_{T_3}\rangle$	$\lvert\Phi_{Q_3}\rangle$	$\lvert\Phi_{P_3}\rangle$	$\cdots$
	$\lvert\Phi_{S_4}\rangle^{(1)}$	$\lvert\Phi_{D_4}\rangle$	$\lvert\Phi_{T_4}\rangle$	$\lvert\Phi_{Q_4}\rangle$	$\lvert\Phi_{P_4}\rangle^{(2)}$	$\cdots$
	$\lvert\Phi_{S_5}\rangle$	$\lvert\Phi_{D_5}\rangle^{(-3)}$	$\lvert\Phi_{T_5}\rangle$	$\lvert\Phi_{Q_5}\rangle$	$\lvert\Phi_{P_5}\rangle$	$\cdots$
	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$

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$\lvert\Phi_0\rangle^{(1)}$	$\lvert\Phi_{S_1}\rangle$	$\lvert\Phi_{D_1}\rangle$	$\lvert\Phi_{T_1}\rangle^{(4)}$	$\lvert\Phi_{Q_1}\rangle$	$\lvert\Phi_{P_1}\rangle$	$\cdots$
	$\lvert\Phi_{S_2}\rangle^{(-1)}$	$\lvert\Phi_{D_2}\rangle$	$\lvert\Phi_{T_2}\rangle$	$\lvert\Phi_{Q_2}\rangle$	$\lvert\Phi_{P_2}\rangle^{(-1)}$	$\cdots$
	$\lvert\Phi_{S_3}\rangle$	$\lvert\Phi_{D_3}\rangle$	$\lvert\Phi_{T_3}\rangle$	$\lvert\Phi_{Q_3}\rangle$	$\lvert\Phi_{P_3}\rangle$	$\cdots$
	$\lvert\Phi_{S_4}\rangle^{(1)}$	$\lvert\Phi_{D_4}\rangle$	$\lvert\Phi_{T_4}\rangle$	$\lvert\Phi_{Q_4}\rangle$	$\lvert\Phi_{P_4}\rangle^{(2)}$	$\cdots$
	$\lvert\Phi_{S_5}\rangle$	$\lvert\Phi_{D_5}\rangle^{(-2)}$	$\lvert\Phi_{T_5}\rangle$	$\lvert\Phi_{Q_5}\rangle$	$\lvert\Phi_{P_5}\rangle$	$\cdots$
	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$

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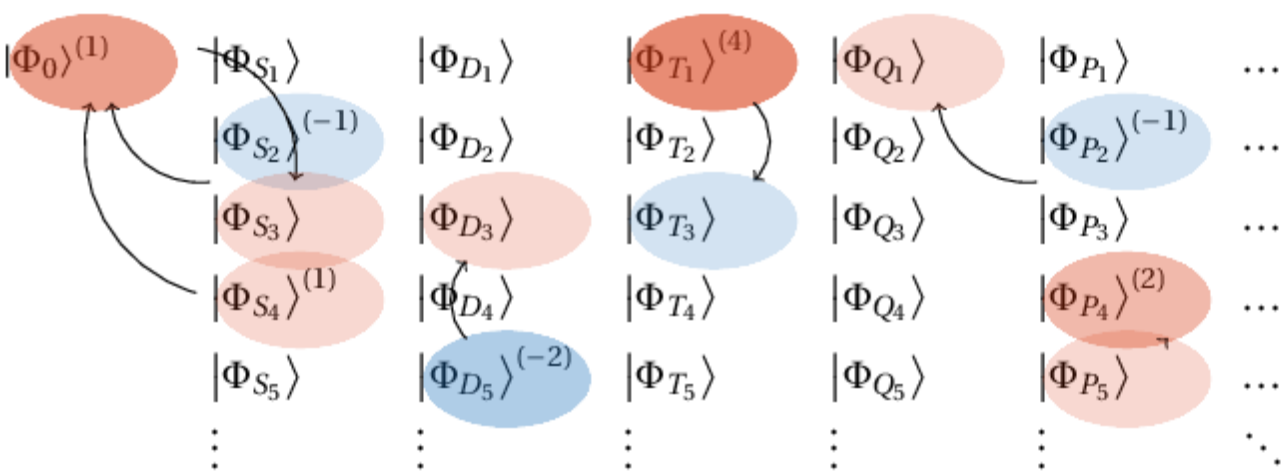

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$\lvert\Phi_0\rangle^{(4)}$	$\lvert\Phi_{S_1}\rangle$	$\lvert\Phi_{D_1}\rangle$	$\lvert\Phi_{T_1}\rangle^{(4)}$	$\lvert\Phi_{Q_1}\rangle^{(2)}$	$\lvert\Phi_{P_1}\rangle$	$\cdots$
	$\lvert\Phi_{S_2}\rangle^{(-2)}$	$\lvert\Phi_{D_2}\rangle$	$\lvert\Phi_{T_2}\rangle$	$\lvert\Phi_{Q_2}\rangle$	$\lvert\Phi_{P_2}\rangle$	$\cdots$
	$\lvert\Phi_{S_3}\rangle$	$\lvert\Phi_{D_3}\rangle^{(0)}$	$\lvert\Phi_{T_3}\rangle^{(-1)}$	$\lvert\Phi_{Q_3}\rangle$	$\lvert\Phi_{P_3}\rangle$	$\cdots$
	$\lvert\Phi_{S_4}\rangle^{(2)}$	$\lvert\Phi_{D_4}\rangle$	$\lvert\Phi_{T_4}\rangle$	$\lvert\Phi_{Q_4}\rangle$	$\lvert\Phi_{P_4}\rangle^{(2)}$	$\cdots$
	$\lvert\Phi_{S_5}\rangle$	$\lvert\Phi_{D_5}\rangle^{(-2)}$	$\lvert\Phi_{T_5}\rangle$	$\lvert\Phi_{Q_5}\rangle$	$\lvert\Phi_{P_5}\rangle^{(2)}$	$\cdots$
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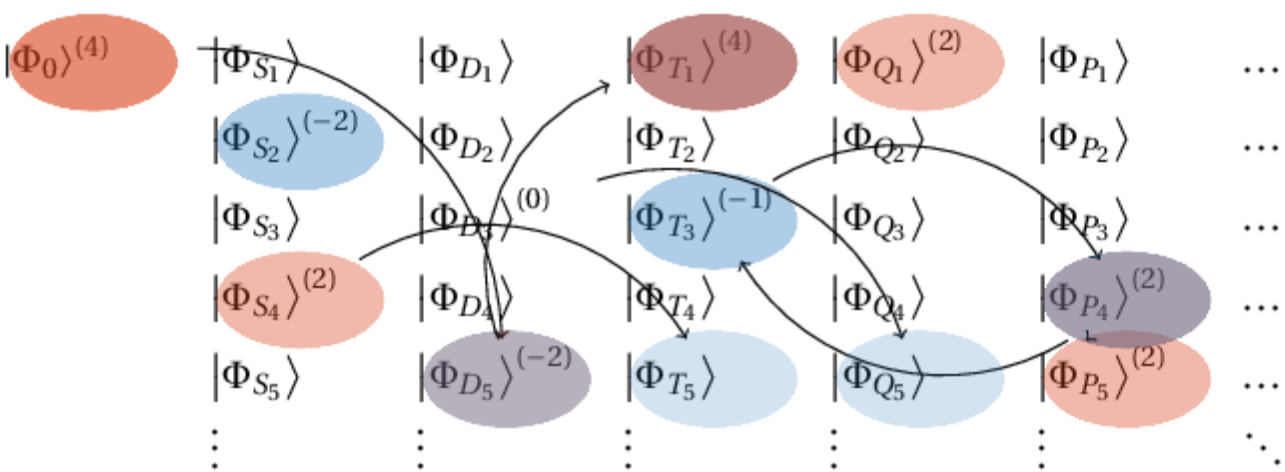

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	$\lvert\Phi_{S_2}\rangle^{(-2)}$	$\lvert\Phi_{D_2}\rangle$	$\lvert\Phi_{T_2}\rangle$	$\lvert\Phi_{Q_2}\rangle$	$\lvert\Phi_{P_2}\rangle$	$\cdots$
	$\lvert\Phi_{S_3}\rangle$	$\lvert\Phi_{D_3}\rangle$	$\lvert\Phi_{T_3}\rangle^{(-2)}$	$\lvert\Phi_{Q_3}\rangle$	$\lvert\Phi_{P_3}\rangle$	$\cdots$
	$\lvert\Phi_{S_4}\rangle^{(2)}$	$\lvert\Phi_{D_4}\rangle$	$\lvert\Phi_{T_4}\rangle$	$\lvert\Phi_{Q_4}\rangle$	$\lvert\Phi_{P_4}\rangle$	$\cdots$
	$\lvert\Phi_{S_5}\rangle$	$\lvert\Phi_{D_5}\rangle^{(-1)}$	$\lvert\Phi_{T_5}\rangle^{(-1)}$	$\lvert\Phi_{Q_5}\rangle^{(-1)}$	$\lvert\Phi_{P_5}\rangle^{(2)}$	$\cdots$
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$\lvert\Phi_0\rangle^{(5)}$	$\lvert\Phi_{S_1}\rangle$	$\lvert\Phi_{D_1}\rangle$	$\lvert\Phi_{T_1}\rangle^{(2)}$	$\lvert\Phi_{Q_1}\rangle^{(3)}$	$\lvert\Phi_{P_1}\rangle$	$\cdots$
	$\lvert\Phi_{S_2}\rangle^{(-3)}$	$\lvert\Phi_{D_2}\rangle$	$\lvert\Phi_{T_2}\rangle$	$\lvert\Phi_{Q_2}\rangle$	$\lvert\Phi_{P_2}\rangle$	$\cdots$
	$\lvert\Phi_{S_3}\rangle$	$\lvert\Phi_{D_3}\rangle$	$\lvert\Phi_{T_3}\rangle^{(-1)}$	$\lvert\Phi_{Q_3}\rangle$	$\lvert\Phi_{P_3}\rangle$	$\cdots$
	$\lvert\Phi_{S_4}\rangle^{(1)}$	$\lvert\Phi_{D_4}\rangle$	$\lvert\Phi_{T_4}\rangle$	$\lvert\Phi_{Q_4}\rangle$	$\lvert\Phi_{P_4}\rangle$	$\cdots$
	$\lvert\Phi_{S_5}\rangle$	$\lvert\Phi_{D_5}\rangle^{(-1)}$	$\lvert\Phi_{T_5}\rangle^{(-2)}$	$\lvert\Phi_{Q_5}\rangle^{(-1)}$	$\lvert\Phi_{P_5}\rangle^{(2)}$	$\cdots$
	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\ddots$

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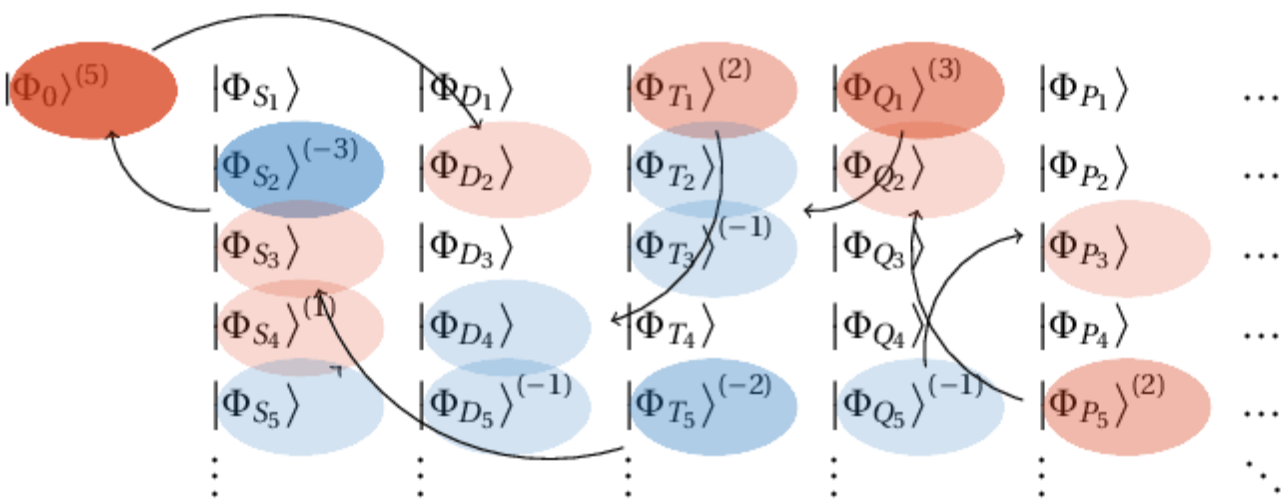

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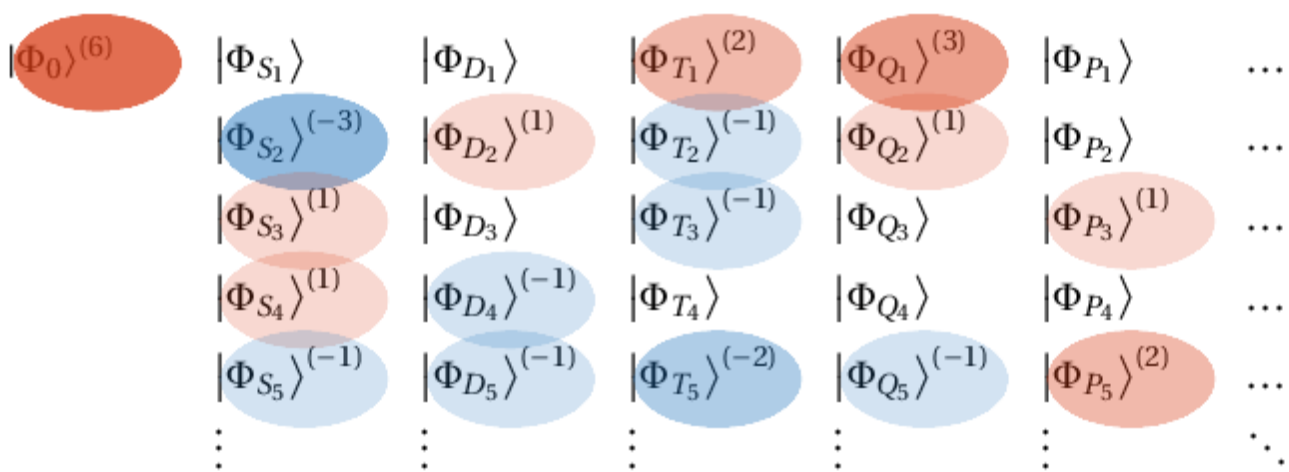

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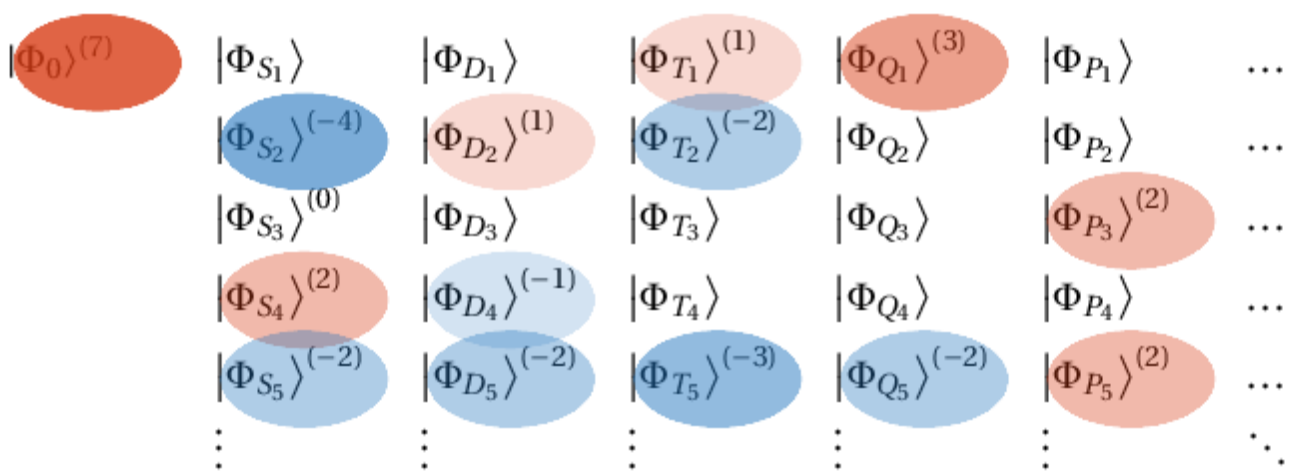

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CCMC (CCSDT-MC, CCSDTQ-MC, etc.)

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/excip population exceeding a preset value n_a are allowed to spawn new walkers onto empty determinants/excitors. One can start *i*-CIQMC and *i*-CCMC simulations by placing a certain, sufficiently large, number of walkers/excips 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)]
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THE JOURNAL OF CHEMICAL PHYSICS **144**, 084108 (2016)

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

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[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*

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

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

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.

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

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.

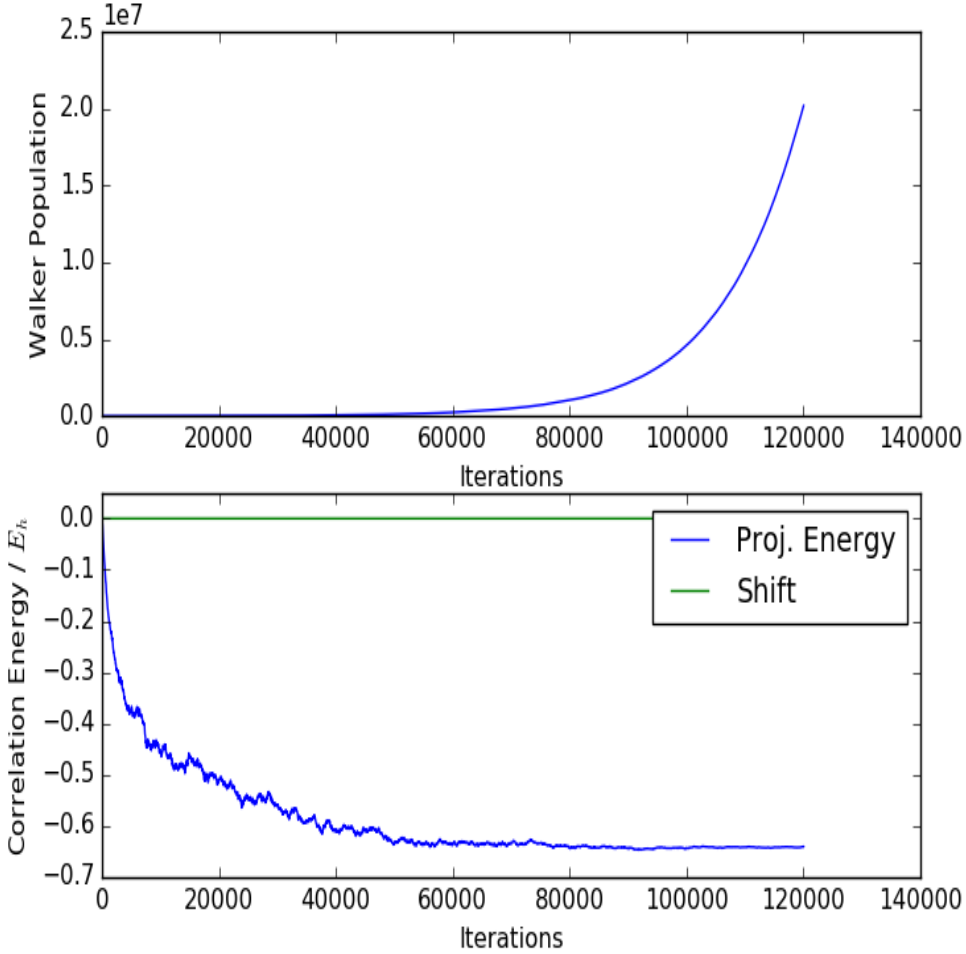
2. Extract a list of the most important determinants or cluster amplitude types relevant to the CC theory of interest (triples for CCSDT; triples and quadruples for CCSDTQ, etc.) from the CIQMC or CCMC propagation at a given time τ to define the *P* space for CC(*P*) calculations as follows:

- **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.**

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

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

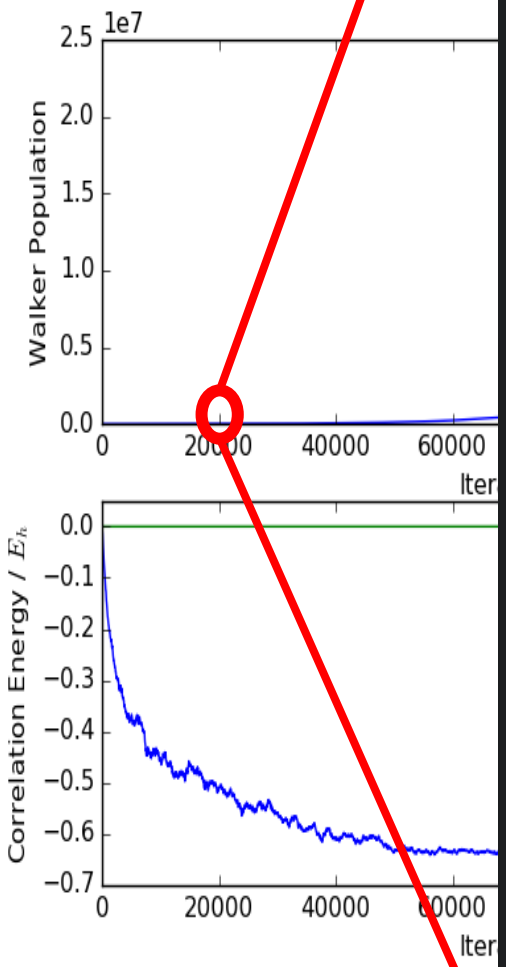
F_2 /cc-pVDZ, $R = 2\ R_e$, *i*-FCIQMC



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

Developing a Stochas

F_2 /cc-pVDZ, R =



[J.E. Deustua, J. Shen, and P. Piecuch

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3	-10	3	4	5	6	7	8	9	10	11	12	13	14	15	16
4	1	2	3	4	5	6	7	8	9	10	11	12	13	14	17
5	1	1	2	3	4	7	8	9	10	11	12	14	15	16	17
6	-1	2	3	5	6	7	8	9	10	11	12	13	14	15	18
7	3	1	4	5	6	7	8	9	10	11	12	13	14	15	18
8	-3	1	2	3	4	5	6	7	8	9	10	11	12	17	18
9	1	1	5	6	7	8	9	10	11	12	14	15	16	17	18
10	1	1	2	4	6	7	8	9	10	11	12	13	14	15	19
11	-1	1	2	3	4	6	7	8	9	10	11	12	15	16	19
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:set nonu

Developing a Stochas

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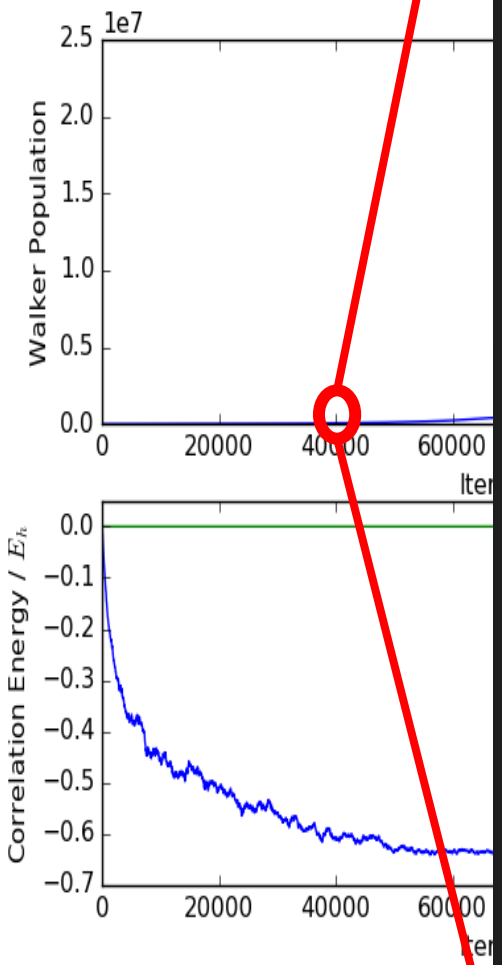

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NORMAL walkers-0 unix 〈 utf-8 〈 no ft 0% 50063:9

[J.E. Deustua, J. Shen, and P. Piecuc

ochastic CC(*P*;*Q*) Approach

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

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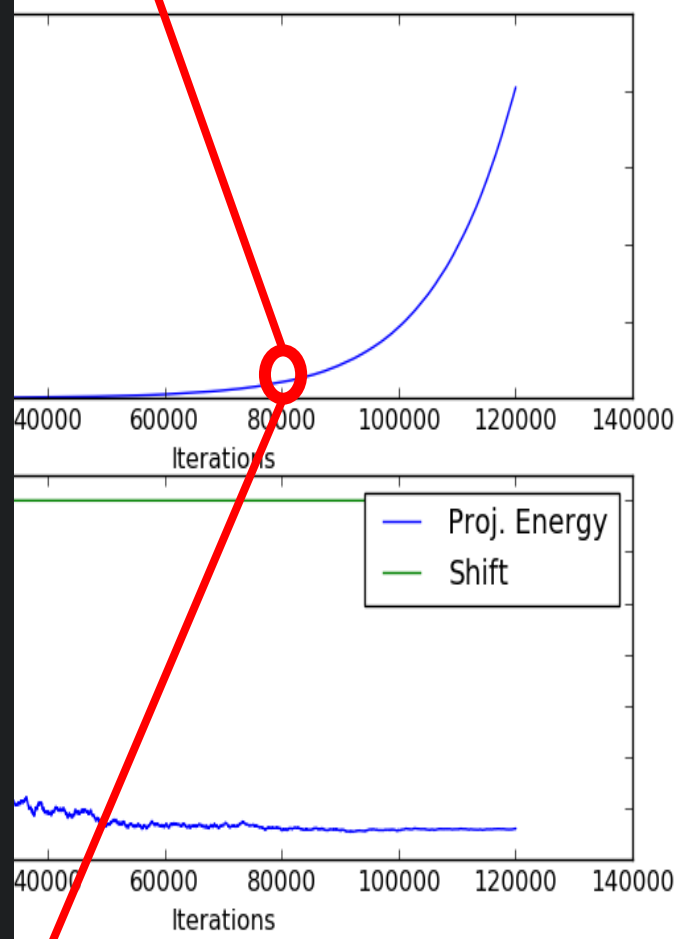
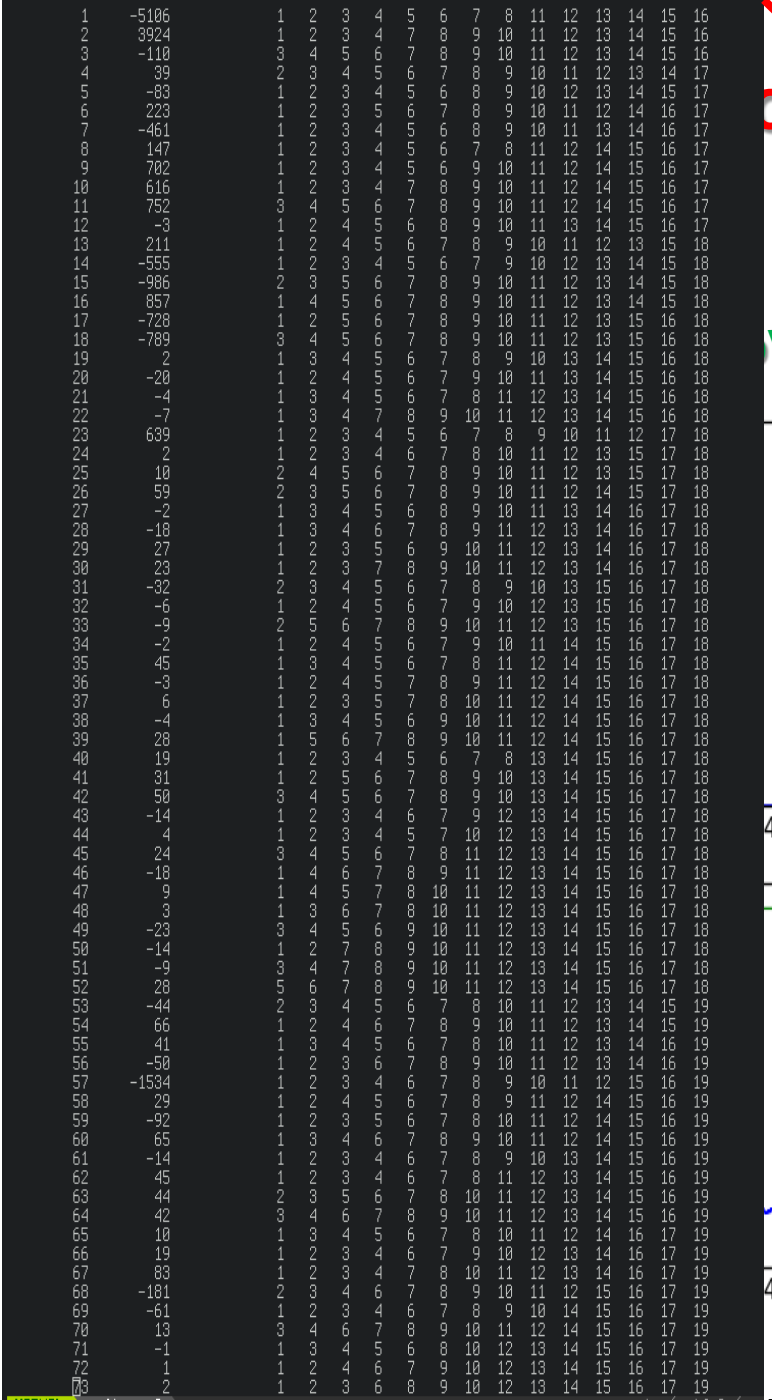


[and P. Piecuch, Phys. Rev. Lett. 119, 223003 (2017)]

ochastic CC(*P*;*Q*) Approach

VDZ, $R = 2\ R_e$, *I*-FCIQMC



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18	-789	3	4	5	6	7	8	9	10	11	12	13	15	16	18
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20	-20	1	2	4	5	6	7	9	10	11	13	14	15	16	18
21	-4	1	3	4	5	6	7	8	11	12	13	14	15	16	18
22	-7	1	3	4	7	8	9	10	11	12	13	14	15	16	18
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24	2	1	2	3	4	6	7	8	10	11	12	13	15	17	18
25	10	2	4	5	6	7	8	9	10	11	12	13	15	17	18
26	59	2	3	5	6	7	8	9	10	11	12	14	15	17	18
27	-2	1	3	4	5	6	8	9	10	11	13	14	16	17	18
28	-18	1	3	4	6	7	8	9	11	12	13	14	16	17	18
29	27	1	2	3	5	6	9	10	11	12	13	14	16	17	18
30	23	1	2	3	7	8	9	10	11	12	13	14	16	17	18
31	-32	2	3	4	5	6	7	8	9	10	13	15	16	17	18
32	-6	1	2	4	5	6	7	9	10	12	13	15	16	17	18
33	-9	2	5	6	7	8	9	10	11	12	13	15	16	17	18
34	-2	1	2	4	5	6	7	9	10	11	14	15	16	17	18
35	45	1	3	4	5	6	7	8	11	12	14	15	16	17	18
36	-3	1	2	4	5	7	8	9	11	12	14	15	16	17	18
37	6	1	2	3	5	7	8	10	11	12	14	15	16	17	18
38	-4	1	3	4	5	6	9	10	11	12	14	15	16	17	18
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40	19	1	2	3	4	5	6	7	8	13	14	15	16	17	18
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42	50	3	4	5	6	7	8	9	10	13	14	15	16	17	18
43	-14	1	2	3	4	6	7	9	12	13	14	15	16	17	18
44	4	1	2	3	4	5	7	10	12	13	14	15	16	17	18
45	24	3	4	5	6	7	8	11	12	13	14	15	16	17	18
46	-18	1	4	6	7	8	9	11	12	13	14	15	16	17	18
47	9	1	4	5	7	8	10	11	12	13	14	15	16	17	18
48	3	1	3	6	7	8	10	11	12	13	14	15	16	17	18
49	-23	3	4	5	6	9	10	11	12	13	14	15	16	17	18
50	-14	1	2	7	8	9	10	11	12	13	14	15	16	17	18
51	-9	3	4	7	8	9	10	11	12	13	14	15	16	17	18
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54	66	1	2	4	6	7	8	9	10	11	12	13	14	15	19
55	41	1	3	4	5	6	7	8	10	11	12	13	14	16	19
56	-50	1	2	3	6	7	8	9	10	11	12	13	14	16	19
57	-1534	1	2	3	4	6	7	8	9	10	11	12	15	16	19
58	29	1	2	4	5	6	7	8	9	11	12	14	15	16	19
59	-92	1	2	3	5	6	7	8	10	11	12	14	15	16	19
60	65	1	3	4	6	7	8	9	10	11	12	14	15	16	19
61	-14	1	2	3	4	6	7	8	9	10	13	14	15	16	19
62	45	1	2	3	4	6	7	8	11	12	13	14	15	16	19
63	44	2	3	5	6	7	8	10	11	12	13	14	15	16	19
64	42	3	4	6	7	8	9	10	11	12	13	14	15	16	19
65	10	1	3	4	5	6	7	8	10	11	12	14	16	17	19
66	19	1	2	3	4	6	7	9	10	12	13	14	16	17	19
67	83	1	2	3	4	7	8	10	11	12	13	14	16	17	19
68	-181	2	3	4	6	7	8	9	10	11	12	15	16	17	19
69	-61	1	2	3	4	6	7	8	9	10	14	15	16	17	19
70	13	3	4	6	7	8	9	10	11	12	14	15	16	17	19
71	-1	1	3	4	5	6	8	10	12	13	14	15	16	17	19
72	1	1	2	4	6	7	9	10	12	13	14	15	16	17	19
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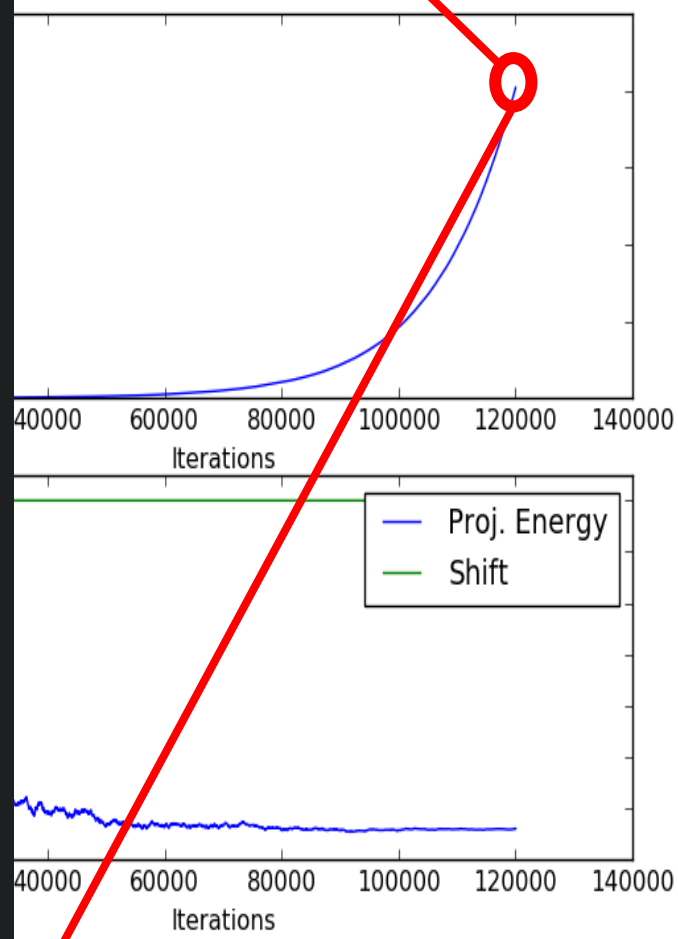

nd P. Piecuch, Phys. Rev. Lett. 119, 223003 (2017)]

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

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3. Solve the CC(*P*) equations.

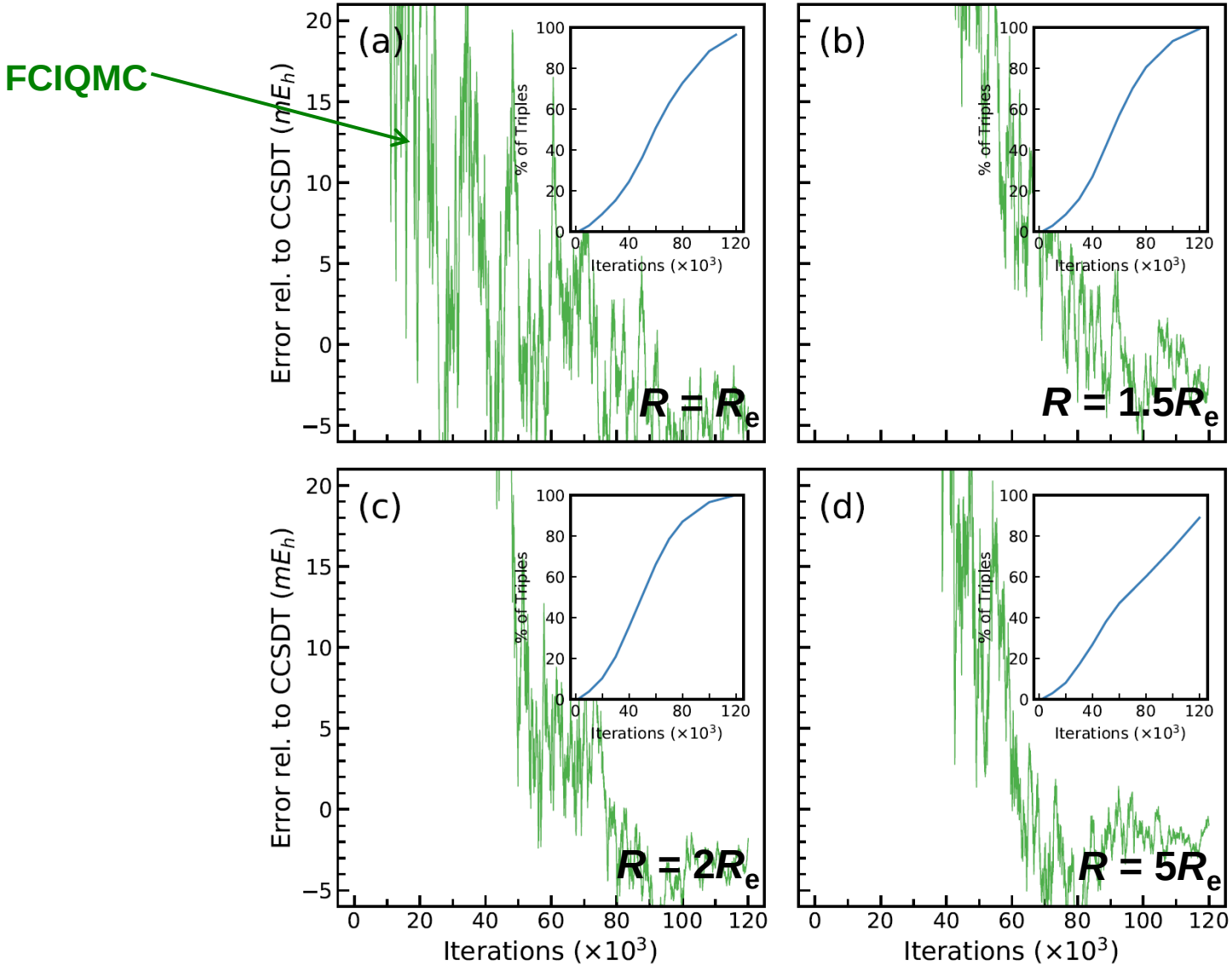
- **if the target approach is CCSDT, use** $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})}$
- **if the target approach is CCSDTQ, use** $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})} + T_4^{(\mathrm{MC})}$

  etc.

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

RECOVERING CCSDT ENERGETICS FOR F_2/cc-pVDZ

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



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

RECOVERING CCSDT ENERGETICS FOR F_2/cc-pVDZ

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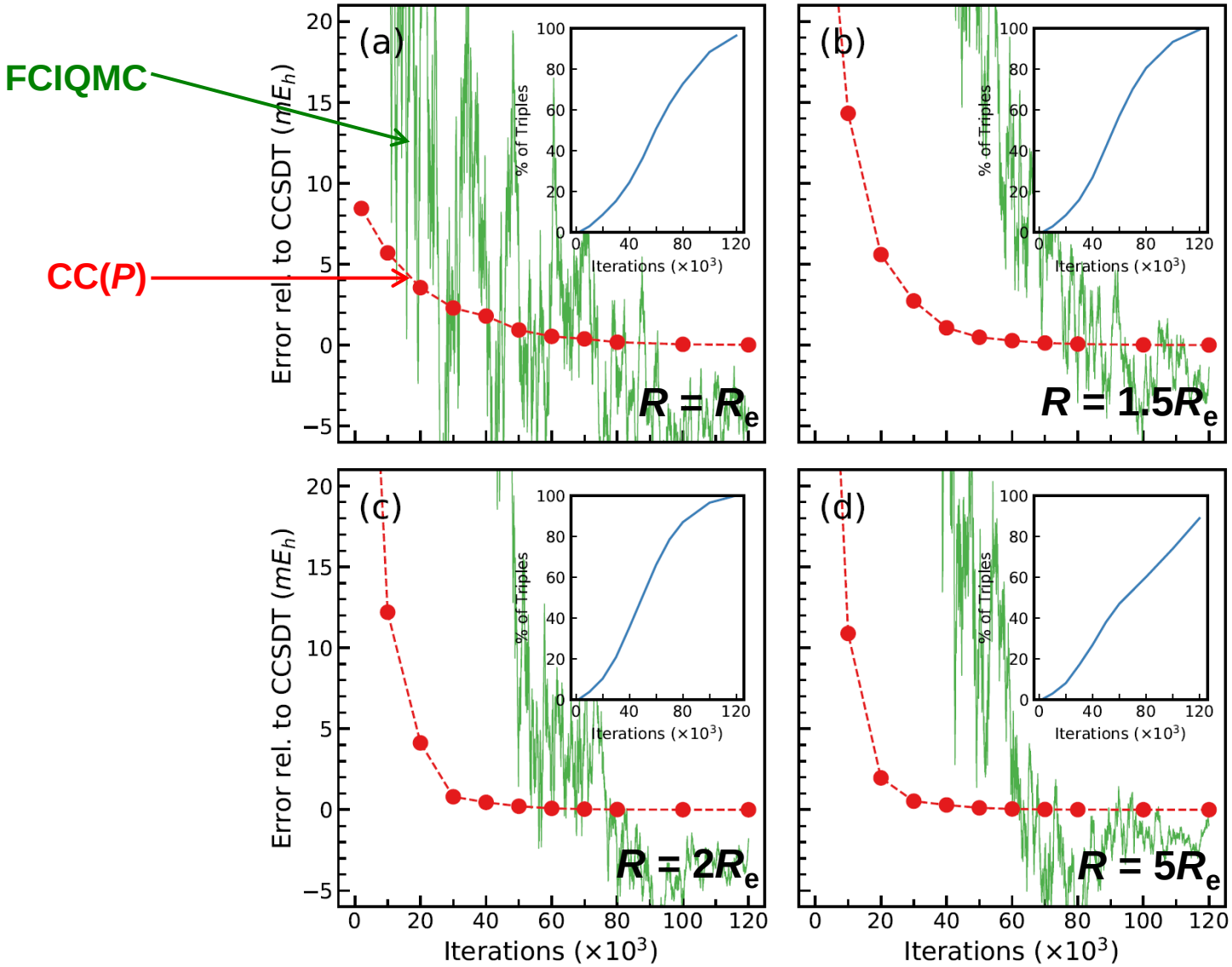

[J.E. Deustua, J. Shen, and P. Piecuch, Phys. Rev. Lett. 119, 223003 (2017)]

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

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3. Solve the CC(*P*) equations.

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

  etc.

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

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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.

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3. Solve the CC(*P*) equations.

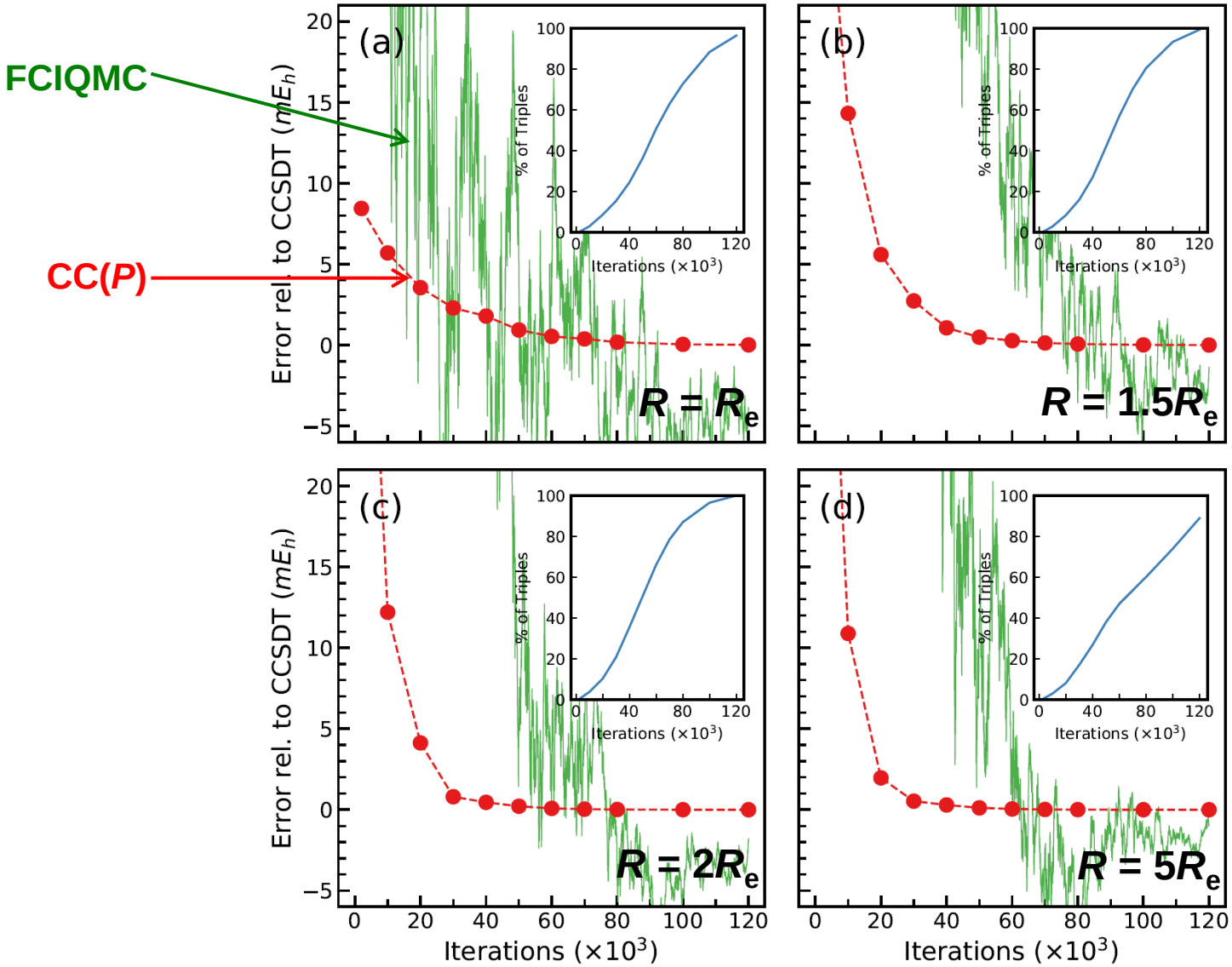
- **if the target approach is CCSDT, use** $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})}$
- **if the target approach is CCSDTQ, use** $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})} + T_4^{(\mathrm{MC})}$
  etc.

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 δ(*P*;*Q*).

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

RECOVERING CCSDT ENERGETICS FOR F_2/cc-pVDZ

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



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

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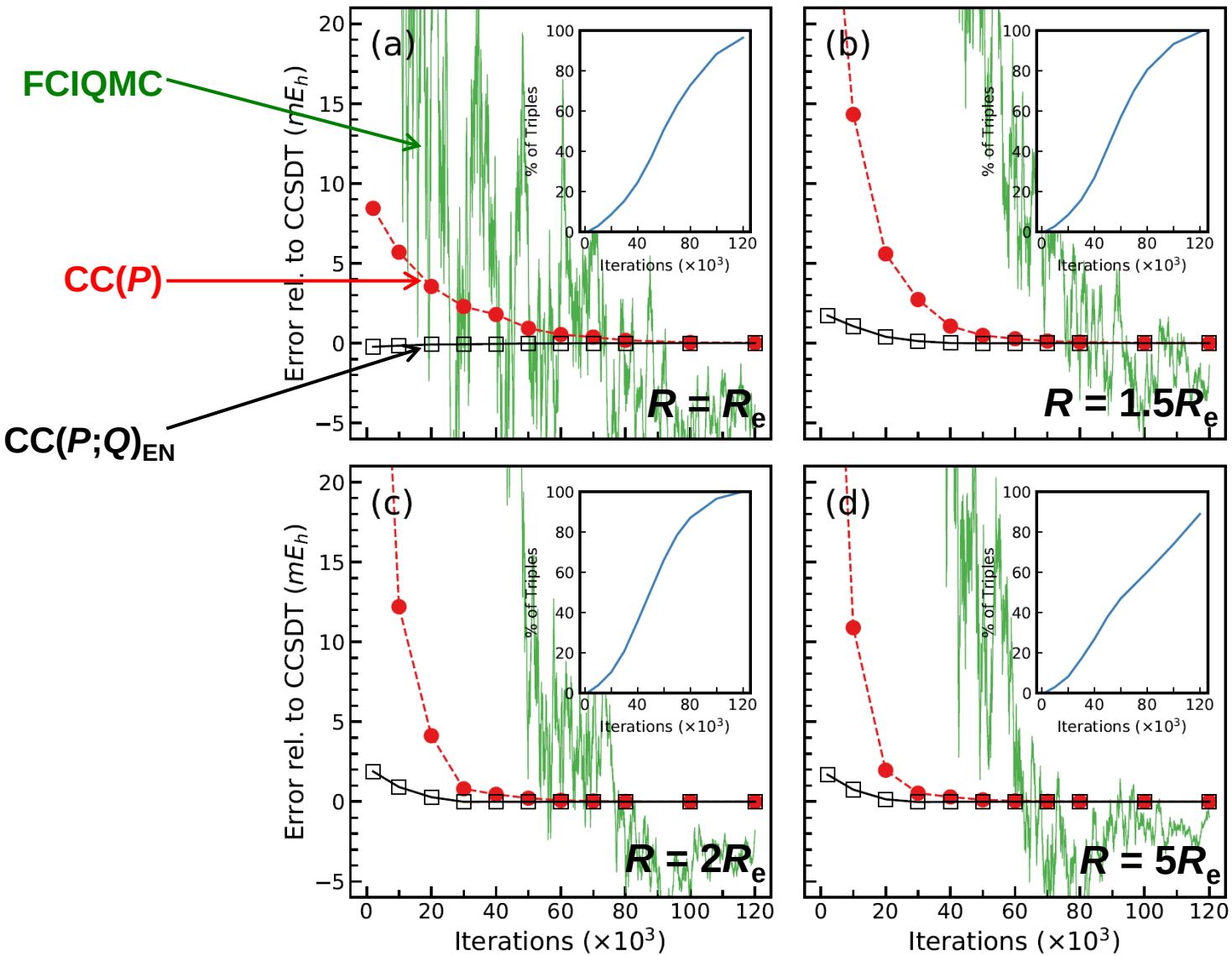
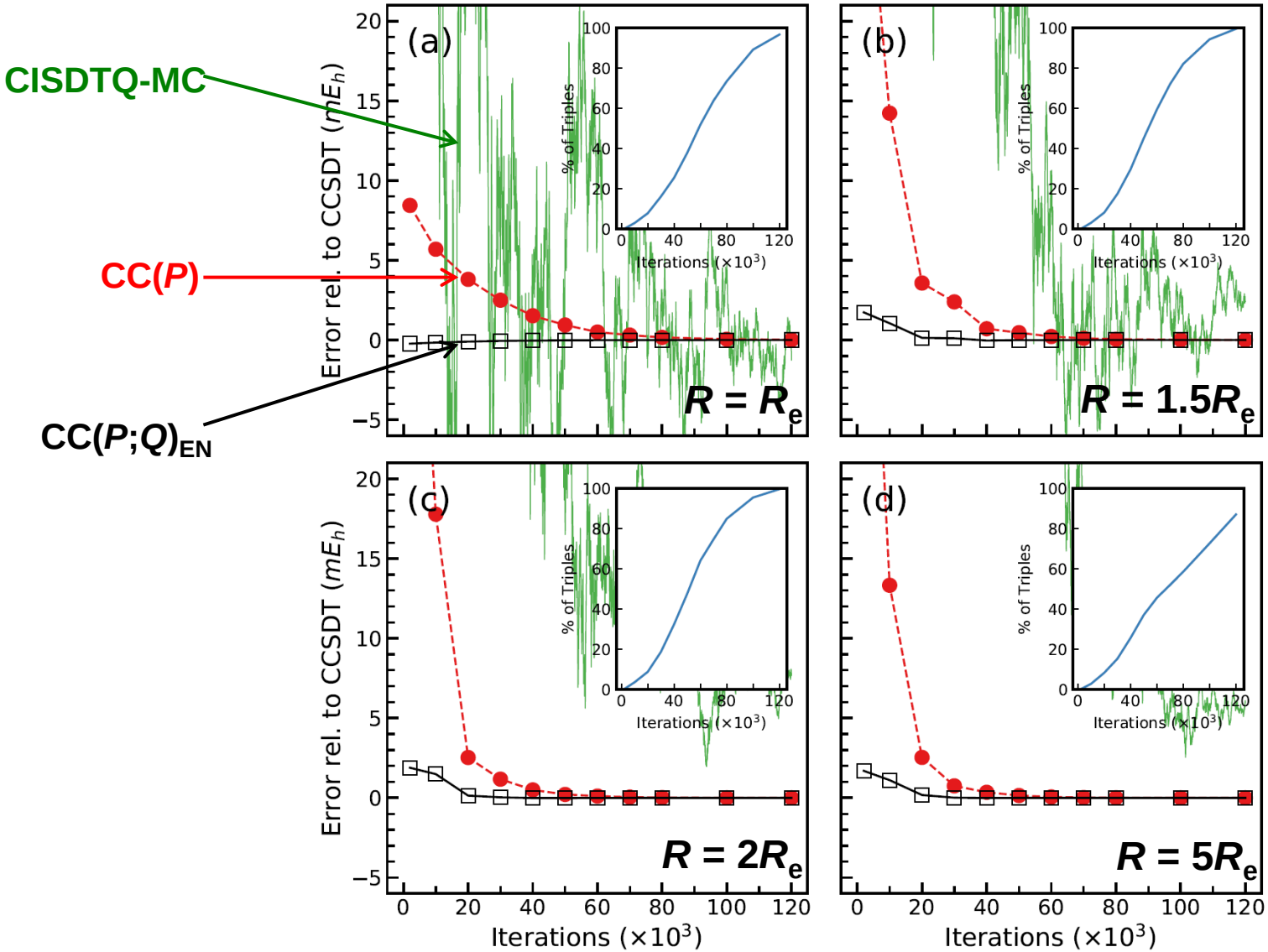


[J.E. Deustua, J. Shen, and P. Piecuch, Phys. Rev. Lett. 119, 223003 (2017)]

RECOVERING CCSDT ENERGETICS FOR F_2/cc-pVDZ

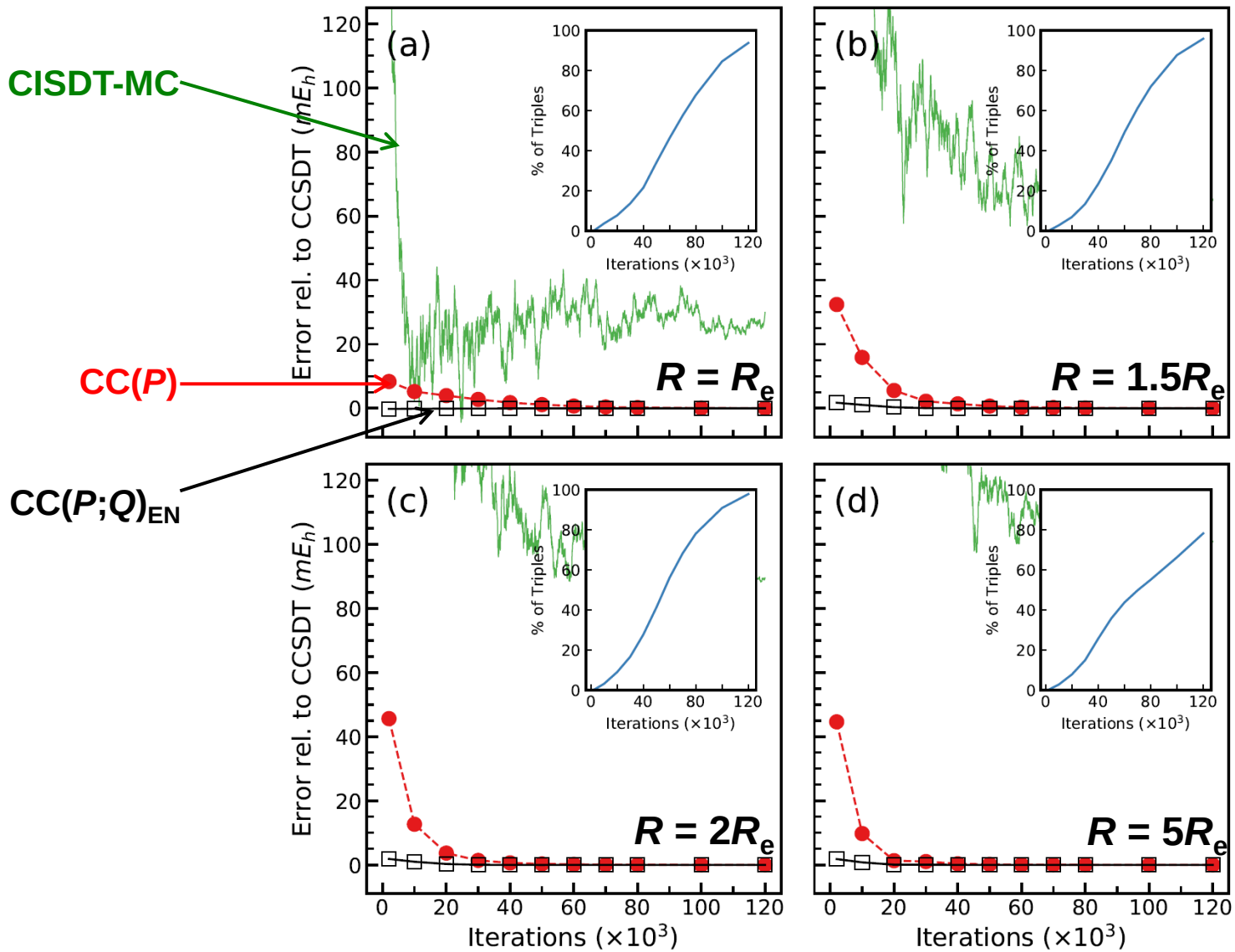
MONTE CARLO APPROACH = *i*-CISDTQ-MC ($\Delta\tau$ = 0.0001 a.u., n_a = 3)



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

RECOVERING CCSDT ENERGETICS FOR F_2/cc-pVDZ

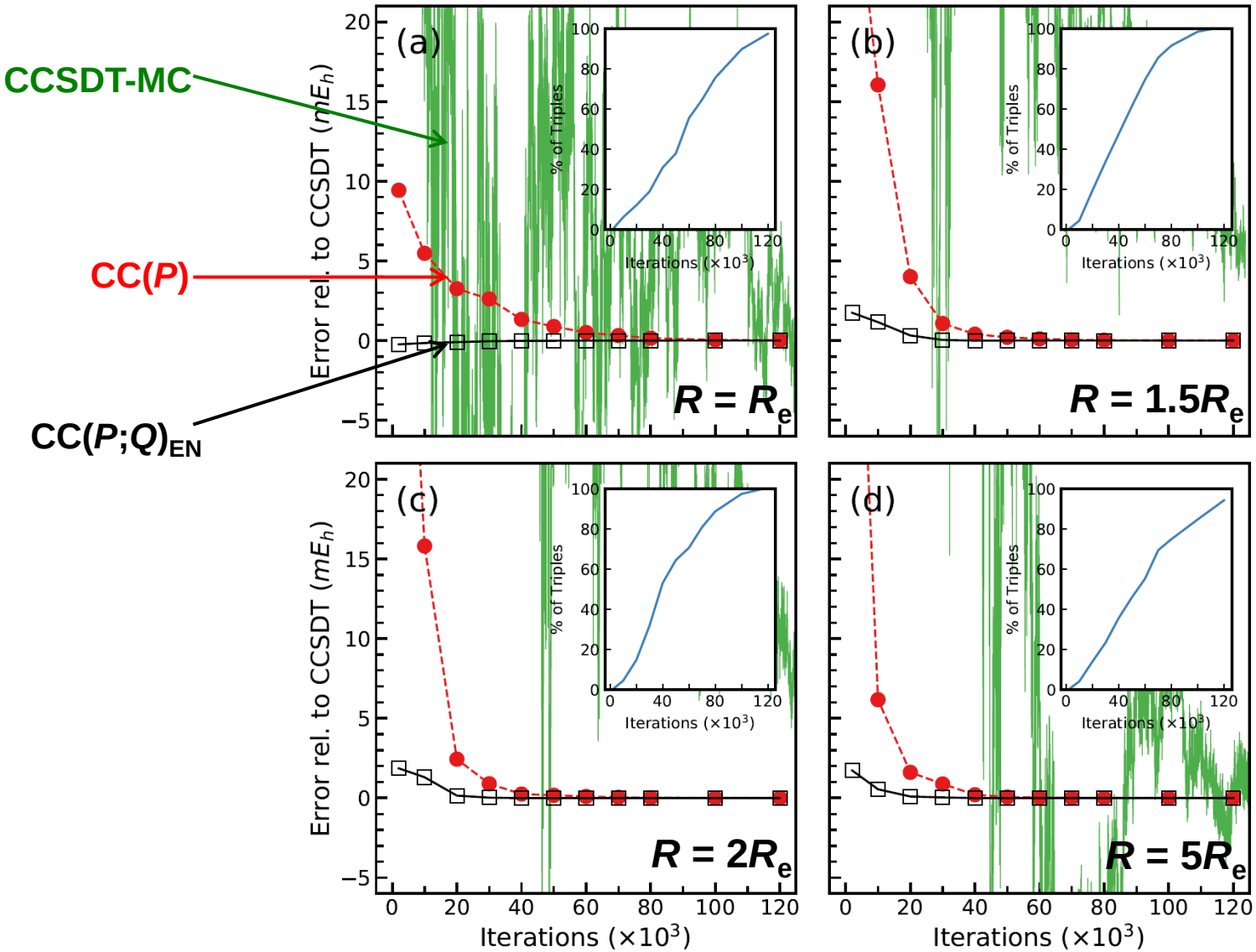
MONTE CARLO APPROACH = *i*-CISDT-MC ($\Delta\tau$ = 0.0001 a.u., n_a = 3)



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

RECOVERING CCSDT ENERGETICS FOR F_2/cc-pVDZ

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



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

RECOVERING CCSDT ENERGETICS FOR F_2/cc-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

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

RECOVERING CCSDT ENERGETICS FOR F_2/cc-pVDZ

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

$R = 2\,R_e$

Errors relative to CCSDT

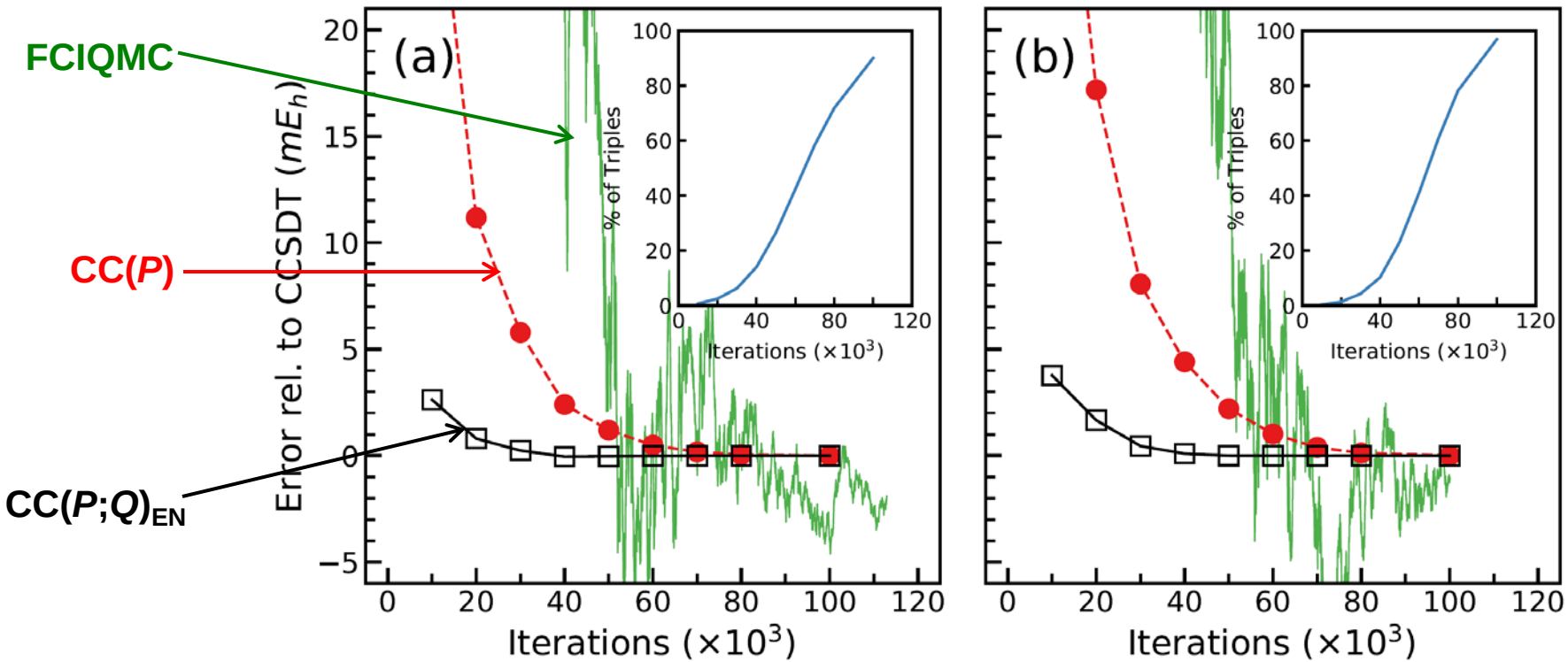
MC Iter.	% of Triples in *P* space	CC(*P*) (mE_h)	CC(*P*;*Q*)$_{MP}$ (mE_h)	CC(*P*;*Q*)$_{EN}$ (mE_h)	Wall Time (s)		
					MC	CC(*P*;*Q*)	Total
0	0	45.638 CCSD	6.357 CCSD(2)$_T$	1.862 CR-CC(2,3)	0	2	2
10,000	3	12.687	2.069	0.978	3	2	5
20,000	9	3.672	0.583	0.280	9	3	12
30,000	17	1.393	0.154	0.030	17	8	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

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

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 , $R = 2R_e$

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

RECOVERING CCSDT ENERGETICS FOR F_2/aug-cc-pVTZ

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

$R = 2\,R_e$

Errors relative to CCSDT

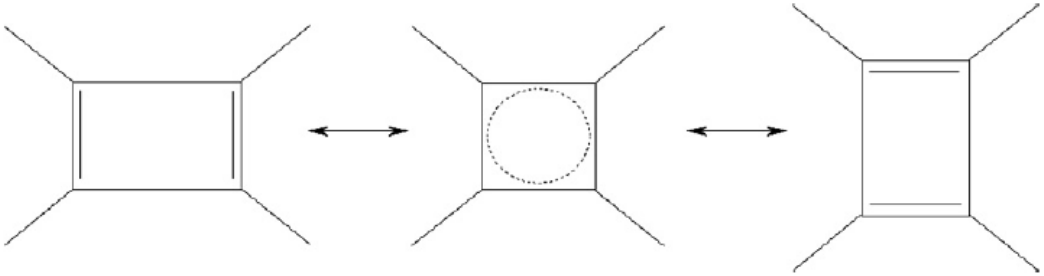
MC Iter.	% of Triples in *P* space	CC(*P*) (mE_h)	CC(*P*;*Q*)$_{MP}$ (mE_h)	CC(*P*;*Q*)$_{EN}$ (mE_h)	Speedup rel. to CCSDT
0	0	65.036 CCSD	9.808 CCSD(2)$_T$	5.595 CR-CC(2,3)	~300
30,000	4	8.065	0.858	0.454	90
40,000	10	4.408	0.330	0.093	30
50,000	23	2.208	0.125	0.002	10
∞	100	-199.253022 E_h			1

Errors relative to CCSDT
CCSD: 65.036 mE_h
CCSD(T): –27.209 mE_h

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

RECOVERING CCSDT ENERGETICS FOR AUTOMERIZATION OF CYCLOBUTADIENE/cc-pVDZ

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



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

RECOVERING CCSDT ENERGETICS FOR AUTOMERIZATION OF CYCLOBUTADIENE/cc-pVDZ

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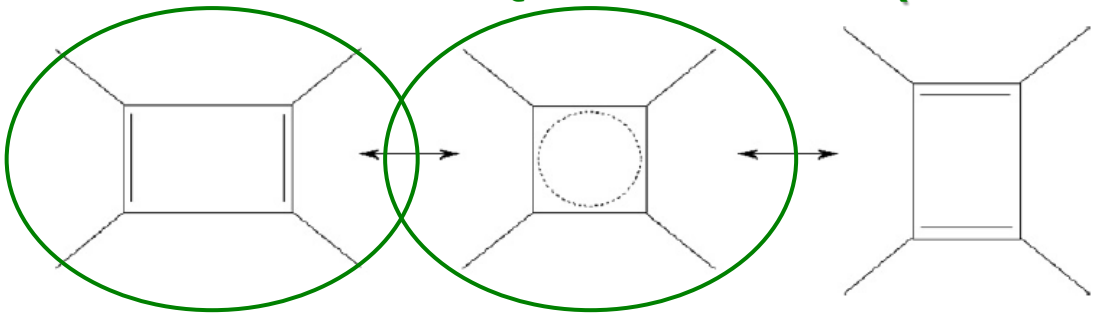


Errors relative to CCSDT

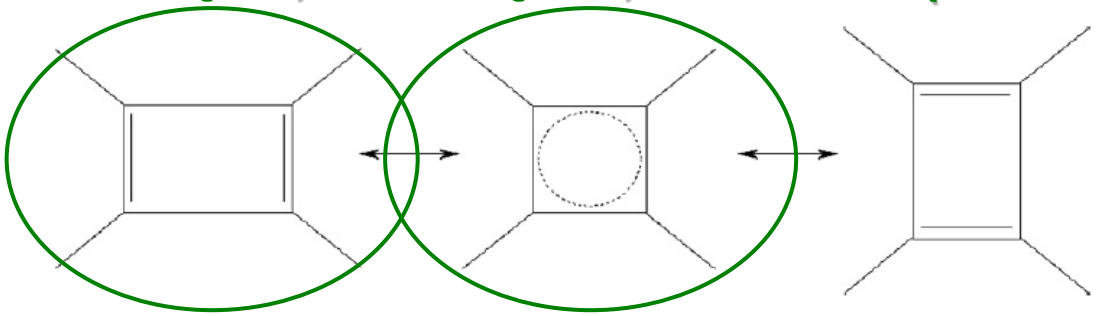
MC Iter.	% of Triples in *P* space	CC(*P*;*Q*)$_{MP}$ (kcal/mol	CC(*P*;*Q*)$_{EN}$ (kcal/mol	Total Wall Time (hrs)		
				MC	CC(*P*;*Q*)	Total
0	0/0	9.6 CCSD(2)$_T$	8.7 CR-CC(2,3)	0/0	0.4/0.4	0.4/0.4
40,000	15-22/14-18	1.5/3.5	1.7/3.5	1.0/0.3	1.9/1.4	2.9/1.7
50,000	31-41/26-34	0.5/1.1	0.6/1.2	3.1/0.7	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		

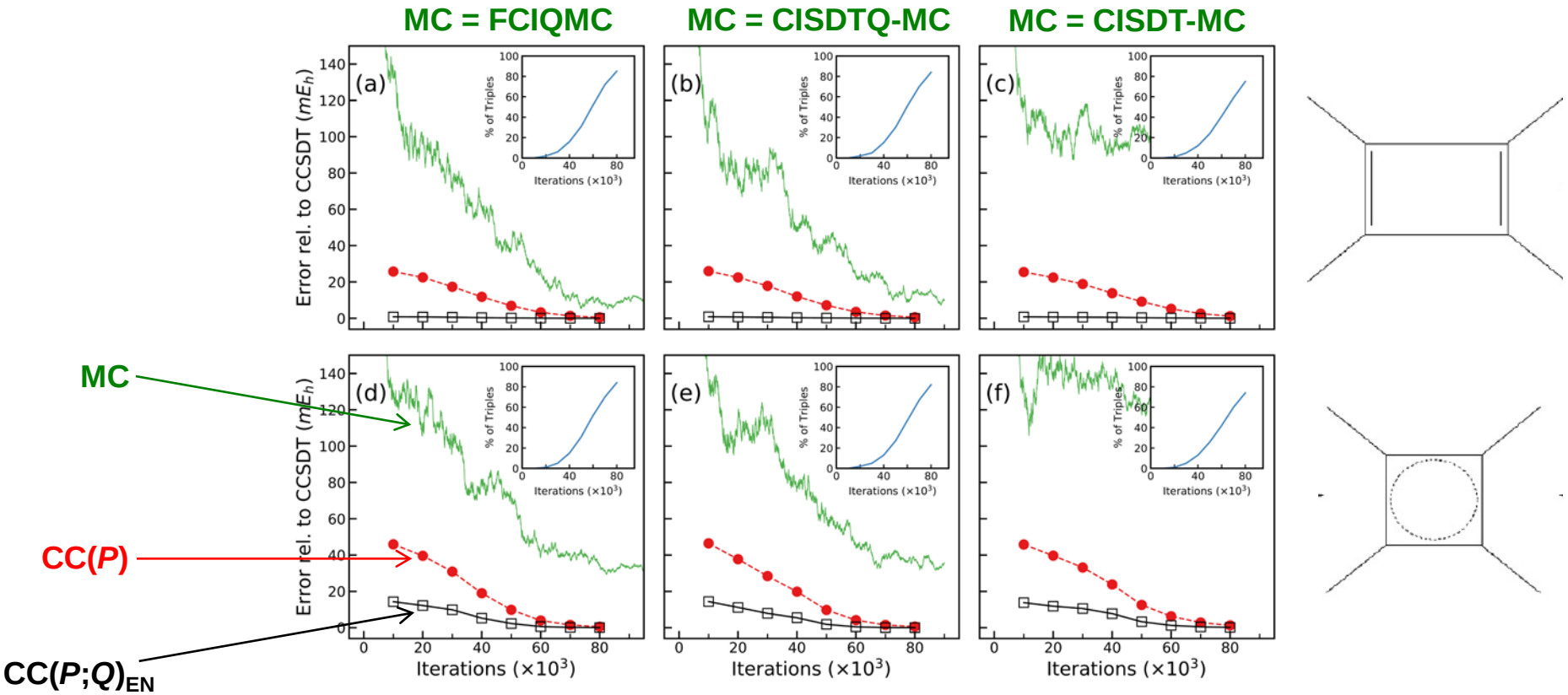
Errors relative to CCSDT
CCSD: 13.3 kcal/mol
CCSD(T): 8.2 kcal/mol

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

RECOVERING CCSDT ENERGETICS 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)



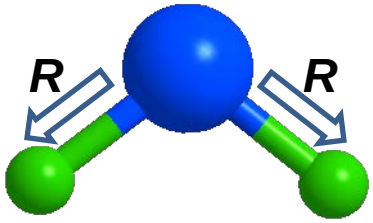


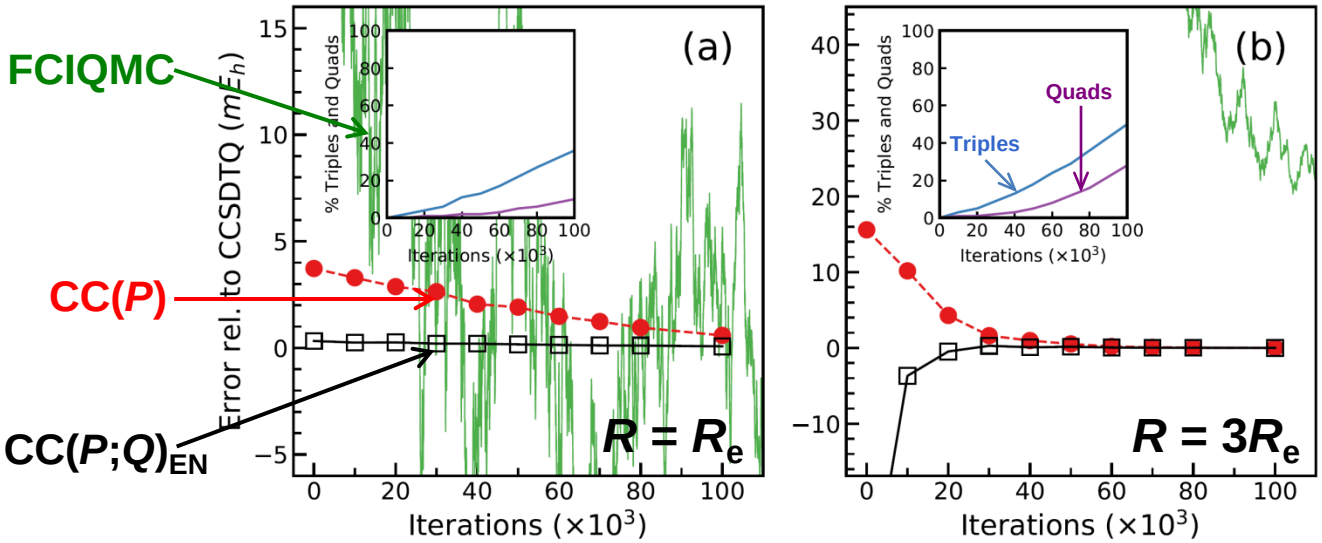
[J.E. Deustua, J. Shen, and P. Piecuch, Phys. Rev. Lett. 119, 223003 (2017); in preparation]

RECOVERING CCSDTQ ENERGETICS FOR H_2O/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

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- **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,

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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)]
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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)

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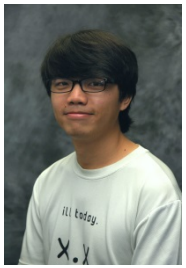

"Algebraic and Diagrammatic Methods for Many-Fermion Systems"

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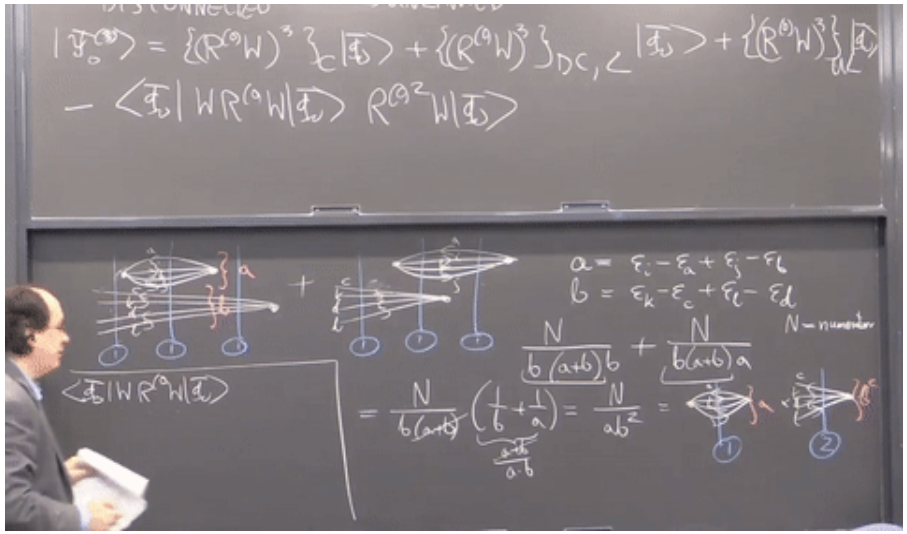

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