TOWARD EXACT QUANTUM CHEMISTRY: ACCURATE ELECTRONIC ENERGIES BY STOCHASTIC WAVE FUNCTION SAMPLING AND DETERMINISTIC COUPLED-CLUSTER COMPUTATIONS

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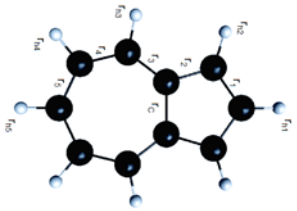
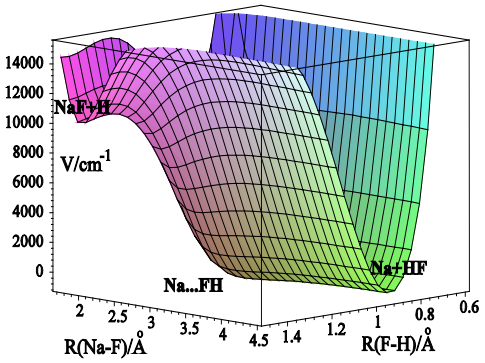
THE ELECTRONIC SCHRÖDINGER EQUATION

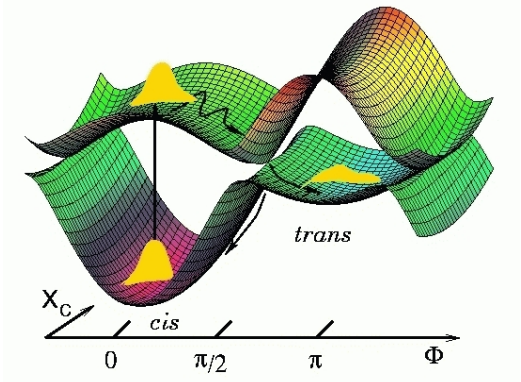
$$\hat{H}_e \Psi_\mu(\mathbf{X};\mathbf{R}) = E_\mu(\mathbf{R})\Psi_\mu(\mathbf{X};\mathbf{R})$$

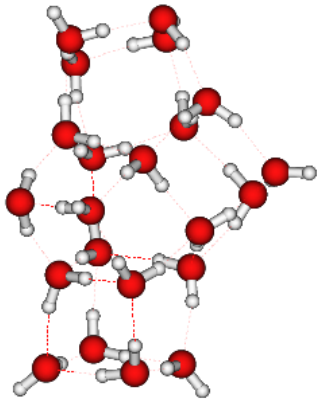
$$\hat{H}_e = \sum_{i=1}^{N} \hat{z}(\mathbf{x}_i) + \sum_{i=1}^{N}\sum_{j=i+1}^{N} \hat{v}(\mathbf{x}_i,\mathbf{x}_j)$$

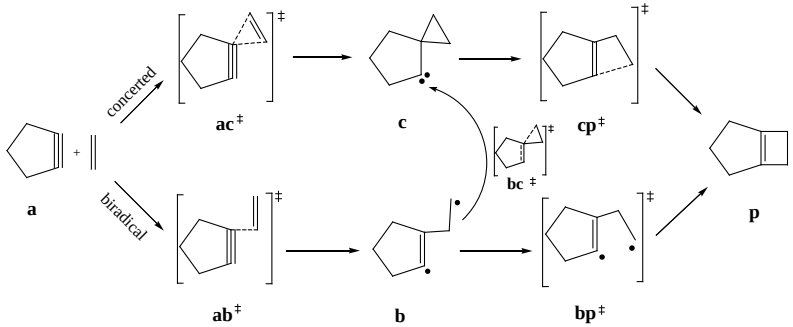
$$\hat{z}(\mathbf{x}_i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{Z_A}{R_{Ai}}, \qquad \hat{v}(\mathbf{x}_i,\mathbf{x}_j) = \frac{1}{r_{ij}}$$

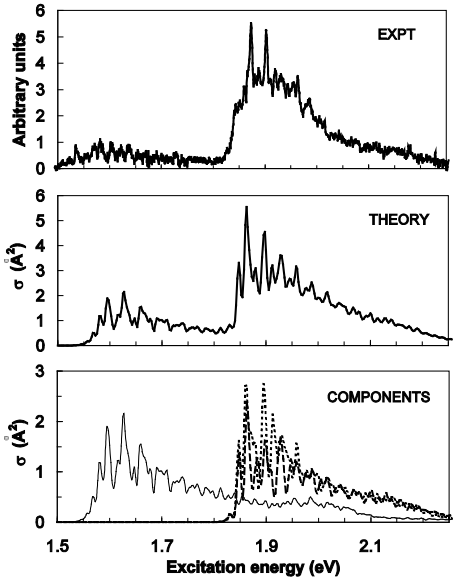












SOLVING THE ELECTRONIC SCHRÖDINGER EQUATION

- Define a basis set of one-electron functions, e.g., LCAO-type molecular spin-orbitals obtained by solving mean-field (e.g., Hartree-Fock) equations

$$V \equiv \left\{ \varphi_r(\mathbf{x}), r = 1, \ldots, \dim V \right\}$$

Exact case : $\dim V = \infty$, in practice : $\dim V < \infty$

- Construct all possible Slater determinants that can be formed from these one-electron states

$$\Phi_{r_1 \ldots r_N}(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{r_1}(\mathbf{x}_1) & \cdots & \varphi_{r_1}(\mathbf{x}_N) \\ \vdots & \ddots & \vdots \\ \varphi_{r_N}(\mathbf{x}_1) & \cdots & \varphi_{r_N}(\mathbf{x}_N) \end{vmatrix}$$

SOLVING THE ELECTRONIC SCHRÖDINGER EQUATION

- The exact wave function can be written as a linear combination of all Slater determinants

$$\Psi_\mu(\mathbf{x}_1,\ldots,\mathbf{x}_N) = \sum_{r_1<\cdots<r_N} c^\mu_{r_1\ldots r_N}\Phi_{r_1\ldots r_N}(\mathbf{x}_1,\ldots,\mathbf{x}_N)$$

$$= \sum_I c^\mu_I \Phi_I(\mathbf{x}_1,\ldots,\mathbf{x}_N)$$

- Determine the coefficients *c* and the energies E_μ by solving the matrix eigenvalue problem:

$$\mathbf{HC}^\mu = E_\mu \mathbf{C}^\mu$$

where the matrix elements of the Hamiltonian are

$$H_{IJ} = \left\langle \Phi_I \middle| \hat{H} \middle| \Phi_J \right\rangle = \int d\mathbf{x}_1 \ldots d\mathbf{x}_N \Phi^*_I(\mathbf{x}_1,\ldots,\mathbf{x}_N)\hat{H}\Phi_J(\mathbf{x}_1,\ldots,\mathbf{x}_N)$$

- This procedure, referred to as the full configuration interaction approach (FCI), yields the exact solution within a given one-electron basis set

THE PROBLEM WITH FCI

Dimensions of the FCI spaces for many-electron systems

	Number of correlated electrons			
Orbitals	6	8	10	12
20	379×10^3	5.80×10^6	52.6×10^6	300×10^6
30	4.56×10^6	172×10^6	4.04×10^9	62.5×10^9
100	6.73×10^9	3.20×10^{12}	9.94×10^{14}	2.16×10^{17}

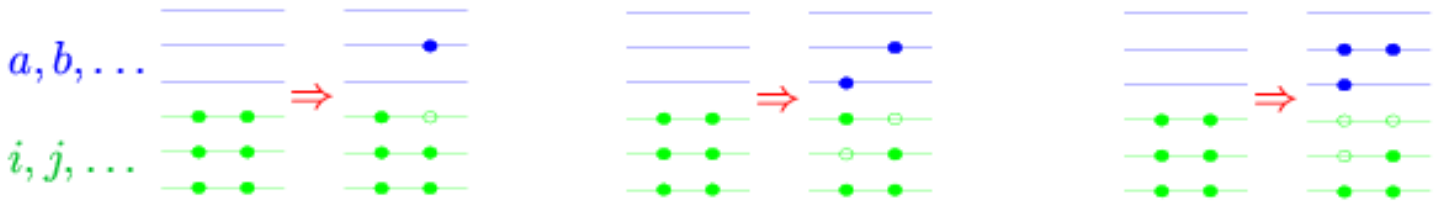
- The high dimensionality of the FCI eigenvalue problem makes this approach inapplicable to systems with more than a few electrons and realistic basis sets
- Alternative approaches are needed in order to study the majority of chemical problems of interest

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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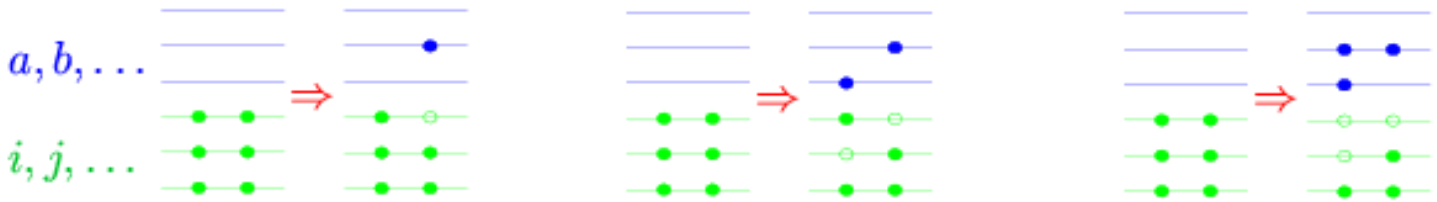


1p-1h, singles (S) **2p-2h, doubles (D)** **3p-3h, triples (T)**

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

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

Standard CC Equations

(J. Čížek, 1966)

We do not minimize

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

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

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

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

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

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

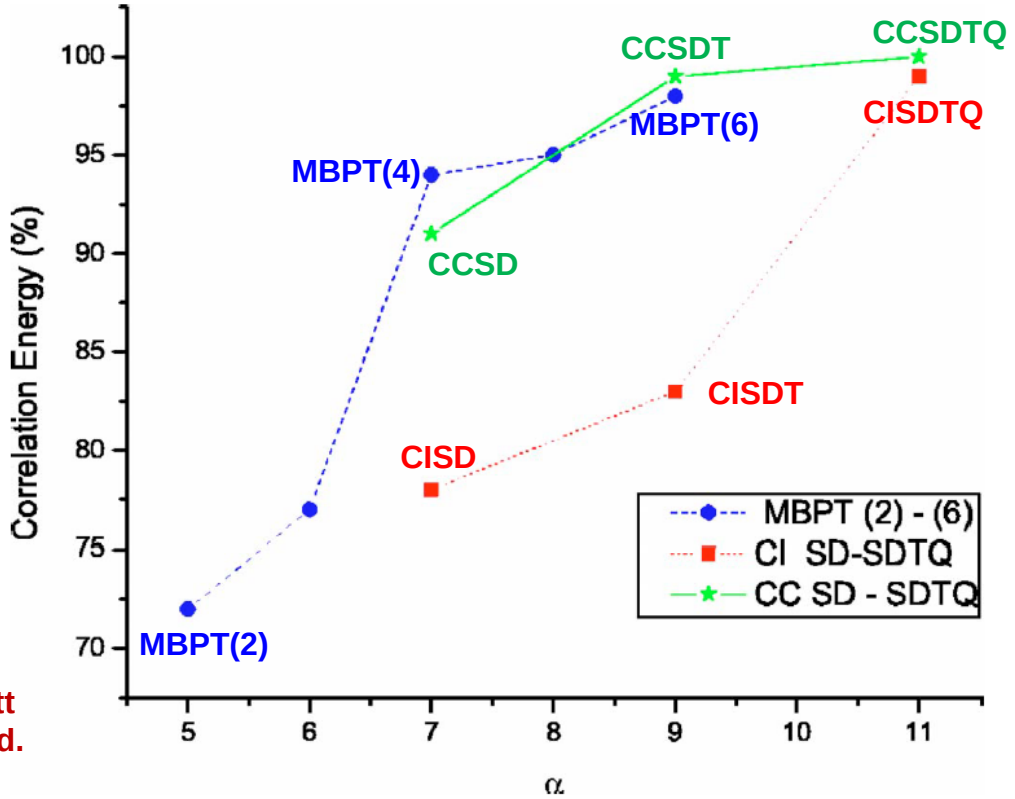
$$\bar{H} = H + [H,T] + \tfrac{1}{2}[[H,T],T]] + \tfrac{1}{6}[[[H,T],T],T] + \tfrac{1}{24}[[[[H,T],T],T],T]$$

kp-kh ⟶ $\langle\Phi^{a_1a_2\ldots a_k}_{i_1i_2\ldots i_k}|\left(H_Ne^{T^{(A)}}\right)_C|\Phi\rangle = 0, \quad k = 1\ldots,m_A$

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

ARGUMENTS IN FAVOR OF THE CC THEORY

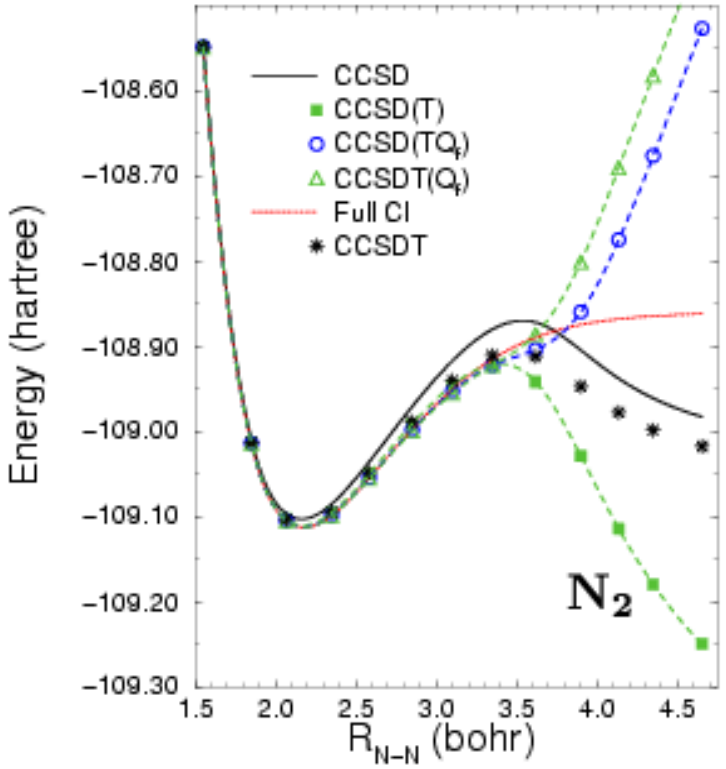
- **Size-extensivity** of the resulting approximations (no loss of accuracy occurs when the system is made larger)
- **Separability** or size consistency if the reference state separates correctly
- **Fastest convergence** toward the exact, full CI, limit



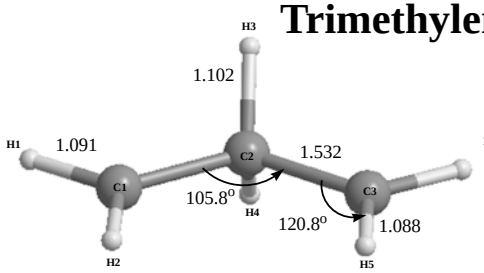
Taken from R.J. Bartlett and M. Musiał, Rev. Mod. Phys., 2007

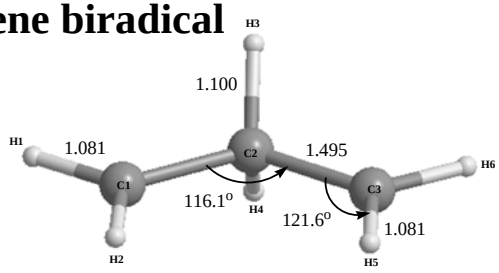
KEY CHALLENGE: How to incorporate T_n and R_n components with $n > 2$, needed to achieve a quantitative description, without running into prohibitive computational costs of CCSDT, CCSDTQ, and similar schemes?

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)



Trimethylene biradical





	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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MMCC functional

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

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

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

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

(moments of CC equations)

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

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before exploiting the resolution of identity, introduce the ansatz:

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

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

before exploiting the resolution of identity, introduce the ansatz:

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

$$E_0 = \frac{\left\langle\Phi\left|L_0 e^{-T^{(A)}} e^{T^{(A)}}\left(He^{T^{(A)}}\right)_C\right|\Phi\right\rangle}{\left\langle\Phi\left|L_0 e^{-T^{(A)}} e^{T^{(A)}}\right|\Phi\right\rangle} = \left\langle\Phi\left|L_0\left(He^{T^{(A)}}\right)_C\right|\Phi\right\rangle$$

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

BIORTHOGONAL MOMENT EXPANSIONS

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

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

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

BIORTHOGONAL MMCC EXPANSION

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

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

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

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

$$\ell^{abc}_{0,ijk}(2) = \left\langle \Phi \middle| L_0^{(\text{CCSD})} \bar{H}^{(\text{CCSD})} \middle| \Phi^{abc}_{ijk} \right\rangle / D^{ijk}_{0,abc}(2), \quad D^{ijk}_{0,abc}(2) = E_0^{(\text{CCSD})} - \left\langle \Phi^{abc}_{ijk} \middle| \bar{H}^{(\text{CCSD})} \middle| \Phi^{abc}_{ijk} \right\rangle$$

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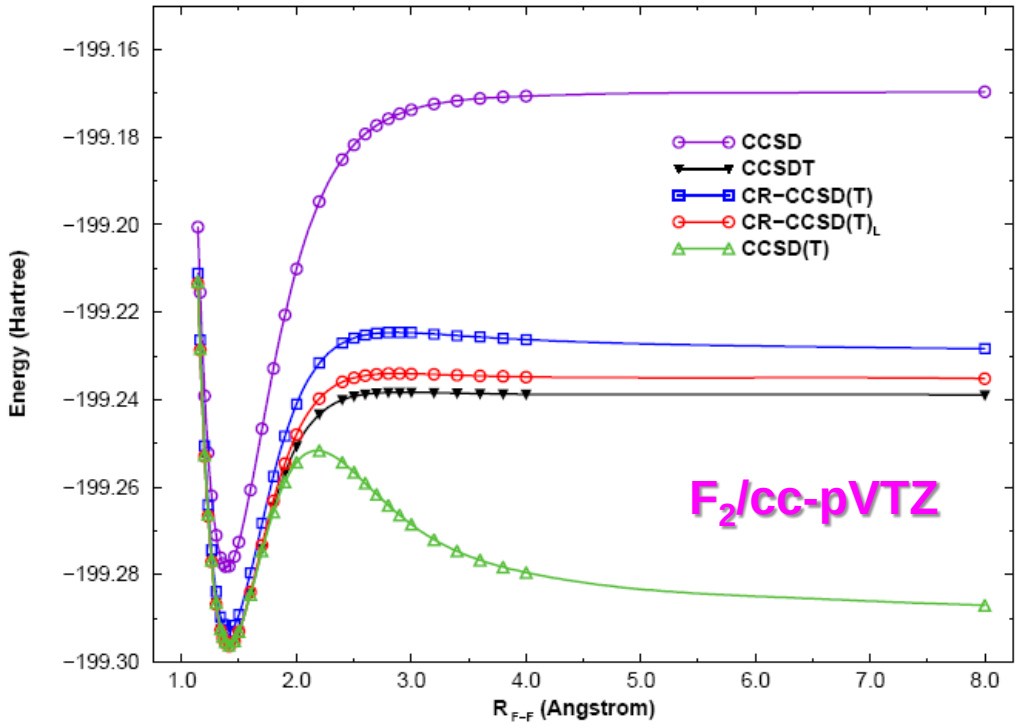

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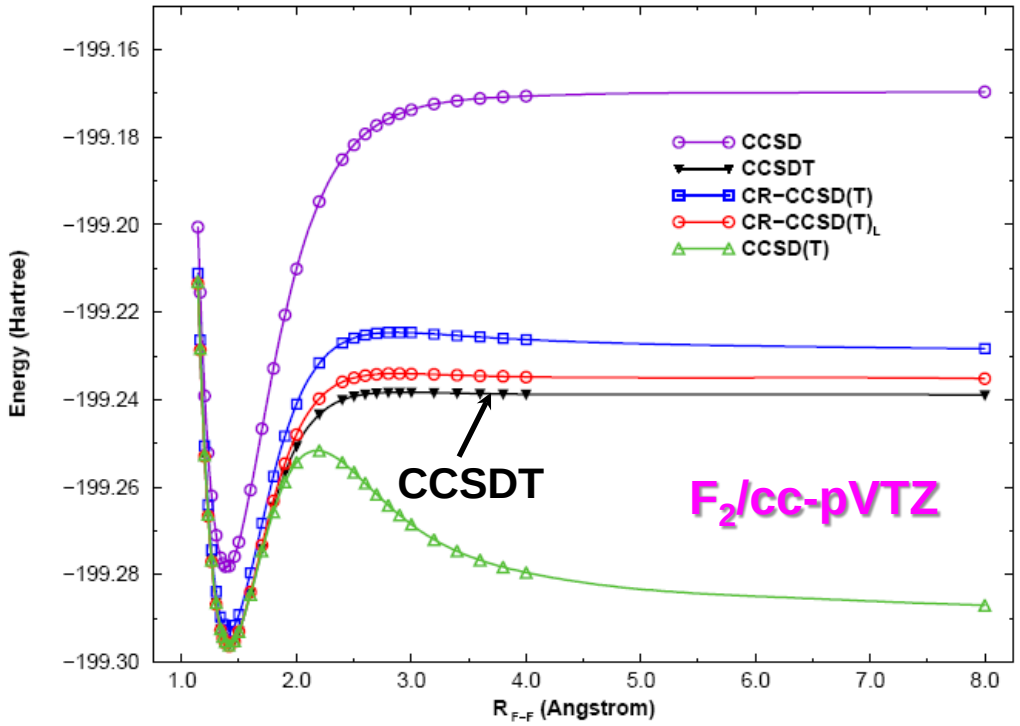

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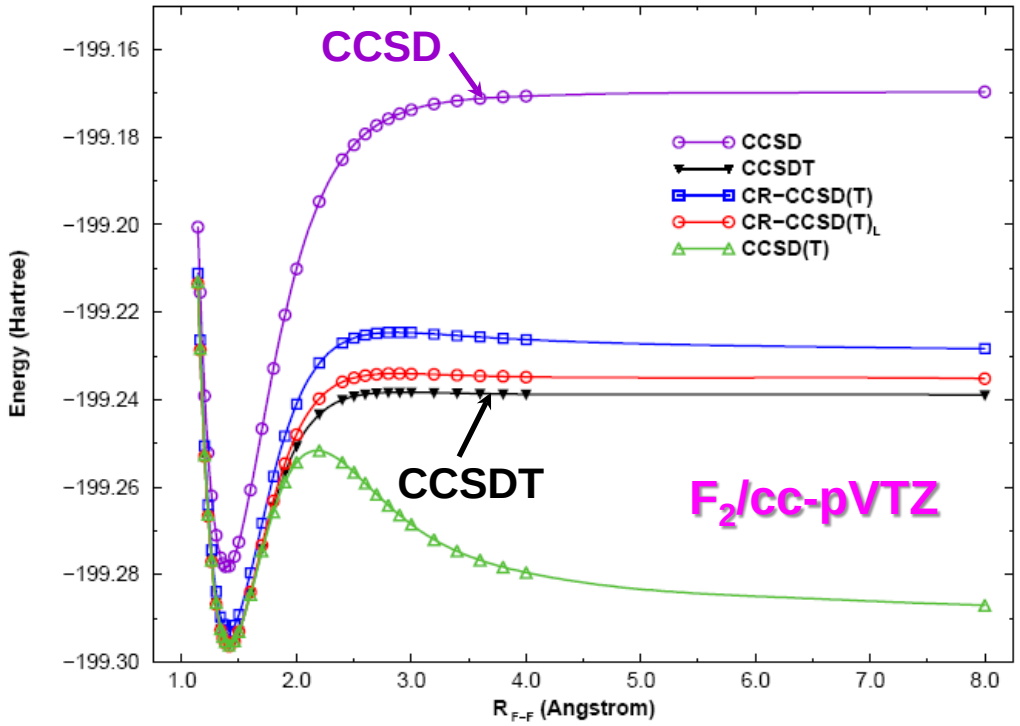

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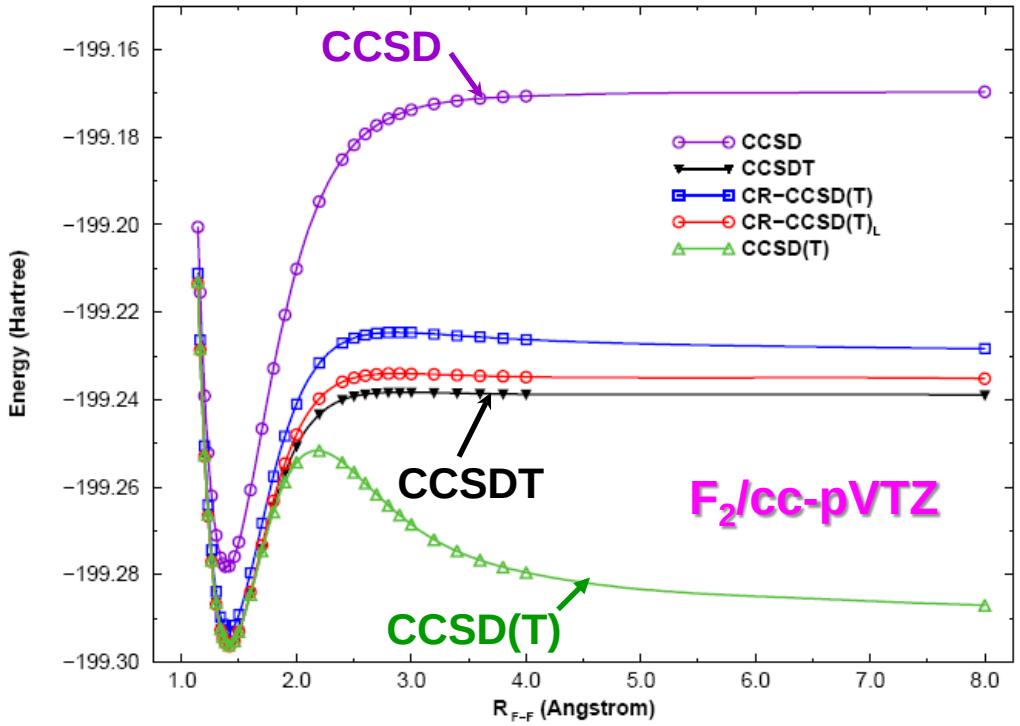

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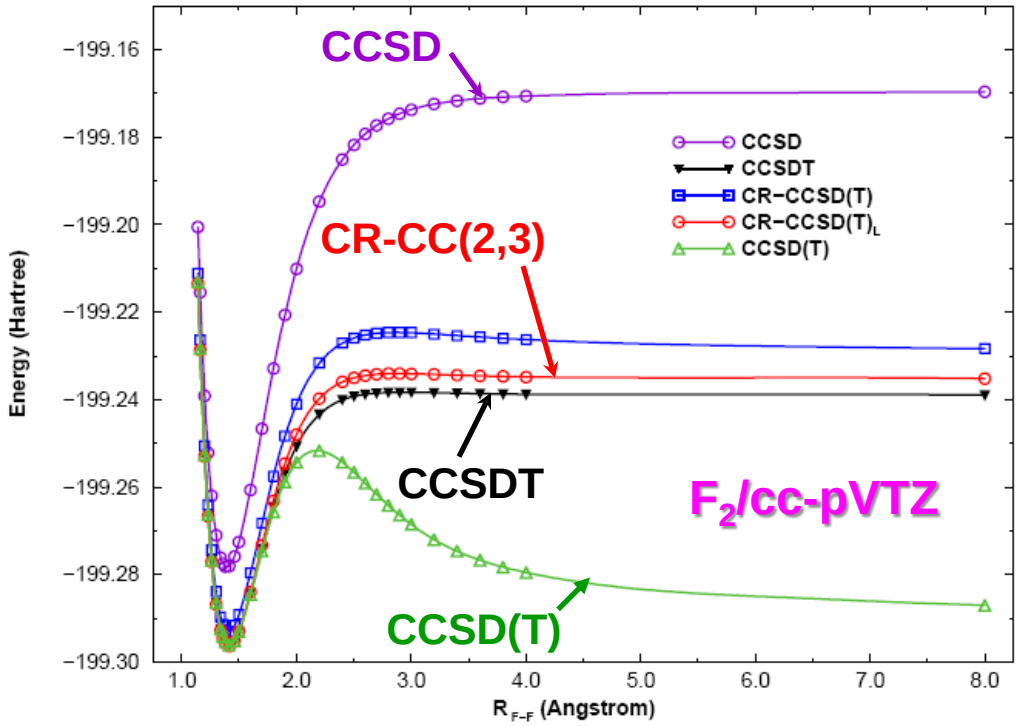
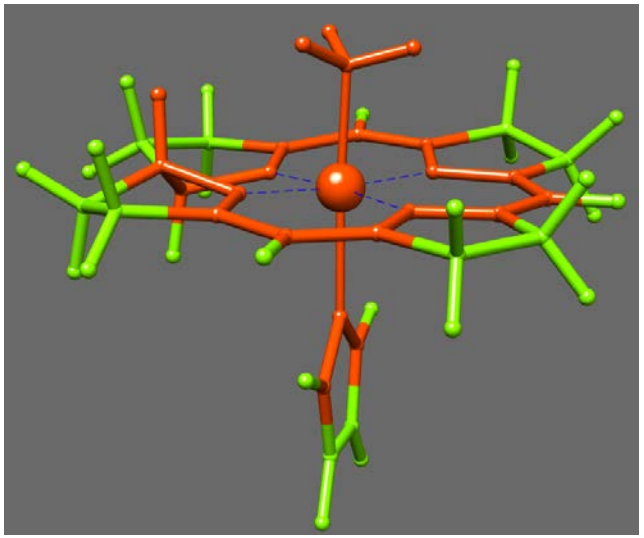


Functional	BDE (with ZPE), kcal/mol, 6-31G(d) / 6-311++G(d,p)
BHandHLYP (50% HF)	1.2 / -2.2
MPW1K (42.8 % HF)	8.9 / 6.0
M06-2X (54 % HF)	13.5 / 9.2
MPW1PW91 (25 % HF)	18.1 / 16.1
B3LYP (20 % HF)	17.8 / 15.9
B3LYP+D3 (20 % HF)	21.2 / 24.7
M06 (27 % HF)	27.4 / 26.2
TPSSh (10 % HF)	24.5 / 23.0
ωB97X-D (22 % 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

DFT

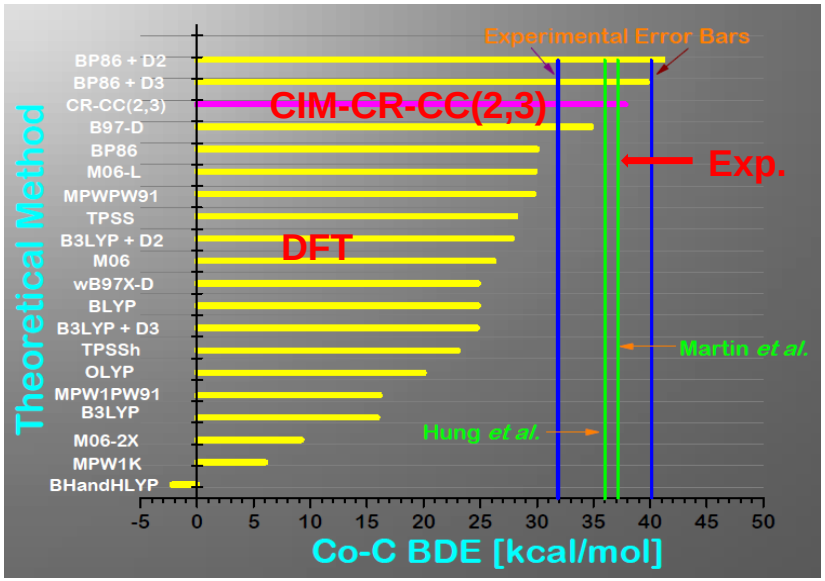
LARGE SYSTEMS (LOCAL CC): CIM-CR-CC(2,3) STUDY OF Co-C BOND DISSOCIATON IN METHYLCOBALAMIN

[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)]



[In GAMESS: CIMTYP = GSECIM]

Structural model: 58 atoms; 234 electrons.



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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

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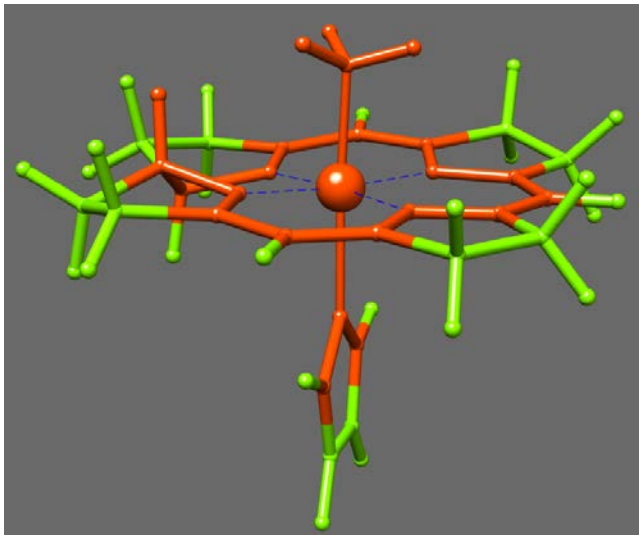

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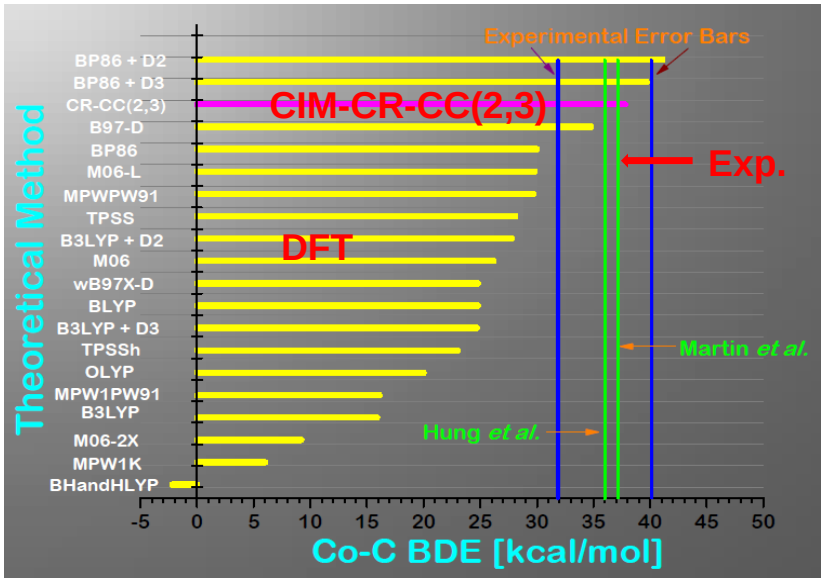
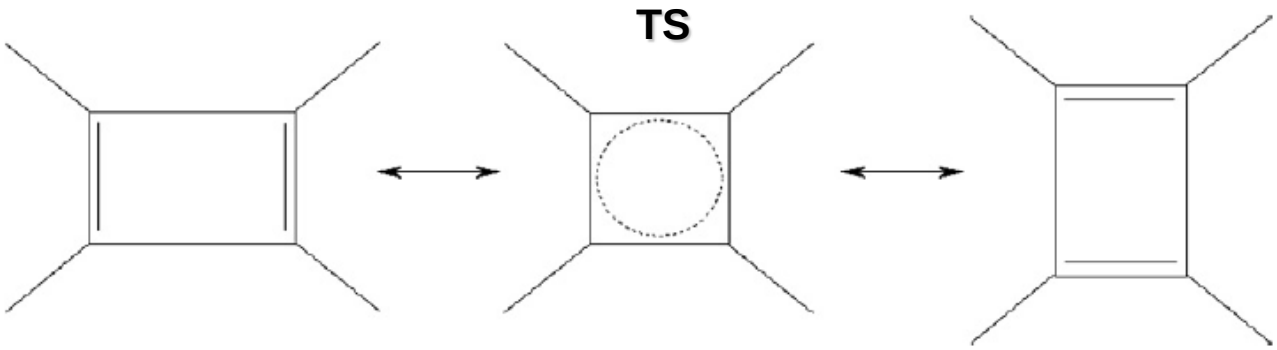


AUTOMERIZATION OF CYCLOBUTADIENE

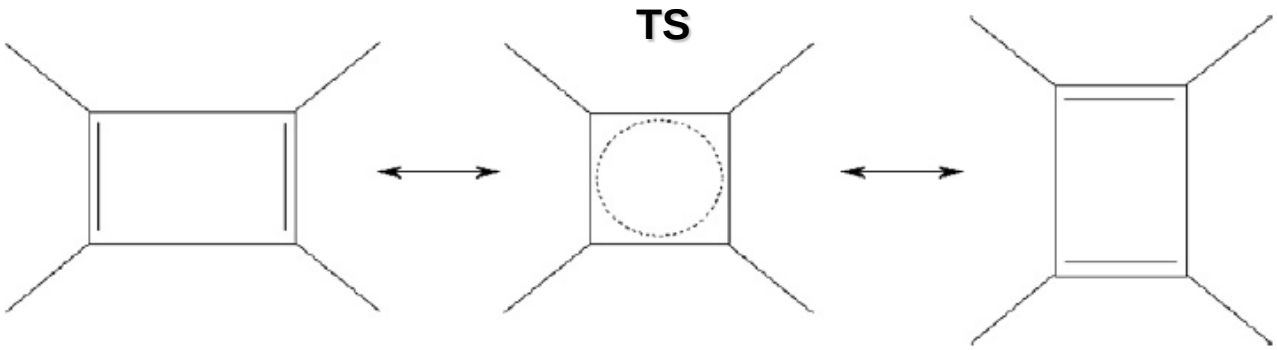


Various CC energies (in millihartree) relative to full CCSDT (in hartree), cc-pVDZ basis set

	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



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T_1 and T_2 decoupled from T_3

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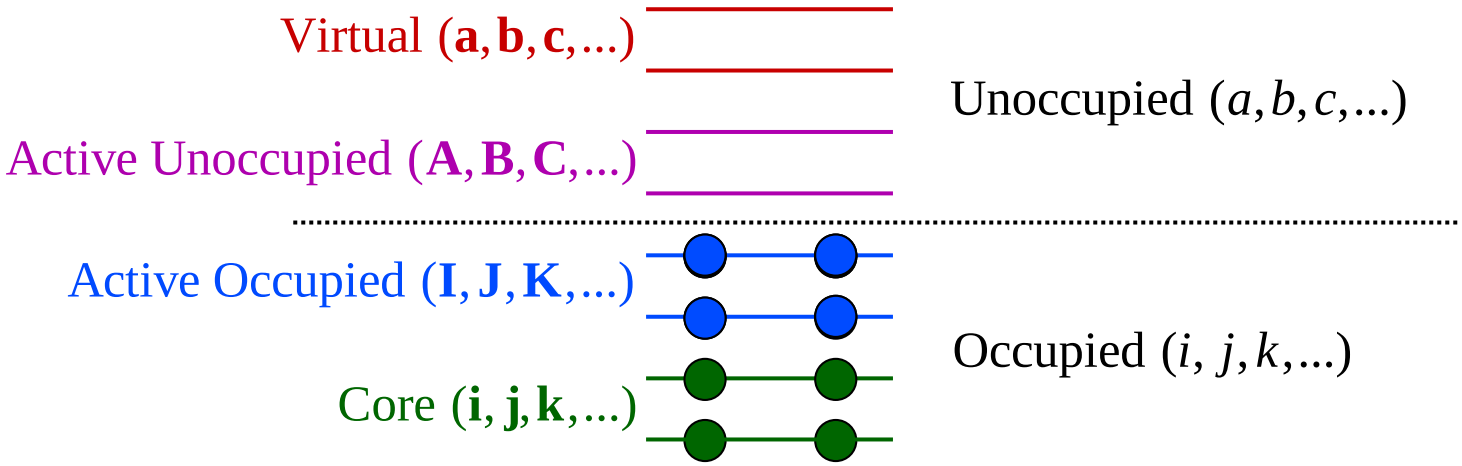
CAPTURING THE COUPLING OF LOWER- AND HIGHER-ORDER CLUSTERS: ACTIVE-SPACE CC APROACHES (CCSDt, CCSDtq, etc.)

[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.]

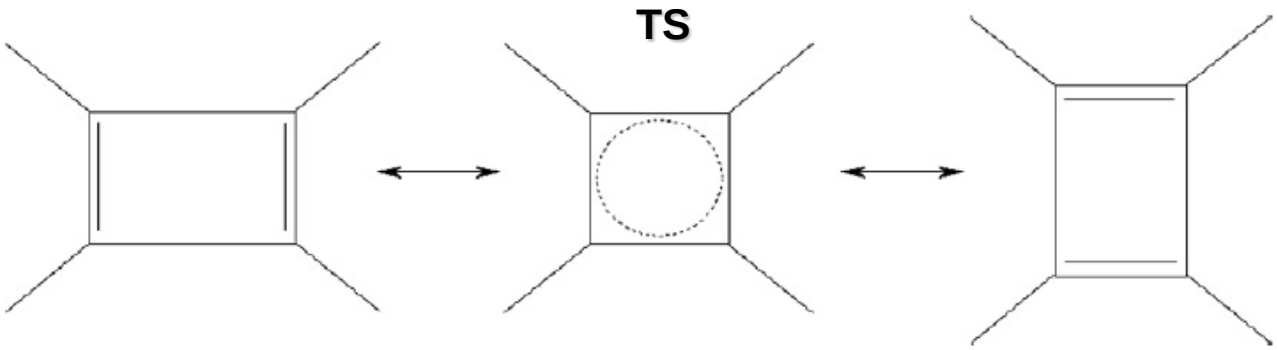


$$T^{(\mathrm{CCSDt})} = T_1 + T_2 + t_3, \quad T^{(\mathrm{CCSDtq})} = T_1 + T_2 + t_3 + t_4, \quad \text{etc.}$$

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

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

AUTOMERIZATION OF CYCLOBUTADIENE



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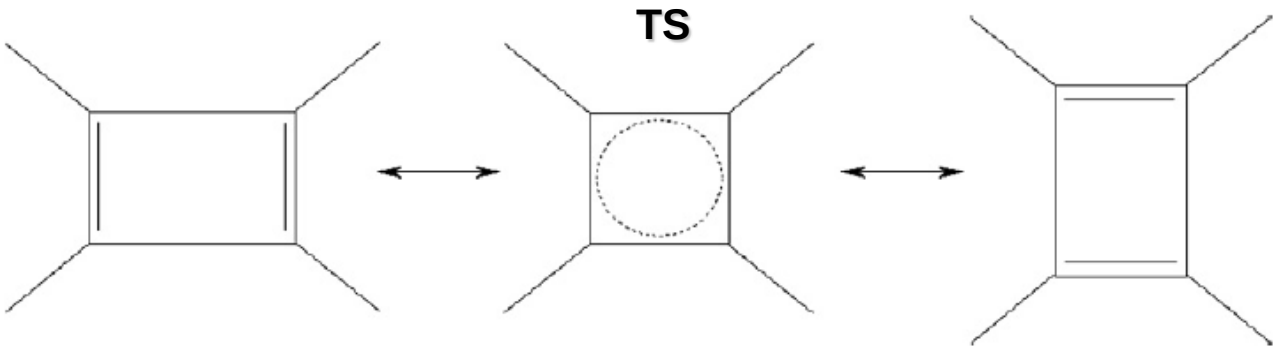

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CCSD	26.827	47.979	20.9
CCSD(T)	1.123	14.198	15.8
CR-CC(2,3)	0.848	14.636	16.3
CCSDt	20.786	20.274	7.3
CCSDT	-154.244157	-154.232002	7.6

T_1 and T_2 decoupled from T_3

t_3 misses some dynamical correlations

[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]

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

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

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

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

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

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moments of CC/EOMCC equations

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Examples:

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

CR-CC(2,3)

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- 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 $\mathcal{H}^{(P)}$

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

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

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

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 $\mathcal{H}^{(Q)}$

Examples:

- P space: singles, doubles, and a subset of triples defined via active orbitals, as in CCSDt
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CC(t;3)

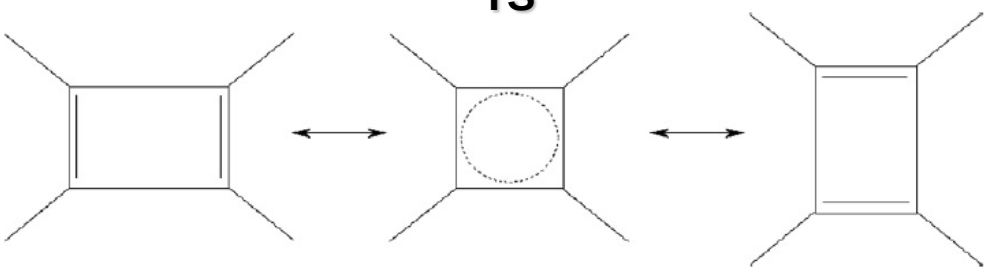
- P space: singles, doubles, and a subset of triples and quadruples defined via active orbitals, as in CCSDtq
- Q space: remaining triples and quadruples not captured by CCSDtq

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
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
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SUCCSD[c]	7.0	8.7
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RMRCCSD[c]	10.4	13.0
SUCCSD(T)[c]	4.8	5.9
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SUCCSD/mcscf[c]	7.2	8.9
MkCCSD/mcscf[c]	7.9	9.7
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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
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[J. Shen and P. Piecuch, *J. Chem. Phys*. 136, 144104 (2012)]

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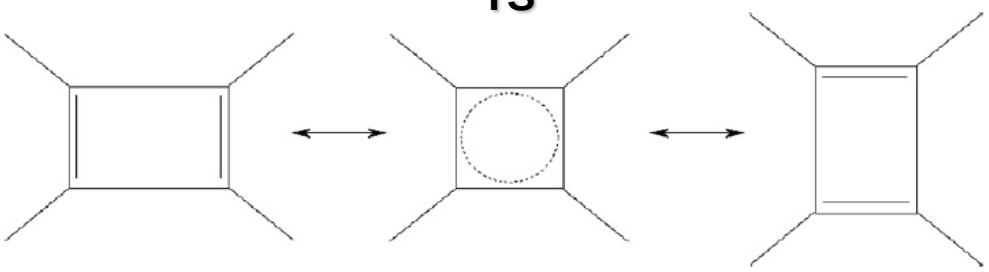

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2D-MRCCSD(T)[d]	6.6	
BWCCSD(a.c.)[e]	6.5	7.6
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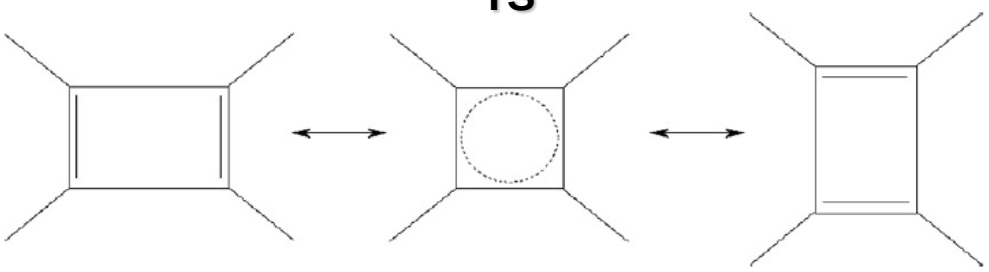

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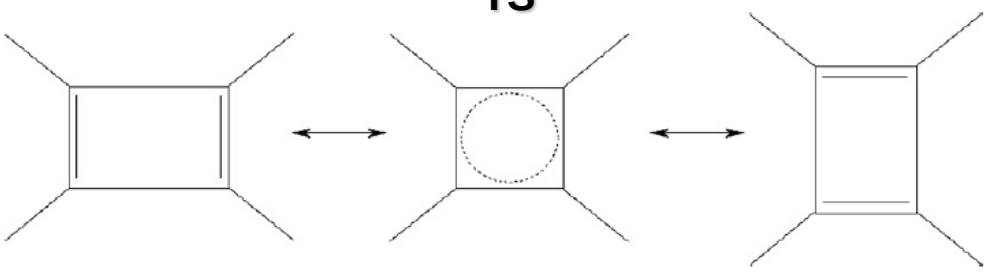
[J. Shen and P. Piecuch, *J. Chem. Phys*. 136, 144104 (2012)]

TS



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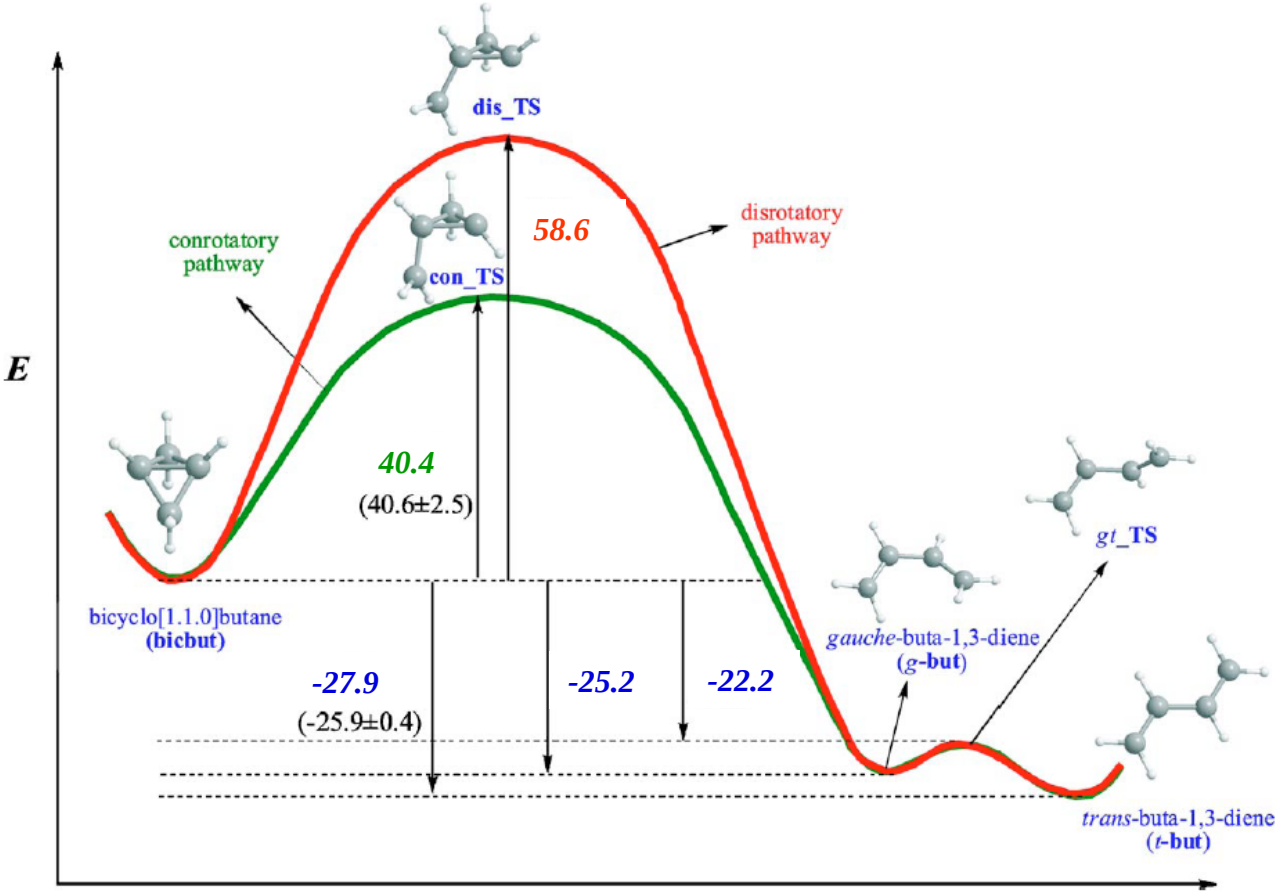
The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]-butane to Butadiene (enthalpies at 0 K in kcal/mol)

	con_TS	dis_TS	g-but	gt_TS	t-but



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	con_TS	dis_TS	g-but	gt_TS	t-but
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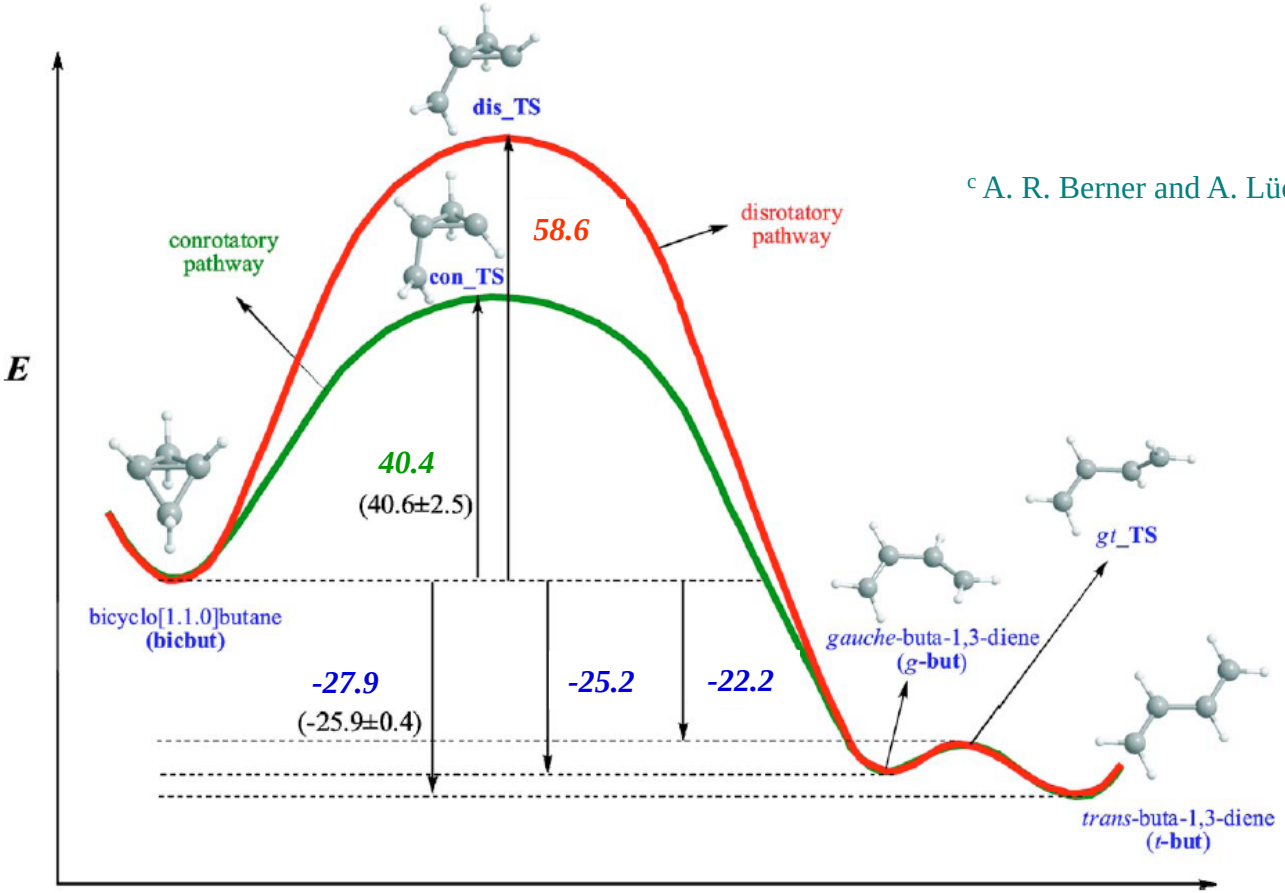

[c] A. R. Berner and A. Lüchow, *J. Phys. Chem. A* **114**, 13222 (2010)

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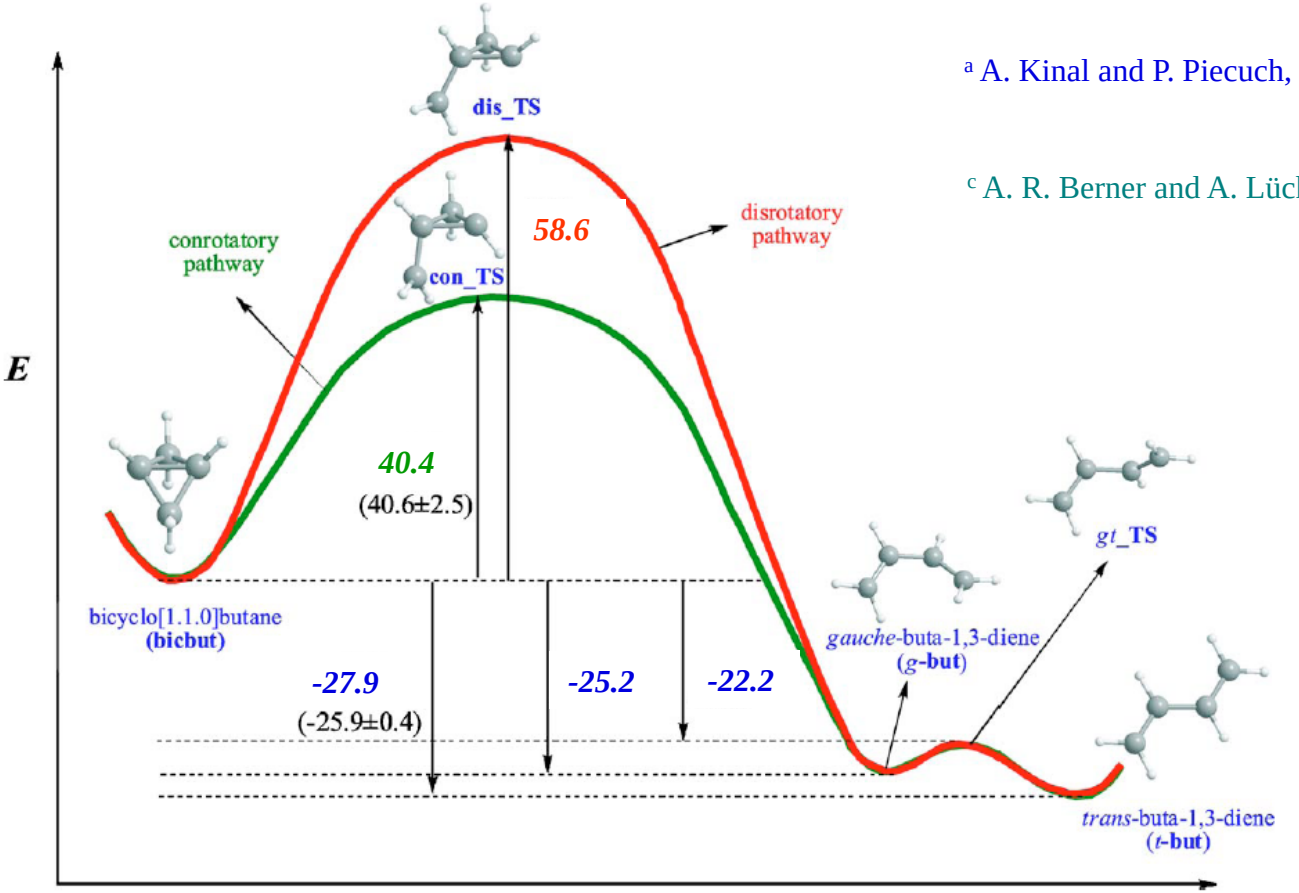

[a] A. Kinal and P. Piecuch, *J. Phys. Chem. A* **111**, 734 (2007)

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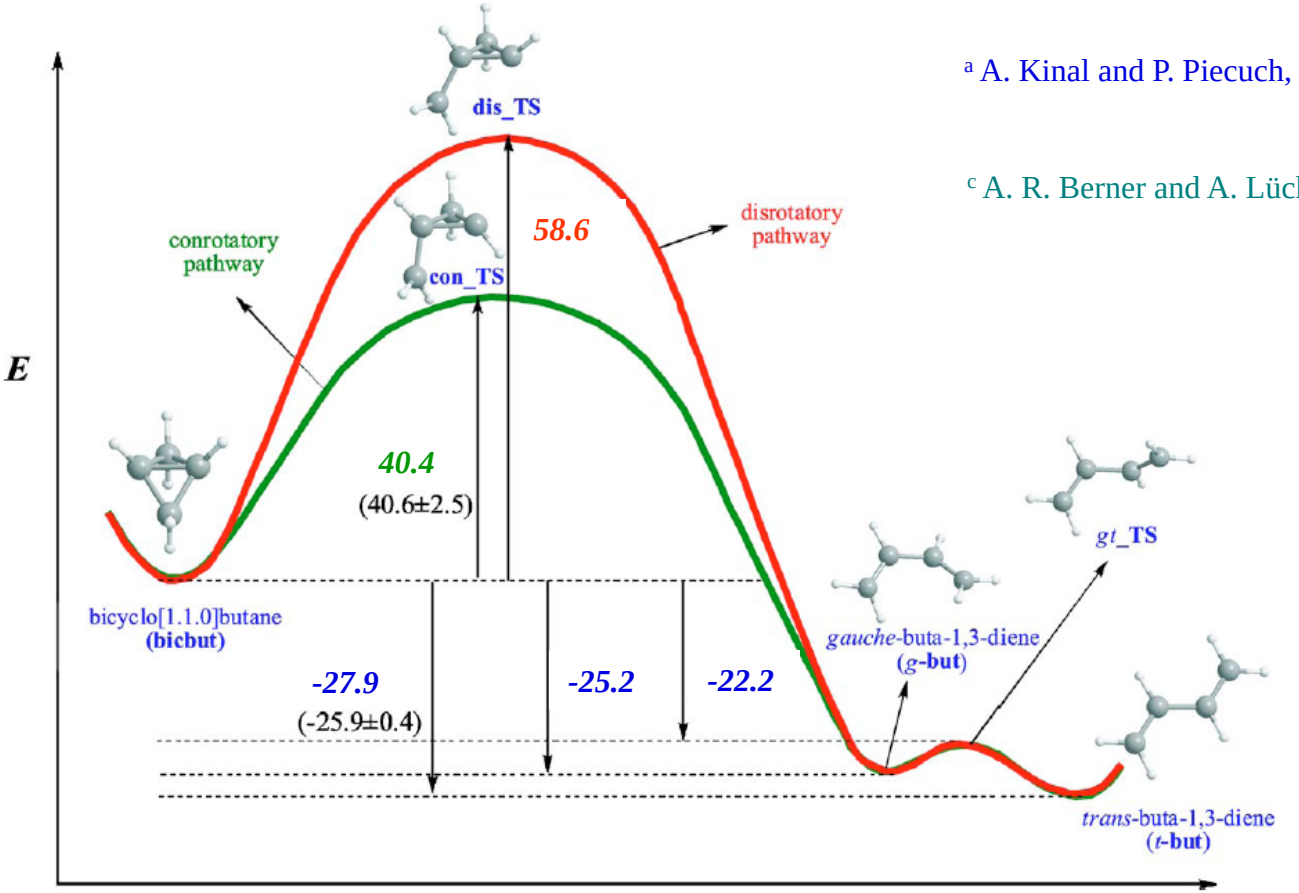
CR-CC(2,3)[a]	41.1	66.1	-24.9	-22.1	-27.9
OMR3-DMC[c]	40.4(5)	58.6(5)	-25.2(5)	-22.2(5)	-27.9(5)



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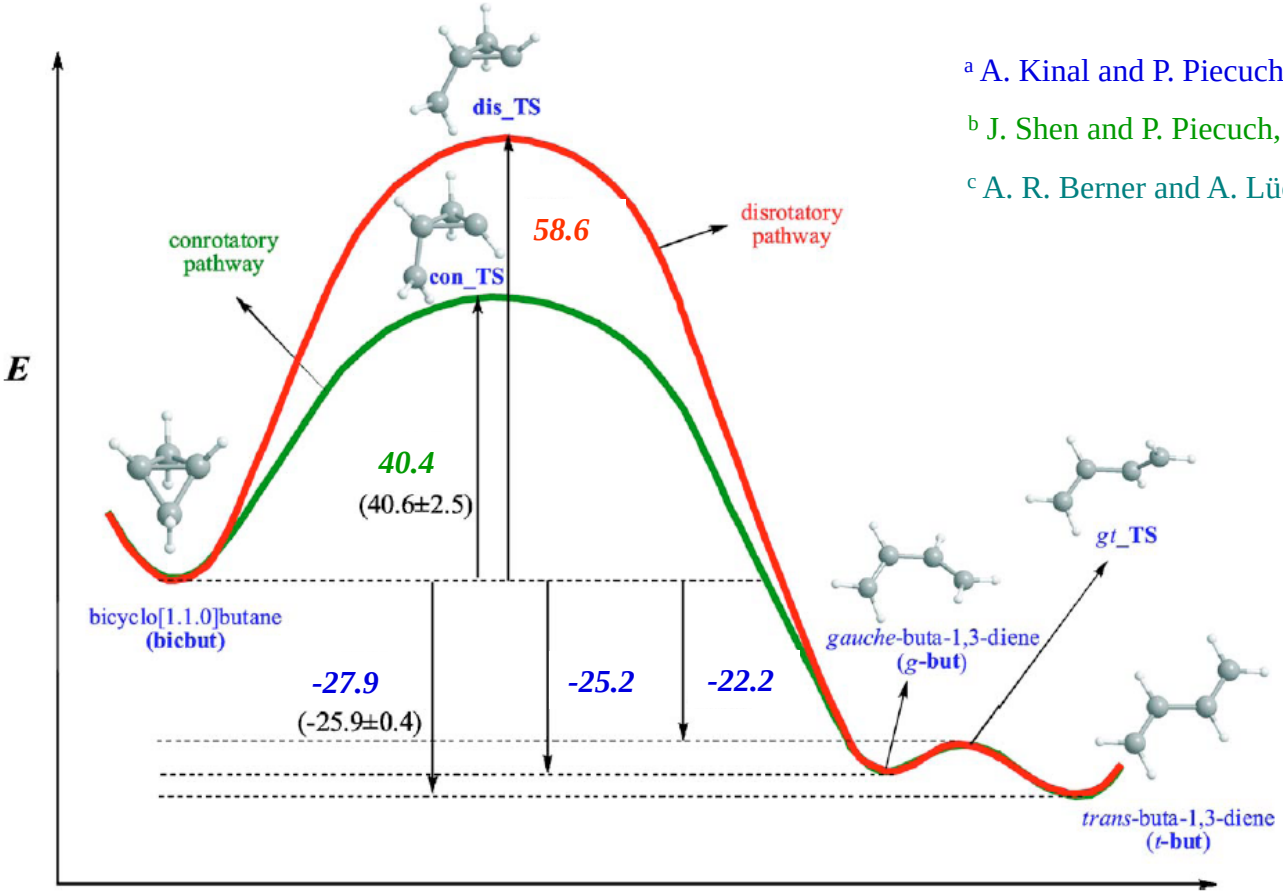
CCSDt[b]	40.1	59.0	-27.2	-25.3	-31.1
OMR3-DMC[c]	40.4(5)	58.6(5)	-25.2(5)	-22.2(5)	-27.9(5)



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

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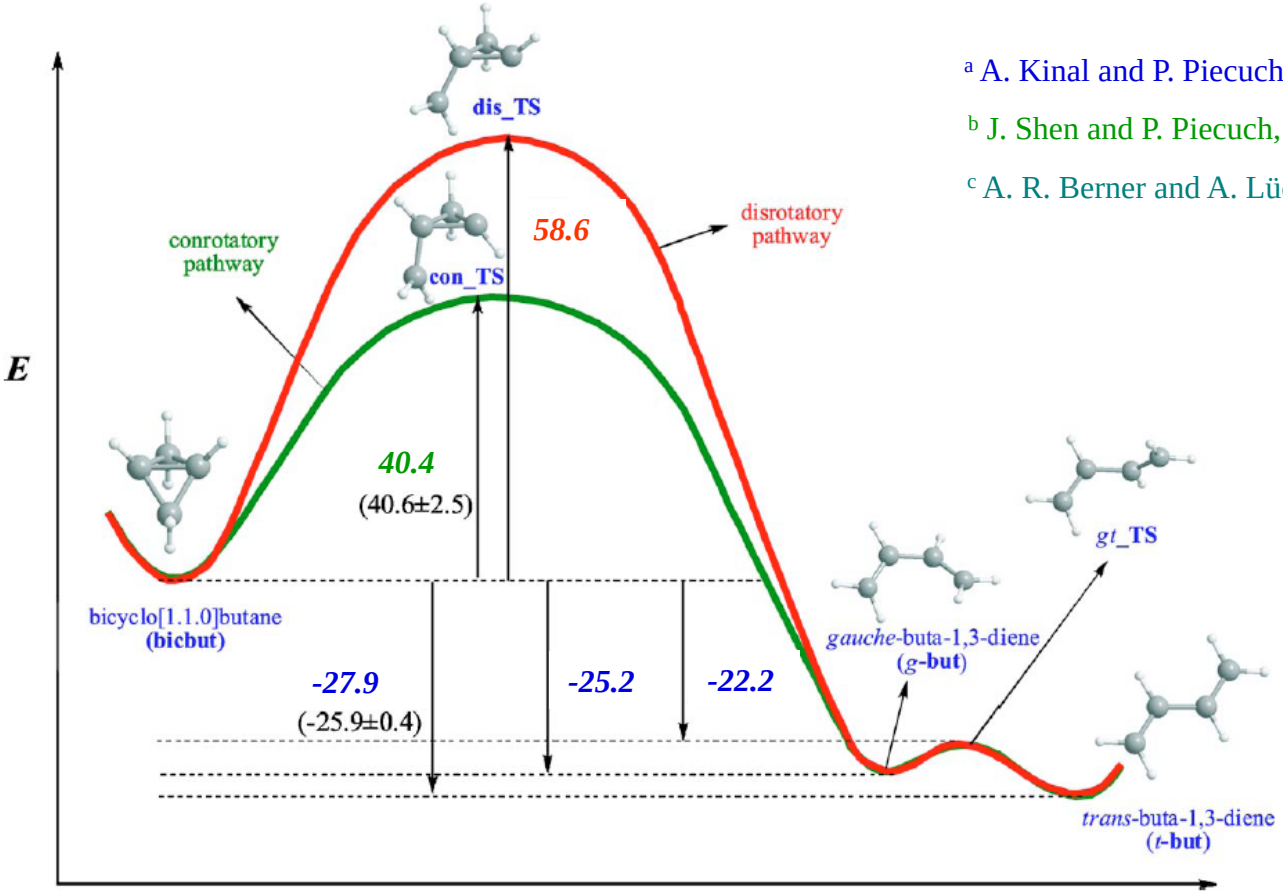
The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]-butane to Butadiene (enthalpies at 0 K in kcal/mol)

	con_TS	dis_TS	g-but	gt_TS	t-but
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)

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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 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.

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QUESTIONS:

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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)]

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.)

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

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

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

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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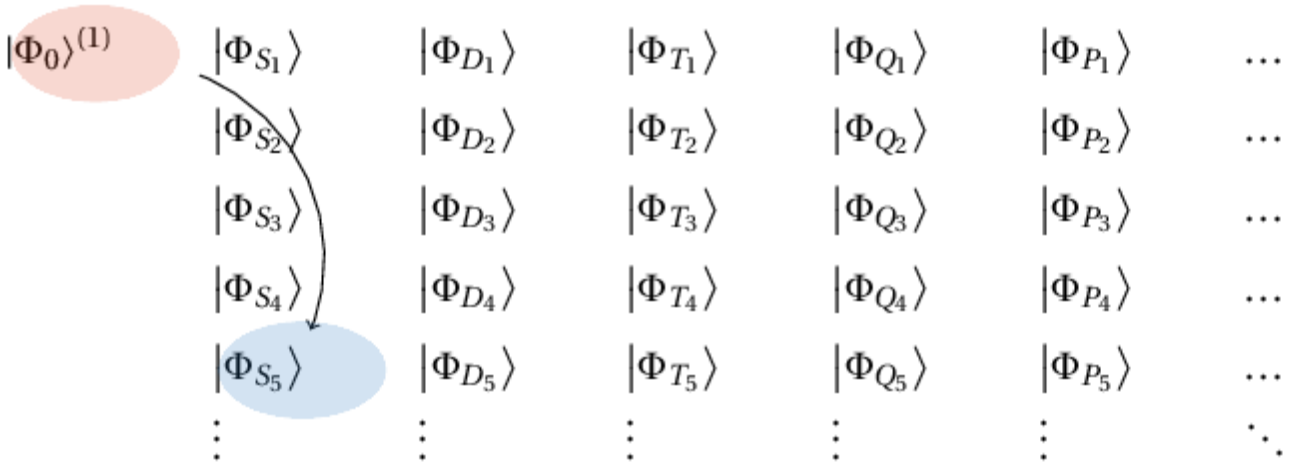

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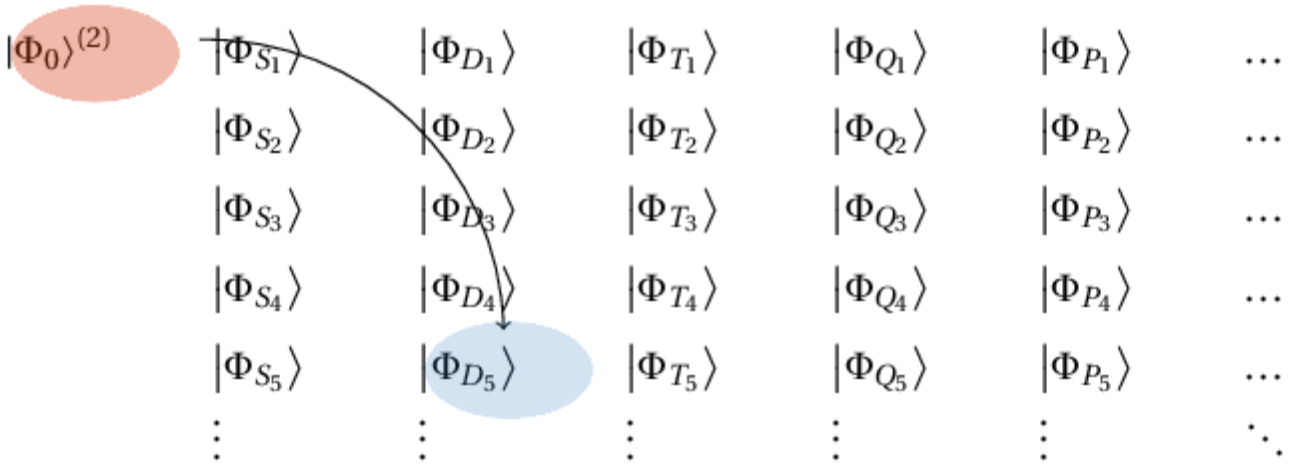

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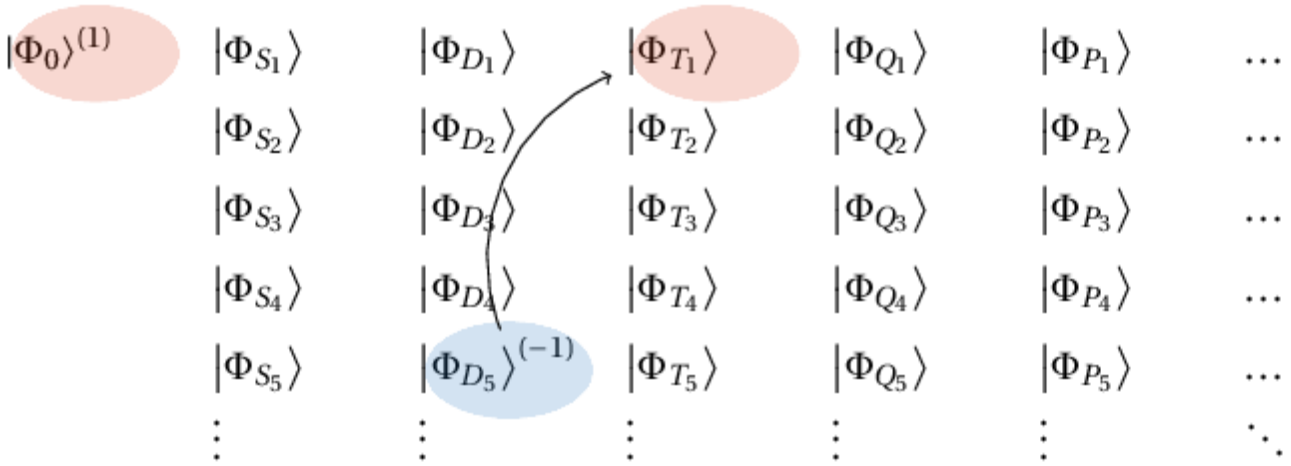

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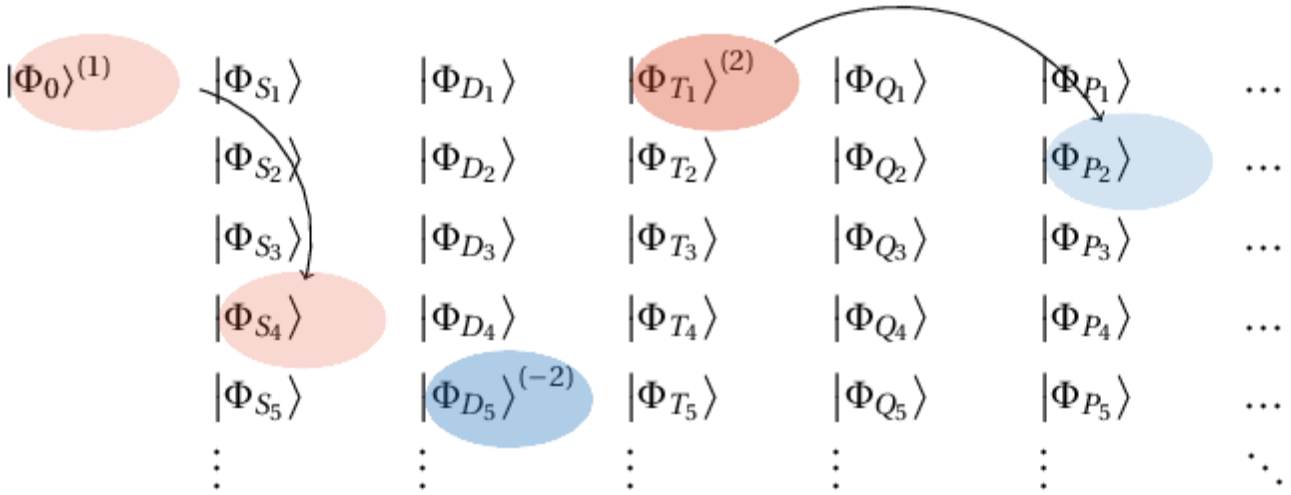

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$$c_K(\tau + \Delta\tau) = c_K(\tau) - \Delta\tau \sum_{L(\neq K)} H_{KL} c_L(\tau)$$

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

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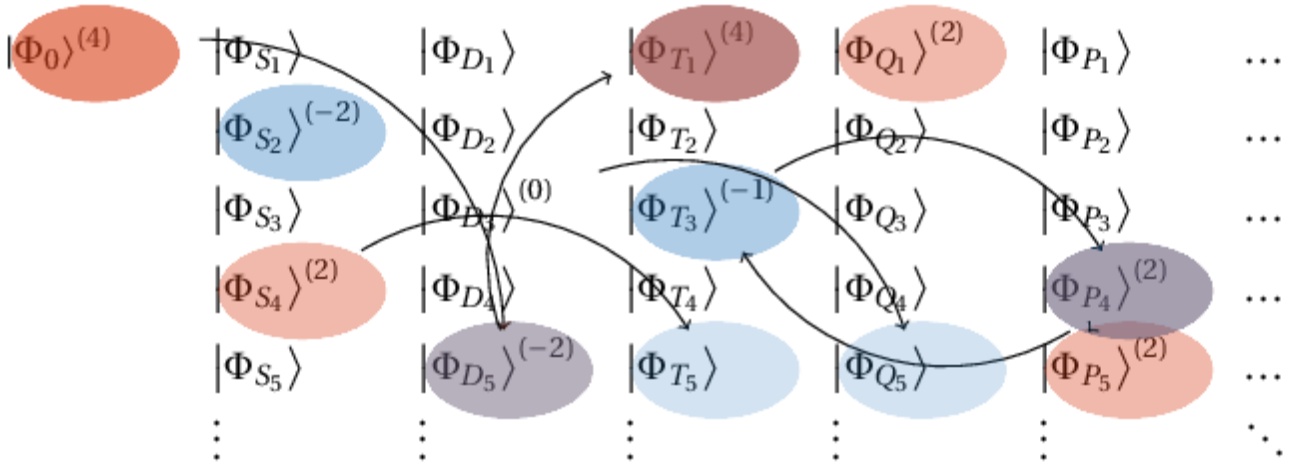

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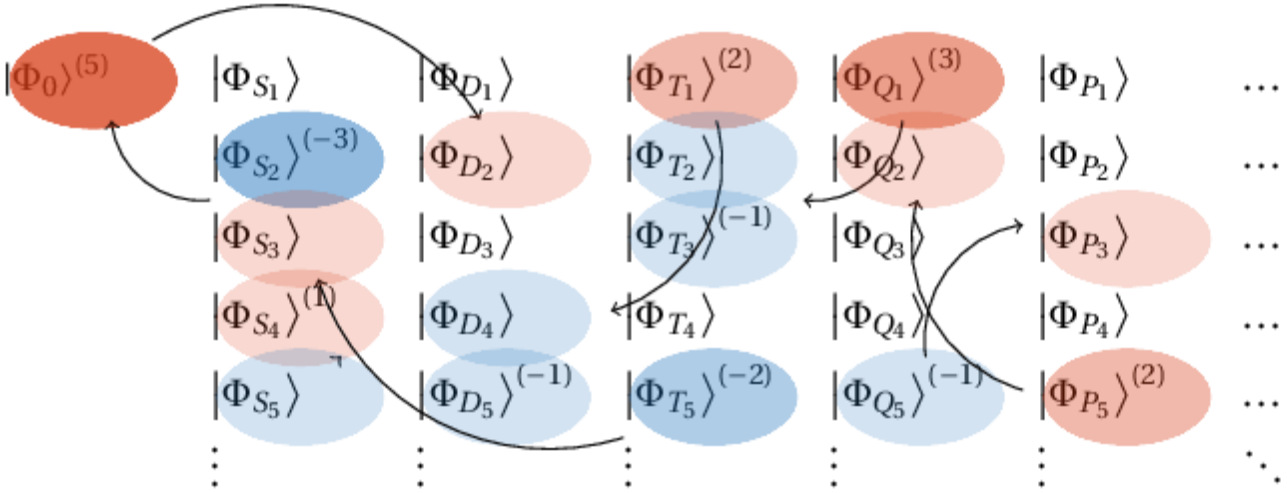

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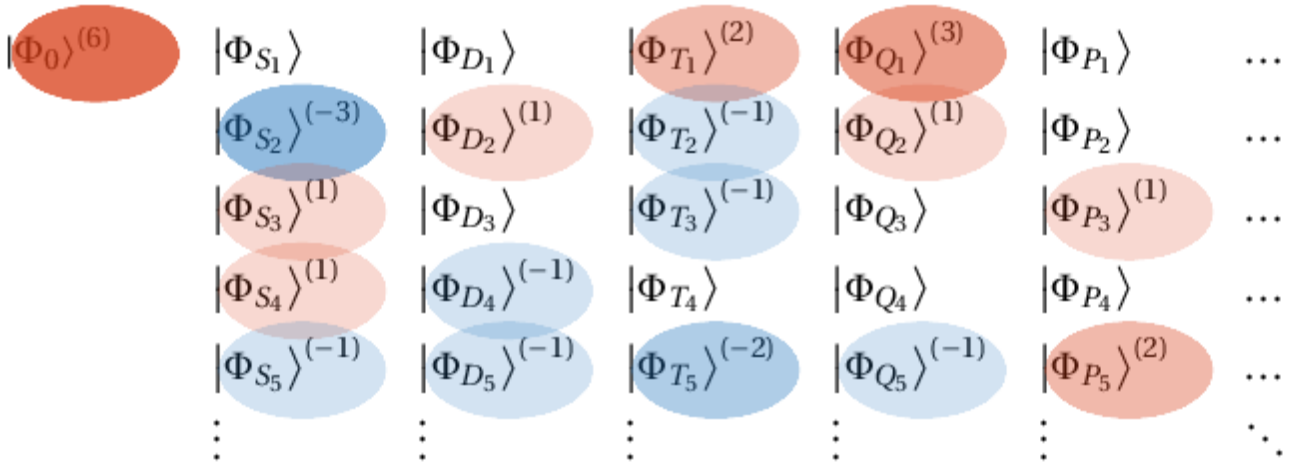

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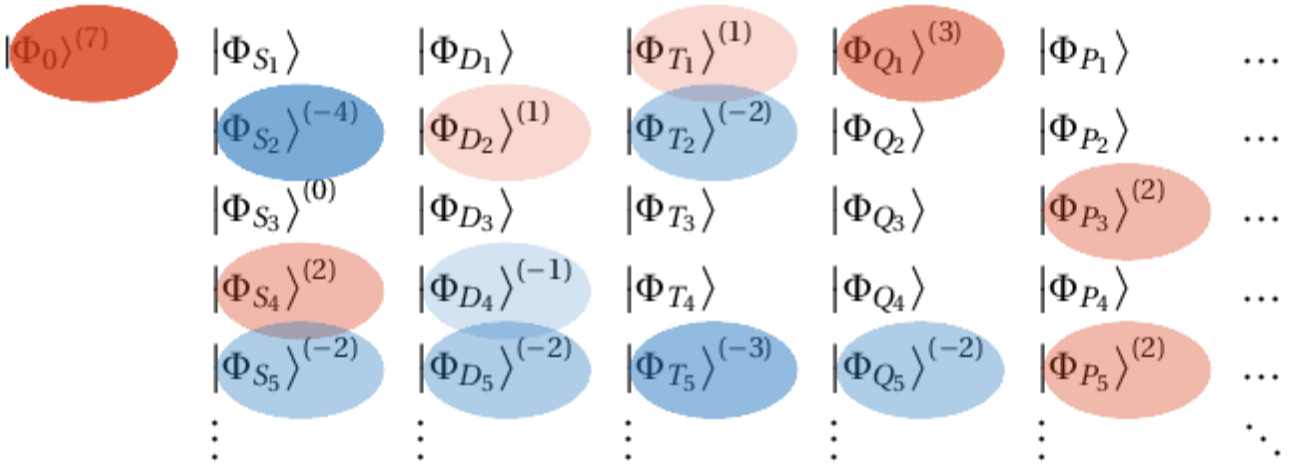

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CCMC (CCSDT-MC, CCSDTQ-MC, etc.)

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)]
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

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[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

[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.

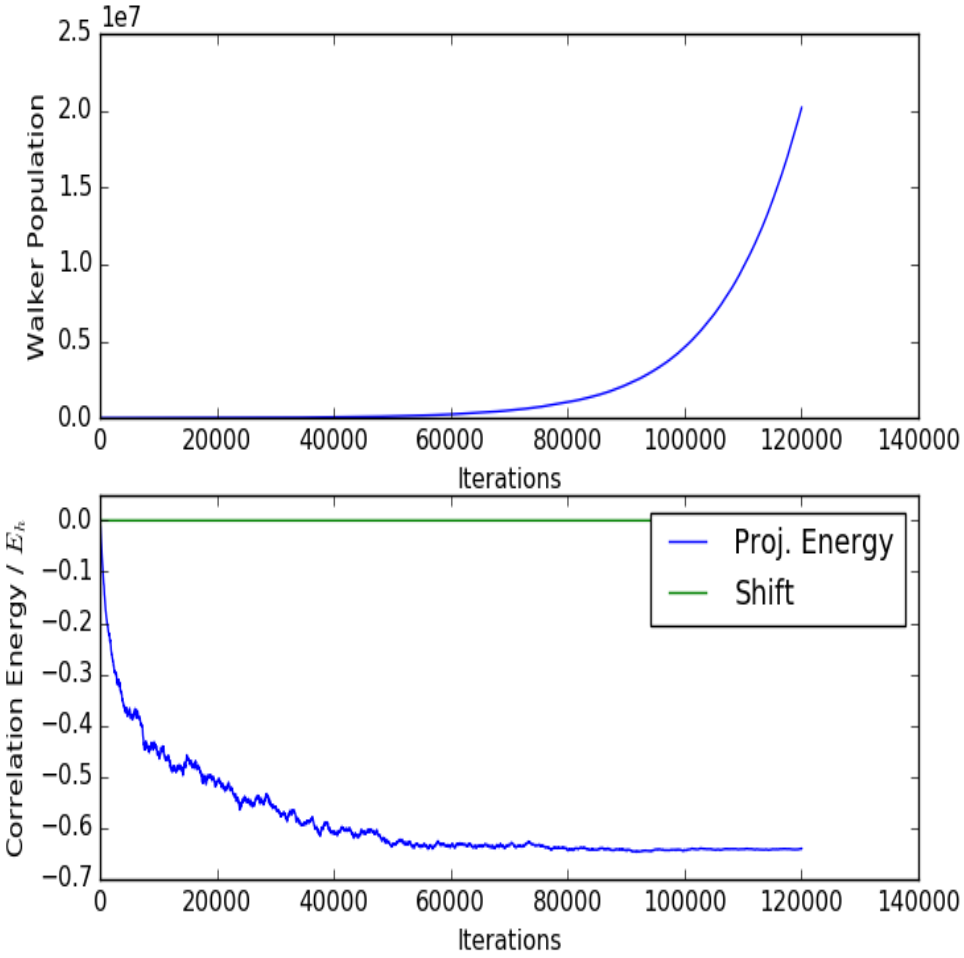
2. Extract a list of the most important determinants or cluster amplitude types relevant to the CC theory of interest (triples for CCSDT; triples and quadruples for CCSDTQ, etc.) from the CIQMC or CCMC propagation at a given time τ to define the *P* space for CC(*P*) calculations as follows:

- **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

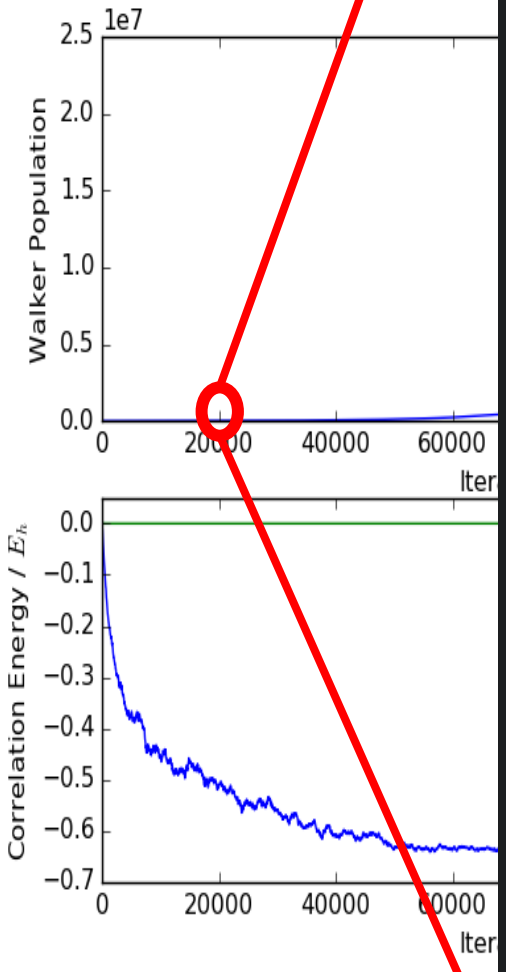
F_2 /cc-pVDZ, $R = 2\,R_e$, *i*-FCIQMC



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

Developing a Stochas

F_2 /cc-pVDZ, R =

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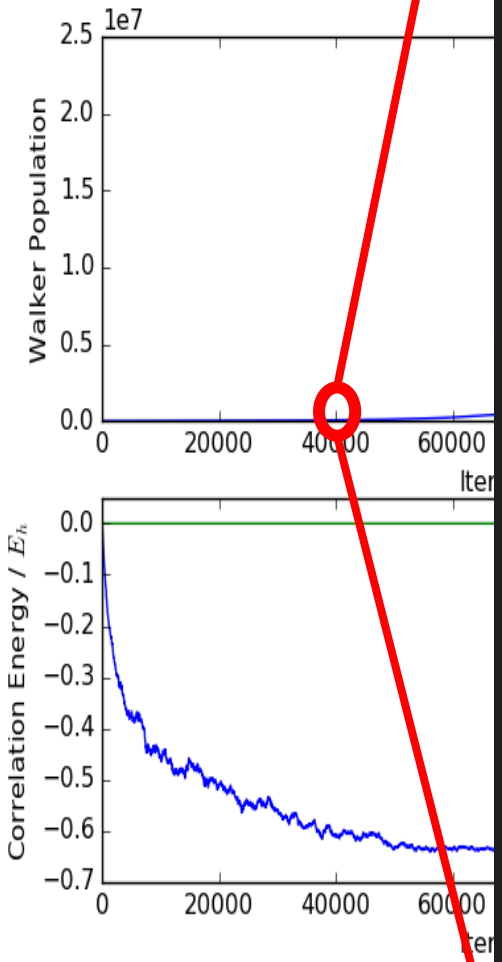
[J.E. Deustua, J. Shen, and P. Piecuch

Developing a Stochas

F_2 /cc-pVDZ, R =



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68	1	1	5	6	7	8	9	10	11	12	13	14	18	19	20
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70	5	1	2	3	4	5	6	7	8	9	10	12	14	15	21
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72	2	2	3	4	5	6	8	9	10	11	12	13	15	16	21
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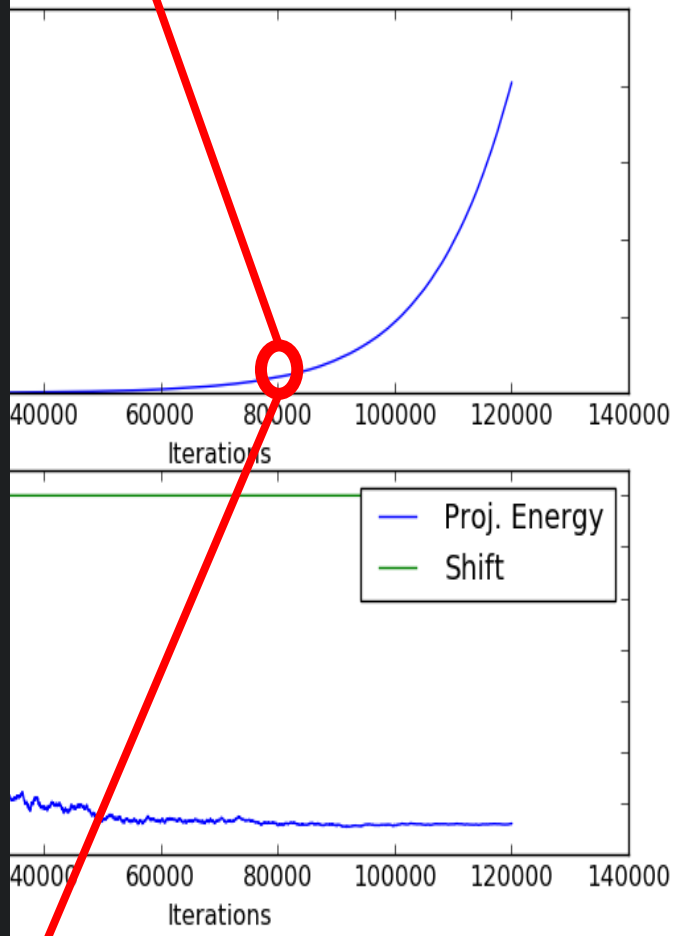
NORMAL walkers-0 unix 〈 utf-8 〈 no ft 0% 50063:9

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

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

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



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14	-33	1	2	3	4	5	6	7	9	10	12	13	14	15	18
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46	-1	1	2	4	5	6	7	8	9	11	12	14	15	16	19
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70	1	2	3	4	6	7	8	9	10	11	12	13	17	18	19
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NORMAL walkers-0 unix 〈 utf-8 〈 n

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

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

VDZ, $R = 2\,R_e$, FCIQMC

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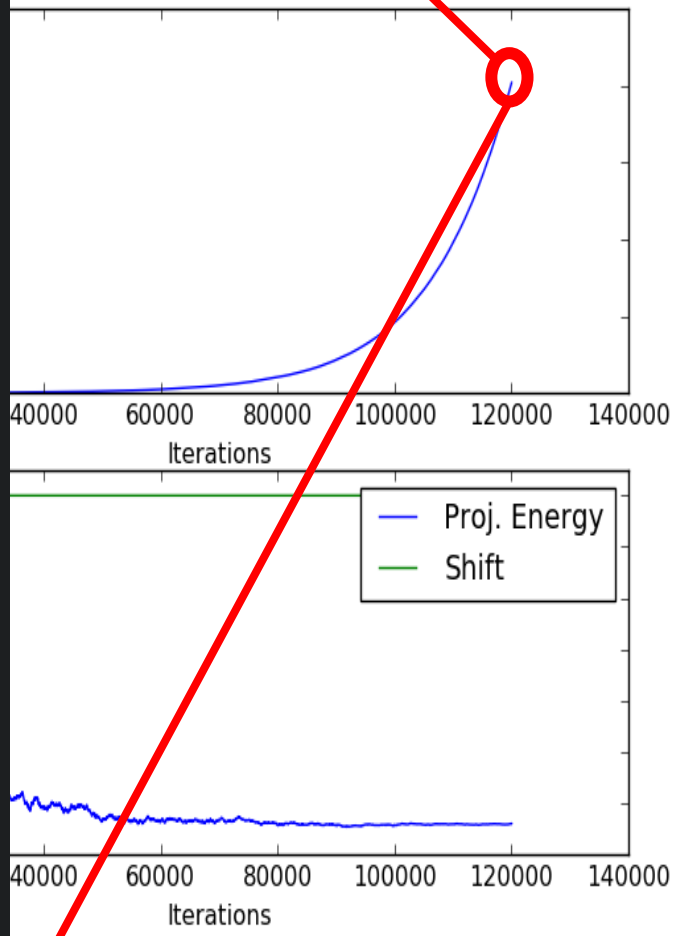

nd P. Piecuch, Phys. Rev. Lett. 119, 223003 (2017)]

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.**
- **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)]

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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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- **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.

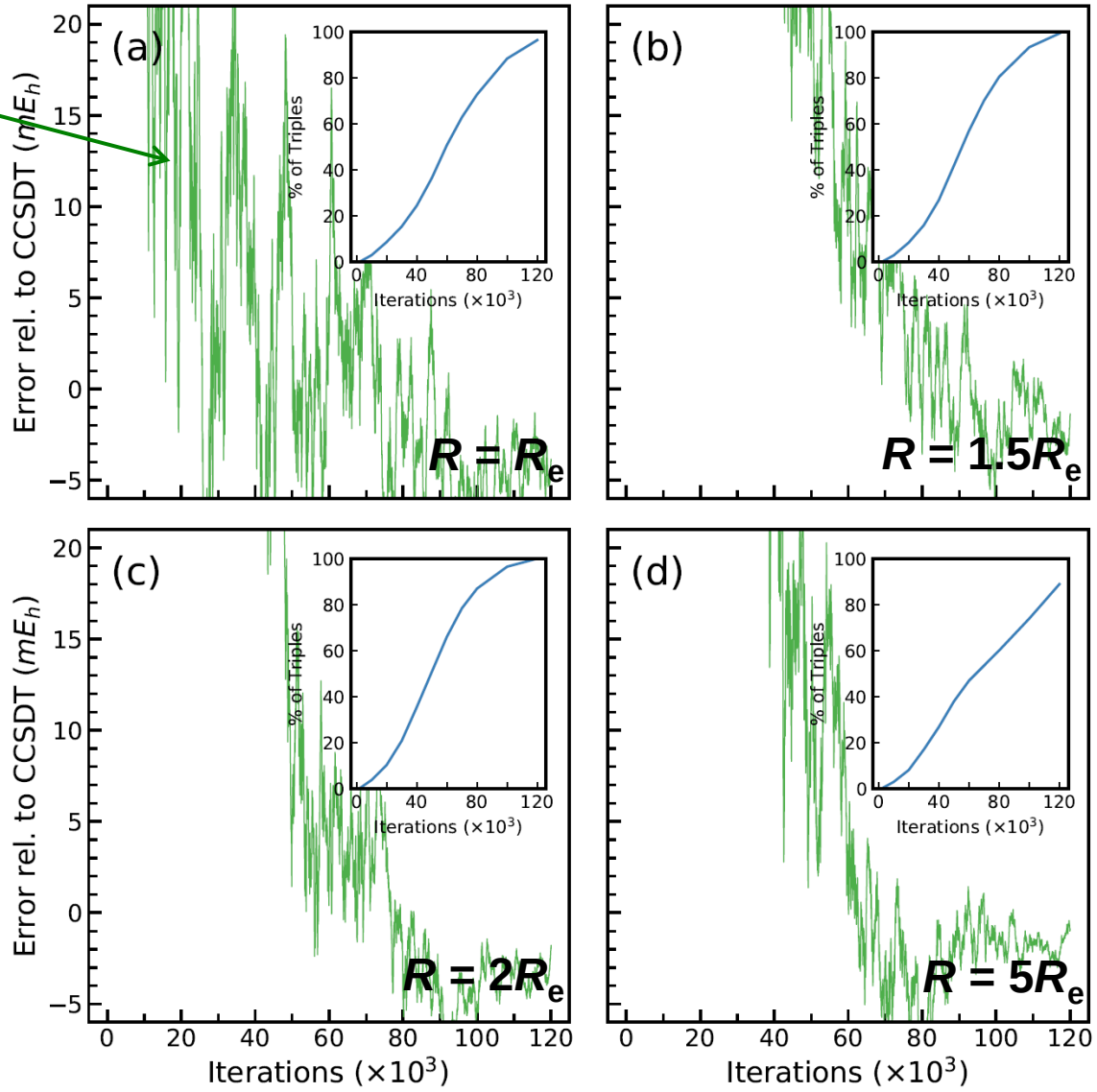
- **if the target approach is CCSDT, use** $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})}$
- **if the target approach is CCSDTQ, use** $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})} + T_4^{(\mathrm{MC})}$

etc.

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

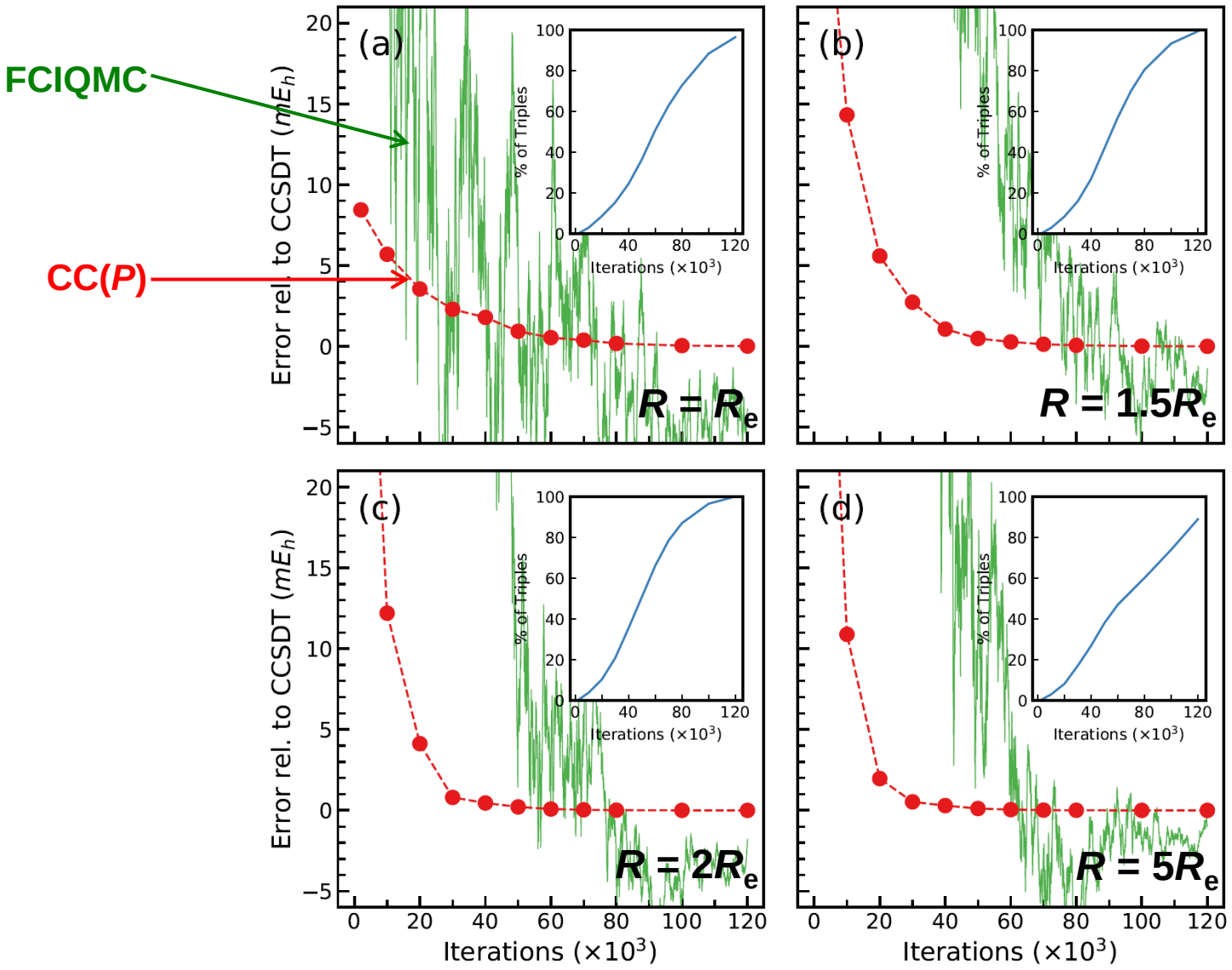
RECOVERING CCSDT ENERGETICS FOR F_2/cc-pVDZ
MONTE CARLO APPROACH = *i*-FCIQMC ($\Delta\tau$ = 0.0001 a.u., n_a = 3)

FCIQMC



[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)]

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** $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})}$
- **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)]

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.

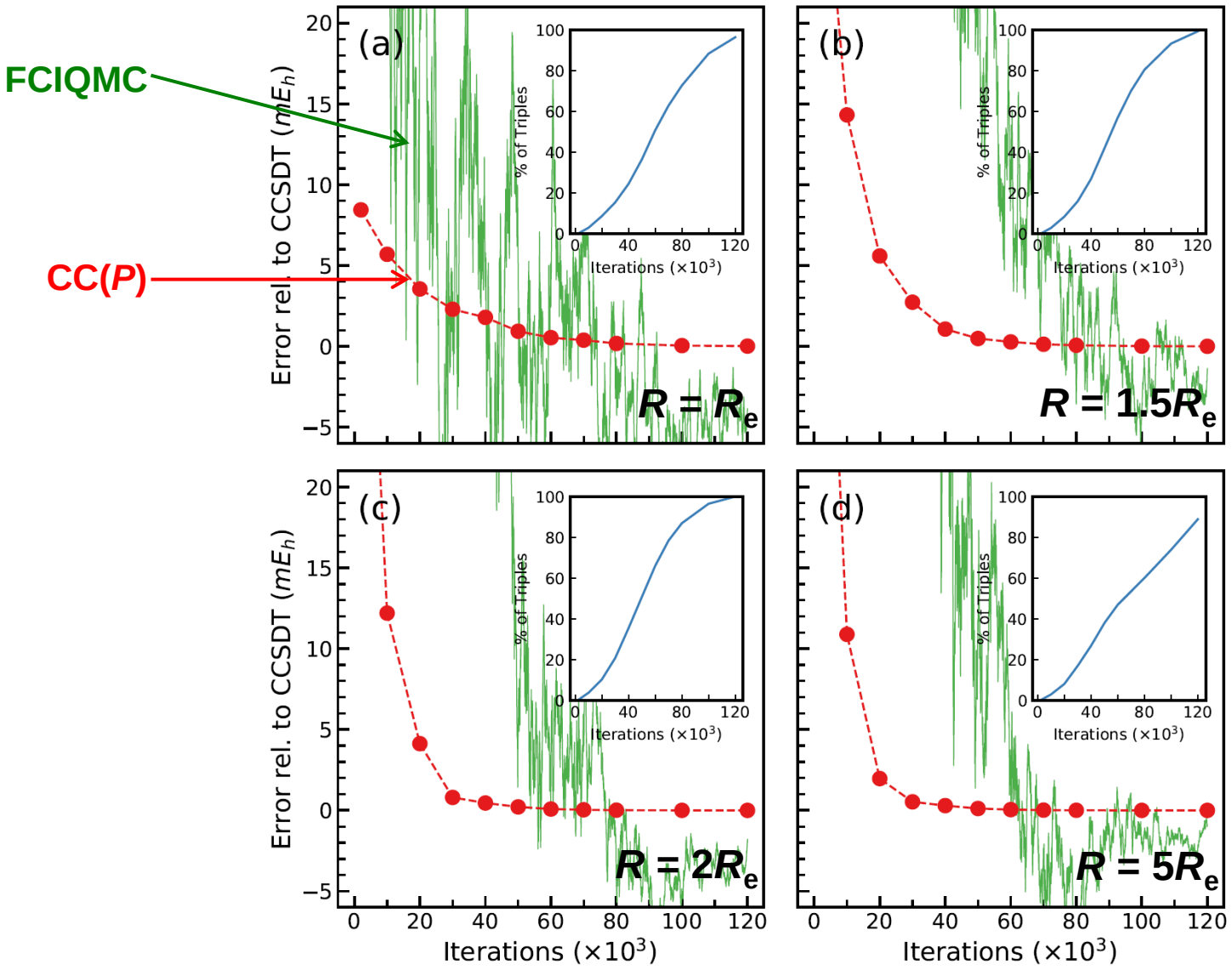
- **if the target approach is CCSDT, use** $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})}$
- **if the target approach is CCSDTQ, use** $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})} + T_4^{(\mathrm{MC})}$

  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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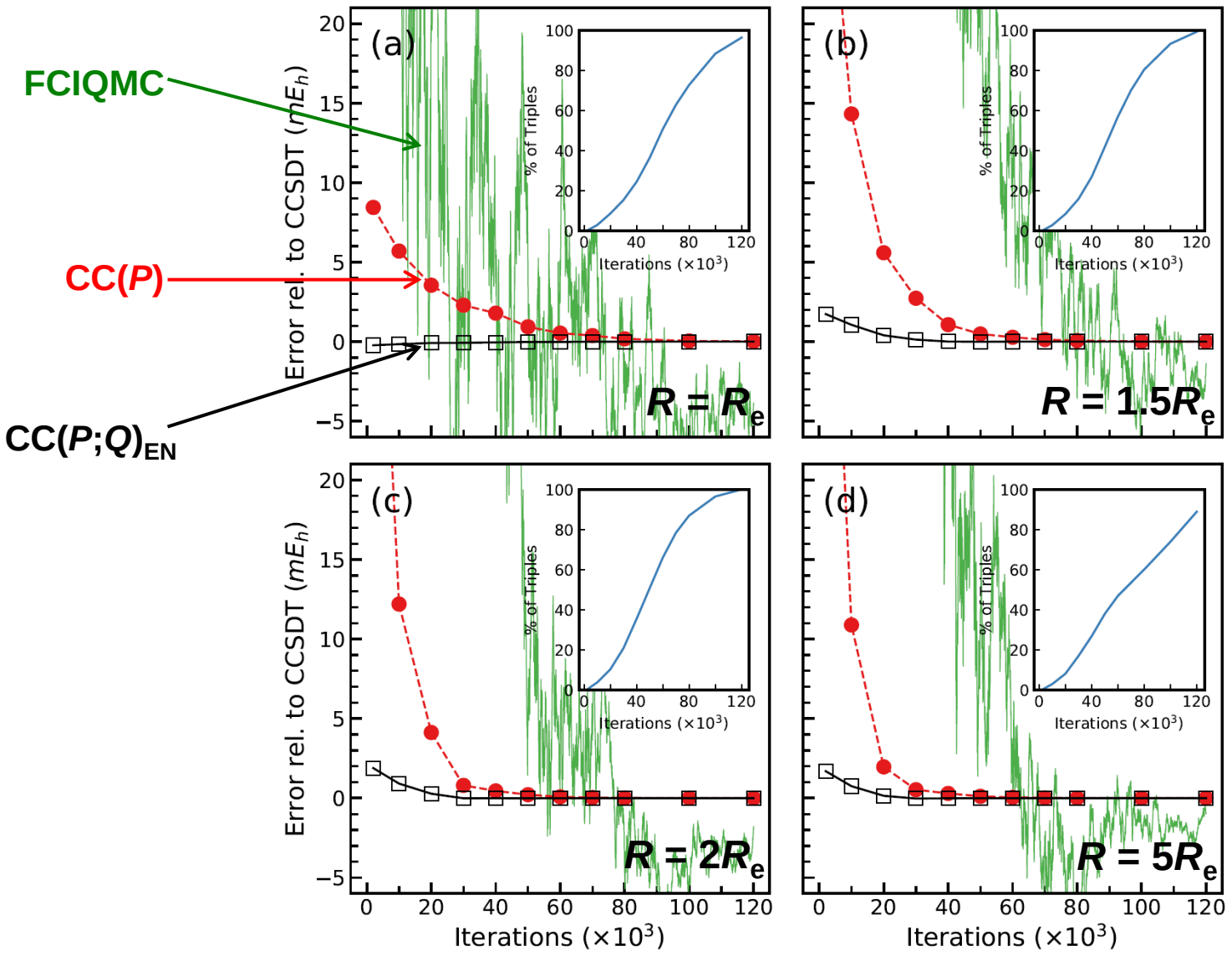
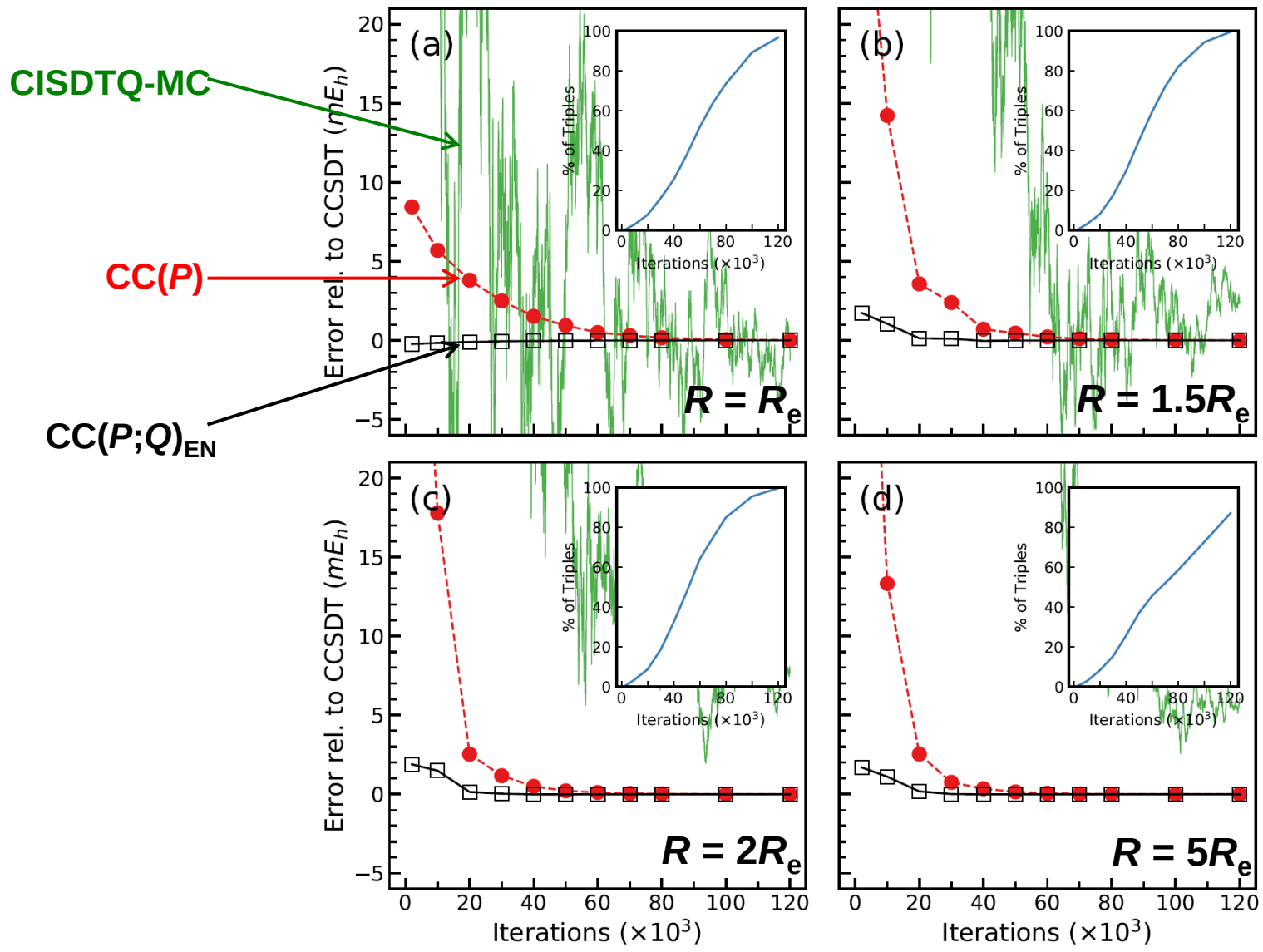


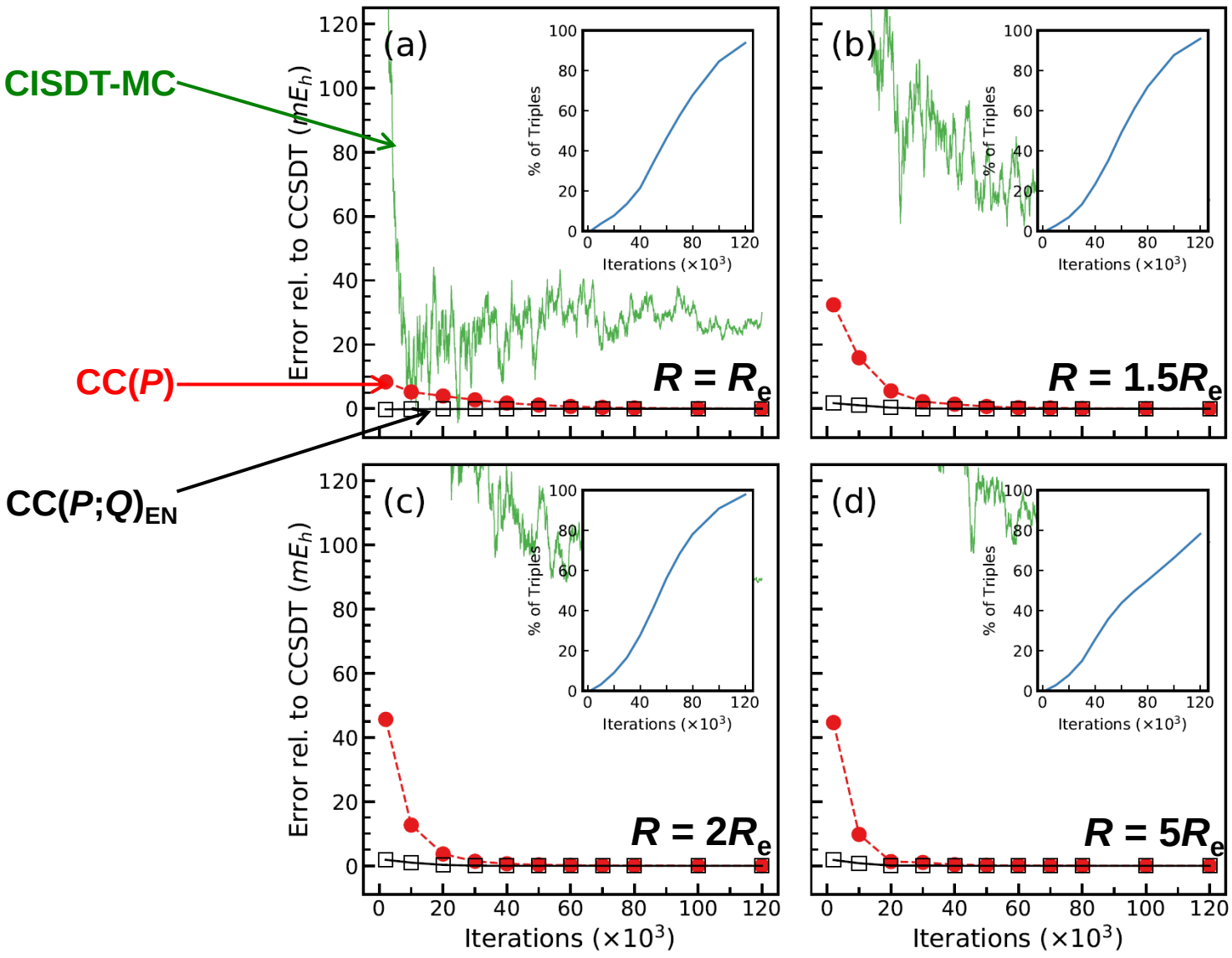
[J.E. Deustua, J. Shen, and P. Piecuch, Phys. Rev. Lett. 119, 223003 (2017)]

RECOVERING CCSDT ENERGETICS FOR F_2/cc-pVDZ
MONTE CARLO APPROACH = *i*-CISDTQ-MC ($\Delta\tau$ = 0.0001 a.u., n_a = 3)



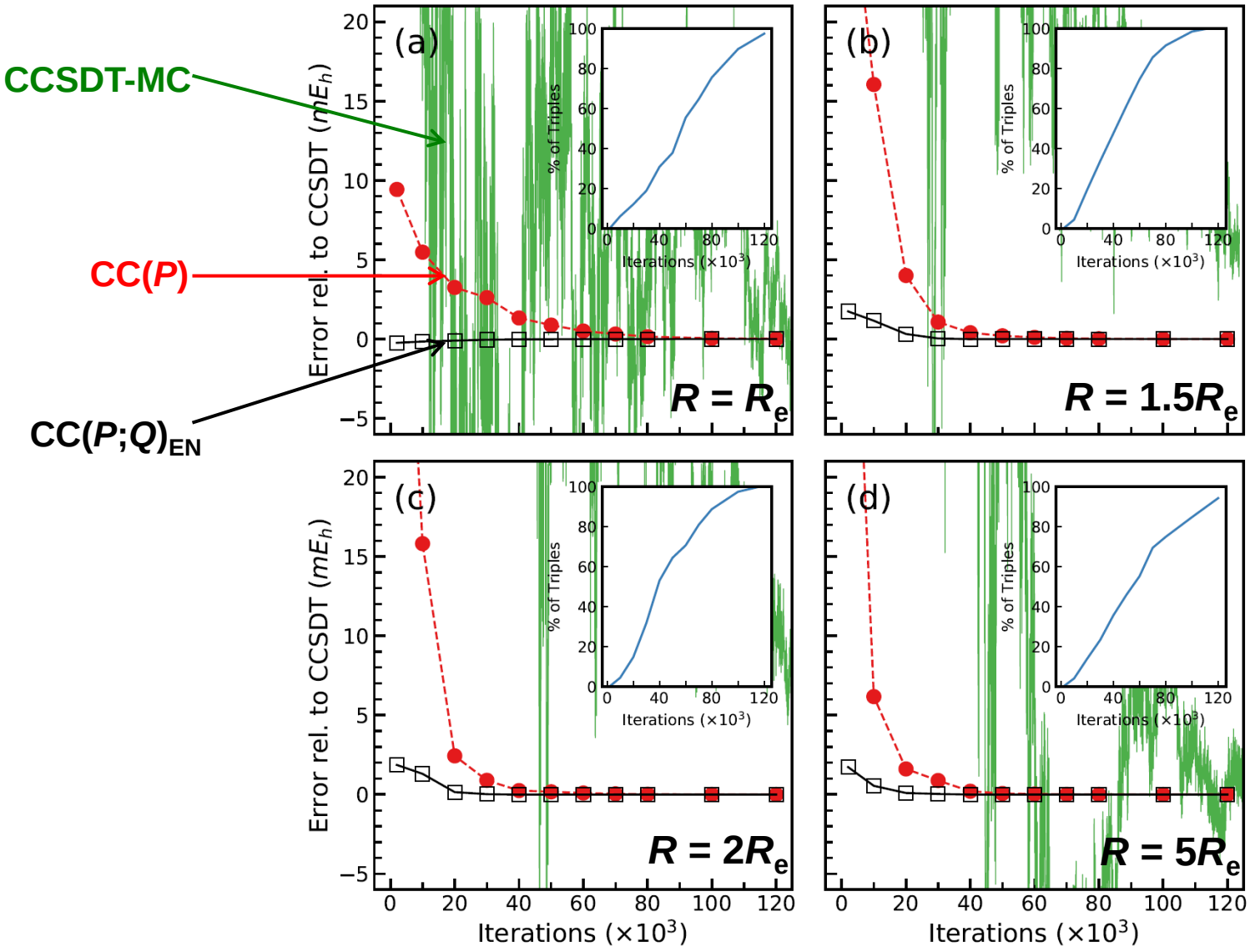
[J.E. Deustua, J. Shen, and P. Piecuch, in preparation]

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

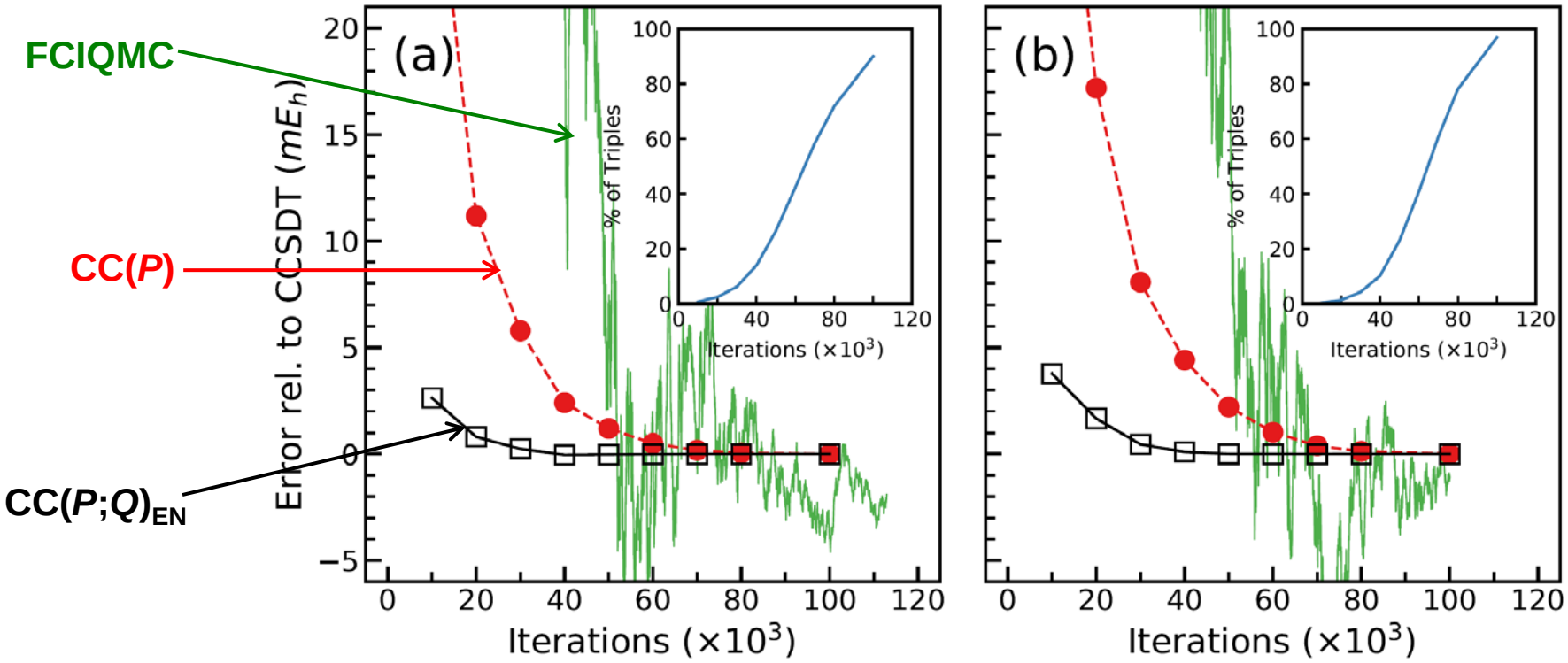
MC Iter.	% of Triples in *P* space	CC(*P*) (mE_h)	CC(*P*;*Q*)$_{MP}$ (mE_h)	CC(*P*;*Q*)$_{EN}$ (mE_h)	Wall Time (s)		
					MC	CC(*P*;*Q*)	Total
0	0	45.638 CCSD	6.357 CCSD(2)$_T$	1.862 CR-CC(2,3)	0	2	2
10,000	3	12.687	2.069	0.978	3	2	5
20,000	9	3.672	0.583	0.280	9	3	12
30,000	17	1.393	0.154	0.030	17	8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

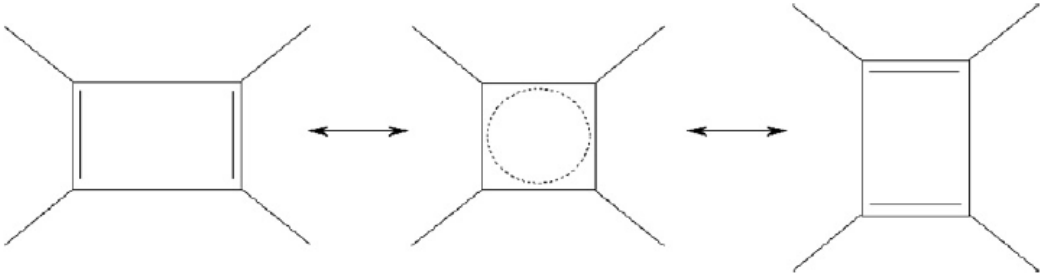
MC Iter.	% of Triples in *P* space	CC(*P*) (mE_h)	CC(*P*;*Q*)$_{MP}$ (mE_h)	CC(*P*;*Q*)$_{EN}$ (mE_h)	Speedup rel. to CCSDT
0	0	65.036 CCSD	9.808 CCSD(2)$_T$	5.595 CR-CC(2,3)	~300
30,000	4	8.065	0.858	0.454	90
40,000	10	4.408	0.330	0.093	30
50,000	23	2.208	0.125	0.002	10
∞	100	-199.253022 E_h			1

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

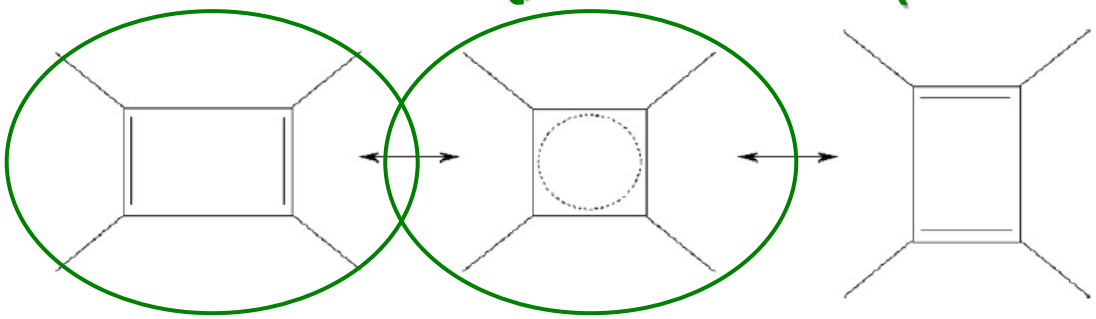
MONTE CARLO APPROACH = *i*-FCIQMC/*i*-CISDT-MC ($\Delta\tau$ = 0.0001 a.u., n_a = 3)



[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

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



Errors relative to CCSDT

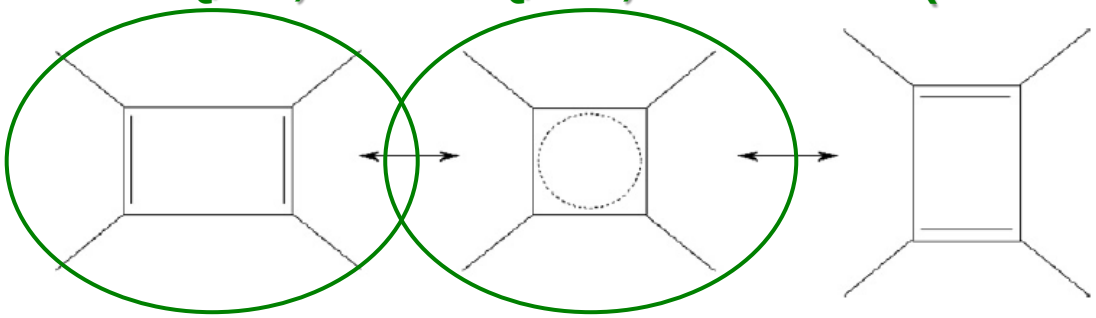
MC Iter.	% of Triples in *P* space	CC(*P*;*Q*)$_{MP}$ (kcal/mol	CC(*P*;*Q*)$_{EN}$ (kcal/mol	Total Wall Time (hrs)		
				MC	CC(*P*;*Q*)	Total
0	0/0	9.6 CCSD(2)$_T$	8.7 CR-CC(2,3)	0/0	0.4/0.4	0.4/0.4
40,000	15-22/14-18	1.5/3.5	1.7/3.5	1.0/0.3	1.9/1.4	2.9/1.7
50,000	31-41/26-34	0.5/1.1	0.6/1.2	3.1/0.7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

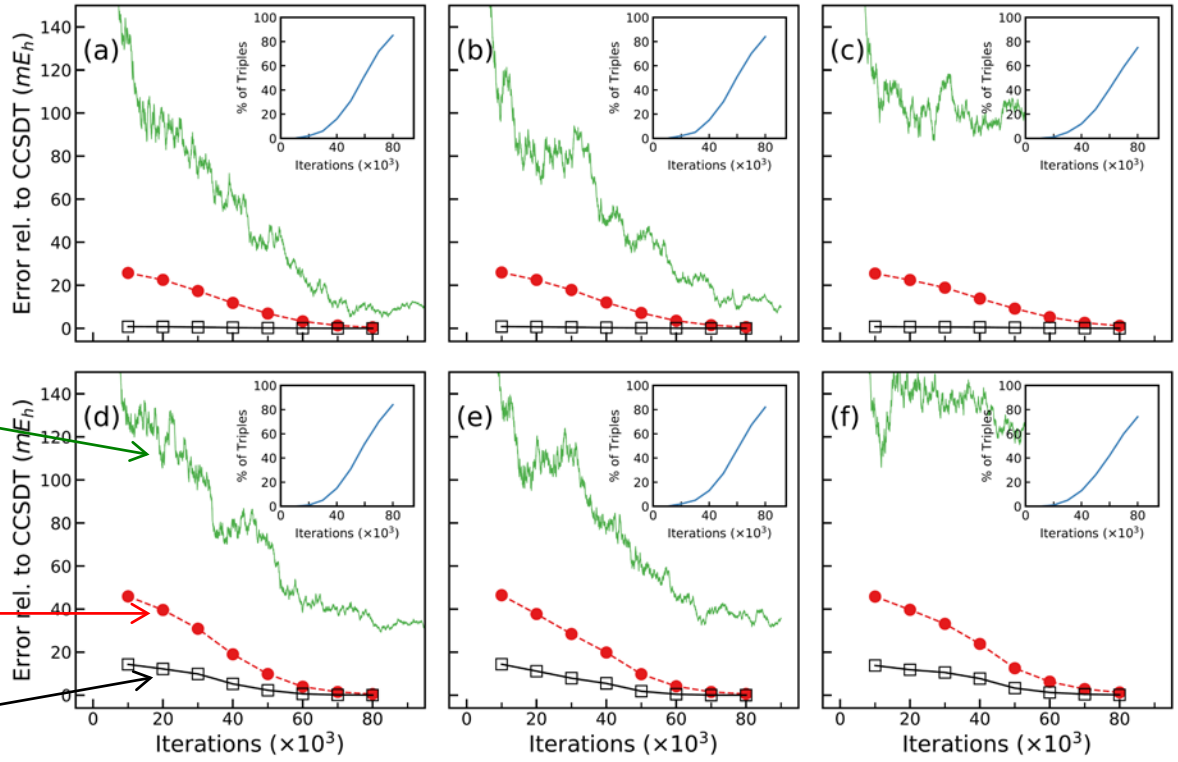
[J.E. Deustua, J. Shen, and P. Piecuch, Phys. Rev. Lett. 119, 223003 (2017); in preparation]

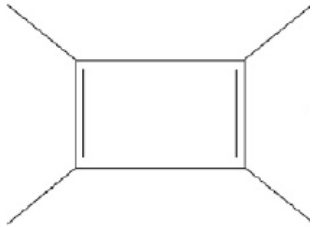
RECOVERING CCSDT ENERGETICS FOR AUTOMERIZATION OF CYCLOBUTADIENE/cc-pVDZ

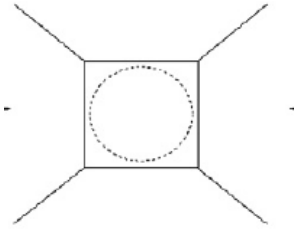
MC APPROACH = *i*-FCIQMC, *i*-CISDTQ-MC, *i*-CISDT-MC ($\Delta\tau$ = 0.0001 a.u., n_a = 3)



MC = FCIQMC | MC = CISDTQ-MC | MC = CISDT-MC







MC

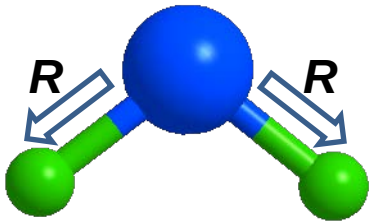
CC(*P*)

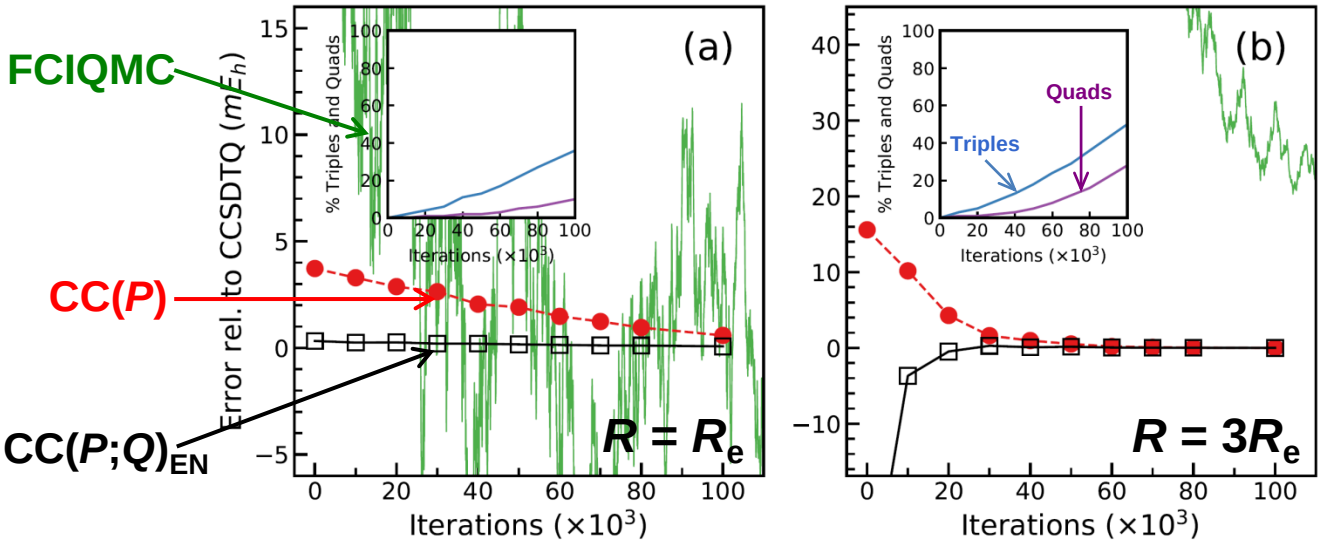
CC(*P*;*Q*)$_{EN}$

[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,

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)

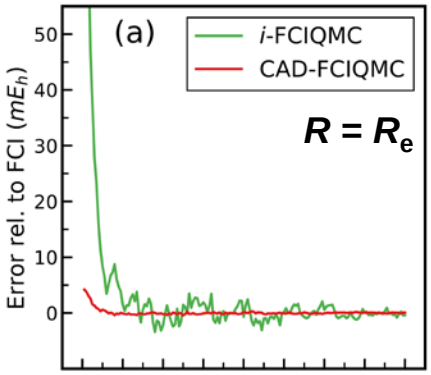
the stochastic CC(*P*;*Q*) formalism is a “game of life, death, and annihilation,” but based on our results one may avoid playing much of it and yet know the outcome.

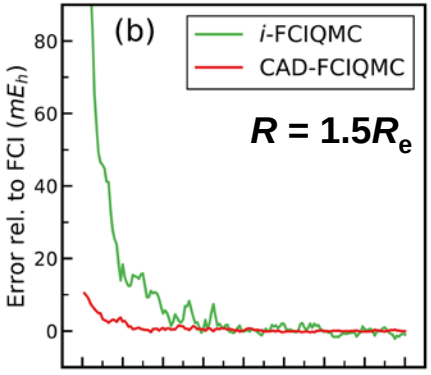
Citing the referee, who reviewed our paper submitted to *Physical Review Letters*:

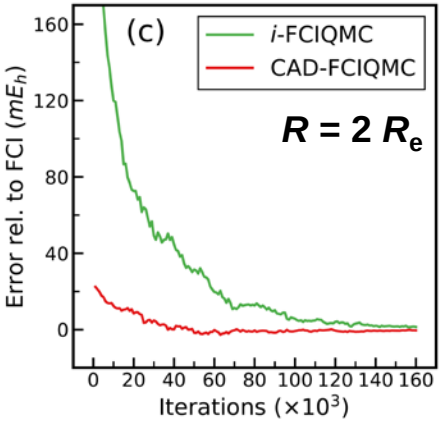
"This is the first work that I've seen where stochastic methods are used to determine what is important, and then deterministic methods are used to solve for the amplitudes of what is important. In this sense, the method is completely original and **OPENS A FULL NEW RESEARCH PARADIGM**. Just because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

WHAT IS NEXT?

Higher-order CC methods, excited states, corrections to FCI, and more … .



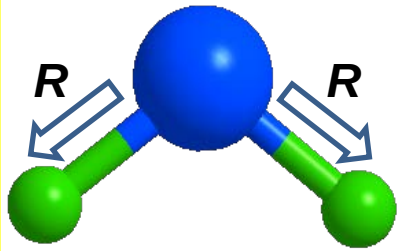




HOW ABOUT ACCELERATING FCIQMC ITSELF?

CAD-FCIQMC

IF YOU WOULD LIKE TO LEARN MORE ABOUT IT, PLEASE JOIN US AT "QUANTUM INTERNATIONAL FRONTIERS 2018" IN CHANGSHA IN OCTOBER!



MC Iters	$R = R_e$		$R = 1.5\ R_e$		$R = 2\ R_e$	
	CAD-FCIQMC	*i*-FCIQMC	CAD-FCIQMC	*i*-FCIQMC	CAD-FCIQMC	*i*-FCIQMC
0	3.744 (CCSD)	217.821 (RHF)	10.043 (CCSD)	269.961 (RHF)	22.032 (CCSD)	363.954 (RHF)
10,000	0.611	8.381	3.335	45.802	12.351	119.896
20,000	-0.073	1.596	2.597	18.345	8.485	72.650
30,000	-0.175	0.586	0.473	15.937	4.794	49.203
40,000	-0.211	-2.217	0.873	4.855	0.138	44.627
50,000	-0.440	1.456	1.310	3.247	-1.693	31.448
60,000	-0.046	1.911	0.501	0.588	-0.225	19.660
70,000	-0.235	0.302	0.685	0.811	-0.377	11.333
80,000	0.189	-0.686	0.063	-0.128	-0.425	12.611
90,000	-0.177	-0.981	-0.171	0.014	-1.657	10.089
100,000	-0.036	0.139	-0.302	1.956	-0.816	5.680
110,000	0.129	-0.710	-0.189	1.088	-0.580	4.797
120,000	-0.035	0.597	0.020	-0.241	-0.555	4.041
130,000	0.086	-0.503	-0.020	-0.720	-1.166	3.107
140,000	0.098	0.080	-0.084	0.497	-0.666	1.981
150,000	-0.055	0.308	-0.156	0.990	-0.620	1.630
160,000	0.078	-0.400	-0.059	-1.002	-0.434	1.328
∞	-76.241860 (FCI)		-76.072348 (FCI)		-75.951665 (FCI)	

[J.E. Deustua, I. Magoulas, J. Shen, and P. Piecuch, J. Chem. Phys., submitted (2018)]

THANK YOU

Emiliano Deustua Jun Shen Ilias Magoulas



"Algebraic and Diagrammatic Methods for Many-Fermion Systems"

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

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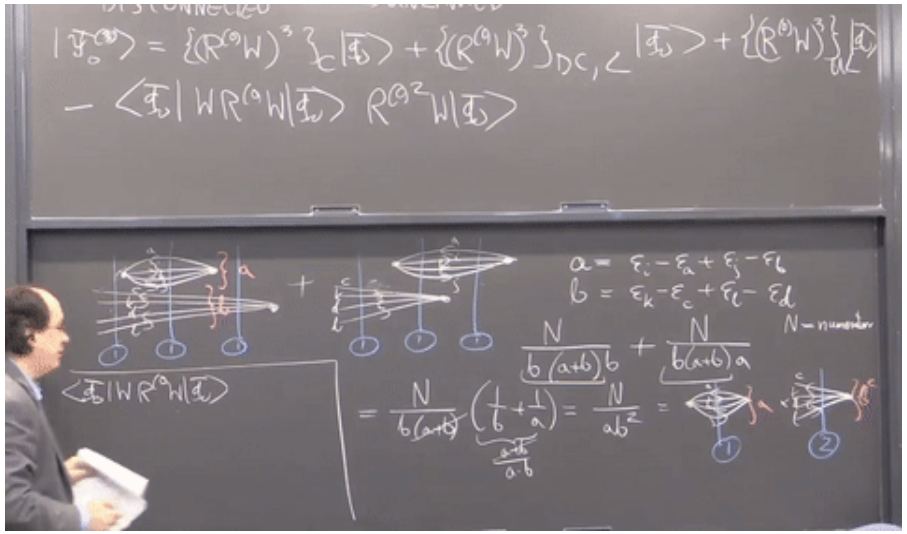
YouTube



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