

SINGLE-REFERENCE COUPLED-CLUSTER METHODS FOR MULTI-REFERENCE MOLECULAR PROBLEMS



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GÅMESS



Nordita Program on “Computational Challenges in Nuclear and Many-Body Physics,”
Stockholm, Sweden, September 15 – October 10, 2014

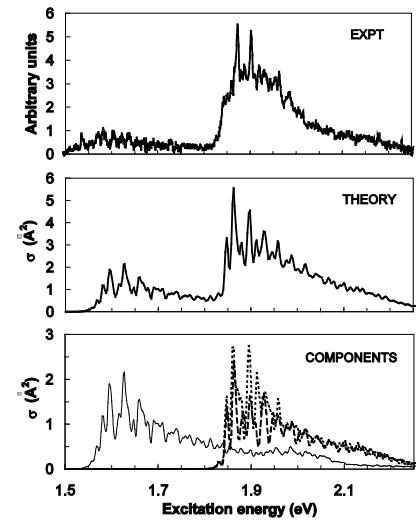
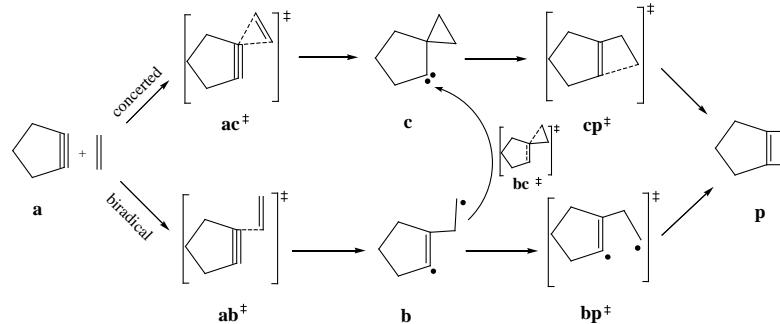
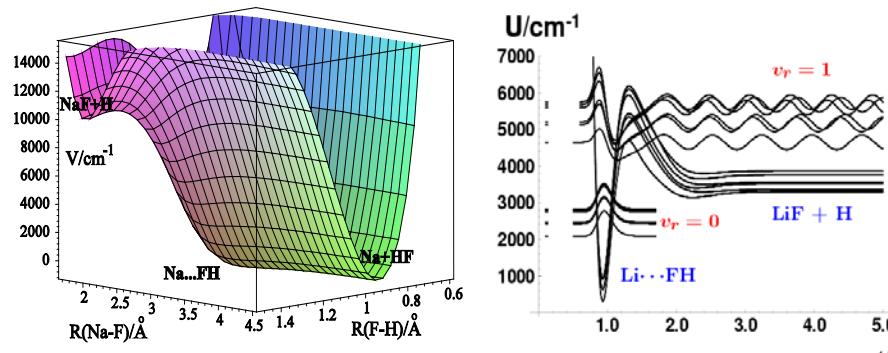
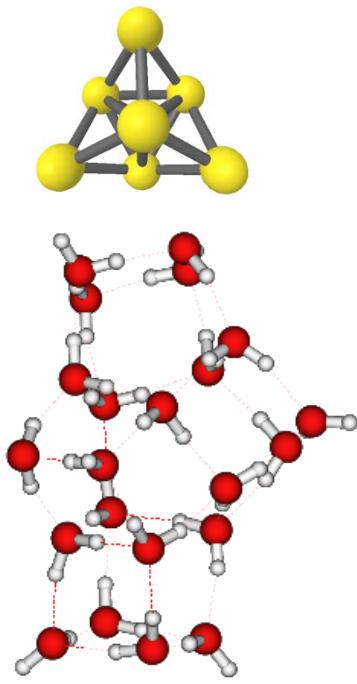
MANY THANKS TO PROFESSORS ALEXANDER BALATSKY, JORGE DUKELSKY,
ROBERTO LIOTTA, AND CHONG QI FOR INVITATION AND WARM HOSPITALITY

THE ELECTRONIC SCHRÖDINGER EQUATION

$$H_e \Psi_K(\mathbf{X}; \mathbf{R}) = E_K(\mathbf{R}) \Psi_K(\mathbf{X}; \mathbf{R})$$

$$H_e = Z + V = \sum_{i=1}^N z(\mathbf{x}_i) + \sum_{i>j=1}^N v(\mathbf{x}_i, \mathbf{x}_j)$$

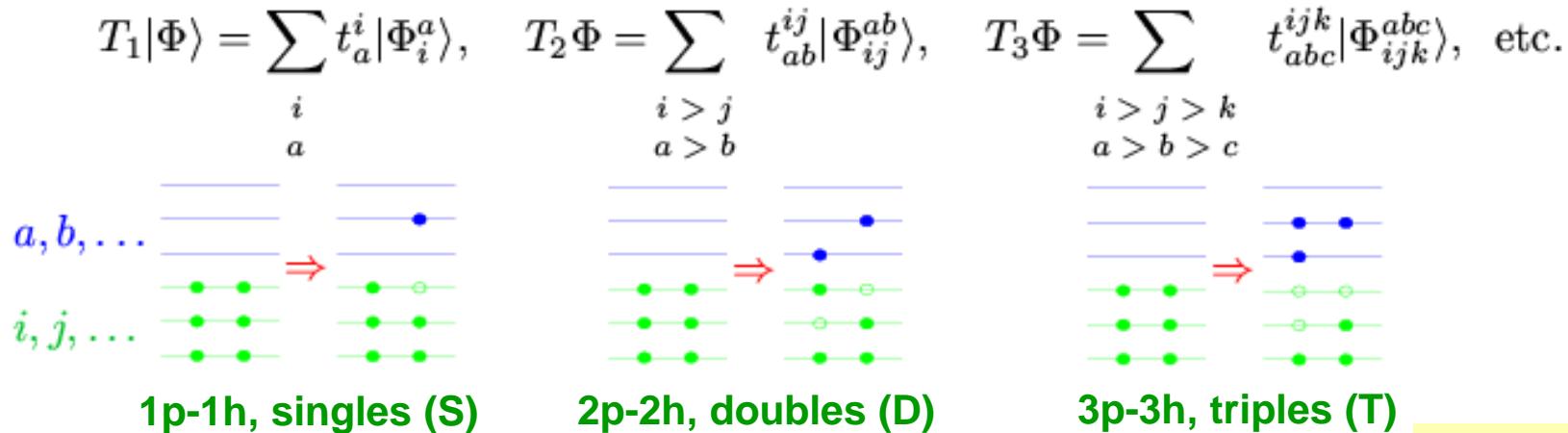
$$z(\mathbf{x}_i) = -\frac{1}{2}\Delta_i + \sum_{A=1}^M \frac{Z_A}{R_{Ai}}, \quad v(\mathbf{x}_i, \mathbf{x}_j) = \frac{1}{r_{ij}}$$



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)

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



$m_A = N \Rightarrow$ exact theory, $m_A < N \Rightarrow$ approximations

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

$$m_A = 3 \quad T = T_1 + T_2 + T_3$$

$$m_A = 4 \quad T = T_1 + T_2 + T_3 + T_4$$

CCSD

CCSDT

CCSDTQ

$$n_o^2 n_u^4 (n_o^2 n_u^2)$$

$$n_o^3 n_u^5 (n_o^3 n_u^3)$$

$$n_o^4 n_u^6 (n_o^4 n_u^4)$$

CPU time
scaling with the
system size

← iterative N^6

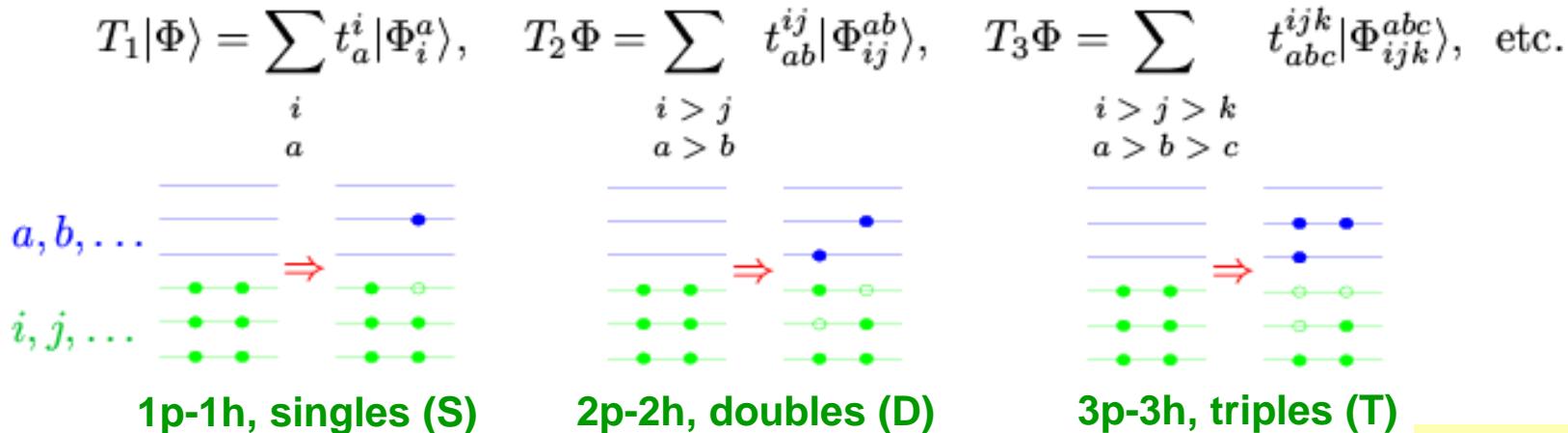
← iterative N^8

← iterative N^{10}

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$m_A = 2$	$T = T_1 + T_2$	CCSD	$n_o^2 n_u^4 (n_o^2 n_u^2)$
$m_A = 3$	$T = T_1 + T_2 + T_3$	CCSDT	$n_o^3 n_u^5 (n_o^3 n_u^3)$
$m_A = 4$	$T = T_1 + T_2 + T_3 + T_4$	CCSDTQ	$n_o^4 n_u^6 (n_o^4 n_u^4)$

CPU time scaling with the system size

← iterative N^6

← iterative N^8

← iterative N^{10}

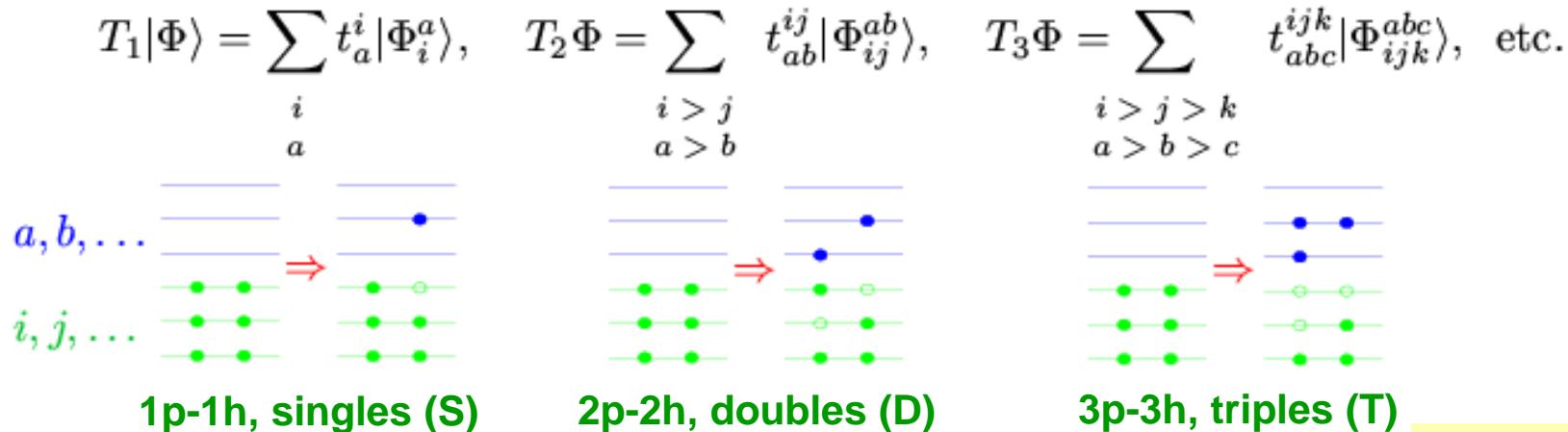
$$\langle \Phi_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k} | \left(H_N e^{T^{(A)}} \right)_C | \Phi \rangle = 0, \quad k = 1 \dots, m_A$$

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

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CCSD

$n_o^2 n_u^4$ ($n_o^2 n_u^2$)

CCSDT

$n_o^3 n_u^5$ ($n_o^3 n_u^3$)

CCSDTQ

$n_o^4 n_u^6$ ($n_o^4 n_u^4$)

CPU time scaling with the system size

← iterative N^6

← iterative N^8

← iterative N^{10}

To reduce prohibitive computer costs of CCSDT, CCSDTQ, etc., one usually approximates T_3 , T_4 , etc. This can be done through, e.g., non-iterative corrections to CCSD energies, as in the CCSD(T), CCSD(TQ), etc. approximations.

← iterative N^6 plus non-iterative N^7 or N^9

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)

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

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

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

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

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

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

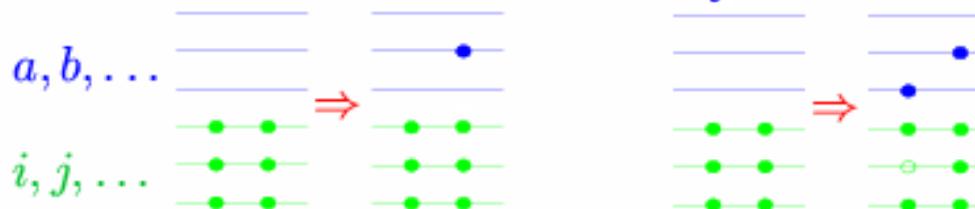
Higher-order methods: EOMCCSDT, EOMCCSDTQ, EOMCCSD(T), etc.

Electron-Attached (EA) and Ionized (IP) EOMCC Methods

$$|\Psi_{\mu}^{(N\pm 1)}\rangle = R_{\mu}^{(N\pm 1)}|\Psi_0\rangle, \quad R_{\mu}^{(N+1)} = \sum_{n=0}^{M_R} R_{\mu,(n+1)p-nh}, \quad R_{\mu}^{(N-1)} = \sum_{n=0}^{M_R} R_{\mu,(n+1)h-np}$$

EA

$$R_{\mu,1p} = \sum_a r_a |\Phi^a\rangle, \quad R_{\mu,2p-1h} = \sum_{\substack{a < b \\ j}} r_{ab}^j |\Phi_{j-1}^{ab}\rangle, \quad etc.$$



IP

$$R_{\mu,1h} = \sum_i r^i |\Phi_i\rangle, \quad R_{\mu,2h-1p} = \sum_{i < j} r_{ij}^b |\Phi_{ij}^b\rangle, \quad etc.$$



Solve the Eigenvalue Problem

$$(\bar{H}_{N,\text{open}} R_{\mu}^{(N\pm 1)})_C |\Phi\rangle = \omega_{\mu}^{(N\pm 1)} R_{\mu}^{(N\pm 1)} |\Phi\rangle,$$

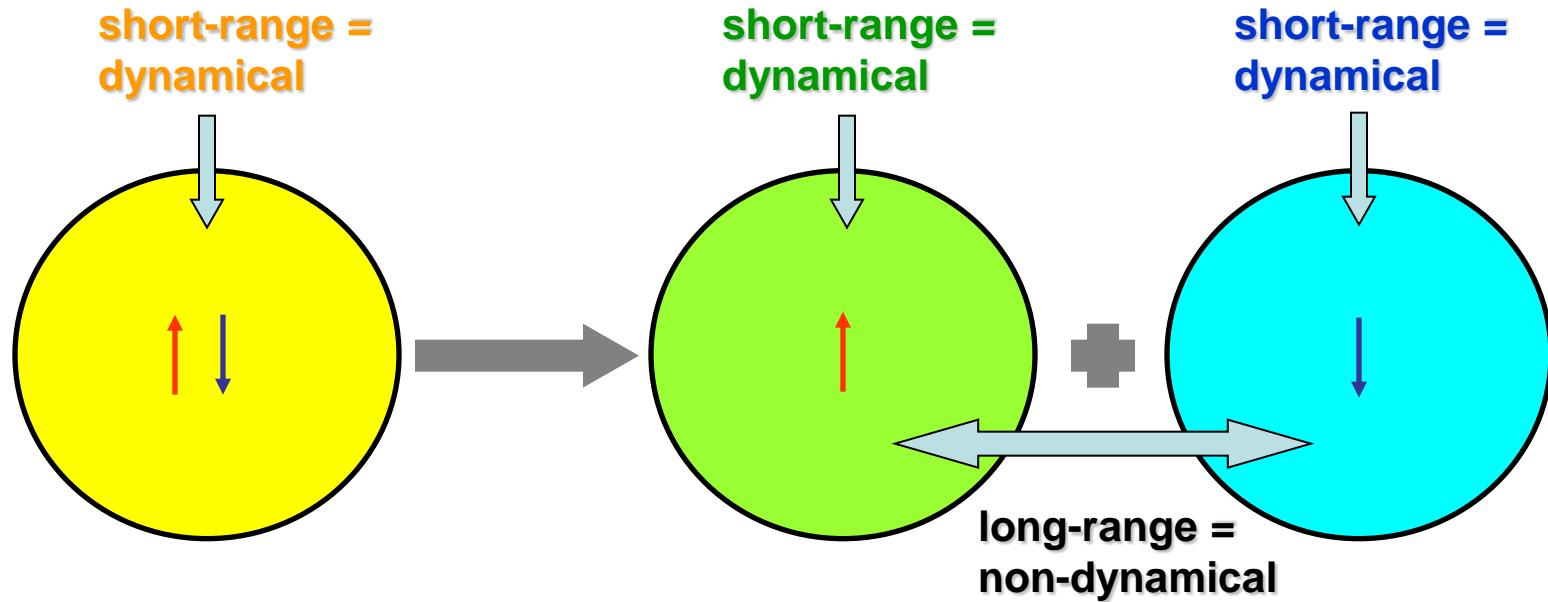
$$\omega_{\mu}^{(N+1)} = E_{\mu}^{(N+1)} - E_0^{(N)}, \quad \omega_{\mu}^{(N-1)} = E_{\mu}^{(N-1)} - E_0^{(N)}$$

M. Nooijen and R.J. Bartlett, 1995; R.J. Bartlett and J.F. Stanton, 1994; M. Nooijen and J.G. Snijders, 1992-1993; J.F. Stanton and J. Gauss, 1994; ...

CHALLENGES IN COUPLED-CLUSTER THEORY (IN FACT, IN ALL *AB INITIO* ELECTRONIC STRUCTURE APPROACHES)

- * Reaction pathways involving bond breaking, biradicals, energy gaps in magnetic systems, electronic excitations dominated by two-electron transitions, ... (**generally, multi-reference problems, systems with strong non-dynamical correlations**).
- * Steep increase of computer costs with the system size (typically, CPU steps and memory requirements that scale as N^6 - N^7 and N^4 , respectively, with the system size N).

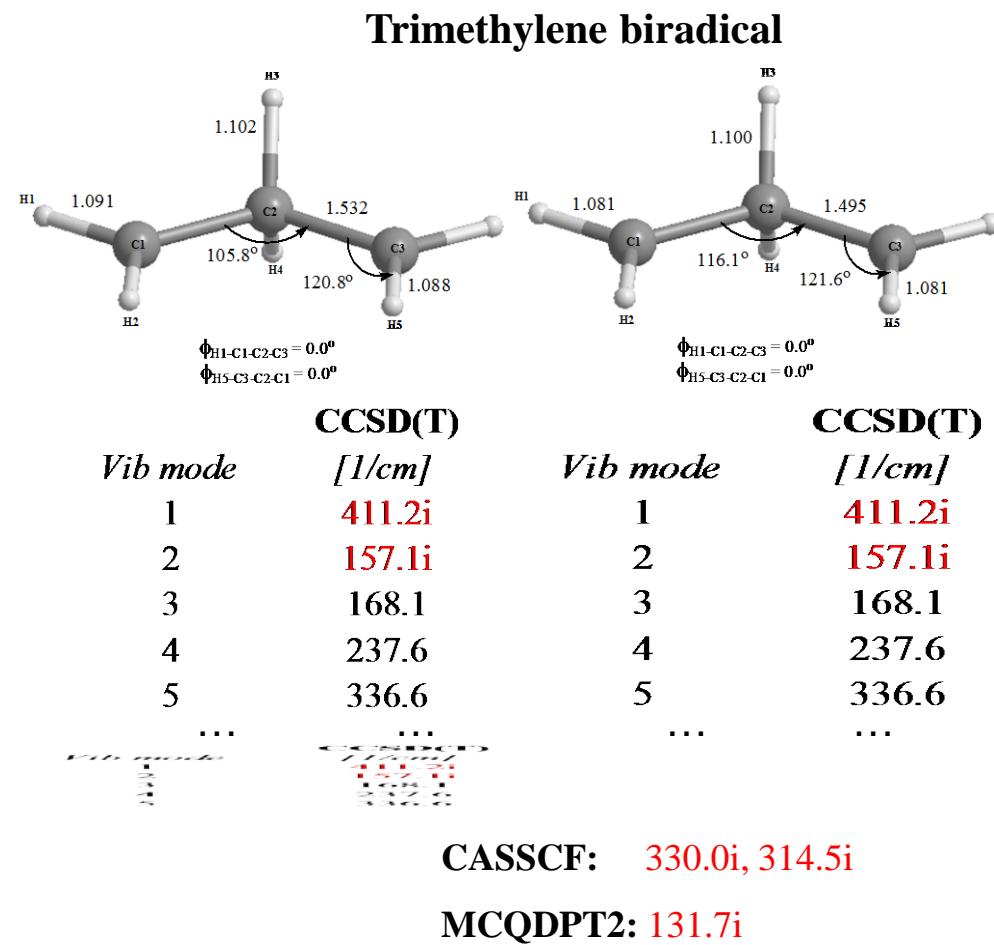
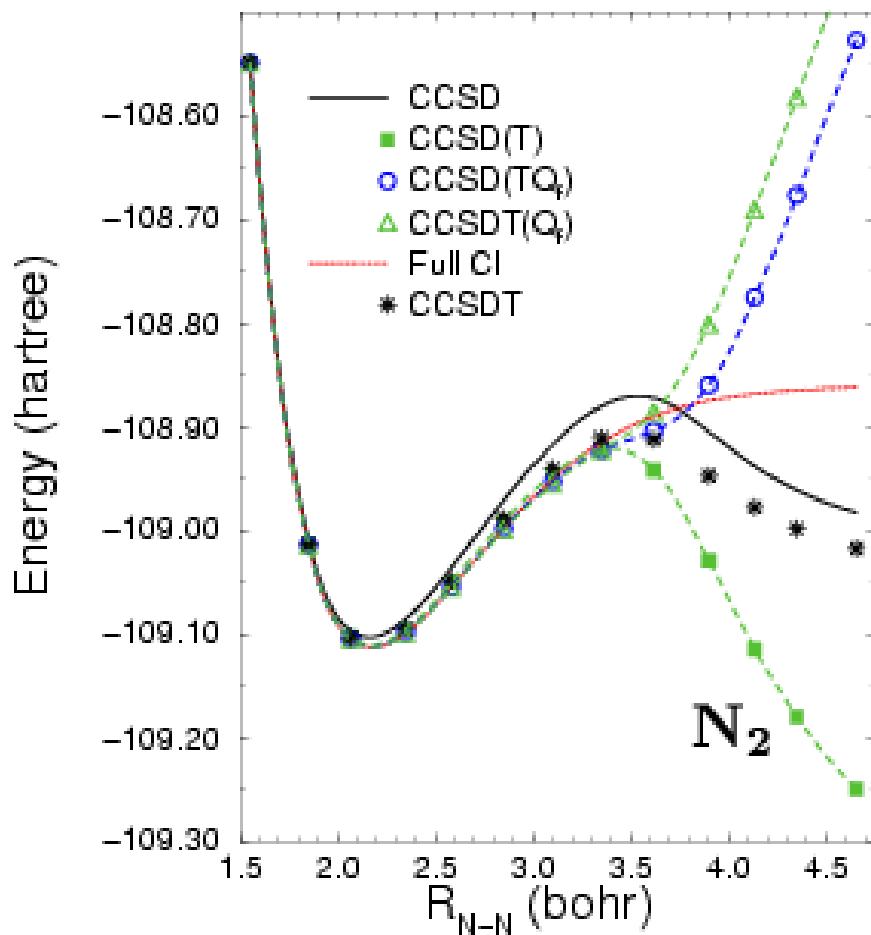
TYPES OF MANY-ELECTRON CORRELATIONS



CONVENTIONAL SINGLE-REFERENCE CC/EOMCC METHODS ARE EXCELLENT IN DESCRIBING DYNAMICAL CORRELATIONS (EVEN WHEN THEY ARE STRONG, AS IN NUCLEI), BUT THEY HAVE SERIOUS PROBLEMS WHEN NON-DYNAMICAL CORRELATIONS BECOME SIGNIFICANT

PROBLEMS WITH THE STANDARD CC/EOMCC APPROXIMATIONS

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



Vertical excitation energies of CH⁺ and C₂ (in eV) [K. Kowalski and P. Piecuch, 2001, 2002]

System	State	Full CI	EOMCCSD	CC3	EOMCCSDT
CH ⁺	2 ¹ Σ ⁺	8.549	0.560	0.230	0.074
	3 ¹ Σ ⁺	13.525	0.055	0.016	0.001
	4 ¹ Σ ⁺	17.217	0.099	0.026	-0.002
	1 ¹ Π	3.230	0.031	0.012	-0.003
	2 ¹ Π	14.127	0.327	0.219	0.060
	1 ¹ Δ	6.964	0.924	0.318	0.040
	2 ¹ Δ	16.833	0.856	0.261	-0.038
C ₂	1 ¹ Π _u	1.385	0.090	-0.068	0.034
	1 ¹ Δ _g	2.293	2.054	0.859	0.407
	1 ¹ Σ _u ⁺	5.602	0.197	-0.047	0.113
	1 ¹ Π _g	4.494	1.708	0.496	0.088

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 Σ ⁻	0.95	0.66	0.65	0.74
A ² Δ	3.33	3.02	3.00	2.88
B ² Σ ⁻	4.41	3.27	3.27	3.23
C ² Σ ⁺	5.29	4.07	4.04	3.94

> 1 eV
 errors

AMONG THE SOLUTIONS WITHIN CC (EXAMPLES):

IMPROVED SINGLE-REFERENCE CC THEORIES, FOR EXAMPLE,

Completely renormalized CC and EOMCC approaches (cf., also, methods based on partitioning of the similarity transformed Hamiltonian)

Objective: Use asymmetric energy formulas and moment expansions to capture the most relevant dynamical and non-dynamical correlations dynamically

Extended CC approaches

Objective: Use two cluster operators and bi-variational formulation to improve cluster amplitudes

Externally corrected and tailored CC approaches

Objective: Use information about non-dynamical correlations extracted from non-CC wave functions

Spin-flip CC and EOMCC approaches

Objective: Use spin-flipping excitation operators to obtain low-spin states from high-spin references

MULTI-REFERENCE CC (MRCC) THEORIES

Genuine MRCC approaches: valence-universal and state-universal MRCC

Objective: Use multi-dimensional reference spaces and the multi-root Bloch wave operator theory

State-selective MRCC methods, e.g., BW-MRCC, Mk-MRCC, MR-expT, BCCC, ic-MRCC, MR-EOMCC, etc.

Objective: Use multi-dimensional reference spaces but focus on one state at a time

ACTIVE-SPACE CC/EOMCC APPROACHES (simplified SSMRCC or SRMRCC; also, CASCC)

Objective: Use active orbitals in single-reference CC/EOMCC to incorporate the leading non-dynamical correlations through selection of higher-than-double excitations

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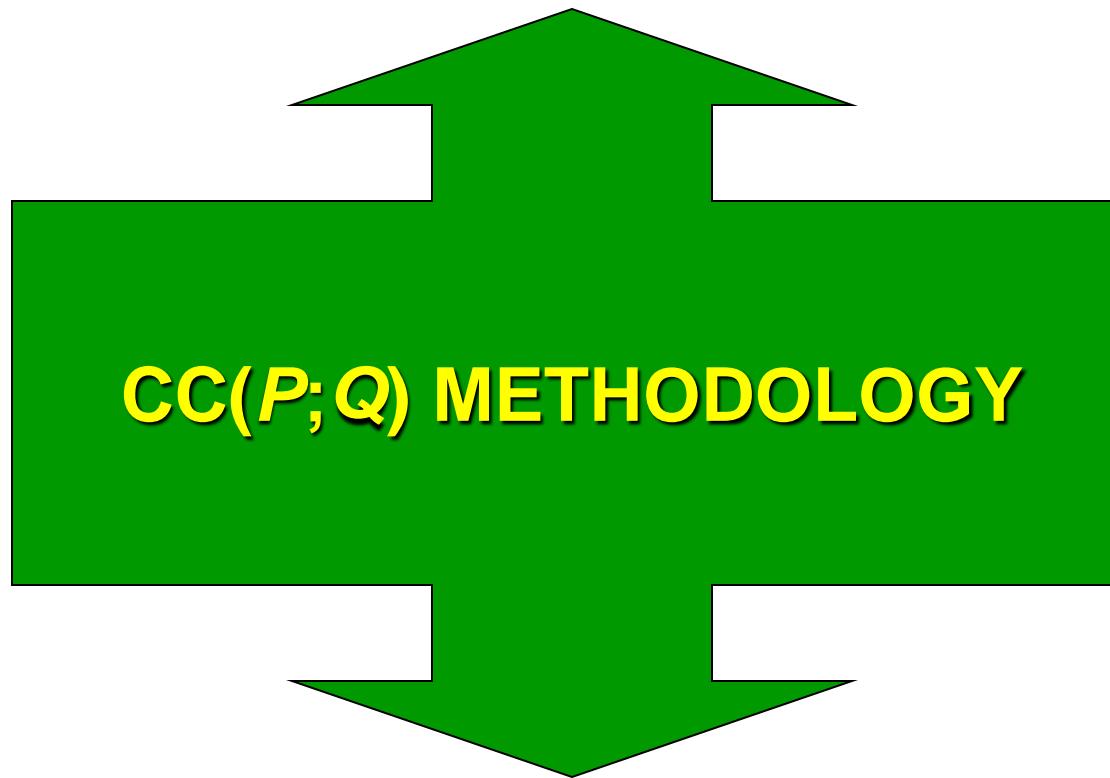
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IN SEARCH FOR BLACK-BOX METHODS FOR BOND BREAKING AND EXCITED STATES:

METHOD OF MOMENTS OF COUPLED-CLUSTER EQUATIONS (MMCC) AND COMPLETELY RENORMALIZED CC/EOMCC APPROACHES

Main idea:

$$\delta_K^{(A)} = E_K - E_K^{(A)} = \Lambda[\Psi_K; \mathcal{M}_{K,i_1 \dots i_k}^{a_1 \dots a_k}(m_A), k > m_A]$$

$E_K^{(A)}$

- the energy of electronic state K obtained using standard coupled-cluster calculations (e.g., CCSD or EOMCCSD)

E_K

- the exact (full CI) energy of state K in a basis set

Ψ_K

- the exact (full CI) wave function in a basis set

$\mathcal{M}_{K,i_1 \dots i_k}^{a_1 \dots a_k}(m_A)$

- the *generalized moments of coupled-cluster equations*

$$E_K^{\text{MMCC}} = E_K^{(A)} + \delta_K^{\text{MMCC}}$$

THE MMCC ENERGY FORMULA

(the ground-state problem, original formulation: P. Piecuch and K. Kowalski, 2000; the excited-state extension within the original formulation: K. Kowalski and P. Piecuch, 2001)

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

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

← MMCC functional
(K.Kowalski and P. Piecuch, 2000)
 $(T^{(A)} = T_1 + \dots + T_{m_A})$

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

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

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

$$\langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} | (H_N e^{T^{(A)}})_C | \Phi \rangle$$

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

$$= \mathcal{M}_{i_1 \dots i_k}^{a_1 \dots a_k}(m_A)$$

(moments of CC equations)

THE MMCC ENERGY FORMULA

(the ground-state problem, original formulation: P. Piecuch and K. Kowalski, 2000)

$$\delta_0^{(A)} = E_0 - E_0^{(A)} = \sum_{n=m_A+1}^N \sum_{k=m_A+1}^n \langle \Psi_0 | C_{n-k}(m_A) M_k(m_A) | \Phi \rangle / \langle \Psi_0 | e^{T^{(A)}} | \Phi \rangle$$

$C_{n-k}(m_A) = \left(e^{T^{(A)}} \right)_{n-k}$, for example, if $m_A = 2$ (the CCSD case),

$$C_0(2) = 1, \quad C_1(2) = T_1, \quad C_2(2) = T_2 + \frac{1}{2}T_1^2, \quad C_3(2) = T_1 T_2 + \frac{1}{6}T_1^3, \quad \text{etc.}$$

$$M_k(m_A) | \Phi \rangle = \sum_{\substack{i_1 < \dots < i_k \\ a_1 < \dots < a_k}} \mathcal{M}_{i_1 \dots i_k}^{a_1 \dots a_k} (m_A) | \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} \rangle,$$

$\mathcal{M}_{i_1 \dots i_k}^{a_1 \dots a_k} (m_A) = \langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} | (H_N e^{T^{(A)}})_C | \Phi \rangle$ – generalized moments of CC equations,

for example, if $m_A = 2$ (the CCSD case),

$$\mathcal{M}_{i_1 \dots i_k}^{a_1 \dots a_k} (2) = \langle \Phi_{i_1 \dots i_k}^{a_1 \dots a_k} | (H_N e^{T_1 + T_2})_C | \Phi \rangle, \quad k = 3 - 6.$$

COMPLETELY RENORMALIZED CC METHODS

(original formulation; P. Piecuch and K. Kowalski, 2000; available in GAMESS; CCTYP=CR-CC, CR-CC(Q))

$$E_0(2, 3) = E_0^{\text{CCSD}} + \langle \Psi_0 | \textcolor{red}{M}_3(2) | \Phi \rangle / \langle \Psi_0 | e^{T_1 + T_2} | \Phi \rangle$$

$$E_0(2, 4) = E_0^{\text{CCSD}} + \langle \Psi_0 | \textcolor{red}{M}_3(2) + [\textcolor{blue}{M}_4(2) + T_1 \textcolor{red}{M}_3(2)] | \Phi \rangle / \langle \Psi_0 | e^{T_1 + T_2} | \Phi \rangle$$

$$\textcolor{red}{M}_3(2) | \Phi \rangle = \sum_{\substack{i < j < k \\ a < b < c}} \mathcal{M}_{ijk}^{abc}(2) | \Phi_{ijk}^{abc} \rangle, \quad \mathcal{M}_{ijk}^{abc}(2) = \langle \Phi_{ijk}^{abc} | (H_N e^{T_1 + T_2})_C | \Phi \rangle$$

$$\textcolor{blue}{M}_4(2) | \Phi \rangle = \sum_{\substack{i < j < k < l \\ a < b < c < d}} \mathcal{M}_{ijkl}^{abcd}(2) | \Phi_{ijkl}^{abcd} \rangle, \quad \mathcal{M}_{ijkl}^{abcd}(2) = \langle \Phi_{ijkl}^{abcd} | (H_N e^{T_1 + T_2})_C | \Phi \rangle$$

COMPLETELY RENORMALIZED CC METHODS (original formulation; P. Piecuch and K. Kowalski, 2000; available in GAMESS; CCTYP=CR-CC, CR-CC(Q))

$$E_0(2,3) = E_0^{\text{CCSD}} + \langle \Psi_0 | \textcolor{red}{M}_3(2) | \Phi \rangle / \langle \Psi_0 | e^{T_1+T_2} | \Phi \rangle \quad \textcolor{green}{\leftarrow} \quad T_3 \text{ correction to CCSD}$$

$$E_0(2,4) = E_0^{\text{CCSD}} + \langle \Psi_0 | \textcolor{red}{M}_3(2) + [\textcolor{blue}{M}_4(2) + T_1 \textcolor{red}{M}_3(2)] | \Phi \rangle / \langle \Psi_0 | e^{T_1+T_2} | \Phi \rangle$$

$$M_3(2) | \Phi \rangle = \sum_{\substack{i < j < k \\ a < b < c}} \mathcal{M}_{ijk}^{abc}(2) | \Phi_{ijk}^{abc} \rangle, \quad \textcolor{red}{\mathcal{M}_{ijk}^{abc}(2) = \langle \Phi_{ijk}^{abc} | (H_N e^{T_1+T_2})_C | \Phi \rangle}$$

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COMPLETELY RENORMALIZED CC METHODS

(original formulation; P. Piecuch and K. Kowalski, 2000; available in GAMESS; CCTYP=CR-CC, CR-CC(Q))

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$$E_0(2,4) = E_0^{\text{CCSD}} + \langle \Psi_0 | \mathbf{M}_3(2) + [\mathbf{M}_4(2) + T_1 \mathbf{M}_3(2)] | \Phi \rangle / \langle \Psi_0 | e^{T_1+T_2} | \Phi \rangle \quad \text{--- } T_3 + T_4 \text{ correction to CCSD}$$

$$\mathbf{M}_3(2) | \Phi \rangle = \sum_{\substack{i < j < k \\ a < b < c}} \mathcal{M}_{ijk}^{abc}(2) | \Phi_{ijk}^{abc} \rangle, \quad \mathcal{M}_{ijk}^{abc}(2) = \langle \Phi_{ijk}^{abc} | (H_N e^{T_1+T_2})_C | \Phi \rangle$$

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COMPLETELY RENORMALIZED CC METHODS

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$$M_3(2) | \Phi \rangle = \sum_{\substack{i < j < k \\ a < b < c}} \mathcal{M}_{ijk}^{abc}(2) | \Phi_{ijk}^{abc} \rangle, \quad \boxed{\mathcal{M}_{ijk}^{abc}(2) = \langle \Phi_{ijk}^{abc} | (H_N e^{T_1+T_2})_C | \Phi \rangle}$$

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Example: The CR-CCSD(T) approach

$$|\Psi_0^{\text{CCSD(T)}}\rangle = (1 + T_1 + T_2 + T_3^{[2]} + Z_3) | \Phi \rangle \quad \leftarrow \text{MBPT(2)-like}$$

$$\boxed{E_0^{\text{CR-CCSD(T)}} = E_0^{\text{CCSD}} + N^{\text{CR(T)}} / D^{\text{(T)}}}$$

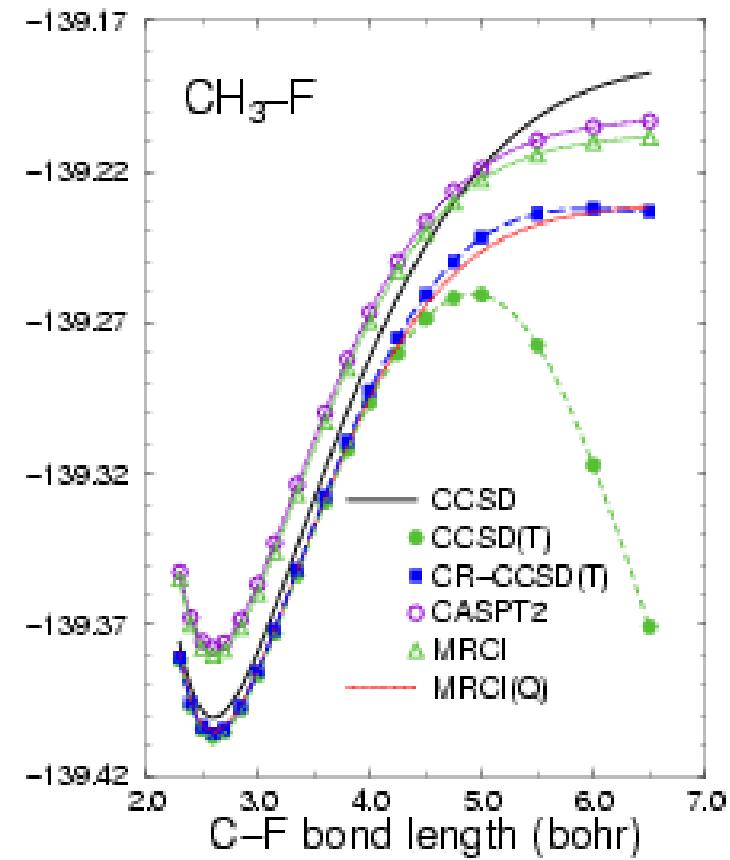
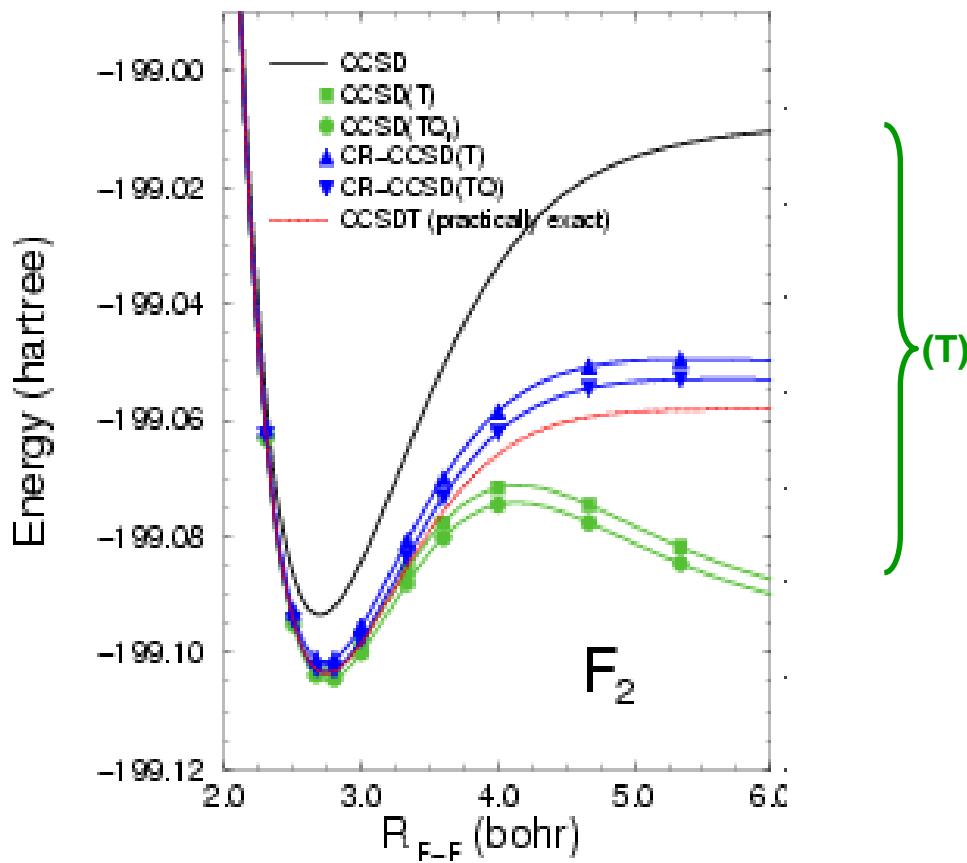
$$N^{\text{CR(T)}} = \langle \Psi_0^{\text{CCSD(T)}} | M_3(2) | \Phi \rangle = \langle \Phi | (T_3^{[2]} + Z_3)^\dagger M_3(2) | \Phi \rangle$$

$$D^{\text{(T)}} = \langle \Psi_0^{\text{CCSD(T)}} | e^{T_1+T_2} | \Phi \rangle = \boxed{1 + \langle \Phi | T_1^\dagger T_1 | \Phi \rangle + \langle \Phi | T_2^\dagger (T_2 + \frac{1}{2} T_1^2) | \Phi \rangle} \\ + \langle \Phi | (T_3^{[2]} + Z_3)^\dagger (T_1 T_2 + \frac{1}{6} T_1^3) | \Phi \rangle$$

(reduces to CCSD(T), when $M_3(2) \rightarrow (V_N T_2)_C$ and $D^{\text{(T)}} \rightarrow 1$).

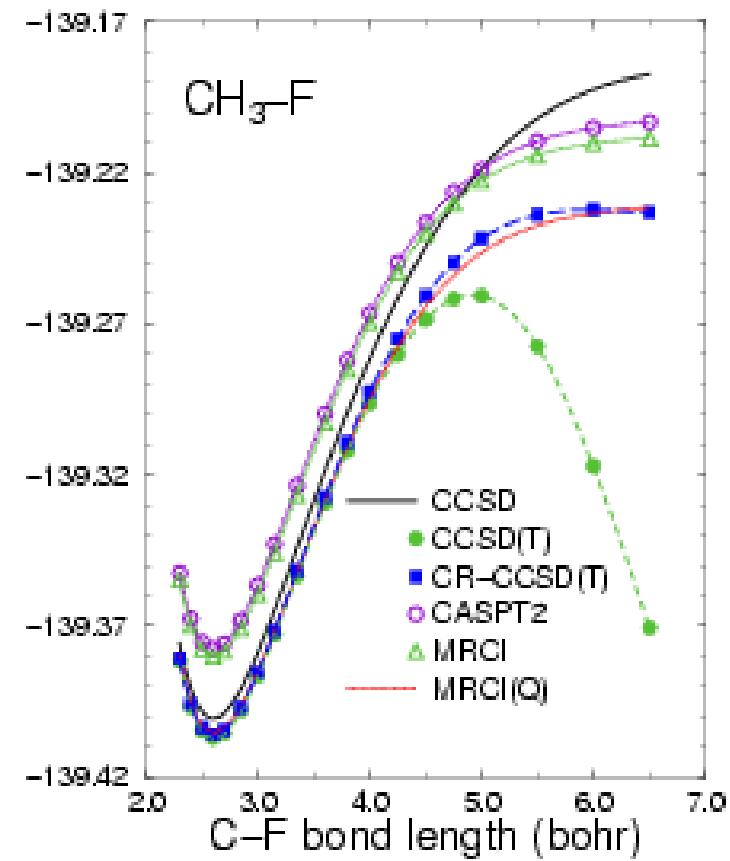
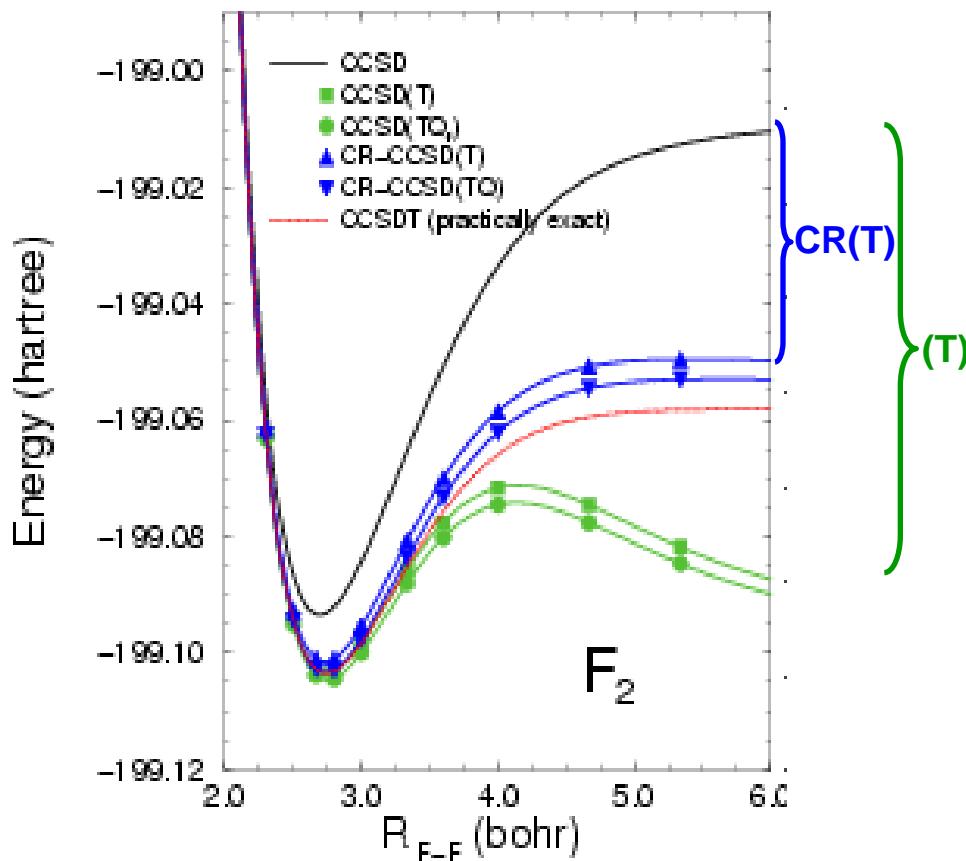
Examples: Single bond breaking in F_2 and CH_3F

(K. Kowalski and P. Piecuch, Chem. Phys. Lett., 2001; P. Piecuch et al., Int. Rev. Phys. Chem., 2002)



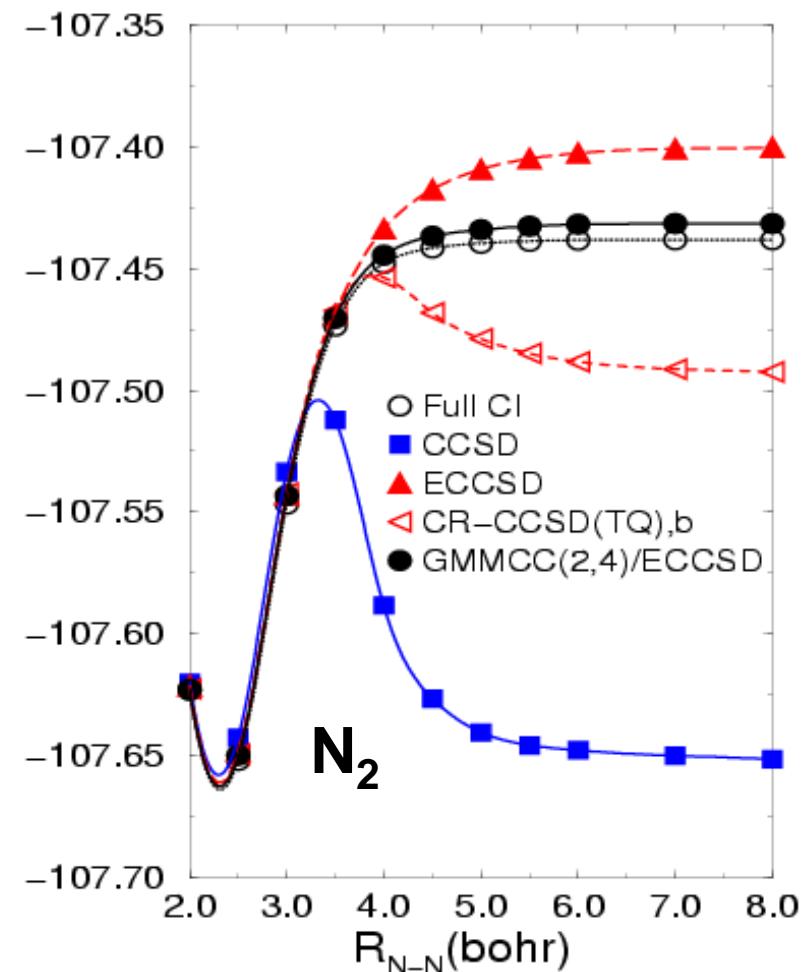
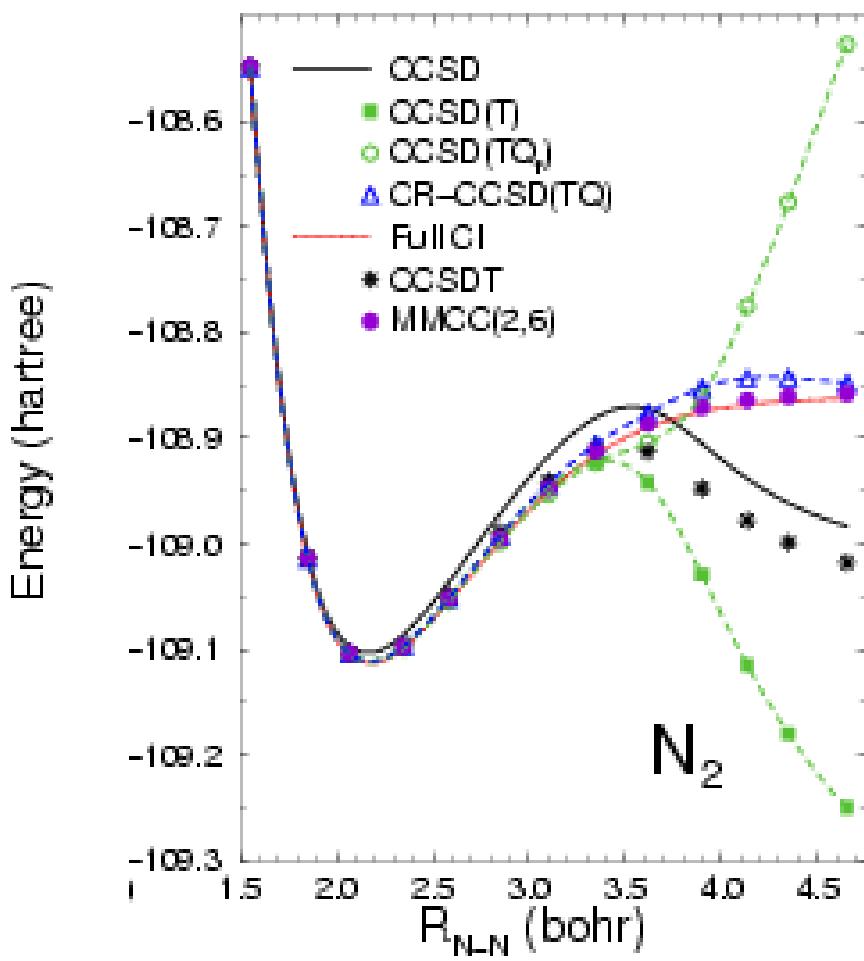
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- Multiple Bond Breaking [the MMCC(2,6) Method and the GMMCC(2,4) Approach Using the Extended CCSD (ECCSD) Amplitudes]

(K. Kowalski and P. Piecuch, J. Chem. Phys., 2000; P. Piecuch et al., Int. Rev. Phys. Chem., 2002; I.S.O. Pimienta, K. Kowalski, and P. Piecuch, J. Chem. Phys., 2003; P. Piecuch et al., Theor. Chem. Acct., 2004; P.-D. Fan, K. Kowalski, and P. Piecuch, Mol. Phys., 2005)



The newest generation of CR-CC corrections: the CR-CC(m_A, m_B) methods

(P. Piecuch and M. Włoch, 2005; P. Piecuch et al., 2006, 2007)

Instead of

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

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

before exploiting the resolution of identity, introduce the ansatz:

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

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

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

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

BIORTHOGONAL MMCC EXPANSION

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

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

Example: CR-CC(2,3)=CR-CCSD(T)_L, robust, size extensive T₃ correction to CCSD

[in GAMESS since February 2006 (closed-shells) and August 2007 (open-shells); CCTYP=CR-CCL]

$$E_0(2,3) = E_0^{(\text{CCSD})} + \langle \Phi | L_3 M_3(2) | \Phi \rangle = E_0^{(\text{CCSD})} + \sum_{i_1 < j < k, a < b < c} \ell_{abc}^{ijk} M_{ijk}^{abc}(2)$$

← $\langle \Phi_{ijk}^{abc} | (H_N e^{T_1+T_2})_C | \Phi \rangle$

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

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

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

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

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

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

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

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)_Λ; 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) \rightarrow CCSD(T)

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

CR-CC(2,3) \rightarrow CCSD(T)

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$$M_{abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \overline{H}^{\text{(CCSD)}} | \Phi \rangle \implies \langle \Phi_{ijk}^{abc} | (V_N T_2)_C | \Phi \rangle$$

CR-CC(2,3) \rightarrow CCSD(T)

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

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(3)

(4)

(2)

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

CR-CC(2,3) \rightarrow CCSD(T)

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

$$M_{abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \overline{H}^{(\text{CCSD})} | \Phi \rangle \implies \langle \Phi_{ijk}^{abc} | (V_N T_2)_C | \Phi \rangle$$

(3)	(4)	(2)
$\ell_{abc}^{ijk} = \langle \Phi [(L_1^{(\text{CCSD})} \overline{H}_2^{(\text{CCSD})})_{DC} + (L_2^{(\text{CCSD})} \overline{H}_1^{(\text{CCSD})})_{DC} + (L_2^{(\text{CCSD})} \overline{H}_2^{(\text{CCSD})})_C \Phi_{ijk}^{abc} \rangle / D_{abc}^{ijk}$	$\ell_{abc}^{ijk} = \langle \Phi [(L_1^{(\text{CCSD})} \overline{H}_2^{(\text{CCSD})})_{DC} + (L_2^{(\text{CCSD})} \overline{H}_1^{(\text{CCSD})})_{DC} + (L_2^{(\text{CCSD})} \overline{H}_2^{(\text{CCSD})})_C \Phi_{ijk}^{abc} \rangle / D_{abc}^{ijk}$	$\ell_{abc}^{ijk} = \langle \Phi (T_2^+ V_N)_C \Phi_{ijk}^{abc} \rangle / D_{abc}^{ijk}$
$(T_1^+ V_N)_{DC}$	$(T_2^+ V_N)_{DC}$	$(T_2^+ V_N)_C$

CR-CC(2,3) \rightarrow CCSD(T)

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

$$M_{abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \overline{H}^{(\text{CCSD})} | \Phi \rangle \implies \langle \Phi_{ijk}^{abc} | (V_N T_2)_C | \Phi \rangle$$

(3)	(4)	(2)
$\ell_{abc}^{ijk} = \langle \Phi [(L_1^{(\text{CCSD})} \overline{H}_2^{(\text{CCSD})})_{DC} + (L_2^{(\text{CCSD})} \overline{H}_1^{(\text{CCSD})})_{DC} + (L_2^{(\text{CCSD})} \overline{H}_2^{(\text{CCSD})})_C \Phi_{ijk}^{abc} \rangle / D_{abc}^{ijk}$	$(L_2^{(\text{CCSD})} \overline{H}_1^{(\text{CCSD})})_{DC}$	$(T_2^+ V_N)_C$
\downarrow		\downarrow
$(T_1^+ V_N)_{DC}$		

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

CR-CC(2,3) \rightarrow CCSD[T]=CCSD+T

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

$$M_{abc}^{ijk}(2) = \langle \Phi_{ijk}^{abc} | \overline{H}^{(\text{CCSD})} | \Phi \rangle \implies \langle \Phi_{ijk}^{abc} | (V_N T_2)_C | \Phi \rangle$$

(3)	(4)	(2)
$\ell_{abc}^{ijk} = \langle \Phi [(L_1^{(\text{CCSD})} \overline{H}_2^{(\text{CCSD})})_{DC} + (L_2^{(\text{CCSD})} \overline{H}_1^{(\text{CCSD})})_{DC} + (L_2^{(\text{CCSD})} \overline{H}_2^{(\text{CCSD})})_C \Phi_{ijk}^{abc} \rangle / D_{abc}^{ijk}$	$\ell_{abc}^{ijk} = \langle \Phi [(L_1^{(\text{CCSD})} \overline{H}_2^{(\text{CCSD})})_{DC} + (L_2^{(\text{CCSD})} \overline{H}_1^{(\text{CCSD})})_{DC} + (L_2^{(\text{CCSD})} \overline{H}_2^{(\text{CCSD})})_C \Phi_{ijk}^{abc} \rangle / D_{abc}^{ijk}$	$\ell_{abc}^{ijk} = \langle \Phi [(L_1^{(\text{CCSD})} \overline{H}_2^{(\text{CCSD})})_{DC} + (L_2^{(\text{CCSD})} \overline{H}_1^{(\text{CCSD})})_{DC} + (L_2^{(\text{CCSD})} \overline{H}_2^{(\text{CCSD})})_C \Phi_{ijk}^{abc} \rangle / D_{abc}^{ijk}$
$(T_1^+ V_N)_{DC}$	$(T_2^+ V_N)_C$	$(T_2^+ V_N)_C$

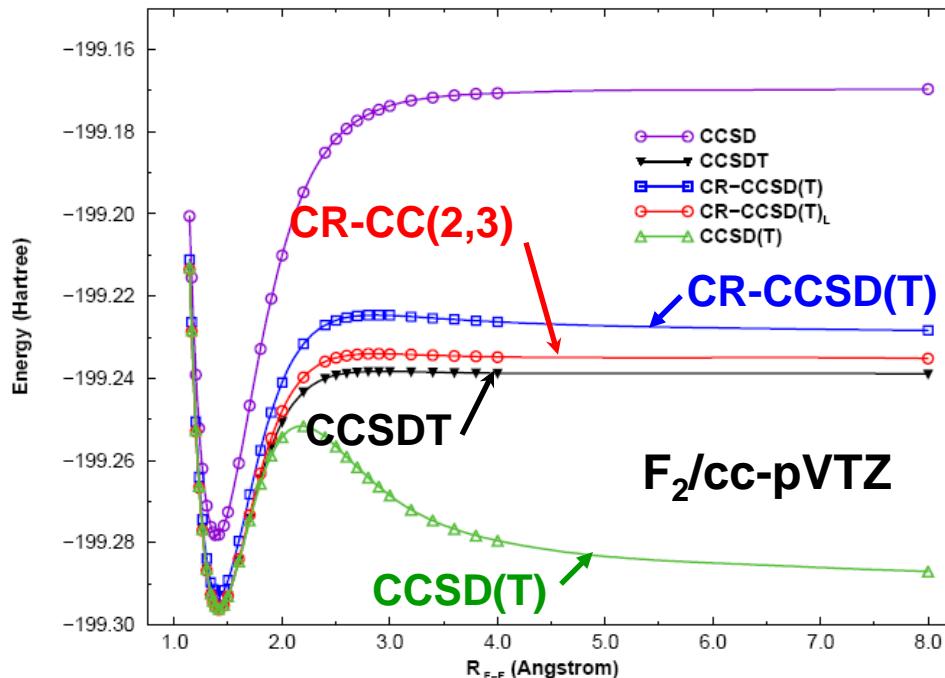
$$D_{abc}^{ijk} = E_0^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \overline{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle \implies \varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c$$

The CR-CC(2,3) method is more accurate than all other non-iterative triples CC methods formulated to date. Example: potential energy curve of OH⁻.

Method	$R_{\text{O-H}}$												
	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) _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

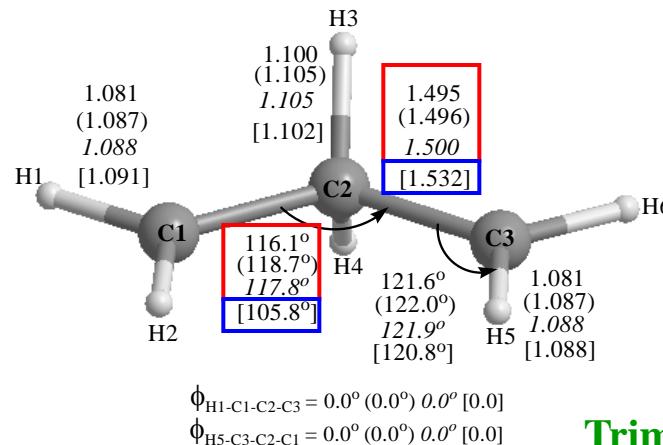
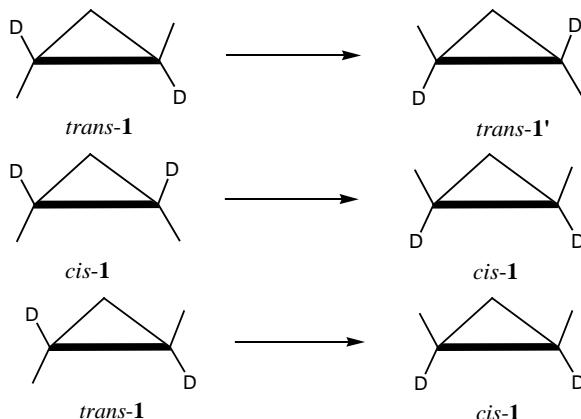
↑
CR-CC(2,3)

Another example ...



Thermal Stereomutations of Cyclopropane

(A. Kinal, P. Piecuch, M.J. McGuire, and M. Włoch, in preparation)



MRCI
 (CR-CCSD(T))
 CR-CC(2,3),A
 [CCSD(T)]

Trimethylene biradical (TS1)

vib mode	MRCI (Isborn et al., 2004)	CR-CCSD(T)	CR-CC(2,3)	CCSD(T)
1	<i>139i</i>	<i>129i</i>	<i>122i</i>	<i>411i</i>
2	61	147	161	<i>157i</i>
3	278	334	340	168
4	361	362	358	238
...
21	3361	3282	3270	3255
Av. %Err.		4.2	4.1	9.4

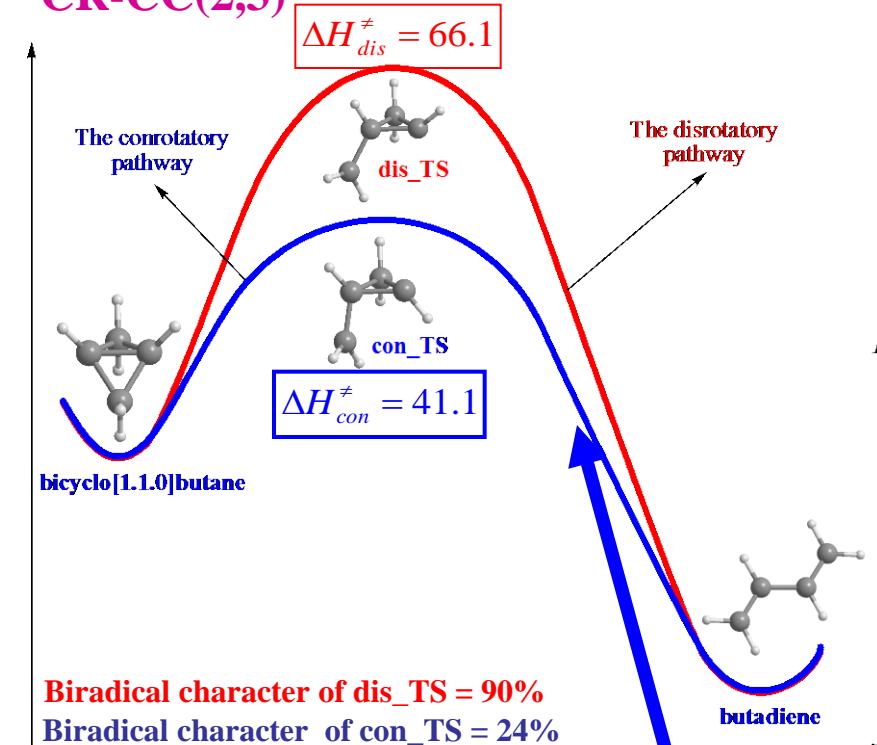
	MRCI(Q)	CR-CCSD(T)	Experiment
$\Delta H_{\text{geom}}^\ddagger$	59.7	67.8	63.6 ± 0.5

CR-CC(2,3) : 63.3 kcal/mol

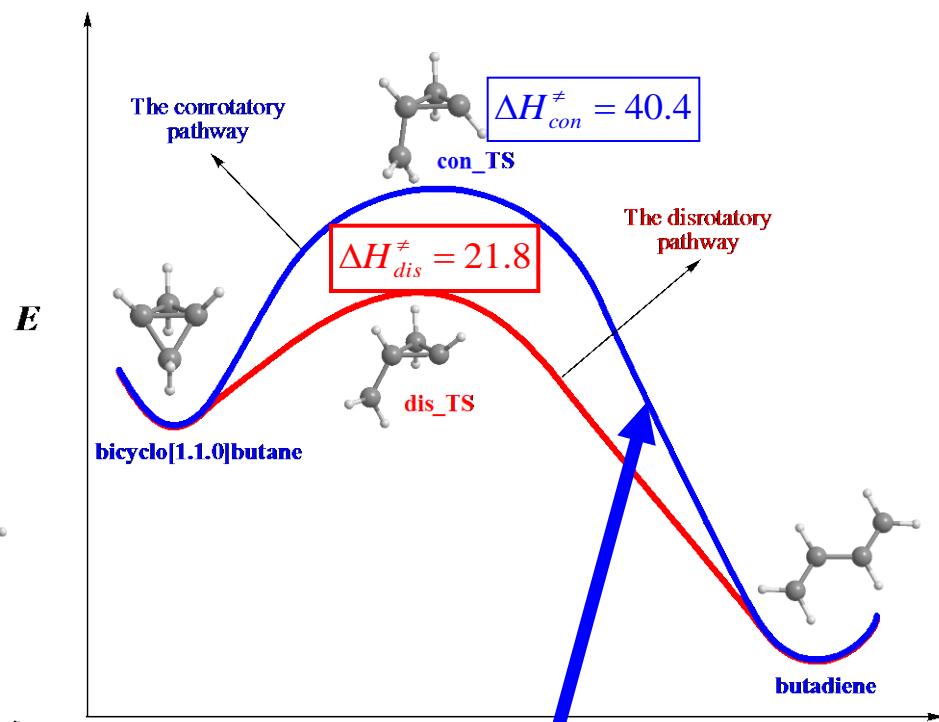
The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]butane to Butadiene

(A. Kinal and P. Piecuch, J. Phys. Chem. A, 2007; J.J. Lutz and P. Piecuch, J. Chem. Phys., 2008)

CR-CC(2,3)



CCSD(T)

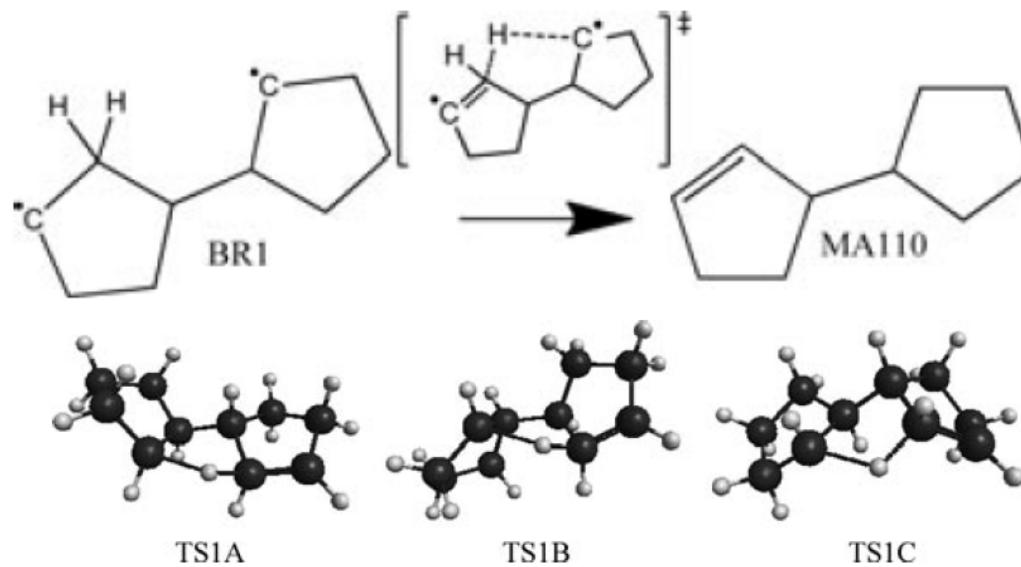


Physical pathway: CONROTATORY

The experimental activation energy is 40.6 ± 2.5 kcal/mol

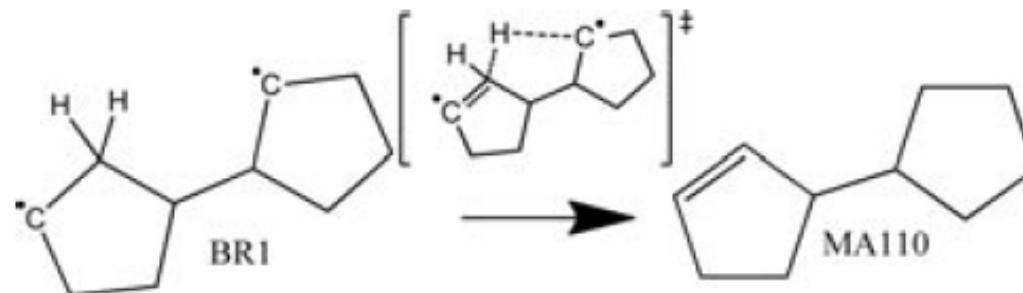
Kinetic Modeling of JP-10 (exo-Tetrahydrodicyclopentadiene) High-Temperature Oxidation: Role of Biradical Species in Initial Decomposition Steps

[G.R. Magoon, J. Aguilera-Iparraguirre, W.H. Green, J.J. Lutz, P. Piecuch, H.-W. Wong, and O.O. Oluwole, Int. J. Chem. Kin., 2012]

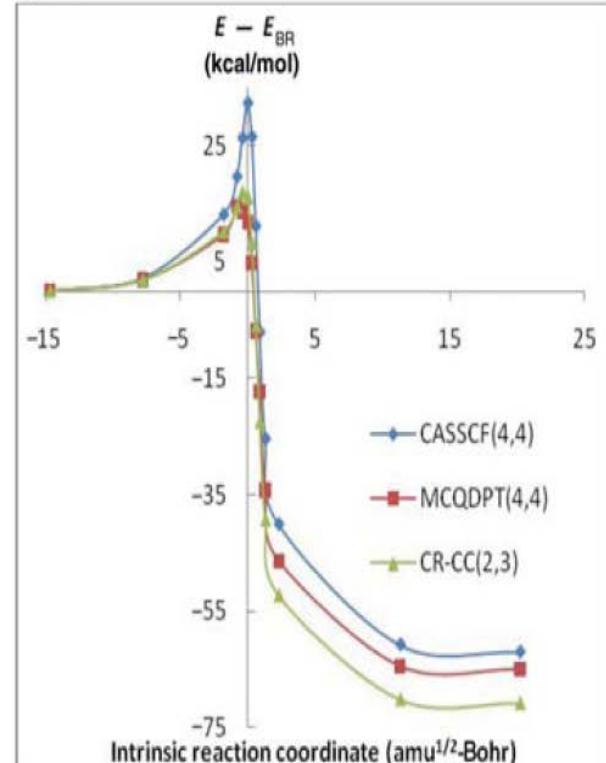


Kinetic Modeling of JP-10 (exo-Tetrahydrodycyclopentadiene) High-Temperature Oxidation: Role of Biradical Species in Initial Decomposition Steps

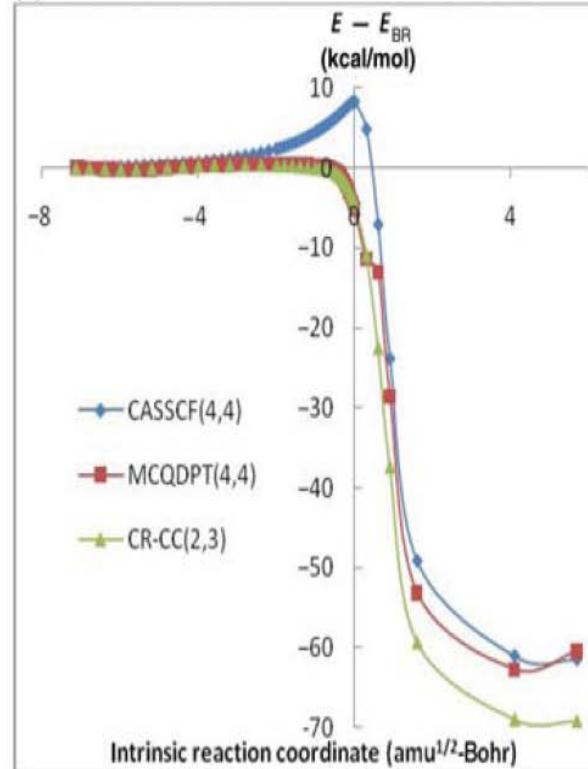
[G.R. Magoon, J. Aguilera-Iparraguirre, W.H. Green, J.J. Lutz, P. Piecuch, H.-W. Wong, and O.O. Oluwole, Int. J. Chem. Kin., 2012]



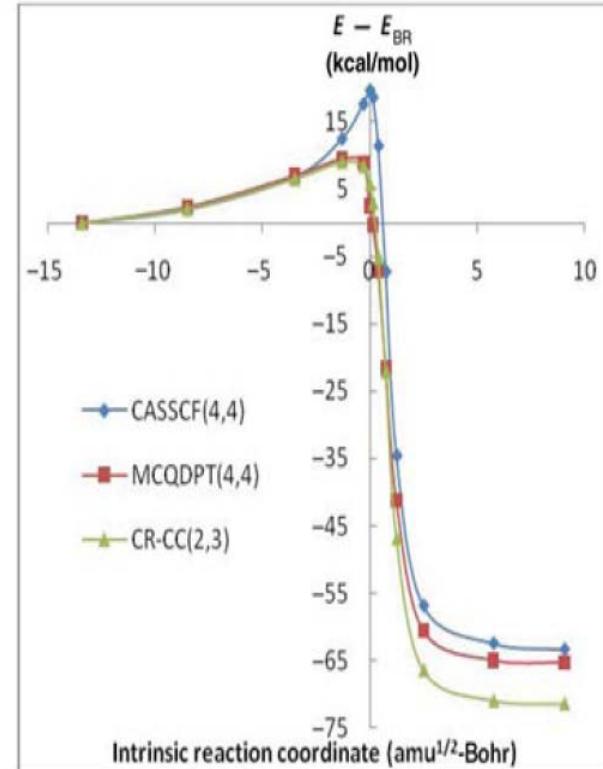
(a) TS1A



(b) TS1B



(c) TS1C



THE MMCC ENERGY FORMULA FOR EXCITED STATES

(original formulation; K. Kowalski and P. Piecuch, 2001; biorthogonal extension, P. Piecuch et al., 2006, 2009)

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

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

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

MMCC(2,3), MMCC(2,4), CR-EOMCCSD(T), etc.

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

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

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

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

ADIABATIC EXCITATIONS IN CH, CNC, C₂N: COMPARISON WITH EOMCCSDT & EA-EOMCCSD(3p-2h)

CH

[Piecuch, Gour, Włoch, IJQC (2009)]

State	Theory	E/Hartree	T _e /eV	REL	State	Theory	E/Hartree	T _e /eV	REL
<i>B</i> ² Σ^-	EOMCCSD	-38.228 924	4.241	1.79	<i>C</i> ² Σ^+	EOMCCSD	-38.194 213	5.185	1.87
	EOMCCSDT ^b	-38.267 435	3.273			EOMCCSDT ^b	-38.238 031	4.073	
	EA-EOMCCSD(2 <i>p</i> -1 <i>h</i>)	-38.160 687	6.105			EA-EOMCCSD(2 <i>p</i> -1 <i>h</i>)	-38.180 332	5.570	
	EA-EOMCCSD(3 <i>p</i> -2 <i>h</i>)	-38.262 600	3.377			EA-EOMCCSD(3 <i>p</i> -2 <i>h</i>)	-38.236 024	4.100	
	EA-EOMCCSD(3 <i>p</i> -2 <i>h</i>) ^{3}	-38.261 677	3.357			EA-EOMCCSD(3 <i>p</i> -2 <i>h</i>) ^{3}	-38.234 680	4.092	
	CR-EOMCCSD(T),ID ^c	-38.270 424	3.181			CR-EOMCCSD(T),ID ^c	-38.236 048	4.117	
	CR-EOMCC(2,3),A	-38.257 269	3.529			CR-EOMCC(2,3),A	-38.224 449	4.422	
	CR-EOMCC(2,3),B	-38.255 709	3.569			CR-EOMCC(2,3),B	-38.222 634	4.469	
	CR-EOMCC(2,3),C	-38.272 744	3.123			CR-EOMCC(2,3),C	-38.238 514	4.055	
	CR-EOMCC(2,3),D	-38.272 498	3.130			CR-EOMCC(2,3),D	-38.238 118	4.065	
Experiment ^d		3.23			Experiment ^e			3.94	

ADIABATIC EXCITATIONS IN CH, CNC, C₂N: COMPARISON WITH EOMCCSDT & EA-EOMCCSD(3p-2h)

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	CR-EOMCC(2,3),D	-38.272 498	3.130	(<0.1 eV error)		CR-EOMCC(2,3),D		-38.238 118	4.065
Experiment ^d		3.23			Experiment ^e			3.94	

ADIABATIC EXCITATIONS IN CH, CNC, C₂N: COMPARISON WITH EOMCCSDT & EA-EOMCCSD(3p-2h)

CH

[Piecuch, Gour, Włoch, IJQC (2009)]

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Experiment ^d		3.23			Experiment ^e			3.94	

CNC, C₂N

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

Molecule	State	REL	EA-EOMCCSD				CR-EOMCC(2,3)				Experiment ^b	
			(2p-1h)	(3p-2h)	(3p-2h){4}	EOMCCSD	CR-EOMCCSD(T),ID	A	B	C	D	
CNC	A ² Δ _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 S _u ⁺	1.979	7.639	4.718	4.704	7.123	4.675	5.432	5.595	4.582	4.599	4.315
C ₂ N	A ² Δ	1.090	6.190	3.055	3.028	3.191	3.344	3.377	3.368	3.389	3.388	2.636
	B ² S ⁻	1.856	7.856	3.677	3.648	5.514	3.351	4.018	4.160	3.091	3.110	2.779
	C ² S ⁺	1.897	6.722	3.809	3.788	6.358	4.023	4.741	4.901	3.799	3.824	3.306

**Completely renormalized CC/EOMCC methods can offer great help ...
but there are situations where this is not sufficient ...**

Example: excited states of metallic clusters (Be_3)

(K. Kowalski et al., J. Chem. Phys. 2005, P. Piecuch et al., Int. J. Quantum Chem., 2006)

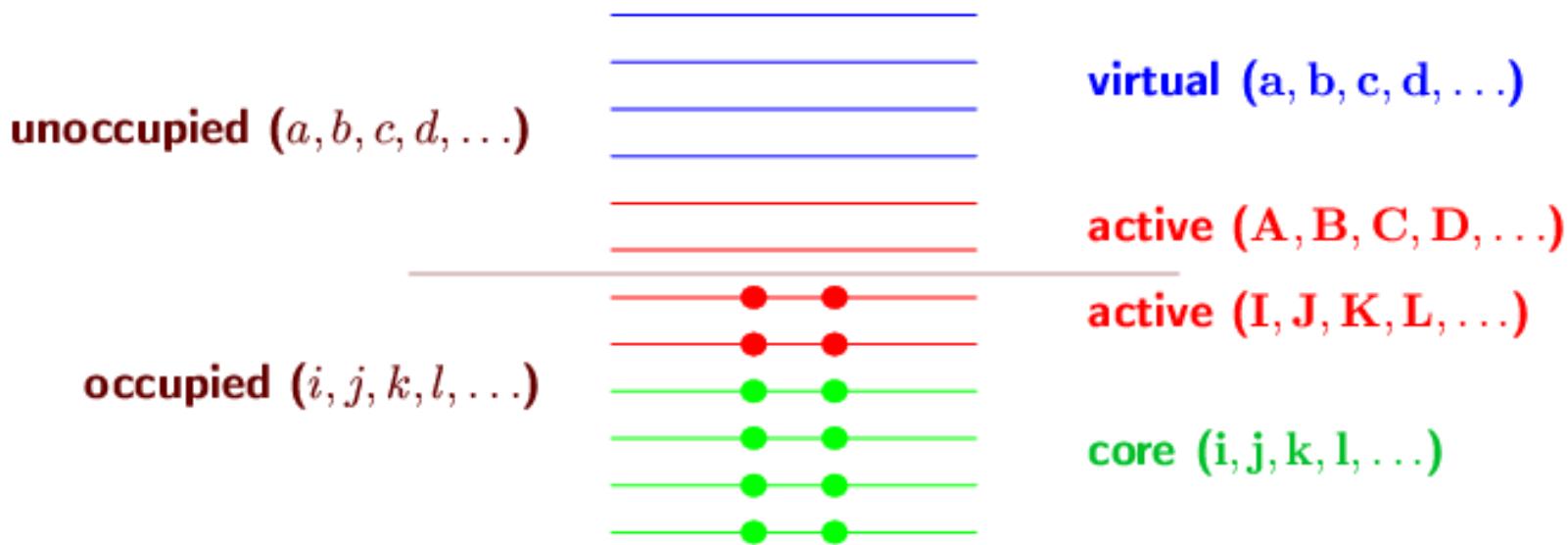
State	Full CI	EOMCCSD	CR-EOMCCSD(T)
$X\ ^1A'_1$	-43.882330	-43.864904	-43.873110
$1\ ^1E^{\#}$	1.67 (S)	1.718	1.647
$1\ ^1A''_1$	1.78 (D)		
$1\ ^1E'$	2.04 (S)	2.122	1.988
$2\ ^1E^{\#}$	2.61 (D)		
$2\ ^1E'$	2.68 (D)	9.315	3.032
$1\ ^1A'_2$	2.89 (S)	2.982	2.790
$2\ ^1A'_1$	2.91 (S)	3.029	2.896
$3\ ^1E^{\#}$	3.04 (D)	4.232	3.546
$3\ ^1E'$	3.08 (D)	4.823	3.338
$1\ ^1A''_2$	3.16 (S,D)	3.993	3.358
$2\ ^1A''_1$	3.31 (D)	5.271	3.601
$4\ ^1E'$	3.48 (D)	4.570	3.633
$3\ ^1A'_1$	3.64 (D)	4.935	4.033
$4\ ^1E^{\#}$	3.90 (D)	5.286	3.954
$3\ ^1A''_1$	3.99 (S,D)	4.244	3.891
$2\ ^1A''_2$	4.12 (D)	5.995	4.384

Av. errors (eV): 1.33 0.20

ACTIVE-SPACE CC/EOMCC APROACHES FOR QUASI-DEGENERATE STATES (CCSDt, CCSDtq, EOMCCSDt, etc.)

[~ state-selective MRCC methods exploiting a single-reference formalism]

[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.]



$$|\Psi\rangle = e^T |\Phi\rangle, \quad T = \mathcal{T}^{\text{int}} + \mathcal{T}^{\text{ext}}, \quad [\mathcal{T}^{\text{int}}, \mathcal{T}^{\text{ext}}] = 0$$

$$|\Psi\rangle = e^{\mathcal{T}^{\text{ext}}} |\Phi^{\text{int}}\rangle, \quad |\Phi^{\text{int}}\rangle = e^{\mathcal{T}^{\text{int}}} |\Phi\rangle \quad \text{(CAS)}$$

\mathcal{T}^{int} – **nondynamic correlation**, \mathcal{T}^{ext} – **dynamic correlation**
(long-range correlations) (short-range correlations)

REPRESENTATIVE APPROXIMATIONS: CCSDt OR SSMRCCSD(T) AND EOMCCSDt

$$T^{\text{int}} = T_1^{\text{int}} + T_2^{\text{int}} + T_3^{\text{int}}, \quad T^{\text{ext}} = T_1^{\text{ext}} + T_2^{\text{ext}} + T_3^{\text{ext}} \left(\begin{array}{c} ab\mathbf{C} \\ Ijk \end{array} \right)$$

$$T^{\text{CCSDt}} = T_1 + T_2 + T_3 \left(\begin{array}{c} ab\mathbf{C} \\ Ijk \end{array} \right), \quad R_K^{\text{CCSDt}} = R_{K,0} + R_{K,1} + R_{K,2} + R_{K,3} \left(\begin{array}{c} ab\mathbf{C} \\ Ijk \end{array} \right)$$

$$\bar{\mathbf{H}}^{\text{CCSDt}} = \begin{pmatrix} \bar{\mathbf{H}}_{\text{SS}} & \bar{\mathbf{H}}_{\text{SD}} & \bar{\mathbf{H}}_{\text{St}} \\ \bar{\mathbf{H}}_{\text{DS}} & \bar{\mathbf{H}}_{\text{DD}} & \bar{\mathbf{H}}_{\text{Dt}} \\ \bar{\mathbf{H}}_{\text{tS}} & \bar{\mathbf{H}}_{\text{tD}} & \bar{\mathbf{H}}_{\text{tt}} \end{pmatrix}, \quad \bar{H} = e^{-T} H e^T = (H e^T)_C$$

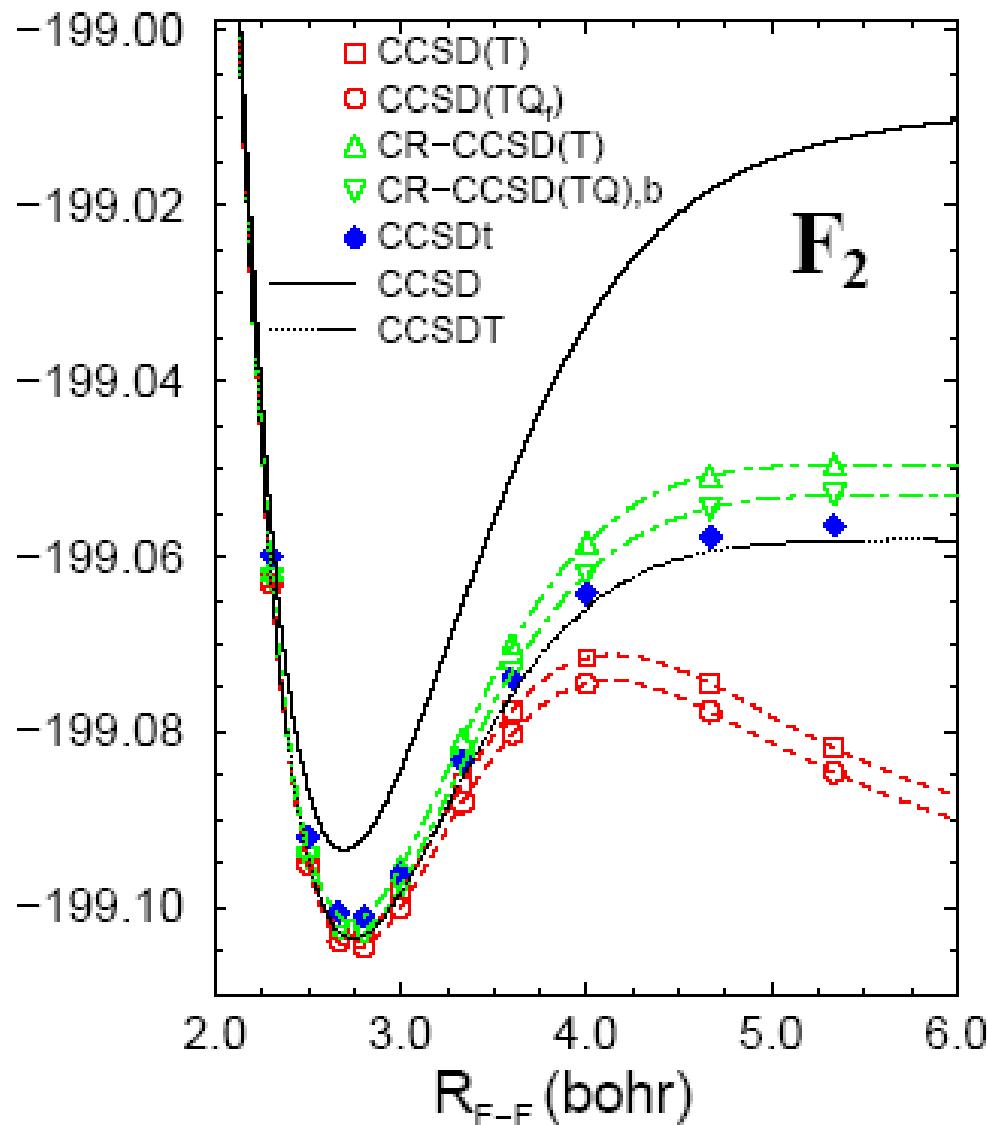
Other approximations: SSMRCCSD(TQ) or CCSDtq, EOMCCSDtq, etc.

Because of the use of active orbitals, the numbers of t, q, ... excitations are small fractions (~10-30 %) of all T, Q, ... excitations.

The most expensive CPU steps of (EOM)CCSDt and (EOM)CCSDtq scale as $\sim N_o N_u n_o^2 n_u^4$ and $\sim N_o^2 N_u^2 n_o^2 n_u^4$, respectively.

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 F₂

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

Potential energy curves for F₂/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;
P. Piecuch et al., Chem. Phys. Lett., 2006)

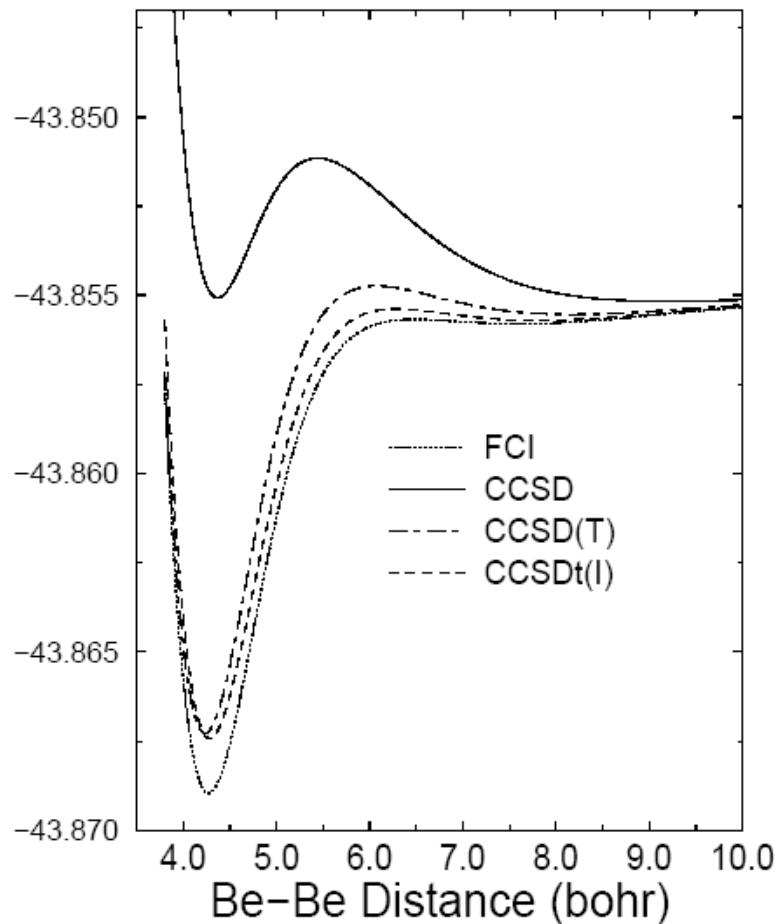
Potential energy curves for F_2 /cc-pVDZ. Differences with CCSDT (in millihartree)

Method	$0.75R_e$	R_e	$1.25R_e$	$1.5R_e$	$1.75R_e$	$2R_e$	$3R_e$	$5R_e$	NPE
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

Ground and excited states of Be_3

(K. Kowalski et al., J. Chem. Phys. 2005, P. Piecuch et al., Int. J. Quantum Chem., 2006)

Energy (hartree)



State	Full CI	EOMCCSD	CR-EOMCCSD(T)	EOMCCSDt
$X^1A'_1$	-43.882330	-43.864904	-43.873110	-43.879340
$1^1E''$	1.67 (S)	1.718	1.647	1.658
$1^1A''_1$	1.78 (D)			1.877
$1^1E'$	2.04 (S)	2.122	1.988	2.031
$2^1E''$	2.61 (D)			2.683
$2^1E'$	2.68 (D)	9.315	3.032	2.708
$1^1A'_2$	2.89 (S)	2.932	2.790	2.871
$2^1A'_1$	2.91 (S)	3.029	2.896	2.937
$3^1E''$	3.04 (D)	4.232	3.546	3.115
$3^1E'$	3.08 (D)	4.823	3.338	3.247
$1^1A''_2$	3.16 (S,D)	3.993	3.358	3.302
$2^1A''_1$	3.31 (D)	5.271	3.601	3.439
$4^1E'$	3.48 (D)	4.570	3.633	3.541
$3^1A'_1$	3.64 (D)	4.935	4.033	3.846
$4^1E''$	3.90 (D)	5.286	3.954	4.018
$3^1A''_1$	3.99 (S,D)	4.244	3.891	4.112
$2^1A''_2$	4.12 (D)	5.995	4.384	4.183

Average errors (eV): 1.33

0.20

0.08

Radicals via the active-space electron-attached (EA) and ionized (IP) EOMCC

(J.R. Gour, P. Piecuch, and M. Włoch, J. Chem. Phys., 2005; Int. J. Quantum Chem., 2006, J.R. Gour and P. Piecuch, J. Chem. Phys., 2006; Piecuch et al., 2007-2011)

$$(\bar{H}_{N,\text{open}} R_{\mu}^{(N\pm 1)}(\text{CCSDt}))_C |\Phi\rangle = \omega_{\mu}^{(N\pm 1)} R_{\mu}^{(N\pm 1)}(\text{CCSDt}) |\Phi\rangle$$

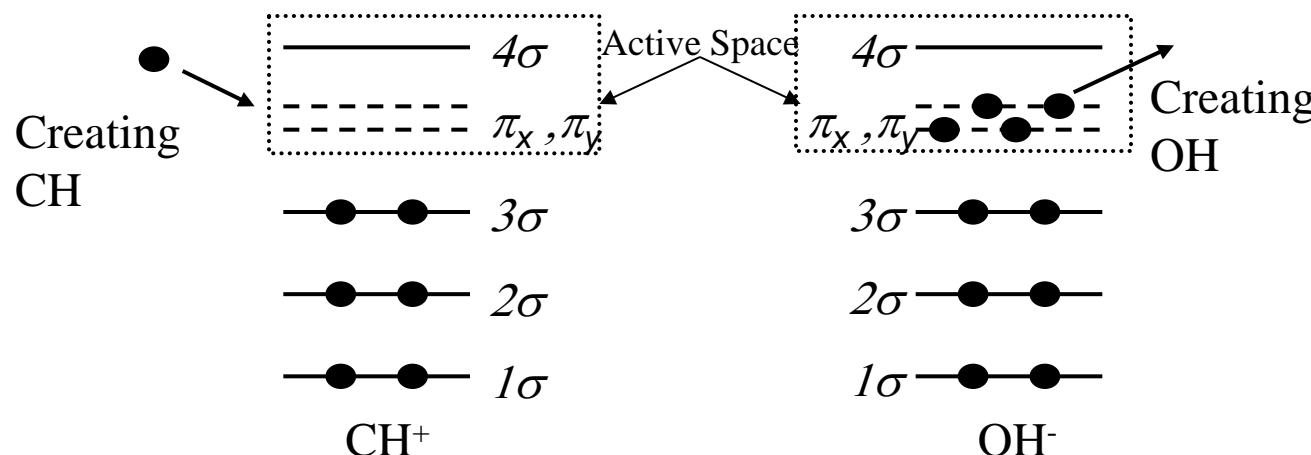
$$R_{\mu}^{(N+1)}(\text{CCSDt}) = R_{\mu,1p} + R_{\mu,2p-1h} + r_{\mu,3p-2h}$$

$$R_{\mu}^{(N-1)}(\text{CCSDt}) = R_{\mu,1h} + R_{\mu,2h-1p} + r_{\mu,3h-2p}$$

where

$$r_{\mu,3p-2h} = \sum_{j>k, A < b < c} r_{A_{bc}}^{jk} a^A a^b a^c a_k a_j,$$

$$r_{\mu,3h-2p} = \sum_{I>j>k, b < c} r_{b_c}^{Ik} a^b a^c a_k a_j a_I.$$



(CCTYP=EA-EOM3A and IP-EOM3A, respectively, in GAMESS)

Adiabatic Excitation Energies of CH (in eV)

State	CCSD/	CCSDT/	EA-EOM				Exp.
	EOMCCSD	EOMCCSDT	CCSD(2p-1h)	CCSD(3p-2h)	CCSDt	MRCl(Q)	
aug-cc-pVTZ							
$X\ ^2\Pi$	-38.409 320	-38.413 493	-38.409 823	-38.412 070	-38.409 413	-38.413 811	
$a\ ^4\Sigma^-$	1.03	0.74	2.661	0.743	0.704	0.718	0.74
$A\ ^2\Delta$	3.28	2.94	5.120	2.964	2.931	2.911	2.87
$B\ ^2\Sigma^-$	4.62	3.27	6.453	3.393	3.359	3.251	3.23
$C\ ^2\Sigma^+$	5.48	4.03	5.815	4.053	4.040	3.980	3.94
aug-cc-pVQZ							
$X\ ^2\Pi$	-38.415 848	-	-38.416 559	-38.418 732	-38.415 905	-38.420 576	
$a\ ^4\Sigma^-$	1.06	-	2.741	0.766	0.724	0.741	0.74
$A\ ^2\Delta$	3.27	-	5.181	2.952	2.917	2.896	2.87
$B\ ^2\Sigma^-$	4.67	-	6.538	3.390	3.355	3.245	3.23
$C\ ^2\Sigma^+$	5.52	-	5.878	4.037	4.021	3.962	3.94

Timings in Multiples of the EA-EOMCCSD(2p-1h) Time

Method	aug-cc-pVTZ	aug-cc-pVQZ		
EA-EOMCCSD(3p-2h)	61.42	56.42	$\sim n_o^2 n_u^5$	
EA-EOMCCSDt	5.57	3.45	$\sim N_u n_o^2 n_u^4$	Active orbitals in EA-EOMCCSDt:
EOMCCSD	1.00	1.19	$\sim n_o^2 n_u^4$	$1\pi_x, 1\pi_y, 4\sigma$

Adiabatic Excitation Energies of CH (in eV)

State	CCSD/	CCSDT/	EA-EOM				Exp.
	EOMCCSD	EOMCCSDT	CCSD(2p-1h)	CCSD(3p-2h)	CCSDt	MRCI(Q)	
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Biradicals via the active-space DEA- and DIP-EOMCC

(J. Shen and P. Piecuch, J. Chem. Phys., 2013, Mol. Phys., 2014)

M. Nooijen and R.J. Bartlett, 1997; M. Nooijen, 2002; K.W. Sattetmeyer, H.F. Schaefer III, and J.F. Stanton, 2003; M. Musiał, R.J. Bartlett, et al., 2011-2013; T. Kuś and A.I. Krylov, 2011-2012; ...

$$R_{\mu}^{(N+2)}\{N_u\} = R_{\mu,2p} + R_{\mu,3p-1h} + r_{\mu,4p-2h}$$

$$R_{\mu}^{(N-2)}\{N_o\} = R_{\mu,2h} + R_{\mu,3h-1p} + r_{\mu,4h-2p}$$

$$r_{\mu,4p-2h} = \sum_{k>l, \mathbf{A}<\mathbf{B}<c<d} r_{\mathbf{AB}cd}^{kl}(\mu) a^{\mathbf{A}} a^{\mathbf{B}} a^c a^d a_l a_k$$

$$r_{\mu,4h-2p} = \sum_{\mathbf{I}>\mathbf{J}>k>l, c<d} r_{\mathbf{IJ}cd}^{kl}(\mu) a^c a^d a_l a_k a_{\mathbf{J}} a_{\mathbf{I}}$$

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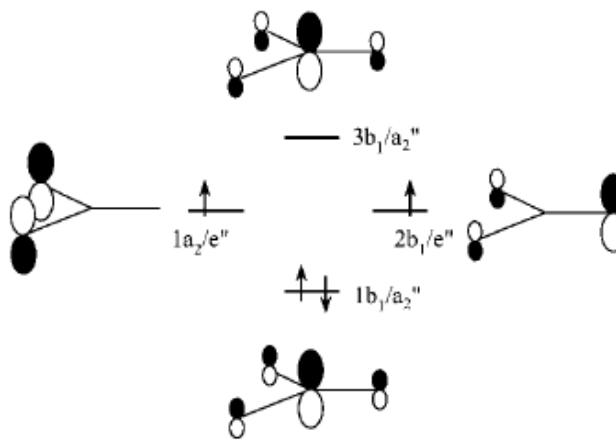
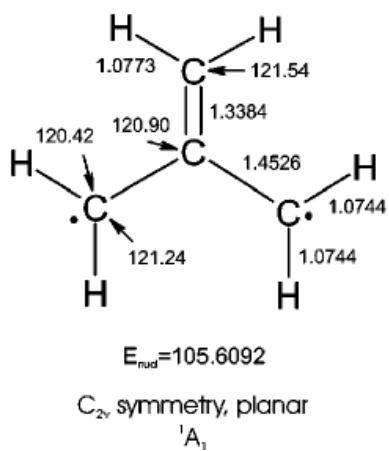
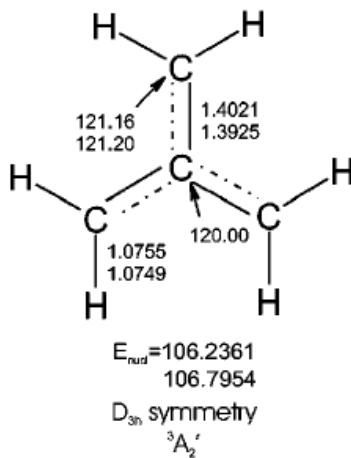
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$$r_{\mu,4h-2p} = \sum_{\mathbf{I} > \mathbf{J} > k > l, c < d} r_{cd}^{\mathbf{IJ}kl}(\mu) a^c a^d a_l a_k a_{\mathbf{J}} a_{\mathbf{I}}$$

Example: Singlet-triplet gap in trimethylenemethane (TMM)



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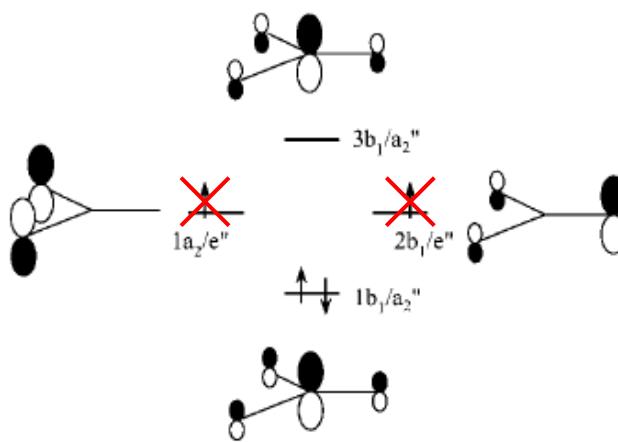
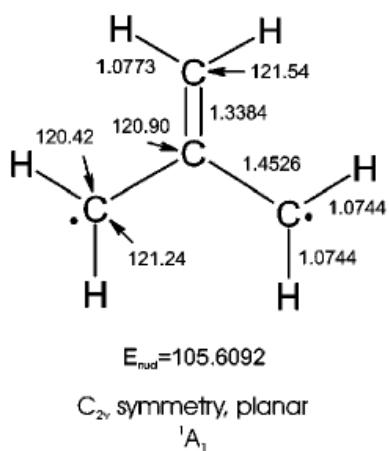
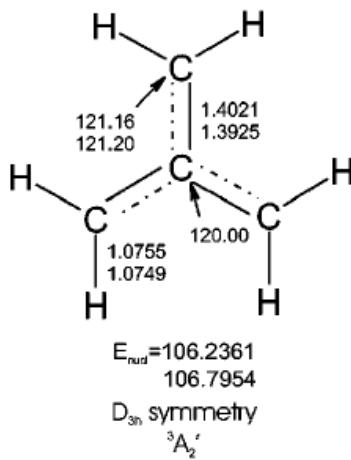
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$$r_{\mu,4h-2p} = \sum_{\mathbf{I}>\mathbf{J}>k>l, c<d} r_{cd}^{\mathbf{IJ}kl}(\mu) a^c a^d a_l a_k a_{\mathbf{J}} a_{\mathbf{I}}$$

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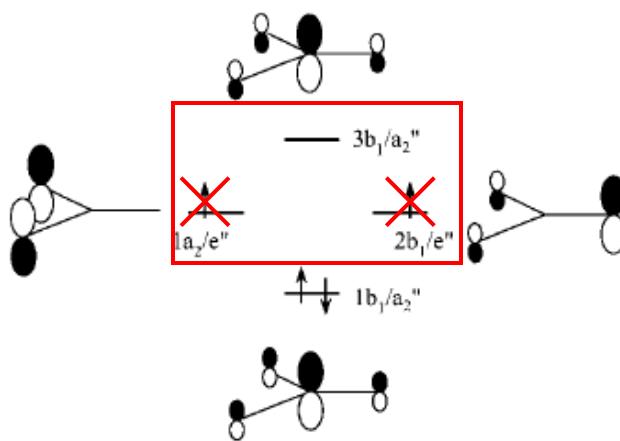
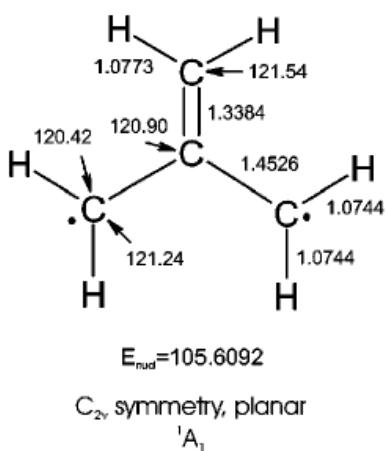
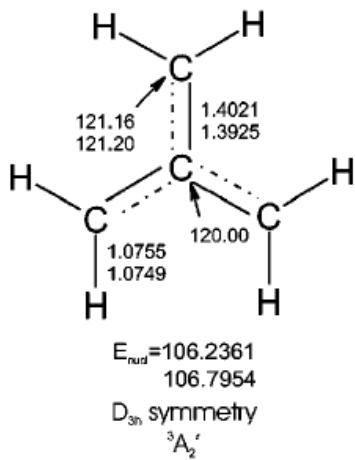
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$$r_{\mu,4h-2p} = \sum_{\mathbf{I} > \mathbf{J} > k > l, c < d} r_{cd}^{\mathbf{IJ}kl}(\mu) a^c a^d a_l a_k a_{\mathbf{J}} a_{\mathbf{I}}$$

Example: Singlet-triplet gap in trimethylenemethane (TMM)



$n_o^2 n_u^6 \rightarrow N_u^2 n_o^2 n_u^4$
DEA: TMM²⁺

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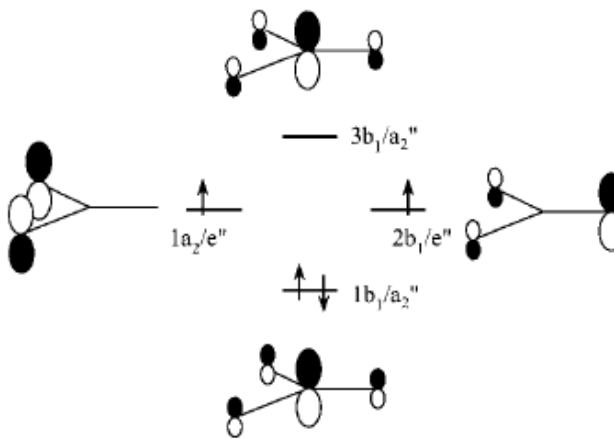
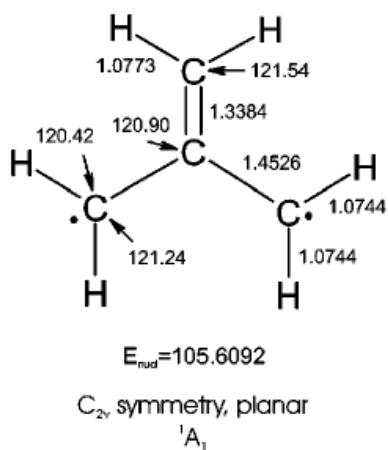
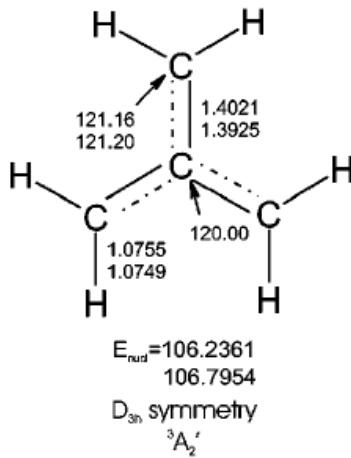
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$$r_{\mu,4p-2h} = \sum_{k>l, \mathbf{A} < \mathbf{B} < c < d} r_{\mathbf{AB}cd}^{kl}(\mu) a^{\mathbf{A}} a^{\mathbf{B}} a^c a^d a_l a_k$$

$$r_{\mu,4h-2p} = \sum_{\mathbf{I} > \mathbf{J} > k > l, c < d} r_{cd}^{\mathbf{IJ}kl}(\mu) a^c a^d a_l a_k a_{\mathbf{J}} a_{\mathbf{I}}$$

Example: Singlet-triplet gap in trimethylenemethane (TMM)



Biradicals via the active-space DEA- and DIP-EOMCC

(J. Shen and P. Piecuch, J. Chem. Phys., 2013, Mol. Phys., 2014)

M. Nooijen and R.J. Bartlett, 1997; M. Nooijen, 2002; K.W. Sattetmeyer, H.F. Schaefer III, and J.F. Stanton, 2003; M. Musiał, R.J. Bartlett, et al., 2011-2013; T. Kuś and A.I. Krylov, 2011-2012; ...

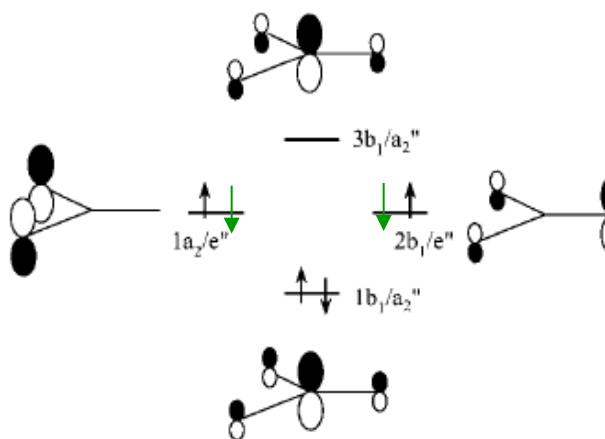
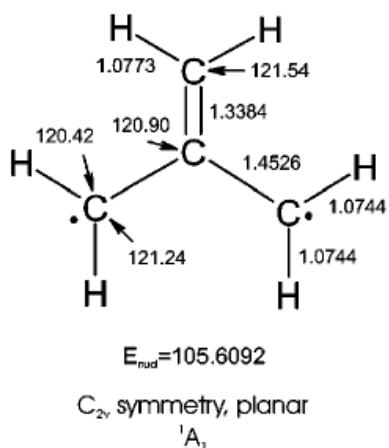
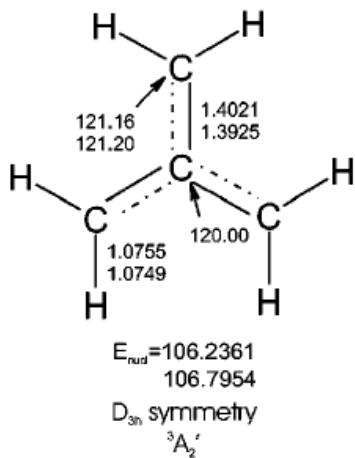
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DIP: TMM^{2-}
 $n_o^4 n_u^4$

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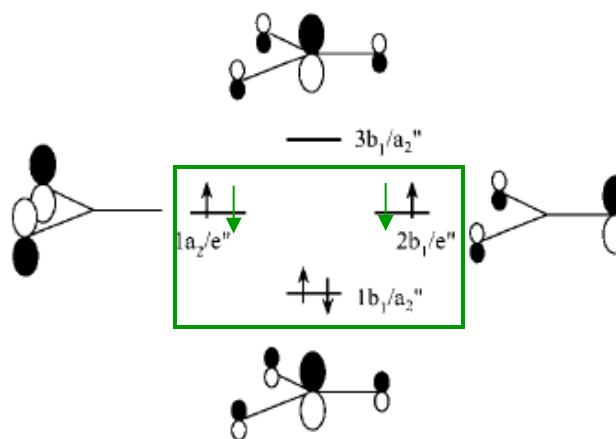
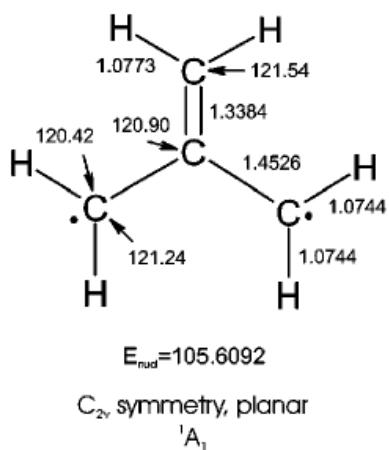
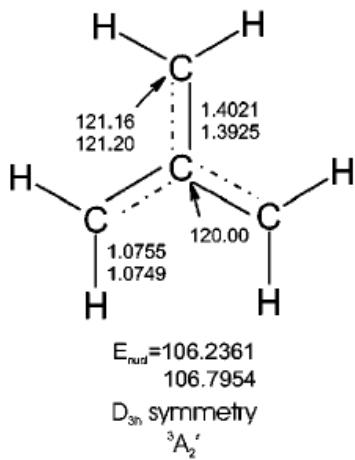
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Example: Singlet-triplet gap in trimethylenemethane (TMM)



DIP: TMM^{2-}

$$n_o^4 n_u^4 \rightarrow N_o^2 n_o^2 n_u^4$$

Biradicals via the active-space DEA- and DIP-EOMCC

(J. Shen and P. Piecuch, J. Chem. Phys., 2013, Mol. Phys., 2014)

Method	ΔE_{S-T}
DEA-EOMCC(3p-1h)	20.9
DEA-EOMCC(4p-2h){3} ^b	18.9
DIP-EOMCC(3h-1p)	22.0
DIP-EOMCC(4h-2p){3} ^c	18.8
DIP-EOMCC(4h-2p)	18.8
Expt. ^d	16.0 ± 0.1
Expt. – $\Delta ZPVE^e$	18.1

Example: Singlet-triplet gap in trimethylenemethane (TMM), in kcal/mol

[geometries from L.V. Slipchenko and A.I. Krylov,
J. Chem. Phys. 117, 4694 (2002)]

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15 times
faster



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15 times
faster

Method	cc-pVDZ	cc-pVTZ
CCSD ^{a,b}	46.1	46.9
CCSD(T) ^{a,b}	24.4	27.1
CR-CC(2,3) _A ^{a,b,c}	32.3	33.6
CR-CC(2,3) _D ^{a,b}	29.9	31.8
CCSDt ^{a,b}	21.6	22.6
CCSD(T)-h ^{a,b}	19.8	19.3
CC(t;3) _A ^{a,b}	21.2	21.8
CC(t;3) _D ^{a,b}	21.2	21.7
CCSDT ^{a,b}	21.7	
2R SUCCSD/RHF ^d		19.9
2R SUCCSD/MCSCF ^d		16.1
2R RMRCCSD/RHF ^d		30.6
2R RMRCCSD/MCSCF ^d		23.8
2R RMRCCSD(T) _f /RHF ^d		25.8
2R RMRCCSD(T) _f /MCSCF ^d		23.6
2R RMRCCSD(T) _{se} /RHF ^d		23.8
2R RMRCCSD(T) _{se} /MCSCF ^d		22.6
SF-CIS ^{b,e}		20.4
SF-CIS(D) ^{b,e}		20.6
SF-OD ^{b,e}		21.7
EOM-SF-CCSD ^{b,f}		21.5
EOM-SF-CC(2,3) ^{b,f}		18.2
4R BWCCSD it ^g	18.2	17.8
4R BWCCSDT-1 α ^g	14.9	
4R BWCCSDT- α ^g	15.6	
Expt. ^h		16.0 ± 0.1
Expt.– $\Delta ZPVE^i$		18.1

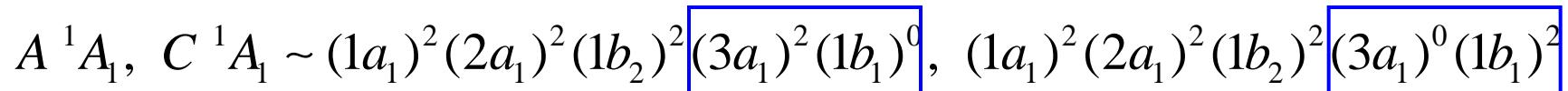
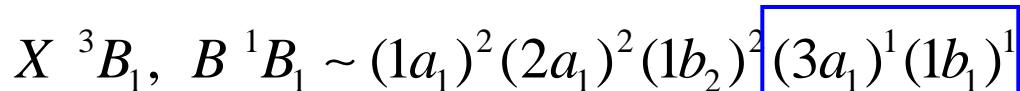
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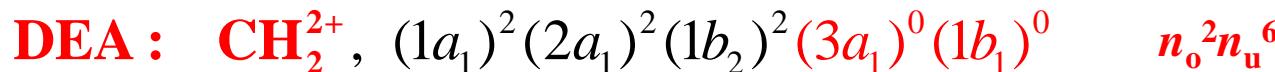
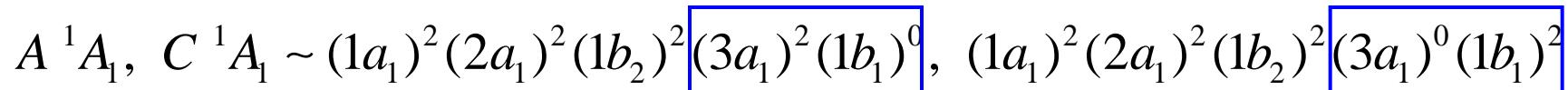
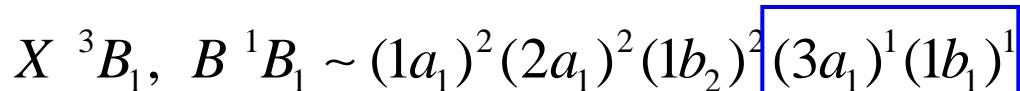


Method	$A \ ^1A_1 - X \ ^3B_1$	$B \ ^1B_1 - X \ ^3B_1$	$C \ ^1A_1 - X \ ^3B_1$	MUE	NPE
DEA-EOMCC($3p-1h$)	1.53	1.09	0.93	1.53	0.60
DEA-EOMCC($4p-2h\{2\}^c$)	0.12	-0.56	-0.82	0.82	0.94
DEA-EOMCC($4p-2h$)	0.19	0.14	0.43	0.43	0.29
DIP-EOMCC($3h-1p$)	6.03	8.47	10.94	10.94	4.91
DIP-EOMCC($4h-2p\{2\}^c$)	1.17	0.64	0.90	1.17	0.53
DIP-EOMCC($4h-2p$)	1.24	0.69	0.95	1.24	0.55
Full CI ^a	11.14	35.59	61.67		

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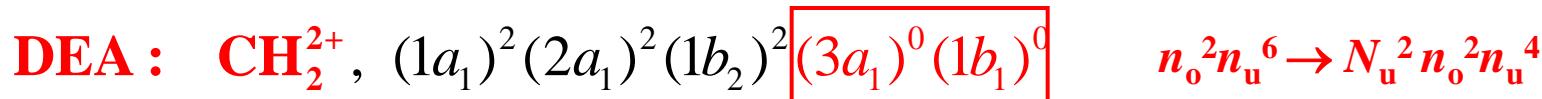
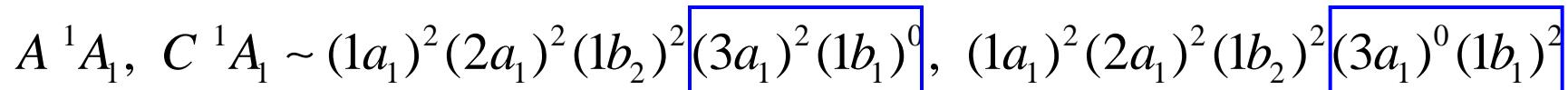
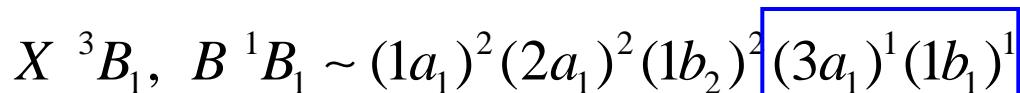


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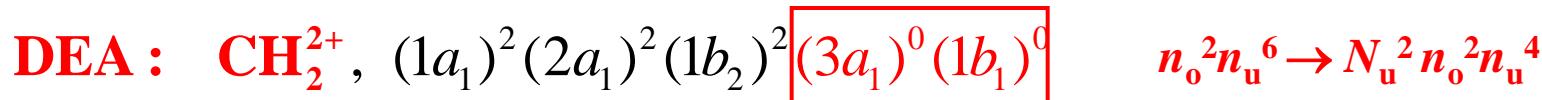
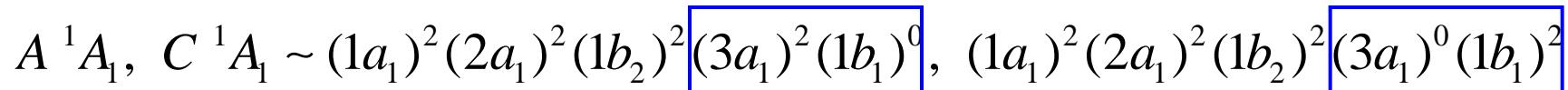
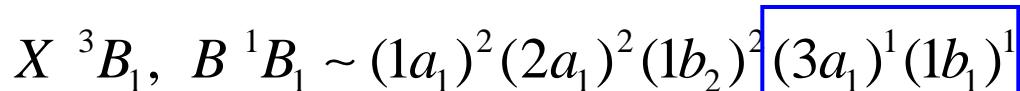


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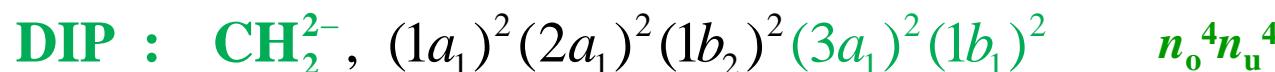
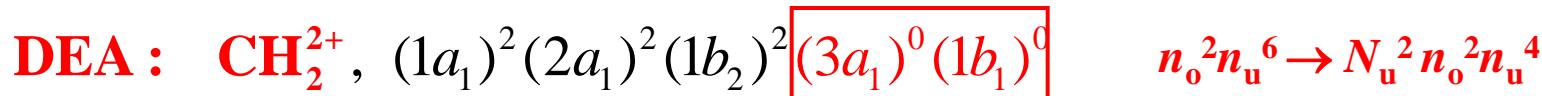
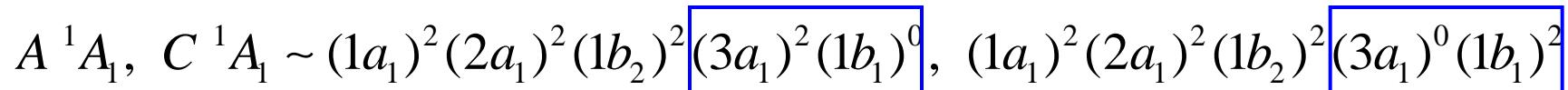
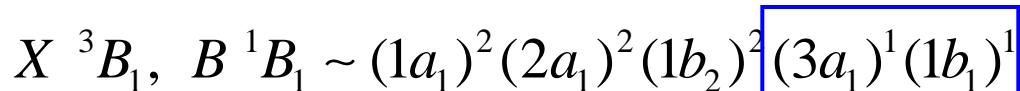


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DEA-EOMCC($3p-1h$)	1.53	1.09	0.93	1.53	0.60	2 s/iter
DEA-EOMCC($4p-2h\{2\}^c$)	0.12	-0.56	-0.82	0.82	0.94	6 s/iter.
DEA-EOMCC($4p-2h$)	0.19	0.14	0.43	0.43	0.29	2621 s/iter.
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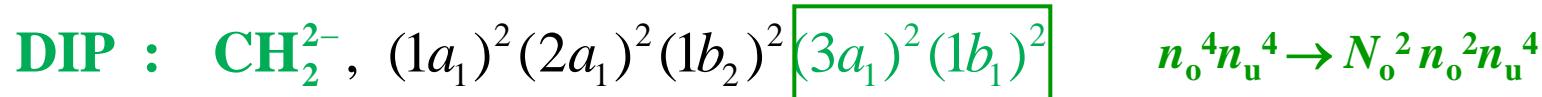
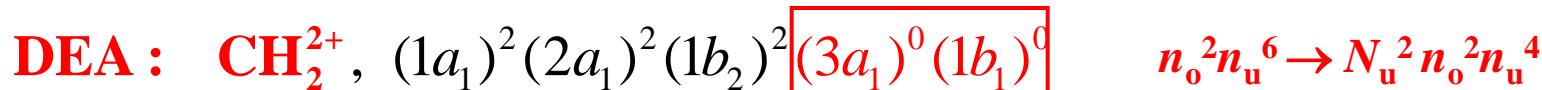
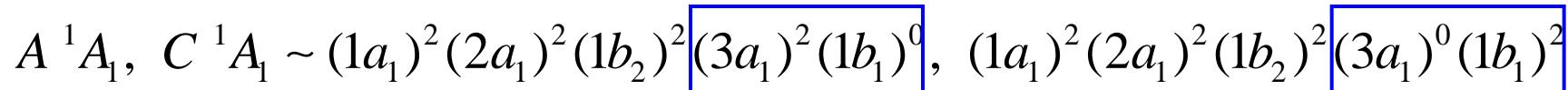
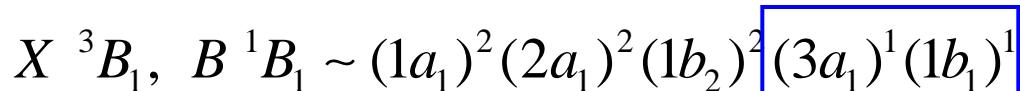


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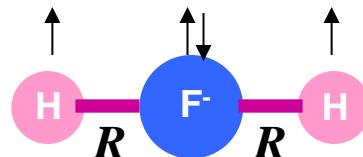


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Singlet-Triplet Splitting in $(\text{HFH})^\cdot$ (in cm^{-1})

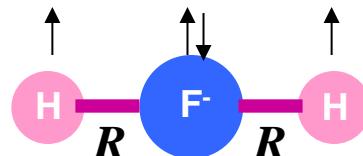


$R_{\text{H-F}}$	RHF			UHF	
	Full CI	CCSD	CCSD(T)	CCSD	CCSD(T)
1.5	9525	7320	9468	7398	8418
1.625	7008	4372	7066	4981	5776
1.750	4911	1838	5179	3156	3693
1.875	3304	-172	3902	1913	2244
2.000	2147	-1656	3212	1122	1323
2.125	1353	-2668	3023	638	766
2.250	827	-3282	3225	350	438
2.375	488	-3572	3714	182	247
2.500	277	-3605	4394	88	137
3.000	17	-2369	7370	1	10
4.000	0	-230	8899	0	0

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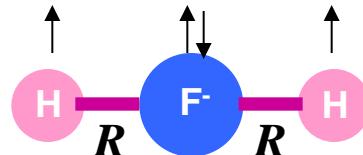


$R_{\text{H-F}}$	RHF			UHF	
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1.5	9525	7320	-57	7398	8418
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1.750	4911	1838	268	3156	3693
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Biradicals via the active-space DEA- and DIP-EOMCC

(J. Shen and P. Piecuch, J. Chem. Phys., 2013, Mol. Phys., 2014)

Singlet-Triplet Splitting in $(\text{HFH})^\cdot$ (in cm^{-1})

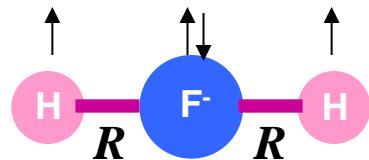


$R_{\text{H-F}}$	RHF			UHF	
	Full CI	CCSD	CCSD(T)	CCSD	CCSD(T)
1.5	9525	7320	-57	7398	-1107
1.625	7008	4372	58	4981	-1232
1.750	4911	1838	268	3156	-1218
1.875	3304	-172	598	1913	-1060
2.000	2147	-1656	1065	1122	-824
2.125	1353	-2668	1670	638	-587
2.250	827	-3282	2398	350	-389
2.375	488	-3572	3226	182	-241
2.500	277	-3605	4117	88	-140
3.000	17	-2369	7353	1	-7
4.000	0	-230	8899	0	0

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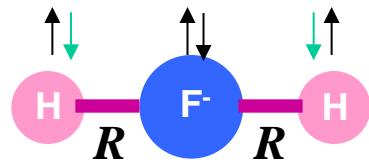
Singlet-Triplet Splitting in $(\text{HFH})^\cdot$ (in cm^{-1})



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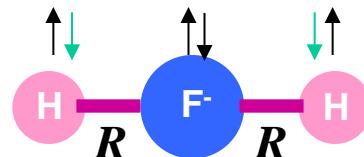


DIP, reference system $(\text{HFH})^{3-}$

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Singlet-Triplet Splitting in $(\text{HFH})^{\cdot}$ (in cm^{-1})



Orbitals	Method	H–F distance (\AA)												MUE	NPE
		1.500	1.625	1.750	1.875	2.000	2.125	2.250	2.375	2.500	3.000	4.000			
ROHF ^b	DIP-EOMCC(3h-1p)	317	327	307	266	216	167	122	85	57	6	0	327	327	
	DIP-EOMCC(4h-2p){3} ^c	-24	-18	-13	-9	-6	-4	-3	-2	-1	0	0	24	24	
	DIP-EOMCC(4h-2p)	-9	-1	3	4	5	4	3	2	2	1	0	9	14	
RHF ^d	DIP-EOMCC(3h-1p)	481	478	435	367	293	222	159	108	71	7	0	481	481	
	DIP-EOMCC(4h-2p){3} ^c	-40	-36	-77	-58	-40	-27	-17	-12	-8	-8	0	77	77	
	DIP-EOMCC(4h-2p)	-22	-19	-16	-12	-8	-6	-4	-3	-1	1	0	22	23	
ROHF/RHF ^e	DIP-EOMCC(3h-1p)	674	725	719	672	603	525	447	374	311	153	79	725	646	
	DIP-EOMCC(4h-2p){3} ^c	160	186	88	113	132	142	144	139	132	103	148	186	98	
	DIP-EOMCC(4h-2p)	155	182	206	224	237	245	247	245	240	202	148	247	99	
Full CI ^a		9525	7008	4911	3304	2147	1353	827	489	277	17	0			

Active orbitals for selecting 4h-2p excitations: 3 MOs correlating with the 1s shells of the H atoms and the 2p_z orbital of F

MERGING ACTIVE-SPACE AND RENORMALIZED COUPLED-CLUSTER METHODS, $\text{CC}(P;Q)$, $\text{CC}(\mathbf{t};3)$, $\text{CC}(\mathbf{t},\mathbf{q};3)$, $\text{CC}(\mathbf{t},\mathbf{q};3,4)$, $\text{CC}(\mathbf{q};4)$, ETC. SCHEMES

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

Key idea: Replace the previously developed moment expansions, which aim at describing the differences between the exact (full CI) energies E_μ and the corresponding CC/EOMCC energies obtained using conventional truncation schemes for the cluster operator T and, in the case of excited states, excitation operator R_μ by the expansions that enable us to correct the energies obtained with arbitrary truncations of T and R_μ for the selected higher-order correlation effects of interest.

Examples (and motivation):

Correct the results of CCSDt calculations, where $T \approx T^{(\text{CCSDt})} = T_1 + T_2 + t_3$, for the remaining triples effects neglected in CCSDt calculations, or correct EOMCCSDtq energies, obtained with $T \approx T^{(\text{CCSDtq})} = T_1 + T_2 + t_3 + t_4$ and and $R_\mu \approx R_\mu^{(\text{CCSDtq})} = R_1 + R_2 + r_3 + r_4$ for the remaining triples and quadruples.

Replace

$$E_\mu = E_\mu^{(A)} + \sum_{n=m_A+1}^{N_{\mu,A}} \langle \Phi | L_{\mu,n} M_{\mu,n}(m_A) | \Phi \rangle = E_\mu^{(A)} + \sum_{n=m_A+1}^{N_{\mu,A}} \sum_{i_1 < \dots < i_n, a_1 < \dots < a_n} \ell_{\mu,a_1 \dots a_n}^{i_1 \dots i_n} M_{\mu,i_1 \dots i_n}^{a_1 \dots a_n}(m_A),$$

where $E_\mu^{(A)}$ is obtained with $T^{(A)} = T_1 + \dots + T_{m_A}$ and $R_\mu^{(A)} = R_1 + \dots + R_{m_A}$, with

$$M_{\mu,i_1 \dots i_n}^{a_1 \dots a_n}(m_A) = \langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | \bar{H}^{(A)} R_\mu^{(A)} | \Phi \rangle, \quad \bar{H}^{(A)} = e^{-T^{(A)}} H e^{T^{(A)}},$$

by

$$E_\mu^{(P+Q)} = E_\mu^{(P)} + \delta_\mu(P;Q) = E_\mu^{(P)} + \sum_{\substack{\Phi_K \in \mathcal{H}_Q \\ \text{rank}(\Phi_K) \leq \min(N_\mu^{(P)}, \Xi^{(P)})}} \ell_{\mu,K}(P) M_{\mu,K}(P),$$

where $E_\mu^{(P)}$ is obtained with $T^{(P)} = \sum_{\Phi_K \in \mathcal{H}_P} t_K E_K$ and $R_\mu^{(P)} = r_0 \mathbf{1} + \sum_{\Phi_K \in \mathcal{H}_P} r_K E_K$, using

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

CC($P; Q$) HIERARCHY.

CC(t;3), CC(t,q;3), CC(t,q;3,4), CC(q;4), etc. schemes

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

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

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

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

CC(P;Q) HIERARCHY.

CC(t;3), CC(t,q;3), CC(t,q;3,4), CC(q;4), etc. schemes

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$$E_\mu^{(\text{CC(t;3)})} = E_\mu^{(\text{CCSDt})} + \delta_\mu(\text{t}; 3)$$

$$\delta_\mu(\text{t}; 3) = \sum_{|\Phi_{ijk}^{abc}\rangle \in \mathcal{H}^{(\text{T})} \ominus \mathcal{H}^{(\text{t})}} \ell_{\mu,ijk}^{abc}(\text{CCSDt}) \mathfrak{M}_{\mu,abc}^{ijk}(\text{CCSDt})$$

} → CC(t;3)

CC(P ; Q) HIERARCHY.

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

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$$E_\mu^{(\text{CC(t,q;3)})} = E_\mu^{(\text{CCSDtq})} + \delta_\mu(\text{t, q}; 3)$$

$$\delta_\mu(\text{t, q}; 3) = \sum_{|\Phi_{ijk}^{abc}\rangle \in \mathcal{H}^{(\text{T})} \ominus \mathcal{H}^{(\text{t})}} \ell_{\mu,ijk}^{abc}(\text{CCSDtq}) \mathfrak{M}_{\mu,abc}^{ijk}(\text{CCSDtq}),$$

} → CC(t;3)
} → CC(t,q;3)

CC(P ; Q) HIERARCHY.

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$$E_{\mu}^{(\text{CC(t,q;3,4)})} = E_{\mu}^{(\text{CCSDtq})} + \delta_{\mu}(\text{t, q}; 3, 4)$$

$$\delta_{\mu}(\text{t, q}; 3, 4) = \sum_{|\Phi_{ijk}^{abc}\rangle \in \mathcal{H}^{(\text{T})} \ominus \mathcal{H}^{(\text{t})}} \ell_{\mu,ijk}^{abc}(\text{CCSDtq}) \mathfrak{M}_{\mu,abc}^{ijk}(\text{CCSDtq})$$

$$+ \sum_{|\Phi_{ijkl}^{abcd}\rangle \in \mathcal{H}^{(\text{Q})} \ominus \mathcal{H}^{(\text{q})}} \ell_{\mu,ijkl}^{abcd}(\text{CCSDtq}) \mathfrak{M}_{\mu,abcd}^{ijkl}(\text{CCSDtq})$$

} → **CC(t;3)**
} → **CC(t,q;3)**
} → **CC(t,q;3,4)**

EXAMPLE: THE CC(t;3) APPROACH: Correcting CCSDt for the remaining triples with CR-CC(2,3)-like expressions

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

$$T^{(\text{CCSDt})} = T_1 + T_2 + t_3, \quad Q \Rightarrow T_3 - t_3$$

$$E_{\mu}^{(\text{CC(t;3)})} = E_{\mu}^{(\text{CCSDt})} + \sum_{\{i < j < k, a < b < c\} \in Q} \ell_{\mu,abc}^{ijk} (\text{CCSDt}) M_{\mu,ijk}^{abc} (\text{CCSDt})$$

$$M_{\mu,ijk}^{abc} (\text{CCSDt}) = \left\langle \Phi_{ijk}^{abc} \left| \bar{H}^{(\text{CCSDt})} R_{\mu}^{(\text{CCSDt})} \right| \Phi \right\rangle$$

$$\ell_{\mu,abc}^{ijk} (\text{CCSDt}) = \left\langle \Phi \left| L_{\mu}^{(\text{CCSDt})} \bar{H}^{(\text{CCSDt})} \right| \Phi_{ijk}^{abc} \right\rangle / (E_{\mu}^{(\text{CCSDt})} - \left\langle \Phi_{ijk}^{abc} \left| \bar{H}^{(\text{CCSDt})} \right| \Phi_{ijk}^{abc} \right\rangle)$$

$$t_3(\text{I}) = \sum_{i < j < \mathbf{K}, \mathbf{A} < b < c} t_{\mathbf{Abc}}^{ij\mathbf{K}} E_{ij\mathbf{K}}^{\mathbf{Abc}}, \quad t_3(\text{II}) = \sum_{i < \mathbf{J} < \mathbf{K}, \mathbf{A} < \mathbf{B} < c} t_{\mathbf{ABc}}^{i\mathbf{JK}} E_{i\mathbf{JK}}^{\mathbf{ABC}}, \quad t_3(\text{III}) = \sum_{\mathbf{I} < \mathbf{J} < \mathbf{K}, \mathbf{A} < \mathbf{B} < \mathbf{C}} t_{\mathbf{ABC}}^{\mathbf{IJK}} E_{\mathbf{IJK}}^{\mathbf{ABC}}$$

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Example: Bond breaking in F₂ (cc-pVTZ basis set; the F-F distance R in multiples of R_e)

R	CCSD			CCSD(T)			CCSDt			CCSD(T)-h			CC(t,3)			CCSDT
	CCSD	CCSD(T)	CR-CC(2,3)	(III)	(II)	(I)	(III)	(II)	(I)	(III)	(II)	(I)	(III)	(II)	(I)	
0.75	11.361	0.021	-0.364	10.401	7.516	2.290	-0.059	-0.163	-0.113	-0.351	-0.308	-0.162	-199.123383			
1	17.979	-0.008	-0.282	16.173	9.907	1.969	-0.273	-0.679	-0.154	-0.341	-0.401	-0.152	-199.296095			
1.25	30.089	-0.881	1.190	25.907	14.577	1.746	-1.617	-2.317	-0.224	0.806	0.069	-0.136	-199.267730			
1.5	45.495	-6.165	3.305	38.405	21.103	1.630	-7.006	-6.962	-0.327	2.536	0.917	-0.124	-199.245756			
1.75	56.750	-16.418	4.193	47.862	26.112	1.588	-16.224	-13.754	-0.410	3.355	1.355	-0.104	-199.239464			
2	62.819	-26.354	4.254	53.126	28.850	1.574	-24.799	-19.507	-0.462	3.493	1.442	-0.088	-199.238344			
3	68.361	-41.789	3.906	58.315	31.260	1.559	-37.814	-27.114	-0.520	3.289	1.265	-0.065	-199.238825			
5	69.103	-47.179	3.733	58.889	31.429	1.558	-41.803	-28.715	-0.524	3.084	1.106	-0.052	-199.238928			
NPE	57.742	47.200	4.618	48.488	23.912	0.732	41.744	28.552	0.410	3.844	1.842	0.110				

EXAMPLE: THE CC(t;3) APPROACH: Correcting CCSDt for the remaining triples with CR-CC(2,3)-like expressions

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

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$$M_{\mu,ijk}^{abc} (\text{CCSDt}) = \left\langle \Phi_{ijk}^{abc} \left| \bar{H}^{(\text{CCSDt})} R_{\mu}^{(\text{CCSDt})} \right| \Phi \right\rangle$$

$$\ell_{\mu,abc}^{ijk} (\text{CCSDt}) = \left\langle \Phi \left| L_{\mu}^{(\text{CCSDt})} \bar{H}^{(\text{CCSDt})} \right| \Phi_{ijk}^{abc} \right\rangle / (E_{\mu}^{(\text{CCSDt})} - \left\langle \Phi_{ijk}^{abc} \left| \bar{H}^{(\text{CCSDt})} \right| \Phi_{ijk}^{abc} \right\rangle)$$

$$t_3(\text{I}) = \sum_{i < j < \mathbf{K}, \mathbf{A} < b < c} t_{\mathbf{A}bc}^{ij\mathbf{K}} E_{ij\mathbf{K}}^{\mathbf{A}bc}, \quad t_3(\text{II}) = \sum_{i < \mathbf{J} < \mathbf{K}, \mathbf{A} < \mathbf{B} < c} t_{\mathbf{A}\mathbf{B}c}^{i\mathbf{J}\mathbf{K}} E_{i\mathbf{J}\mathbf{K}}^{\mathbf{A}\mathbf{B}c}, \quad t_3(\text{III}) = \sum_{\mathbf{I} < \mathbf{J} < \mathbf{K}, \mathbf{A} < \mathbf{B} < \mathbf{C}} t_{\mathbf{A}\mathbf{B}\mathbf{C}}^{\mathbf{I}\mathbf{J}\mathbf{K}} E_{\mathbf{I}\mathbf{J}\mathbf{K}}^{\mathbf{A}\mathbf{B}\mathbf{C}}$$

Example: Bond breaking in F₂ (cc-pVTZ basis set; the F-F distance R in multiples of R_e)

R	CCSD			CCSD(T)			CCSDt			CCSD(T)-h			CC(t,3)			CCSDT
	CCSD	CCSD(T)	CR-CC(2,3)	(III)	(II)	(I)	(III)	(II)	(I)	(III)	(II)	(I)	(II)	(I)		
0.75	11.361	0.021	-0.364	10.401	7.516	2.290	-0.059	-0.163	-0.113	-0.351	-0.308	-0.162	-0.162	-0.162	-199.123383	
1	17.979	-0.008	-0.282	16.173	9.907	1.969	-0.273	-0.679	-0.154	-0.341	-0.401	-0.152	-0.152	-0.152	-199.296095	
1.25	30.089	-0.881	1.190	25.907	14.577	1.746	-1.617	-2.317	-0.224	0.806	0.069	-0.136	-0.136	-0.136	-199.267730	
1.5	45.495	-6.165	3.305	38.405	21.103	1.630	-7.006	-6.962	-0.327	2.536	0.917	-0.124	-0.124	-0.124	-199.245756	
1.75	56.750	-16.418	4.193	47.862	26.112	1.588	-16.224	-13.754	-0.410	3.355	1.355	-0.104	-0.104	-0.104	-199.239464	
2	62.819	-26.354	4.254	53.126	28.850	1.574	-24.799	-19.507	-0.462	3.493	1.442	-0.088	-0.088	-0.088	-199.238344	
3	68.361	-41.789	3.906	58.315	31.260	1.559	-37.814	-27.114	-0.520	3.289	1.265	-0.065	-0.065	-0.065	-199.238825	
5	69.103	-47.179	3.733	58.889	31.429	1.558	-41.803	-28.715	-0.524	3.084	1.106	-0.052	-0.052	-0.052	-199.238928	
NPE	57.742	47.200	4.618	48.488	23.912	0.732	41.744	28.552	0.410	3.844	1.842	0.110	0.110	0.110		

EXAMPLE: THE CC(t;3) APPROACH: Correcting CCSDt for the remaining triples with CR-CC(2,3)-like expressions

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

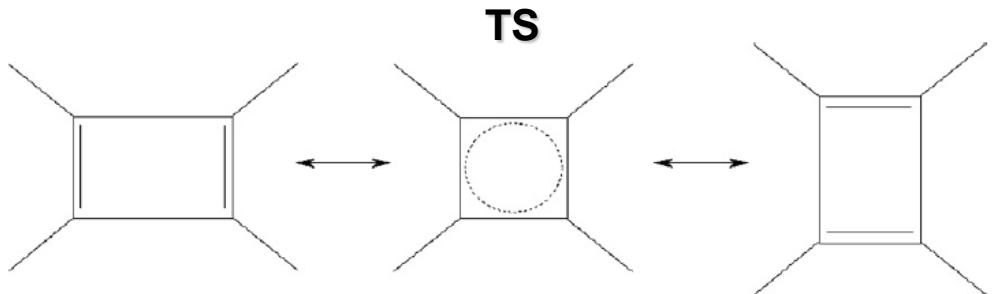
The mean unsigned error (MUE) and non-parallelity error (NPE) values (in millihartree) characterizing the results of various CC calculations for the potential energy curves of the HF, F₂, and F₂⁺ molecules relative to the corresponding full CCSDT energies

Molecular system ^a	CCSD	CCSD(T)	CR-CC(2,3)	CCSDt	CCSD(T)-h	CC(t;3)
MUE						
HF($R/R_e = 0.75 - 5.0$)	36.029	71.762	1.553	3.779	0.350	0.187
F ₂ ($R/R_e = 0.75 - 5.0$)	69.103	47.179	4.254	2.290	0.524	0.162
F ₂ ⁺ ($R/R_e = 0.75 - 3.0$)	89.240	22.032	14.305	1.840	0.727	0.254
NPE						
HF($R/R_e = 0.75 - 5.0$)	29.733	71.770	1.433	1.385	0.330	0.202
F ₂ ($R/R_e = 0.75 - 5.0$)	57.742	47.200	4.618	0.732	0.410	0.110
F ₂ ⁺ ($R/R_e = 0.75 - 3.0$)	77.510	22.132	15.262	0.717	0.604	0.081

^aIn each case, R/R_e designates the range of internuclear separations, in multiples of the equilibrium distance, which was used in the MUE and NPE evaluation. The active spaces used in the CCSDt, CCSD(T)-h, and CC(t;3) calculations consisted of the $N_o = 3$ highest-energy occupied and $N_u = 10$ lowest-energy unoccupied orbitals that correlate with the 1s, 2s, and 2p shells of the H atom and the 2p, 3s, 3p, and 4s shells of the F atom in the HF case, and the $N_o = 5$ highest occupied and $N_u = 9$ lowest unoccupied orbitals that correlate with the 2p, 3s, and 3p shells of the F atoms in the case of F₂ and F₂⁺. See Ref. 152 for further details.

AUTOMERIZATION OF CYCLOBUTADIENE

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



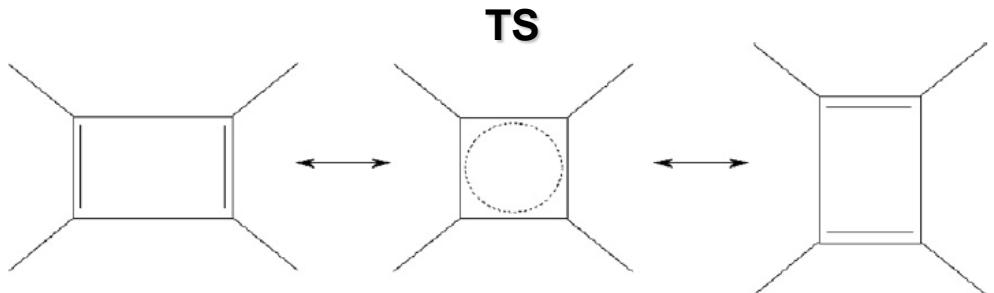
Method	cc-pVDZ	cc-pVTZ
CCSD	20.9	22.6
CCSD(T)	15.8	18.1
CR-CC(2,3)	16.3	18.6
CCSDt(I)	7.3	9.5
CCSD(T)-h(I)	5.0	6.8
CC(t;3)(I)	7.8	10.0
CCSDT	7.6	10.6
ACCSD(T) ^a	16.8	19.2
TCCSD ^a	9.4	12.9
TCCSD(T) ^a	4.6	7.0
CAS-BCCC4 ^b	7.6	8.7
CASPT2 ^b	3.4	3.8
SUCCSD ^c	7.0	8.7
MkCCSD ^c	7.8	9.6
RMRCCSD ^c	10.4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

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

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

AUTOMERIZATION OF CYCLOBUTADIENE

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



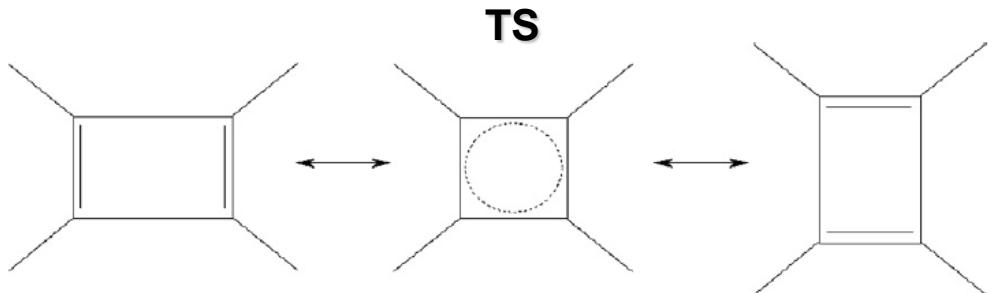
Method	cc-pVDZ	cc-pVTZ
CCSD	20.9	22.6
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CR-CC(2,3)	16.3	18.6
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CCSD(T)-h(I)	5.0	6.8
CC(t;3)(I)	7.8	10.0
CCS DT	7.6	10.6
ACCSD(T) ^a	16.8	19.2
TCCSD ^a	9.4	12.9
TCCSD(T) ^a	4.6	7.0
CAS-BCCC4 ^b	7.6	8.7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

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

	Reactant	TS
CCS DT	-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

AUTOMERIZATION OF CYCLOBUTADIENE

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



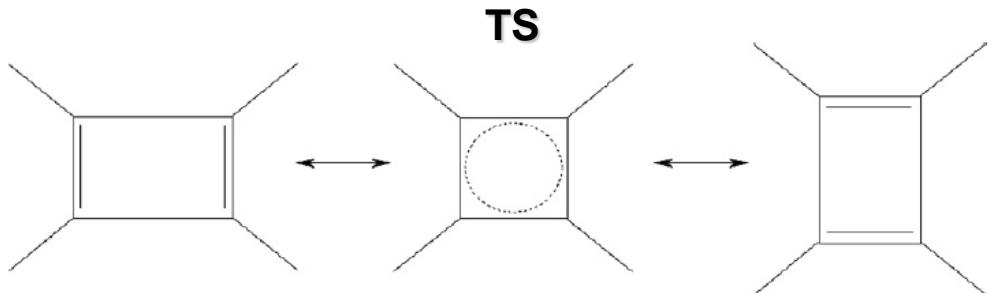
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	Reactant	TS
CCSDT	-154.244157	-154.232002
CCSD	26.827	47.979
CCSD(T)	1.123	14.198
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CCSDt(I)	20.786	20.274
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CC(t;3)(I)	-0.137	0.071

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
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CASPT2 ^b	3.4	3.8
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SUCCSD/mcsfc ^c	7.2	8.9
MkCCSD/mcsfc ^c	7.9	9.7
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2D-MRCCSD(T) ^d	6.6	
BWCCSD(a.c.) ^e	6.5	7.6
BWCCSD(i.c.) ^e	6.2	7.4
BWCCSD(T)(a.c.) ^e	6.1	7.0
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DIP-EOM-CCSD ^a	8.3	10.7
SS-EOM-CCSD[+2] ^g	8.3	9.5
Experimental range ^h	1.6-10	
$\Delta ZPVE^i$		-2.5

AUTOMERIZATION OF CYCLOBUTADIENE

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



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

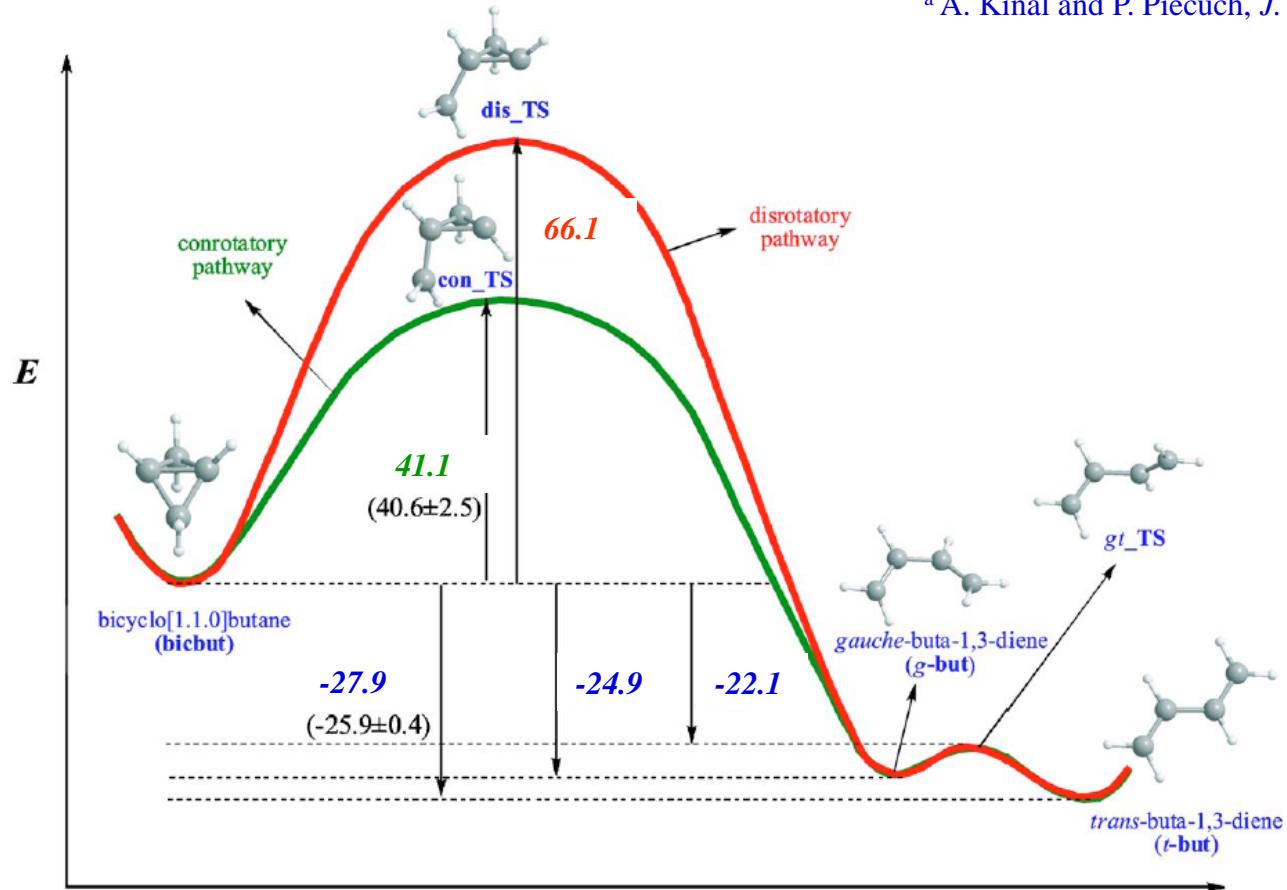
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CCSDT	-154.244157	-154.232002
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ACCSD(T) ^a	16.8	19.2
TCCSD ^a	9.4	12.9
TCCSD(T) ^a	4.6	7.0
CAS-BCCC4 ^b	7.6	8.7
CASPT2 ^b	3.4	3.8
SUCCSD ^c	7.0	8.7
MkCCSD ^c	7.8	9.6
RMRCCSD ^c	10.4	13.0
SUCCSD(T) ^c	4.8	5.9
RMRCCSD(T) ^c	7.2	9.5
SUCCSD/mcsfc ^c	7.2	8.9
MkCCSD/mcsfc ^c	7.9	9.7
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DIP-EOM-CCSD ^a	8.3	10.7
SS-EOM-CCSD[+2] ^g	8.3	9.5
Experimental range ^h	1.6-10	
$\Delta ZPVE^i$		-2.5

The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]-butane to Butadiene Revisited

	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

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



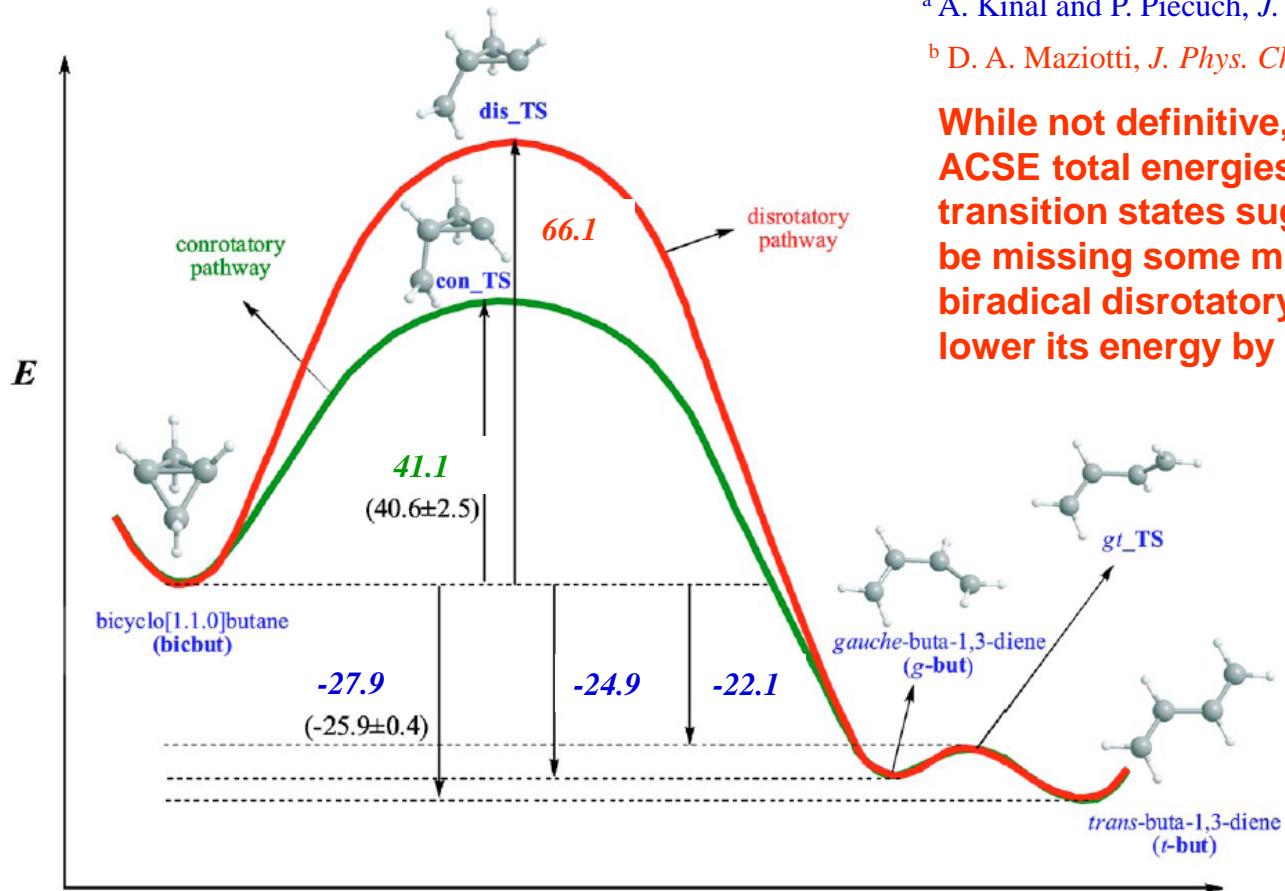
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CR-CC(2,3) ^a	41.1	66.1	-24.9	-22.1	-27.9
ACSE ^b	41.2	55.7	-23.8		

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

^b D. A. Maziotti, *J. Phys. Chem. A* **112**, 13684 (2008)

While not definitive, comparison of the CR-CC and ACSE total energies for reactant, product, and transition states suggests the CR-CC method may be missing some multireference correlation of the biradical disrotatory transition state that would lower its energy by about 9.5 kcal/mol.

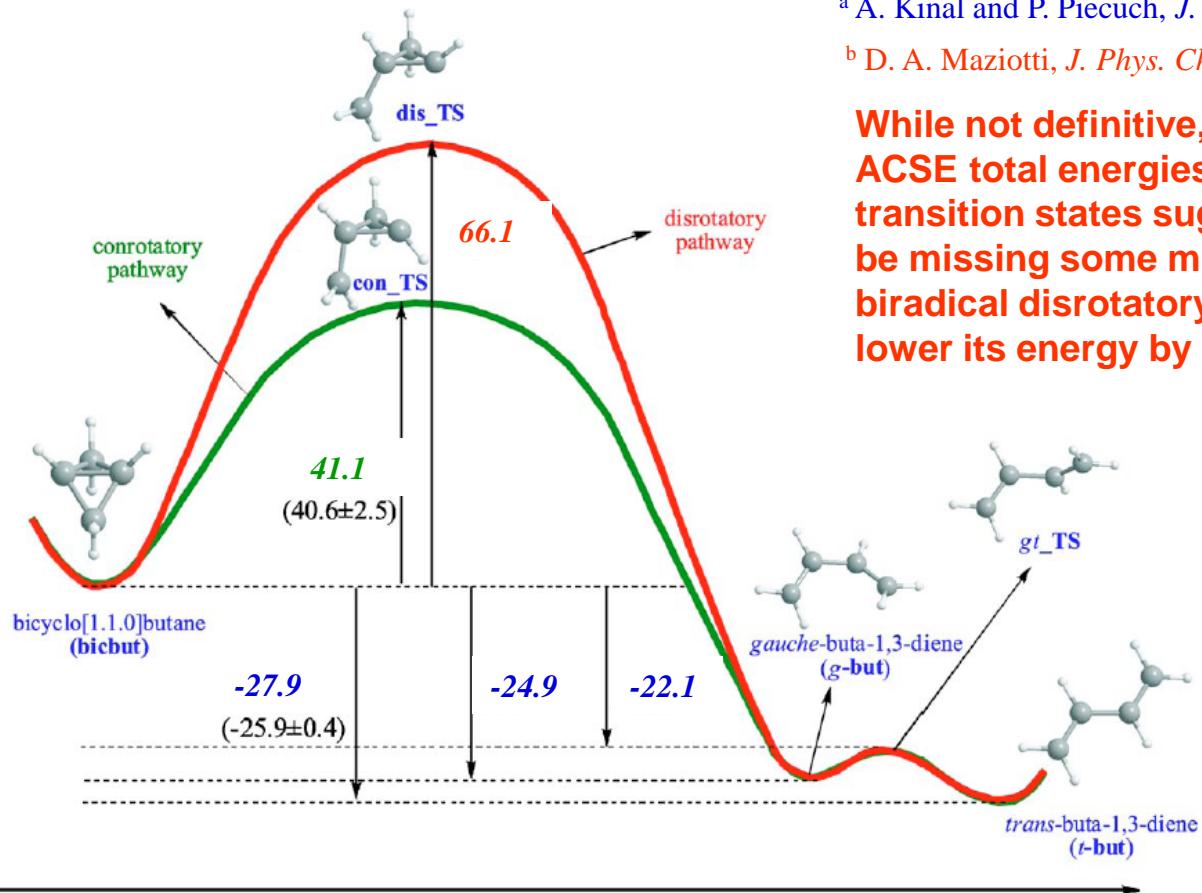


The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]-butane to Butadiene Revisited

	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
ACSE ^b	41.2	55.7	-23.8		
CCSDt ^c	40.1	59.0	-27.2	-25.3	-31.1
CC(t;3) ^c	40.2	60.1	-25.3	-22.6	-28.3

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

^b D. A. Maziotti, *J. Phys. Chem. A* **112**, 13684 (2008)



While not definitive, comparison of the CR-CC and ACSE total energies for reactant, product, and transition states suggests the CR-CC method may be missing some multireference correlation of the biradical disrotatory transition state that would lower its energy by about 9.5 kcal/mol.

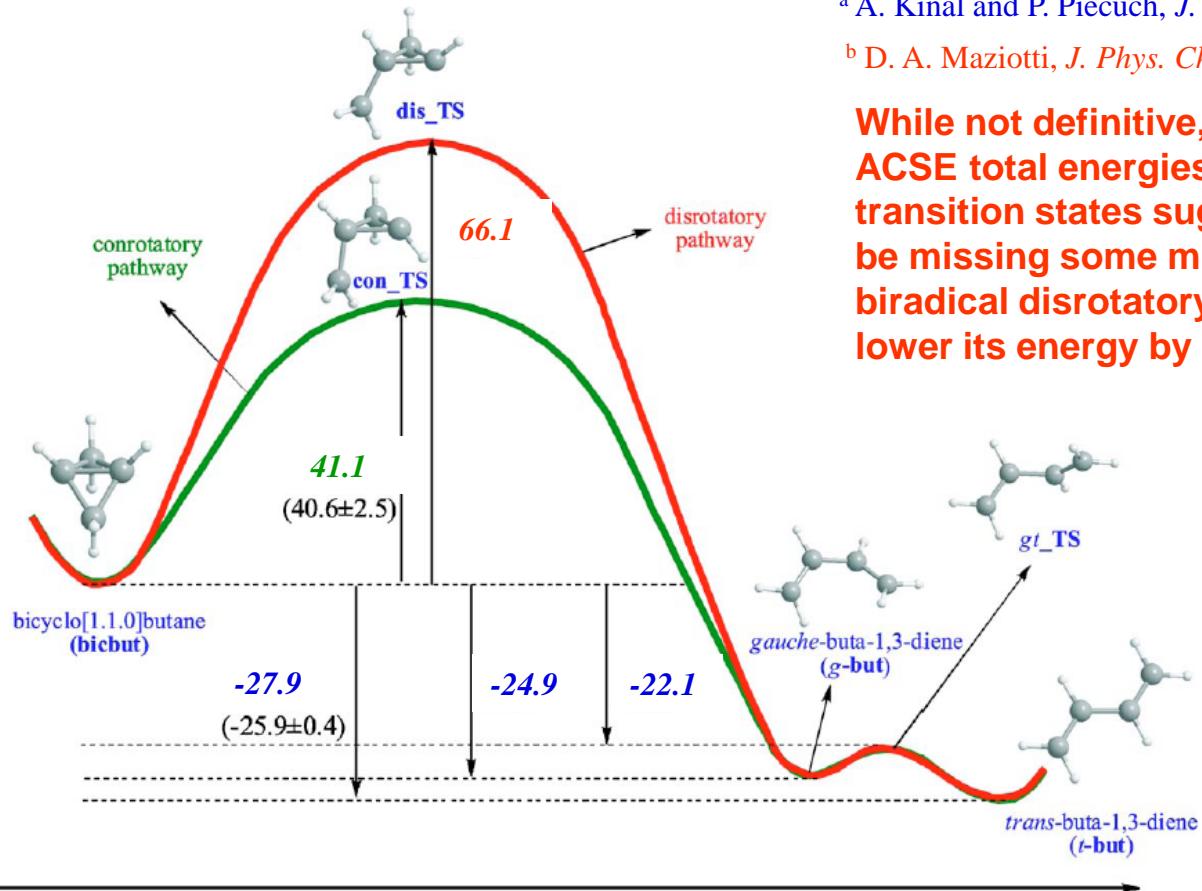
^c J. Shen and P. Piecuch, *J. Chem. Phys.* **136**, 144104 (2012)

The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]-butane to Butadiene Revisited

	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
ACSE ^b	41.2	55.7	-23.8		
CCSDt ^c	40.1	59.0	-27.2	-25.3	-31.1
CC(t;3) ^c	40.2	60.1	-25.3	-22.6	-28.3
OMR3-DMC ^d	40.4(5)	58.6(5)	-25.2(5)	-22.2(5)	-27.9(5)

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

^b D. A. Maziotti, *J. Phys. Chem. A* **112**, 13684 (2008)



While not definitive, comparison of the CR-CC and ACSE total energies for reactant, product, and transition states suggests the CR-CC method may be missing some multireference correlation of the biradical disrotatory transition state that would lower its energy by about 9.5 kcal/mol.

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

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

The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]-butane to Butadiene Revisited

Method	con_TS	dis_TS	g-but	gt_TS	t-but
cc-pVDZ					
CCSD	45.0	75.7	-25.6	-23.1	-28.5
CCSD(T)	39.9	13.5	-26.1	-23.4	-29.0
CCSD(2) _T	43.9	68.3	-25.0	-22.0	-28.0
CR-CC(2,3) ^a	40.3	62.1	-26.1	-23.3	-29.0
CCSDt	39.5	55.7	-28.4	-25.6	-31.6
CCSD(T)-h	39.4	53.9	-26.5	-23.7	-29.4
CC(t;3)	39.7	57.4	-26.4	-23.6	-29.3
CCSDT	39.8	57.5	-26.5	-23.7	-29.4
MCQDPT2 ^b	37.0	53.7	-26.4	-23.4	-29.4
cc-pVTZ					
CCSD	45.6	78.9	-24.8	-22.2	-27.6
CCSD(T) ^a	40.4	21.8	-25.1	-22.3	-28.0
CCSD(2) _T	41.7	67.8	-25.0	-22.3	-27.9
CR-CC(2,3) ^{a,b}	41.1	66.1	-24.9	-22.1	-27.9
CCSDt	40.1	59.0	-27.2	-25.3	-31.1
CCSD(T)-h	39.7	53.6	-25.4	-22.6	-28.4
CC(t;3)	40.2	60.1	-25.3	-22.6	-28.3
MRMP2/6-31G(d) ^c	38.0	54.0	-26.6		
MRMP2/6-311G(d,p) ^c	35.7	52.2	-27.0		
CASPT2/6-31G(d) ^d	41.5	56.3	-23.2		-26.0
MRCI(Q)/6-31G(d) ^d	41.5	56.7	-29.8		-32.4
ACSE/6-31G(d) ^c	41.8	56.4	-24.2		
ACSE/6-311G(d,p) ^c	41.2	55.7	-23.8		
OMR3-DMC ^e	40.4(5)	58.6(5)	-25.2(5)	-22.2(5)	-27.9(5)
Experiment	40.6 ± 2.5^f				-25.9 ± 0.4^g

The Conrotatory and Disrotatory Isomerization Pathways of Bicyclo[1.1.0]- butane to Butadiene Revisited

**Errors in the calculated total electronic energies relative to full CCSDT, in millihartree
(the cc-pVDZ basis set)**

Species ^b	CCSD	CCSD(T)	CCSD(2) _T	CR-CC(2,3) ^c	CCSDt	CCSD(T)-h	CC(t;3)
bicbut	21.863	0.450	3.107	0.134	14.427	-0.200	-0.263
con_TS	30.130	0.573	5.305	0.968	14.024	-0.826	-0.418
dis_TS	50.760	-69.648	14.052	7.345	11.487	-5.918	-0.491
g-but	23.259	1.009	3.786	0.794	11.377	-0.183	-0.065
gt_TS	22.836	0.964	3.658	0.782	11.402	-0.139	-0.028
t-but	23.396	1.036	3.837	0.840	10.963	-0.192	-0.056

PRELIMINARY CC(t,q;3) AND CC(t,q;3,4) RESULTS: Correcting CCSDtq for the missing triples or triples and quadruples

[P. Piecuch, J. Shen, N.P. Bauman, and M. Ehara, in preparation]

Double dissociation of the H₂O molecule (DZ basis set)

Method	$R = R_e$	$R = 1.5R_e$	$R = 2R_e$	MUE	NPE
CCSD	1.790	5.590	9.335	9.335	7.545
CCSDT	0.434	1.473	-2.210	2.210	3.683
CCSDTQ	0.015	0.141	0.108	0.141	0.126
Full CI	-76.157866	-76.014521	-75.905247		

Method	$R = R_e$	$R = 1.5R_e$	$R = 2R_e$	MUE	NPE
CCSD(TQ _f)	0.151(0.166)	-0.047(0.094)	-6.022(-5.914)	6.022(5.914)	6.173(6.080)
CR-CC(2,4)	0.041(0.056)	0.238(0.379)	-1.039(-0.931)	1.039(0.931)	1.277(1.310)
CCSDtq{2,2}	0.970(0.985)	1.091(1.232)	1.229(1.337)	1.229(1.337)	0.259(0.352)
CC(t,q;3){2,2}	0.309(0.324)	0.497(0.638)	0.713(0.821)	0.713(0.821)	0.403(0.496)
CC(t,q;3,4){2,2}	0.022(0.037)	0.049(0.190)	0.411(0.519)	0.411(0.519)	0.389(0.482)
CCSDTQ	-76.157851	-76.014380	-75.905139		
Full CI	-76.157866	-76.014521	-75.905247		

PRELIMINARY CC(t,q;3) AND CC(t,q;3,4) RESULTS: Correcting CCSDtq for the missing triples or triples and quadruples

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Method	$R = R_e$	$R = 1.5R_e$	$R = 2R_e$	MUE	NPE
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CR-CC(2,4)	0.041(0.056)	0.238(0.379)	-1.039(-0.931)	1.039(0.931)	1.277(1.310)
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[P. Piecuch, J. Shen, N.P. Bauman, and M. Ehara, in preparation]

Double dissociation of the H₂O molecule (DZ basis set)

Method	$R = R_e$	$R = 1.5R_e$	$R = 2R_e$	MUE	NPE
CCSD	1.790	5.590	9.335	9.335	7.545
CCSDT	0.434	1.473	-2.210	2.210	3.683
CCSDTQ	0.015	0.141	0.108	0.141	0.126
Full CI	-76.157866	-76.014521	-75.905247		

Method	$R = R_e$	$R = 1.5R_e$	$R = 2R_e$	MUE	NPE
CCSD(TQ _f)	0.151(0.166)	-0.047(0.094)	-6.022(-5.914)	6.022(5.914)	6.173(6.080)
CR-CC(2,4)	0.041(0.056)	0.238(0.379)	-1.039(-0.931)	1.039(0.931)	1.277(1.310)
CCSDtq{2,2}	0.970(0.985)	1.091(1.232)	1.229(1.337)	1.229(1.337)	0.259(0.352)
CC(t,q;3){2,2}	0.309(0.324)	0.497(0.638)	0.713(0.821)	0.713(0.821)	0.403(0.496)
CC(t,q;3,4){2,2}	0.022(0.037)	0.049(0.190)	0.411(0.519)	0.411(0.519)	0.389(0.482)
CCSDTQ	-76.157851	-76.014380	-75.905139		
Full CI	-76.157866	-76.014521	-75.905247		

PRELIMINARY CC(t,q;3) AND CC(t,q;3,4) RESULTS: Correcting CCSDtq for the missing triples or triples and quadruples

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[P. Piecuch, J. Shen, N.P. Bauman, and M. Ehara, in preparation]

The Be+H₂→BeH₂ reaction (C_{2v} pathway; DZP basis set)

Method	A	B	C	D	E	F	G	H	I	NPE	MUE
CCSD	0.391	0.378	0.479	1.092	3.481	0.791	0.311	0.180	0.036	3.445	3.481
CCSDT	0.021	0.003	0.041	-0.104	-2.205	0.058	0.042	0.015	0.004	2.263	2.205
CCSDTQ	0.000	-0.001	0.001	-0.001	0.000	0.016	-0.001	-0.001	0.000	0.018	0.016
Full CI	-15.779172	-15.737224	-15.674818	-15.622883	-15.602919	-15.624981	-15.693194	-15.736688	-15.760878		

Method	A	B	C	D	E	F	G	H	I	NPE	MUE
CR-CC(2,4) _{AA}	0.165	0.141	0.153	0.473	-0.737	0.254	0.093	0.050	0.009	1.209	0.737
CR-CC(2,4) _{DA}	0.058	0.036	0.009	0.162	-0.936	0.036	-0.001	-0.003	0.001	1.098	0.936
CCSDtq{(1,1)}	0.238	0.191	0.239	0.367	0.908	0.314	0.185	0.117	0.024	0.885	0.908
CC(t,q;3) _A {1,1}	0.097	0.074	0.097	0.133	0.412	0.124	0.058	0.036	0.007	0.406	0.412
CC(t,q;3) _D {1,1}	0.033	0.022	0.036	0.036	0.210	0.033	-0.003	0.003	0.002	0.213	0.210
CC(t,q;3,4) _{AA} {1,1}	0.094	0.073	0.095	0.114	0.466	0.126	0.054	0.032	0.006	0.460	0.466
CC(t,q;3,4) _{DA} {1,1}	0.030	0.021	0.034	0.017	0.263	0.035	-0.007	0.000	0.001	0.270	0.263
CCSDTQ	-15.779172	-15.737225	-15.674819	-15.622884	-15.602919	-15.624965	-15.693195	-15.736689	-15.760878		
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Method	A	B	C	D	E	F	G	H	I	NPE	MUE
CCSD	0.391	0.378	0.479	1.092	3.481	0.791	0.311	0.180	0.036	3.445	3.481
CCSDT	0.021	0.003	0.041	-0.104	-2.205	0.058	0.042	0.015	0.004	2.263	2.205
CCSDTQ	0.000	-0.001	0.001	-0.001	0.000	0.016	-0.001	-0.001	0.000	0.018	0.016
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CCSDtq{(1,1)}	0.238	0.191	0.239	0.367	0.908	0.314	0.185	0.117	0.024	0.885	0.908
CC(t,q;3) _A {1,1}	0.097	0.074	0.097	0.133	0.412	0.124	0.058	0.036	0.007	0.406	0.412
CC(t,q;3) _D {1,1}	0.033	0.022	0.036	0.036	0.210	0.033	-0.003	0.003	0.002	0.213	0.210
CC(t,q;3,4) _{AA} {1,1}	0.094	0.073	0.095	0.114	0.466	0.126	0.054	0.032	0.006	0.460	0.466
CC(t,q;3,4) _{DA} {1,1}	0.030	0.021	0.034	0.017	0.263	0.035	-0.007	0.000	0.001	0.270	0.263
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PRELIMINARY CC(t,q;3) AND CC(t,q;3,4) RESULTS: Correcting CCSDtq for the missing triples or triples and quadruples

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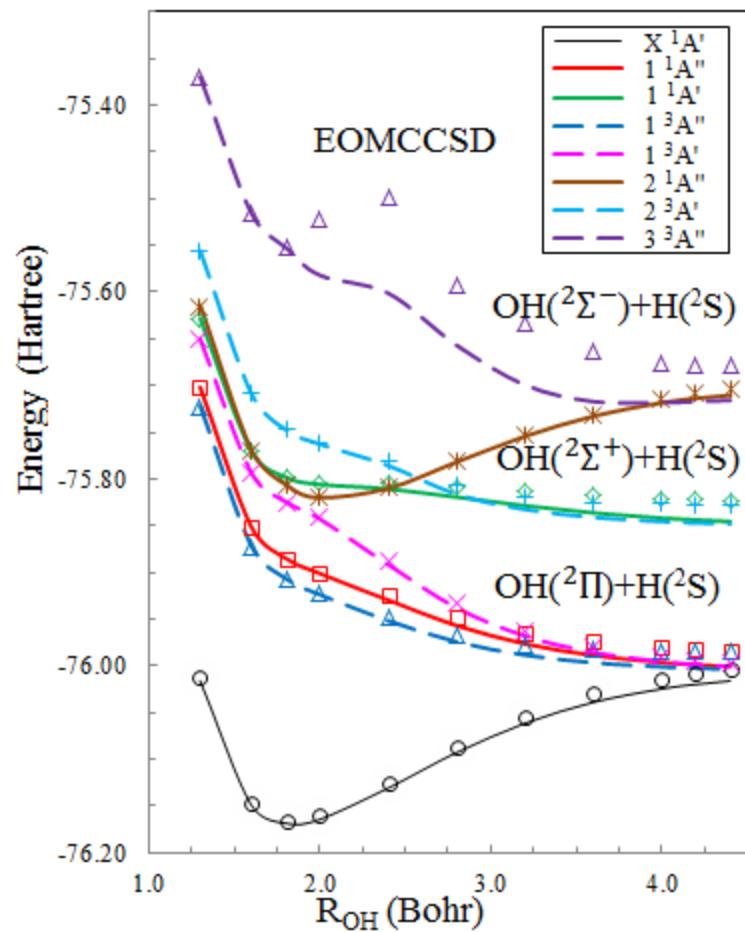
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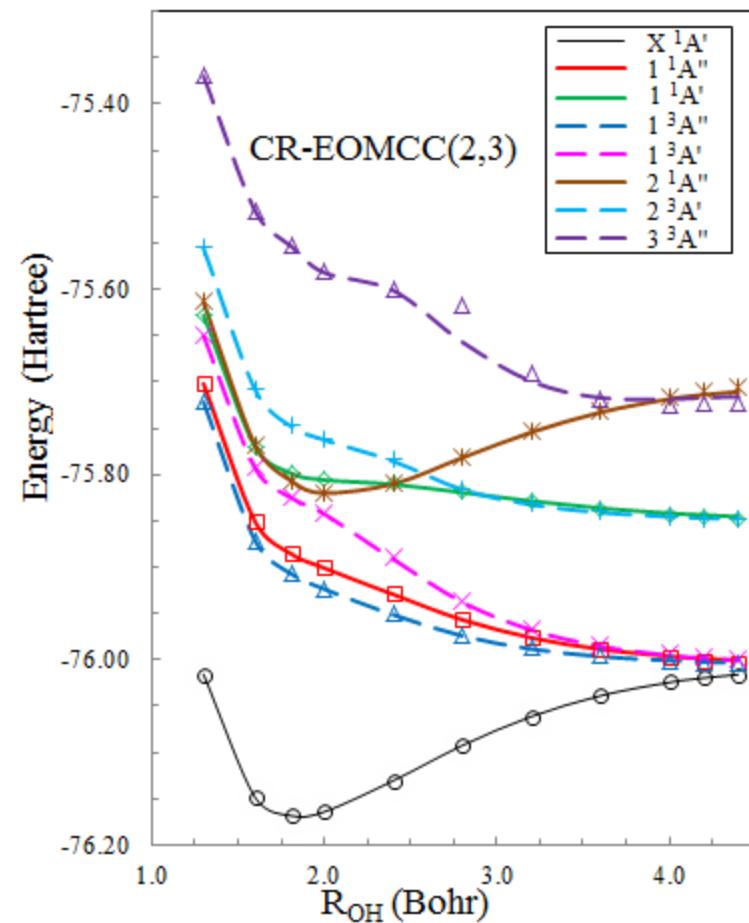
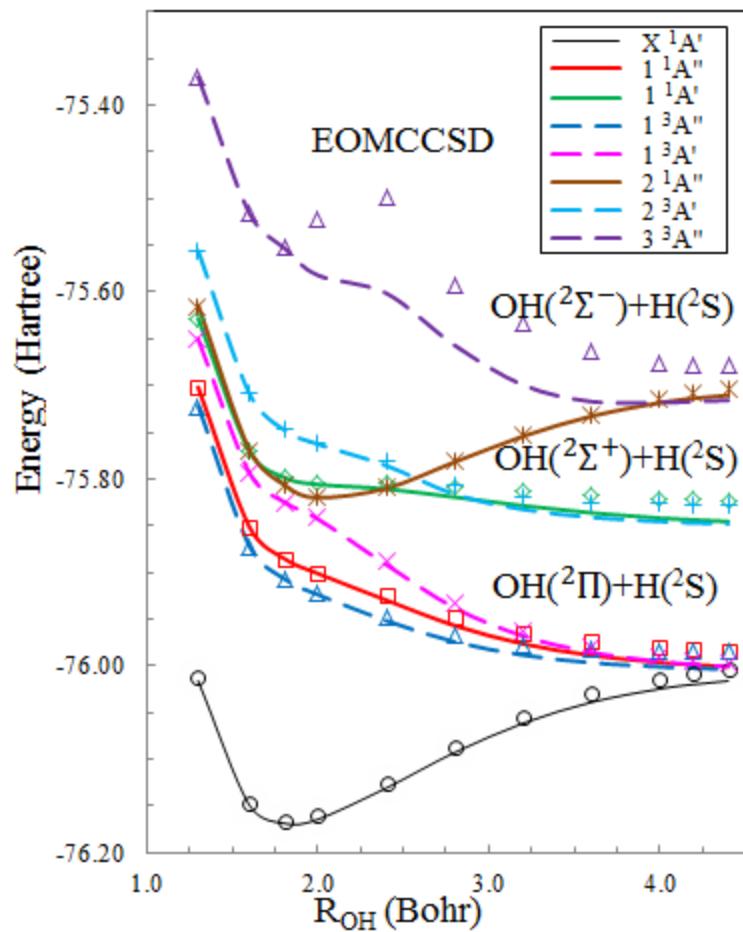
EXCITED-STATE POTENTIAL ENERGY SURFACES OF THE WATER MOLECULE

[J. Shen and P. Piecuch, in preparation; cf., also, J.J. Lutz and P. Piecuch, Comput. Theor. Chem., 2014]



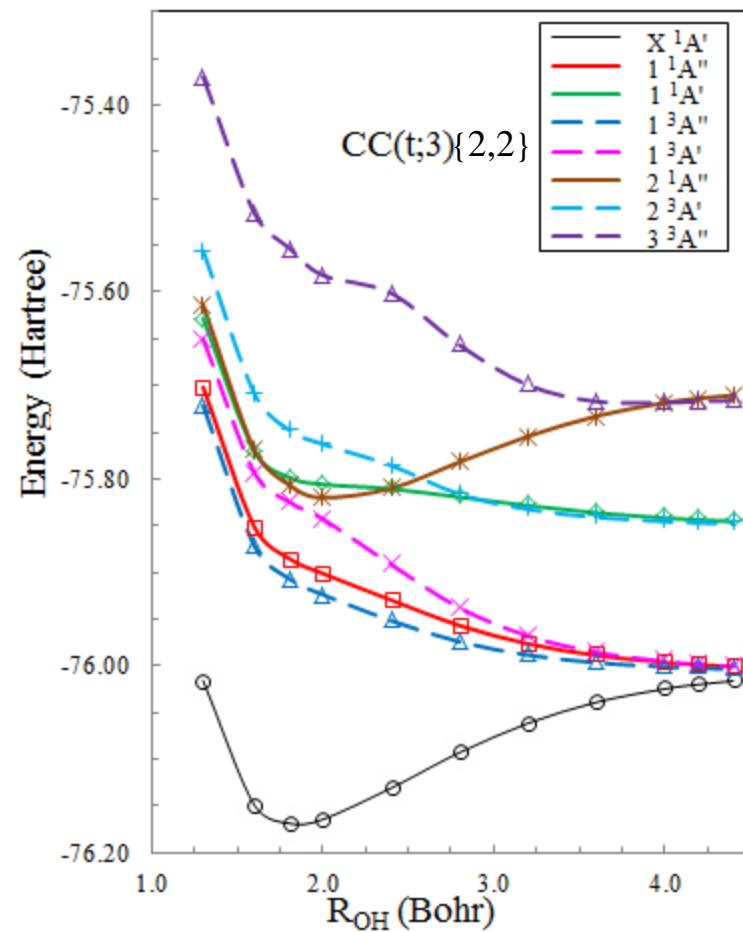
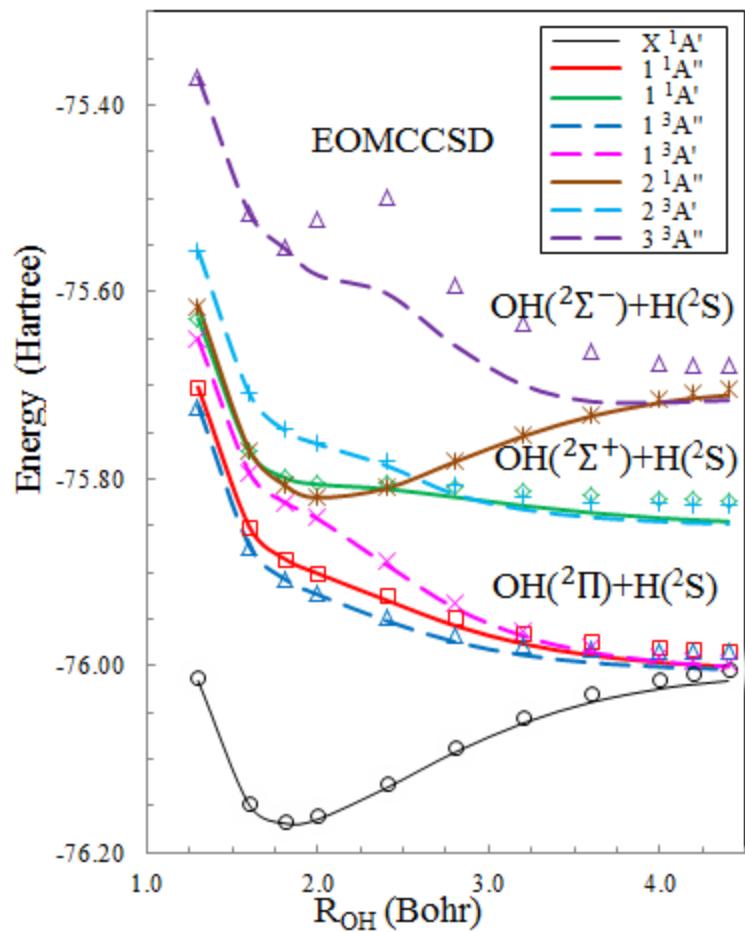
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Mean unsigned errors (MUEs) rel. to full CI, in mH, for the A' and A'' excited states

STATE	7R-SU-CCSD [1]	EOMCCSD	CR-EOMCC(2,3)	CC(t;3)
1 ¹ A'	3.94	10.80	0.88	1.10
2 ¹ A'	3.12	15.59	1.89	1.61
3 ¹ A'	12.44	14.86	3.86	2.12
1 ³ A'	4.25	3.03	1.31	0.92
2 ³ A'	4.15	9.67	0.68	1.25
3 ³ A'	6.48	11.09	4.89	2.08
AVERAGE MUE	5.73	10.84	3.38	1.51

STATE	4R-SU-CCSD [1]	(8,4)-CCSD [1]	EOMCCSD	CR-EOMCC(2,3)	CC(t;3)
1 ¹ A''	2.85	1.32	8.31	0.87	0.99
2 ¹ A''	6.22	3.80	1.54	0.89	0.19
1 ³ A''	3.88	2.82	8.53	0.58	1.19
2 ³ A''	12.62	1.95	8.95	4.13	0.63
AVERAGE MUE	6.39	2.47	6.83	1.62	0.75

[1] X. Li and J. Paldus, *J. Chem. Phys.* 133, 024102 (2010).

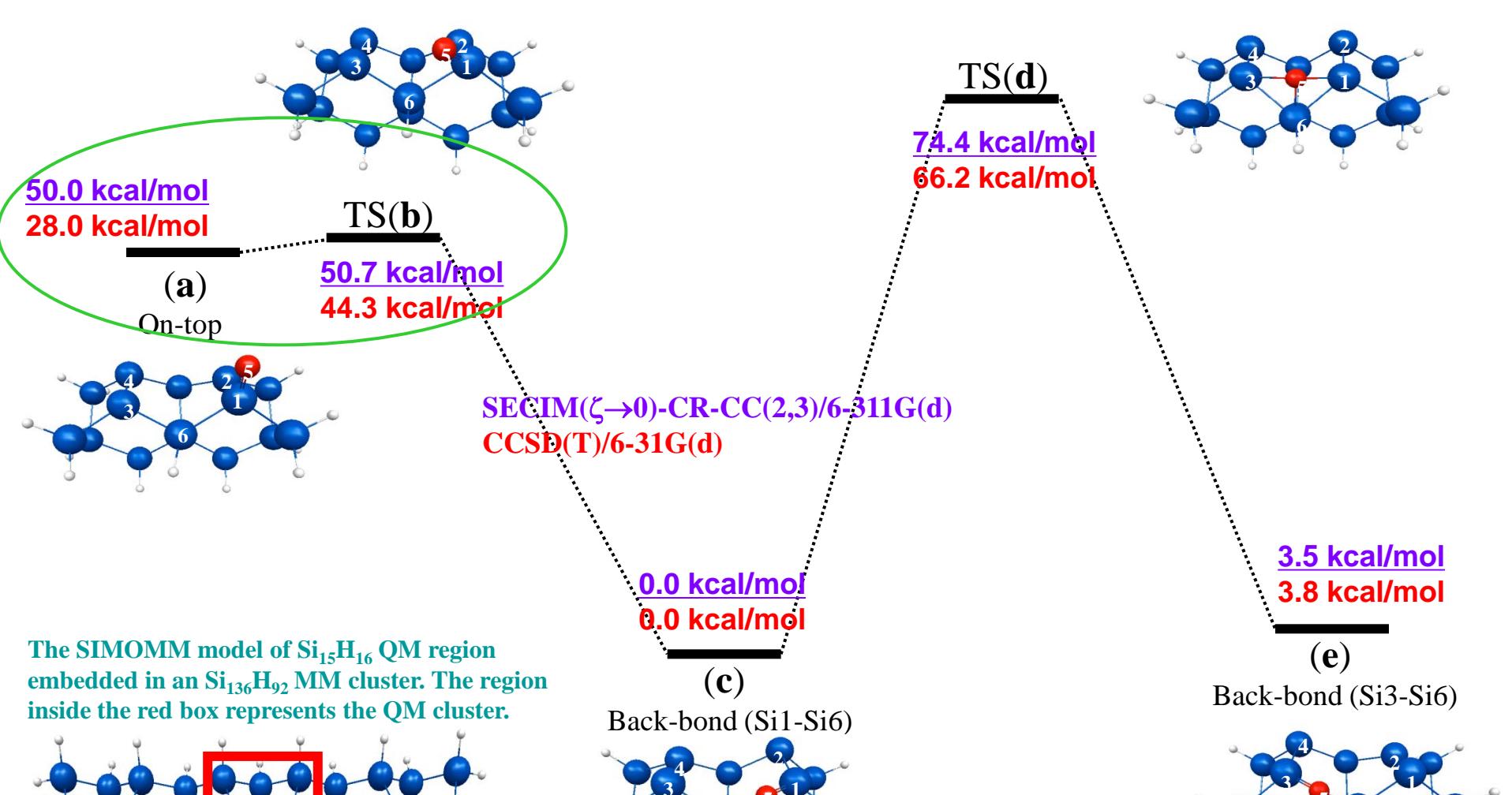
(SUB)LINEAR SCALING LOCAL CORRELATION CC METHODS: CLUSTER-IN-MOLECULE (CIM) CCSD, CCSD(T), AND CR-CC(2,3) APPROACHES

[W. Li, P. Piecuch, and J.R. Gour, AIP Proceedings, 2009; W. Li, P. Piecuch, J.R. Gour, and S. Li, J. Chem. Phys., 2009;
W. Li, P. Piecuch, and J.R. Gour, Prog. Theor. Chem. Phys., 2009; W. Li and P. Piecuch, J. Phys. Chem. A, 2010 (x2)]

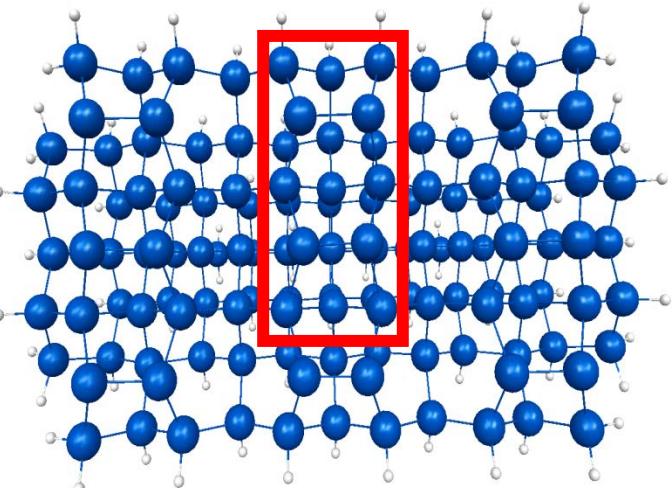
$$\Delta E = \sum_{i'} \delta E_{i'}, \quad \delta E_{i'} = \frac{1}{M_{i'}} \sum_{\{P_{i'}\}} \delta E_{i'} (\{P_{i'}\}) \quad (\text{CIMTYP in GAMESS})$$

Our CIM-CC and CIM-MBPT algorithms are characterized by:

- The use of (virtually) orthonormal LMO bases (one can use canonical CC/MBPT codes for orthonormal orbitals to perform the CIM-CC and CIM-MBPT calculations)
- The linear scaling of the CPU time when the same theory level is applied to all CIM subsystems (CIM subsystems do not grow with the system size, reflecting on the immediate chemical environment)
- The natural and coarse-grain parallelism that can be further enhanced by fine-grain parallelism (each CC subsystem calculation can run on a different processor or node in serial or parallel; fast connection among nodes is not needed)
- The non-iterative character of triples (and other perturbative) energy corrections through the use of subsystem-specific quasi-canonical MOs (QCMOs) (usually, local CC and MBPT approaches convert the determination of non-iterative energy corrections into relatively expensive iterative steps).
- The possibility to mix different levels of CC theory or CC and non-CC (e.g., MP n or MBPT(n)) methods within a single computation.



The SIMOMM model of $\text{Si}_{15}\text{H}_{16}$ QM region embedded in an $\text{Si}_{136}\text{H}_{92}$ MM cluster. The region inside the red box represents the QM cluster.



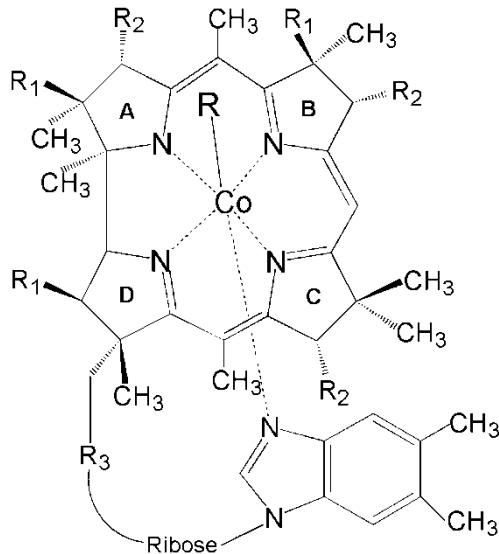
DIFFUSION OF ATOMIC OXYGEN ON THE Si(100) SURFACE

[P. Arora, W. Li, P. Piecuch, J.W. Evans, M. Alba, and M.S. Gordon, *J. Phys. Chem. C*, 2010]

MULTI-LEVEL CIM-CC METHODS WITH A CANONICAL TREATMENT OF CHEMICALLY INACTIVE REGIONS

CIM-CR-CC(2,3)/MP2 or CCSD vs DFT study of the Co-C Bond dissociation in methylcobalamin (MeCbl)

[P.M. Kozłowski, M. Kumar, P. Piecuch, W. Li, N.P. Bauman, J.A. Hansen, P. Lodziński, and M. Jaworska, J. Chem. Theory Comput., 2012]

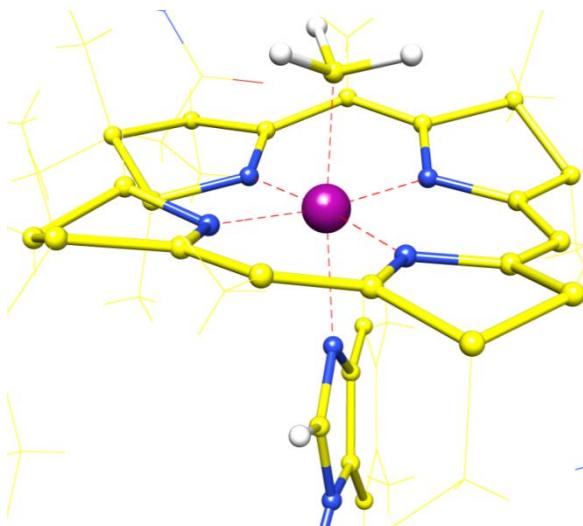
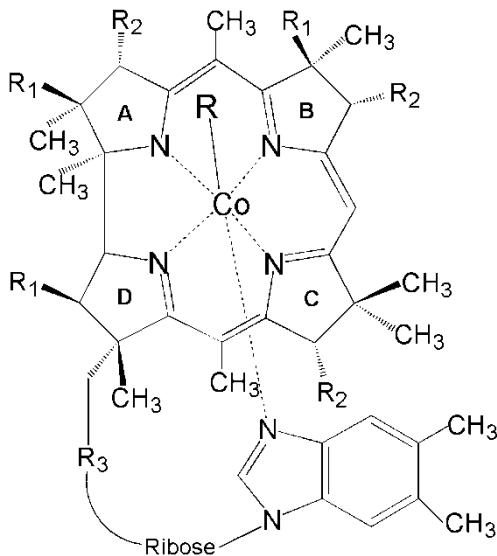


Molecular structure of B₁₂ cofactors
(R = Me or Ado) R₁ = CH₂CONH₂,
R₂ = CH₂CH₂CONH₂, R₃ =
(CH₂)₂CONHCH₂CH(CH₃)OPO₃⁻.

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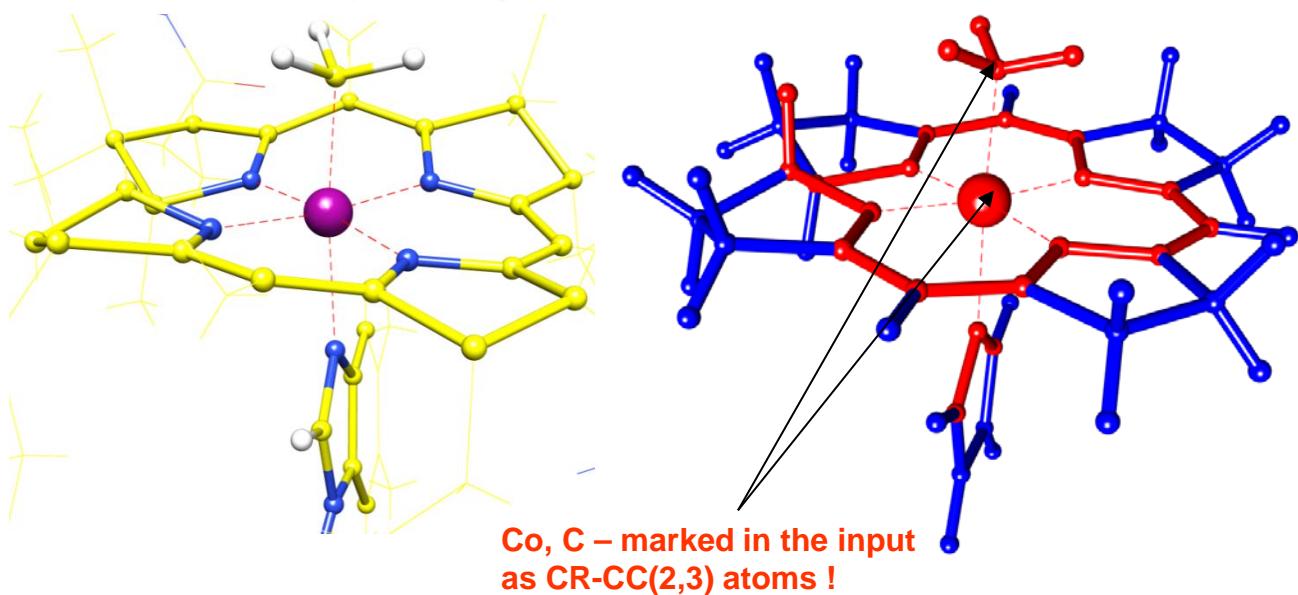
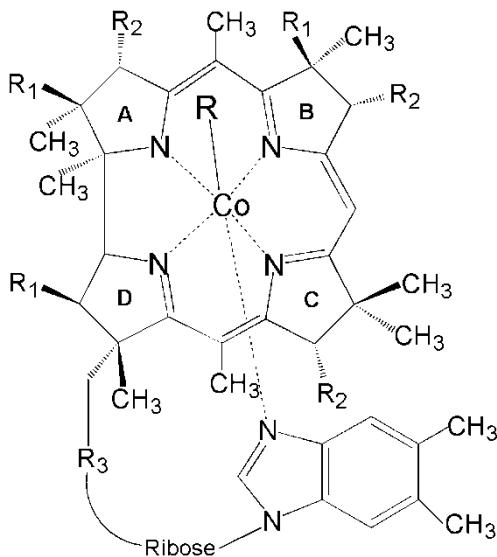
Molecular structure of B_{12} cofactors
($R = Me$ or Ado) $R_1 = CH_2CONH_2$,
 $R_2 = CH_2CH_2CONH_2$, $R_3 =$
 $(CH_2)_2CONHCH_2CH(CH_3)OPO_3^-$.

The $Im\text{-}[Co^{III}\text{corrin}]\text{-}Me^+$ structural model of MeCbl employed by us (58 atoms; 234 electrons, 530 basis functions in the 6-31G* description; the 6-311++G** results extrapolated from the analysis of Co-C bond dissociation in the $Co(NH_3)_5Me^{2+}$).

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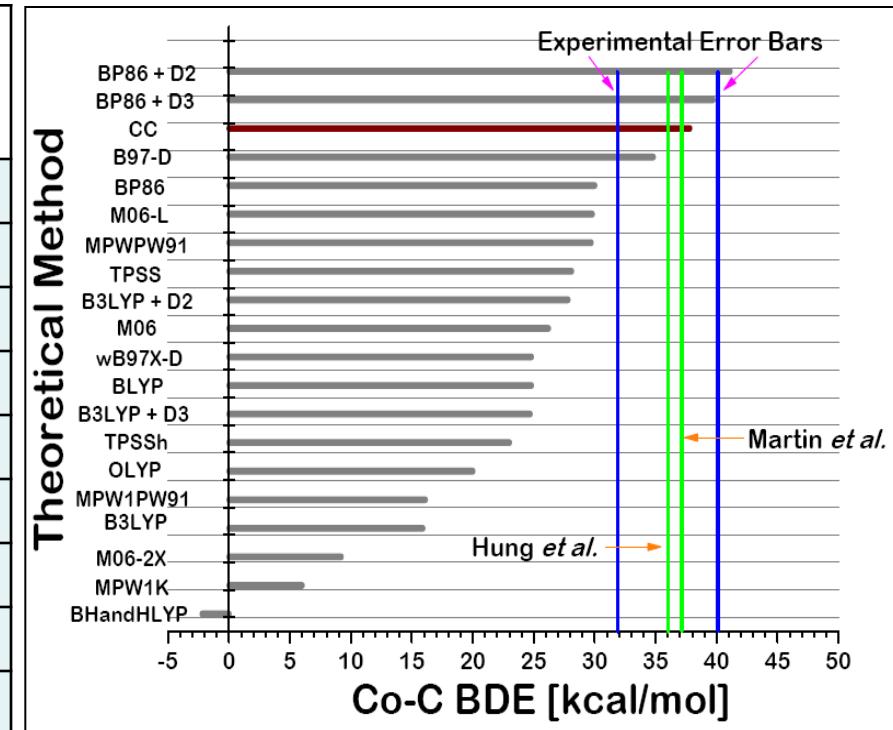
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The $Im-[Co^{III}corrin]-Me^+$ structural model of MeCbl where the red colored zone marks the atoms that can be assigned to the CIM subsystem which in the multi-level GSECIM-X/Y calculations is treated by the higher-level method X.

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
ω B97X-D (22 % HF)	26.8 / 24.8
BLYP	25.7 / 24.8
TPSS	29.1 / 28.1
MPWPW91	30.3 / 29.7
M06-L	31.3 / 29.8
BP86	30.6 / 30.0
BP86+D3	35.2 / 39.7
B97-D	35.1 / 34.8
CIM-CR-CC(2,3)/CCSD	39.8 (calc.) / 37.8 (est.)
Experiment	37 ± 3, 36 ± 4



CPU timings of CIM-CR-CC(2,3)/MP2 and CIM-CR-CC(2,3)/CCSD:

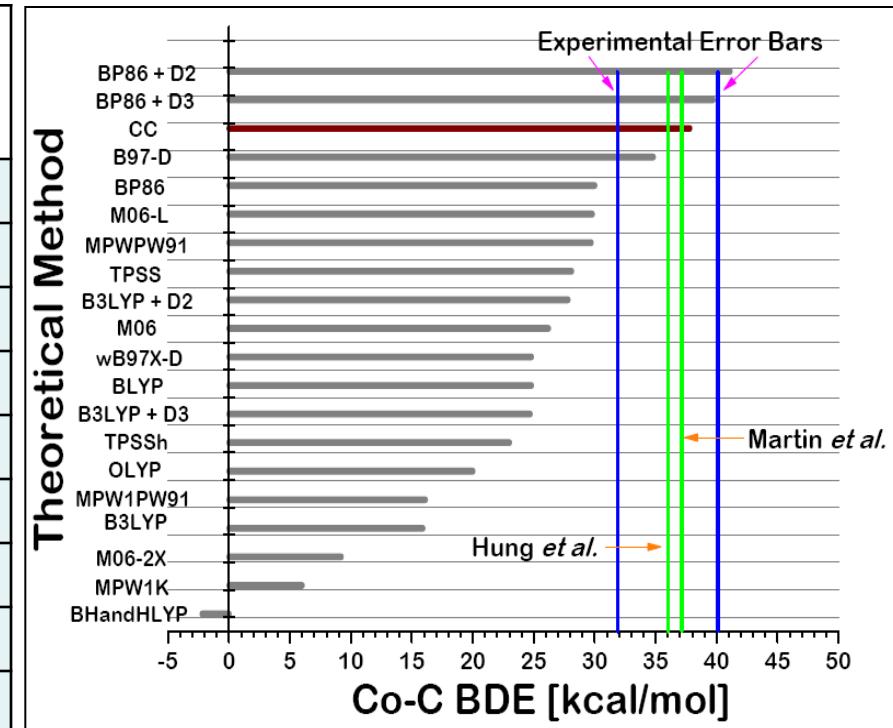
Canonical MP2 on 16 cores: ~9 minutes

Canonical CCSD on 16 cores: ~60 hours

Local CR-CC(2,3) triples correction on 1 CPU (one CC subsystem): ~74 hours

~ CHEMICAL ACCURACY IN ~3 DAYS ON UP TO 16 CORES! (think of 1,000 cores ...)

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CASSCF(11,10), CASPT2(11,10)	15.1, 53.8



CPU timings of CIM-CR-CC(2,3)/MP2 and CIM-CR-CC(2,3)/CCSD:

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THANK YOU

