NEW COUPLED-CLUSTER METHODS FOR MOLECULAR POTENTIAL ENERGY SURFACES: II. EXCITED-STATE APPROACHES

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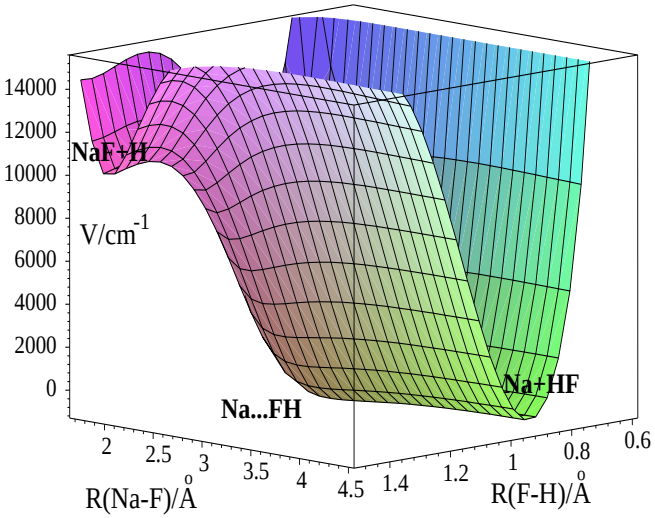
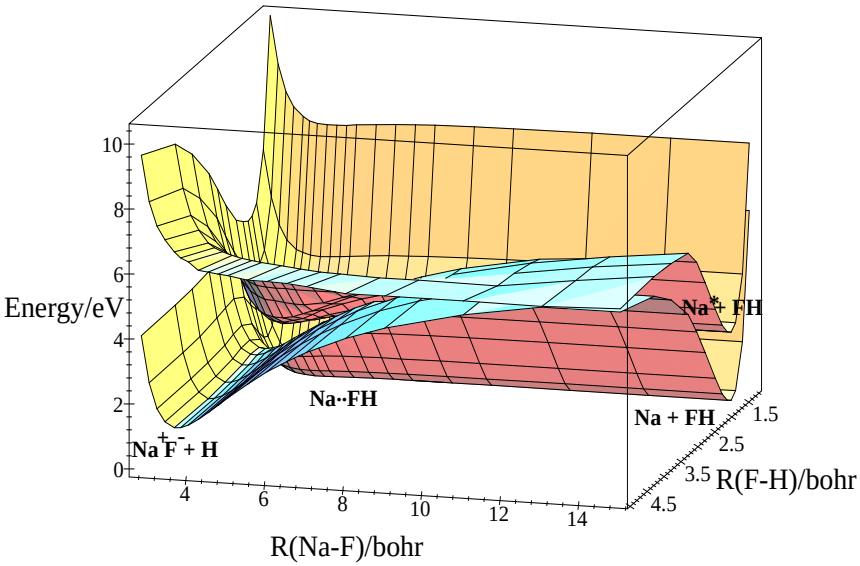
P. Piecuch and K. Kowalski, in: *Computational Chemistry: Reviews of Current Trends*, edited by J. Leszczyński (World Scientific, Singapore, 2000), Vol. 5, pp. 1-104; K. Kowalski and P. Piecuch, *J. Chem. Phys.* **113**, 18-35 (2000); **113**, 5644-5652 (2000); *J. Molec. Struct.: THEOCHEM* **547**, 191-208 (2001); *Chem. Phys. Lett.* **344**, 165-175 (2001); P. Piecuch, S.A. Kucharski, and K. Kowalski, *Chem. Phys. Lett.* **344**, 176-184 (2001); P. Piecuch, S.A. Kucharski, V. Špirko, and K. Kowalski, *J. Chem. Phys.* **115**, 5796-5804 (2001); P. Piecuch, K. Kowalski, and I.S.O. Pimienta, *Int. J. Mol. Sci.*, submitted (2001); P. Piecuch and K. Kowalski, *Int. J. Mol. Sci.*, submitted (2001); K. Kowalski and P. Piecuch, *J. Chem. Phys.* **115**, 2966-2978 (2001); P. Piecuch, K. Kowalski, I.S.O. Pimienta, and S.A. Kucharski, in: *Accurate Description of Low-Lying Electronic States and Potential Energy Surfaces*, ACS Symposium Series, Vol. XXX, edited by M.R. Hoffmann and K.G. Dyall (ACS, Washington, D.C., 2002), pp. XXX-XXXX; K. Kowalski and P. Piecuch, *J. Chem. Phys.*, submitted (2001); P. Piecuch, S.A. Kucharski, and V. Špirko, *J. Chem. Phys.* **111**, 6679-6692 (1999); K. Kowalski and P. Piecuch, *J. Chem. Phys.* **113**, 8490-8502 (2000); **115**, 643-651 (2001); K. Kowalski and P. Piecuch, *Chem. Phys. Lett.* **347**, 237-246 (2001).

The "holy grail" of the *ab initio* electronic structure theory:

The development of simple, "black-box," and affordable methods that can provide highly accurate ($\sim$ spectroscopic) description of ENTIRE GROUND- AND EXCITED-STATE POTENTIAL ENERGY SURFACES





Examples of applications:

- dynamics of reactive collisions
- highly excited and metastable ro-vibrational states of molecules
- rate constant calculations
- collisional quenching of electronically excited molecular species

Motivation:

- elementary processes that occur in combustion (e.g., reactions involving OH and N_xO_y)
- collisional quenching of the OH and other radical species

IN THIS PRESENTATION, WE FOCUS ON NEW "BLACK-BOX" COUPLED-CLUSTER METHODS FOR EXCITED-STATE POTENTIAL ENERGY SURFACES

EQUATION-OF-MOTION (OR RESPONSE) COUPLED CLUSTER THEORY (EOMCC)

(R.J. Bartlett, P. Jørgensen, and others)

$$|\Psi_K\rangle = R_K^{(A)} e^{T^{(A)}} |\Phi\rangle, \quad T^{(A)} = \sum_{n=1}^{m_A} T_n, \quad R_K^{(A)} = \sum_{n=0}^{m_A} R_{K,n}$$

$m_A = N$ – exact theory
$m_A < N$ – approximate methods

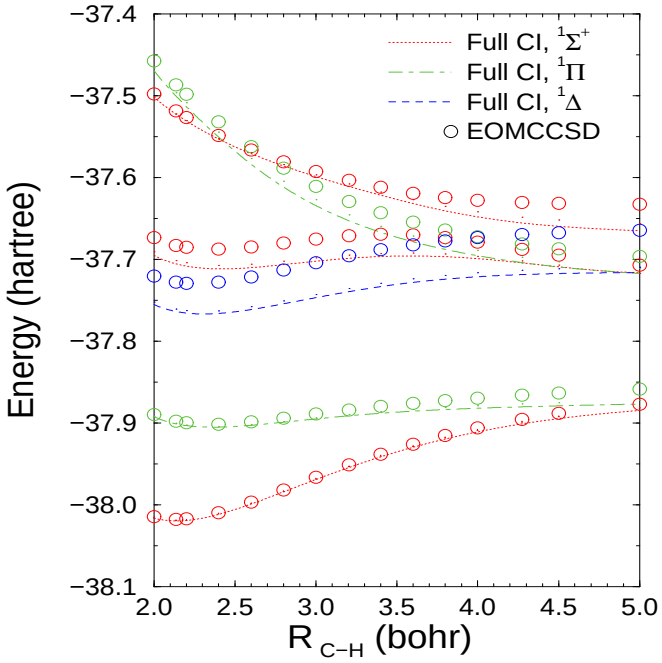
$m_A = 2$	$T = T_1 + T_2,\ R_K = R_{K,0} + R_{K,1} + R_{K,2}$	EOMCCSD
$m_A = 3$	$T = T_1 + T_2 + T_3,\ R_K = R_{K,0} + R_{K,1} + R_{K,2} + R_{K,3}$	EOMCCSDT

PROBLEMS WITH THE STANDARD EOMCC APPROXIMATIONS

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

Example: CH^+

[K. Kowalski and P. Piecuch, *J. Chem. Phys.* **115**, 2966 (2001)]



Existing solutions

- **Multi-Reference CC Methods (Jeziorski, Monkhorst, Paldus, Piecuch, Bartlett, Mukherjee, Lindgren, Kaldor *et al.*)**
  [also, Multi-Reference CI and MBPT Approaches; cf. the presentation by Professor Mark S. Gordon]
- **EOMCC Methods with the Complete Inclusion of Higher-Than-Doubly Excited Clusters (e.g., the Full EOMCCSDT Method of Kowalski and Piecuch; cf., also, Kucharski *et al.*)**

THE PROPOSED RESEARCH FOCUSES ON METHODS THAT COMBINE THE SIMPLICITY OF THE STANDARD EOMCC APPROACHES, SUCH AS EOMCCSD, EOMCCSD(T), or CC3, WITH THE EFFICIENCY WITH WHICH THE MULTI-REFERENCE METHODS DESCRIBE EXCITED-STATE POTENTIAL ENERGY SURFACES

SPECIFIC GOALS

- New CC methods for excited-state potential energy surfaces:
  - method of moments of CC equations
  - active-space EOMCC approaches

EXTENSION OF THE METHOD OF MOMENTS OF COUPLED-CLUSTER EQUATIONS (MMCC) TO EXCITED STATES

$$H|\Psi_K\rangle = E_K|\Psi_K\rangle$$

Via the State-Universal Multi-Reference CC Formalism

$$|\Psi_K^{\text{SUCC-A}}\rangle = U|\chi_K^{(A)}\rangle = \sum_{p=1}^{M} c_{pK} e^{T_A^{(p)}}|\Phi_p\rangle, \quad T_A^{(p)} = \sum_{m=1}^{m_A} T_m^{(p)} \quad (m_A < N)$$

$$\delta_K = E_K - E_K^{(A)} = \sum_{p=1}^{M} \sum_{n=m_A+1}^{N} \sum_{m=m_A+1}^{n} \langle\Psi_K|(e^{T_A^{(p)}})_{n-m}\,\Gamma_m^{(p)}(m_A)|\Phi_p\rangle \times \langle\Phi_p|\chi_K^A\rangle / \langle\Psi_K|\Psi_K^{\text{SUCC-A}}\rangle \quad (K = 1, \ldots, M)$$

$\Gamma_m^{(p)}(m_A)|\Phi_p\rangle \Longleftarrow$ generalized moments of the SUCC equations

Via the Equation-of-Motion CC Formalism

$$|\Psi_K^{(A)}\rangle = R_K^{(A)} e^{T^{(A)}}|\Phi\rangle, \quad T^{(A)} = \sum_{n=1}^{m_A} T_n, \quad R_K^{(A)} = \sum_{n=0}^{m_A} R_{K,n} \quad (m_A < N)$$

$$(Q^{(A)}\bar{H}^{(A)}Q^{(A)})R_K^{(A)}|\Phi\rangle = \omega_K^{(A)} R_K^{(A)}|\Phi\rangle, \quad \omega_K^{(A)} = E_K^{(A)} - E_0^{(A)}, \quad \bar{H}^{(A)} = e^{-T^{(A)}} H e^{T^{(A)}}$$

$$\delta_K = E_K - E_K^{(A)} = \sum_{n=m_A+1}^{N} \sum_{j=m_A+1}^{n} \langle\Psi_K|Q_n C_{n-j}(m_A) M_{K,j}^{\text{EOMCC}}(m_A)|\Phi\rangle / \langle\Psi_K|e^{T^{(A)}} R_K^{(A)}|\Phi\rangle$$

$M_{K,j}^{\text{EOMCC}}(m_A)|\Phi\rangle \Longleftarrow$ generalized moments of the EOMCC equations

Extension of the MMCC Theory to the EOMCC Formalism

$$\delta_K^{(A)} \equiv E_K - E_K^{(A)} = \sum_{n=m_A+1}^{N} \sum_{j=m_A+1}^{n} \langle \Psi_K | Q_n \, C_{n-j}(m_A) \, M_{K,j}^{\rm EOMCC}(m_A) | \Phi \rangle / \langle \Psi_K | e^{T^{(A)}} R_K^{(A)} | \Phi \rangle$$

$$C_{n-j}(m_A) = (e^{T^{(A)}})_{n-j}$$

$$M_{K,j}^{\rm EOMCC}(m_A)|\Phi\rangle = Q_j(\bar{H}^{(A)} R_K^{(A)})|\Phi\rangle = \sum_J \mathcal{M}_{K,J}^{(j)}(m_A) \, |\Phi_J^{(j)}\rangle$$

$\mathcal{M}_{K,J}^{(j)}(m_A) = \langle \Phi_J^{(j)} | (\bar{H}^{(A)} R_K^{(A)}) | \Phi \rangle$ – generalized moments of the EOMCC equations (we only need moments with $j > m_A$)

The MMCC(m_A,m_B) Approaches

$$E_K(m_A, m_B) = E_K^{(A)} + \delta_K(m_A, m_B)$$

$$\delta_K(m_A, m_B) = \sum_{n=m_A+1}^{m_B} \sum_{j=m_A+1}^{n} \langle \Psi_K | Q_n \, C_{n-j}(m_A) \, M_{K,j}^{\rm EOMCC}(m_A) | \Phi \rangle / \langle \Psi_K | e^{T^{(A)}} R_K^{(A)} | \Phi \rangle$$

Various approximate forms of $|\Psi\rangle$ lead to different classes of MMCC(m_A, m_B) schemes.

The MMCC(2,3) Approximation

$$E_K(2,3) = E_K^{\rm EOMCCSD} + \delta_K(2,3)$$
$$\delta_K(2,3) = \langle \Psi_K | M_{K,3}^{\rm EOMCC}(2) | \Phi \rangle / \langle \Psi_K | e^{T^{\rm CCSD}} R_K^{\rm CCSD} | \Phi \rangle$$
$$T^{\rm CCSD} = T_1 + T_2, \quad R_K^{\rm CCSD} = R_{K,0} + R_{K,1} + R_{K,2}$$

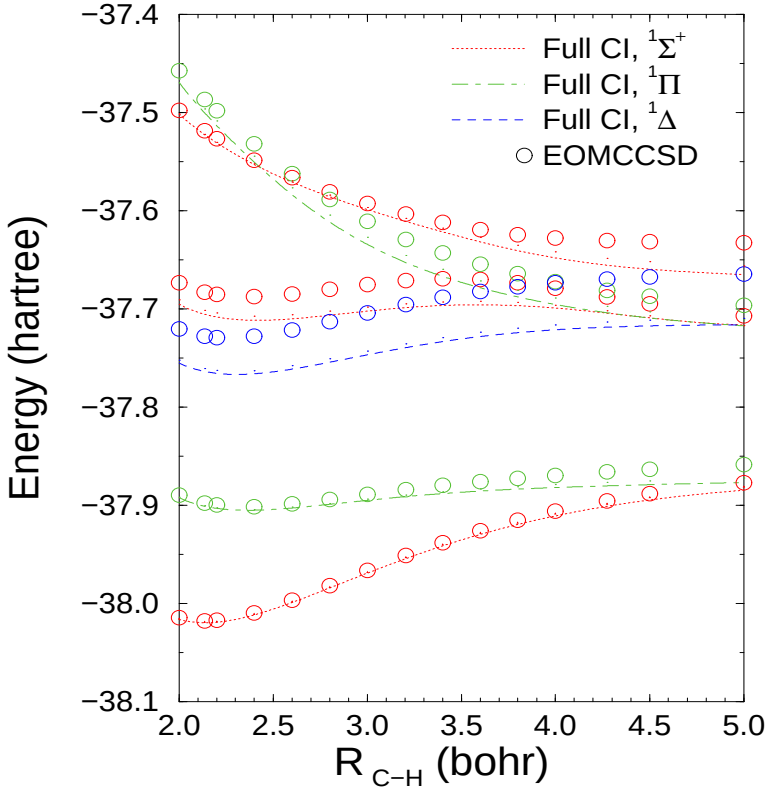
$$M_{K,3}^{\rm EOMCC}(2)|\Phi\rangle = \sum_{\substack{i<j<k \\ a<b<c}} \mathcal{M}_{K,ijk}^{abc}(2) |\Phi_{ijk}^{abc}\rangle$$

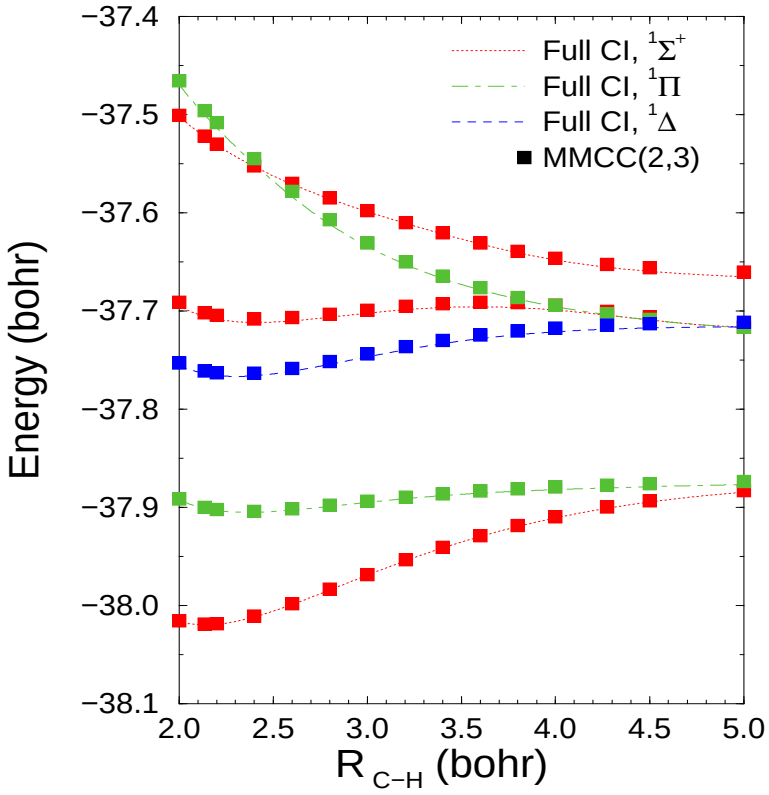
$$\mathcal{M}_{K,ijk}^{abc}(2) = \langle \Phi_{ijk}^{abc}| \left(\bar{H}_{\rm open}^{\rm CCSD} R_{K,\rm open}^{\rm CCSD} \right)_C |\Phi\rangle + r_{K,0}^{\rm CCSD} \langle \Phi_{ijk}^{abc}| \bar{H}^{\rm CCSD} |\Phi\rangle$$

$$\begin{array}{rcl} & & \mathbf{\bar{H}_{TD}} \qquad\qquad\qquad\qquad \mathbf{\bar{H}_{TS} + \bar{H}_{TD}} \\ \mathcal{M}_{K,ijk}^{abc}(2) & = & \langle \Phi_{ijk}^{abc}| (\bar{H}_2^{\rm CCSD} R_{K,2})_C |\Phi\rangle + \langle \Phi_{ijk}^{abc}| [\bar{H}_3^{\rm CCSD} (R_{K,1} + R_{K,2})]_C |\Phi\rangle \\ & & + \langle \Phi_{ijk}^{abc}| (\bar{H}_4^{\rm CCSD} R_{K,1})_C |\Phi\rangle + r_{K,0}^{\rm CCSD} \langle \Phi_{ijk}^{abc}| \bar{H}^{\rm CCSD} |\Phi\rangle \\ & & \mathbf{\bar{H}_{TS}} \qquad\qquad\qquad\qquad \mathbf{\bar{H}_{T0}} \end{array}$$

$$|\Psi_K\rangle \simeq |\Psi_K^{\rm CISDt}\rangle = \left[1 + C_1 + C_2 + C_3 \begin{pmatrix} ab\mathbf{C} \\ \mathbf{I}jk \end{pmatrix} \right] |\Phi\rangle$$

Example: Potential Energy Surfaces for CH^+ (the MMCC(2,3) Study)





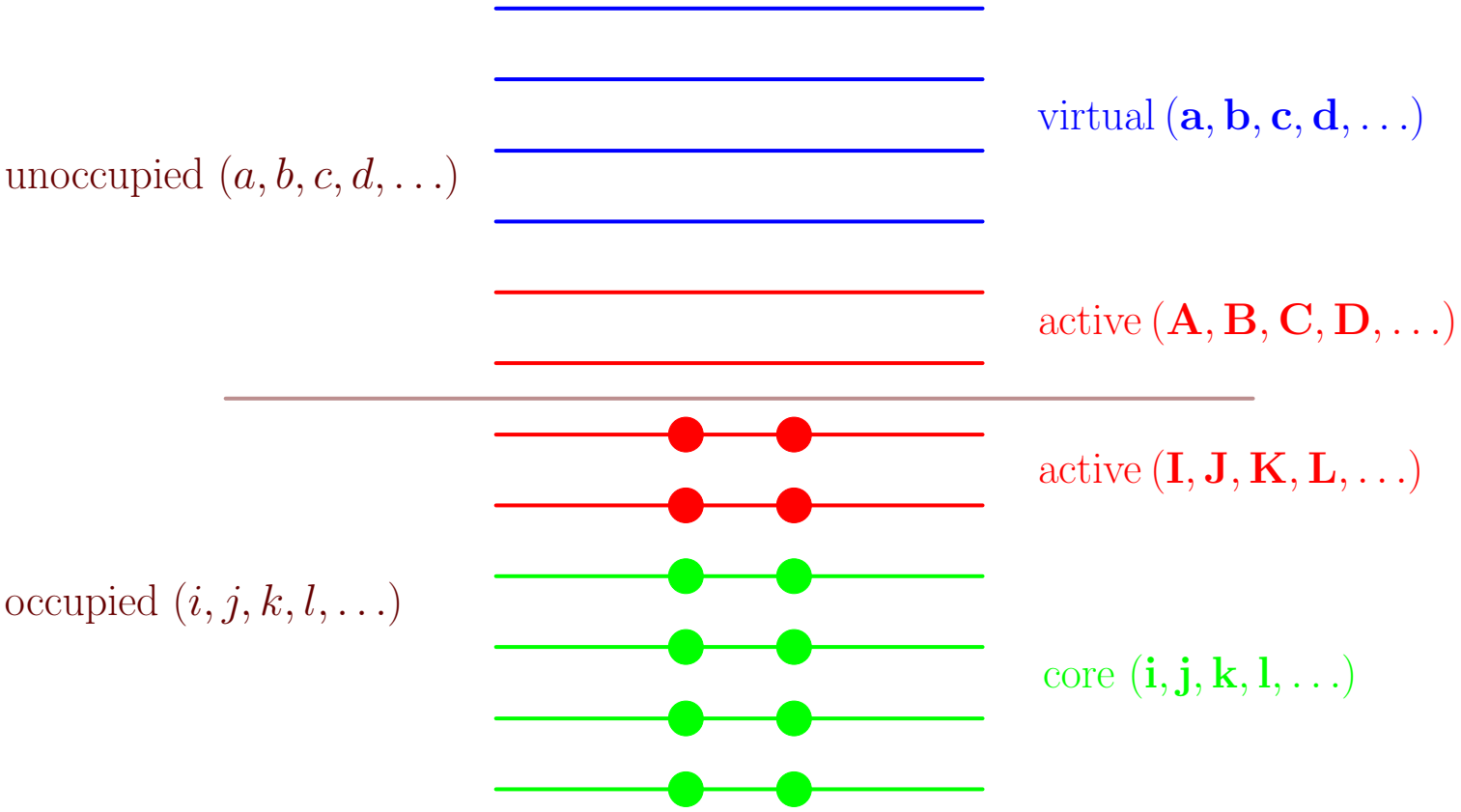
Vertical excitation energies (in eV) of CH^+, N_2, and C_2. The full CI values represent the excitation energies, whereas all remaining values are the deviations from the full CI results.

Molecule	State	Full CI	EOMCCSD	CC3	EOMCCSDt	EOMCCSDT	MMCC(2,3)	MMCC(2,4)
CH^+	$2\,^1\Sigma^+$	8.549	0.560	0.230	0.092	0.074	0.084	0.023
	$3\,^1\Sigma^+$	13.525	0.055	0.016	0.000	0.001	0.000	-0.001
	$4\,^1\Sigma^+$	17.217	0.099	0.026	0.012	-0.002	0.015	0.008
	$1\,^1\Pi$	3.230	0.031	0.012	0.003	-0.003	0.007	0.010
	$2\,^1\Pi$	14.127	0.327	0.219	0.094	0.060	0.105	0.037
	$1\,^1\Delta$	6.964	0.924	0.318	0.057	0.040	0.051	0.031
	$2\,^1\Delta$	16.833	0.856	0.261	0.016	-0.038	0.006	0.061
N_2	$^1\Pi_g$	9.584	0.081	0.033	0.029		0.092	0.080
	$^1\Sigma_u^-$	10.329	0.136	0.007	-0.005		0.008	0.032
	$^1\Delta_u$	10.718	0.180	0.009	0.001		0.024	0.039
	$^1\Pi_u$	13.609	0.400	0.177	0.090		0.246	0.085
C_2	$1\,^1\Pi_u$	1.385	0.090	-0.068	-0.062		-0.078	-0.043
	$1\,^1\Delta_g$	2.293	2.054	0.859	0.269		0.130	0.011
	$1\,^1\Sigma_u^+$	5.602	0.197	-0.047	0.085		-0.032	-0.039
	$1\,^1\Pi_g$	4.494	1.708	0.496	0.076		-0.026	0.057

Mean absolute errors in the calculated vertical excitation energies relative to the corresponding full CI values (in eV).

	Mean Absolute Error						
Molecule	EOMCCSD	EOMCCSDt	EOMCCSDT	MMCC(2,3)	MMCC(2,4)	CISDt	CISDtq
$CH^+(R_e)$	0.407	0.039	0.031	0.038	0.024	0.500	0.232
$CH^+(1.5R_e)$	0.704	0.047	0.037	0.048	0.022	0.467	0.134
$CH^+(2R_e)$	1.062	0.070	0.066	0.047	0.016	0.348	0.112
N_2	0.199	0.031		0.093	0.059	0.409	0.183
C_2	1.012	0.123		0.067	0.038	0.781	0.250

THE ACTIVE-SPACE EQUATION-OF-MOTION COUPLED-CLUSTER METHODS: THE EOMCCSDt APPROACH



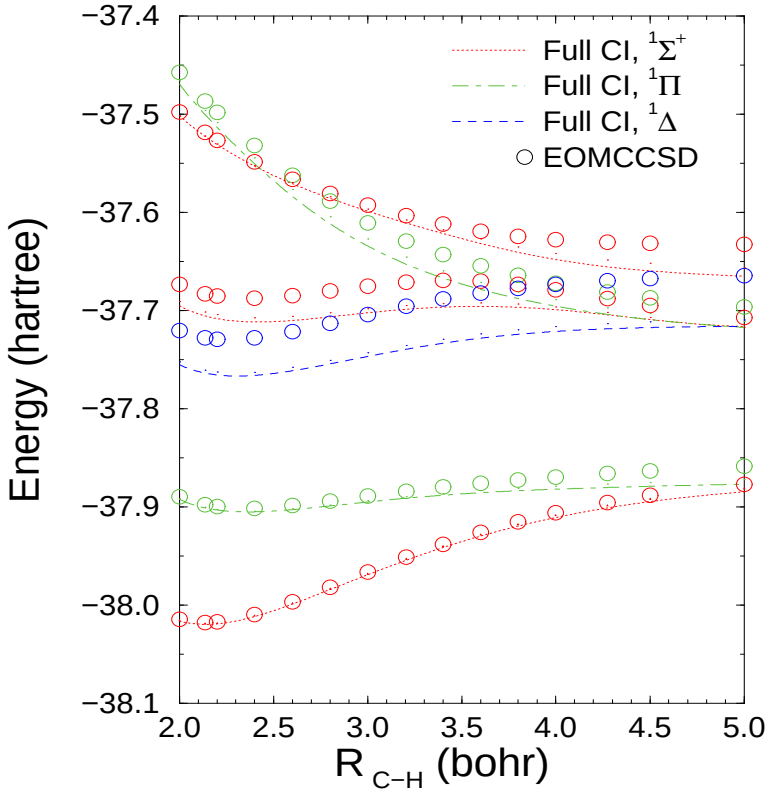
$$T \approx T^{\mathrm{CCSDt}} = T_1 + T_2 + T_3 \left(\begin{array}{c} ab\mathbf{C} \\ \mathbf{I}jk \end{array} \right)$$

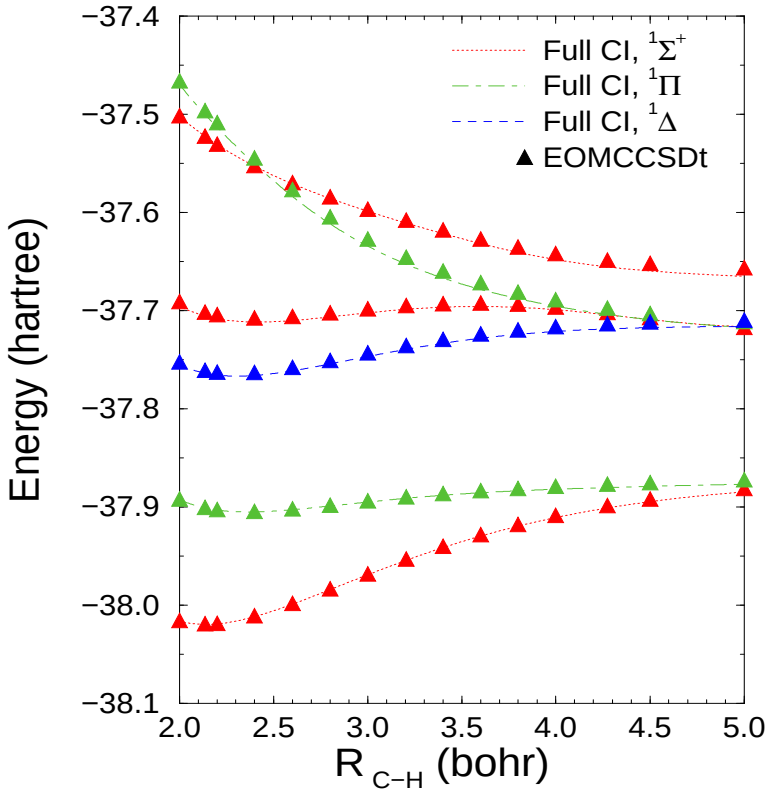
$$R_K \approx R_K^{\mathrm{CCSDt}} = R_{K,0} + R_{K,1} + R_{K,2} + R_{K,3} \left(\begin{array}{c} ab\mathbf{C} \\ \mathbf{I}jk \end{array} \right)$$

$$T_3 \left(\begin{array}{c} ab\mathbf{C} \\ \mathbf{I}jk \end{array} \right) = \sum_{\substack{\mathbf{I}>j>k \\ a>b>\mathbf{C}}} t_{ab\mathbf{C}}^{\mathbf{I}jk} \, G_{\mathbf{I}jk}^{ab\mathbf{C}}, \qquad R_{K,3} \left(\begin{array}{c} ab\mathbf{C} \\ \mathbf{I}jk \end{array} \right) = \sum_{\substack{\mathbf{I}>j>k \\ a>b>\mathbf{C}}} r_{ab\mathbf{C}}^{\mathbf{I}jk}(K) \, G_{\mathbf{I}jk}^{ab\mathbf{C}}$$

$$\bar{\mathbf{H}}^{\mathrm{CCSDt}} = \left(\begin{array}{ccc} \bar{\mathbf{H}}_{\mathbf{SS}} & \bar{\mathbf{H}}_{\mathbf{SD}} & \bar{\mathbf{H}}_{\mathbf{St}} \\ \bar{\mathbf{H}}_{\mathbf{DS}} & \bar{\mathbf{H}}_{\mathbf{DD}} & \bar{\mathbf{H}}_{\mathbf{Dt}} \\ \bar{\mathbf{H}}_{\mathbf{tS}} & \bar{\mathbf{H}}_{\mathbf{tD}} & \bar{\mathbf{H}}_{\mathbf{tt}} \end{array} \right)$$

Example: Potential Energy Surfaces for CH^+ (the EOMCCSDt Study)





Computer effort

Numbers of the symmetry-adapted, spin-orbital, $S_z = 0$ triexcited coefficients t_{abc}^{ijk} [or $r_{abc}^{ijk}(K)$] used in the EOMCCSDt and EOMCCSDT calculations (examples).

Molecule	Basis Set	Abelian Group	State Symmetry	EOMCCSDt	EOMCCSDT
CH_2	$[4s2p1d/2s1p]$	C_{2v}	A_1	4092 $\{3a_1, 1b_1\}$	68912
CH^+	$[5s3p1d/3s1p]$	C_{2v}	A_1 (Σ, Δ)	4956 $\{3\sigma, 1\pi \equiv 1\pi_x, 2\pi \equiv 1\pi_y\}$	31912
CH^+	$[5s3p1d/3s1p]$	C_{2v}	A_2 (Δ)	5132 $\{3\sigma, 1\pi \equiv 1\pi_x, 2\pi \equiv 1\pi_y\}$	22012
CH^+	$[5s3p1d/3s1p]$	C_{2v}	B_1, B_2 (Π)	5260 $\{3\sigma, 1\pi \equiv 1\pi_x, 2\pi \equiv 1\pi_y\}$	27180
C_2	$[4s3p1d]$	D_{2h}	A_g (Σ_g, Δ_g)	30176 $\{1\pi_u, 2\pi_u; 3\sigma_g, 3\sigma_u, 1\pi_g, 2\pi_g\}$	99924
C_2	$[4s3p1d]$	D_{2h}	A_u (Δ_u)	31368 $\{1\pi_u, 2\pi_u; 3\sigma_g, 3\sigma_u, 1\pi_g, 2\pi_g\}$	100460
C_2	$[4s3p1d]$	D_{2h}	B_{1g} (Δ_g)	31308 $\{1\pi_u, 2\pi_u; 3\sigma_g, 3\sigma_u, 1\pi_g, 2\pi_g\}$	100400
C_2	$[4s3p1d]$	D_{2h}	B_{1u} (Σ_u, Δ_u)	30236 $\{1\pi_u, 2\pi_u; 3\sigma_g, 3\sigma_u, 1\pi_g, 2\pi_g\}$	99984
C_2	$[4s3p1d]$	D_{2h}	B_{2g}, B_{3g} (Π_g)	30764 $\{1\pi_u, 2\pi_u; 3\sigma_g, 3\sigma_u, 1\pi_g, 2\pi_g\}$	100192
C_2	$[4s3p1d]$	D_{2h}	B_{2u}, B_{3u} (Π_u)	30764 $\{1\pi_u, 2\pi_u; 3\sigma_g, 3\sigma_u, 1\pi_g, 2\pi_g\}$	100192

Scalings

EOMCCSDt – $N_o N_u n_o^2 n_u^4$ (iterative)

MMCC(2,3) – $n_o^2 n_u^4$ (iterative) $+ n_o^3 n_u^4$ (noniterative)

EOMCCSDT – $n_o^3 n_u^5$ (iterative)

MRCISD – $M n_o^2 n_u^4$ (iterative, $M \gg N_o N_u$)

Future Work (Methods and Algorithms, Excited-State Problem)

- Extension of the MMCC theory to the MMCC(2,4) case and extension of the active-space EOMCC theory to the EOMCCSDtq case (years 1 and 2)
- Development of efficient computer codes for the MMCC and active-space EOMCC methods and incorporation of these codes in GAMESS (years 1 and 2)
- Development of the MMCC and active-space EOMCC methods for non-singlet states and formulation of the EA and IP extensions of the active-space EOMCC approaches (years 2 and 3)
- Extension of the active-space EOMCC approaches to properties other than energy (years 2 and 3)
- Development of the MMCC schemes with the perturbative choices of Ψ (renormalized EOMCCSD(T) method ?) (years 2 and 3)
- Work with Professor Mark S. Gordon and coworkers on parallelizing the excited-state MMCC codes within GAMESS (year 3)

- **Personnel:** 3 (PI, 1 postdoc, 1 student)
- **Present computer resources:** 2- and 32-CPU Origin systems at MSU
- **Collaborations:** Professor Mark S. Gordon and coworkers at Iowa State University and Ames Laboratory; also, Professor Stanisław A. Kucharski (Silesian University)
- **Expected computer needs:** 55,000 MPP hours at NERSC