

NEW COUPLED-CLUSTER METHODS FOR MOLECULAR POTENTIAL ENERGY SURFACES: I. GROUND-STATE APPROACHES

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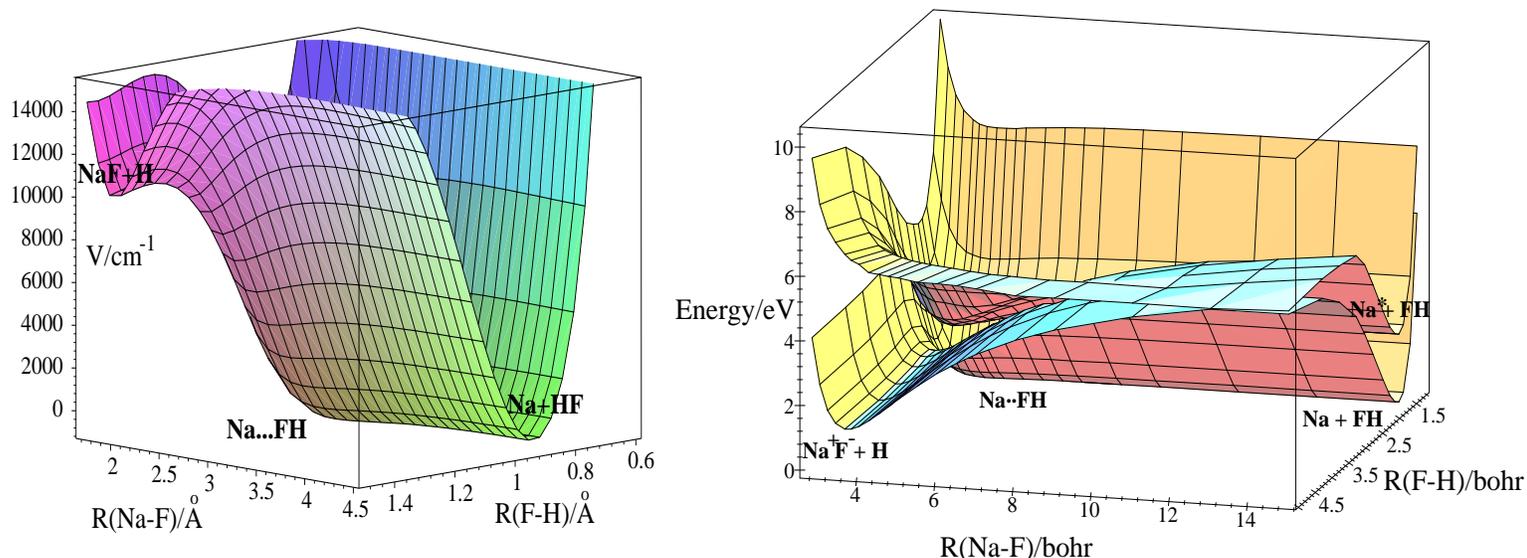
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P. Piecuch and K. Kowalski, in: *Computational Chemistry: Reviews of Current Trends*, edited by J. Leszczyński (World Scientific, Singapore, 2000), Vol. 5, pp. 1-104; K. Kowalski and P. Piecuch, *J. Chem. Phys.* **113**, 18-35 (2000); **113**, 5644-5652 (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 GROUND-STATE POTENTIAL ENERGY SURFACES

SINGLE-REFERENCE COUPLED-CLUSTER (CC) THEORY

(J. Čížek, 1966, 1969; J. Čížek and J. Paldus, 1971)

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

$$T_1|\Phi\rangle = \sum_{\substack{i \\ a}} t_a^i |\Phi_i^a\rangle, \quad T_2\Phi = \sum_{\substack{i > j \\ a > b}} t_{ab}^{ij} |\Phi_{ij}^{ab}\rangle, \quad T_k|\Phi\rangle = \sum_{\substack{i_1 > i_2 > \dots > i_k \\ a_1 > a_2 > \dots > a_k}} t_{a_1 a_2 \dots a_k}^{i_1 i_2 \dots i_k} |\Phi_{i_1 i_2 \dots i_k}^{a_1 a_2 \dots a_k}\rangle$$

$m_A = N$ – exact theory

$m_A < N$ – approximate methods

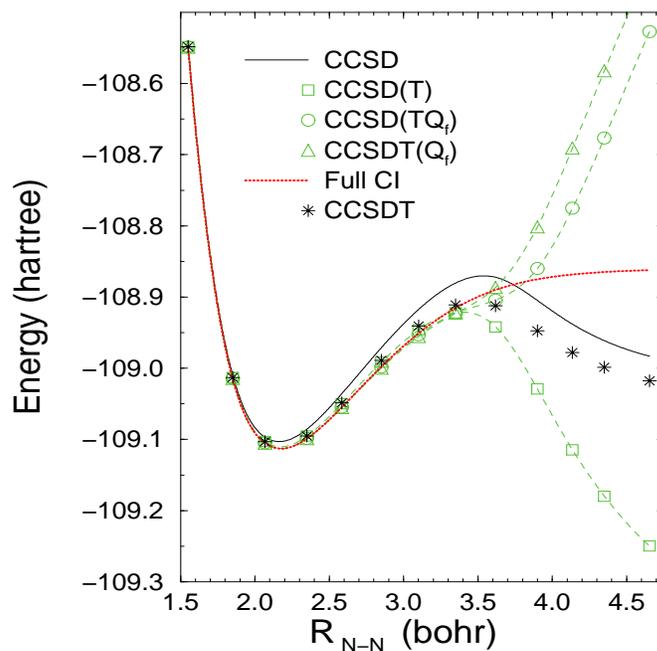
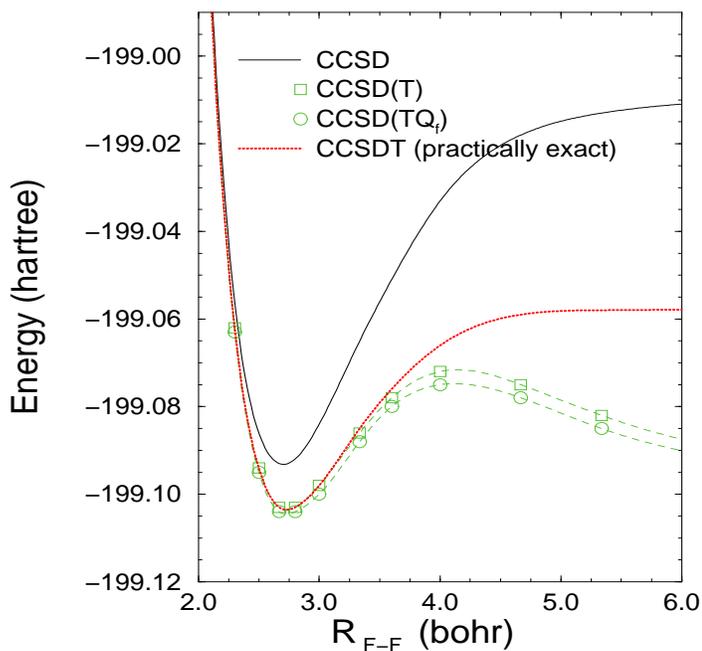
$m_A = 2$	$T = T_1 + T_2$	CCSD	$n_o^2 n_u^4 (n_o^2 n_u^2)$
$m_A = 3$	$T = T_1 + T_2 + T_3$	CCSDT	$n_o^3 n_u^5 (n_o^3 n_u^3)$
$m_A = 4$	$T = T_1 + T_2 + T_3 + T_4$	CCSDTQ	$n_o^4 n_u^6 (n_o^4 n_u^4)$

PROBLEMS WITH THE STANDARD CC APPROXIMATIONS

$$(T^{(A)} = \sum_{k=1}^{m_A} T_k, \quad m_A < N)$$

Example: N₂

[K. Kowalski and P. Piecuch, *J. Chem. Phys.* **113**, 5644 (2000); K. Kowalski and P. Piecuch, *Chem. Phys. Lett.* **344**, 165 (2001); P. Piecuch, S.A. Kucharski, and K. Kowalski, *ibid.* **344**, 176 (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]
- State-Selective, Active-Space CC Methods (e.g., the CCSDt and CCSDtq approaches of Piecuch *et al.*)
- Externally-Corrected CC Methods (e.g., the RMRCCSD approach of Paldus and Li)

THE PROPOSED RESEARCH FOCUSES ON METHODS THAT COMBINE THE SIMPLICITY OF THE STANDARD SINGLE-REFERENCE CC APPROACHES, SUCH AS CCSD(T), WITH THE EFFICIENCY WITH WHICH THE MULTI-REFERENCE METHODS DESCRIBE GROUND-STATE POTENTIAL ENERGY SURFACES

SPECIFIC GOALS

- New CC methods for ground-state potential energy surfaces:
 - method of moments of CC equations
 - renormalized CC approaches

METHOD OF MOMENTS OF COUPLED-CLUSTER EQUATIONS: A NEW APPROACH TO THE MANY-ELECTRON CORRELATION PROBLEM

A new relationship in quantum-mechanical theory of many-fermion (many-electron) systems

$$\delta = E - E^{(A)} = \Lambda[\Psi; \mathcal{M}_j^{(j)}(m_A), j > m_A]$$

- $E^{(A)}$ – the electronic energy obtained using the approximate *coupled-cluster* calculations (e.g., CCSD)
- E – the exact energy (the exact eigenvalue of the electronic Hamiltonian)
- Ψ – the exact wave function
- $\mathcal{M}_j^{(j)}(m_A)$ – the *generalized moments of coupled-cluster equations*

$$E^{\text{MMCC}} = E^{(A)} + \delta^{\text{MMCC}}$$

MMCC - *the method of moments of coupled-cluster equations* - provides us with fundamentally new ways of performing electronic structure calculations and **renormalizing** the failing standard tools of quantum chemistry.

The MMCC Energy Formula (the Ground-State Problem)

$$\delta = E - E^{(A)} = \sum_{n=m_A+1}^N \sum_{j=m_A+1}^n \langle \Psi | Q_n C_{n-j}(m_A) M_j(m_A) | \Phi \rangle / \langle \Psi | e^{T^{(A)}} | \Phi \rangle$$

$$M_j(m_A) = \left(H_N e^{T^{(A)}} \right)_{C,j}, \quad C_{n-j}(m_A) = \left(e^{T^{(A)}} \right)_{n-j}$$

$$M_j(m_A) | \Phi \rangle = Q_j \left(H_N e^{T^{(A)}} \right)_C | \Phi \rangle = \sum_J \mathcal{M}_J^{(j)}(m_A) | \Phi_J^{(j)} \rangle$$

$\mathcal{M}_J^{(j)}(m_A) = \langle \Phi_J^{(j)} | \left(H_N e^{T^{(A)}} \right)_C | \Phi \rangle$ – generalized moments of the CC equations

Approximate MMCC Methods: The MMCC(m_A, m_B) Approaches

$$E(m_A, m_B) = E^{(A)} + \sum_{n=m_A+1}^{m_B} \sum_{j=m_A+1}^n \langle \Psi | Q_n C_{n-j}(m_A) M_j(m_A) | \Phi \rangle / \langle \Psi | e^{T^{(A)}} | \Phi \rangle$$

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

The MMCC(2,3), MMCC(2,4), and MMCC(3,4) Methods

$$E(2, 3) = E^{\text{CCSD}} + \langle \Psi | Q_3 M_3(2) | \Phi \rangle / \langle \Psi | e^{T_1+T_2} | \Phi \rangle$$

$$E(2, 4) = E^{\text{CCSD}} + \langle \Psi | Q_3 M_3(2) + Q_4 [M_4(2) + T_1 M_3(2)] | \Phi \rangle / \langle \Psi | e^{T_1+T_2} | \Phi \rangle$$

$$E(3, 4) = E^{\text{CCSDT}} + \langle \Psi | Q_4 M_4(3) | \Phi \rangle / \langle \Psi | e^{T_1+T_2+T_3} | \Phi \rangle$$

$$M_3(2) | \Phi \rangle = Q_3 (H_N e^{T_1+T_2})_C | \Phi \rangle = \sum_{\substack{i < j < k \\ a < b < c}} \mathcal{M}_{ijk}^{abc}(2) | \Phi_{ijk}^{abc} \rangle$$

$$M_4(2) | \Phi \rangle = Q_4 (H_N e^{T_1+T_2})_C | \Phi \rangle = \sum_{\substack{i < j < k < l \\ a < b < c < d}} \mathcal{M}_{ijkl}^{abcd}(2) | \Phi_{ijkl}^{abcd} \rangle$$

$$M_4(3) | \Phi \rangle = Q_4 (H_N e^{T_1+T_2+T_3})_C | \Phi \rangle = \sum_{\substack{i < j < k < l \\ a < b < c < d}} \mathcal{M}_{ijkl}^{abcd}(3) | \Phi_{ijkl}^{abcd} \rangle$$

$$\mathcal{M}_{ijk}^{abc}(2) = \langle \Phi_{ijk}^{abc} | (H_N e^{T_1+T_2})_C | \Phi \rangle$$

$$\mathcal{M}_{ijkl}^{abcd}(2) = \langle \Phi_{ijkl}^{abcd} | (H_N e^{T_1+T_2})_C | \Phi \rangle$$

$$\mathcal{M}_{ijkl}^{abcd}(3) = \langle \Phi_{ijkl}^{abcd} | (H_N e^{T_1+T_2+T_3})_C | \Phi \rangle$$

The MMCC(2,3)/CISDT, MMCC(2,3)/CISDt,
MMCC(2,4)/CISDTQ, and MMCC(2,4)/CISDtq Methods

MMCC(2,3)/CISDT

$$|\Psi^{\text{CISDT}}\rangle = (1 + C_1 + C_2 + C_3) |\Phi\rangle$$

MMCC(2,3)/CISDt (CISDt = active-space CISDT)

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

MMCC(2,4)/CISDTQ

$$|\Psi^{\text{CISDTQ}}\rangle = (1 + C_1 + C_2 + C_3 + C_4) |\Phi\rangle$$

MMCC(2,4)/CISDtq (CISDtq = active-space CISDTQ)

$$|\Psi^{\text{CISDtq}}\rangle = \left[1 + C_1 + C_2 + C_3 \begin{pmatrix} ab\mathbf{C} \\ \mathbf{I}jk \end{pmatrix} + C_4 \begin{pmatrix} ab\mathbf{CD} \\ \mathbf{I}Jkl \end{pmatrix} \right] |\Phi\rangle$$

The Renormalized and Completely Renormalized CCSD[T], CCSD(T), CCSD(TQ), and CCSDT(Q) Methods

MBPT(2)-like choices of Ψ lead to the renormalized (R) and completely renormalized (CR) CCSD[T], CCSD(T), CCSD(TQ), CCSDT(Q), etc. approaches. Here are some examples of these methods:

CR-CCSD(T) ← completely renormalized CCSD(T)

$$|\Psi^{\text{CCSD(T)}}\rangle = \left(1 + T_1 + T_2 + R_0^{(3)}(V_N T_2)_C + R_0^{(3)}V_N T_1\right) |\Phi\rangle$$

$$E^{\text{CR-CCSD(T)}} = E^{\text{CCSD}} + \langle \Psi^{\text{CCSD(T)}} | Q_3 M_3(2) | \Phi \rangle / \langle \Psi^{\text{CCSD(T)}} | e^{T_1+T_2} | \Phi \rangle$$

R-CCSD(T) ← renormalized CCSD(T)

$$M_3(2) \approx (V_N T_2)_{C,3}$$

$$E^{\text{R-CCSD(T)}} = E^{\text{CCSD}} + \langle \Psi^{\text{CCSD(T)}} | Q_3 (V_N T_2)_C | \Phi \rangle / \langle \Psi^{\text{CCSD(T)}} | e^{T_1+T_2} | \Phi \rangle$$

\downarrow
 1.0 → CCSD(T)

CR-CCSD(TQ)

$$|\Psi^{\text{CCSD(TQ)}}\rangle = |\Psi^{\text{CCSD(T)}}\rangle + \frac{1}{2}T_2^2|\Phi\rangle$$

$$E^{\text{CR-CCSD(TQ)}} = E^{\text{CCSD}} + \langle \Psi^{\text{CCSD(TQ)}} | \{Q_3 M_3(2) + Q_4 [M_4(2) + T_1 M_3(2)]\} | \Phi \rangle / \langle \Psi^{\text{CCSD(TQ)}} | e^{T_1+T_2} | \Phi \rangle$$

CR-CCSDT(Q)

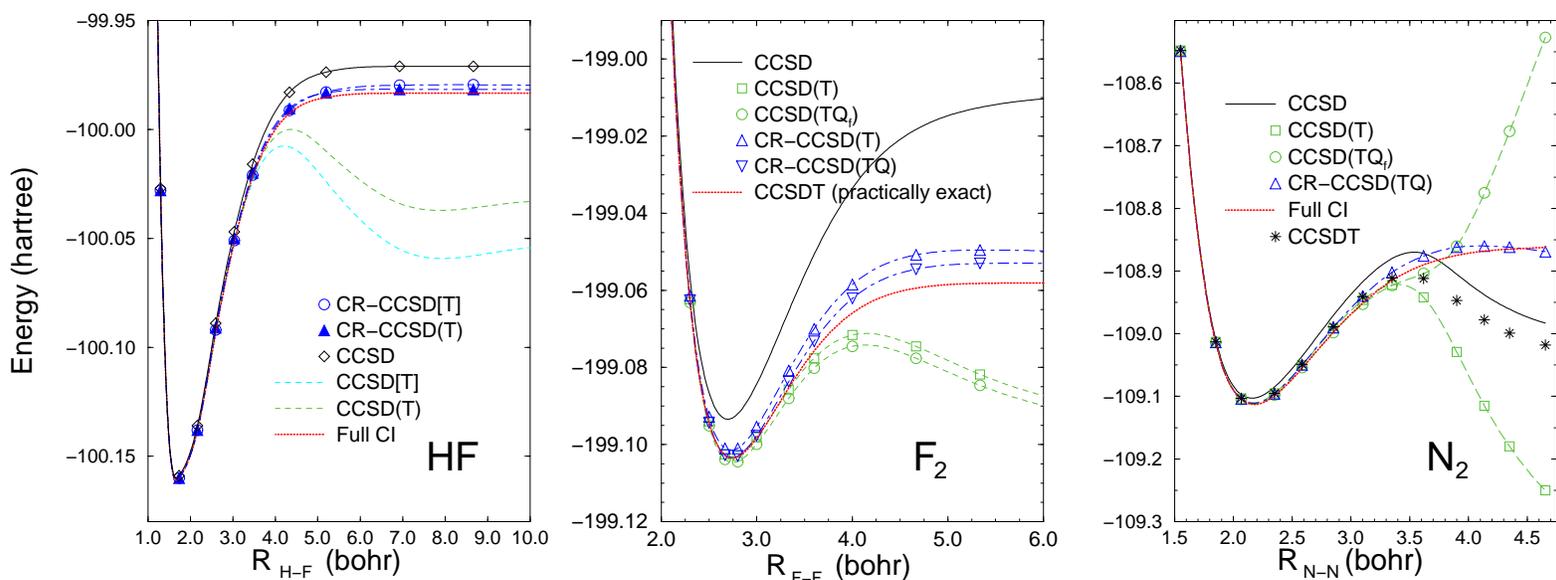
$$|\Psi^{\text{CCSDT(Q)}}\rangle = \left(1 + T_1 + T_2 + T_3 + T_1T_2 + \frac{1}{2}T_2^2\right) |\Phi\rangle$$

$$E^{\text{CR-CCSDT(Q)}} = E^{\text{CCSDT}} + \langle \Psi^{\text{CCSDT(Q)}} | Q_4 M_4(3) | \Phi \rangle / \langle \Psi^{\text{CCSDT(Q)}} | e^{T_1+T_2+T_3} | \Phi \rangle$$

The (C)R-CCSD[T], (C)R-CCSD(T), (C)R-CCSD(TQ), and (C)R-CCSDT(Q) methods can be viewed as the extensions of the standard CCSD[T], CCSD(T), CCSD(TQ_f), and CCSDT(Q_f) methods, respectively.

The computer costs of the (C)R-CCSD[T], (C)R-CCSD(T), (C)R-CCSD(TQ), and (C)R-CCSDT(Q) calculations are the same as the costs of the corresponding standard CCSD[T], CCSD(T), (C)R-CCSD(TQ), and (C)R-CCSDT(Q) calculations. For example, the cost of calculating the noniterative (T) correction of the standard CCSD(T) approximation is $kn_o^3n_u^4$. The costs of calculating the noniterative (T) corrections of the R-CCSD(T) and CR-CCSD(T) methods are $kn_o^3n_u^4$ and $2kn_o^3n_u^4$, respectively.

Representative Results

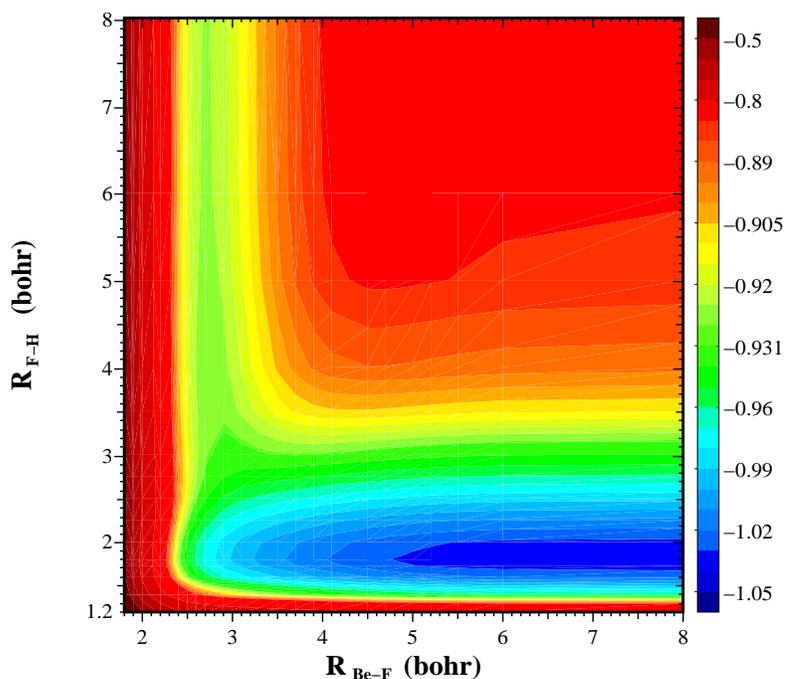


Selected vibrational energies $G(v)$ (v is the vibrational quantum number) and dissociation energies D_e (in cm^{-1}) of the HF molecule as described by the aug-cc-pVTZ basis set. The RKR represent total energies and all theoretically computed energies represent errors relative to RKR.

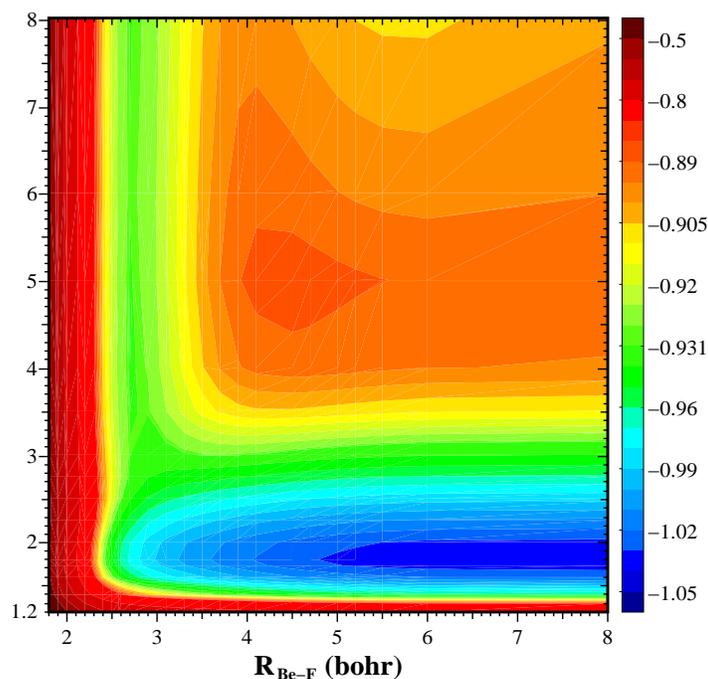
v	RKR	CCSD	CCSDT	CCSD(T)	CCSD(TQ _f)	R-CCSD(T)	CR-CCSD(T)	CR-CCSD(TQ)
0	2051	15	-7	-7	-7	-4	-3	-6
1	6012	52	-19	-18	-17	-9	-4	-16
2	9802	96	-28	-25	-23	-9	-2	-22
3	13424	144	-36	-32	-29	-9	2	-27
5	20182	252	-54	-47	-43	-6	12	-37
10	34363	623	-116	-136	-124	1	49	-70
11	36738	728	-131	-175	-159	1	60	-77
12	38955	850	-148	-232	-211	-2	72	-84
13	41007	993	-166			-9	87	-91
15	44576	1370	-207			-55	123	-109
19	49027	2881	-325				227	-159
D_e	49362	5847	-453				207	-156

The PES for the $\text{Be} + \text{FH} \rightarrow \text{BeF} + \text{H}$ Reaction

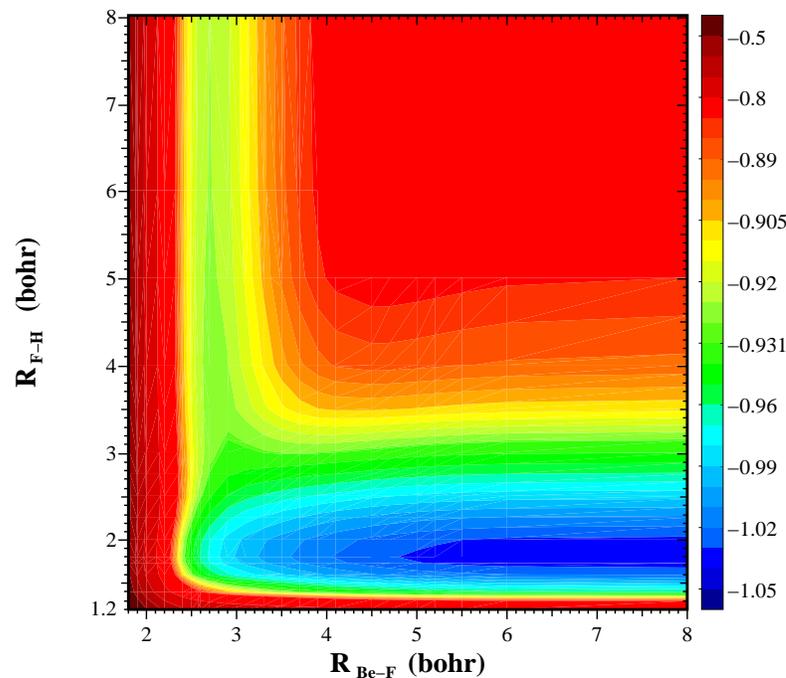
Full CI Results



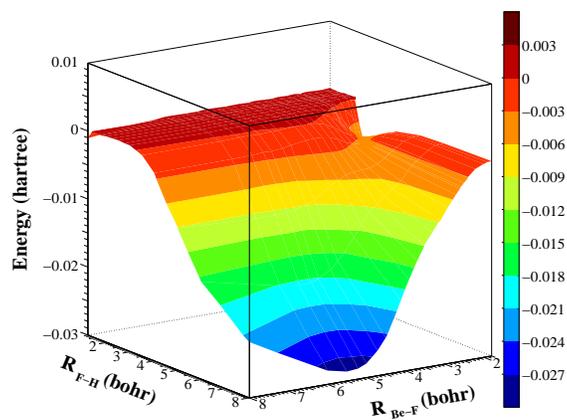
CCSD(T) Results



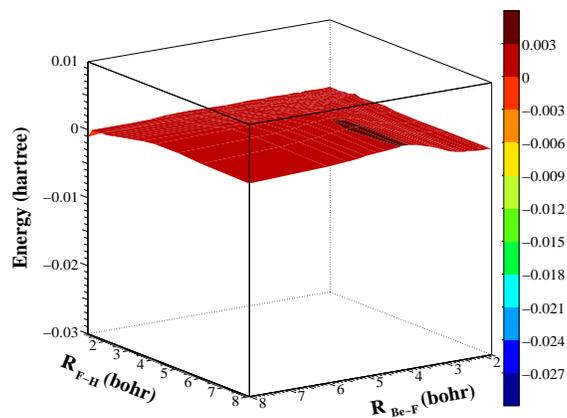
CR-CCSD(T) Results



Differences with Full CI for CCSD(T)



Differences with Full CI for CR-CCSD(T)



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

- Incorporation of the standard and renormalized CCSD(T), CCSD(TQ), and CCSDT(Q) methods in GAMESS (years 1 and 2)
- Development of the ground-state MMCC schemes with the non-perturbative choices of Ψ (years 1–3)
- Extensions of the MMCC and renormalized CC methods to open-shell states and reference configurations of the ROHF type (years 2 and 3)
- Work with Professor Mark S. Gordon and coworkers on parallelizing the MMCC and renormalized CC methods within GAMESS (years 2 and 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