COUPLED-CLUSTER THEORY: FROM QUANTUM CHEMISTRY TO APPLICATIONS IN NUCLEAR PHYSICS

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MANY THANKS TO PROFESSORS WOJCIECH SATUŁA, MAREK PFŰTZNER, AND BOGUMIŁ JEZIORSKI FOR INVITATION AND SEMINAR ARRANGEMENTS

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MANY-PARTICLE SCHRÖDINGER EQUATION

NUCLEAR PHYSICS: THE NUCLEAR SCHRÖDINGER EQUATION

$$\boxed{H_n\Psi_\mu(\mathbf{X}) = E_\mu\Psi_\mu(\mathbf{X})}$$

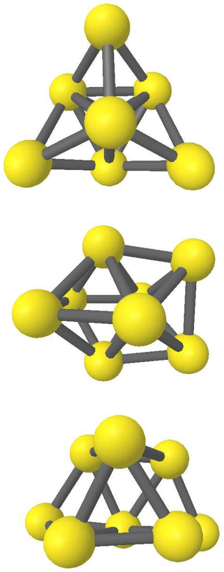
$$H_n = Z + V_2 + V_3(+???) = \sum_{i=1}^{N} z(\mathbf{x}_i) + \sum_{i>j=1}^{N} v_2(\mathbf{x}_i,\mathbf{x}_j) + \sum_{i>j>k=1}^{N} v_3(\mathbf{x}_i,\mathbf{x}_j,\mathbf{x}_k)(+???)$$

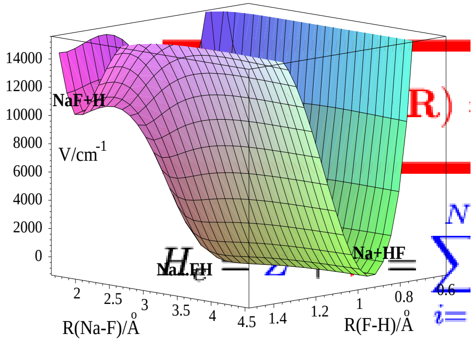
$$z(\mathbf{x}_i) = \frac{p_i^2}{2m_i}, \quad v_2(\mathbf{x}_i,\mathbf{x}_j) =? \text{ (Argonne } v_{18}\text{, CD Bonn, Idaho-A, etc.),}$$

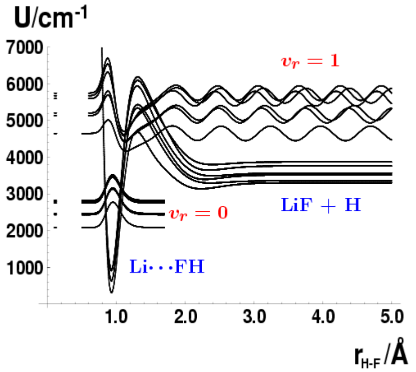
$$v_3(\mathbf{x}_i,\mathbf{x}_j,\mathbf{x}_k) =? \text{ (Tucson-Melbourne, Urbana IX, etc.)}$$

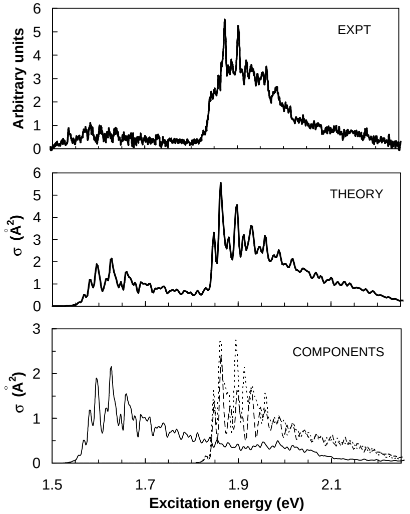
or NLO, N^2LO, N^3LO, etc.

QUANTUM CHEMISTRY: THE ELECTRONIC SCHRÖDINGER EQUATION

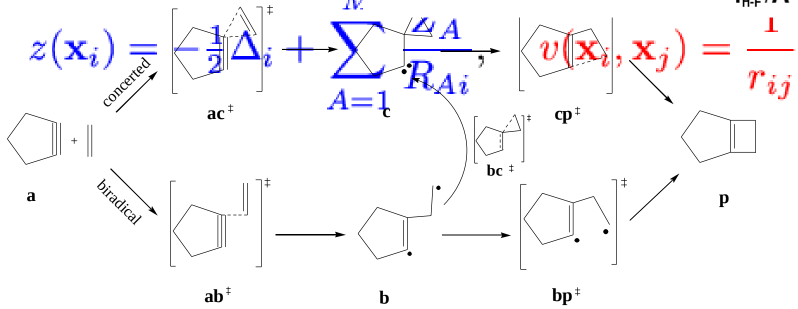




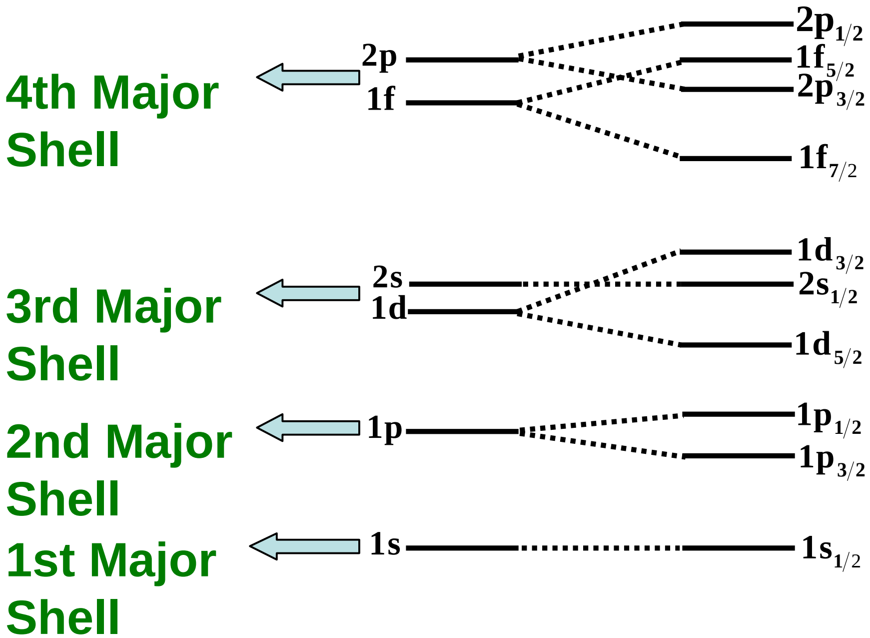




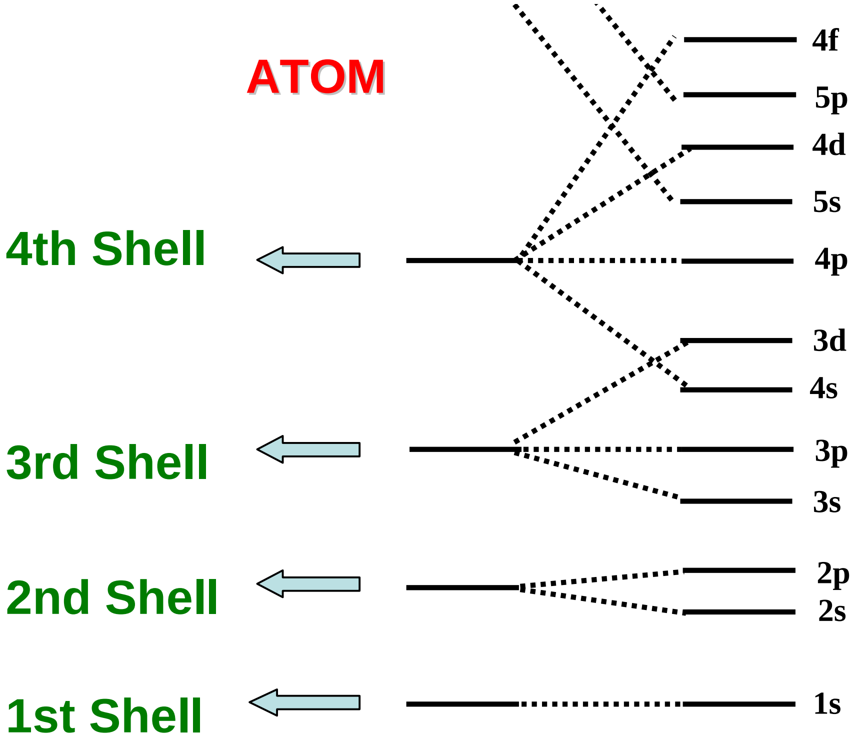
$$z(\mathbf{x}_i) = \left[-\frac{1}{2}\Delta_i + \sum_{A=1}^{M}\frac{Z_A}{R_{Ai}}\right], \quad v(\mathbf{x}_i,\mathbf{x}_j) = \frac{1}{r_{ij}}$$



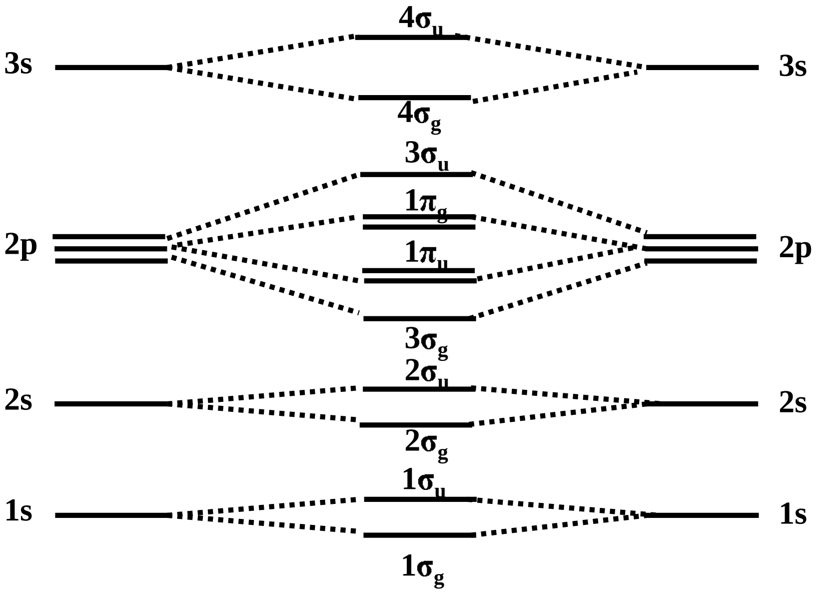
NUCLEUS



ATOM



MOLECULE (EXAMPLE, HOMONUCLEAR DIATOMIC)



ALGEBRAIC APPROACH

(IN CHEMISTRY, MOLECULAR ORBITAL THEORY)

$$\{\psi_r(\mathbf{x}),\ r=1,2,\ldots\} \equiv \mathcal{V}, \quad \dim\mathcal{V}=\infty$$

$$\Psi(\mathbf{x}_1,\ldots,\mathbf{x}_N) = \sum_{r_1>\cdots>r_N} c_{r_1\ldots r_N}\Psi_{r_1\ldots r_N}(\mathbf{x}_1,\ldots,\mathbf{x}_N)$$

$$\Psi_{r_1\ldots r_N}(\mathbf{x}_1,\ldots,\mathbf{x}_N) \equiv |\psi_{r_1}\ldots\psi_{r_N}| = (N!)^{-\frac{1}{2}} \begin{vmatrix} \psi_{r_1}(\mathbf{x}_1) & \ldots & \psi_{r_1}(\mathbf{x}_N) \\ \ldots & \ldots & \ldots \\ \psi_{r_N}(\mathbf{x}_1) & \ldots & \psi_{r_N}(\mathbf{x}_N) \end{vmatrix}$$

$$\text{In practice: } \dim\mathcal{V}<\infty$$

MOLECULAR ELECTRONIC STRUCTURE:

Molecular orbital (MO) basis set (usually, linear combination of atomic orbitals (LCAO) obtained with Hartree-Fock or MCSCF). Examples of AO basis sets: 6-311G++(2df,2pd), cc-pVDZ, MIDI, aug-cc-pVTZ.

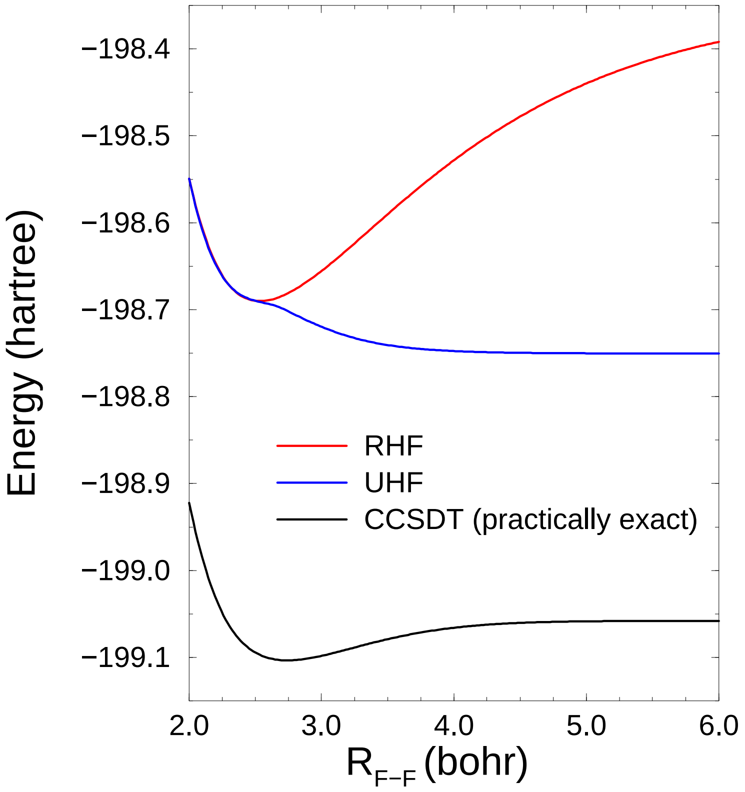
NUCLEAR STRUCTURE:

Example: Harmonic-oscillator (HO) basis set.

The key to successful description of atoms, molecules, condensed matter systems, and nuclei is an accurate determination of the MANY-PARTICLE CORRELATION EFFECTS. INDEPENDENT-PARTICLE-MODEL APPROXIMATIONS, such as the Hartree-Fock method, ARE INADEQUATE

ELECTRONIC STRUCTURE:

Bond breaking in F_2



NUCLEAR STRUCTURE:

Binding energy of ^{4}He
(4 shells)

Method	**Energy (MeV)**
$\langle \Phi_{osc} \lvert H' \rvert \Phi_{osc} \rangle$	**-7.211**
$\langle \Phi_{HF} \lvert H' \rvert \Phi_{HF} \rangle$	**-10.520**
CCSD	**-21.978**
CR-CCSD(T)	**-23.524**
Full Shell Model (Full CI)	**-23.484**

Many-particle correlation problem in atoms, molecules, nuclei, and other many-body systems is extremely complex …

Dimensions of the full CI spaces for many-electron systems

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

Dimensions of the full shell model spaces for nuclei

Nucleus	**4 shells**	**7 shells**
^{4}He	**4E4**	**9E6**
^{8}B	**4E8**	**5E13**
^{12}C	**6E11**	**4E19**
^{16}O	**3E14**	**9E24**

Full CI = Full Shell Model (=exact solution of the Schrödinger equation in a finite basis set) has a FACTORIAL scaling with the system size ("N! catastrophe")

APPROXIMATE METHODS THAT PROVIDE AN ACCURATE DESCRIPTION OF MANY-PARTICLE CORRELATION EFFECTS WITH RELATIVELY LOW COSTS ARE NEEDED

COUPLED-CLUSTER (CC) FORMALISMS

SINGLE-REFERENCE (SR) CC

(single reference determinant)

- Ground-state CC
- Excited-state CC, EOMCC, response CC, SAC-CI
- Bi-variational CC, ECC
- Renormalized CC, CR-CC

MULTI-REFERENCE (MR) CC

(multiple references; ground and excited states)

- Genuine:
  - Fock-space or valence-universal MRCC
  - Hilbert-space or state-universal MRCC
- State-selective or state-specific MRCC (several formulations)

EXTERNALLY-CORRECTED CC

(mix SRCC or MRCC with non-CC wave functions)

ACTIVE-SPACE CC or EOMCC

(mix SRCC/EOMCC with elements of MRCC)

GENERALIZED CC (???)

(single- or multi-determinantal reference, generalized form of the cluster operator adjusted to the Hamiltonian, virtually exact, but not well understood)

$$|\Psi\rangle = e^{T_1+T_2+T_3+T_4+\cdots}|\Phi\rangle$$

$T_3, T_4, \ldots$ determined directly from the Schrödinger equation ⇒ (CCSDT, CCSDTQ, etc.)

$T_3, T_4, \ldots$ estimated from perturbation theory ⇒ [CCSD(T), CCSD(TQ), etc.]

$T_3, T_4, \ldots$ extracted from non-CC wave functions ⇒ externally corrected CC methods

$T_3, T_4, \ldots$ selected via active orbitals ⇒ active-space CC methods (CCSDt, CCSDtq, etc.)

$T_3, T_4, \ldots$ from moment expansions ⇒ CR-CCSD(T), CR-CCSD(TQ), CR-CC(2,3), CR-CC(2,4), MMCC(2,3), MMCC(2,4), etc.

$$|\Psi\rangle = R\,e^{T_1+T_2+T_3+T_4+\cdots}|\Phi\rangle$$

$R_3, R_4, \ldots$ determined directly ⇒ excited states [EOMCCSDT, EOMCCSDTQ, etc.]

$R = R_{1p} + R_{2p\text{-}1h} + R_{3p\text{-}2h} + R_{4p\text{-}3h} + \cdots$ ⇒ electron-attached states [EA-EOMCCSD(3p-2h), EA-EOMCCSD(4p-3h), SAC-CI(4p-3h), etc.]

$R = R_{1h} + R_{2h\text{-}1p} + R_{3h\text{-}2p} + R_{4h\text{-}3p} + \cdots$ ⇒ ionized states [IP-EOMCCSD(3h-2p), IP-EOMCCSD(4h-3p), SAC-CI(4h-3p), etc.]

$R_3, R_4, R_{3p\text{-}2h}, R_{4p\text{-}3h}, R_{3h\text{-}2p}, R_{4h-3p}, \ldots$ selected via active orbitals ⇒ active-space EOMCC methods [EOMCCSDt, EA/IP-EOMCCSDt, SAC-CI(4p-3h){N$_o$,N$_u$}, SAC-CI(4h-3p){N$_o$,N$_u$}, etc.]

$R_3, R_4, T_3, T_4, \ldots$ from moment expansions ⇒ CR-EOMCCSD(T), CR-EOMCC(2,3), CR-EOMCC(2,4), MM-EOMCC(2,3), MM-EOMCC(2,4), etc.

$$|\Psi\rangle = \sum_{p=1}^{M} c_p\, e^{T_1^{(p)}+T_2^{(p)}+\cdots}|\Phi_p\rangle$$

State-universal multi-reference CC (SUMRCC) [SUMRCCSD, SUMRCCSD(1), CR-SUMRCC, MM-SUMRCC, etc.]

Mukherjee multi-reference CC (Mk-MRCC)

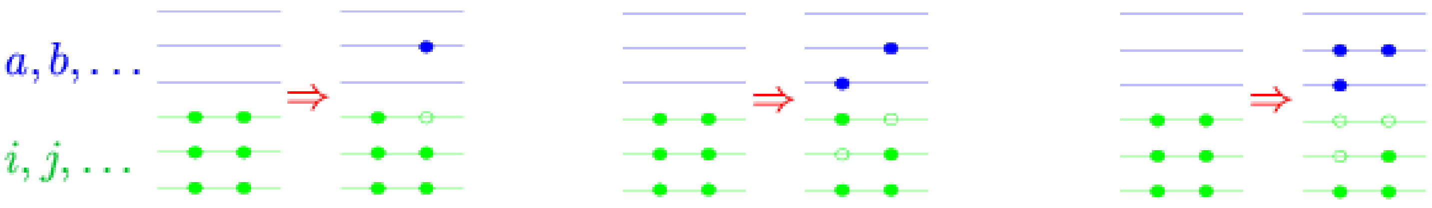
Brillouin-Wigner multi-reference CC (BW-MRCC)

SINGLE-REFERENCE COUPLED-CLUSTER (CC) THEORY

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

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

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



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

$$m_A = N \Rightarrow \text{exact theory}, \quad m_A < N \Rightarrow \text{approximations}$$

				CPU time scaling with the system size
$m_A = 2$	$T = T_1 + T_2$	CCSD	$n_o^2 n_u^4 \ (n_o^2 n_u^2)$	← iterative N^6
$m_A = 3$	$T = T_1 + T_2 + T_3$	CCSDT	$n_o^3 n_u^5 \ (n_o^3 n_u^3)$	← iterative N^8
$m_A = 4$	$T = T_1 + T_2 + T_3 + T_4$	CCSDTQ	$n_o^4 n_u^6 \ (n_o^4 n_u^4)$	← iterative N^{10}

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), CR-CC(2,3), CR-CC(2,4), CCSD(2), etc. approximations.

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

Standard CC Equations

(J. Čížek, 1966)

We do not minimize

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

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

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

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

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

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

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

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

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

- Iterative full methods: full CCSD, full CCSDT, full CCSDTQ, etc.

  CCSD equations (one- and two-body terms in the Hamiltonian) – $n_o^2 n_u^4$ $(\mathcal{N}^6)$

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

$$\begin{aligned} \langle \Phi_{ij}^{ab} | (H_N e^{T_1+T_2})_C | \Phi \rangle \quad \equiv \quad & \langle \Phi_{ij}^{ab} | [H_N (1 + T_1 + T_2 + \tfrac{1}{2} T_1^2 + T_1 T_2 + \tfrac{1}{6} T_1^3 \\ & + \tfrac{1}{2} T_2^2 + \tfrac{1}{2} T_1^2 T_2 + \tfrac{1}{24} T_1^4)]_C | \Phi \rangle = 0 \end{aligned}$$

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

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

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

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

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

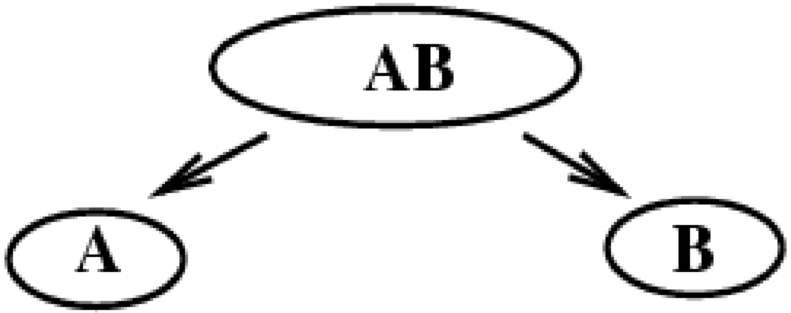
- Non-iterative perturbative methods: CCSD(T), $\mathrm{CCSD(TQ_f)}$, $\mathrm{CCSDT(Q_f)}$, etc.

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

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

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

Arguments in favor of CC: Separability or size consistency (provided that the reference state separates correctly)



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

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

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

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

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

Arguments in favor of CC: CC vs. CI

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

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

CIS = CI(1p-1h) → $C_1 = T_1$

CISD = CI(2p-2h) → $C_2 = T_2 + \frac{1}{2}(T_1)^2$

CISDT = CI(3p-3h) → $C_3 = T_3 + T_1T_2 + \frac{1}{6}(T_1)^3$

CISDTQ = CI(4p-4h) → $C_4 = T_4 + \frac{1}{2}(T_2)^2 + T_1T_3 + \frac{1}{2}(T_1)^2T_2 + \frac{1}{24}(T_1)^4$, etc.

→ CCSDT

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

CCSDT ~ CISDTQ

CC up to 3p-3h excitations in *T* ~ CI up to 4p-4h excitations in *C*

Arguments in favor of CC: Linked and connected cluster theorems

Linked cluster (diagram) theorem (Brueckner, 1955; Goldstone, 1957; Hubbard, 1957,1958; Hugenholtz, 1957)

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

Connected cluster theorem (Hubbard, 1957,1958)

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

$$C \Leftrightarrow \text{connected diagrams (including EPV terms)}$$

CC THEORY LEADS TO SIZE-EXTENSIVE APPROXIMATIONS

Arguments in favor of CC: CC vs. MBPT

$$\Delta E^{\mathrm{CCSD}} = \Delta E^{(2)} + \Delta E^{(3)} + \Delta E^{(4)}_{\mathrm{SDQ}} + \cdots$$

$$\mathbf{CCSD \sim MBPT(4)[SDQ] = MP4(SDQ)}$$

$$\Delta E^{\mathrm{CCSDT}} = \Delta E^{(2)} + \Delta E^{(3)} + \Delta E^{(4)} + \Delta E^{(5)}_{\mathrm{SDT}} + \cdots$$

$$\mathbf{CCSDT > MBPT(4)[SDTQ] = MBPT(4) = MP4}$$

COUPLED-CLUSTER METHODS PROVIDE THE EXCELLENT COMPROMISE BETWEEN HIGH ACCURACY AND RELATIVELY LOW COMPUTER COST …

Equilibrium bond length (in Å) and harmonic vibrational frequency (in cm^{-1}) of N_2

Method	r_e	ω_e	Scaling
DZP basis set, 32 orbitals, 2 lowest orbitals frozen			
CISD	1.1123	2444	$n_o^2 n_u^4$ (iterative)
CISDT	1.1158	2409	$n_o^3 n_u^5$ (iterative)
CISDTQ	1.1264	2296	$n_o^4 n_u^6$ (iterative) $\leftarrow \mathcal{N}^{10}$
MBPT(2)=MP2	1.1400	2105	$n_o^2 n_u^2$ (noniterative)
MBPT(3)=MP3	1.1126	2480	$n_o^2 n_u^4$ (noniterative)
MBPT(4)=MP4	1.1355	2145	$n_o^3 n_u^4$ (noniterative)
CCSD	1.1210	2352	$n_o^2 n_u^4$ (iterative)
CCSD(T)	1.1269	2287	$n_o^2 n_u^4$ (iterative)+$n_o^3 n_u^4$ (noniterative) $\leftarrow \mathcal{N}^6 + \mathcal{N}^7$
CCSDT-1	1.1275	2280	$n_o^3 n_u^4$ (iterative) $\leftarrow \mathcal{N}^7$
CCSDT	1.1265	2294	$n_o^3 n_u^5$ (iterative) $\leftarrow \mathcal{N}^8$
aug-cc-pVTZ basis set, 92 orbitals, 2 lowest orbitals frozen			
CCSD(T)	1.1040	2340	
Experiment	1.0977	2359	

EXAMPLES OF SINGLE-REFERENCE CC METHODS THAT ARE PARTICULARLY USEFUL

CCSD – basic CC method; recovers bulk, often >90%, of the correlation energy; also needed to define a posteriori T_3 corrections

$$E^{(\text{CCSD})} = E^{(\text{ref})} + \Delta E^{(\text{CCSD})}$$

$$\Delta E^{(\text{CCSD})} = \sum_{i,a} f_i^{\,a} t_a^i + \sum_{i<j,a<b} v_{ij}^{ab} \tau_{ab}^{ij} \qquad \tau_{ab}^{ij} = t_{ab}^{ij} + t_a^i t_b^j - t_a^j t_b^i$$

CCSD(T) – CCSD plus correction due to T_3, 'gold standard' of quantum chemistry;
CR-CC(2,3) – CCSD plus correction due to T_3, 'black-box' extension of CCSD(T) to single bond breaking and biradicals; recover >99 % of the correlation energy ('chemical accuracy')

$$E^{(\text{CR-CC(2,3)})} = E^{(\text{ref})} + \Delta E^{(\text{CR-CC(2,3)})} = E^{(\text{ref})} + \Delta E^{(\text{CCSD})} + \delta E^{(2,3)}$$

$$\delta E^{(2,3)} = \sum_{i<j<k,a<b<c} \ell_{ijk}^{abc} \, \mathrm{M}_{abc}^{ijk}$$

CR-CC(2,3)

CCSD(T)

$$\mathrm{M}_{abc}^{ijk} = \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi \rangle \Longleftarrow \bar{H}^{(\text{CCSD})} = \left(H e^{T_1+T_2} \right)_C = e^{-T_1-T_2} H e^{T_1+T_2} \Longrightarrow \mathrm{M}_{abc}^{ijk} = \langle \Phi_{ijk}^{abc} | (V_N T_2)_C | \Phi \rangle$$

$$\ell_{ijk}^{abc} = \langle \Phi | (1+\Lambda_1+\Lambda_2) \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle / D_{abc}^{ijk}$$

$$\ell_{ijk}^{abc} = \langle \Phi | [(T_1^{\dagger} V_N)_{DC} + (T_2^{\dagger} V_N)_C] | \Phi_{ijk}^{abc} \rangle / D_{abc}^{ijk}$$

$$= \langle \Phi | [(\Lambda_1 \bar{H}_2^{(\text{CCSD})})_{DC} + (\Lambda_2 \bar{H}_1^{(\text{CCSD})})_{DC} + (\Lambda_2 \bar{H}_2^{(\text{CCSD})})_C] | \Phi_{ijk}^{abc} \rangle / D_{abc}^{ijk}$$

$$D_{abc}^{ijk} = E^{(\text{CCSD})} - \langle \Phi_{ijk}^{abc} | \bar{H}^{(\text{CCSD})} | \Phi_{ijk}^{abc} \rangle = -\sum_{n=1}^{3} \bar{H}_n^{(\text{CCSD})}$$

$$D_{abc}^{ijk} = \varepsilon_i + \varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b - \varepsilon_c$$

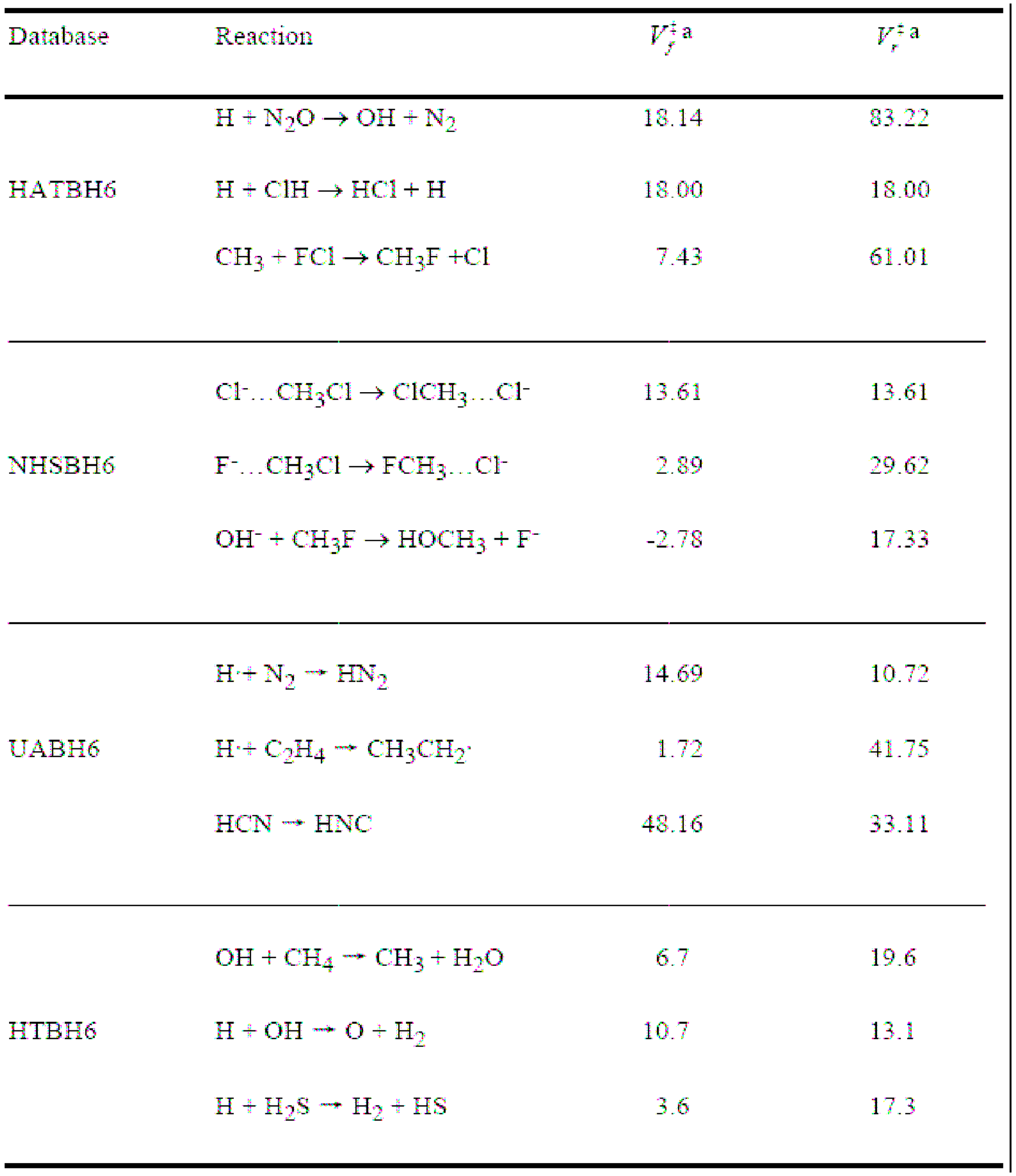
Example: The DBH24 Representative Benchmark Suite for Thermochemical Kinetics

Heavy-Atom Transfer

Nucleophilic Substitution

Unimolecular and Association

Hydrogen Transfer



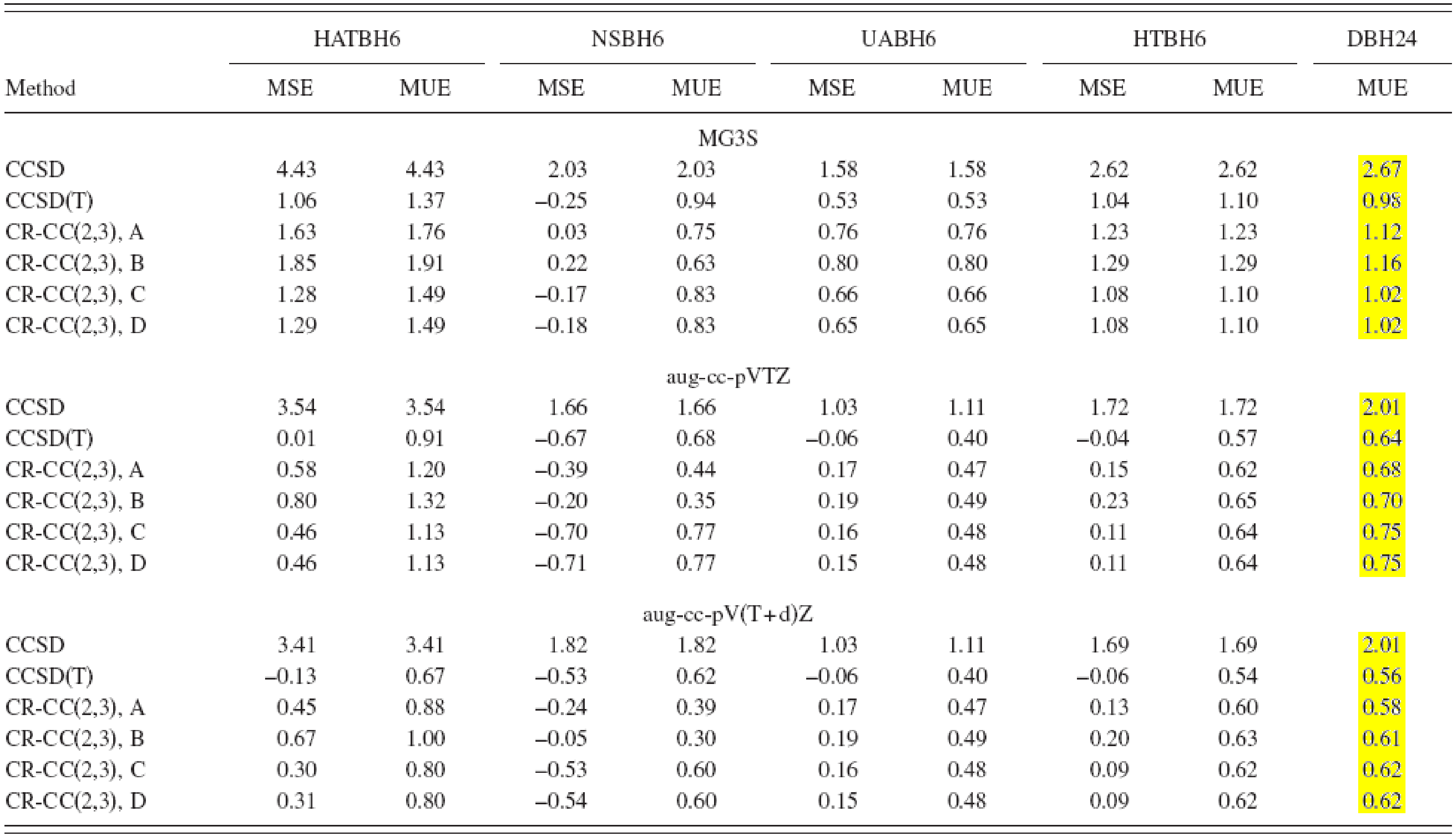
Database	Reaction	$V_f^{\ddagger\,a}$	$V_r^{\ddagger\,a}$
HATBH6	$H + N_2O \rightarrow OH + N_2$	18.14	83.22
	$H + ClH \rightarrow HCl + H$	18.00	18.00
	$CH_3 + FCl \rightarrow CH_3F + Cl$	7.43	61.01
NHSBH6	$Cl^-\ldots CH_3Cl \rightarrow ClCH_3\ldots Cl^-$	13.61	13.61
	$F^-\ldots CH_3Cl \rightarrow FCH_3\ldots Cl^-$	2.89	29.62
	$OH^- + CH_3F \rightarrow HOCH_3 + F^-$	-2.78	17.33
UABH6	$H\cdot + N_2 \rightarrow HN_2$	14.69	10.72
	$H\cdot + C_2H_4 \rightarrow CH_3CH_2\cdot$	1.72	41.75
	$HCN \rightarrow HNC$	48.16	33.11
HTBH6	$OH + CH_4 \rightarrow CH_3 + H_2O$	6.7	19.6
	$H + OH \rightarrow O + H_2$	10.7	13.1
	$H + H_2S \rightarrow H_2 + HS$	3.6	17.3

(kcal/mol)

(J. Zheng, Y. Zhao, and D.G. Truhlar, J. Chem. Theory Comput., 2007)

Performance of various CC methods and basis sets for the DBH24 benchmark suite for thermochemical kinetics

(reported as errors relative to benchmark values in kcal/mol)



	HATBH6		NSBH6		UABH6		HTBH6		DBH24
Method	MSE	MUE	MSE	MUE	MSE	MUE	MSE	MUE	MUE
				MG3S					
CCSD	4.43	4.43	2.03	2.03	1.58	1.58	2.62	2.62	2.67
CCSD(T)	1.06	1.37	−0.25	0.94	0.53	0.53	1.04	1.10	0.98
CR-CC(2,3), A	1.63	1.76	0.03	0.75	0.76	0.76	1.23	1.23	1.12
CR-CC(2,3), B	1.85	1.91	0.22	0.63	0.80	0.80	1.29	1.29	1.16
CR-CC(2,3), C	1.28	1.49	−0.17	0.83	0.66	0.66	1.08	1.10	1.02
CR-CC(2,3), D	1.29	1.49	−0.18	0.83	0.65	0.65	1.08	1.10	1.02
				aug-cc-pVTZ					
CCSD	3.54	3.54	1.66	1.66	1.03	1.11	1.72	1.72	2.01
CCSD(T)	0.01	0.91	−0.67	0.68	−0.06	0.40	−0.04	0.57	0.64
CR-CC(2,3), A	0.58	1.20	−0.39	0.44	0.17	0.47	0.15	0.62	0.68
CR-CC(2,3), B	0.80	1.32	−0.20	0.35	0.19	0.49	0.23	0.65	0.70
CR-CC(2,3), C	0.46	1.13	−0.70	0.77	0.16	0.48	0.11	0.64	0.75
CR-CC(2,3), D	0.46	1.13	−0.71	0.77	0.15	0.48	0.11	0.64	0.75
				aug-cc-pV(T+d)Z					
CCSD	3.41	3.41	1.82	1.82	1.03	1.11	1.69	1.69	2.01
CCSD(T)	−0.13	0.67	−0.53	0.62	−0.06	0.40	−0.06	0.54	0.56
CR-CC(2,3), A	0.45	0.88	−0.24	0.39	0.17	0.47	0.13	0.60	0.58
CR-CC(2,3), B	0.67	1.00	−0.05	0.30	0.19	0.49	0.20	0.63	0.61
CR-CC(2,3), C	0.30	0.80	−0.53	0.60	0.16	0.48	0.09	0.62	0.62
CR-CC(2,3), D	0.31	0.80	−0.54	0.60	0.15	0.48	0.09	0.62	0.62

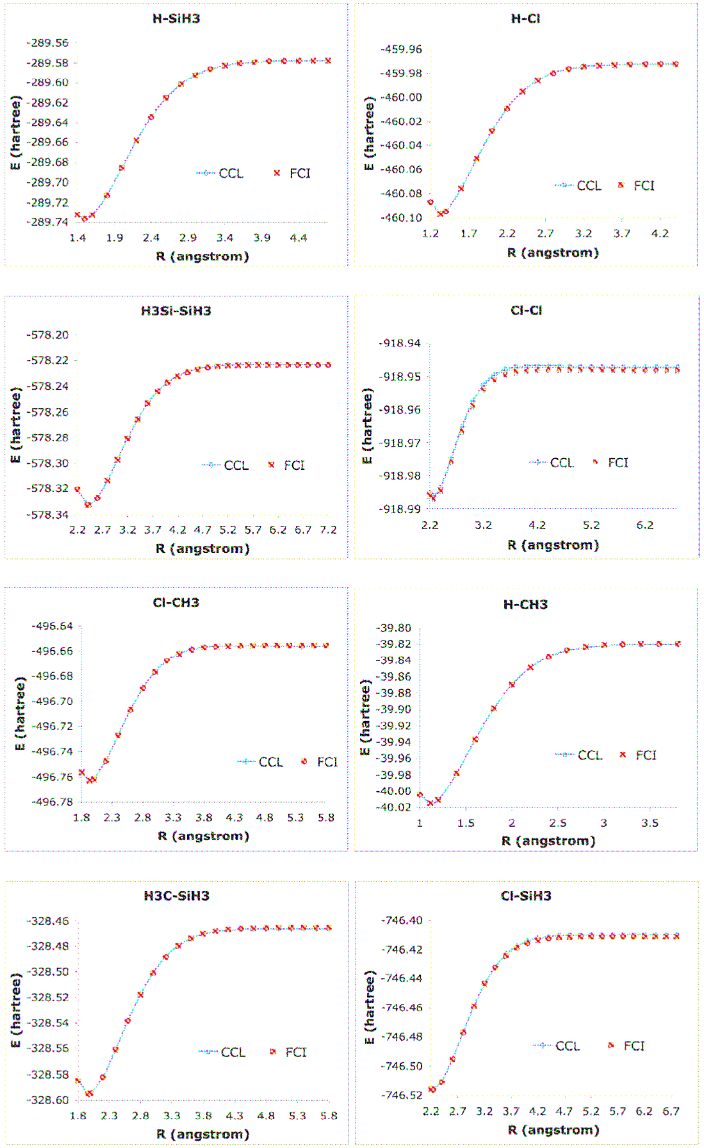
(J. Zheng, J.R. Gour, J.J. Lutz, M. Wloch, P. Piecuch and D.G. Truhlar, J. Chem. Phys., 2008)

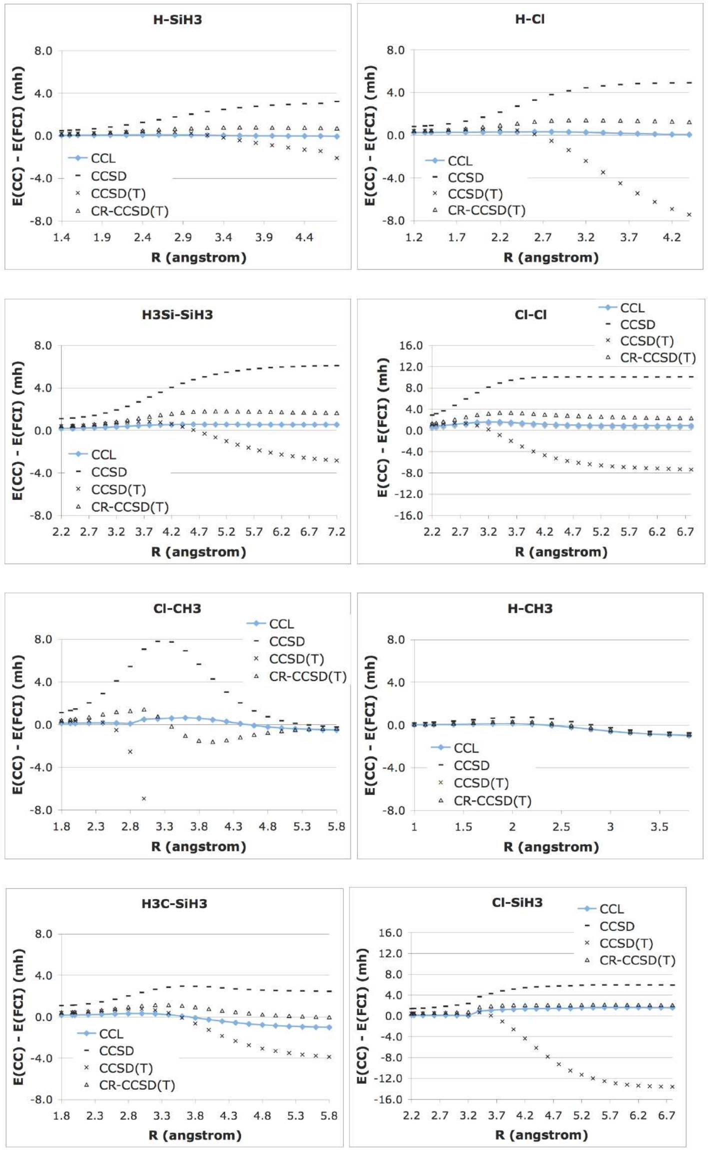
Reactions relevant to gas-phase chemistry of SiC

(Y. Ge, M.S. Gordon, and P. Piecuch, J. Chem. Phys., 2007)

CCL =

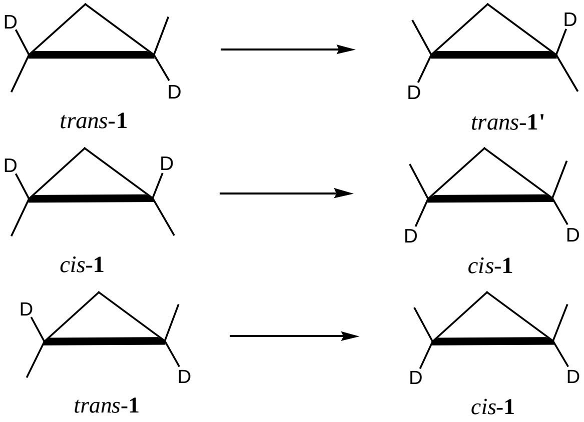
CR-CC(2,3)

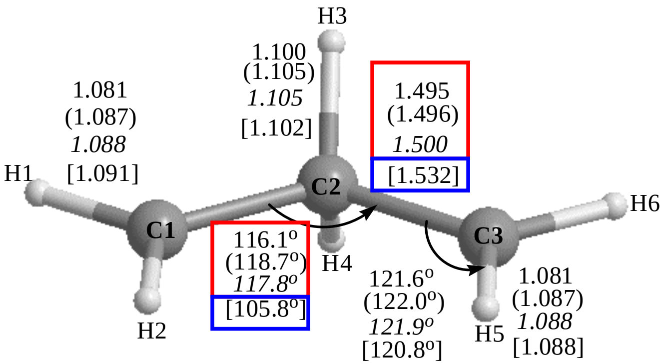




Example: Thermal Stereomutations of Cyclopropane

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





$\phi_{H1\text{-}C1\text{-}C2\text{-}C3}$ = 0.0° (0.0°) *0.0°* [0.0]

$\phi_{H5\text{-}C3\text{-}C2\text{-}C1}$ = 0.0° (0.0°) *0.0°* [0.0]

MRCI

(CR-CCSD(T))

CR-CC(2,3),A

[CCSD(T)]

Trimethylene biradical (TS1)

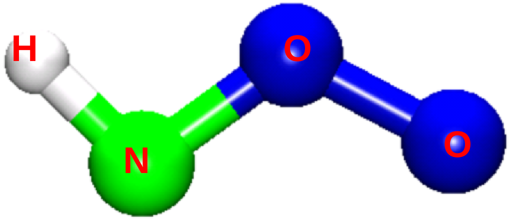
vib mode	MRCI (Isborn et al., 2004)	CR-CCSD(T)	CR-CC(2,3)	CCSD(T)
1	*139i*	*129i*	*122i*	*411i*
2	61	147	161	*157i*
3	278	334	340	168
4	361	362	358	238
…	…	…	…	…
21	3361	3282	3270	3255
Av. %Err.		**4.2**	**4.1**	**9.4**

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

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

THE HNOO CONTROVERSY

- **LBSW:** P. Ling, A.I. Boldyrev, J. Simons, and C.A. Wight, "Laser Photolysis of Matrix-Isolated Methyl Nitrate: Experimental and Theoretical Characterization of the Infrared Spectrum of Imine Peroxide (HNOO)," *J. Am. Chem. Soc.* 120, 12327 (1998).
- **LGDS:** S.L. Laursen, J.E. Grace Jr., R.L. DeKock, and S.A. Spronk, "Reaction of NH (X) with Oxygen in a Solid Xenon Matrix: Formation and Infrared Spectrum of Imine Peroxide, HNOO," *J. Am. Chem. Soc.* 120, 12583 (1998).



Fundamental Frequency	Exp: LBSW	Exp.:LGDS	CCSD(T)	CR-CCSD(T)	CCSD(TQ$_f$)	CCSDT-3(Q$_f$)
ν_1 (NH stretch)	3287.7	3165.5	3189	3198	3188	3188
ν_2 (HNO bend)	not observed	1485.5	1492	1509	1494	1499
ν_3 (NO stretch)	1381.6	1092.3	1147	1116	1123	1126
ν_4 (OO stretch)	843.2	1054.5	1042	1078	1047	1071
ν_5 (NOO bend)	670.1	not observed	650	653	650	650
ν_6 (torsion)	790.7	764.0	764	777	757	757

R.L. DeKock, M.J. McGuire, P. Piecuch, W.D. ALLEN, H.F. SCHAEFER III, K. Kowalski, S.A. Kucharski, M. Musiał, A.R. Bonner, S.A. Spronk, D.B. Lawson, and S.L. Laursen, *J. Phys. Chem. A* (2004)

CAN WE EXTEND CC METHODS TO LARGE MOLECULAR SYSTEMS?

- **CODE PARALLELIZATION**

Example: CCSD(T) or CR-CC(2,3): CPU time scaling: N^7

In order to triple the system size without increasing the CPU time one needs **$3^7 = 2187$** processors (assuming perfect scalability)

⇓

PARALLELIZATION ALONE IS NOT SUFFICIENT (!)

ONE MUST ATTACK INTRINSIC POWER SCALING LAWS CAUSED, IN PARTICULAR, BY THE USE OF DELOCALIZED MOLECULAR ORBITALS.

HINT:

ELECTRON CORRELATIONS IN NON-METALLIC SYSTEMS ARE LOCAL

⇓

USE LOCALIZED ORBITALS AND LIMIT EXCITATIONS TO LOCAL ORBITAL DOMAINS THAT (HOPEFULLY) DO NOT GROW WITH THE SYSTEM SIZE

⇓

- **LOCAL CORRELATION METHODS AND LINEAR SCALING ALGORITHMS**

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)]

C_nH_{2n+2}, 6-31G(d)

n	n_o	n_u	CCSD Correlation Energy/H			CR-CC(2,3) Correlation Energy/H		
			Canonical	CIM (level 1)[a]	CIM (level 2)[a]	Canonical	CIM (level 1)[a]	CIM (level 2)[a]
12	37	183	-1.72201	-1.72032 (99.90%)	-1.72062 (99.92%)	-1.77148	-1.77160 (100.01%)	-1.77180 (100.02%)
16	49	243	-2.29168	-2.28888 (99.88%)	-2.28932 (99.90%)	-2.35724	-2.35779 (100.02%)	-2.35811 (100.04%)
20	61	303	-2.86170	-2.85778 (99.86%)	-2.85883 (99.90%)	-	-2.94426	-2.94548
24	73	363	-	-3.42639	-3.42772	-	-3.53049	-3.53167
28	85	423	-	-3.99501	-3.99662	-	-4.11673	-4.11817
32	97	483	-	-4.56362	-4.56551	-	-4.70297	-4.70466

n	CCSD Iterations/CPU hours			CR-CC(2,3) triples/CPU hours			No. of Subsystems
	Canonical	CIM (level 1)[a]	CIM (level 2)[a]	Canonical	CIM (level 1)[a]	CIM (level 2)[a]	
12	8.8	3.3 (0.7)	3.6 (0.7)	49.0	29.3 (6.5)	46.0 (8.0)	7/7
16	41.3	3.1 (0.4)	8.0 (1.1)	330.9	43.0 (4.8)	92.9 (15.7)	11/11
20	143.2	5.8 (0.5)	24.3 (1.5)	[1580]	57.0 (5.2)	224.3 (13.8)	15/43
24	[418]	7.2 (0.4)	28.6 (1.5)	[5383]	69.9 (4.0)	289.3 (10.0)	19/55
28	[1038]	8.8 (0.6)	38.5 (1.0)	[15683]	111.1 (8.2)	421.5 (12.0)	23/67
32	[2300]	9.9 (0.6)	49.8 (1.2)	[39700]	101.1 (5.1)	499.4 (12.0)	27/79

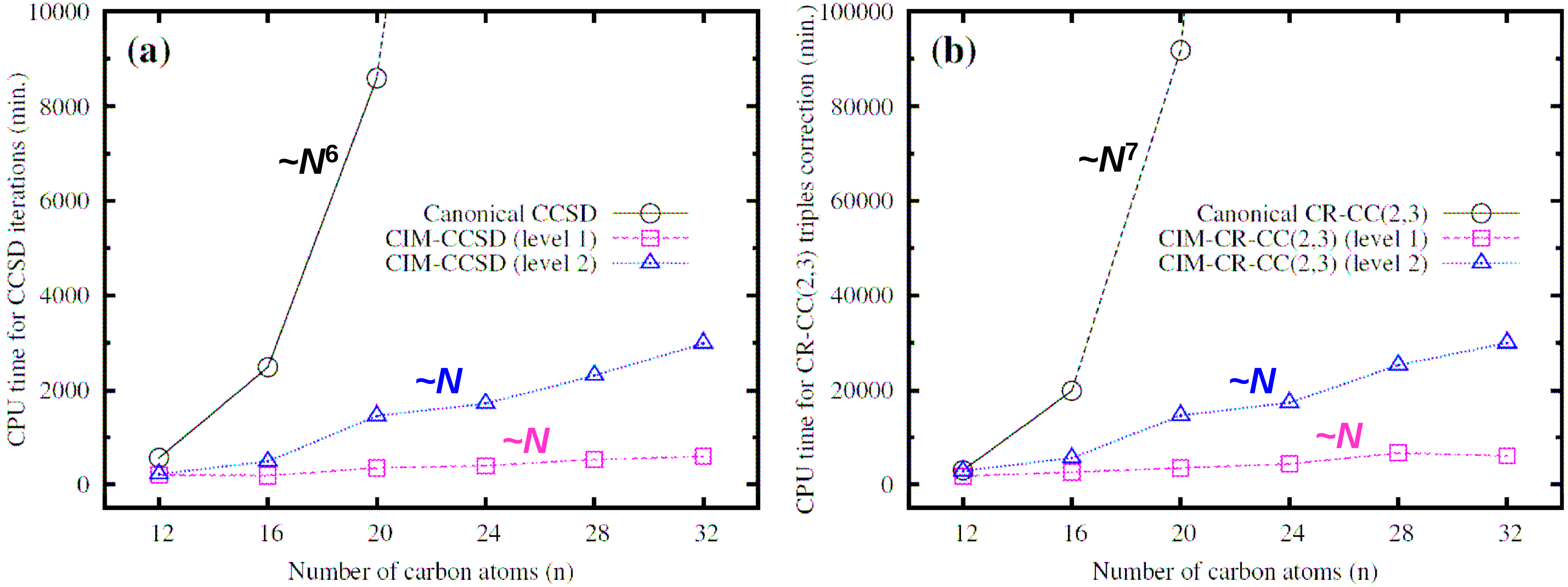
[a] The numbers in parentheses represent the fractions of the canonical correlation energies recovered by the CIM approach. In level 1 of the CIM theory, ζ_1=0.01 and ζ_2=0.05; in level 2, ζ_1=0.01 and ζ_2=0.02

[a] The numbers in parentheses represent the CPU times required by the calculations for the largest CIM subsystems. In level 1 of the CIM theory, ζ_1=0.01 and ζ_2=0.05; in level 2, ζ_1=0.01 and ζ_2=0.02

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)]

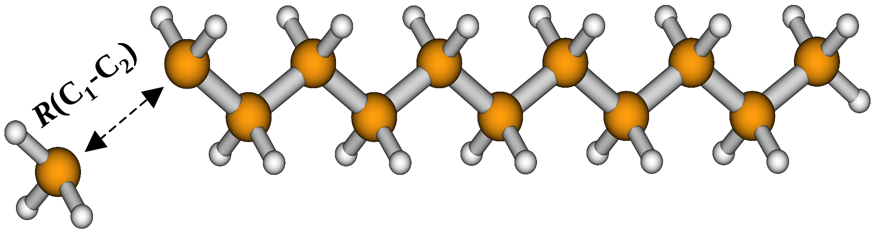
C_nH_{2n+2}, 6-31G(d)

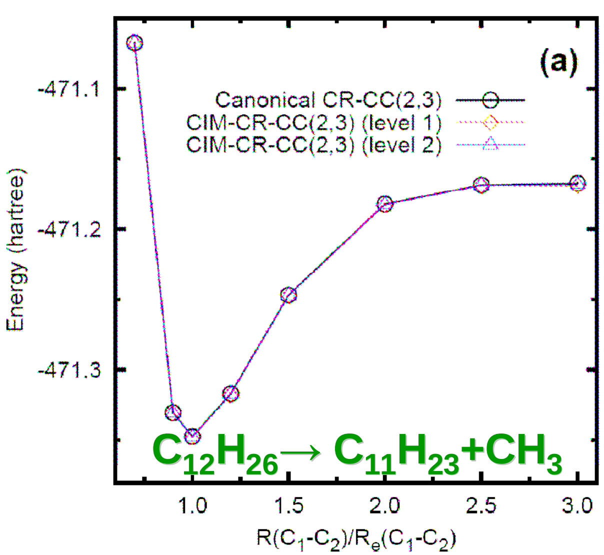


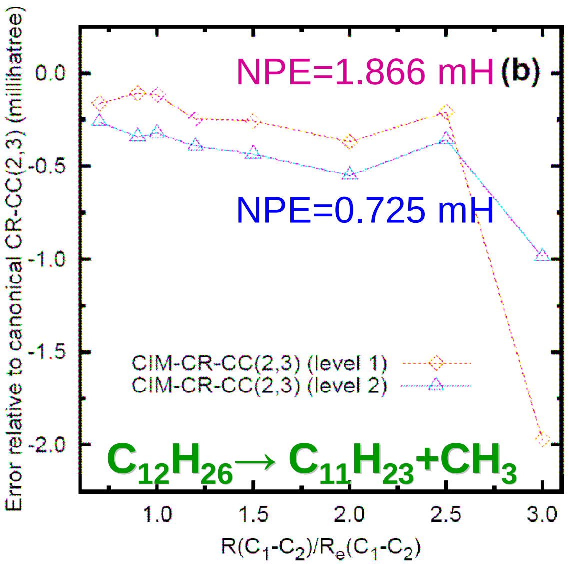
LINEAR SCALING LOCAL CORRELATION CC METHODS: CLUSTER-IN-MOLECULE (CIM) CCSD, CCSD(T), AND CR-CC(2,3) APPROACHES

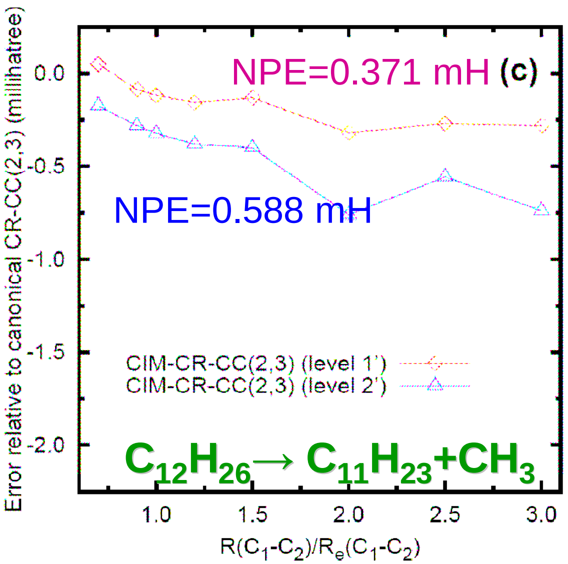
[W. Li, P. Piecuch, and J.R. Gour, AIP Proceedings, 2009; W. Li, P. Piecuch, J.R. Gour, and S. Li, J. Chem. Phys., 2009; W. Li, P. Piecuch, and J.R. Gour, Prog. Theor. Chem. Phys., 2009; W. Li and P. Piecuch, J. Phys. Chem. A, 2010 (x2)]

C_nH_{2n+2}, 6-31G(d)

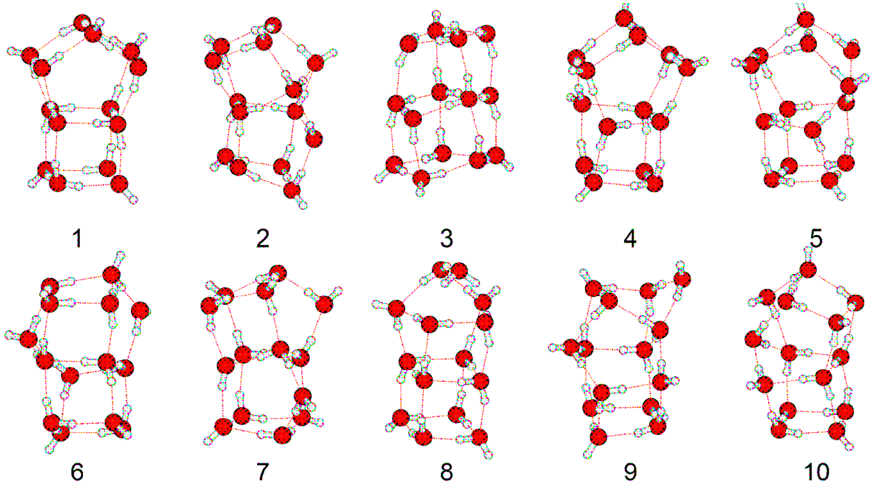


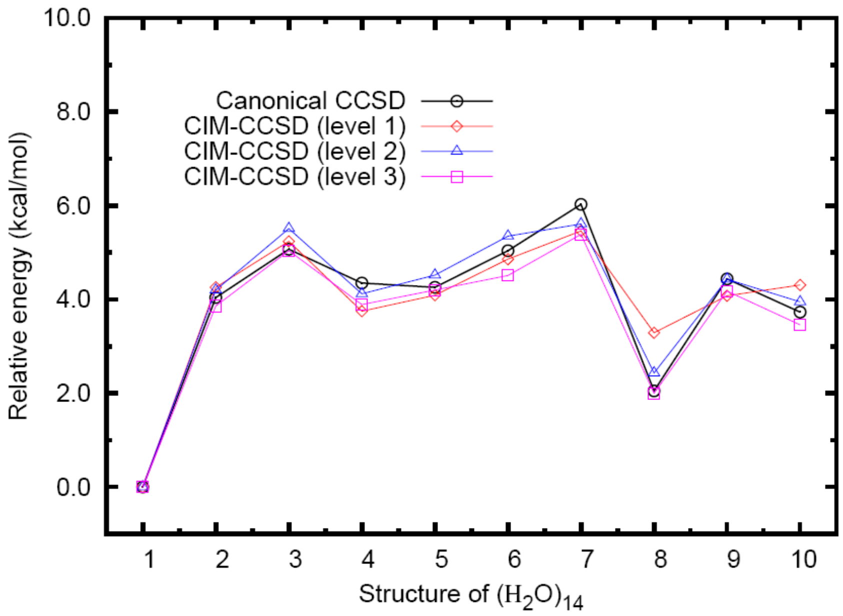






$(H_2O)_{14}$





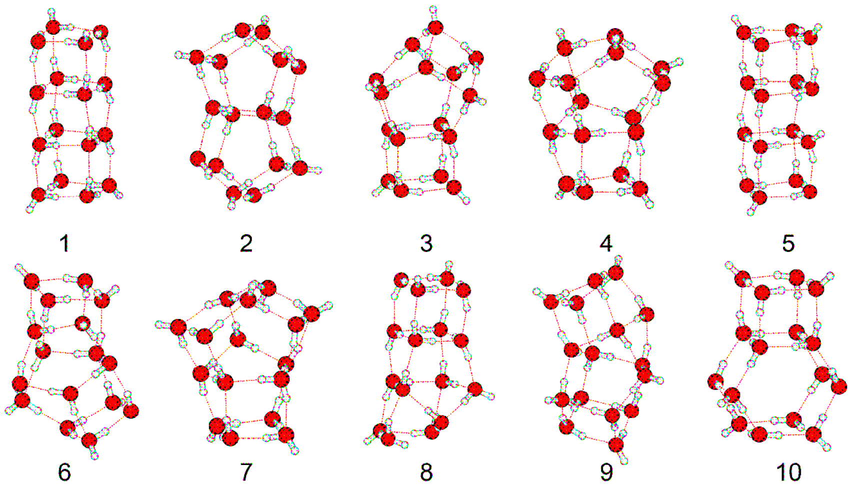
Canonical CCSD: 1758-1870 min

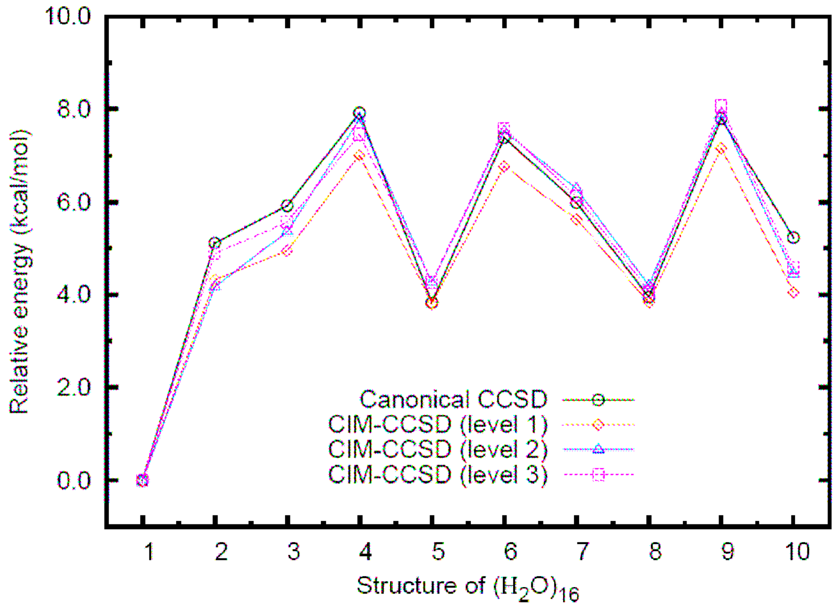
CIM CCSD level 1: 30-70 min; 2-9 min/subsystem

CIM CCSD level 2: 54-153 min; 5-17 min/subsystem

CIM CCSD level 3: 204-474 min; 21-89 min/subsystem

$(H_2O)_{16}$



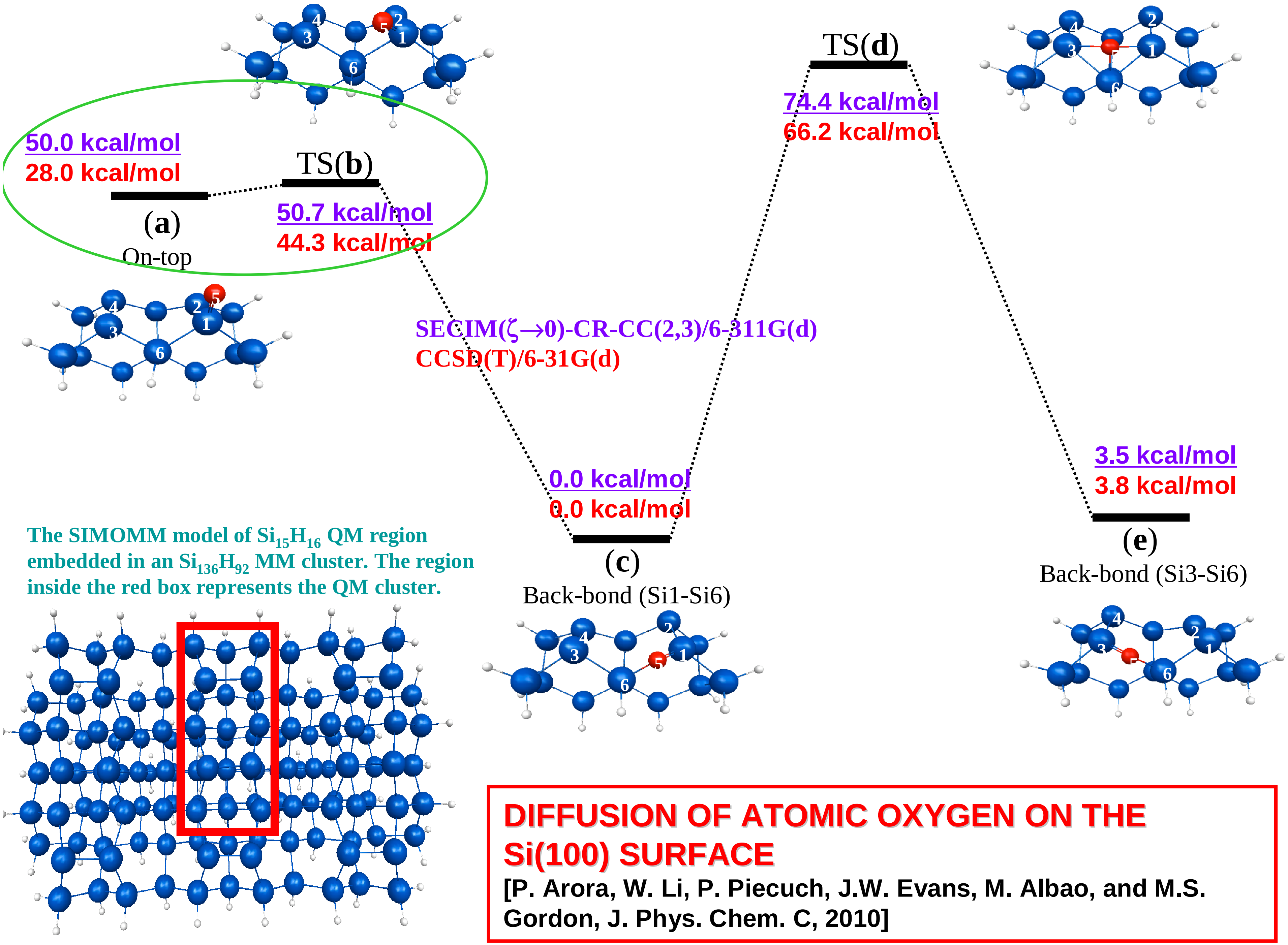


Canonical CCSD: 4045-4265 min

CIM CCSD level 1: 45-99 min; 3-10 min/subsystem

CIM CCSD level 2: 74-229 min; 5-19 min/subsystem

CIM CCSD level 3: 324-724 min; 28-67 min/subsystem



SECIM(ζ→0)-CR-CC(2,3)/6-311G(d)

CCSD(T)/6-31G(d)

The SIMOMM model of $Si_{15}H_{16}$ QM region embedded in an $Si_{136}H_{92}$ 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. Albao, and M.S. Gordon, J. Phys. Chem. C, 2010]

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)

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

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

Example: EOMCC

In the exact theory,

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

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

In approximate methods,

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

Basic approximation: EOMCCSD

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

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

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

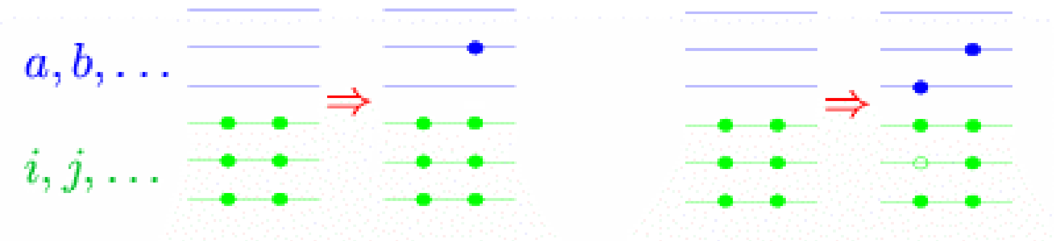
Higher-order iterative methods: EOMCCSDT, EOMCCSDTQ, etc., or non-iterative corrections, such as CR-EOMCCSD(T), CR-EOMCC(2,3), etc.

Particle (Electron) Attached and Particle Removed (Ionized) EOMCC Methods

$$|\Psi_\mu^{(N\pm1)}\rangle = R_\mu^{(N\pm1)}|\Psi_0\rangle, \quad R_\mu^{(N+1)} = \sum_{n=0}^{M_R} R_{\mu,(n+1)p-nh}, \quad R_\mu^{(N-1)} = \sum_{n=0}^{M_R} R_{\mu,(n+1)h-np}$$

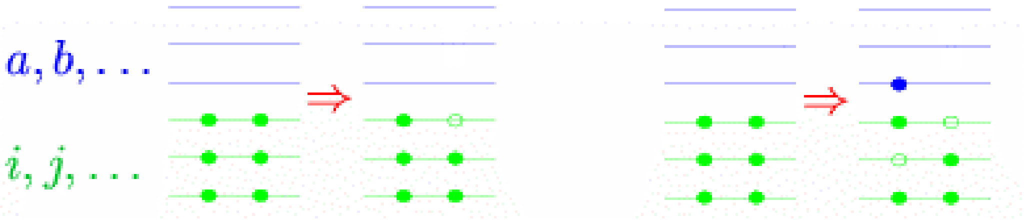
Particle Attaching (EA or PA)

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



Particle Removing (IP or PR)

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

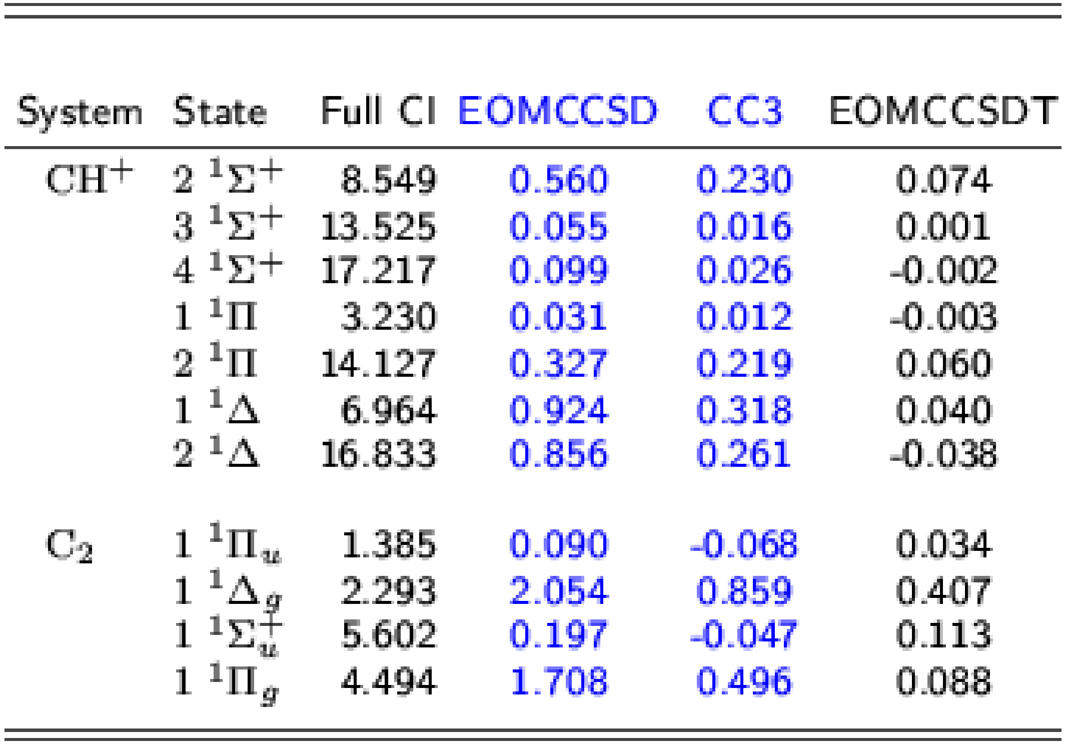


Solve the Eigenvalue Problem

$$(\bar{H}_{N,\text{open}}\, R_\mu^{(N\pm1)})_C|\Phi\rangle = \omega_\mu^{(N\pm1)} R_\mu^{(N\pm1)}|\Phi\rangle,$$

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

Vertical excitation energies of CH^+ and C_2 (in eV) [K. Kowalski and P. Piecuch, 2001, 2002]



System	State	Full CI	EOMCCSD	CC3	EOMCCSDT
CH^+	$2\ {}^1\Sigma^+$	8.549	0.560	0.230	0.074
	$3\ {}^1\Sigma^+$	13.525	0.055	0.016	0.001
	$4\ {}^1\Sigma^+$	17.217	0.099	0.026	-0.002
	$1\ {}^1\Pi$	3.230	0.031	0.012	-0.003
	$2\ {}^1\Pi$	14.127	0.327	0.219	0.060
	$1\ {}^1\Delta$	6.964	0.924	0.318	0.040
	$2\ {}^1\Delta$	16.833	0.856	0.261	-0.038
C_2	$1\ {}^1\Pi_u$	1.385	0.090	-0.068	0.034
	$1\ {}^1\Delta_g$	2.293	2.054	0.859	0.407
	$1\ {}^1\Sigma_u^+$	5.602	0.197	-0.047	0.113
	$1\ {}^1\Pi_g$	4.494	1.708	0.496	0.088

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

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

Excited states of ozone: adiabatic excitation energies T_e (T_0)

State	EOMCCSD	CR-EOMCCSD(T)	MRDCI	CASPT2	Expt.
$2\,^1A_1^\alpha$	10.018 (9.951)	3.649 (3.582)	2.50		3.45–4.02 Huggins band
$2\,^1A_1^\beta$	9.500 (9.433)	4.437 (4.370)	3.61		
$1\,^1B_2$	4.871	4.520	4.34	3.87 (3.84)	4.13–6.20 Hartley band
$1\,^1B_1$	2.288	2.174	1.82	1.67 (1.65)	1.46–2.82, 2.05 Chappuis band
$1\,^1A_2$	1.668 (1.598)	1.615 (1.545)	1.44	1.20 (1.10)	1.46–2.82, 1.58 Chappuis band

(K. Kowalski and P. Piecuch, J. Chem. Phys., 2004)

Properties (including density matrices)

$$|\Psi_K\rangle = R_K e^T|\Phi\rangle$$

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

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

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

$$\langle\Psi_K| = \langle\Phi|L_K e^{-T}$$

$$\langle\Phi|L_K\, R_{K'}|\Phi\rangle = \delta_{K,K'}$$

$$L_K = \delta_{K,0} + L_{K,\mathrm{open}}, \quad L_{K,\mathrm{open}} = L_{K,1} + L_{K,2} + \cdots$$

$$\boxed{\langle\Phi|L_K \bar{H}_{N,\mathrm{open}} = \omega_K \langle\Phi|L_K}$$

For the ground $(K = 0)$ state, $|\Psi_0\rangle = e^T|\Phi\rangle$, $\langle\Psi_0| = \langle\Phi|(1+\Lambda)e^{-T}$

$$\bar{H}_N|\Phi\rangle = \Delta E_0|\Phi\rangle, \quad \langle\Phi|(1+\Lambda)\,\bar{H}_N = \Delta E_0\langle\Phi|(1+\Lambda)$$

Expectation values, transition matrix elements

$$\langle \Psi_K | \Theta | \Psi_{K'} \rangle = \langle \Phi | L_K \bar{\Theta} R_{K'} | \Phi \rangle,$$

$$\bar{\Theta} = e^{-T} \Theta e^{T} = (\Theta e^{T})_C$$

1-RDMs

$$\gamma_q^p(K, K') \equiv \langle \Psi_K | a^p a_q | \Psi_{K'} \rangle = \langle \Phi | L_K \overline{a^p a_q} R_{K'} | \Phi \rangle,$$

$$\overline{a^p a_q} = e^{-T} a^p a_q \, e^{T}$$

2-RDMs

$$\gamma_{rs}^{pq}(K, K') \equiv \langle \Psi_K | a^p a^q a_s a_r | \Psi_{K'} \rangle = \langle \Phi | L_K \overline{a^p a^q a_s a_r} R_{K'} | \Phi \rangle,$$

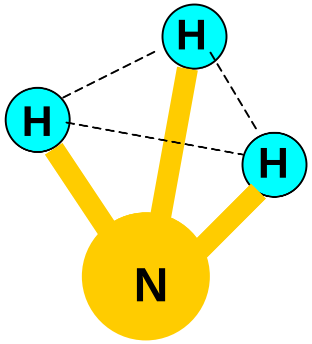
$$\overline{a^p a^q a_s a_r} = e^{-T} (a^p a^q a_s a_r) \, e^{T}$$

For example,

$$\langle \Psi_K | \Theta | \Psi_{K'} \rangle = \theta_p^q \, \gamma_q^p(K, K'), \quad \Theta = \theta_p^q a^p a_q$$

$$\gamma_K(\mathbf{x}|\mathbf{x}') = \sum_{p,q} \gamma_p^q(K, K) [\psi_p(\mathbf{x})]^* \psi_q(\mathbf{x}')$$

Dipole Moment Function of Ammonia

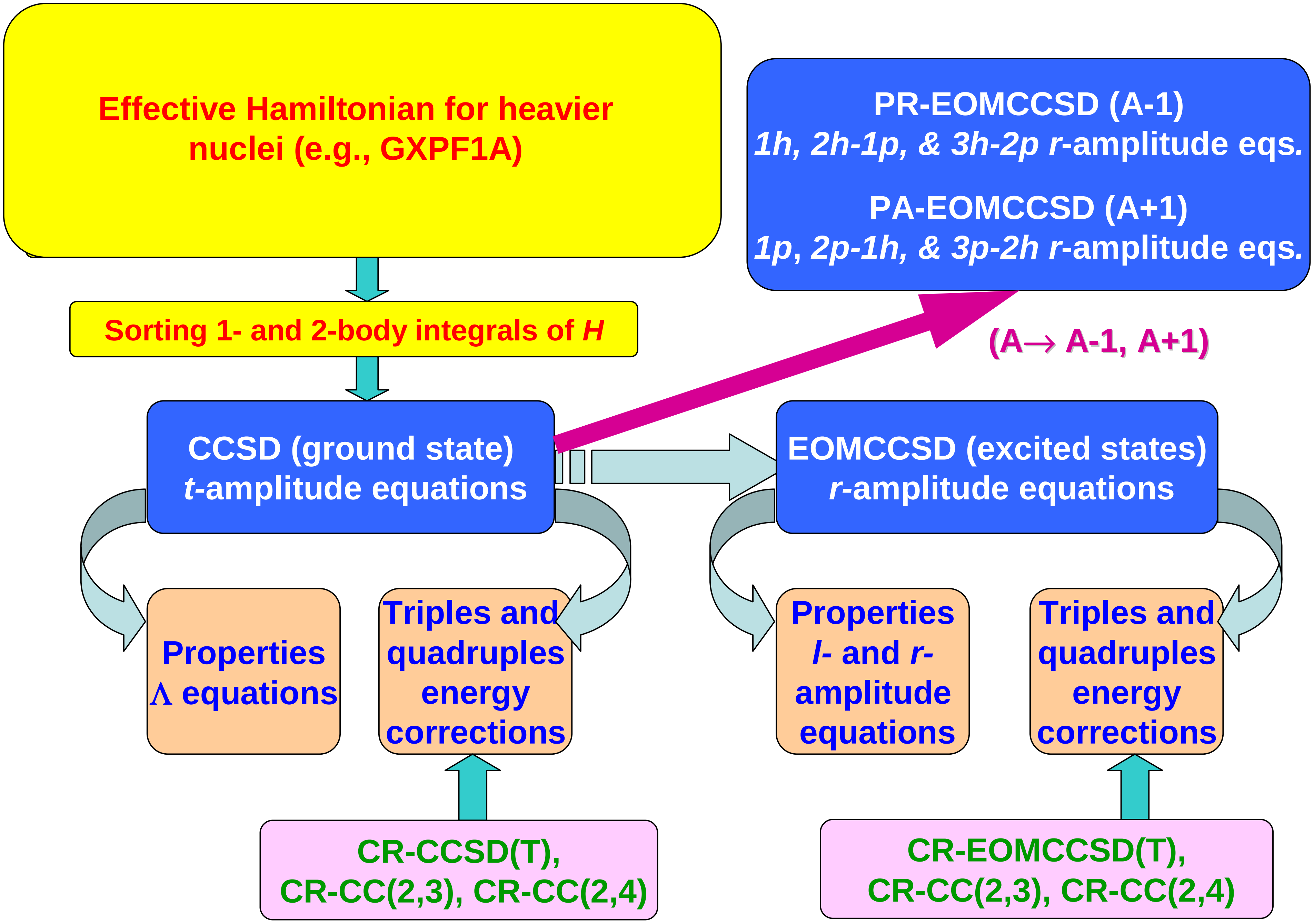


μ
(D

[From P. Piecuch, V. Špirko, and J. Paldus, Pol. J. Chem. **72** (7S), 1635 (1998)]

The vibrational transition moments $\langle v_2''; 0, 0 | \hat{\mu}_z | v_2'; 0, 0 \rangle$ of $^{14}NH_3$ (in Debye).

v_2''	v_2'	Exp.	CISD	CASSCF^c	Fit I	CCSD	LRCCSD – Fit I
0^+	0^-	1.47147(6)	1.536	1.653	1.471	1.473	0.002
0^+	1^-	0.236(4)	0.258	0.236	0.237	0.245	0.008
0^+	2^-	0.011	0.007	0.002	0.000	0.004	0.004
0^-	1^+	0.248(7)	0.269	0.239	0.247	0.254	0.007
0^-	2^+	0.02261(21)	0.027	0.006	0.019	0.024	0.005
1^+	2^-	0.285(10)	0.313	0.335	0.287	0.296	0.009
1^-	2^+		0.557	0.442	0.525	0.532	0.007
2^+	2^-	1.02(18)	0.995	1.122	0.948	0.954	0.006



Effective Hamiltonian for heavier nuclei (e.g., GXPF1A)

Sorting 1- and 2-body integrals of *H*

CCSD (ground state)
***t*-amplitude equations**

Properties
Λ equations

Triples and quadruples energy corrections

CR-CCSD(T), CR-CC(2,3), CR-CC(2,4)

PR-EOMCCSD (A-1)
***1h, 2h-1p, & 3h-2p r*-amplitude eqs.**

PA-EOMCCSD (A+1)
***1p*, *2p-1h, & 3p-2h r*-amplitude eqs.**

(A→ A-1, A+1)

EOMCCSD (excited states)
***r*-amplitude equations**

Properties
***l*- and *r*-amplitude equations**

Triples and quadruples energy corrections

CR-EOMCCSD(T), CR-CC(2,3), CR-CC(2,4)

Comparison of Shell Model and Coupled-Cluster Results for the Total Binding Energies of ^{4}He and ^{16}O (Argonne $V_{8'}$)

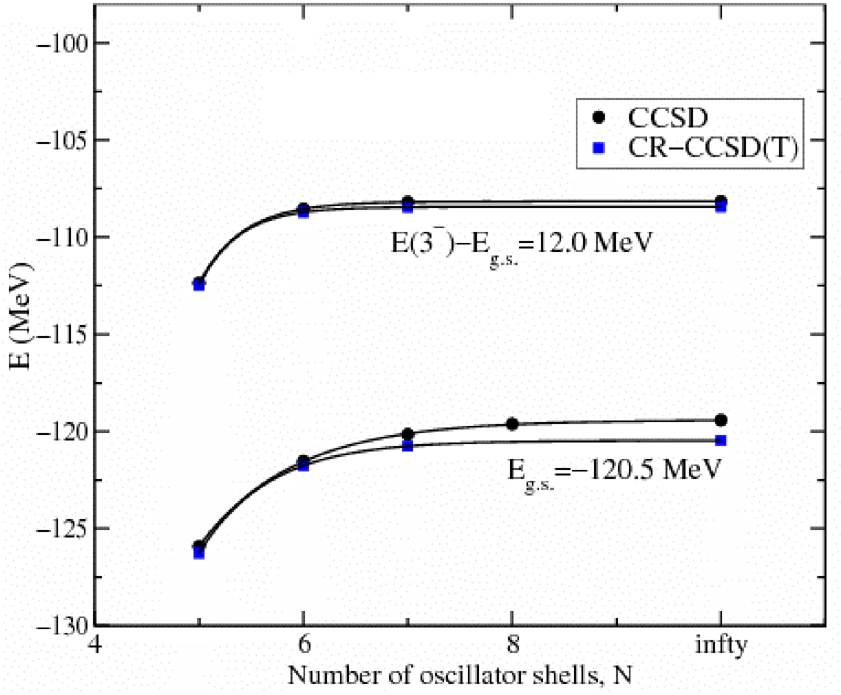
(M. Włoch, P. Piecuch, M. Horoi, M. Hjorth-Jensen, unpublished)

^{4}He		$\hbar\Omega = 10$	$\hbar\Omega = 15$	$\hbar\Omega = 20$	$\hbar\Omega = 25$	$\hbar\Omega = 30$
4 MS	Shell Model^a	-24.894	-28.207	-28.164	-27.170	-25.869
	CCSD	-24.606	-28.027	-28.033	-26.917	-25.308
	CR-CCSD(T)$_{\mathcal{L}}$	-24.822	-28.156	-28.118	-27.101	-25.766
5 MS	Shell Model^a	-26.484	-28.336	-27.228	-25.900	-24.702
	CCSD	-26.156	-28.101	-27.015	-25.439	-23.738
	CR-CCSD(T)$_{\mathcal{L}}$	-26.365	-28.272	-27.175	-25.817	-24.602
6 MS	Shell Model^a	-26.604	-27.526	-26.189	-25.053	-24.147
	CCSD	-25.860	-27.195	-25.903	-24.380	-22.755
CR-CC(2,3)⇨	CR-CCSD(T)$_{\mathcal{L}}$	-26.396	-27.460	-26.134	-24.967	-24.077
7 MS	Shell Model^a			-25.180		
	CCSD	-25.833	-26.256	-24.802	-23.385	-21.857
	CR-CCSD(T)$_{\mathcal{L}}$	-26.447	-26.574	-25.147	-24.261	-23.762

^{16}O		$\hbar\Omega = 10$	$\hbar\Omega = 14$	$\hbar\Omega = 16$	$\hbar\Omega = 18$	$\hbar\Omega = 20$
4 MS	Shell Model^a	-143.5	-165.5	-165.5	-161.5	-153.7
	CCSD	-144.448	-165.841	-165.67	-160.785	-152.87
	CR-CCSD(T)$_{\mathcal{L}}$	-143.502	-165.106	-165.211	-160.744	-153.406
5 MS	Shell Model^a	-132	-150.5	-149.6	-143	-136
	CCSD	-137.950	-151.909	-148.607	-141.997	-133.338
	CR-CCSD(T)$_{\mathcal{L}}$	-138.107	-152.507	-149.626	-143.609	-136.338
6 MS	Shell Model^a	-129	-142	-138.5	-134	-126
	CCSD	-150.582	-148.854	-139.943	-130.949	-122.801
	CR-CCSD(T)$_{\mathcal{L}}$	-149.329	-149.42	-141.591	-133.716	-126.716

The coupled-cluster approach accurately reproduces the very expensive full shell model results at a fraction of a cost.

Ground and Excited States of ^{16}O (Idaho-A, N^{3}LO, G-matrix)



M. Włoch, D.J. Dean, J.R. Gour, M. Hjorth-Jensen, K. Kowalski, T. Papenbrock, and P. Piecuch, Phys. Rev. Lett., 2005.

Ground State

Idaho-A Binding Energy, No Coulomb: -7.46 MeV/nucleon (CCSD), -7.53 MeV/nucleon (CR-CCSD(T))

Approx. Coulomb: +0.7 MeV/nucleon

Idaho-A + Approx. Coulomb: -6.8 MeV/nucleon

N^{3}LO (with Coulomb): -7.0 MeV/nucleon

Experiment: -8.0 MeV/nucleon (approx. -1 MeV due to three-body interations and, perhaps, remaining center-of-mass contaminations)

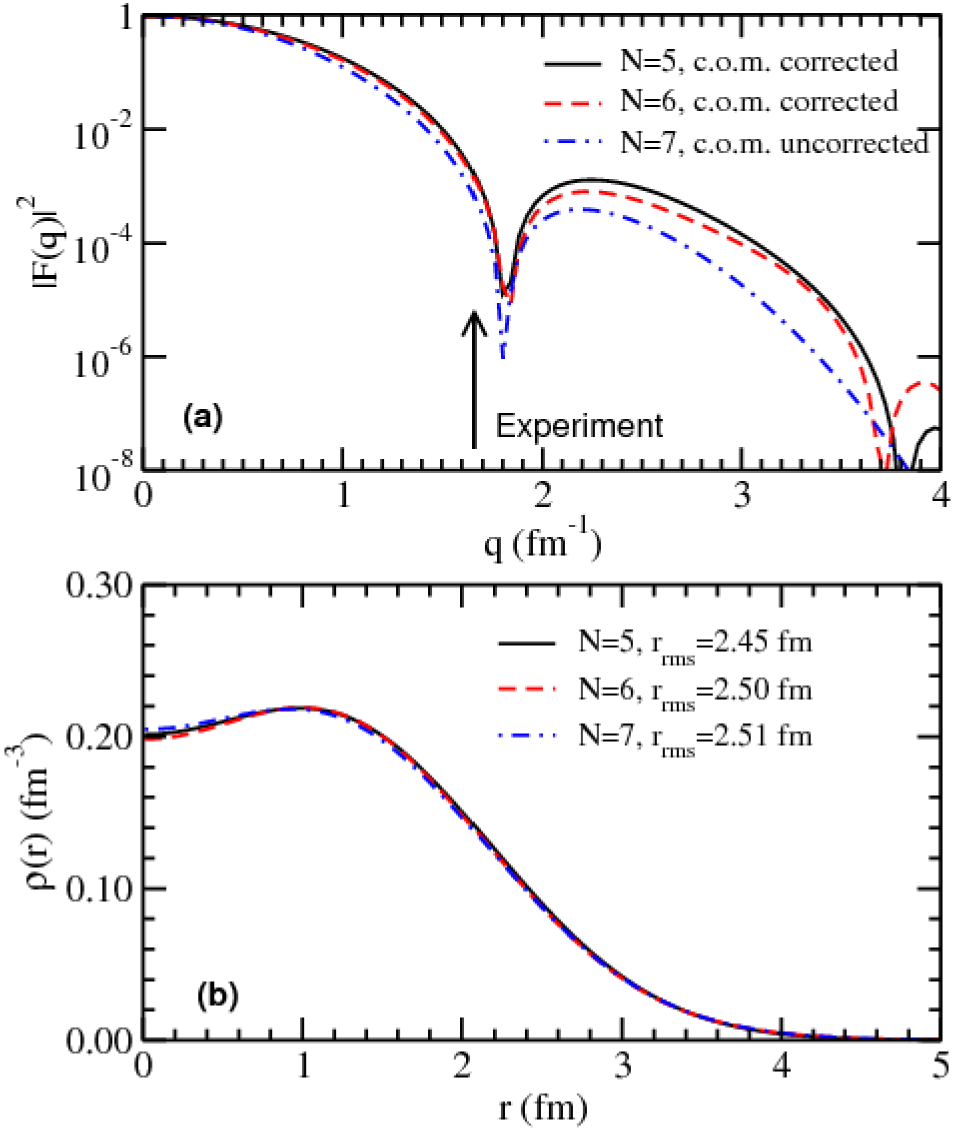
J=3- Excited State

Idaho-A Excitation Energy: 11.3 MeV (EOMCCSD)
12.0 MeV (CR-EOMCCSD(T))

Experiment: 6.12 MeV (5-6 MeV difference due to three-body interactions and, to some extent, remaining center-of-mass contaminations)

Ground-state properties of ^{16}O, Idaho-A

Form factor



M. Włoch, D.J. Dean, J.R. Gour, M. Hjorth-Jensen, K. Kowalski, T. Papenbrock, and P. Piecuch, Phys. Rev. Lett., 2005.

Exp.: 2.73±0.025 fm

CCSD: 2.51 fm

Ground and Excited States of Valence Nuclei Around ^{16}O with Various Potentials

(J.R. Gour, P. Piecuch, M. Hjorth-Jensen, M. Włoch, and D.J. Dean, Phys. Rev. C, 2006)

Binding Energy per Nucleon (MeV)

	Interaction			
Nucleus	N3LO	CD-Bonn	V_{18}	Expt
^{15}O	6.158	6.643	4.789	7.464
^{15}N	6.339	6.810	4.957	7.699
^{16}O	6.951	7.444	5.469	7.976
^{17}O	6.722	7.201	5.214	7.751
^{17}F	6.559	7.048	5.059	7.542

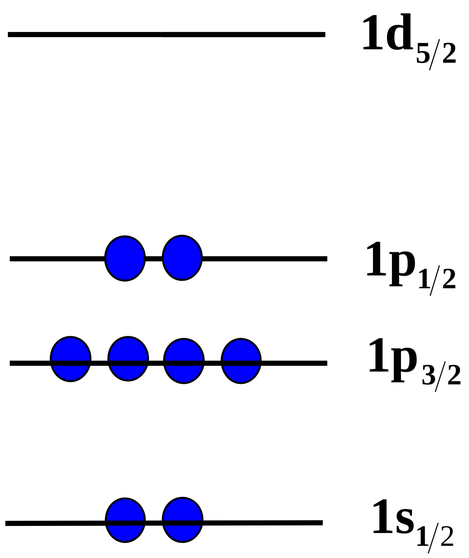
Excitation Energies (MeV)

	Interaction			
Excited state	N3LO	CD-Bonn	V_{18}	Expt
^{15}O $(3/2)^-_1$	6.264	7.351	4.452	6.176
^{15}N $(3/2)^-_1$	6.318	7.443	4.499	6.323
^{17}O $(3/2)^+_1$	5.675	6.406	3.946	5.084
^{17}O $(1/2)^+_1$	-0.025	0.311	-0.390	0.870
^{17}F $(3/2)^+_1$	5.891	6.677	4.163	5.000
^{17}F $(1/2)^+_1$	0.428	0.805	0.062	0.495

- The non-local N^{3}LO and CD-Bonn interactions give much stronger binding than the local Argonne V_{18} interaction.
- The different binding energies and spin-orbit splittings indicate that different potentials require different 3-body interactions. Excitation energies of the A=15 systems obtained with N^{3}LO are excellent.
- The relative binding energies of these nuclei for the various potentials are in good agreement with each other and with experiment.

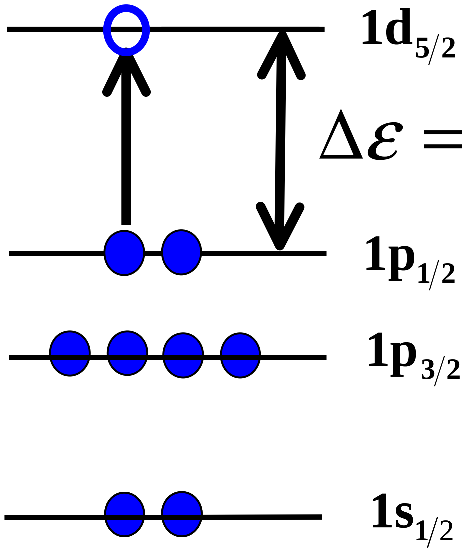
Return to 3^- state of ^{16}O

(J.R. Gour, P. Piecuch, M. Hjorth-Jensen, M. Włoch, and D.J. Dean, Phys. Rev. C, 2006)



Return to 3$^-$ state of ^{16}O

(J.R. Gour, P. Piecuch, M. Hjorth-Jensen, M. Włoch, and D.J. Dean, Phys. Rev. C, 2006)

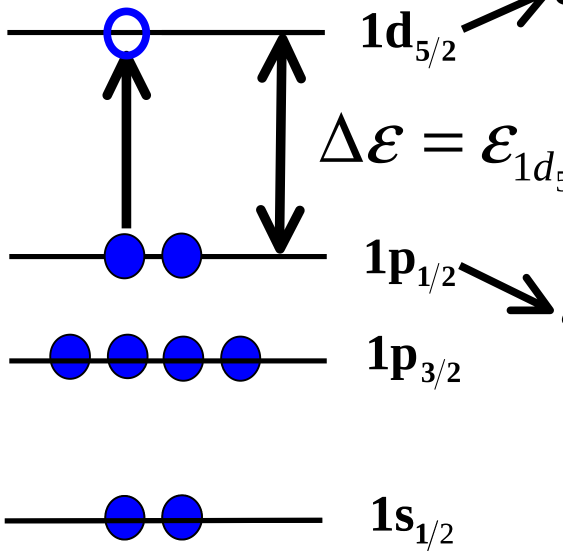


$$\Delta\varepsilon = \varepsilon_{1d_{5/2}} - \varepsilon_{1p_{1/2}} \approx E(3^-) - E(g.s.)$$

- The 3$^-$ state is dominated by a single excitation from the1p$_{1/2}$ level to the 1d$_{5/2}$ level. Thus, the energy difference between these shells gives a zero-order estimate of the excitation energy of the 3$^-$ state.

Return to 3^- state of ^{16}O

(J.R. Gour, P. Piecuch, M. Hjorth-Jensen, M. Włoch, and D.J. Dean, Phys. Rev. C, 2006)



$$\varepsilon_{1\mathrm{d}_{5/2}} = \mathrm{BE}(^{16}\mathrm{O}) - \mathrm{BE}(^{17}\mathrm{O})$$

$$\Delta\varepsilon = \varepsilon_{1d_{5/2}} - \varepsilon_{1p_{1/2}} \approx E(3^-) - E(g.s.)$$

$$\varepsilon_{1\mathrm{p}_{1/2}} = \mathrm{BE}(^{16}\mathrm{O}) - \mathrm{BE}(^{15}\mathrm{O})$$

- The 3^- state is dominated by a single excitation from the $1p_{1/2}$ level to the $1d_{5/2}$ level. Thus, the energy difference between these shells gives a zero-order estimate of the excitation energy of the 3^- state.
- Using the experimental and CC binding energies of the valence systems around ^{16}O to determine this energy gap gives 11.5 and 15.8 MeV, respectively.

Inclusion of NNN interactions: ^{4}He (proof-of-principle)

(G. Hagen, T. Papenbrock, D.J. Dean, A. Schwenk, A. Nogga, M. Włoch, and P. Piecuch, Phys. Rev. C, 2007)

$$H = T + V_{\text{low}\,k}(\Lambda) + V_{3\text{N}}(\Lambda)$$

(derived from Argonne V_{18})

(based on the leading chiral 3NF)

$$\hat{H}_3 = \frac{1}{36} \sum_{pqrstu} \langle pqr||stu\rangle \hat{a}^\dagger_p \hat{a}^\dagger_q \hat{a}^\dagger_r \hat{a}_u \hat{a}_t \hat{a}_s$$

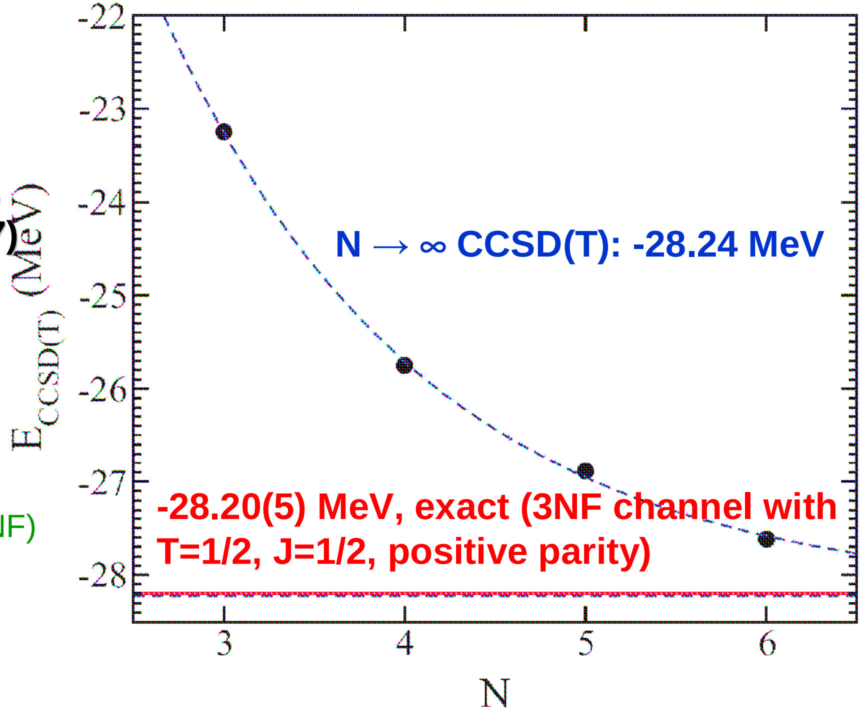
0-body 3NF **1-body 3NF**

$$\hat{H}_3 = \frac{1}{6} \sum_{ijk} \langle ijk||ijk\rangle + \frac{1}{2} \sum_{ijpq} \langle ijp||ijq\rangle \{\hat{a}^\dagger_p \hat{a}_q\}$$

$$+ \frac{1}{4} \sum_{ipqrs} \langle ipq||irs\rangle \{\hat{a}^\dagger_p \hat{a}^\dagger_q \hat{a}_s \hat{a}_r\} + \hat{h}_3,$$

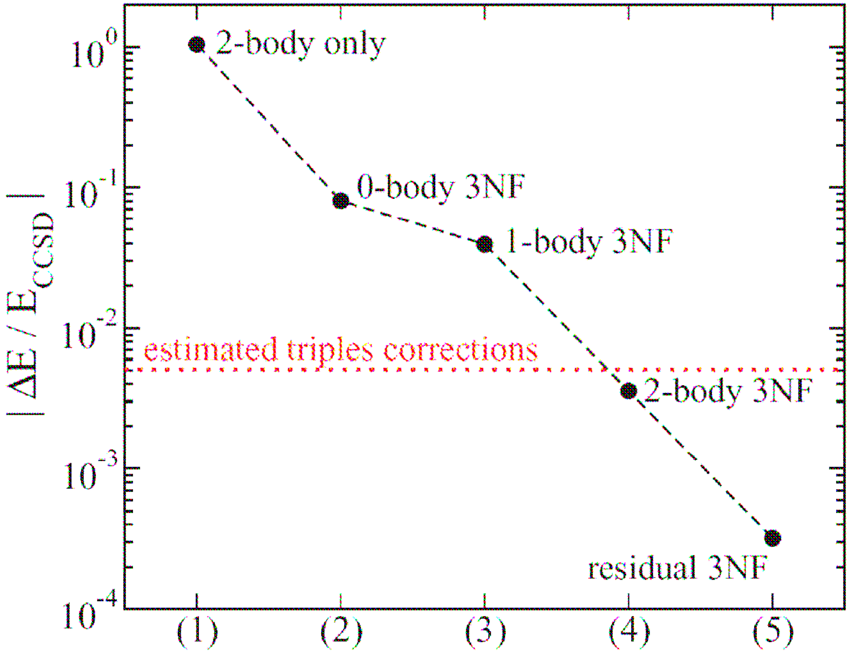
2-body 3NF **residual 3NF**

$$\hat{h}_3 \equiv \frac{1}{36} \sum_{pqrstu} \langle pqr||stu\rangle \{\hat{a}^\dagger_p \hat{a}^\dagger_q \hat{a}^\dagger_r \hat{a}_u \hat{a}_t \hat{a}_s\}$$



N → ∞ CCSD(T): -28.24 MeV

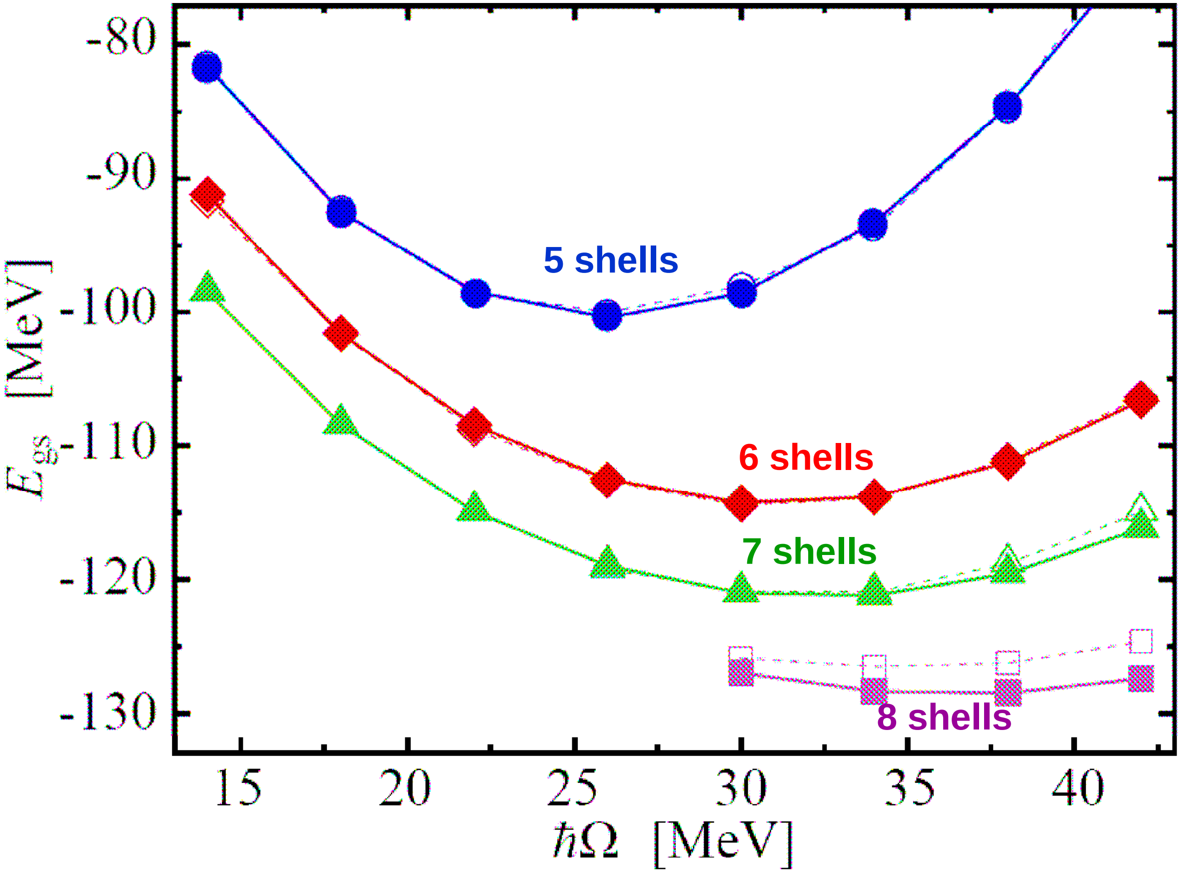
-28.20(5) MeV, exact (3NF channel with T=1/2, J=1/2, positive parity)



Ground State of ^{16}O Using V_{UCOM}

(R. Roth, J.R. Gour, and P. Piecuch, Phys. Rev. C, 2009)

- **Comparison of the CR-CC(2,3) and IT-CI(4p-4h)+MRD results with the Hartree-Fock basis for various model spaces**



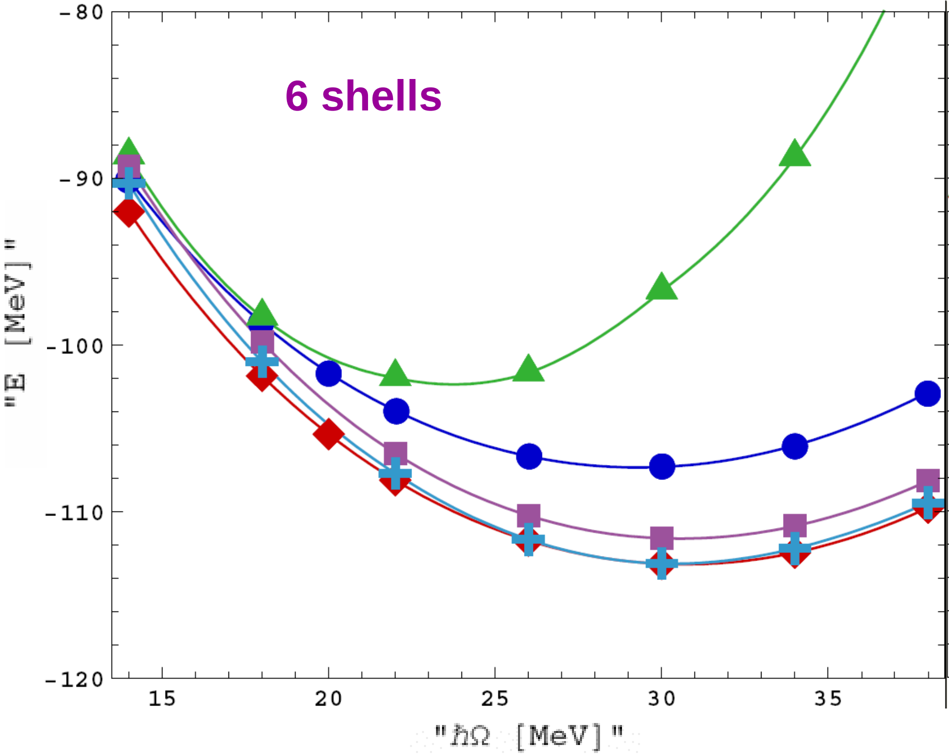
**Open symbols:
IT-CI(4p-4h)+MRD**

**Closed symbols:
CR-CC(2,3)**

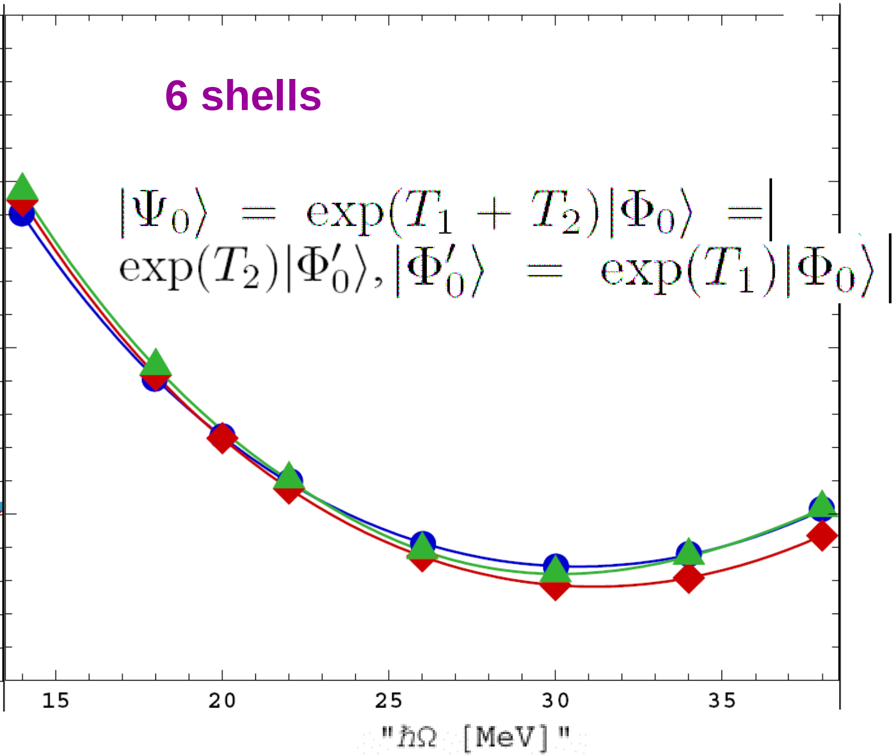
Ground State of ^{16}O Using V_{UCOM}

(R. Roth, J.R. Gour, and P. Piecuch, Phys. Rev. C, 2009)

- **Analysis of the effect of Hartree-Fock vs. harmonic oscillator basis functions with the CC and IT-CI(4p-4h) approaches**



Blue: CCSD – HO
Red: CR-CC(2,3) – HO
Green: IT-CI(4p-4h) – HO
Violet: IT-CI(4p-4h) – HF
Light Blue: IT-CI(4p-4h)+MRD - HF

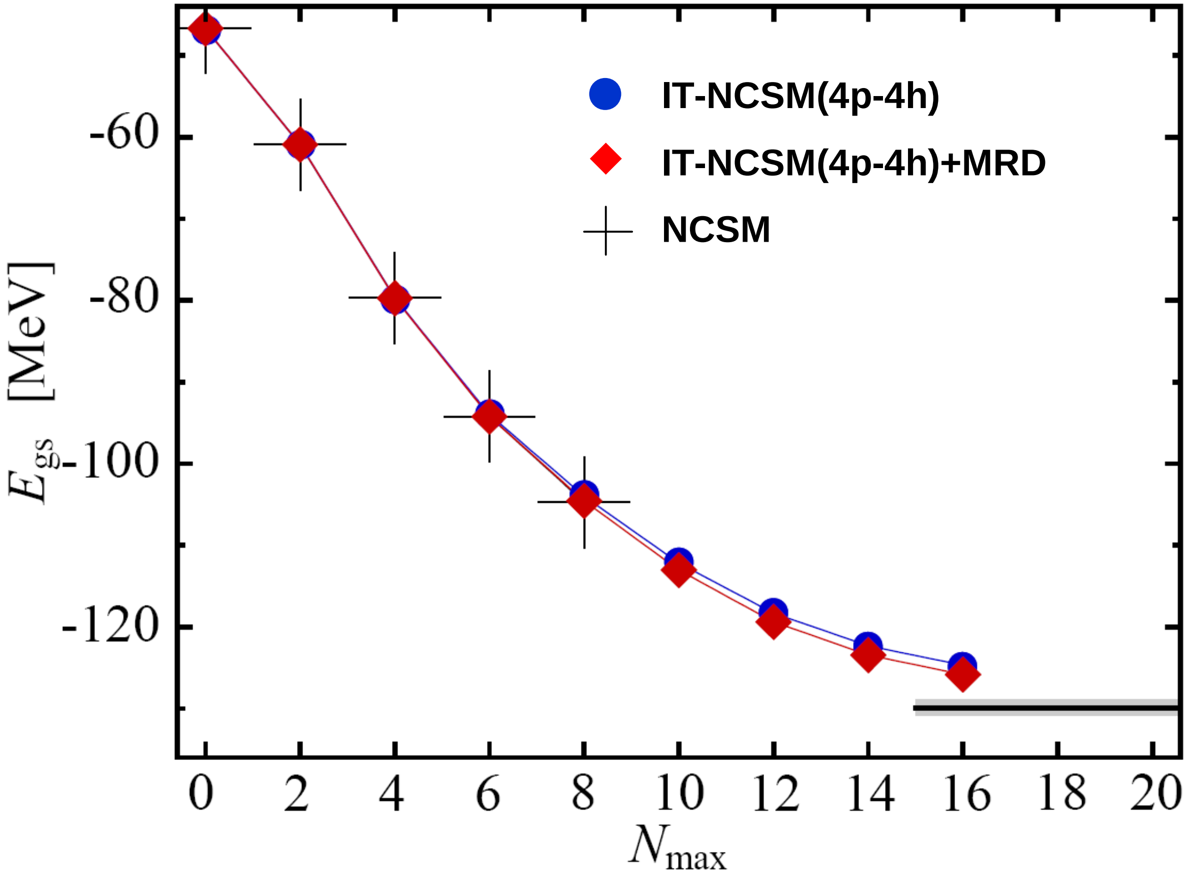


$$|\Psi_0\rangle = \exp(T_1 + T_2)|\Phi_0\rangle = \exp(T_2)|\Phi'_0\rangle, |\Phi'_0\rangle = \exp(T_1)|\Phi_0\rangle$$

Blue: CR-CC(2,3) – HO
Red: CR-CC(2,3) – HF
Green: IT-CI(4p-4h)+MRD – HF

Ground State of ^{16}O Using V_{UCOM}

(R. Roth, J.R. Gour, and P. Piecuch, Phys. Rev. C, 2009)



-130 ± 2 MeV

(8.0-8.25 MeV per nucleon

Experiment: -127.619 MeV. CBS-CR-CC(2,3) rough estimate: (-141) - (-131) MeV

(7.976 MeV per nucleon) **(8.2-8.8 MeV per nucleon)**

Center-of-Mass (CM) Problem in Truncated CC and CI calculations: Ground States of ^{4}He and ^{16}O Using V_{UCOM}

(R. Roth, J.R. Gour, and P. Piecuch, Phys. Lett. B, 2009)

In the exact theory (equivalent to full CI in infinite basis set), the total wave function of the nucleus factorizes,

$$|\Psi\rangle = |\psi_{\mathrm{int}}\rangle \otimes |\psi_{\mathrm{cm}}\rangle$$

The same is true in NCSM calculations, but no longer generally true in truncated CC and CI calculations (even when basis set is infinitely large).

The Lawson prescription for suppressing the CM contaminations

$$H_\beta = H_{\mathrm{int}} + \beta\, H_{\mathrm{cm}}.$$

$$H_{\mathrm{int}} = (T - T_{\mathrm{cm}}) + V = T_{\mathrm{int}} + V\,, \quad T_{\mathrm{int}} = \frac{1}{2mA} \sum_{i<j}^{A} (\mathbf{p}_i - \mathbf{p}_j)^2$$

$$H_{\mathrm{cm}} = \frac{1}{2mA}\mathbf{P}_{\mathrm{cm}}^2 + \frac{mA\Omega^2}{2}\mathbf{X}_{\mathrm{cm}}^2 - \frac{3}{2}\hbar\Omega$$

Some popular beliefs:

- The effect of the CM contaminations varies as 1/A, so the problem is limited to light nuclei.
- CC methods, accounting for higher-order correlation effects beyond a CI model space truncated at the same excitation level via products of cluster operators, have smaller CM contaminations than the analogous CI methods.
- The smallness of the expectation value of H_{cm} for sufficiently large β guarantees the decoupling of the CM and intrinsic degrees of freedom.
- The expectation value of H_{cm} at $\beta=0$ provides a quantitative measure of the impact of CM contamination on intrinsic observables.

Center-of-Mass Diagnostics

(R. Roth, J.R. Gour, and P. Piecuch, Phys. Lett. B, 2009)

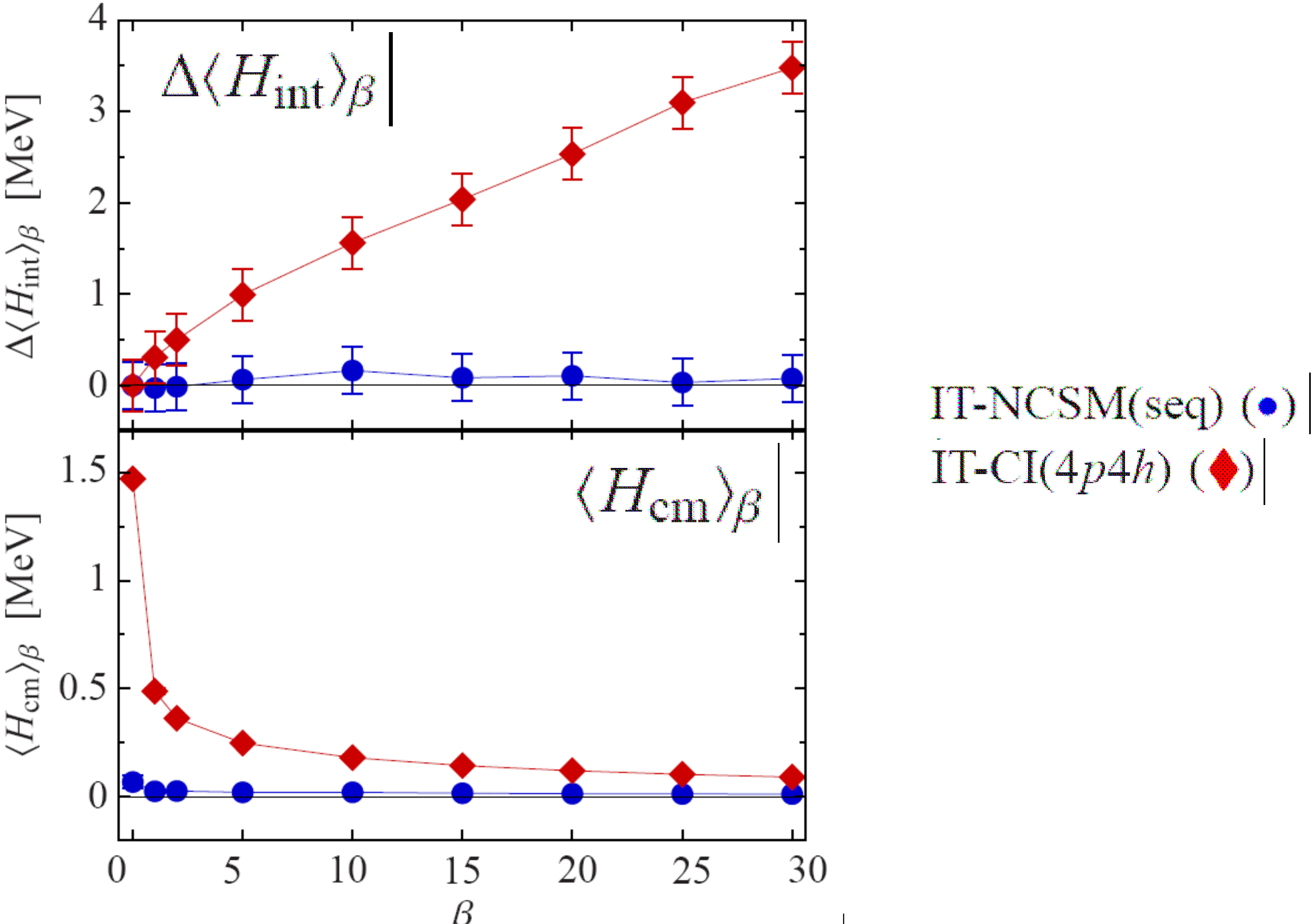
Primary diagnostic: $\Delta\langle H_{\text{int}}\rangle_{\beta} = \langle H_{\text{int}}\rangle_{\beta} - \langle H_{\text{int}}\rangle_{0}$ **, where**
$\langle H_{\text{int}}\rangle_{\beta} = E_{\beta} - \beta\langle H_{\text{cm}}\rangle_{\beta}$
[when the many-body state $|\Psi\rangle$ factorizes, $\Delta\langle H_{\text{int}}\rangle_{\beta} = 0$]

Secondary diagnostic: $\langle H_{\text{cm}}\rangle_{\beta}, \; \beta > 0$
[when the many-body state $|\Psi\rangle$ factorizes, $\langle H_{\text{cm}}\rangle_{\beta}$ vanishes]

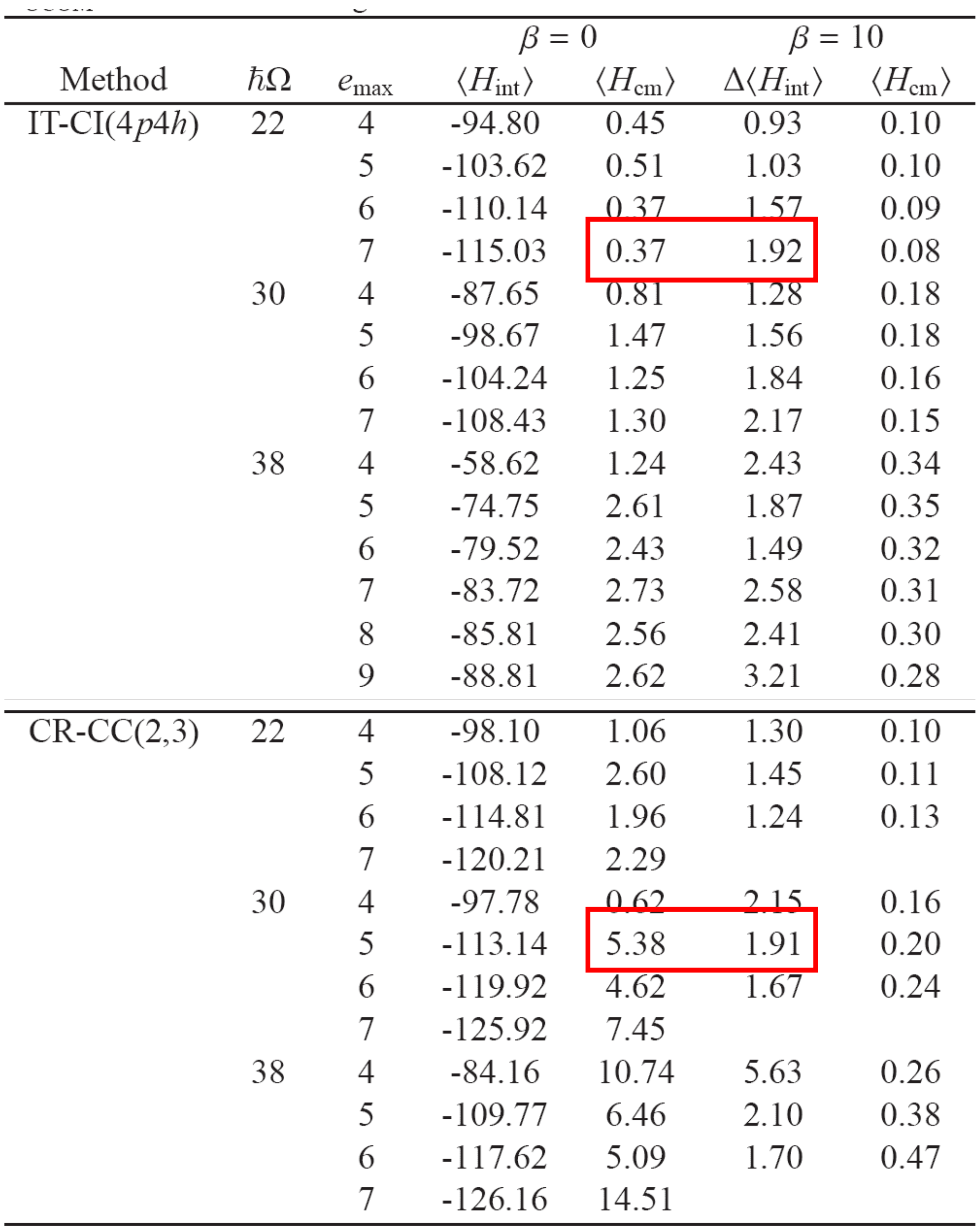
WARNING: $\langle H_{\text{cm}}\rangle_{\beta=0}$ **DOES NOT PROVIDE DEFINITIVE INFORMATION, SINCE IT CAN ASSUME ANY POSITIVE VALUE FOR FACTORIZABLE MANY-BODY STATES**

Example: Ground State of ^{16}O Using V_{UCOM}

(R. Roth, J.R. Gour, and P. Piecuch, Phys. Lett. B, 2009)



Lesson 1: The smallness of $\langle H_{\mathrm{cm}}\rangle_\beta$ is not sufficient to claim that the CM and intrinsic motions decouple.



			$\beta = 0$		$\beta = 10$	
Method	$\hbar\Omega$	$e_{\max}$	$\langle H_{\rm int}\rangle$	$\langle H_{\rm cm}\rangle$	$\Delta\langle H_{\rm int}\rangle$	$\langle H_{\rm cm}\rangle$
IT-CI(4p4h)	22	4	-94.80	0.45	0.93	0.10
		5	-103.62	0.51	1.03	0.10
		6	-110.14	0.37	1.57	0.09
		7	-115.03	0.37	1.92	0.08
	30	4	-87.65	0.81	1.28	0.18
		5	-98.67	1.47	1.56	0.18
		6	-104.24	1.25	1.84	0.16
		7	-108.43	1.30	2.17	0.15
	38	4	-58.62	1.24	2.43	0.34
		5	-74.75	2.61	1.87	0.35
		6	-79.52	2.43	1.49	0.32
		7	-83.72	2.73	2.58	0.31
		8	-85.81	2.56	2.41	0.30
		9	-88.81	2.62	3.21	0.28
CR-CC(2,3)	22	4	-98.10	1.06	1.30	0.10
		5	-108.12	2.60	1.45	0.11
		6	-114.81	1.96	1.24	0.13
		7	-120.21	2.29		
	30	4	-97.78	0.62	2.15	0.16
		5	-113.14	5.38	1.91	0.20
		6	-119.92	4.62	1.67	0.24
		7	-125.92	7.45		
	38	4	-84.16	10.74	5.63	0.26
		5	-109.77	6.46	2.10	0.38
		6	-117.62	5.09	1.70	0.47
		7	-126.16	14.51		

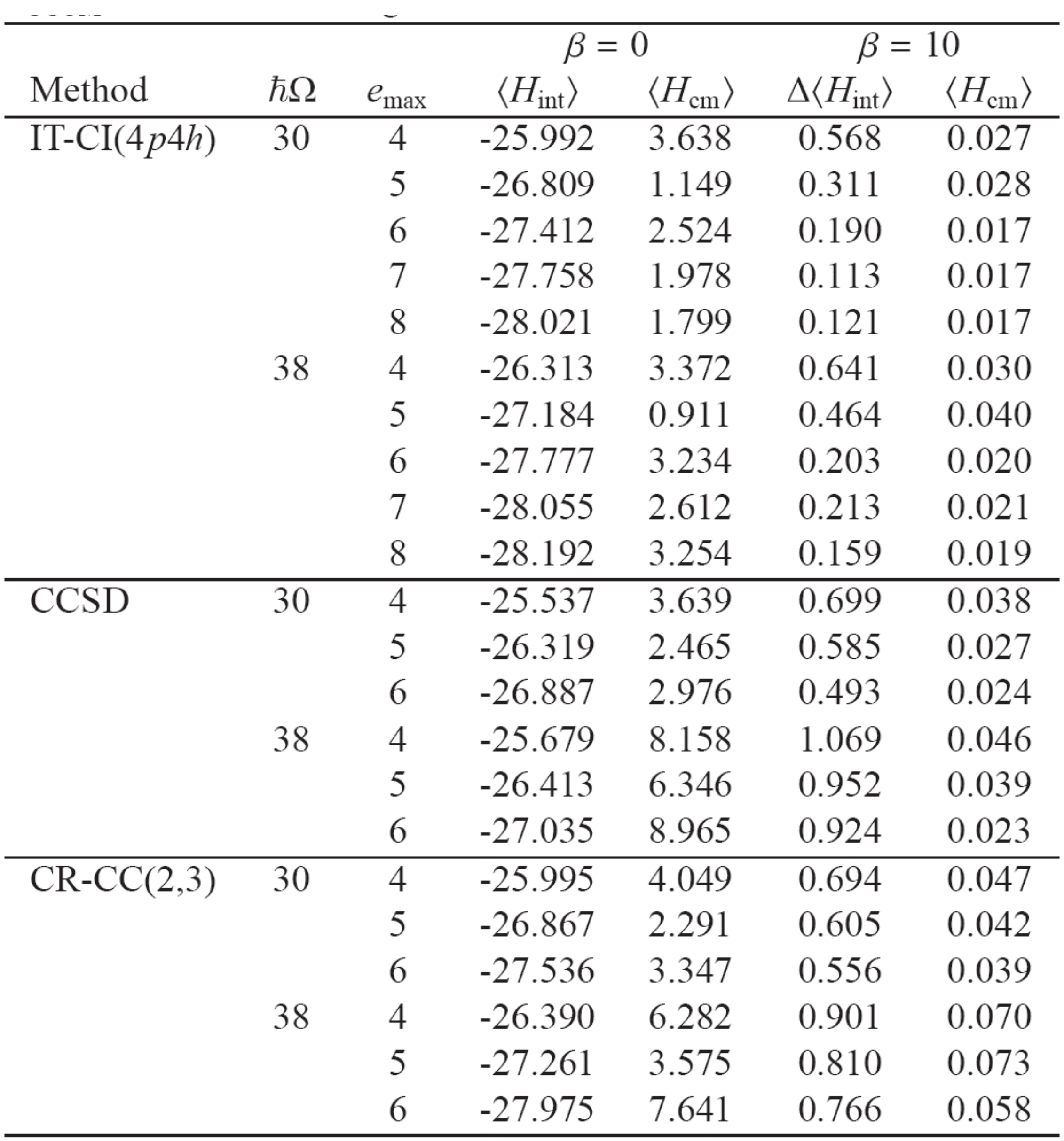
Lesson 2: The value of $\langle H_{\rm cm}\rangle_{\beta=0}$ cannot be used to quantify the degree of CM contaminations.

Lesson 3: The CM contaminations may remain substantial for larger single-particle basis sets.

Lesson 4: The inclusion of higher-order correlation effects via the exponential CC ansatz does not necessarily reduce the CM contaminations compared to the analogous CI calculations.

Example: Ground State of ^{4}He Using V_{UCOM}

(R. Roth, J.R. Gour, and P. Piecuch, Phys. Lett. B, 2009)



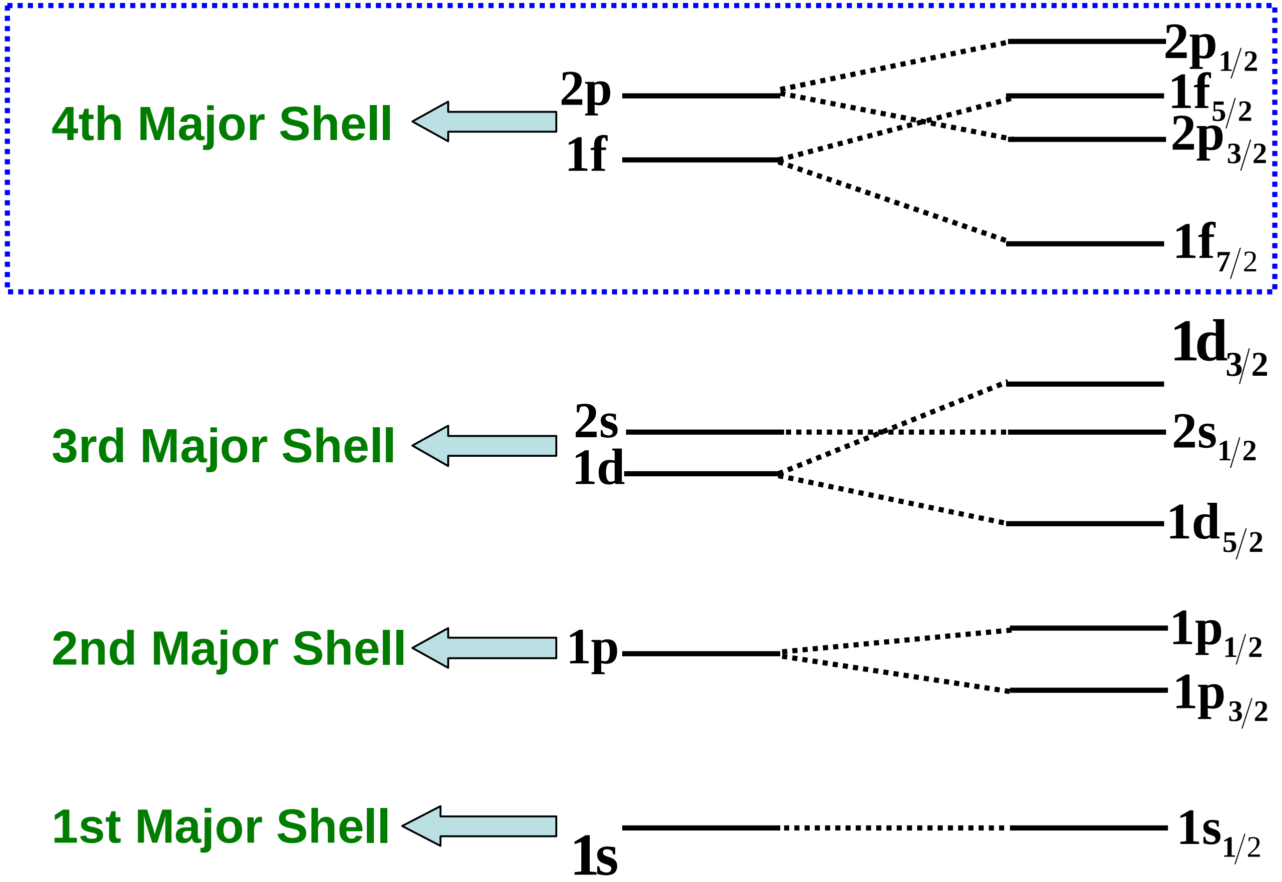
			$\beta = 0$		$\beta = 10$	
Method	$\hbar\Omega$	$e_{\max}$	$\langle H_{\text{int}}\rangle$	$\langle H_{\text{cm}}\rangle$	$\Delta\langle H_{\text{int}}\rangle$	$\langle H_{\text{cm}}\rangle$
IT-CI(4*p*4*h*)	30	4	-25.992	3.638	0.568	0.027
		5	-26.809	1.149	0.311	0.028
		6	-27.412	2.524	0.190	0.017
		7	-27.758	1.978	0.113	0.017
		8	-28.021	1.799	0.121	0.017
	38	4	-26.313	3.372	0.641	0.030
		5	-27.184	0.911	0.464	0.040
		6	-27.777	3.234	0.203	0.020
		7	-28.055	2.612	0.213	0.021
		8	-28.192	3.254	0.159	0.019
CCSD	30	4	-25.537	3.639	0.699	0.038
		5	-26.319	2.465	0.585	0.027
		6	-26.887	2.976	0.493	0.024
	38	4	-25.679	8.158	1.069	0.046
		5	-26.413	6.346	0.952	0.039
		6	-27.035	8.965	0.924	0.023
CR-CC(2,3)	30	4	-25.995	4.049	0.694	0.047
		5	-26.867	2.291	0.605	0.042
		6	-27.536	3.347	0.556	0.039
	38	4	-26.390	6.282	0.901	0.070
		5	-27.261	3.575	0.810	0.073
		6	-27.975	7.641	0.766	0.058

Lesson 5: The popular belief that the CM contaminations are suppressed as 1/A is questionable; other factors, such as the accuracy of a given many-body method relative to full CI may counteract a 1/A scaling

[e.g., for the 4-particle ^{4}He system, the CR-CC(2,3) and IT-CI(4p4h) methods in the limit of an infinite single-particle basis set lead to virtually exact and factorized wave functions in spite of the lightness of ^{4}He; the same approaches are not exact for the heavier ^{16}O, leading to substantial CM contaminations].

Coupled-Cluster Calculations for ^{56}Ni

- The calculations were performed within the *pf* shell, making it possible to perform full CI calculations for comparison



4th Major Shell

2p

1f

$2p_{1/2}$

$1f_{5/2}$

$2p_{3/2}$

$1f_{7/2}$

3rd Major Shell

2s

1d

$1d_{3/2}$

$2s_{1/2}$

$1d_{5/2}$

2nd Major Shell

1p

$1p_{1/2}$

$1p_{3/2}$

1st Major Shell

1s

$1s_{1/2}$

Unoccupied states:

$2p_{3/2}$, $1f_{5/2}$, $2p_{1/2}$

Occupied states:

$1f_{7/2}$

Coupled-Cluster Calculations for ^{56}Ni

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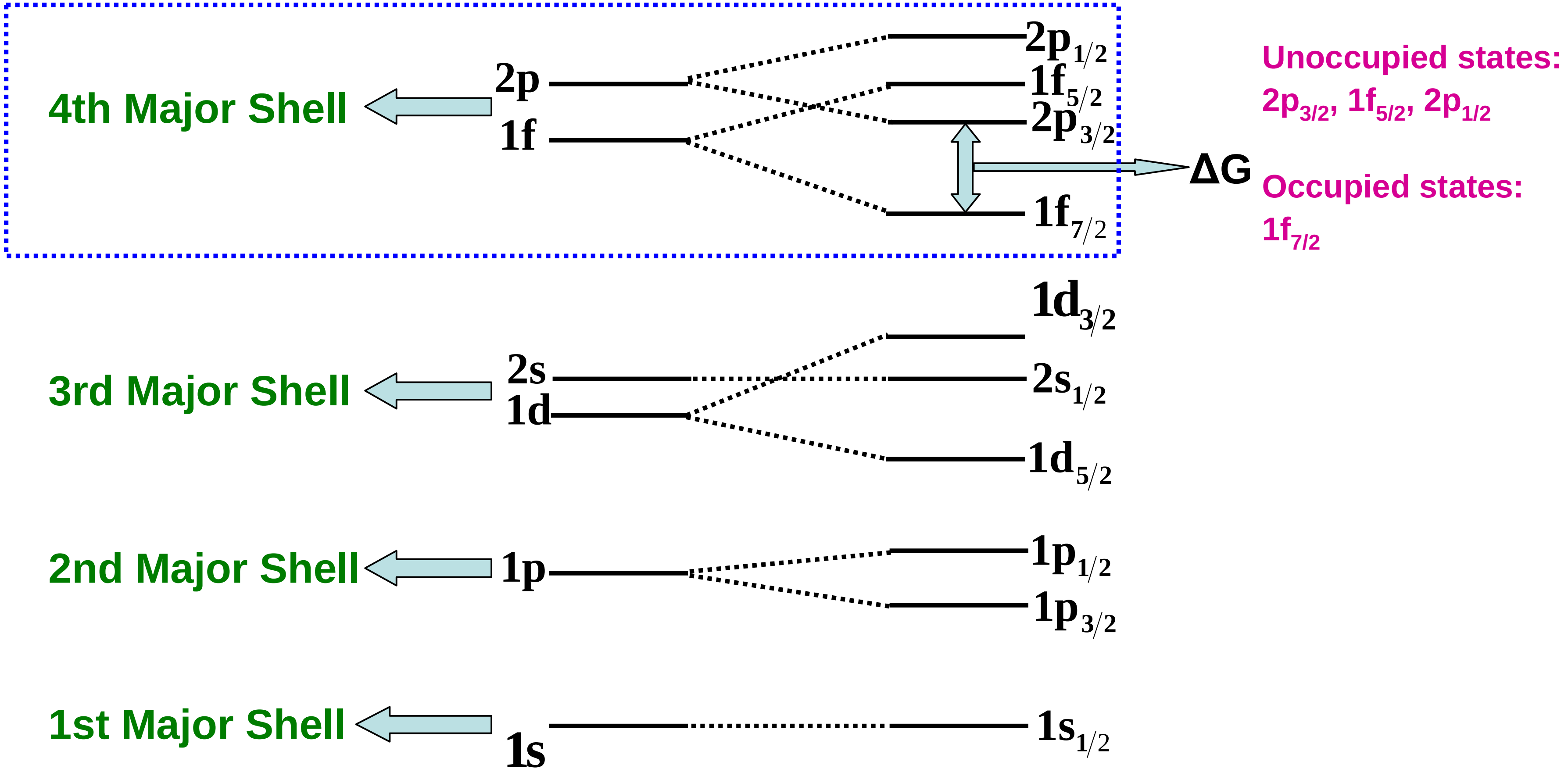
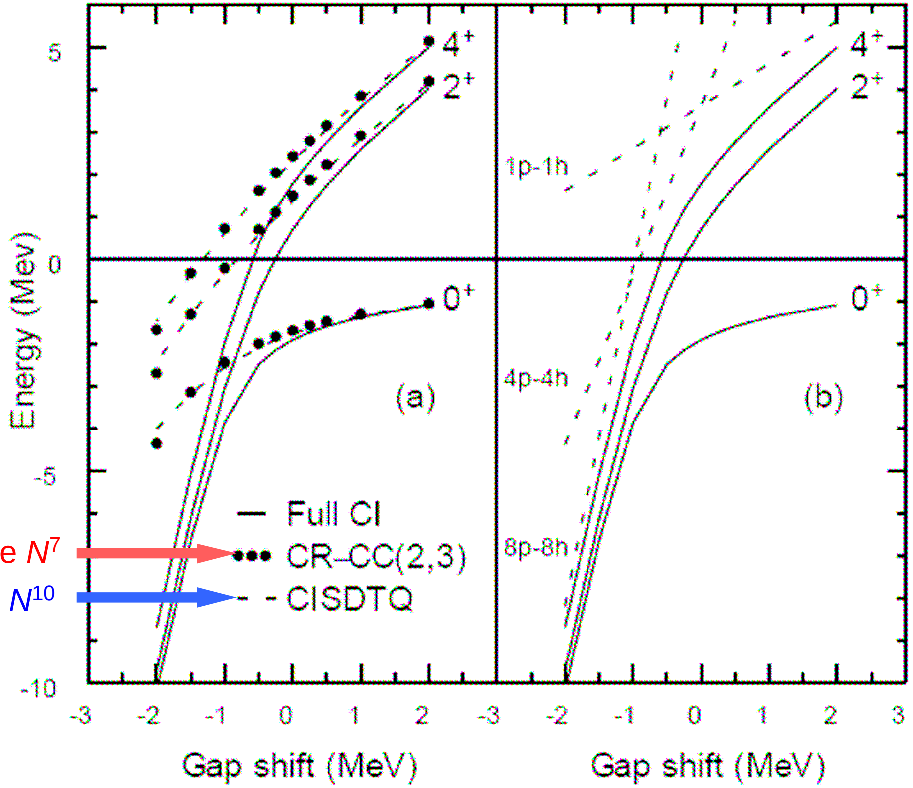


Unoccupied states:
$2p_{3/2}$, $1f_{5/2}$, $2p_{1/2}$

Occupied states:
$1f_{7/2}$

- The gap ΔG was varied to test to the perfomance of the CC methods
- Calculations were performed using the GXPF1A effective Hamiltonian, which is parameterized to fit experimental data for a variety of nuclei in the *A*=47 to *A*=66 region

Coupled-Cluster Calculations for ^{56}Ni

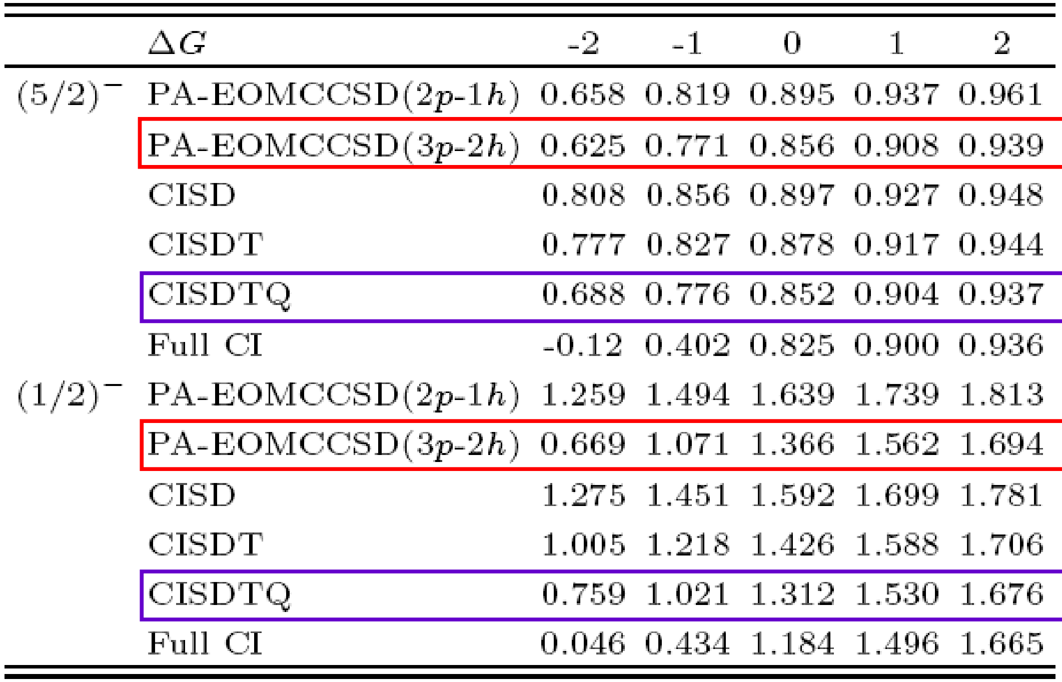


Iterative N^6, non-iterative N^7

Iterative N^{10}

M. Horoi, J. R. Gour, M. Włoch, M. D. Lodriguito, B. A. Brown, and P. Piecuch, Phys. Rev. Lett., 2007

Excitations in ^{57}Ni



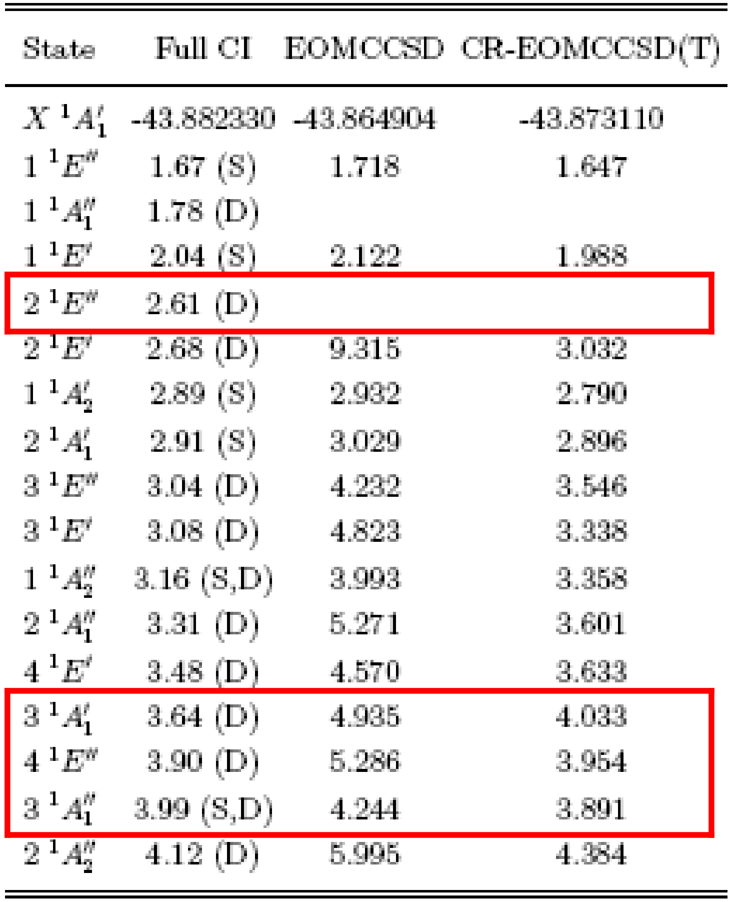
	ΔG	-2	-1	0	1	2	
$(5/2)^-$	PA-EOMCCSD(2p-1h)	0.658	0.819	0.895	0.937	0.961	
	PA-EOMCCSD(3p-2h)	0.625	0.771	0.856	0.908	0.939	N^7
	CISD	0.808	0.856	0.897	0.927	0.948	
	CISDT	0.777	0.827	0.878	0.917	0.944	
	CISDTQ	0.688	0.776	0.852	0.904	0.937	N^{10}
	Full CI	-0.12	0.402	0.825	0.900	0.936	
$(1/2)^-$	PA-EOMCCSD(2p-1h)	1.259	1.494	1.639	1.739	1.813	
	PA-EOMCCSD(3p-2h)	0.669	1.071	1.366	1.562	1.694	N^7
	CISD	1.275	1.451	1.592	1.699	1.781	
	CISDT	1.005	1.218	1.426	1.588	1.706	
	CISDTQ	0.759	1.021	1.312	1.530	1.676	N^{10}
	Full CI	0.046	0.434	1.184	1.496	1.665	

J. R. Gour, M. Horoi, P. Piecuch, B. A. Brown, Phys. Rev. Lett. 2008

Single-reference CC methods can be very successful, but there there are situations where one has to use multi-reference approaches:

Example: excited states of metallic clusters (Be_3)

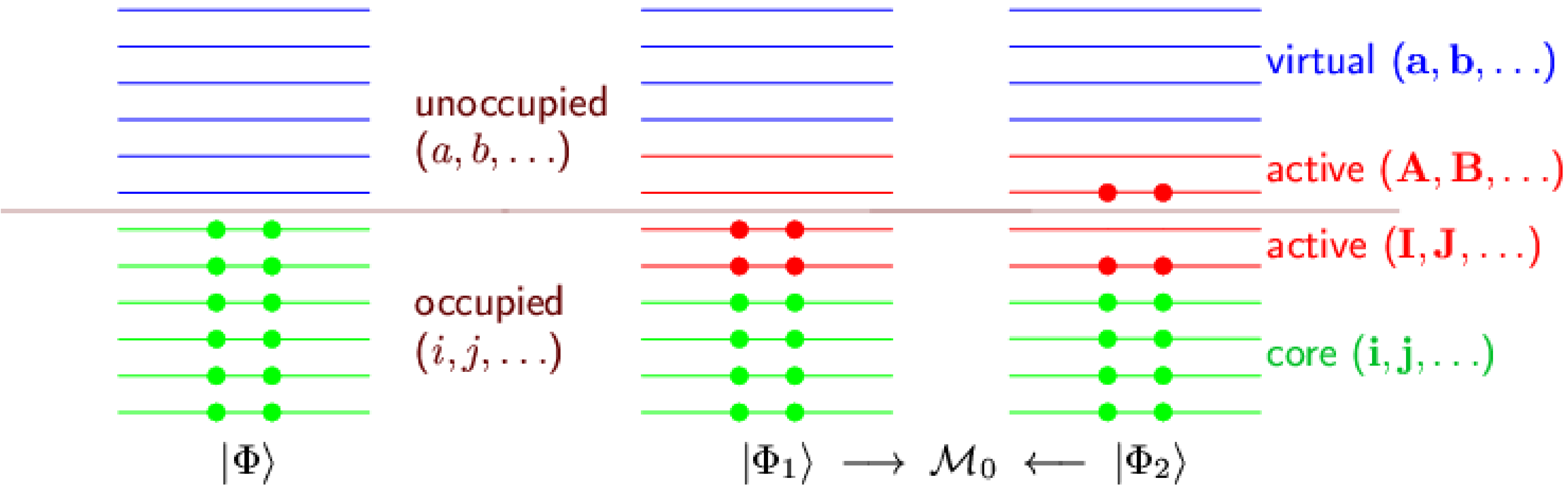
(K. Kowalski et al., J. Chem. Phys. 2005, P. Piecuch et al., Int. J. Quantum Chem., 2006)



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)	2.932	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

MULTI-REFERENCE COUPLED-CLUSTER FORMALISMS



Single-Reference

$$\mathcal{M}_0 = \mathrm{span}\,\{|\Phi\rangle\}$$

$$H|\Psi\rangle = E|\Psi\rangle$$

$$\mathcal{M} = \mathrm{span}\,\{|\Psi\rangle\}$$

$$U : \mathcal{M}_0 \longrightarrow \mathcal{M}$$

$$|\Psi\rangle = U|\Phi\rangle$$

$$U = e^T|\Phi\rangle\langle\Phi|$$

Multi-Reference

$$\mathcal{M}_0 = \mathrm{span}\,\{|\Phi_1\rangle, |\Phi_2\rangle, \ldots, |\Phi_M\rangle\}$$

$$H|\Psi_K\rangle = E_K|\Psi_K\rangle \quad (K = 1, 2, \ldots, M)$$

$$\mathcal{M} = \mathrm{span}\,\{|\Psi_1\rangle, |\Psi_2\rangle, \ldots, |\Psi_M\rangle\}$$

$$U : \mathcal{M}_0 \longrightarrow \mathcal{M}$$

$$|\Psi_K\rangle = U|\chi_K\rangle = U(\sum_{p=1}^{M} c_{p,K}|\Phi_p\rangle)$$

$$U = \mathbf{???}$$

BLOCH WAVE OPERATOR FORMALISM, GENUINE MRCC THEORIES

$$|\chi_K\rangle = P|\Psi_K\rangle = \sum_{p=1}^{M} c_{p,K}|\Phi_p\rangle, \quad P = \sum_{p=1}^{M} |\Phi_p\rangle\langle\Phi_p|$$

$$|\Psi_K\rangle = U|\chi_K\rangle = U\left(\sum_{p=1}^{M} c_{p,K}|\Phi_p\rangle\right) = \sum_{p=1}^{M} c_{p,K}U|\Phi_p\rangle$$

$$U \downarrow \mathcal{M}_0 \equiv (P \downarrow \mathcal{M})^{-1} : \mathcal{M}_0 \to \mathcal{M}, \quad U \downarrow \mathcal{M}_0^{\perp} \equiv 0$$

$UP = U, \quad PU = P$ (intermediate normalization condition), $\quad U^2 = U$

$$\boxed{\begin{gathered} UHU = HU \text{ (generalized Bloch equation)} \\ H^{\text{eff}}|\chi_K\rangle = E_K|\chi_K\rangle, \quad H^{\text{eff}} = PHU = PHUP \end{gathered}}$$

Genuine MRCC Theories

- Fock-space (valence-universal) methods - VUMRCC (Mukherjee, Lindgren, Pal, Kutzelnigg, Kaldor, Meissner, Bartlett, Stolarczyk, Monkhorst, and others) (1974/75 -)

$$U^{(n)} = \Omega P^{(n)} : \mathcal{M}_0^{(n)} \longrightarrow \mathcal{M}^{(n)}, \quad (n = N, N-1, \ldots)$$

For example, Lindgren's ansatz: $\Omega = \mathrm{e}^S \equiv N[e^S]$

- Hilbert-space (state-universal) methods - SUMRCC

The Jeziorski-Monkhorst ansatz:

$$U = \sum_{p=1}^{M} e^{T^{(p)}} |\Phi_p\rangle\langle\Phi_p| \qquad (1981)$$

$$|\Psi_K\rangle = \sum_{p=1}^{M} c_{pK} e^{T^{(p)}} |\Phi_p\rangle$$

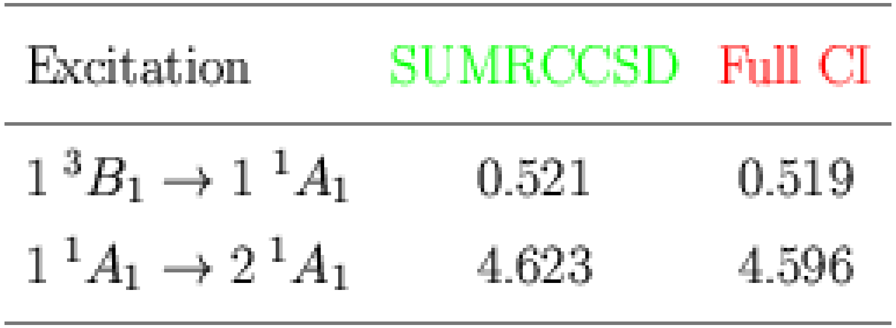
Piecuch, Paldus, and Jeziorski *et al.* spin-adapted SUMRCCSD
Meissner, Kucharski, and Bartlett *et al.* spin-orbital SUMRCCSD (1988-1995)

The X $^3B_1$ (1 $^3B_1$) – A $^1A_1$ (1 $^1A_1$) and 1 $^1A_1$ – 2 $^1A_1$ energy gaps in methylene (CH_2)

Active orbitals: HOMO ($3a_1$), LUMO ($1b_1$); two active electrons

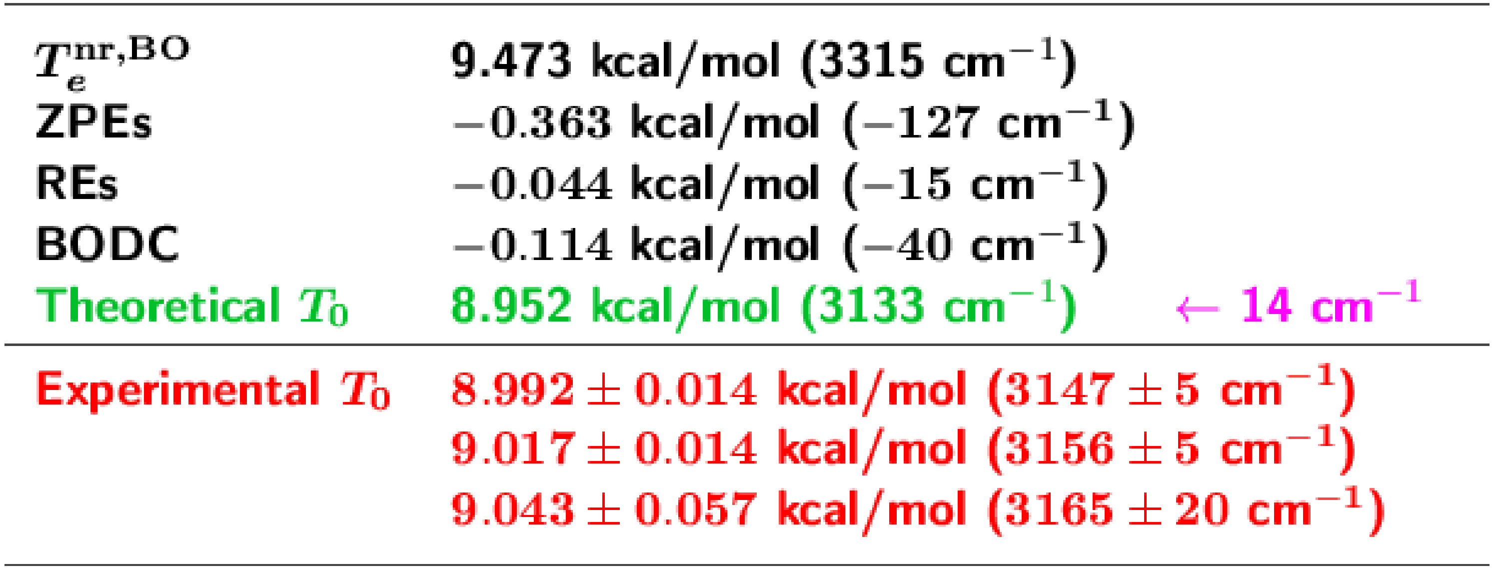
[Piecuch, Li, and Paldus, 1994; Piecuch and Landman, 2000, Kowalski and Piecuch, 2001]

Vertical excitation energies (eV), DZP (4s2p1d/2s1p) basis set



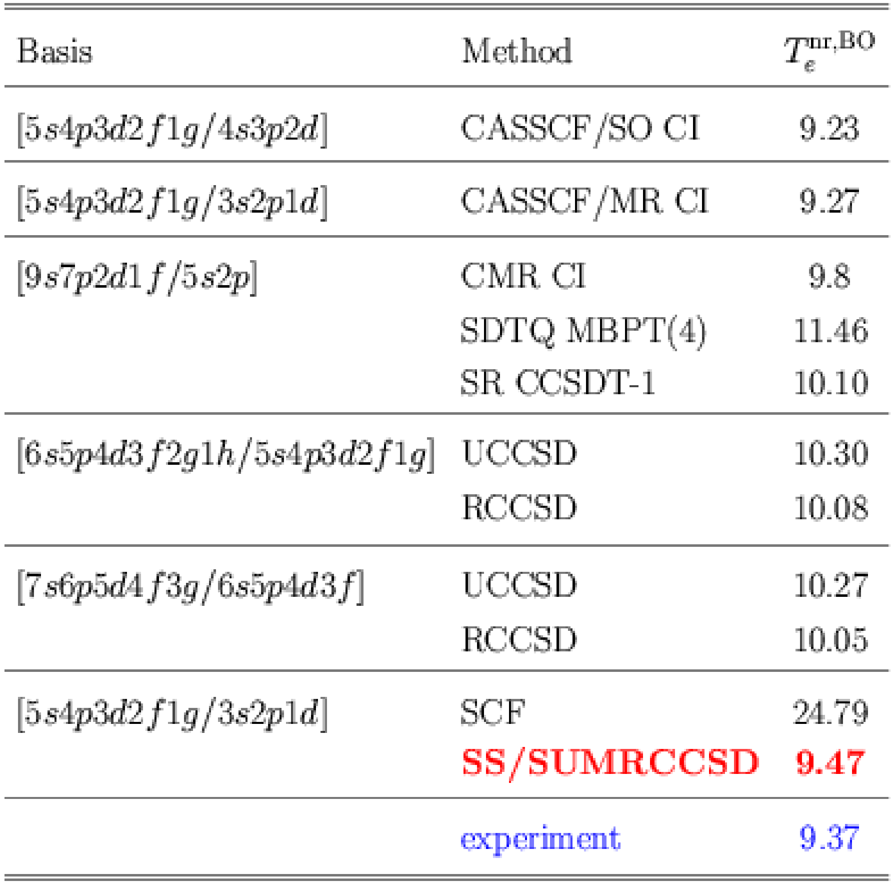
Excitation	SUMRCCSD	Full CI
$1\,^3B_1 \to 1\,^1A_1$	0.521	0.519
$1\,^1A_1 \to 2\,^1A_1$	4.623	4.596

The adiabatic singlet-triplet (X $^3B_1$ – A $^1A_1$) energy gap, 5s4p3d2f1g/3s2p1d basis

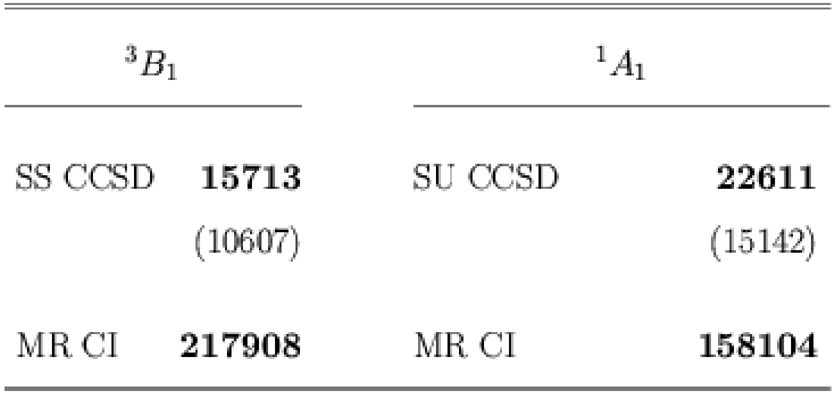


$T_e^{\mathrm{nr,BO}}$	9.473 kcal/mol (3315 cm^{-1})	
ZPEs	-0.363 kcal/mol (-127 cm^{-1})	
REs	-0.044 kcal/mol (-15 cm^{-1})	
BODC	-0.114 kcal/mol (-40 cm^{-1})	
Theoretical T_0	8.952 kcal/mol (3133 cm^{-1})	$\leftarrow$ 14 cm^{-1}
Experimental T_0	8.992 ± 0.014 kcal/mol (3147 ± 5 cm^{-1})	
	9.017 ± 0.014 kcal/mol (3156 ± 5 cm^{-1})	
	9.043 ± 0.057 kcal/mol (3165 ± 20 cm^{-1})	

The singlet-triplet (X $^3B_1$ – A $^1A_1$) separation in CH_2 in different calculations (kcal/mol)



Basis	Method	$T_e^{\mathrm{nr,BO}}$
$[5s4p3d2f1g/4s3p2d]$	CASSCF/SO CI	9.23
$[5s4p3d2f1g/3s2p1d]$	CASSCF/MR CI	9.27
$[9s7p2d1f/5s2p]$	CMR CI	9.8
	SDTQ MBPT(4)	11.46
	SR CCSDT-1	10.10
$[6s5p4d3f2g1h/5s4p3d2f1g]$	UCCSD	10.30
	RCCSD	10.08
$[7s6p5d4f3g/6s5p4d3f]$	UCCSD	10.27
	RCCSD	10.05
$[5s4p3d2f1g/3s2p1d]$	SCF	24.79
	SS/SUMRCCSD	**9.47**
	experiment	9.37



$^3B_1$		$^1A_1$	
SS CCSD	**15713** (10607)	SU CCSD	**22611** (15142)
MR CI	**217908**	MR CI	**158104**

The SUMRCCSD method can provide nice results … but there are problems, such as, for example,

- **intruder multiple solutions; very hard to eliminate in genuine MRCC methods. Among the solutions: the general model space SUMRCC methods of Li and Paldus, the Brillouin-Wigner MRCC theory of Hubač, Pittner, Čarsky, and co-workers, the state-selective MRCC method of Mukherjee et al. (pursued by Mukherjee, Evangelista, Allen, Schaefer III, Gauss, and co-workers), the MRexpT approach of Hanrath et al., and the active-space CC methods of Piecuch, Adamowicz, and co-workers.**

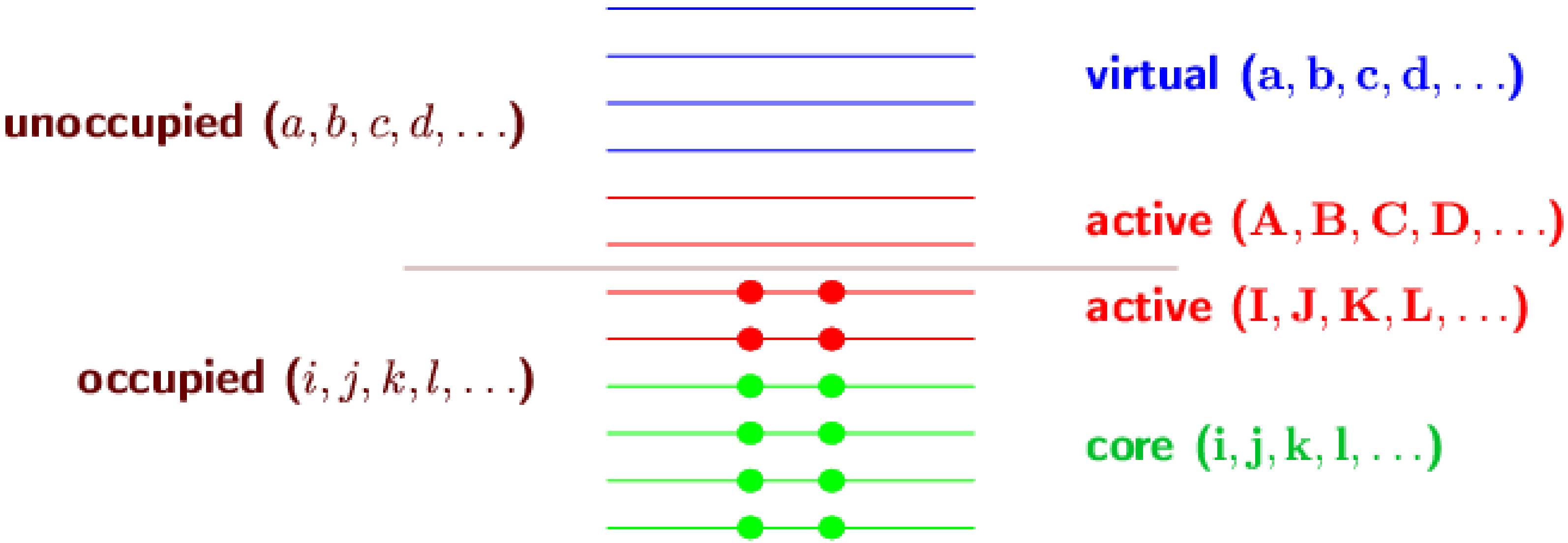
- **large inaccuracies produced by the use of inadequate model spaces, and, in some cases, neglect of higher-than-two-body clusters. Among useful solutions: renormalized corrections to SUMRCC energies due to higher-order excitations of Kowalski and Piecuch (multi-reference analogs of CR-CCSD(T), etc.).**

- **excessive number of cluster operators or amplitudes when larger model spaces are used. The general model space SUMRCC methods of Li and Paldus and the SUMRCCSD(1) approach of Kowalski and Piecuch.**

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

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

[Piecuch, Oliphant, and Adamowicz, 1993, Piecuch, Kucharski, and Bartlett, 1998, Kowalski and Piecuch, 2001, Gour, Piecuch, and Włoch, 2005, 2006]



virtual $(\mathrm{a, b, c, d, \ldots})$

unoccupied $(a, b, c, d, \ldots)$

active $(\mathrm{A, B, C, D, \ldots})$

active $(\mathrm{I, J, K, L, \ldots})$

occupied $(i, j, k, l, \ldots)$

core $(\mathrm{i, j, k, l, \ldots})$

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

$$|\Psi\rangle = e^{T^{\mathrm{ext}}}|\Phi^{\mathrm{int}}\rangle, \quad |\Phi^{\mathrm{int}}\rangle = e^{T^{\mathrm{int}}}|\Phi\rangle \longleftarrow (1 + C^{\mathrm{int}})|\Phi\rangle$$ **(CAS)**

T^{int} – **nondynamic correlation,** T^{ext} – **dynamic correlation**

(long-range correlations) **(short-range correlations)**

REPRESENTATIVE APPROXIMATIONS:
CCSDt OR SSMRCCSD(T) AND EOMCCSDt

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

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

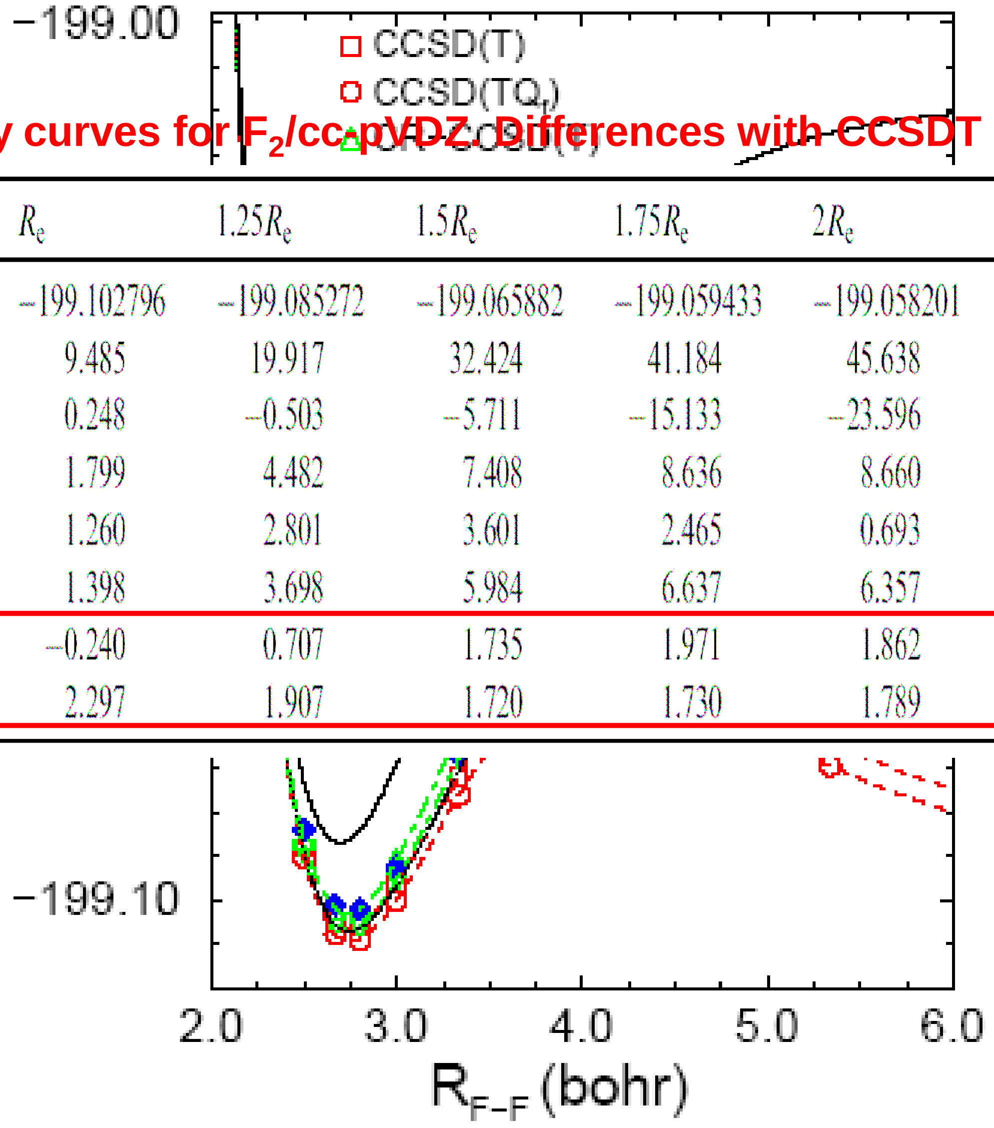
$$\bar{\mathbf{H}}^{\mathrm{CCSDt}} = \begin{pmatrix} \bar{\mathbf{H}}_{\mathbf{SS}} & \bar{\mathbf{H}}_{\mathbf{SD}} & \bar{\mathbf{H}}_{\mathbf{St}} \\ \bar{\mathbf{H}}_{\mathbf{DS}} & \bar{\mathbf{H}}_{\mathbf{DD}} & \bar{\mathbf{H}}_{\mathbf{Dt}} \\ \bar{\mathbf{H}}_{\mathbf{tS}} & \bar{\mathbf{H}}_{\mathbf{tD}}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

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

Because of the use of active orbitals, the numbers of t, q, … excitations are small fractions (a few %) of all T, Q, … excitations.

EXAMPLE: Bond breaking in F_2

(K. Kowalski and P. Piecuch, Chem. Phys. Lett., 2001;
P. Piecuch et al., Chem. Phys. Lett., 2005)

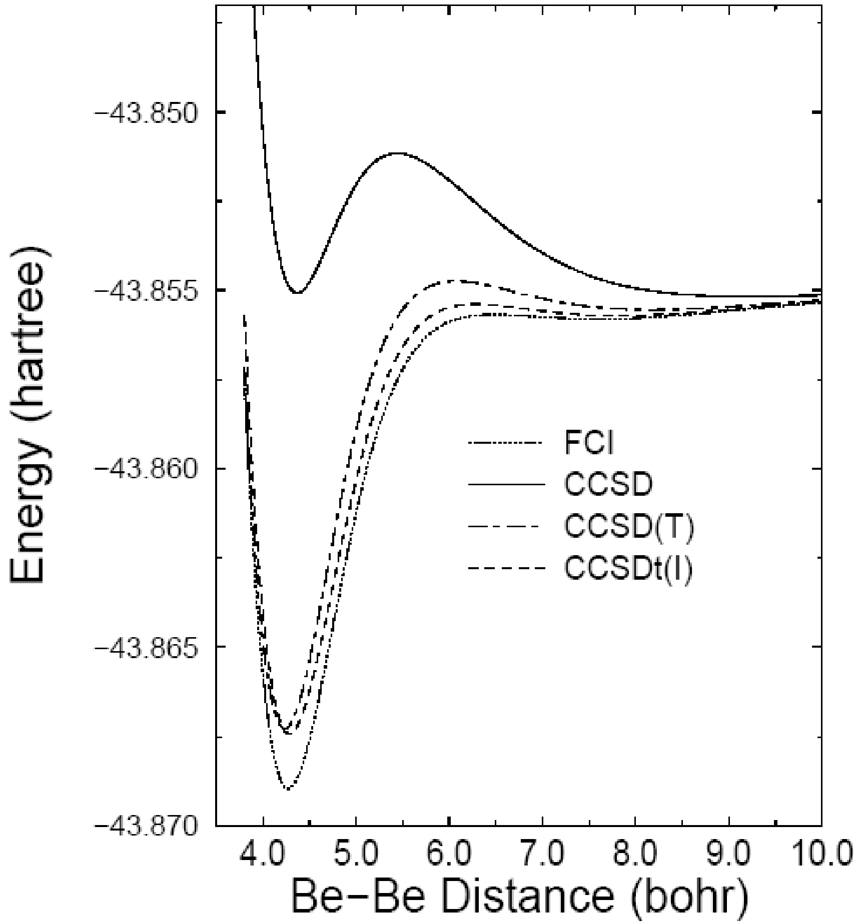


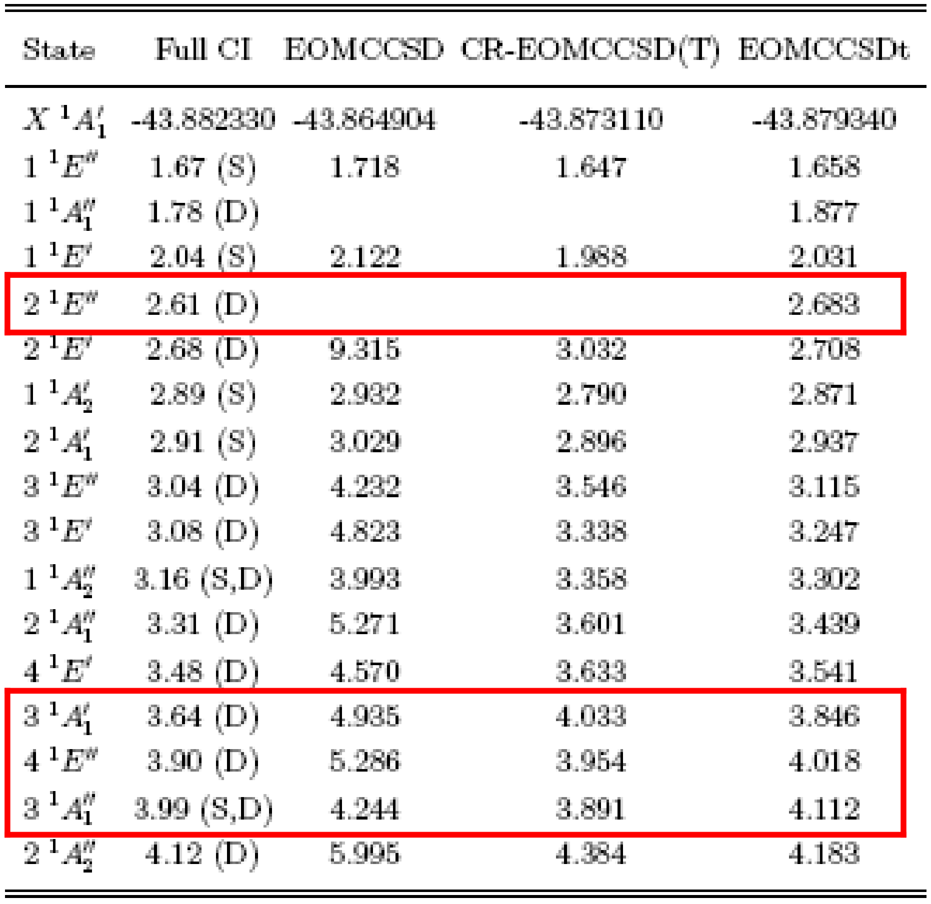
Potential energy curves for F_2/cc-pVDZ. Differences with CCSDT (in millihartree)

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

Ground and excited states of 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)	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

EXTERNALLY CORRECTED CC APPROACHES

An alternative to active-space CC or state-specific MRCC approaches

(J. Paldus, M. Takahashi, J. Čížek, P. Piecuch, X. Li, J. Planelles, et al.; L. Stolarczyk et al.)

$$\langle \Phi_i^a | \mathbf{CCSD} + \cancel{(H_N \boxed{T_3})_C} | \Phi \rangle = 0$$

$$\langle \Phi_{ij}^{ab} | \mathbf{CCSD} + \cancel{[H_N(\boxed{T_3} + T_1 \boxed{T_3} + \boxed{T_4})]_C} | \Phi \rangle = 0$$

$\cancel{(...)}$

$$E = \langle \Phi | H | \Phi \rangle + \langle \Phi | [H_N(T_1 + T_2 + \tfrac{1}{2} T_1^2)]_C | \Phi \rangle$$

In standard CCSD, we neglect equations corresponding to projections on higher-than-2p-2h excited determinants and terms containing T_3 and T_4.

In externally corrected CCSD, we neglect equations corresponding to projections on higher-than-2p-2h excited determinants and extract T_3 and T_4 from a non-CC wave function (for example, PUHF, as in ACCSD of Piecuch, Tobola, and Paldus, or small MRCI, as in RMRCC of Paldus and Li).

Based on the observation: T_3, T_4 extracted from full CI → E becomes exact.

Singlet-triplet (a $^1\Sigma$ – X $^3\Pi$) gap in BN/cc-pVxZ, x=D,T,Q,5

(unusally large and very difficult to balance T_3 and T_4 effects)

(X. Li, J.R. Gour, J. Paldus, and P. Piecuch, Chem. Phys. Lett., 2008)

	$X^3\Pi$		$a^1\Sigma$		T_e			
Method	R_e	ω_e	R_e	ω_e	x=D	x=T	x=Q	x=5
CCSD	1.317	1586	1.272	1705	4196	4391	4459	4471
CCSD(T)	1.329	1510	1.269	1739	-34	-92	-94	-87
CCSDT	1.330	1512	1.277	1702			844	
CR-CC(2,3)	1.329	1518	1.281	1686	404	666	817	919
CR-CC(2,4)					253	289	323	(337)
RMR CCSD(T),A	1.329	1510	1.277	1691	361	264	267	269
RMR CCSD(T),B	1.330	1509	1.277	1700	548	422	408	406
Experiment	1.329	1519.2	1.275	1705.4	15–182			
		1496	1.274	1700.9	153			

MRCI-corrected CCSD, augmented with the dynamical T_3 effects that are not present in MRCI

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THANK YOU !