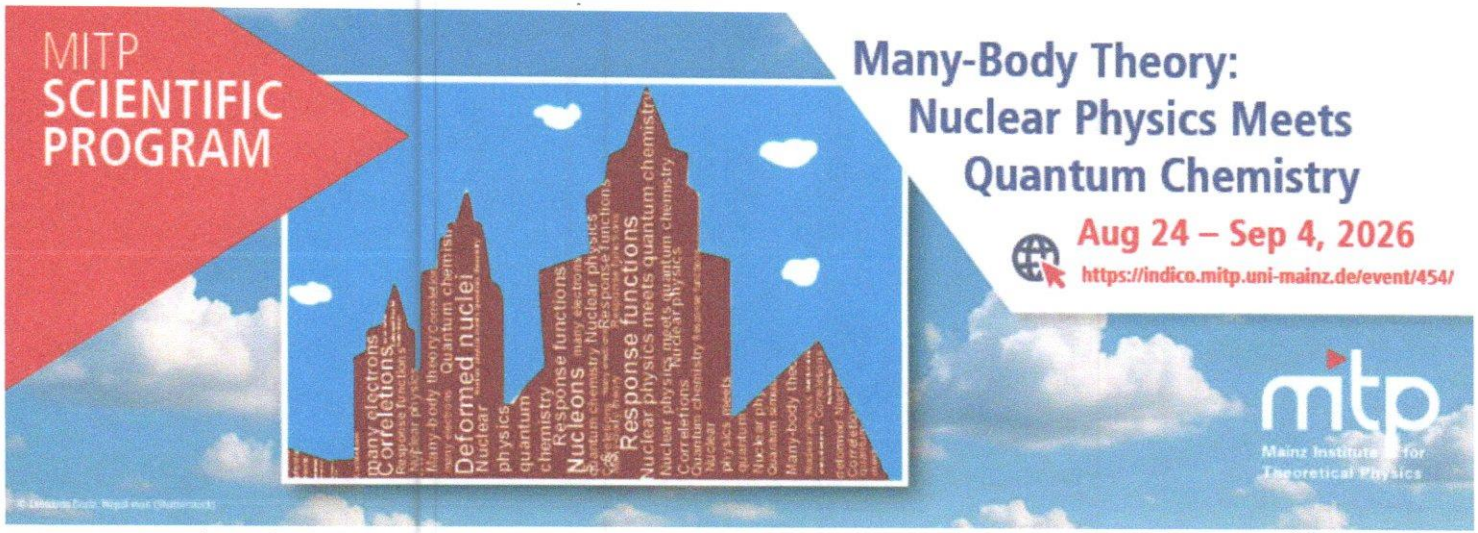

Many-Body Theory: Nuclear Physics Meets Quantum Chemistry

Introduction to Coupled-cluster Theory for Chemistry

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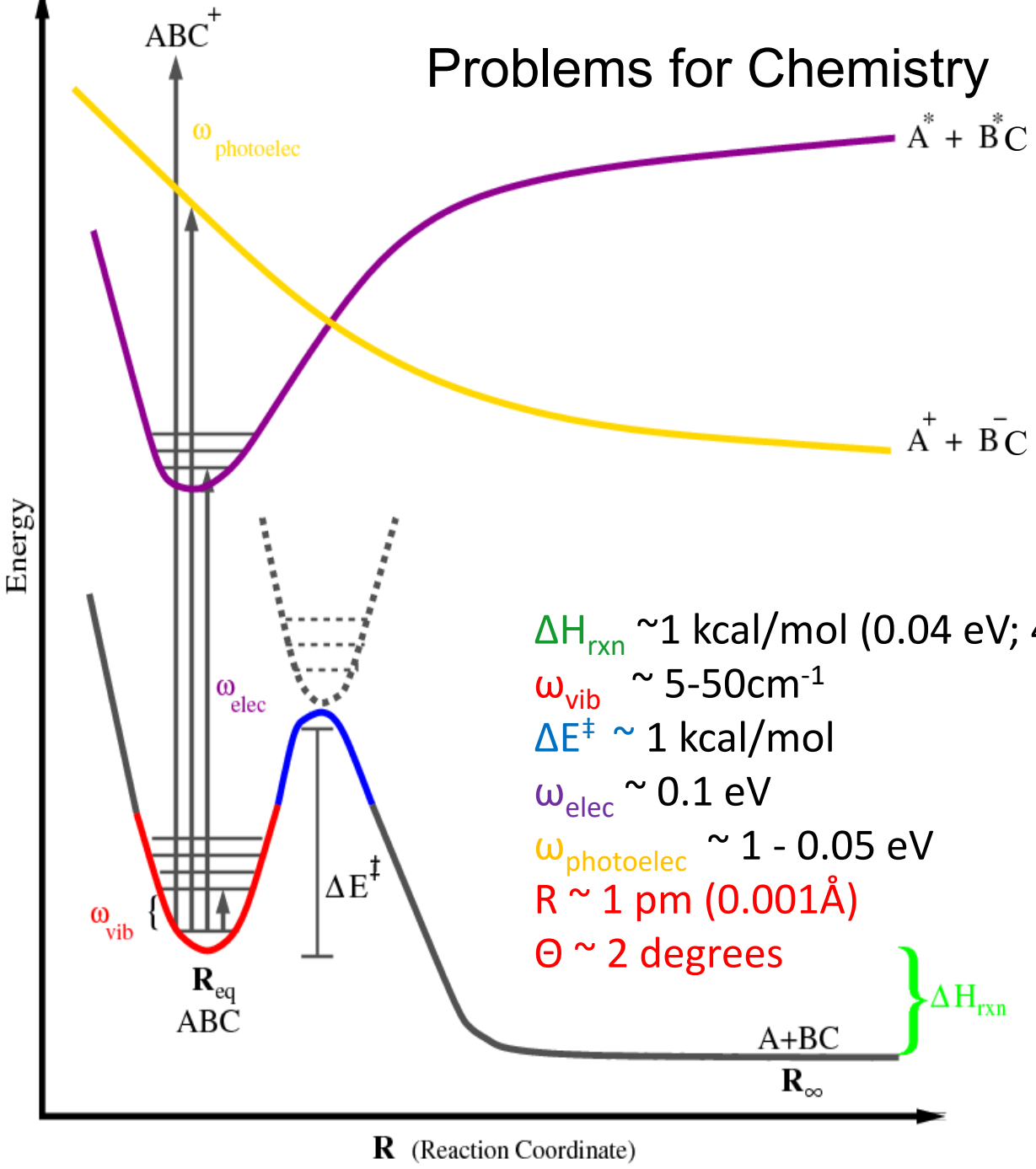
Quantum Theory Project
Depts. of Chemistry and Physics
University of Florida

OUTLINE

- Pedagogical Introduction to CC in chemistry
- CC Numerical Results compared to FCI
- Quasi-linearization of CC eqns.
- Analytical gradients and Property Evaluation
- Triple Excitations, simplified forms, Λ based variants
- Quadruple Excitations and a simplified form
- Equation-of-motion CC methods for excited states

- 'Strong Correlation'. Bond Breaking, MR Tests for SR-CC.
- Changing particle number solutions: DIP and DEA
- Role of Reference Functions, featuring Pccd

Problems for Chemistry



ΔH_{rxn} ~1 kcal/mol (0.04 eV; 4 kj/mol)

ω_{vib} ~ 5-50cm^{-1}

$\Delta E^{\ddagger}$ ~ 1 kcal/mol

ω_{elec} ~ 0.1 eV

$\omega_{photoelec}$ ~ 1 - 0.05 eV

R ~ 1 pm (0.001Å)

Θ ~ 2 degrees

The starting point is Molecular Orbital Theory, an effective independent particle theory whose wavefunction is a single determinant of MO's, that solve the Schrodinger-like eqn,

$h^{eff}(1)\varphi_p(1) = \varepsilon_p \varphi_p(1)$

$\Phi_0 = A(\varphi_1(1)\ \varphi_2(2)...\ \varphi_n(n))$ **A = Anti-symmetrizer makes a determinant of the MO's**

$h^{eff}(1) = F(1) = t(1)+v(1)+J(1) - K(1)$ Hartree-Fock

where all essential two-particle effects
are hidden into an effective one-particle operator.
HF *formally* accomplishes this, as does KS-DFT.

CORRELATION PROBLEM IN MANY-ELECTRON QUANTUM MECHANICS

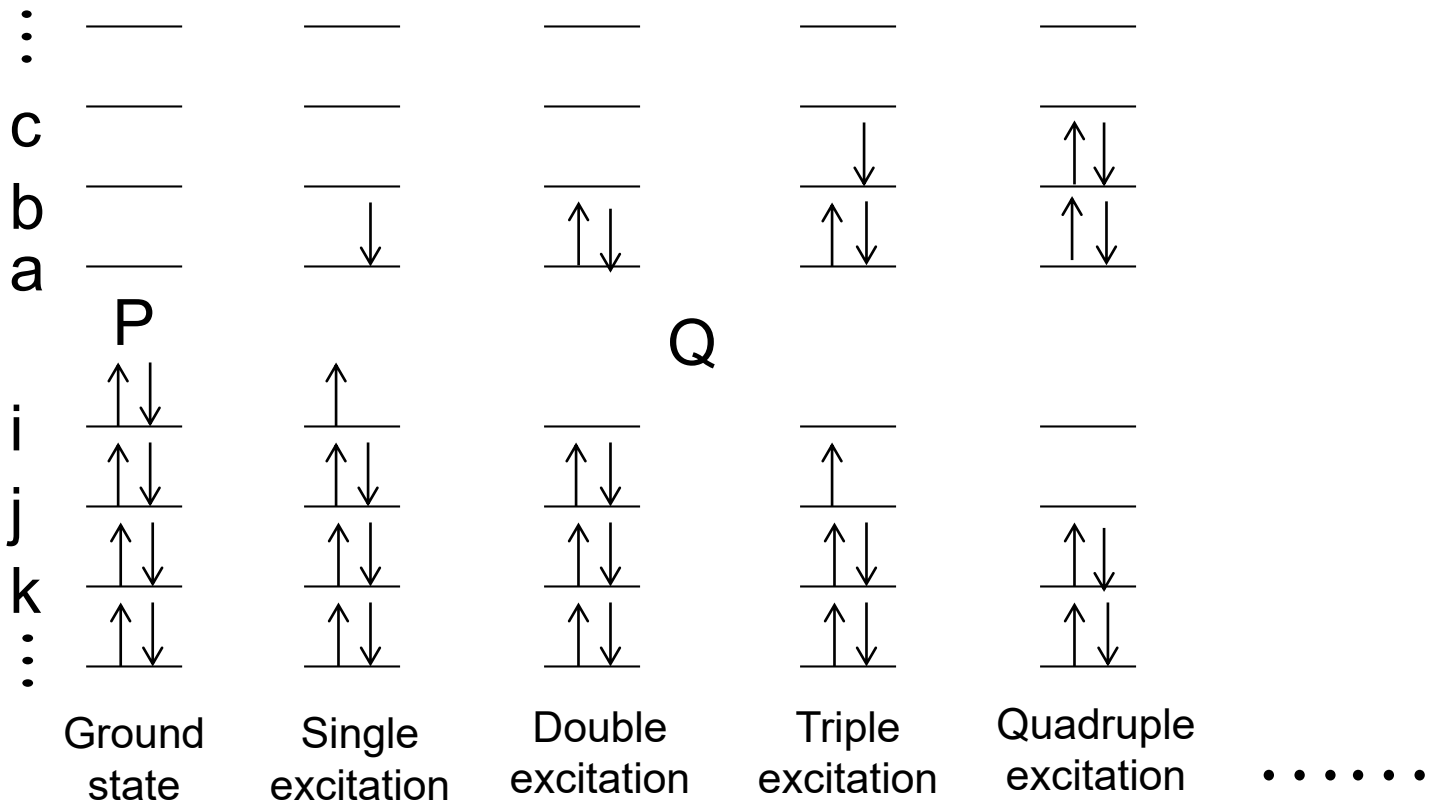
PER OLOV LÖWDIN

Adv. Chem. Phys. Vol II, pg. 207-365 (1959).

"…a wavefunction approximated by a single Slater determinant is usually a rather poor solution to the Schrödinger equation… It has instead turned out that phenomena depending on the individual motions of the different particles are of almost the same importance as the exchange phenomena and that a better theory of many-particle systems can be obtained only if this *correlation* between the individual motions is in some way taken into proper account. The correlation problem is today, therefore, of crucial importance not only in atomic, molecular, and solid-state theory, but also in nuclear physics."

CCSD ~o^2v^4,CCSDT ~o^3v^5, CCSDTQ ~o^4v^6

o=10, v=100, # Triples ~10^9 , # Quads ~10^{12}



CID, CISD, CISDT, CISDTQ, …. Full CI

MBPT2,MBPT3, MBPT4, MBPT5,..Full CI

CCD, CCSD, CCSDT, CCSDTQ…Full CI

Properties of Full CI

- Best possible answer in a basis set
- Invariant to orbital choice
- Variational Upper bound to any electronic state
- Size-extensive, correct scaling with size of molecule
- Size–intensive for excited state energy differences
- Truncated CI (or MR-CI) satisfies none of these exact conditions---except upper bound—but bound is due to the incorrect retention of unlinked digrams.

Many-Body Perturbation Theory

$$\Psi_{MBPT} = \Sigma_{k=0} (R_0 H)^k |0\rangle_{\textbf{Linked}}$$

$$R_0 = (E_0 - H_0)^{-1} Q$$

$$E_{MBPT} = \langle 0|H|\Psi_{MBPT}\rangle = E_0 + E^{(1)} + E^{(2)} + E^{(3)} \ldots$$

TRANSITION TO COUPLED-CLUSTER THEORY

Infinite-order summation of linked MBPT diagrams becomes

$\Psi_{MBPT} = \exp(T)|0\rangle = \Psi_{CC}$. $T = T_1 + T_2 + T_3 + \ldots$

T is ‘connected’

THE NECESSITY OF SIZE-EXTENSIVITY* IN QUANTUM CHEMISTRY

Chemistry depends on energy differences.
We have to know that **$E(AB)=E(A)+E(B)$, $R_{AB}\rightarrow\infty$**

This can be accomplished provided that

$H(AB)\Psi(AB)=[H(A)+H(B)]\ \Psi(A)\Psi(B)=[E(A)+E(B)]\ \Psi(A)\Psi(B)$

With a separable (mean-field) reference function, $|A\rangle|B\rangle$

$\Psi(AB)=\exp[T(AB)]|AB\rangle=\exp[T(A)]|A\rangle\exp[T(B)]|B\rangle$,
where the operator, T, is *connected*.
Guaranteed by evaluating *only* **linked diagrams**.
***RJB, G. Purvis, IJQC (1978)**

Performance of theories for the correlation energy in small molecules. To facilitate comparisons, the ordinate gives the size-scaling parameter of the approximation, $\alpha = \alpha_n + \alpha_N + \alpha_{it}$ in the computational cost function $n^{\alpha_n} N^{\alpha_N} N_{it}^{\alpha_{it}}$.

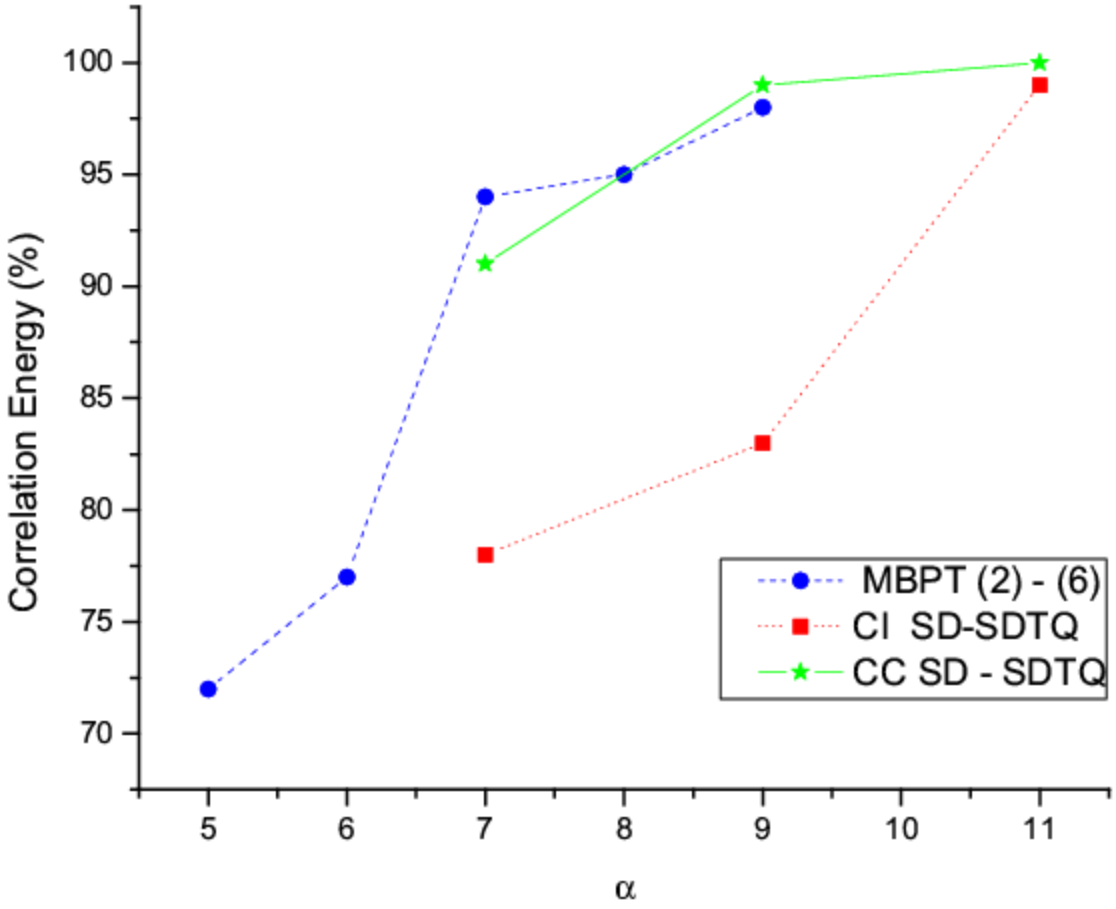


Illustration for FCI Correlation Energies

These are small molecules whose Full CI's are available in a DZP basis. But for a correlation energy study, they are highly demanding at stretched geometries because like all RHF reference functions, it cannot separate correctly to open shell fragments, making the correlation error excessive at large R.

TABLE V. Correlation corrections with various CC methods relative to FCI[a] values [mH].

		CCSD	CCSDT	CCSDTQ	CCSDTQP
	R_e	3.006	0.266	0.018	0.000
HF(DZP)	$1.5R_e$	5.099	0.646	0.041	0.000
	$2.0R_e$	10.181	1.125	0.062	0.001
	R_e	4.122	0.531	0.023	0.002
H_2O(DZP)	$1.5R_e$	10.158	1.784	0.139	0.025
	$2.0R_e$	21.404	−2.472	−0.015	0.026
	R_e	2.843	0.100	0.002	0.001
SiH_2(DZP)	$1.5R_e$	6.685	0.058	−0.015	0.001
	$2.0R_e$	14.869	−3.689	−0.346	0.001
	R_e	3.544	0.206	0.007	0.000
CH_2(DZP)	$1.5R_e$	6.961	0.310	0.026	0.000
	$2.0R_e$[b]	14.648	−1.900	−0.050	0.000

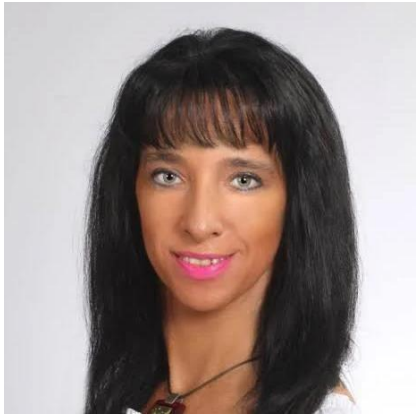
[a]The FCI values, basis sets and geometry taken from Ref. 27 for HF; Ref. 28 for H_2O; Ref. 29 for SiH_2 and Ref. 30 for CH_2.

[b]For CH_2 system the FCI $2R_e$ result is not available; the CCSDTQP value was used as the reference.

TABLE VI. Net correlation effects due to particular cluster operators [mH].

		ΔE(CCSD)	$\Delta E(T_3)$	$\Delta E(T_4)$	$\Delta E(T_5)$
	R_e	−200.876	−2.740	−0.248	−0.018
HF(DZP)	$1.5R_e$	−222.066	−4.453	−0.605	−0.041
	$2.0R_e$	−253.355	−9.056	−1.063	−0.061
	R_e	−211.960	−3.591	−0.508	−0.021
H_2O(DZP)	$1.5R_e$	−260.753	−8.374	−1.645	−0.114
	$2.0R_e$	−348.579	−23.876	2.457	0.041
	R_e	−114.008	−2.743	−0.098	−0.001
SiH_2(DZP)	$1.5R_e$	−137.469	−6.627	−0.073	0.016
	$2.0R_e$	−210.241	−18.558	3.343	0.347
	R_e	−137.342	−3.338	−0.119	−0.007
CH_2(DZP)	$1.5R_e$	−172.173	−6.651	−0.284	−0.026
	$2.0R_e$	−242.752	−16.548	1.850	0.050

CCSDTQP 2002



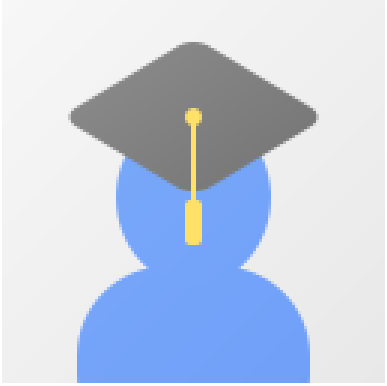
Monika Musial

CCSDT 1987

Josef Noga

George Purvis

CCSD 1982



Stan Kucharski

CCSDTQ 1992

T_3 eqns

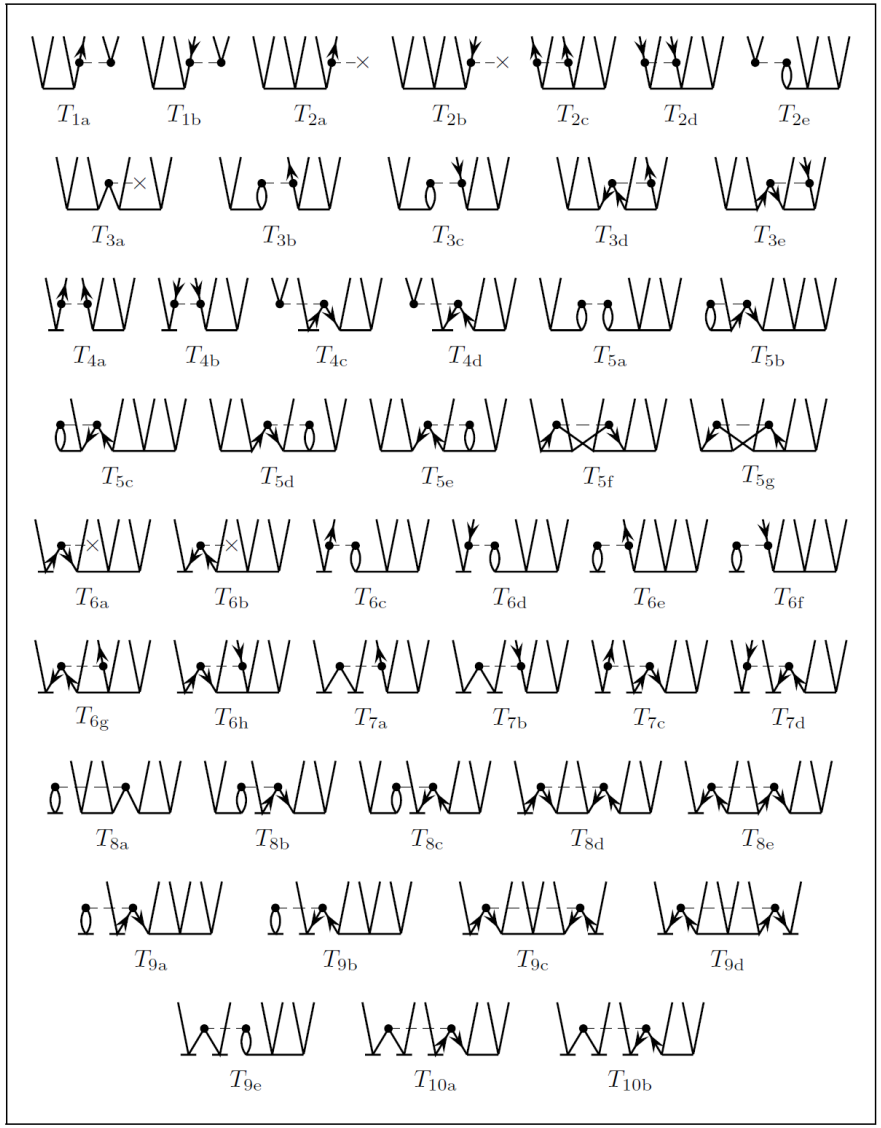


Fig. 10.5. ASG diagrams representing the CCSDT $\hat{T}_3$ equations.

T_4 eqns.

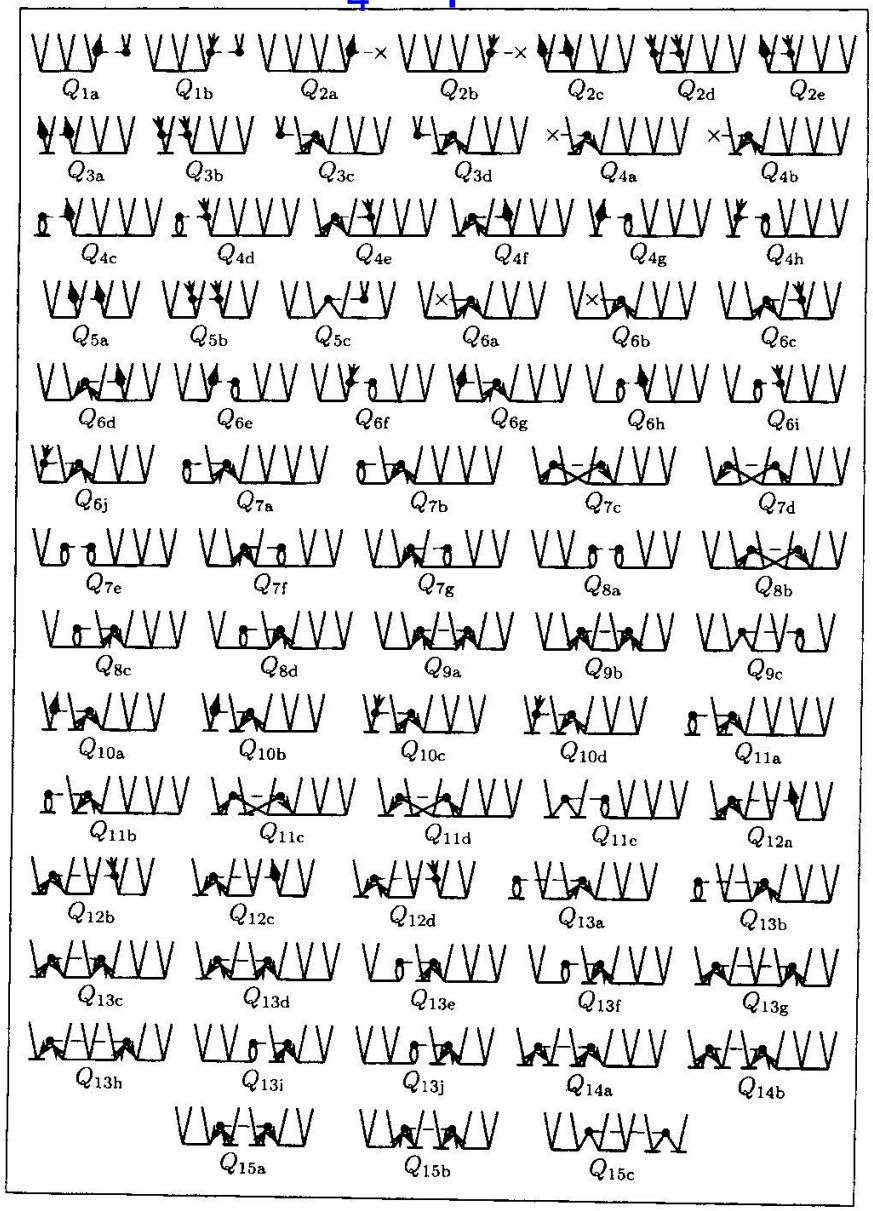
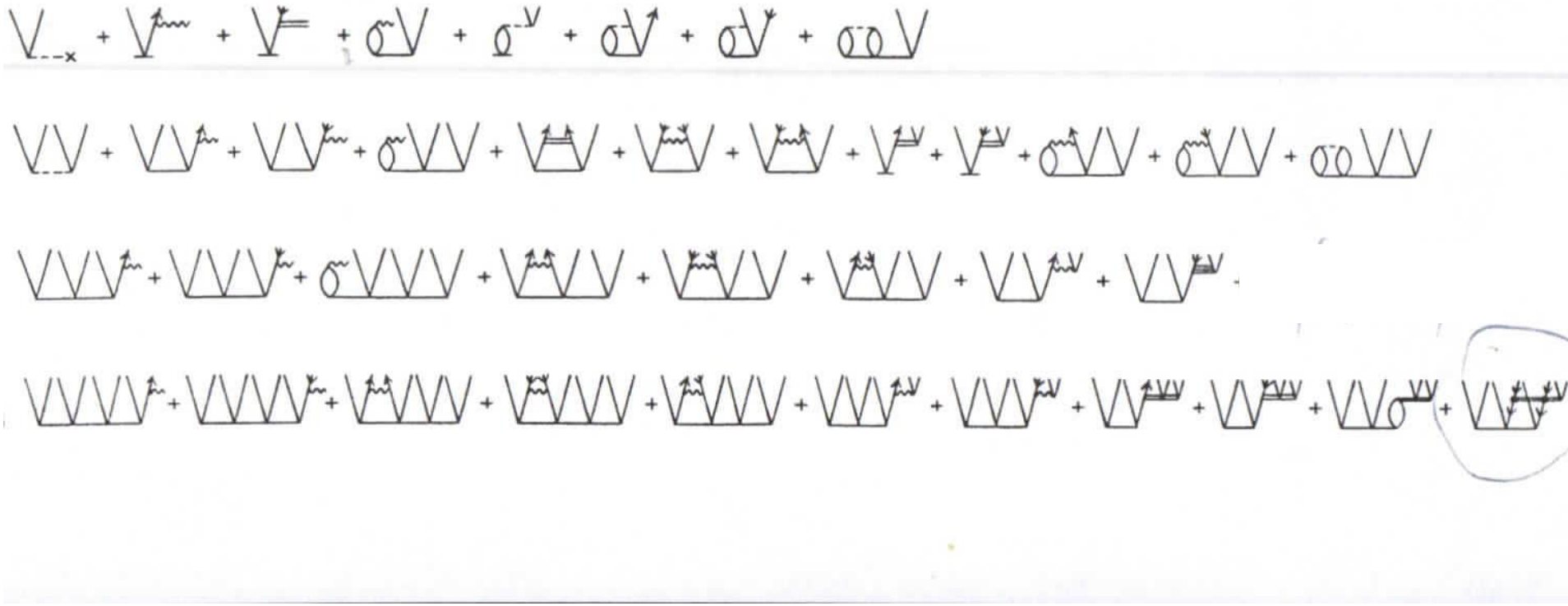


Fig. 10.9. Antisymmetrized Goldstone diagrams representing the CCSDTQ $\hat{T}_4$ equation.

Quasi-linearization of CC eqns. Kucharski, RJB TCA 1991

CCSDTQ eqns, subject to defined intermediates



Now we can hide most details to proceed expediently

Example I: CC theory.

The exact wavefunction has to be $\psi=\exp(T)|0\rangle$, (with potential mods for MR theory) It's multiplicatively separable, size-extensive, suited to infinite systems, etc. Why use any wavefunction form that isn't?

The CC energy is

$EP = P\bar{H}P,$

The similarity transformed Hamiltonian is

$\bar{H} = \exp(-T)H\exp(T)$

and the wavefunction equations are

$Q\bar{H}P = 0.$

EQUATIONS IN CC THEORY

$T=T_1+T_2+T_3+\ldots$CCSDT...

Critical Element is that

$$e^{-T}He^{T}=H+[H,T]+[[H,T]T]/2+[[[H,T]T]T]/3!+[[[[H,T]T]T]T]/4!$$
$$=(He^{T})_C$$
$$=\hat{H}$$

Regardless of what level of excitations are in T.

Thus, the equations for the wavefunction amplitudes are *finite*, even though the wavefunction is *not truncated*.

$$E=\langle 0|\hat{H}|0\rangle$$
$$Q\hat{H}|0\rangle=0$$

Q=single+double+ triple+…excitations.

Analytical Gradients, $\{\partial E/\partial X_\alpha\}$

Chemistry is critically dependent on molecular geometry. Yet they have ~3N degrees of freedom.To explore structure, transition states, and vibrational spectroscopy for polyatomic molecules demands the 3N analytical gradients, $\{\partial E/\partial X_\alpha\}$, computed at the same time and cost as E, itself.

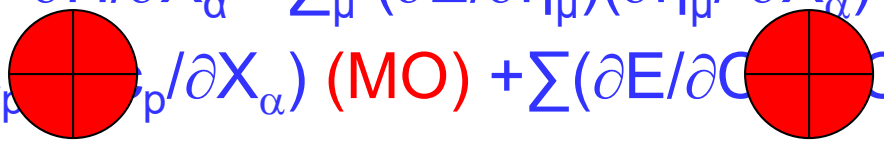
ANALYTICAL GRADIENTS IN CC THEORY

PROBLEMS:

•Before CC theory all quantum chemical methods depended upon being variational to get better approximations and to make it possible to evaluate forces analytically.

$$\partial E/\partial X_\alpha = \langle \partial H/\partial X_\alpha \rangle + \sum_\mu (\partial E/\partial \eta_\mu)(\partial \eta_\mu/\partial X_\alpha) \text{ (AO)}$$

$$+\sum_p (\partial E/\partial c_p)(\partial c_p/\partial X_\alpha) \text{ (MO)} + \sum (\partial E/\partial C_k)(\partial C_k/\partial X_\alpha) \text{ (CI)}$$



•Methods like CI and MCSCF do not correspond to an *unterminated* exponential structure.

Example II. Properties in CC Theory

Take derivative(s) of the CC energy to get $\partial E/\partial X_\alpha = E^\alpha$,

$$EP = P\bar{H}P,$$

$$E^\alpha P = P(\bar{H}^\alpha)P + P(\bar{H}T^\alpha)P$$

And the wavefunction, from first- order PT

$$QT^\alpha P=(E- \bar{H})^{-1}Q\ \bar{H}^\alpha P$$

$$E^\alpha P= P[(\bar{H}^\alpha) + \bar{H}Q(E- \bar{H})^{-1}Q\ \bar{H}^\alpha]P$$

Then, Define $\Lambda = P\bar{H}Q(E- \bar{H})^{-1}Q$

.

$E^\alpha P = P(1+\Lambda)\ \bar{H}^\alpha P$. And

$E = P(1+\Lambda)\bar{H}P,$ is the CC functional.

It is stationary wrt Λ and T.

Expectation Value in CC Properties

Since the expectation value

$$\langle O \rangle = (\exp(T^{\dagger}) O \exp(T))_C$$

Doesn't terminate, this simple
Expression does not work.

Instead $\langle O \rangle = \langle 0 | (1+\Lambda)[(O\exp(T)]_C | 0 \rangle$

This provides an expectation value for an *untruncated* exponential wavefunction, and a generalization of *density matrices* to CC theory and for methods that do not have a wavefunction like CCSD(T).

$$\Upsilon_{pq} = \langle 0|(1+\Lambda)e^{-T}\{p^{\dagger}q\}e^{T}|0\rangle$$

$$\Gamma_{pqrs} = \langle 0|(1+\Lambda)e^{-T}\{p^{\dagger}q^{\dagger}sr\}e^{T}|0\rangle$$

These density matrices enable CC theory to handle all first-order properties, including analytical gradients.

Example III: Non-iterative Triple Excitation Corrections

CCSD(T): "the gold-standard."

Combines MBPT(4) Triple Excitations with CCSD (Purvis, RJB, 82) solutions.

If let $T_3[2] \rightarrow T_2+T_1$ and iterate, have CCSDT-1, 84(Lee,Kucharski,RJB).

If stop after first iteration, get $\Delta E_{(T)}$.

$$H = H_0 + f_{ov} + W$$

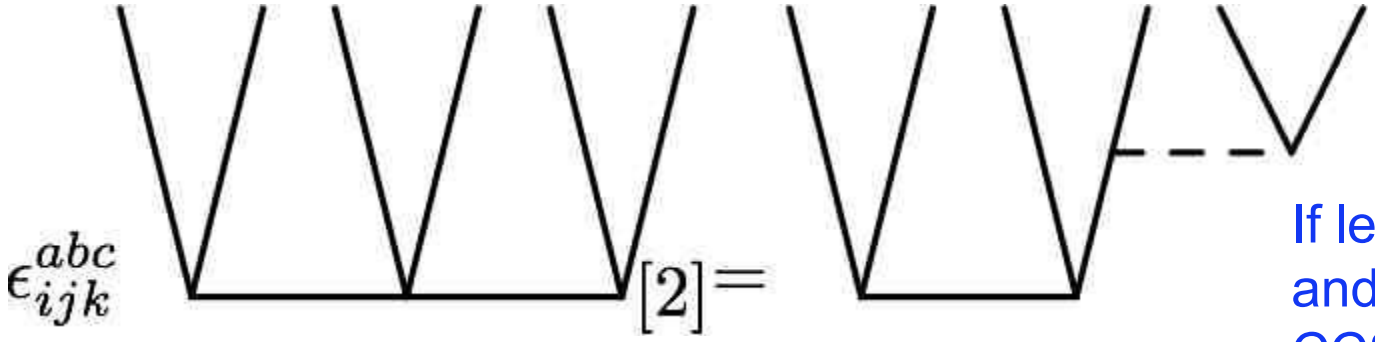
$$\Delta E_{(T)} = \langle 0|(T_1+T_2)^{\dagger}(f_{OV}+W)Q_3D_3\ Q_3(WT_2)|0\rangle$$

Urban,Noga,RJB,85[T],

Raghavchari, Trucks, …Pople 89(T)

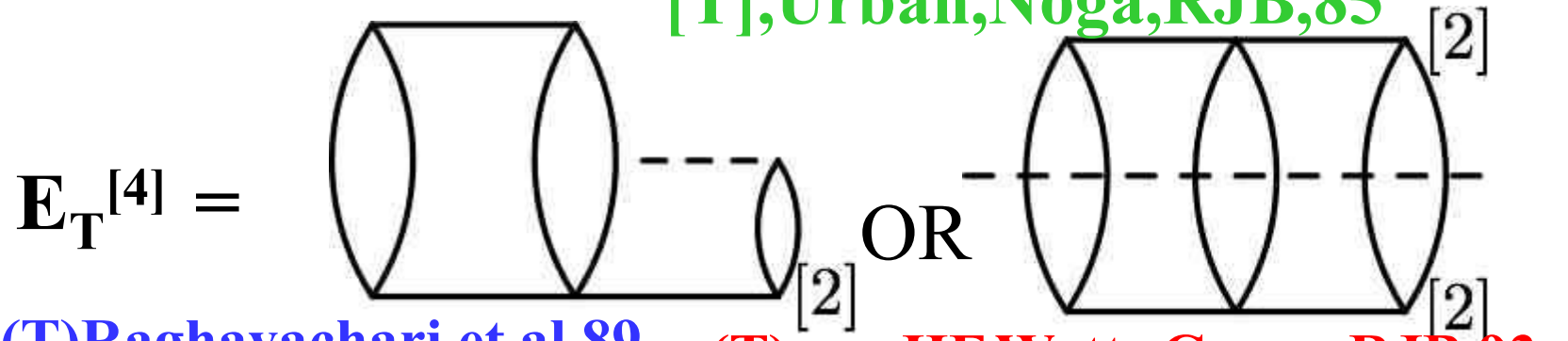
Watts, Gauss, RJB 93
(Generalized (T)).

CCSD(T) arises from assuming that the T_3 amplitudes can be approximated from T_2 and T_1 known from CCSD.



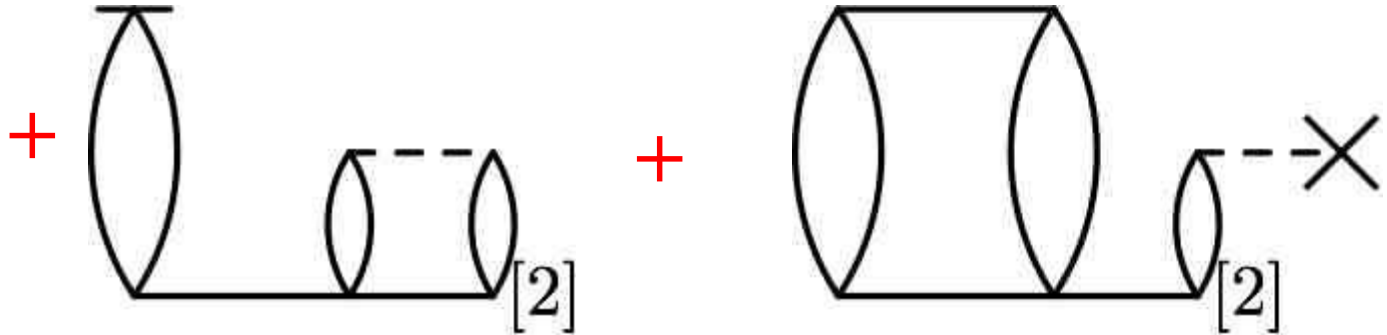
If let $T_3[2] \rightarrow T_2+T_1$ and iterate, have CCSDT-1

[T],Urban,Noga,RJB,85



(T)Raghavachari,et al,89

(T)non HF,Watts,Gauss, RJB,93



Non-iterative triple excitations

$$E_{\mathrm{CC4SD(T)}} = E_{\mathrm{CCSD}} + E_{\mathrm{T}}^{[4]} + E_{\mathrm{ST}}^{[5]} + E_{\mathrm{DT}}^{[4]}\,, \tag{10.38}$$

where

$$E_{\mathrm{T}}^{[4]} = \quad = \quad [2]$$

$$= \frac{1}{36} \sum_{ijkabc} t_{ijk}^{abc\,[2]*} t_{ijk}^{abc\,[2]} \varepsilon_{ijk}^{abc} = \sum_{\substack{i>j>k \\ a>b>c}} t_{ijk}^{abc\,[2]*} t_{ijk}^{abc\,[2]} \varepsilon_{ijk}^{abc}\,, \tag{10.39}$$

$$E_{\mathrm{ST}}^{[4]} =$$

$$= \frac{1}{4} \sum_{ia} t_i^{a\,[1]*} \Big\{ \sum_{jkbc} \langle bc \| jk \rangle t_{ijk}^{abc\,[2]} \Big\} = \sum_{ia} t_i^{a\,[1]*} \Big\{ \sum_{\substack{j>k \\ b>c}} \langle bc \| jk \rangle t_{ijk}^{abc\,[2]} \Big\}\,, \tag{10.40}$$

$$E_{\mathrm{DT}}^{[4]} = \quad \times$$

$$= \frac{1}{4} \sum_{ijab} t_{ij}^{ab\,[1]*} \Big\{ \sum_{kc} f_{kc} t_{ijk}^{abc\,[2]} \Big\} = \sum_{\substack{i>j \\ a>b}} t_{ij}^{ab\,[1]*} \Big\{ \sum_{kc} f_{kc} t_{ijk}^{abc\,[2]} \Big\}\,. \tag{10.41}$$

But what happens when CCSD(T) fails?

CC Functional, $E=\langle 0|(1+\Lambda)\exp(-T)H\exp(T)|0\rangle = \langle 0|(1+\Lambda)\hat{H}|0\rangle$

Assuming the CCSD solution has been obtained, then one can use this half-CI and half-CC biorthogonal expression to improve non-iterative triple excitation corrections like CCSD[T], CCSD(T),, so that despite their perturbative nature, and incorrectly separating reference RHF functions, surprisingly good potential curves can be obtained.

CC functional, E=P(1+Λ)$\hat{H}$P

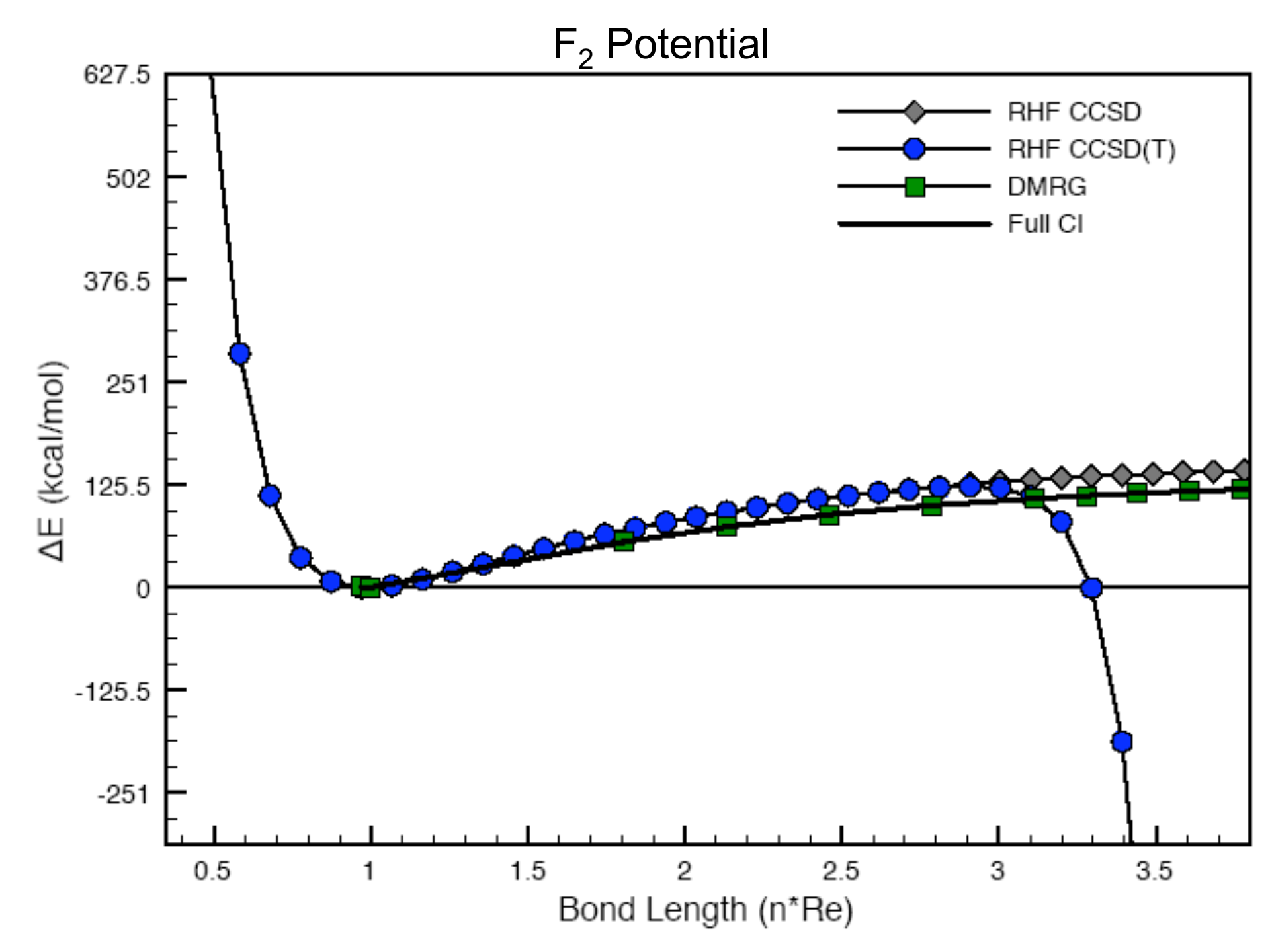
CCSD(T) and ΛCCSD(T)

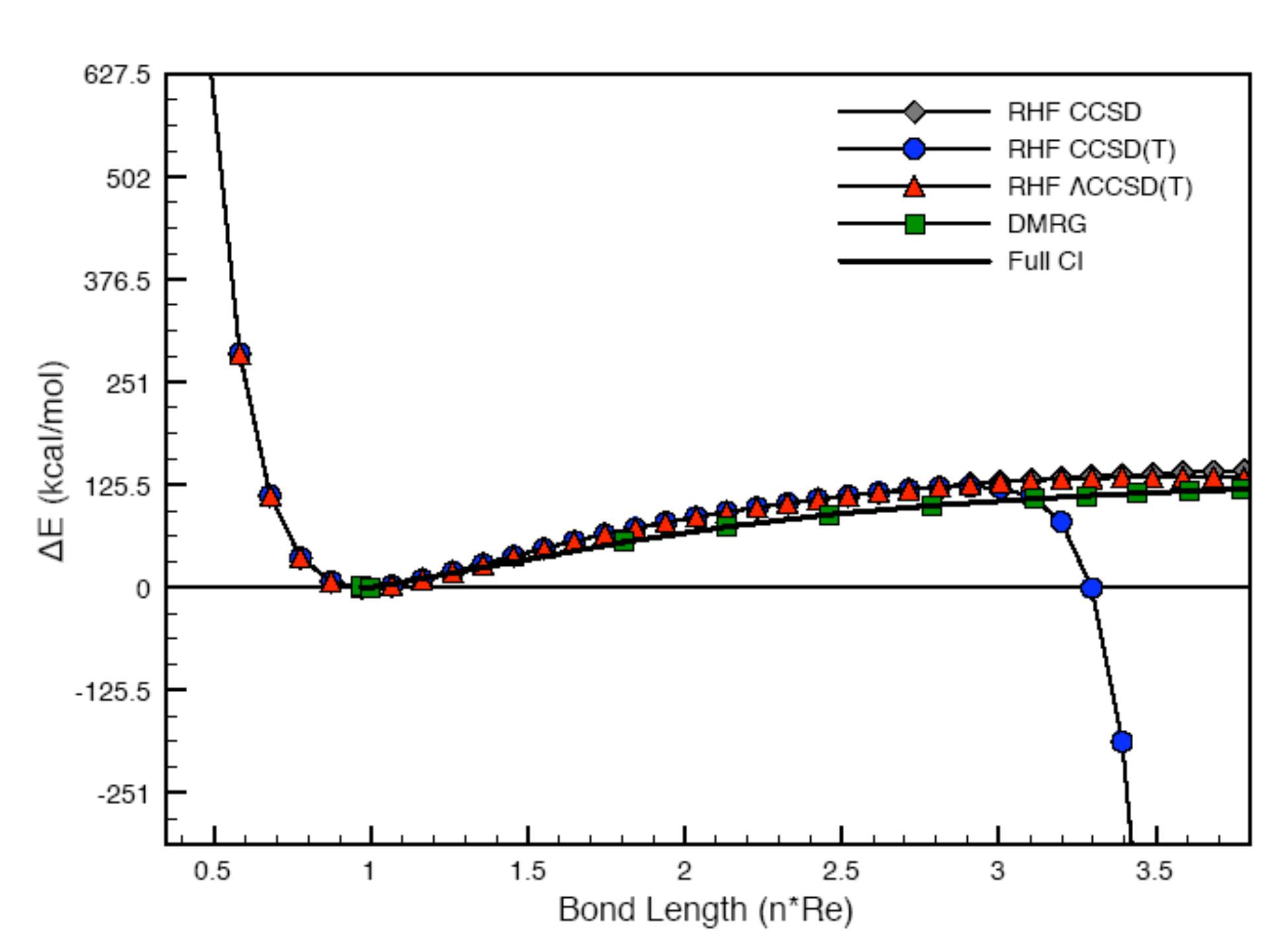
ΛCCSD(T) is the "minimal" formal improvement of CCSD(T)

$$\Delta E_{(T)} = \langle 0 | T^{\dagger} \left(F_{ov} + W \right) | T \rangle D_3 \langle T | \left(W T_2 \right)_C | 0 \rangle$$

$$\Delta E_{\Lambda(T)} = \langle 0 | \Lambda \left(F_{ov} + W \right) | T \rangle D_3 \langle T | \left(W T_2 \right)_C | 0 \rangle$$

Proposed, Kucharski, RJB, 1998, who showed much better agreement with Full CI than CCSD(T).
Crawford, Stanton, 1998 Further applied and discussed gradients
Taube, RJB 2008 implemented gradients.


F_2 Potential
627.5
502
376.5
251
125.5
0
-125.5
-251
ΔE (kcal/mol)
0.5
1
1.5
2
2.5
3
3.5
Bond Length (n*Re)
RHF CCSD
RHF CCSD(T)
DMRG
Full CI


627.5
502
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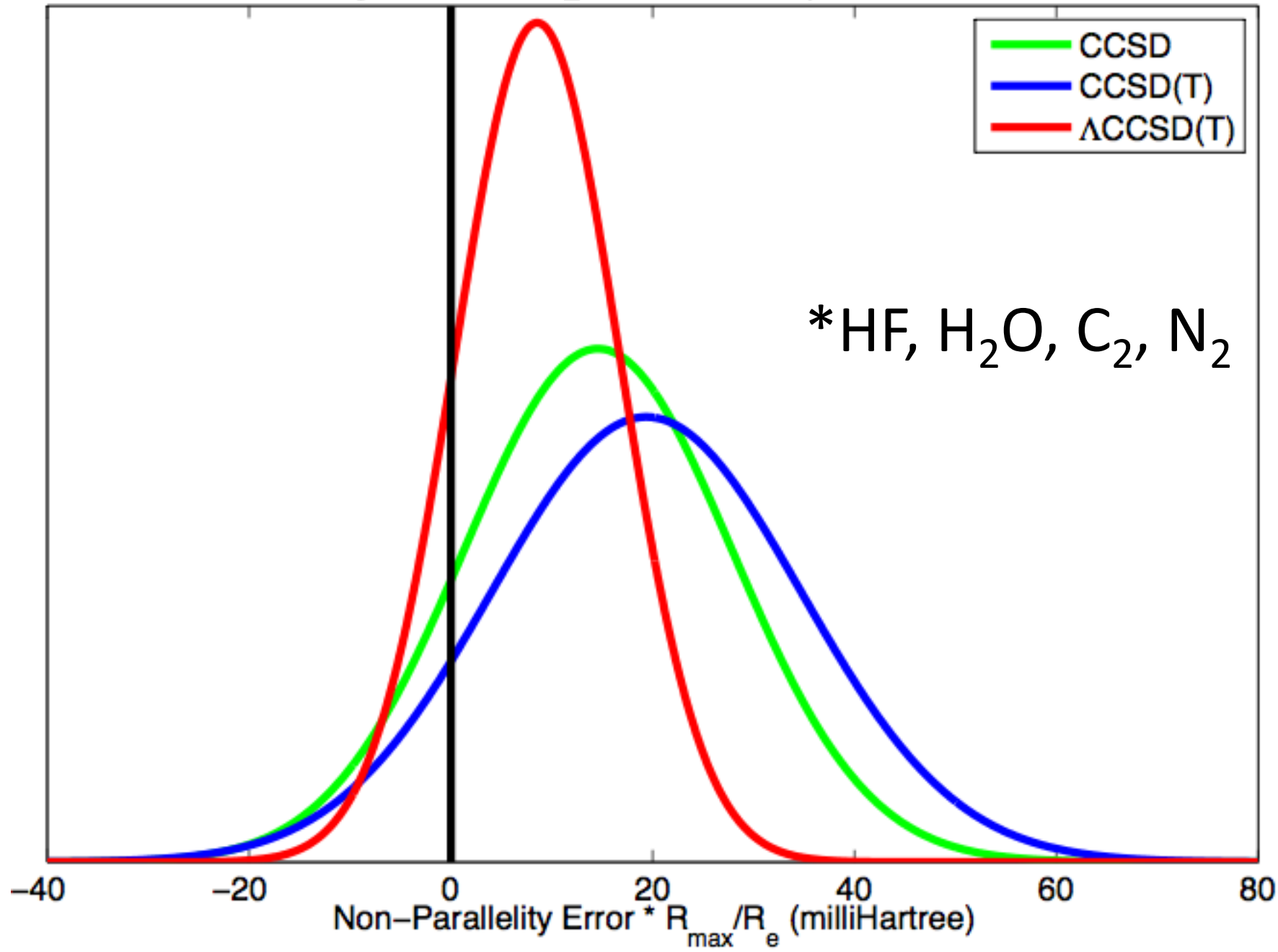
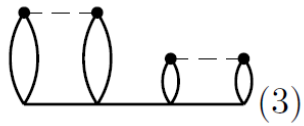
125.5
0
-125.5
-251
ΔE (kcal/mol)
0.5
1
1.5
2
2.5
3
3.5
Bond Length (n*Re)
RHF CCSD
RHF CCSD(T)
RHF ΛCCSD(T)
DMRG
Full CI

Average Non-parallelity Error*

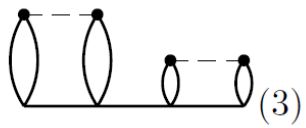


Simplified methods for quadruple excitations?

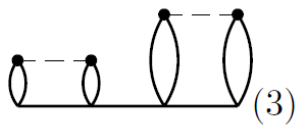
$$\Delta E_{\mathrm{Q}}^{(5)} = \langle 0|\hat{W}\hat{R}_0\hat{W}\hat{T}_4^{(3)}|0\rangle_{\mathrm{C}} =$$



$$= \frac{1}{2}\Bigg\{$$



$$+$$



$$\Bigg\}$$

$$= \frac{1}{32}\sum_{\substack{abcd\\ijkl}}\left\{\frac{\langle ij\|ab\rangle}{\varepsilon_{ij}^{ab}}\langle kl\|cd\rangle + \frac{\langle kl\|cd\rangle}{\varepsilon_{kl}^{cd}}\langle ij\|ab\rangle\right\}t_{ijkl}^{abcd} \qquad (10.48)$$

$$= \frac{1}{32}\sum_{\substack{abcd\\ijkl}}\left\{\frac{1}{\varepsilon_{ij}^{ab}} + \frac{1}{\varepsilon_{kl}^{cd}}\right\}\langle ij\|ab\rangle\langle kl\|cd\rangle t_{ijkl}^{abcd}$$

$$= \frac{1}{32}\sum_{\substack{abcd\\ijkl}}\frac{\langle ij\|ab\rangle}{\varepsilon_{ij}^{ab}}\frac{\langle kl\|cd\rangle}{\varepsilon_{kl}^{cd}}\varepsilon_{ijkl}^{abcd}t_{ijkl}^{abcd}\,.$$

$$\Delta E_{\mathrm{Q}}^{(5)} = \tfrac{1}{2}\langle 0|(\hat{T}_2^{\dagger(1)})^2[\hat{W}(\hat{T}_3 + \tfrac{1}{2}\hat{T}_2^2)]|0\rangle_{\mathrm{C}}\,. \qquad (10.49)$$

$$\Delta E_{\mathrm{Q_f}}^{[5]} = \tfrac{1}{2}\langle 0|\hat{T}_2^{\dagger}\hat{T}_2^{\dagger(1)}[\hat{W}(\hat{T}_3 + \tfrac{1}{2}\hat{T}_2^2)]|0\rangle_{\mathrm{C}}\,. \qquad (10.50)$$

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Article

Factorized Quadruples and a Predictor of Higher-Level Correlation in Thermochemistry

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James H. Thorpe, Zachary W. Windom, Rodney J. Bartlett,* and Devin A. Matthews*

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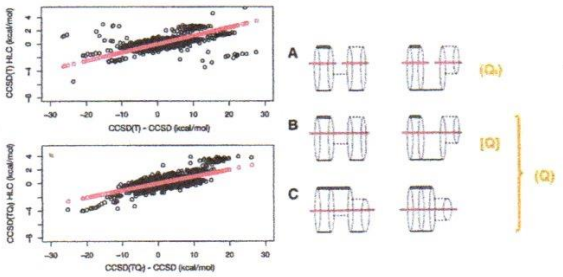
ABSTRACT: Coupled cluster theory has had a momentous impact on the ab initio prediction of molecular properties, and remains a staple ingratiate in high-accuracy thermochemical model chemistries. However, these methods require inclusion of at least some connected quadruple excitations, which generally scale at best as $O(N^9)$ with the number of basis functions. It is very difficult to predict, a priori, the effect correlation of past CCSD(T) on a given reaction energy. The purpose of this work is to examine cost-effective quadruple corrections based on the factorization theorem of the many-body perturbation theory that may address these challenges. We show that the $O(N^7)$ factorized CCSD(TQ$_f$) method introduces minimal error to predicted correlation and reaction energies as compared to the $O(N^9)$ CCSD(TQ). Further, we examine the performance of Goodson's continued fraction method in the estimation of CCSDT(Q)$_\Lambda$ contributions to reaction energies as well as a "new" method related to %TAE[(T)] that we refer to as a scaled perturbation estimator. We find that the scaled perturbation estimator based upon CCSD(TQ$_f$)/cc-pVDZ is capable of predicting CCSDT(Q)$_\Lambda$/cc-pVDZ contributions to reaction energies with an average error of 0.07 kcal mol^{-1} and an L_2D of 0.52 kcal mol^{-1} when applied to a test-suite of nearly 3000 reactions. This offers a means by which to reliably "ballpark" how important post-CCSD(T) contributions are to reaction energies while incurring no more than CCSD(T) formal cost and a little mental math.



So far, we get accurate single state potential surfaces, their vibrational spectra, transition states, and density matrices,
but we also need excited state PES, UV-vis spectroscopy, photo-electron spectra, ionizations and electron-attached processes.

How do we do that?

Equation-of-motion CC…

JCP **98** 7029 (1993)

Example IV: Excited states.

EOM-CC

$(E_0 - H)\Psi_0 = 0$ GROUND STATE

$(E_0 - H)\Psi_K = \omega_K \Psi_K$ EXCITED STATE

$\Psi_K = R_k \exp(T)|0\rangle$ R_k is an operator that can create excited, ionized, or electron attached states---

$[T, R_k] = 0$

Subtract the ground state equation from the excited state, to give

$[(e^{-T}He^{T} - E)R_k]_C|0\rangle = (\bar{H}, R_k)_C|0\rangle = \omega_K R_k|0\rangle$

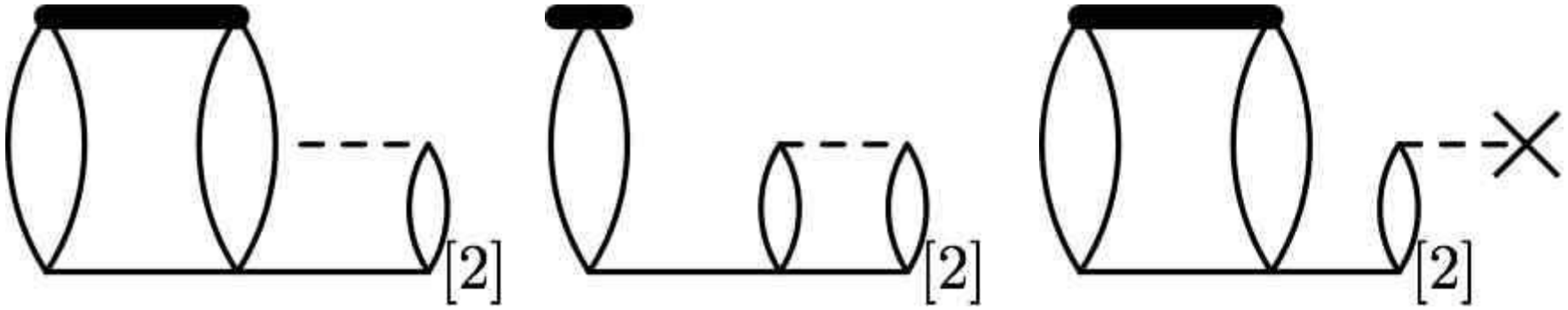
$\langle 0|(L_k \bar{H}) = \langle 0|L_k \omega_K$

$\omega_K = \langle 0|L_k(\bar{H} R_k)_C|0\rangle$

This is the analogous functional for excited states that can be differentiated to get properties.

Following exactly the same strategy as for ΛCCSD(T), triples effect in EOM-CC can be readily approximated….

$$\omega_k = \langle 0|L_K \, \bar{H} \, R_K|0\rangle, \langle L_K|R_L\rangle = \delta_{KL}$$
$$\omega_T = \langle 0|(L_1 + L_2)(\bar{H} \, R_3)_C|0\rangle$$
$$Q_3\bar{H}_0R_3|0\rangle = Q_3[\bar{H}(R_2 + R_1)]_C \, |0\rangle \backsimeq$$
$$Q_3H_0R_3|0\rangle = Q_3WR_2|0\rangle$$



Replacing Λ by L_K and T_3 by R_3 gives EOM-CCSD(T).

ROLE OF TRIPLE EXCITATIONS IN EOM-CC (ev)

Cystosine (aug-pVDZ basis), P. Szalay, et al JPC (2012)

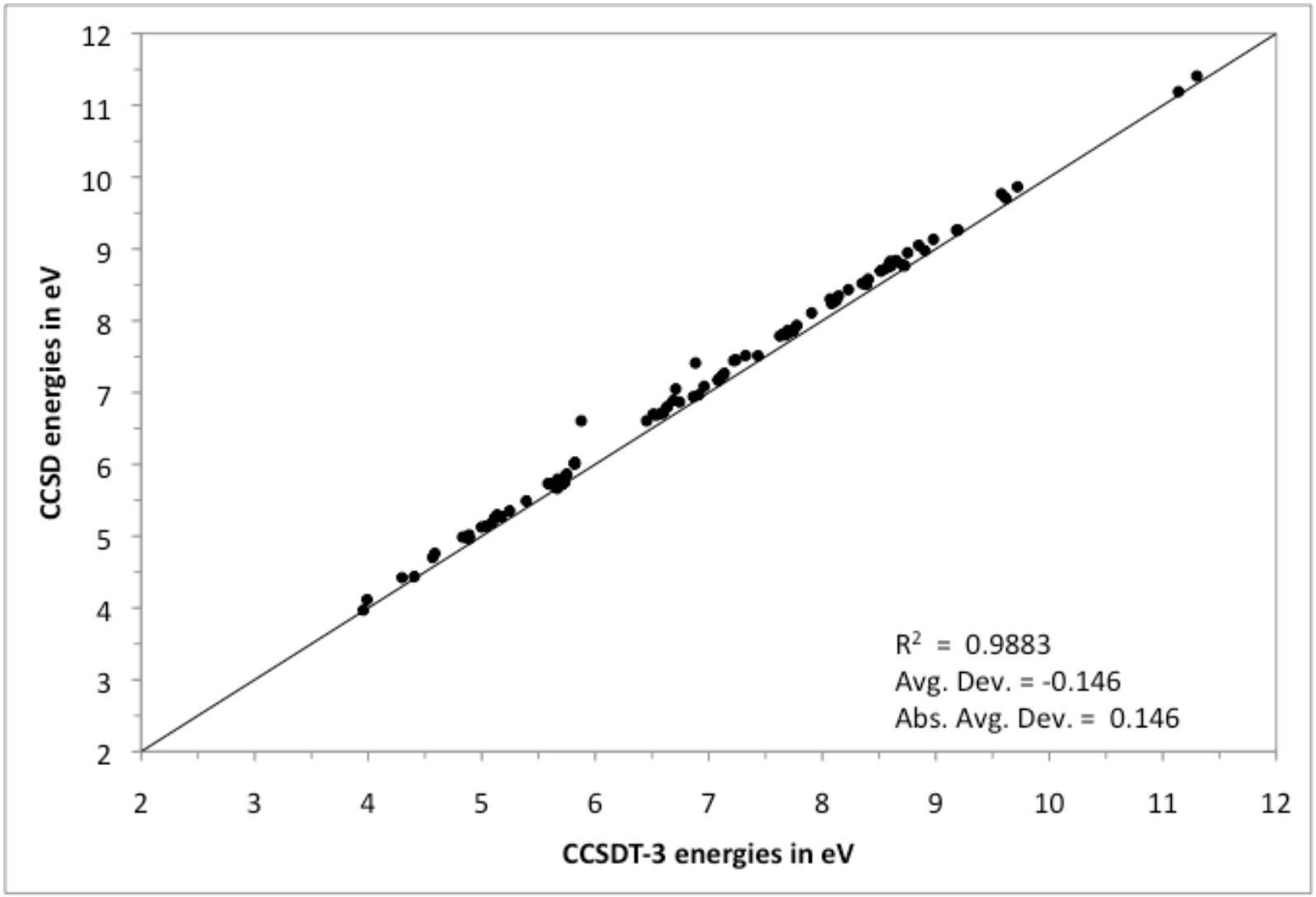
(Tom Watson's ACES III implementation)

STATE	CCSD	CCSDT-3 #	CC3 &	CCSD(T) #
$\pi \rightarrow \pi^*$	4.94	4.79	4.71	4.73
$\Pi_N \rightarrow \pi^*$	5.86	5.65	5.55	5.62
$\pi \rightarrow 2\pi^*$	6.50	6.38	6.30	6.35
$n_{O+N} \rightarrow R$	6.70	6.57	6.43	6.57
$\pi_N \rightarrow 2\pi^*$	6.88	6.72	6.62	6.69

J. Watts, RJB Chem. Phys. Lett. (1994)

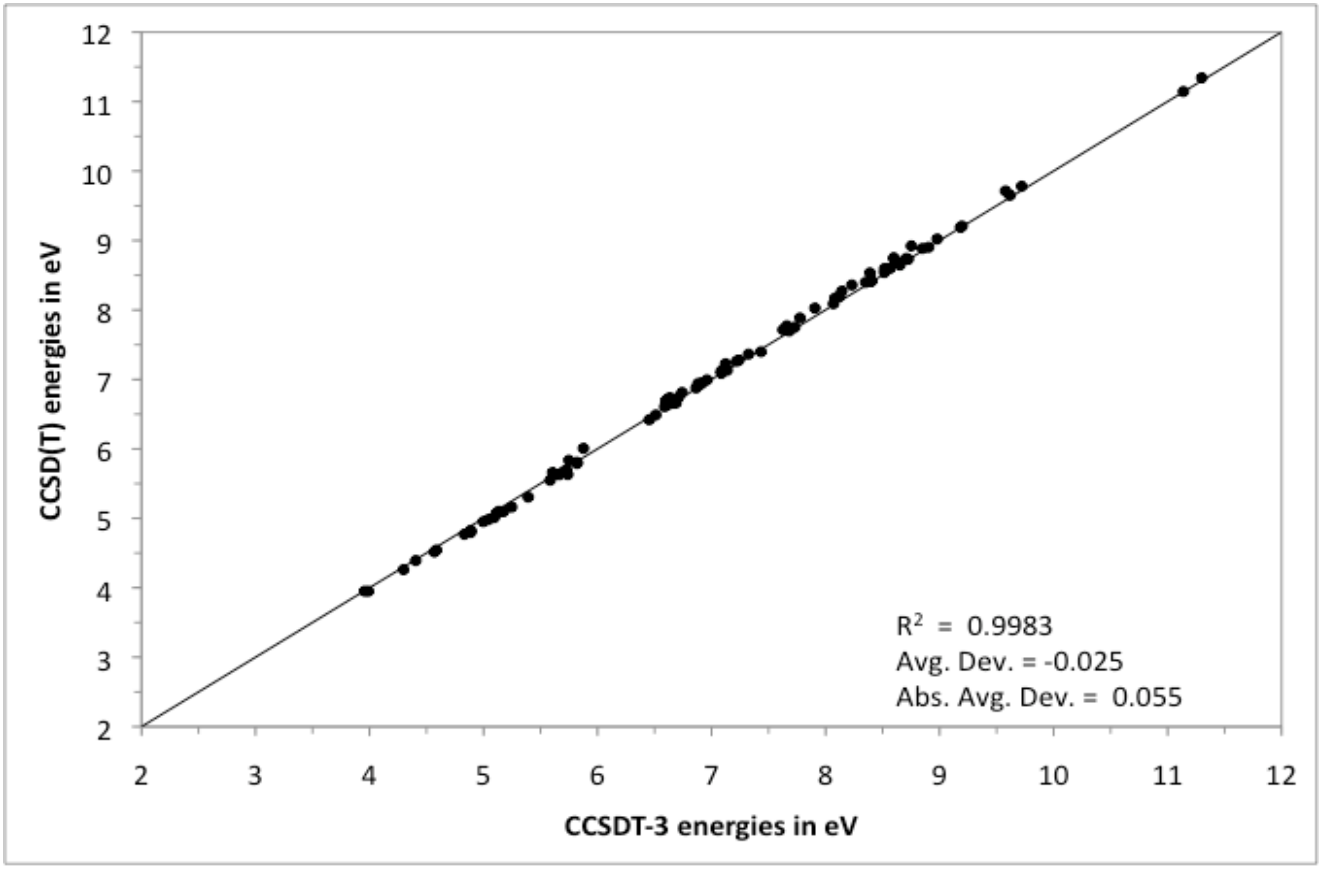
&O. Christiansen, et al J. Chem. Phys. (1997)

EOM-CCSD vs. EOM-CCSDT-3



Reference results, Sauer, Schreiber, Silva-Junior, Thiel, JCTC (2009).

EOM-CCSD(T) vs. EOM-CCSDT-3



Reference results, Sauer, Schreiber, Silva-Junior, Thiel, JCTC (2009).

Example VI.“Strong Correlation” and MR Character

Choice of Reference Function and Bond Breaking Problems

- RHF
- ROHF
- UHF
- QRHF
- Brueckner
- Natural
- KS
- Pccd (New!)

RHF CC vs. UHF CC for Diatomic Molecules

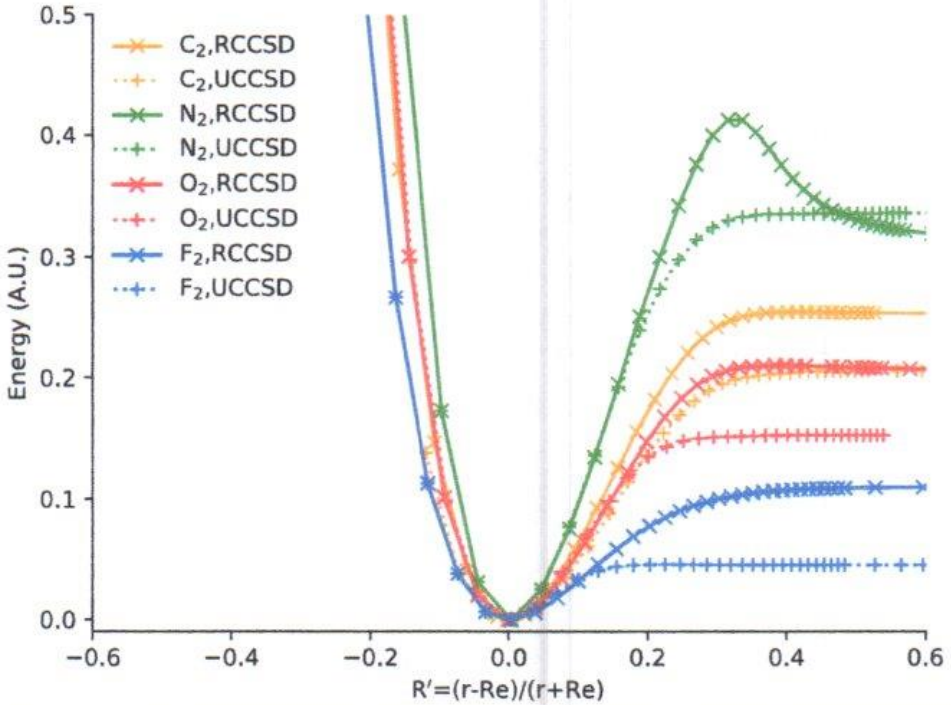
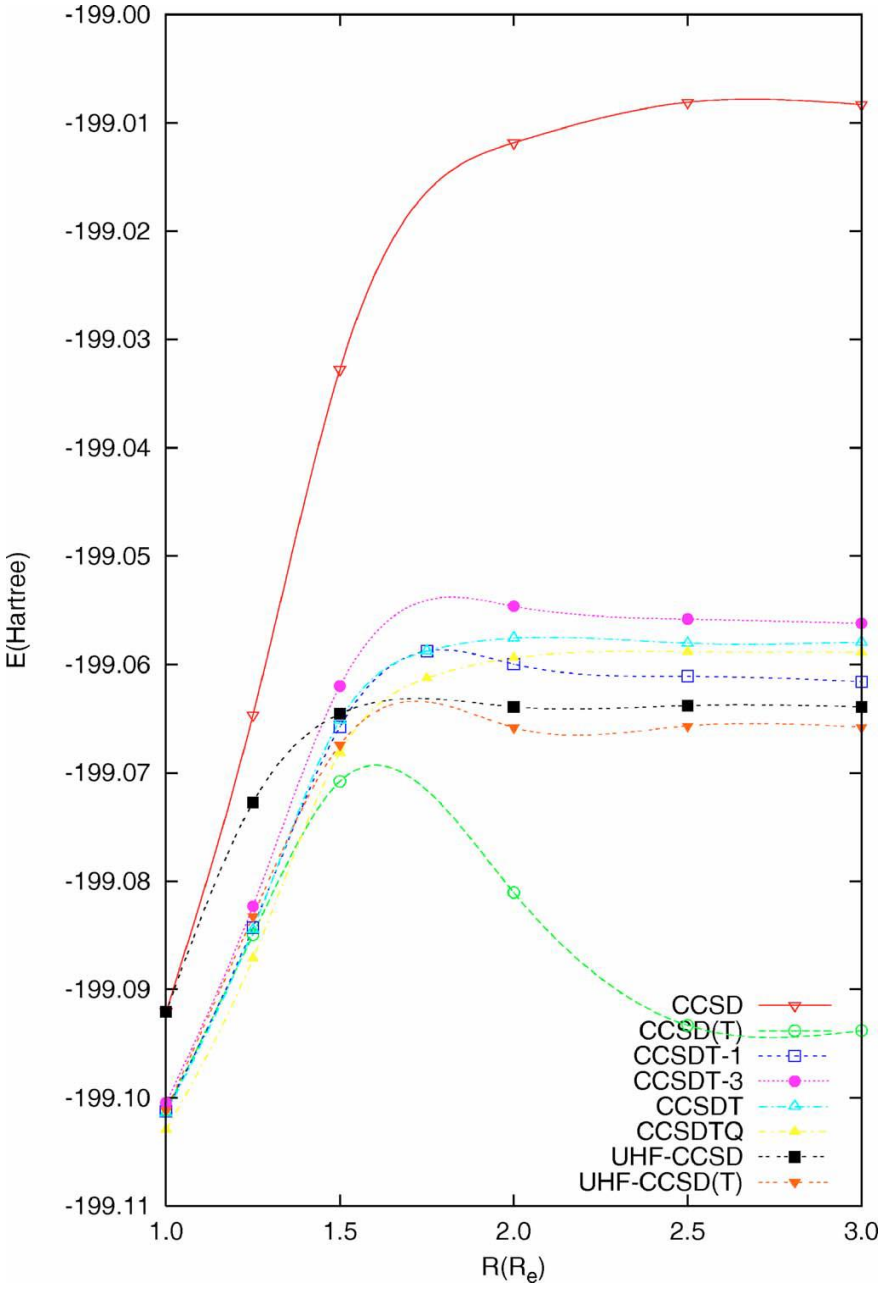
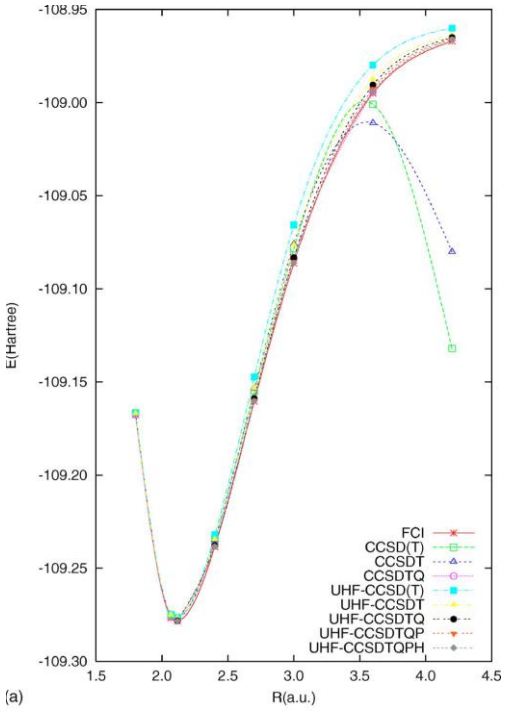


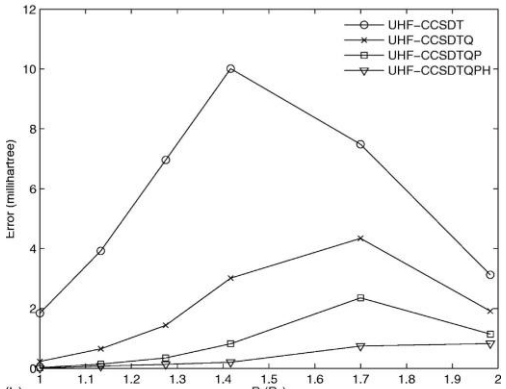
FIG. 14. PESs of diatomic molecules. The x axis (r′) is the distance with respect to the stable bond length (Re). The $^1\Delta_g$ state is used for O_2 RHF-CCSD.

F_2 Potential Curves



UHF vs. RHF for N_2 PES





Chan, Kallay, Gauss
JCP (2004)

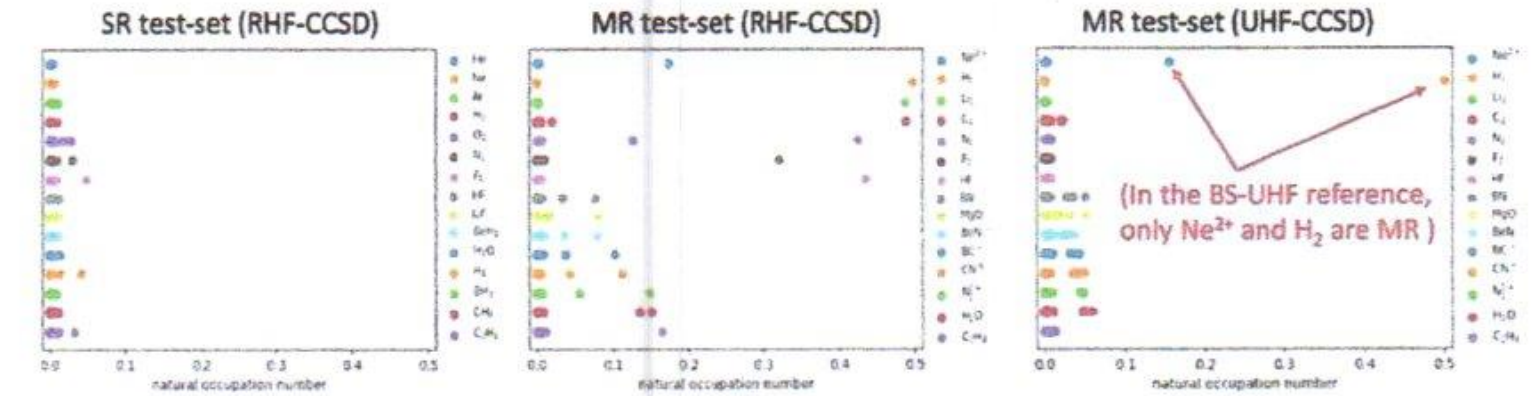


Fig. 2 Plots of NON, the largest virtual orbital natural occupation number vs. for a series of molecules deemed SR, and a set termed MR, at the RHF-CCSD level. For the MR set, these are compared to the NON from UHF-CCSD.

Exploiting different particle numbers for MR: DIP, DEA

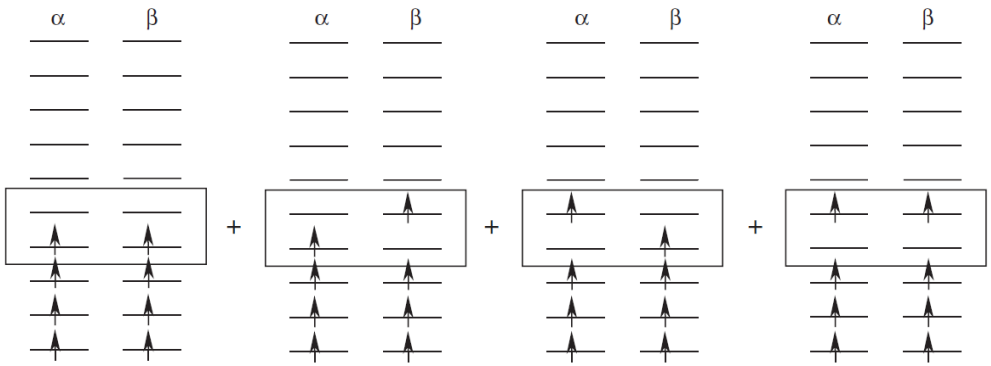


FIG. 1. Orbital occupancy and associated determinants for two electrons in two spatial orbitals.

The EOM-CC equations are

$$[\overline{H}, \widehat{R}_k]\Phi_0 = \omega_k \widehat{R}_k \Phi_0 \,\forall k, \tag{3}$$

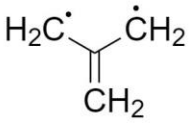
$$\overline{\mathbf{H}}\mathbf{R} = \mathbf{R}\omega \quad . \tag{4}$$

We choose to introduce a vacuum for N +2 electrons
And then depend upon the double ionization operator
To remove two of them to introduce all four determinants
In Fig. 1 in an equivalent manner.

Singlet-Triplet gap of 2 by 2 multi-reference molecules

CH_2:

Methylene

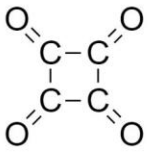


Trimethylenemethane (TMM)

ortho-Benzyne

meta-Benzyne

para-Benzyne



cyclobutane-1,2,3,4-tetraone

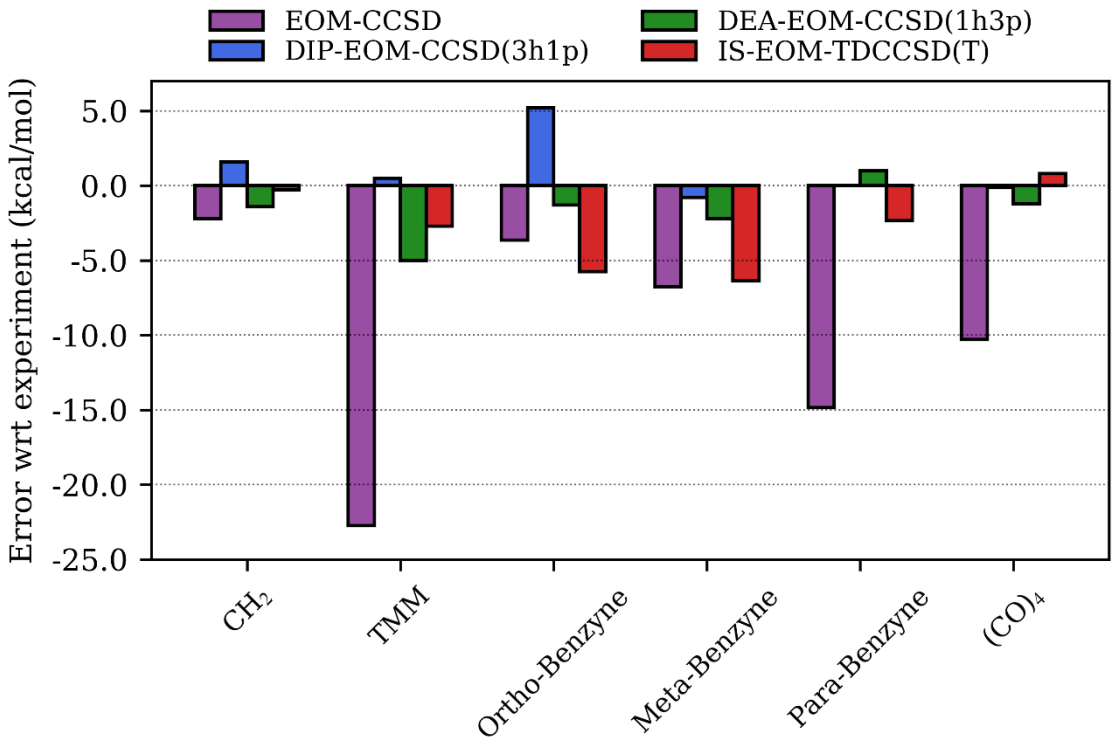
Multi-reference Index (MRI)

	MRI	Highest unoccupied NON
CH2	0.9074	0.0656
TMM	-0.9996	0.4076
ortho-Benzyne	0.0254	0.1182
meta-Benzyne	-0.8121	0.1571
para-Benzyne	-0.9991	0.3482
$(CO)_4$	0.2389	0.1230

*MRI and NON obtained from 1-DM of CCSD

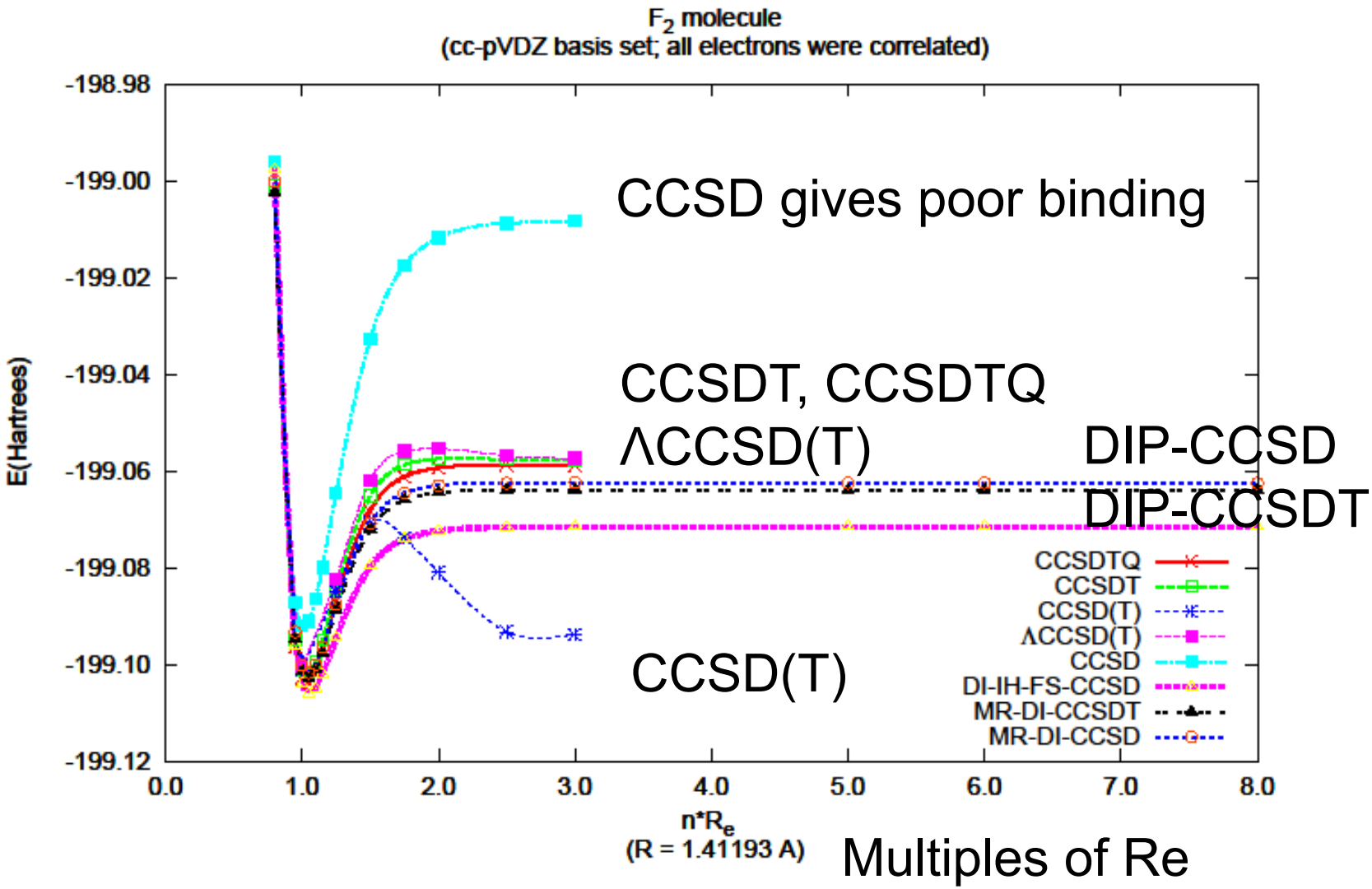
- Perera, Ajith, et al. *Isaiah Shavitt*. Springer, Berlin, Heidelberg, 2016. 153-165.
- R.J. Bartlett, et. al. JCP, 2020, “Index of multi-determinantal and multi-reference character in coupled-cluster theory”

Adiabatic Singlet-Triplet gap with other EOM based methods

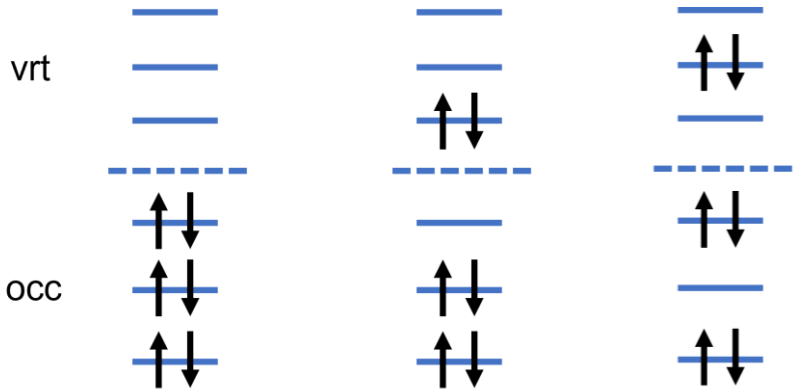


* DIP-EOM and DEA-EOM values taken from Perera, Ajith, et al. *Isaiah Shavitt*. Springer, Berlin, Heidelberg, 2016. 153-165.

Transition to DIP/DEA MR Methods



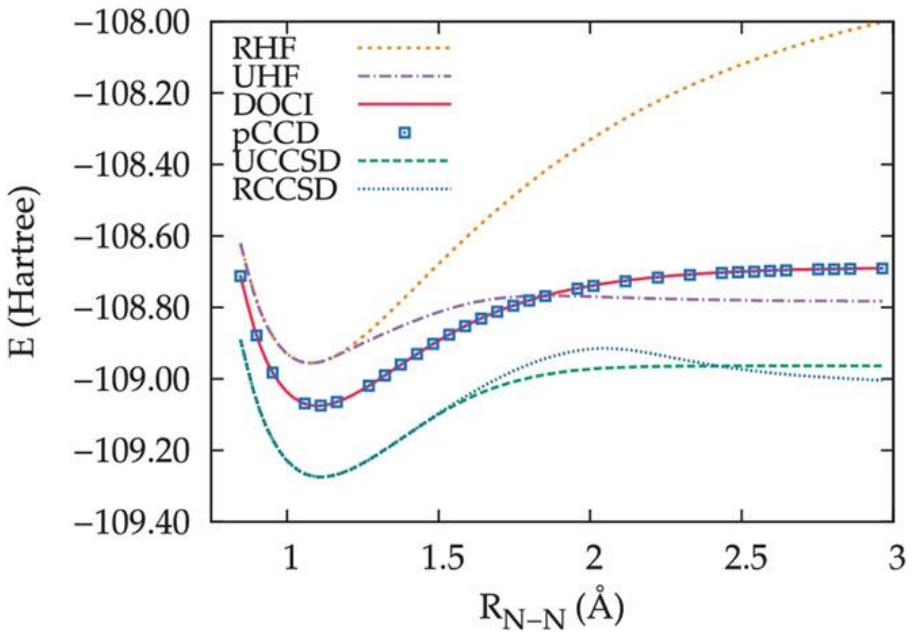
A New Reference Function: Pair CCD (pCCD)



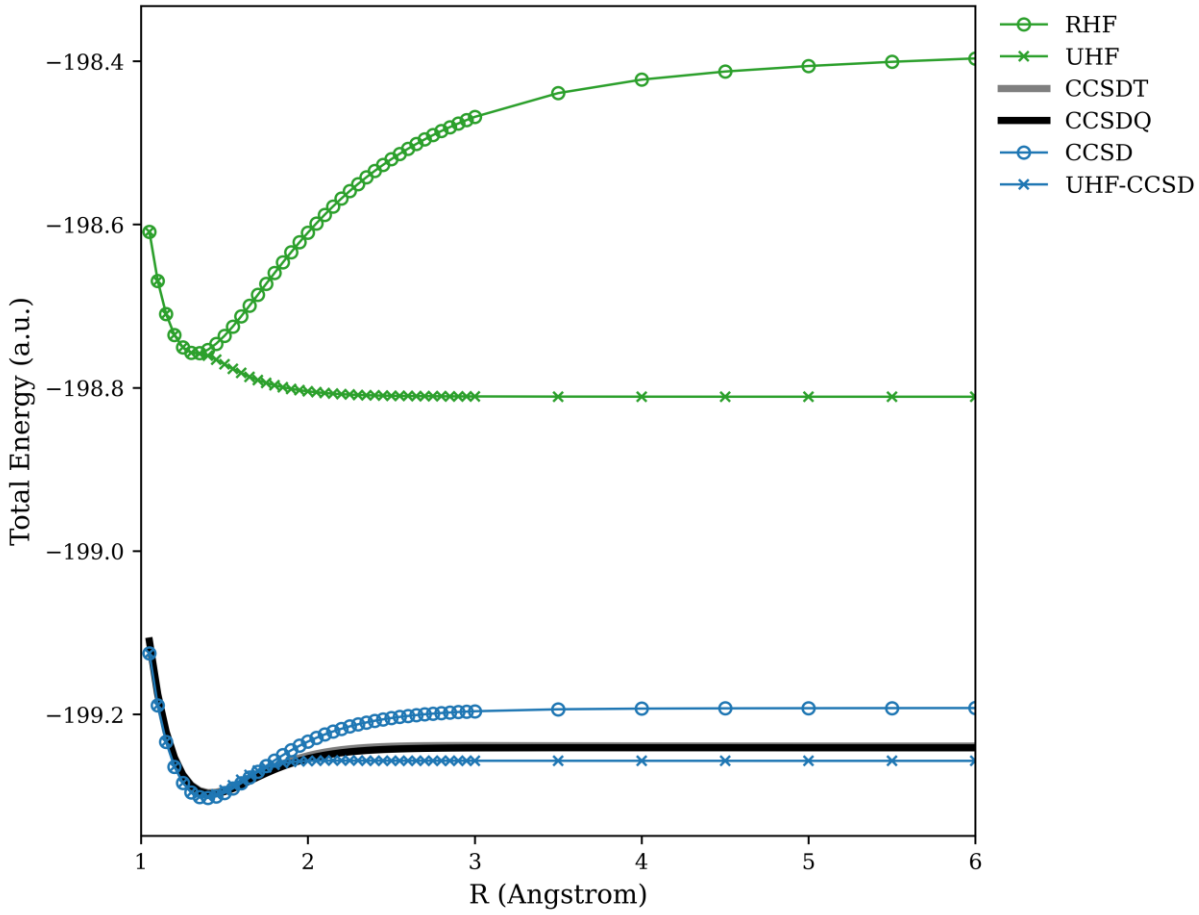
$$|\psi_{pCCD}\rangle = exp(\hat{T}_2^{(pair)})|\phi_0\rangle \equiv |\psi_{GVB}\rangle$$

* J. Cullen, Chem. Phys. **202**, 217–229 (1996).

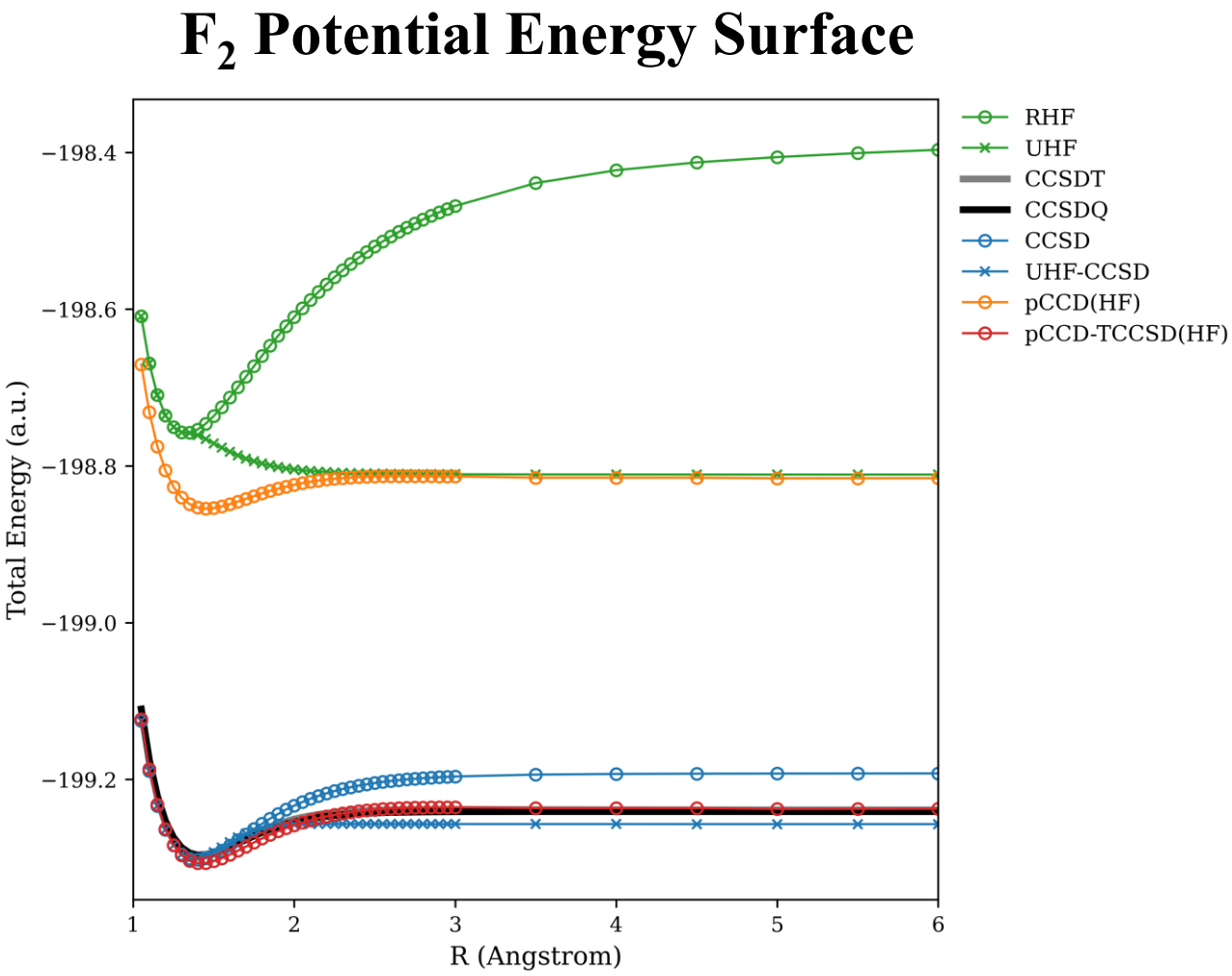
Pccd compared to UHF-CCSD



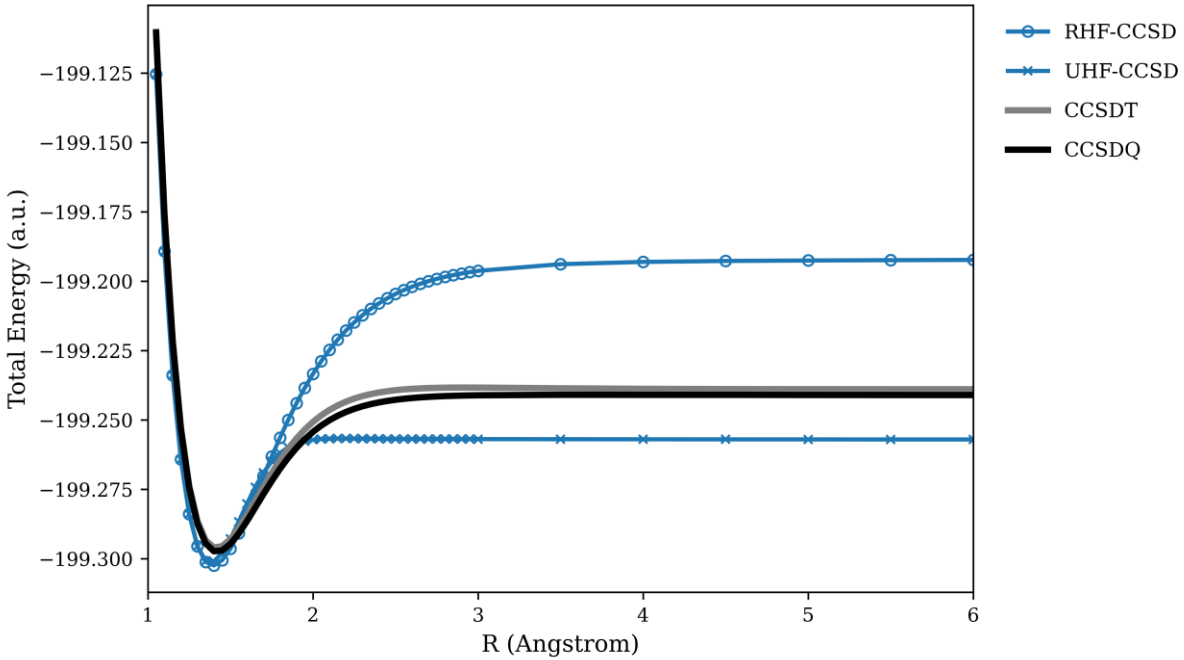
F_2 Potential Energy Surface



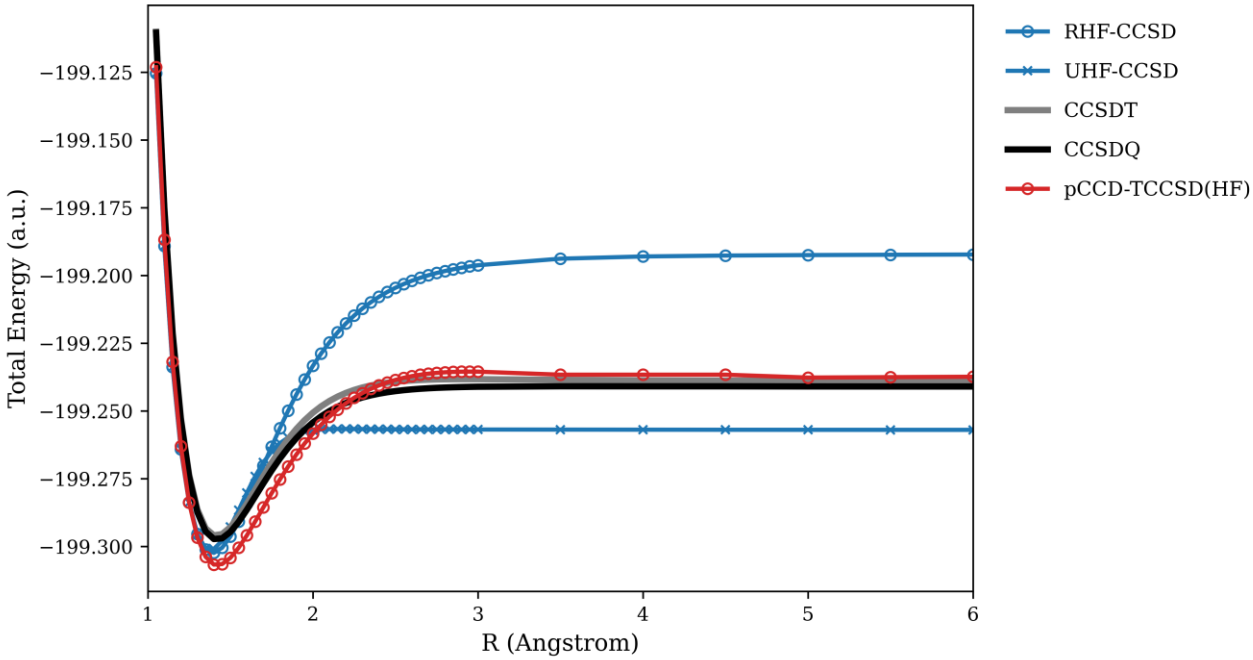
pCCD reference



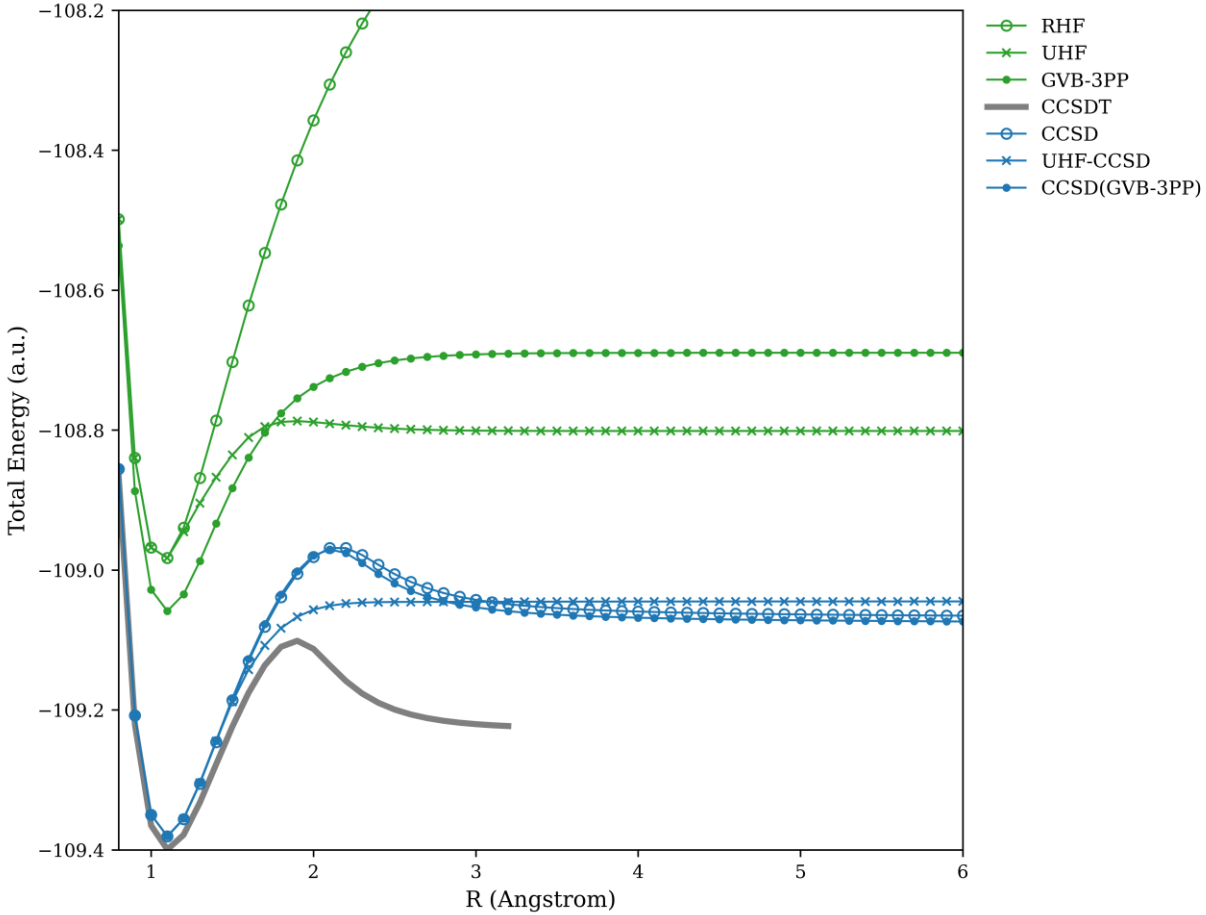
F_2 Potential Energy Surface



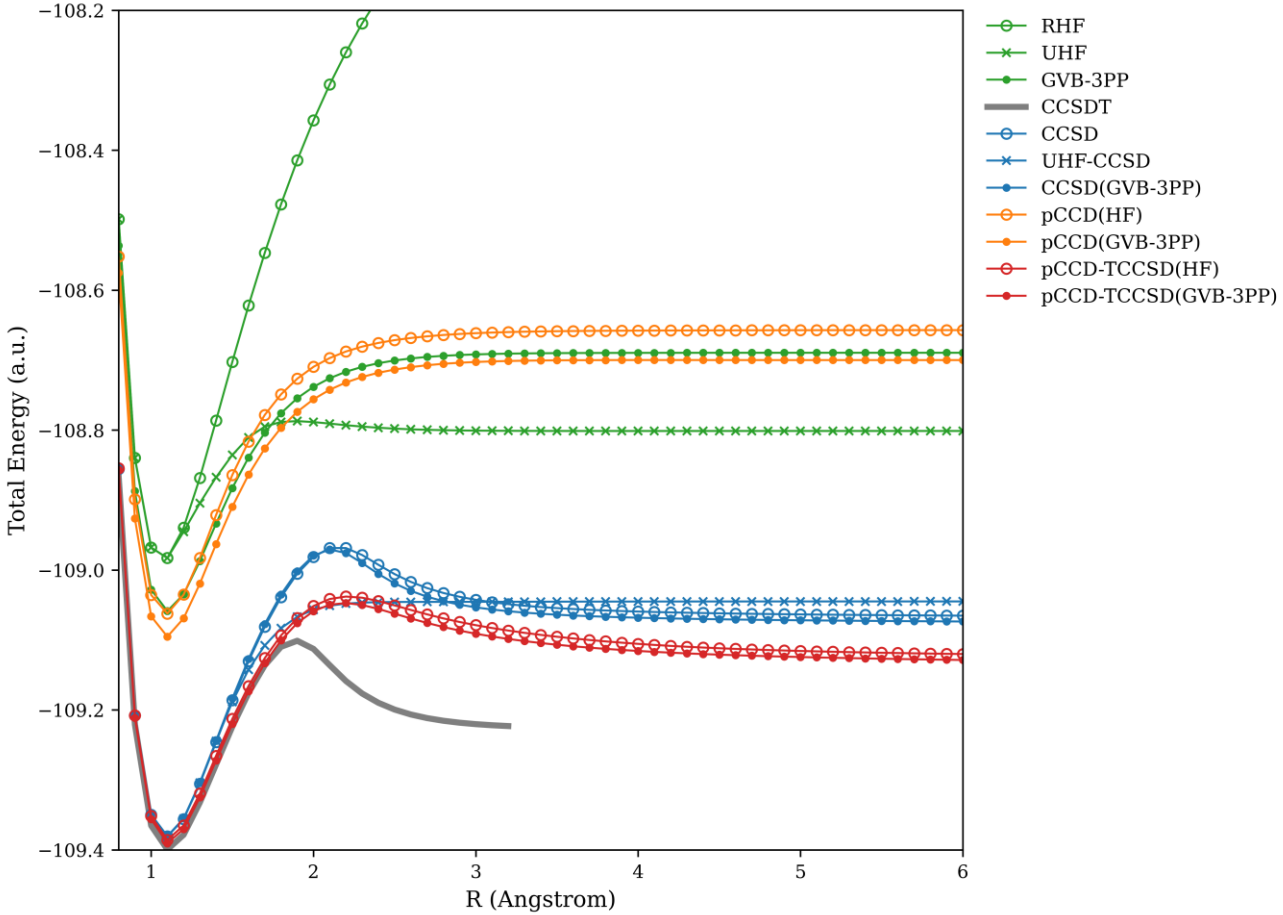
F_2 Potential Energy Surface



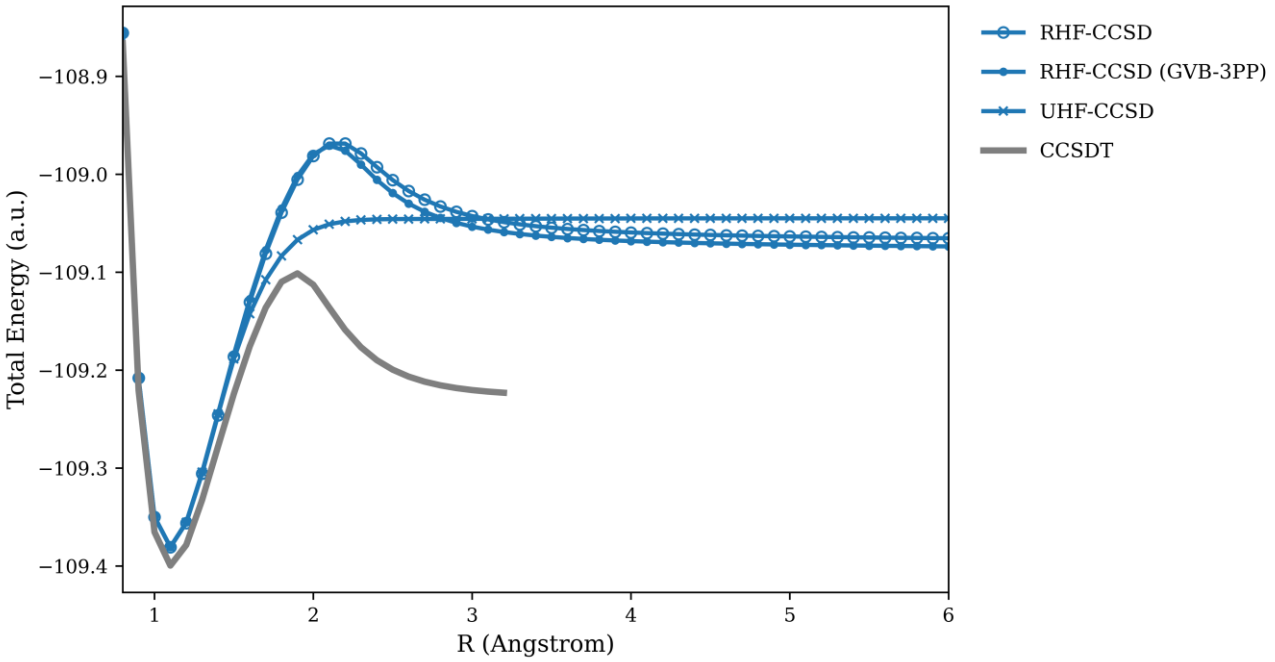
N_2 Potential Energy Surface



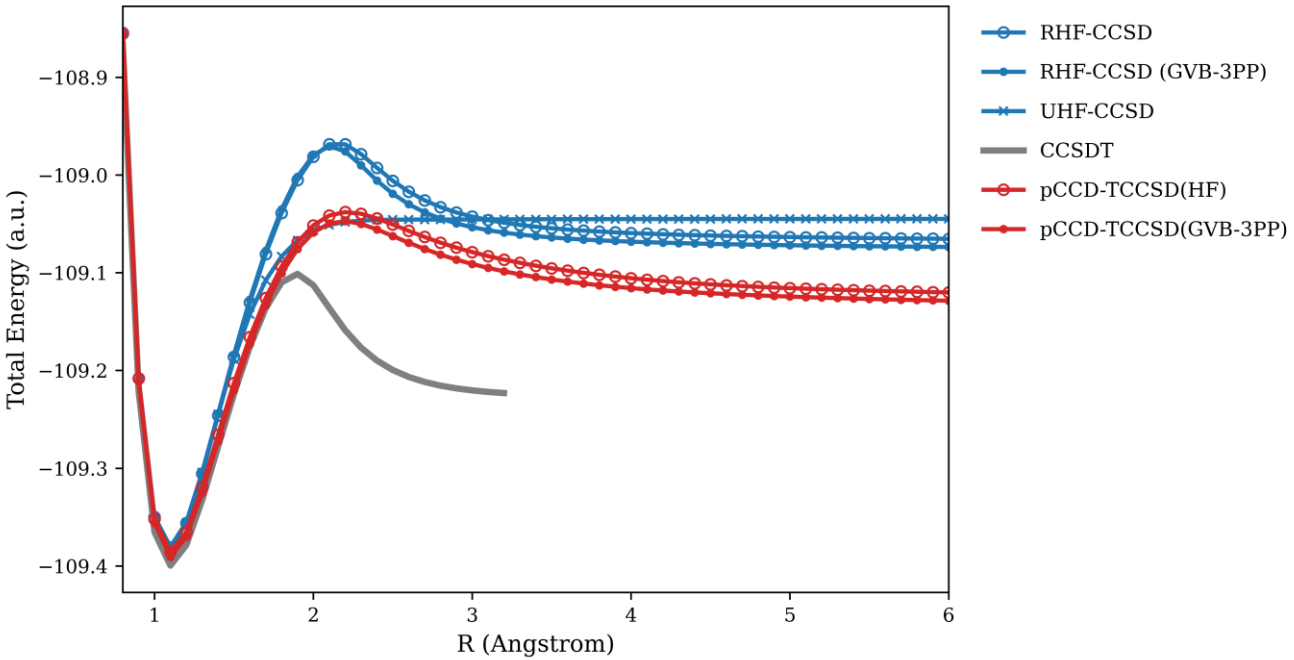
N_2 Potential Energy Surface



N_2 Potential Energy Surface



N_2 Potential Energy Surface



Excited states in Coupled cluster (CC) theory with EOM ansatz

Singly Excited states:

- EOM-CCSD is well established for singly excited states for single reference molecules with error from 0.1 to 0.3 eV.

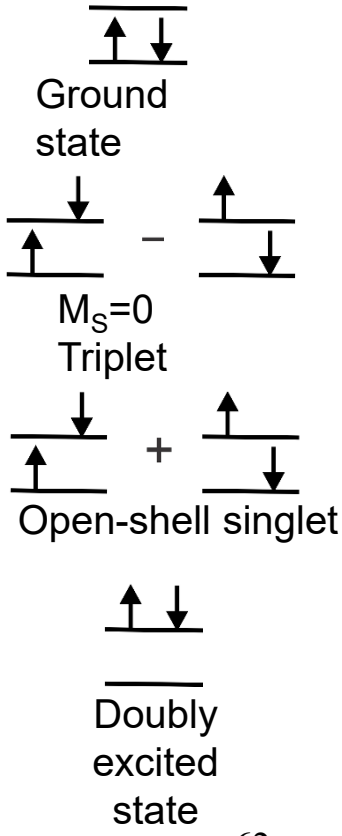
Doubly excited states:

- EOM-CCSD error is usually greater than 1 eV.
- Partial double excitation character can also lead to large error Example: spin multiplets

Excited states of multi-reference molecules:

- EOM-CCSD on a reference function with multireference character can result in a large error for the excitation energies of a molecule.

All the above-mentioned problems are fixed with CCSDT and CCSDTQ which scales as n^8 and n^{10} respectively, while EOM-CCSD that scales as n^6 .



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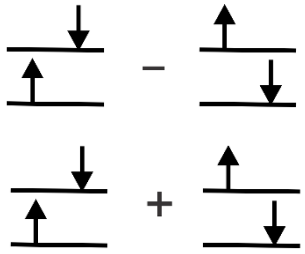
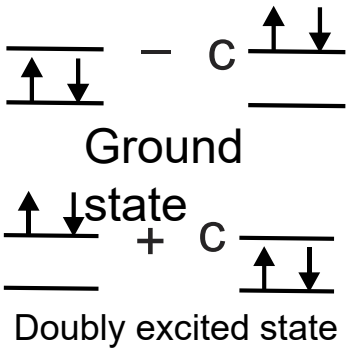
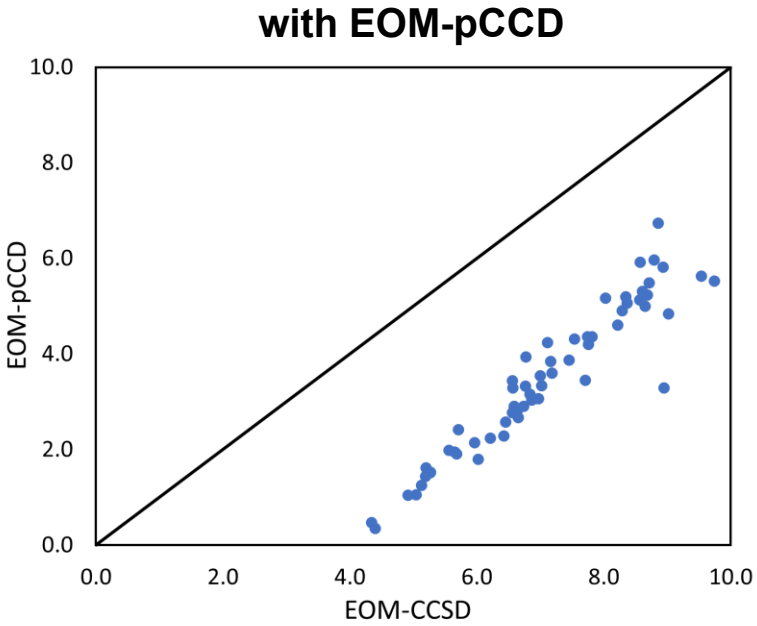
Static correlation:

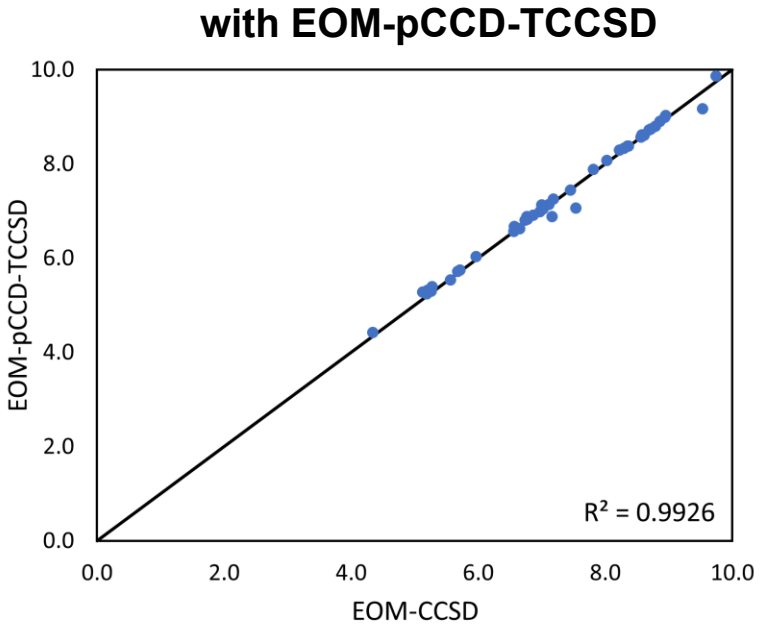


Non-dynamic correlation

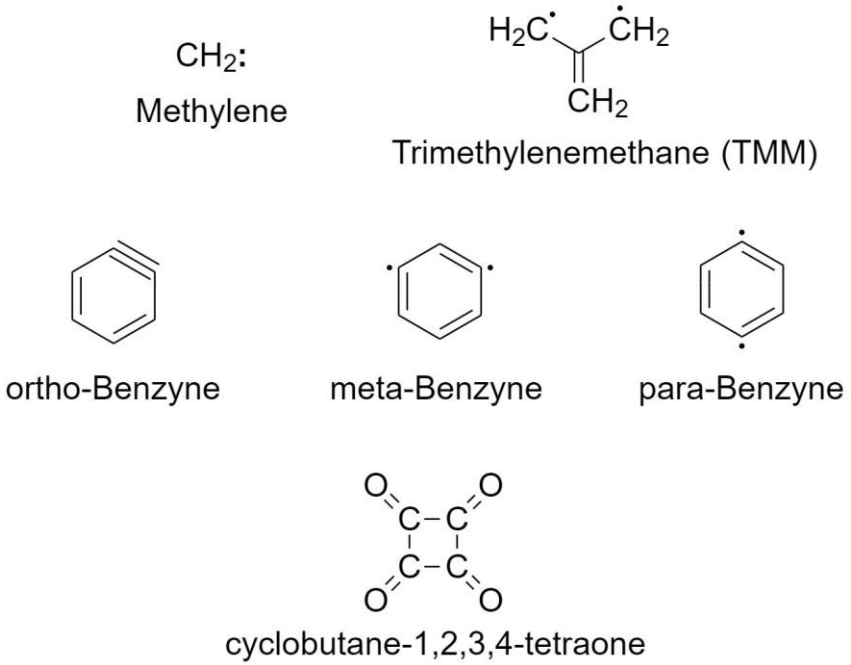


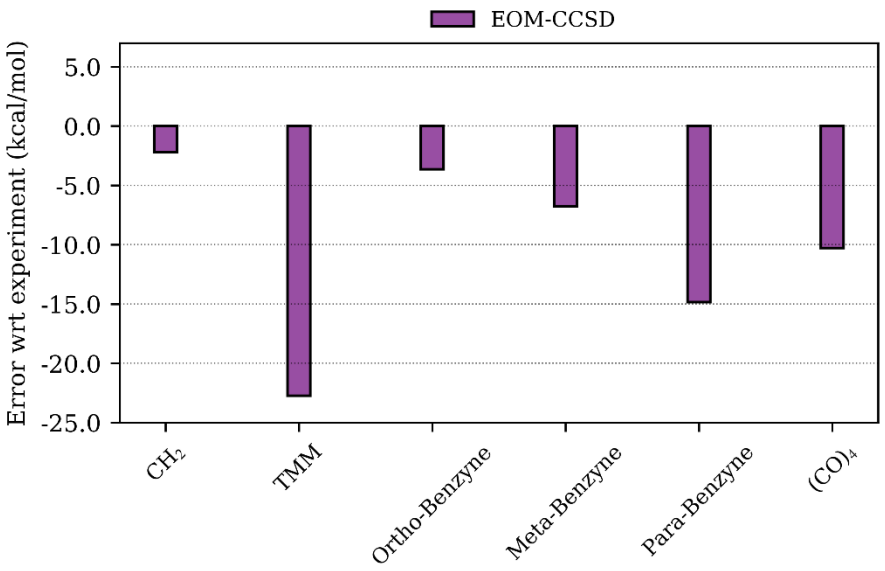
Singly excited states





Singlet-Triplet gap of 2 by 2 multi-reference molecules with EOM-CCSD





- Perera, Ajith, et al. *Isaiah Shavitt*. Springer, Berlin, Heidelberg, 2016. 153-165.

Adiabatic Singlet-Triplet gap with EOM-pCCD-TCCSD

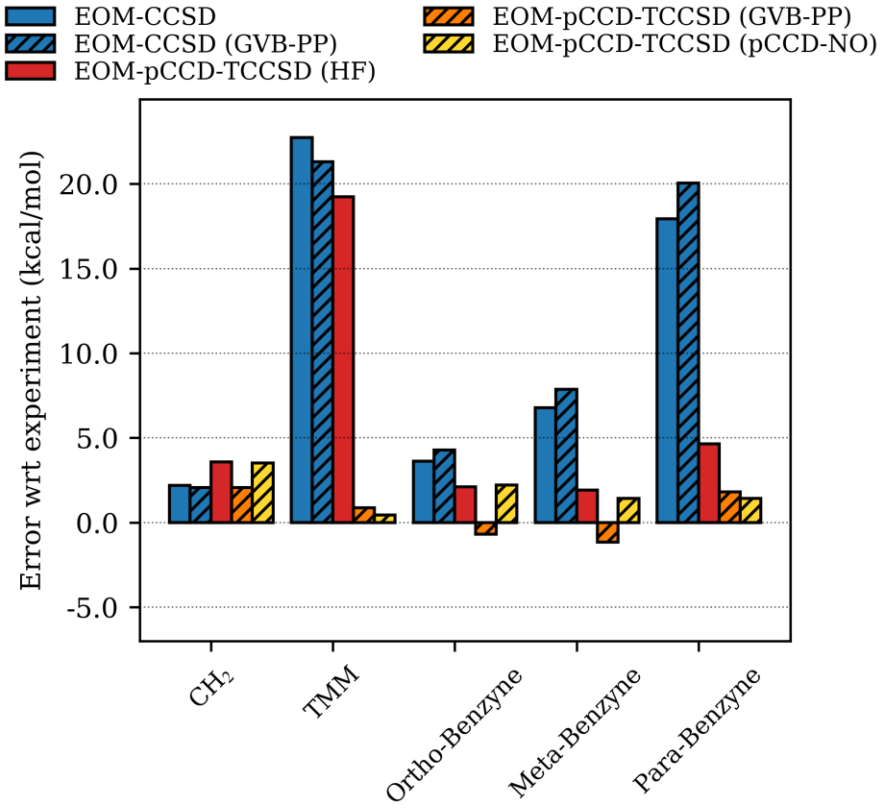


TABLE II. Adiabatic singlet–triplet gap obtained with EOM-pCCD-TCCSD using HF, GVB-PP, and pCCD natural orbitals in kcal/mol.

Molecules	EOM-CCSD (HF)	EOM-CCSD (GVB-PP)	EOM-pCCD-TCCSD (HF)	EOM-pCCD-TCCSD (GVB-PP)	EOM-pCCD-TCCSD (pCCD NO)	Expt.-ZPE-core[a]
CH_2	−11.2	−11.1	−12.6	−11.0	−12.5	−8.99
TMM	−42.1	−40.7	−38.6	−20.3	−19.9	−19.4
Ortho-benzyne	33.8	33.1	35.3	38.1	35.2	37.4 ± 0.3
Meta-benzyne	13.7	12.6	18.6	21.7	19.1	20.5 ± 0.3
Para-benzyne	−13.5	−15.7	−0.2	2.6	3.0	4.4 ± 0.3

[a]Taken from Ref. 33.

CONCLUSIONS

- CC theory now provides the computational benchmark for most of molecular theory.
- Like all *ab initio* methods it is systematically improvable to the exact result in the basis set, correlation limit. (This feature is very different than DFT!).
- For relativistic effects it is used for solutions of the Dirac equation in 1,2 and 4 component forms.
- It is used with explicit consideration of inter-electronic interactions, F12, to more rapidly approach the basis set limit.
- With recent developments, it now offers solutions for essentially all problems encountered for molecules, and now for many MR problems. MIP/MEA-EOM-CC is operationally SR, so suits 'black-box' implementation and calibration.
- The pCCD + TCCSD method is another, operationally 'black-box' SR-CC method that accounts for MR effects.
- It has been applied to polymers and now being used for 2 and 3 dim systems subject to periodic boundary conditions for the wavefunction. CC is doing band structure and all traditional condensed matter applications.
- With the development of the massively parallel ACES III, CC theory and all of its applications are poised to be applied routinely to ~100 atoms, ~500 electrons, ~3000 basis functions.

Example VII. Correlated one-particle theory (COT)

How often do you hear that DFT and its KS implementation need a new idea?

The following presents an alternative approach to an

exact-one particle correlation theory that comes from CC theory.

CC theory to COT

$h^{eff}(1)\varphi_p(1) = \varepsilon_p \varphi_p(1)$

$\Phi_0 = A(\varphi_1(1)\ \varphi_2(2)\ldots\ \varphi_n(n))$

$h^{eff}(1) = t(1)+v(1)+J(1)+V_x(1)+V_c(1)$

Our objective is to find a $V_x(1)+ V_c(1)$ where this is an effective one-particle operator that accounts for electron exchange and correlation, familiar from KS DFT, but we also want to do this in WFT. We build a "constructive proof", not an existence one.

First, start with the Dyson eqn and one-particle Greens' Fxns. Solns have to give Ip, and Ea.
Second, insert a CC ground state into the Dyson eqn, to decouple the I and A parts of the Greens' Fxn.and remove the frequency dependence. This step degenerates into IP-EA/EOM-CC so results must be exact in FCI limit. This is COT.
Third, take this *ab initio* COT and project it onto KS-DFT to provide rapid calcs. (Define QTP functionals) that must satisfy Bartlett's theorem for coorelated orbitals..
COT orbitals have eigenvalues for all principal levels hat correspond to exp.

1. The oldest realization of such a correlation potential is the self-energy of the Dyson Eqn.

$$[h+J-K+\Sigma(1,\omega)]\,\phi_p = [f + \Sigma(1,\omega)]\,\phi_p = \omega_p\,\phi_p$$

(1) The problem with solving this eqn. for our purposes is the frequency dependence, ω, as the solutions, $\phi_{p,}$ are only obtained when $\omega = \omega_p$.

(2) This also causes the self-energy, correlation potential, $\Sigma(1,\omega_p)$ to differ for every orbital as in Hartree-theory, making the (Dyson) orbitals obtained non-orthogonal and over determined.

(3) When used to evaluate the Greens' Fxn the Ip and Ea parts are coupled, contrary to the fact they correspond to different electron numbers

2. The CC and EOM-CC method provide a better route toward a correlation potential.

The CC ground state wavefxn, $\Psi_{CC} = \exp(T)\Phi_0$, causes the Ip and Ea parts of the electron-propagator to decouple, so they can be treated independently.

L. Meissner, RJB (1993)
M. Nooijen J. Snidjers (1992}

Then the electron-propagator can be built by solving the EOM-CC equations separately for the I and A parts, which provide the frequencies as eigenvalues.

$$\bar{H} R_k^I \Phi_0 = \omega_k^I R_k^I \Phi_0 \qquad \bar{H} = \exp(-T) H \exp(T)$$

$$\bar{H} R_k^A \Phi_0 = \omega_k^A R_k^A \Phi_0$$

The total energy is $\bar{H}\Phi_0 = E\Phi_0$

But the good thing is that some of the ω_p's must be exactly the ionization potentials and electron affinities for the 1h and 1p states. Hence, Bartlett's theorem: COT correlated orbitals must offer correct IP/s (EA's) in the FCI limit.

The bad thing is those Ip's and Ea's also include 2h1p, 2p1h, etc resonances. This is great for interpretation of PES, but bad
for generating n-orbitals to define a correlated orbital
effective
Hamiltonian problem, our objective.

Thus, the expression for the correlated one particle theory,

$$h^{eff}(1) = f(1) + \Sigma_{cc}(1) = h(1) + J(1) - K(1) + \Sigma_{cc}(1)$$

$$h^{eff}\varphi_P(1) = \varepsilon_p \varphi_P(1)$$

$$\Sigma_{cc}(1) = V_C(1) \quad \text{'COP'}$$

$\Sigma_{cc}(1)$ is a frequency independent self-energy/correlation potential--
-
expressed in terms of T and R. (RJB, Frontiers Article, CPL, 2009.)

ε_i=-I(i) , the exact principal Ip's for occ orbitals
ε_a=A(a), the Ea's, for bound unoccupied orbitals

Orbitals are biorthogonal in the most general case
This gives us a model COT that we can try to emulate using elements of KS-DFT.

.

MAD of eigenvalues compared to EOM-CCSD/cc-pVTZ basis sets (eV).

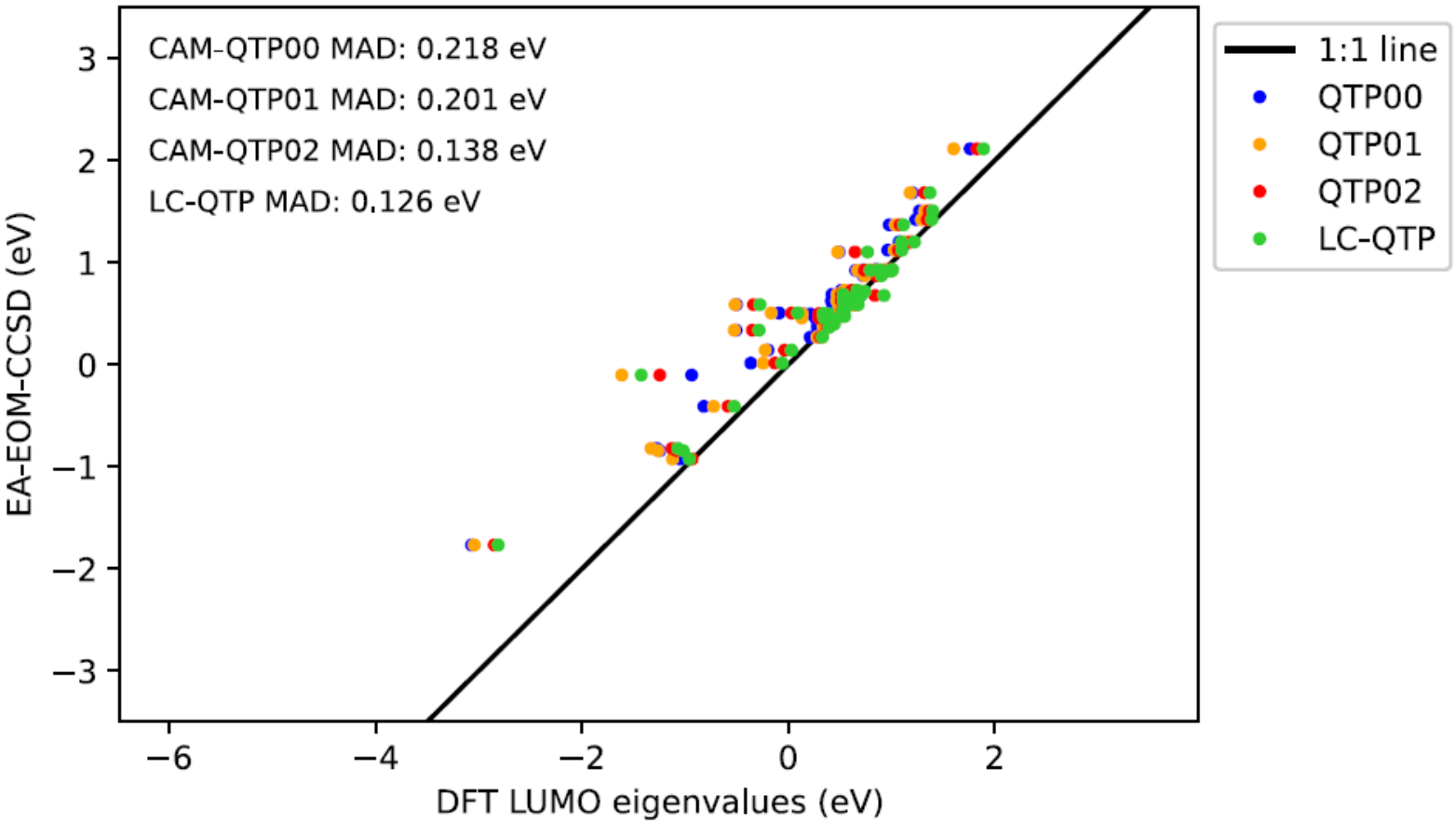
	401IP	HOMO
LDA	4.84	4.34
B3LYP	3.44	3.23
CAM-B3LYP	1.55	1.51
QTP00	0.65	0.32
QTP01	0.31	0.29
QTP02	0.34	0.24
LC-QTP	0.49	0.33
HF	1.69	0.76
EKT(CCSD)	0.80	0.34

Ranasinghe, Margraf, Perera, and Bartlett, J. Chem. Phys. 150, 074108, 2019.

MAD of eigenvalues compared to experimental IP values (eV).

	401IP	HOMO
LDA	4.66	4.33
B3LYP	3.26	3.23
CAM-B3LYP	1.37	1.50
QTP00	0.81	0.32
QTP01	0.40	0.30
QTP02	0.49	0.25
LC-QTP	0.65	0.35
HF	1.86	0.74
EKT(CCSD)	0.97	0.35

Ranasinghe, Margraf, Perera, and Bartlett, J. Chem. Phys. 150, 074108, 2019.



QTP DFT LUMO energies vs EA-EOM-CCSD/aug-cc-pVTZ . Test set composed of 63 EA values.

A. Pavlicek, Z. W. Windom, A. Perera, and R. J. Bartlett, J. Chem. Phys. **160**, 014106 (2024)

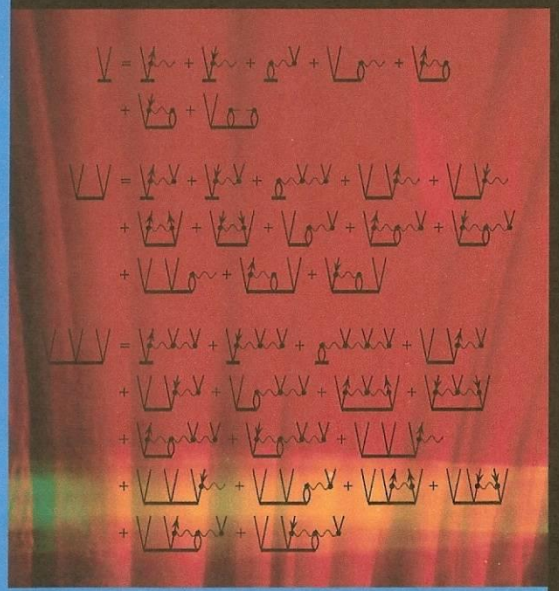
CONCLUSIONS

- CC theory now provides the computational benchmark for most of molecular theory.
- Like all *ab initio* methods it is systematically improvable to the exact result in the basis set, correlation limit. (This feature is very different than DFT!).
- For relativistic effects it is used for solutions of the Dirac equation in 1,2 and 4 component forms.
- It is used with explicit consideration of inter-electronic interactions, F12, to more rapidly approach the basis set limit.
- With recent developments, it now offers solutions for essentially all problems encountered for molecules, and now for many MR problems. MIP/MEA-EOM-CC is operationally SR, so suits ‘black-boximplementation and calibration.
- It has been applied to polymers and now being used for 2 and 3 dim systems subject to periodic boundary conditions for the wavefunction.
- Various kinds of linear scaled implementations exist (Werner, Neese, Flocke+RJB)
- With the development of ACES III, CC theory and all of its applications are poised to be applied to ~100 atoms, ~500 electrons, ~3000 basis functions.

Many-Body Methods in Chemistry and Physics

MBPT and Coupled-Cluster Theory

Isaiah Shavitt and Rodney J. Bartlett



CAMBRIDGE MOLECULAR SCIENCE

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RJB, “How and Why Coupled-cluster Theory Became the Pre-eminent Method in *Ab Initio* Quantum Chemistry?” in *Theory and Applications of Computational Chemistry: The First Forty Years,* (C. Dykstra, G. Frenking, K. Kim and G. Scuseria, editors) Elsevier, 1191-1221 (2005).

RJB and M. Musial, “Coupled-cluster theory in quantum chemistry”, Revs. of Modern Phys. **79,** 291-352 (2007).

I. Shavitt and RJB, “Many-Body Methods in Chemistry and Physics: Many-body Perturbation Theory and Coupled-cluster Methods,” Cambridge Press, 2009.

THANK YOU VERY MUCH!

OUTLINE

I. RSPT→MBPT→exp wavefxn.

Infinite order summation of MBPT.

Extensivity.

Ultimate objective is the full CI, $\Psi_{CI} = \Phi_0 + \Sigma_k^n \Phi_k C_k$, without restriction in excitations up to 'n', the number of electrons.

$\Psi_{CC} = \exp(T)\,\Phi_0 = 1 + T + T^2/2 + T^3/3! + \ldots$

$T = T_1 + T_2 + T_3 + T_4 + \ldots$

Decomposition of CI excitations

$C_2 = T_2 + T_1^2/2$,

$C_3 = T_3 + T_1T_2 + T_1^3/3!$,

$C_4 = T_4 + T_2^2/2 + T_1T_3 + T_1^2T_2/2 + T_1^4/4!$, ...

II. Basic CCD eqns,

Diagrammatic # 10 Diagrams Scaling ~M^6

Algebraic Interpretation

Already includes disconnected quadruples from T_2^2. Physically these are simultaneous doubles, not T_4.

III. Singles; CCSD.

45 Diagrams. Scaling ~M^6

Numerical Illustrations. Insensitive to orbital choice. Numerically important for properties. Can be large for non-HF orbital choices.

IV. Triples; CCSDT.

54 Diagrams. Scaling ~M^8

Since most of CI quadruples come from T_2^2, with HF ref all in fourth -order MBPT, T_3 is most important numerical correction after CCSD.

CCSDT-1, CCSDT-3, CCSD(T) approximations. Scaling, ~M^7

V. Quadruples, CCSDTQ.

81 Diagrams Scaling ~M^{10}

Particularly important when one ref fxn strongly interacts with another determinant (multi-ref example like GVB)

CCSDT(Q_f) approximation. Scaling ~M^7

VI. Analytic gradients and Density matrices. CC functional.

Generalized Hellman-Feynman Theorem

Analytical gradients to search energy surfaces, properties

Illustrations

VII. EOM-CC for excited, ionized, doubly ionized and electron attached and DEA states.

EOM-CCSD(T), EOM-CCSDT-3, EOM-CCSDT

Illustrations.

VIII. Importance of the reference function

Possible reference functions:

RHF, ROHF, UHF, Bruckner, Natural, QRHF, KS, Localized, and Pccd is a new one.

Illustrations

IX. What constitutes "Strong Correlation"?

Some Accommodations for MR situations.

UHF, ΛCCSD(T), DIP, DEA, pCCD

Measure MR Character

Applications to bond breaking.

Illustrations

X. Alternative Ansatz. Unitary CC (UCC)

For quantum computers

Simplicity for Gradients and Properties

Illustrations

XI. Correlated Orbital Theory (COT) and DFT

From the IP/EA-EOM-CC eqns, one can create a correlated one-particle theory (COT).

This is the wavefxn analogue of Kohn-Sham DFT without any direct dependence on the density or use of KS theorems.

Instead, it depends on what we call the CC self-energy, $\Sigma_{cc}(1)$. A one-particle operator defined diagrammatically.

But by choosing well-known DFT expressions like LR(ω)-PBE or CAM B3LYP, one can replace $\Sigma_{cc}(1)$, by a Vxc (ρ, Δρ), and minimum parameterization, to ensure satisfaction of the COT condition that the orbital eigenvalues must correspond to principal IP's and EA's.

This IP-eigenvalue theorem is the *correlated orbital equivalent* of Koopmans' thm in HF.

When we do this, we obtain the (minimally parameterized) QTP family of density functionals.

Illustrations.

Useful Sources:

R. J. Bartlett and M. Musial, Reviews of Modern Physics, **79,** 291-352 (2007).

I. Shavitt and R. J. Bartlett, "Many-body methods in Chemistry and Physics, MBPT and Coupled-cluster Theory, " Cambridge Press, (2009)

RJB, FOREWARD: Some thoughts on coupled-cluster theory for electron correlation from single reference to multireference to "Strong Electron Correlation." What does the latter truly mean? in "Novel Treatments of Strong Correlation", Advances in Quantum Chemistry, vol. 90, Editors, Ramon Quintana and John Stanton, Series Editors, Erkki J. Brändas and Rodney J. Bartlett, Academic Press, (2024).

This Foreward might stimulate a discussion of 'Strong Correlation" from the viewpoint of chemists and physicists.

R. J. Bartlett, "Perspective on DFT: Adventures in DFT by a wavefunction theorist," J. Chem. Phys. **151**, 160901 (2019).

R. J. Bartlett, "Perspective on coupled-cluster theory: The evolution toward simplicity in quantum chemistry," Phys. Chem. Chem. Phys. **26**, 8013 (2024). DOI: 10.1039/d3cp03853

- CC theory now provides the computational benchmark for most of molecular theory.

- Like all *ab initio* methods it is systematically improvable to the exact result in the basis set, correlation limit. (This feature is very different than DFT!).

- For relativistic effects it is used for solutions of the Dirac equation in 1,2 and 4 component forms

- It is used with explicit consideration of inter-electronic interactions, F12, to more rapidly approach the basis set limit.

- UHF based CC correctly describes many MR problems, but still suffers from spin contamination warranting a 'break and restore strategy'.

- With recent developments, it now offers solutions for many MR problems. MIP/MEA-EOM-CC is operationally SR, so suits 'black-box' implementation and calibration.

- pCCD looks like a very useful new single ref that behaves like UHF, but with no symmetry breaking that when combined into pCCD+TCCSD, handles some MR issues also in an operationally SR form.

- CC has been applied to polymers, and is now being used for 2 and 3 dim systems subject to periodic boundary conditions for the wavefunction.

* Various kinds of linear scaled implementations exist (Werner, Neese, Flocke+RJB)

- With the development of ACES III, CC theory and all of its applications are poised to be applied to ~100 atoms, ~500 electrons, ~3000 basis functions.