THE NEXT STEP IN MOLECULAR COUPLED-CLUSTER THEORY:
STRUCTURE, PROPERTIES, AND EXCITED STATES

FIFTY YEARS OF COUPLED-CLUSTER THEORY
INSTITUTE OF NUCLEAR THEORY
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July 1, 2008

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Many co-workers

New Work: Andrew Taube

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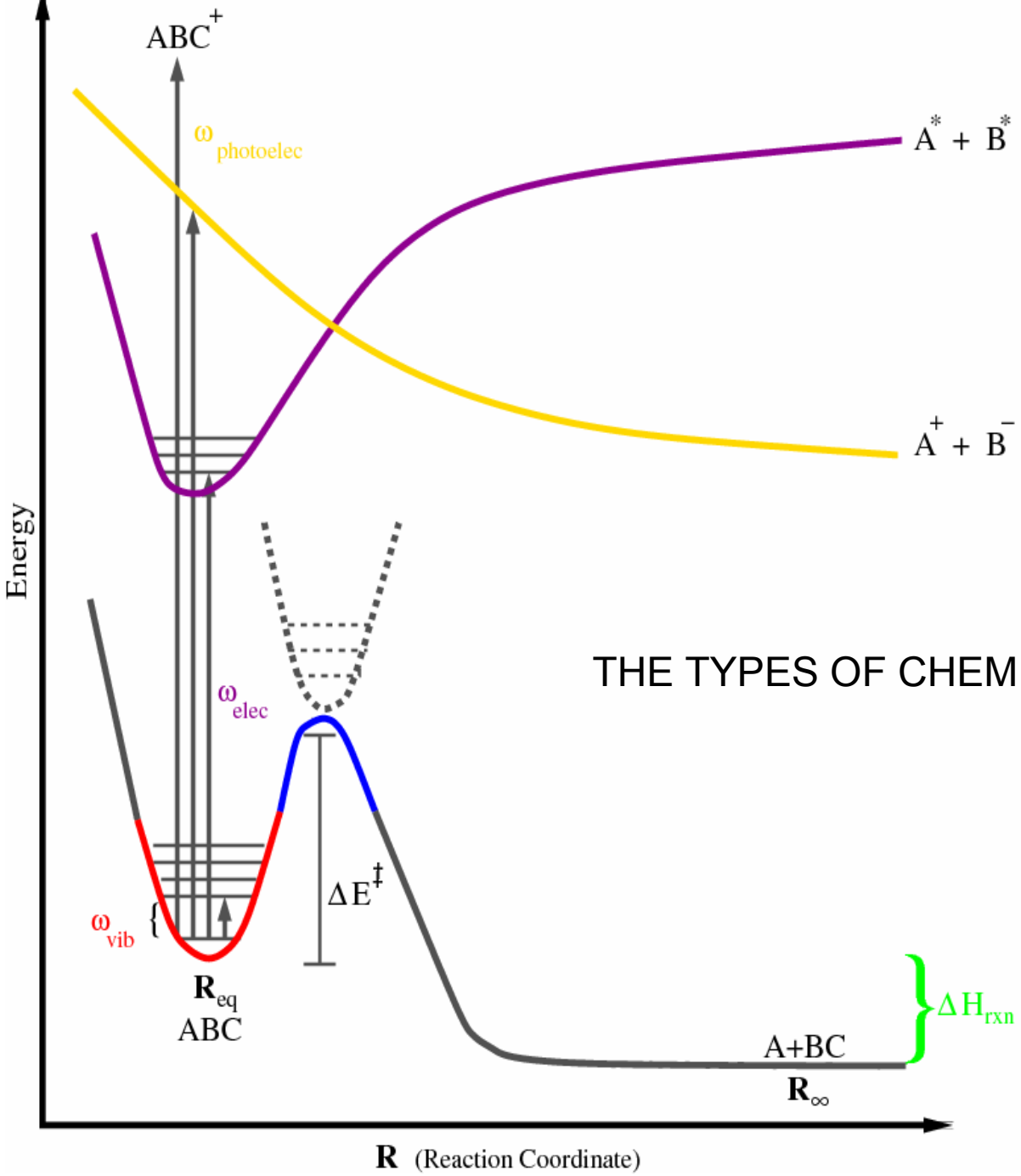
$ AFOSR $



THE TYPES OF CHEMICAL PROBLEMS

PROBLEMS FOR MOLECULES

•Molecular structure. Defined by finding the minima on PES.
•Vibrational frequencies for IR and Raman spectra.

•Energetics of reactions.

•Transition states to describe making and breaking chemical bonds.
•Activation barriers.

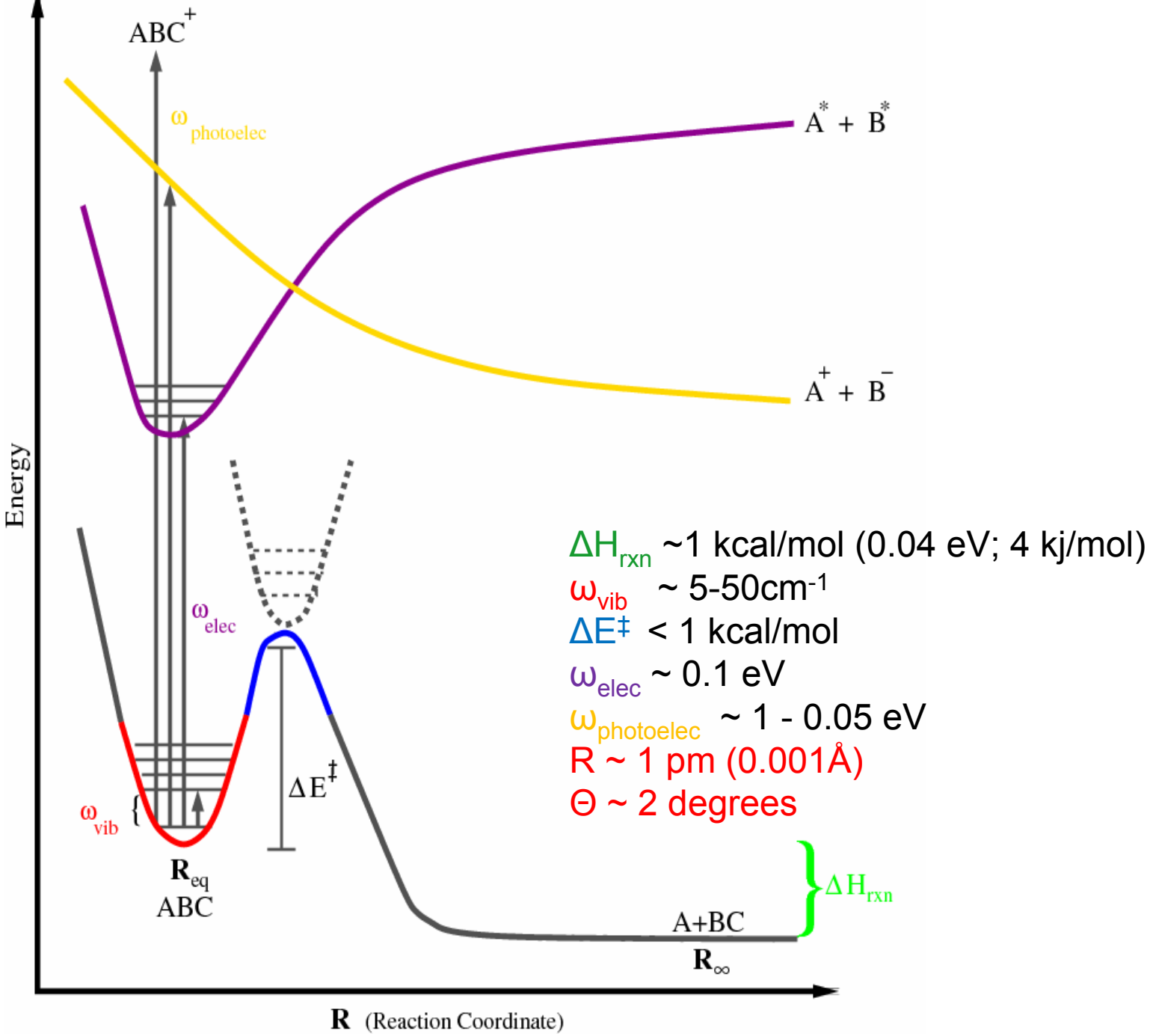
•Electronic excited states for UV-vis spectroscopy
•Photochemical reaction paths.

• Photoionization spectra and reaction paths.

• First order properties obtained from density matrices
•Higher-order properties obtained from response functions.

$\partial E(\mathbf{R})/\partial X_A$ ~3N for N atoms
$\partial^2 E(\mathbf{R})/\partial X_A \partial X_B$ ~$(3N)^2$

- Critical points are identified where the first derivatives (forces/gradients) vanish.
- Second derivatives (hessians) document whether point is a minimum, where they give the harmonic force constants and vibrational frequencies, or a saddle point, which identifies a transition state, whose energy provides an activation barrier.
- **In modern quantum chemistry it is absolutely essential to evaluate all ~3N forces in about the same time as the energy, itself. Hence, this has to be done analytically.**



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

Objectives of Quantum Chemistry

- Solve the Schroedinger Eqn. for the many-body problem for molecules,
- Repeat for *many* fixed molecular geometries,
- Provide spectra, decomposition paths, activation barriers, heats of reaction, etc.

PROBLEMS?

CORRELATION PROBLEM IN MANY-ELECTRON QUANTUM MECHANICS

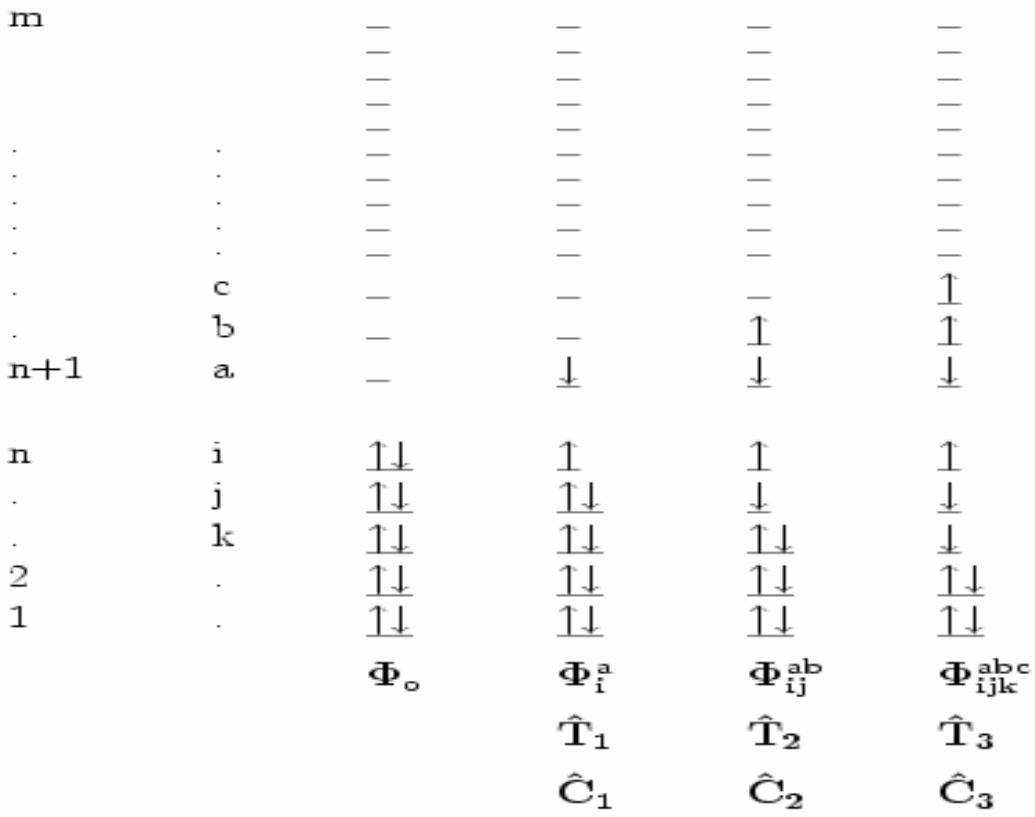
PER OLOV LÖWDIN

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."

The correlation energy for a certain state with respect to a specified Hamiltonian is the difference between the exact eigenvalue of the Hamiltonian and its expectation value in the Hartree-Fock approximation.

Fig. 2



CCD, CCSD, CCSDT, CCSDTQ,…,FULL CI.

- When I studied QC (*in the last millenium)* it was not possible to provide very accurate answers for molecules with several electrons. Most such *ab initio* applications were from Hartree-Fock (HF) theory, while for small molecules, modest amounts of configuration interaction (CI) could be added.

- All knew the latter was a necessity to describe the *correlated motions* of the electrons, but it was not generally appreciated that truncated CI itself had critical failures, that today we call *size-inextensivity.*

- The *size-extensivity* failure of CI affects obtaining the correct relative energies on a potential energy surface, or getting the correct excitation energies, or density matrices. **In short, it does not allow the development of a suitably accurate and**

THE NECESSITY OF SIZE-EXTENSIVITY* IN QUANTUM CHEMISTRY

Chemistry depends on energy differences. We have to know tha

$$E(AB)=E(A)+E(B),\ R_{AB}\rightarrow\infty$$

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, $|A\rangle|B\rangle$

$$\Psi(AB)=\exp[T(AB)]|AB\rangle=\exp[T(A)]|A\rangle\exp[T(B)]|B\rangle,$$

Exact Wavefunction has to be an exponential!
of a *connected* operator, T.

Guaranteed by evaluating *only* linked diagrams.

***RJB, G. Purvis, IJQC (1978)**

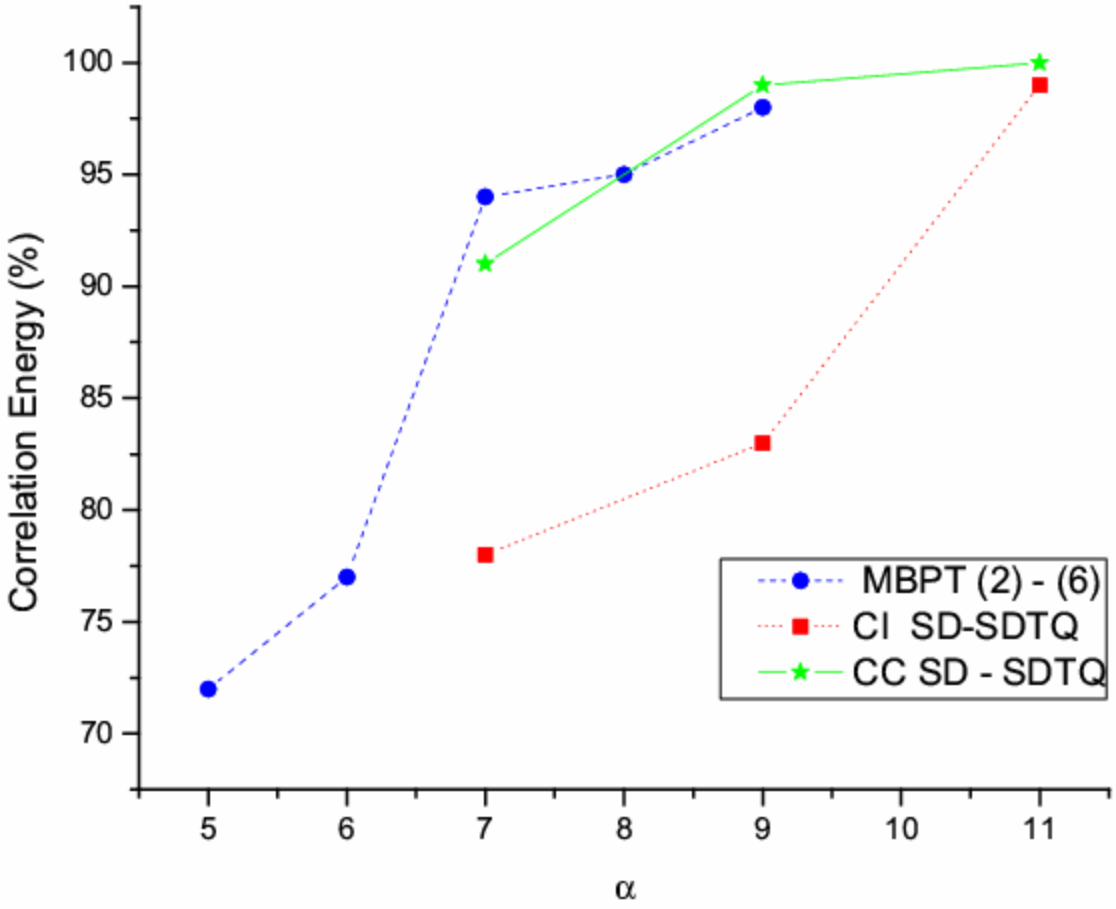
CORRECT WAVEFUNCTION HAS TO BE AN EXPONENTIAL OF CONNECTED OPERATORS!

$$\Psi = \exp(T)|0\rangle$$

Hence, coupled-cluster theory!!!

- **SIZE-EXTENSIVE (No unlinked diagrams).**
- **RAPID SATURATION OF DYNAMIC CORRELATION**
- **CONNECTED EXPRESSIONS FOR AMPLITUDES (No CI evaluation.)**
- **INFINITE SUMMATION OF MBPT DIAGRAMS**
- **ITERATIONS GIVE MBPT(2), (3), (4), …**

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 $n^{\alpha_n} N^{\alpha_N} N_{it}^{\alpha_{it}}$.



SOME RELEVANT HISTORY

•Brueckner Goldstone Linked Diagram Theorem, MBPT, 1955-1957

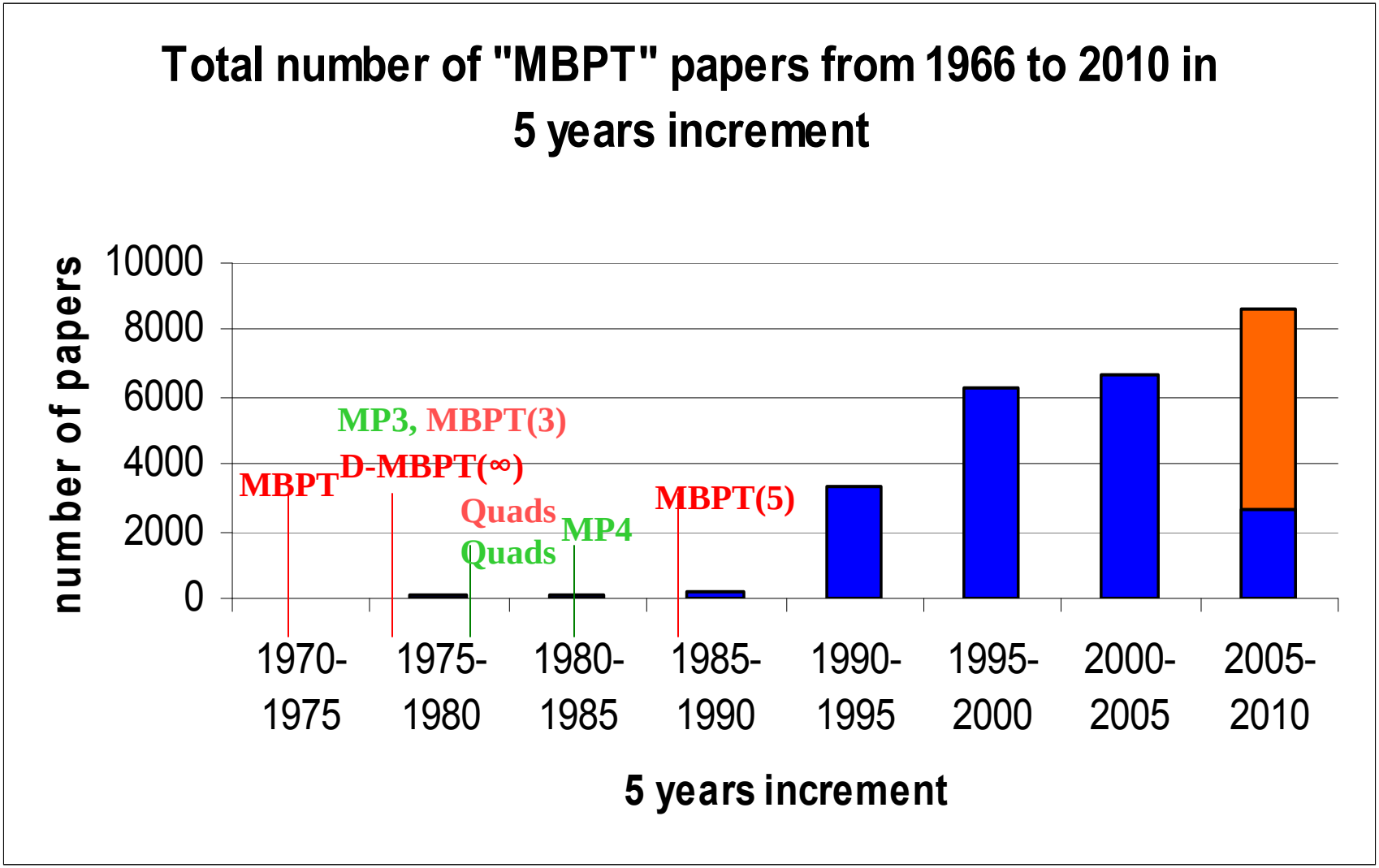
•Hubbard first wrote down the exponential ansatz ,1957

•Coester and Kuemmel considered such wavefunctions for nuclei, 1958-60

•H.P. Kelly, provided MBPT solutions for atoms, 1962.

•Ćĭźek presented the first CC equations, for molecules, 1966.

• Paldus, Ćĭźek, and Shavitt made some initial semi-empirical (1970) and one ab initio application to BH_3 (1972) with only 8 basis functions.



Bartlett Group

Pople Group

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*.

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

Q=single+double+ triple+…excitations.

SOME MANIFESTATIONS OF SIZE-EXTENSIVITY

• $\Psi_{CCD}=\exp(T_2)|0\rangle=(1+T_2+T_2^2/2+\ldots)|0\rangle$ COMPARED TO CI ($T_1=0$)

disc. con.

$$C_4 = T_2^2/2 + T_4$$

$\sim n^{10}$ $\sim n^6$ $\sim n^{10}$

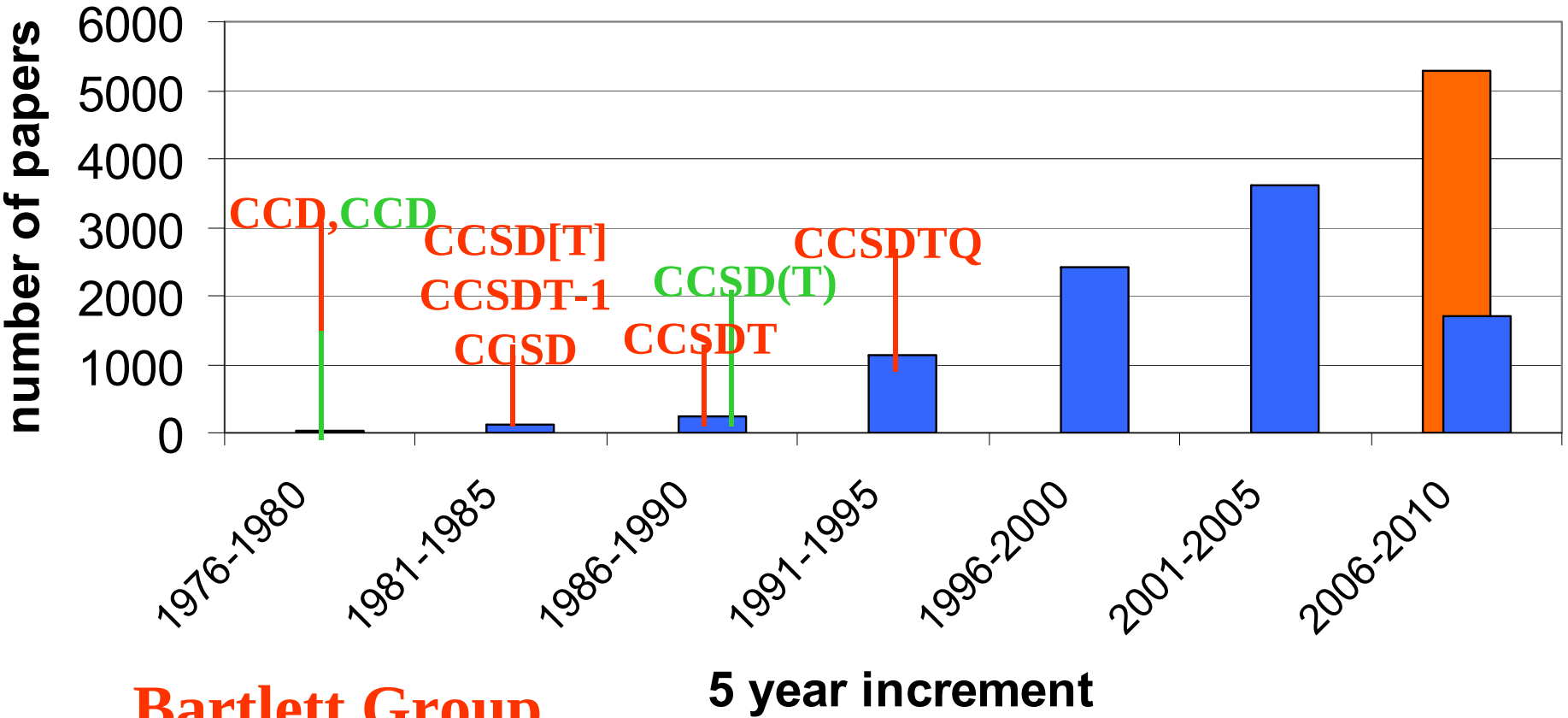
$$C_6 = T_2^3/3! + T_6 + T_3^2/2$$

$\sim n^{14}$ $\sim n^6$ $\sim n^{14}$ $\sim n^8$

Etc.

• C_4 accounts for >40% of the correlation energy, even for C_6H_6.
• CC is applicable to infinite systems.
• Correct relative energies on PES, or even between units with different numbers of electrons.
• CI density matrix in the limit of infinite system reduces to $|0\rangle\langle 0|$.

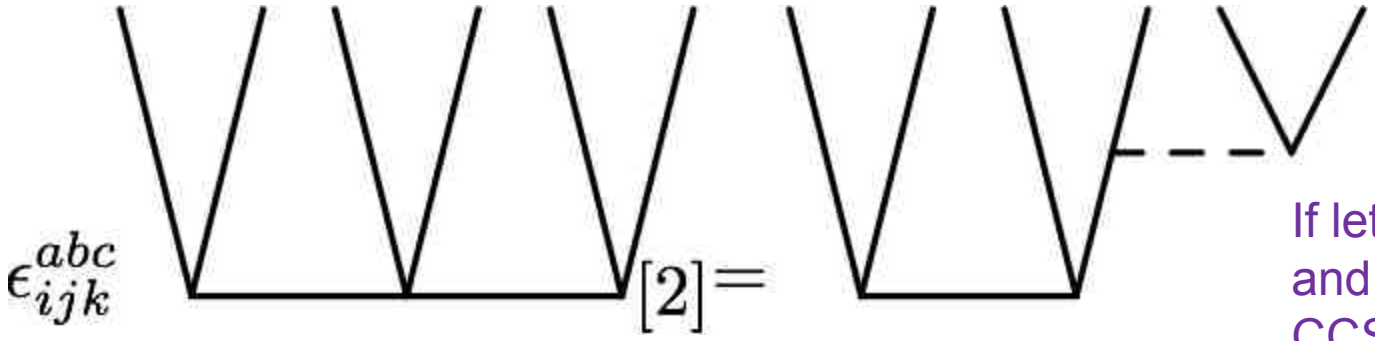
Total number of "coupled cluster" papers from 1975 to 2010 in 5 year increments



Bartlett Group

Pople Group

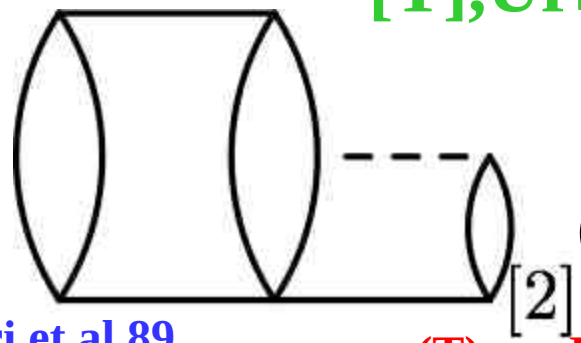
CCSD(T) arises from assuming that the T_3 amplitudes can be approximated from T_2 known from CCSD...



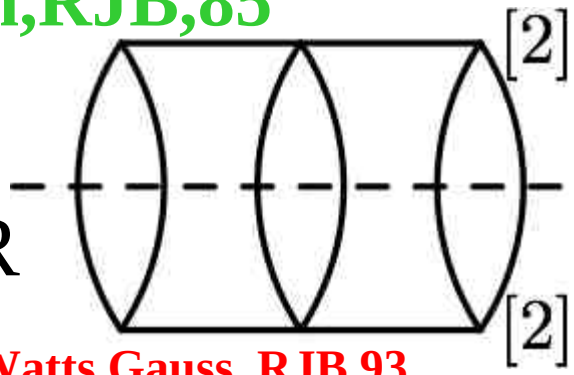
If let $T_3[2] \rightarrow T_2+T_1$ and iterate, have CCSDT-1

[T],Urban,RJB,85

$E_T^{[4]}$ =



OR



(T)Raghavachari,et al,89

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

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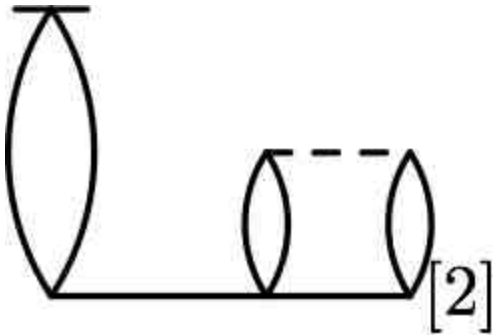

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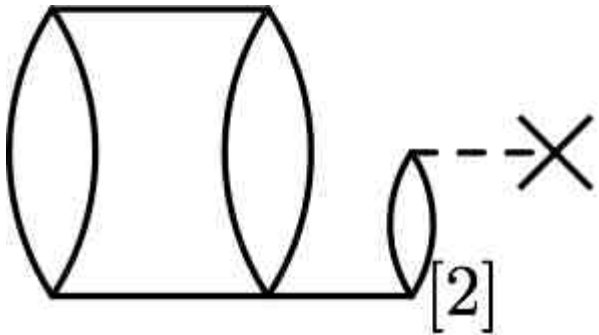


AB INITIO, CORRELATED, SIZE EXTENSIVE WAVEFUNCTION METHODS COMBINED WITH CONVERGING BASIS SETS HAVE ...

Established the now widely used paradigm for ground state

Ab Initio Calculations

MBPT(2)<CCD <CCSD<CCSD[T] <CCSD(T) <CCSDT-1

1978 1982 1985 1989 1984

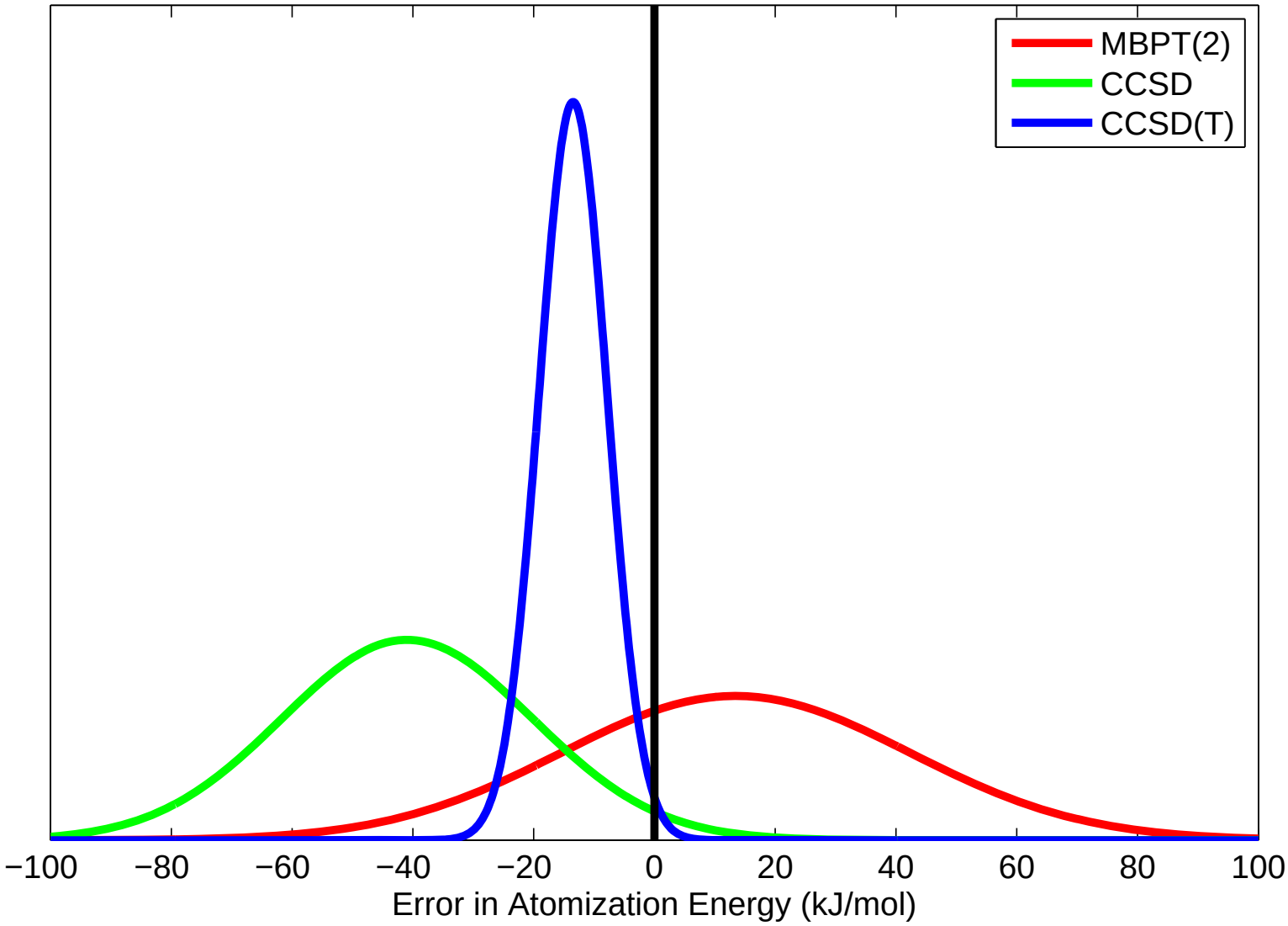
<CCSDT<CCSDT(Q_f) <CCSDTQ<**CCSDTQP** <FULL CI

1987 1998 1992 2002

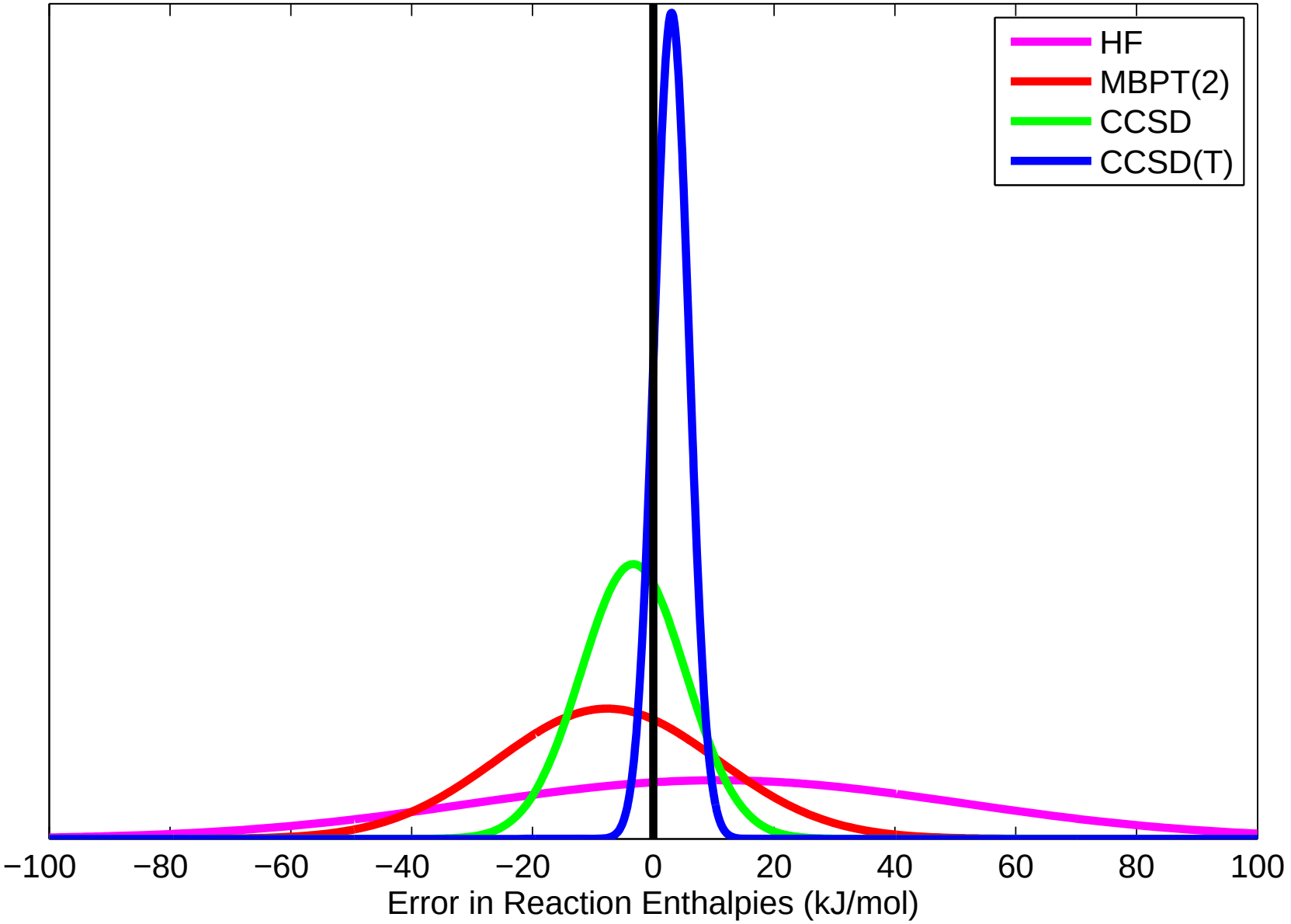
Automatic Code Generation by Hirata, Kallay, Olsen adds

Hextuples!

Distribution of Atomization Energy Errors for 16 Small Molecules in a cc-pCVQZ basis – ACES II calculations, from Bak, et.al. JCP, v.112, p. 9229 (2000)



Distribution of Reaction Enthalpy Errors for 13 Rxns of 16 Small Molecules in a cc-pCVQZ basis – from Bak, et.al. op.cit.



- To make these **many-body methods** universally applicable to molecules required a lot more than simply a way to compute an energy.
- We required the **energy derivatives** evaluated analytically at comparable cost, to enable the prediction of structure, transition states, and vibrational spectra.
- We also had to develop methods for **density matrices, excited states**, and **second and higher-order properties** to treat response properties, anharmonic forces and non-linear optical effects.

OTHER REQURIED EXTENSIONS FOR A GENERALLY APPLICABLE THEORY

Analytical gradients for CC Theory (1984-1991)

- $\partial E/\partial X_\alpha = \langle 0|(1+\Lambda)\exp(-T)(\partial H/\partial X_\alpha)\exp(T)|0\rangle$.
- CC Functional, $E = \langle 0|(1+\Lambda)\exp(-T)H\exp(T)|0\rangle$.

- CC generalization for response and relaxed density matrices and properties,
  $\gamma_{pq} = \langle 0|(1+\Lambda)\exp(T)\{p^\tau q\}\exp(T)|0\rangle$ (1989)

- EOM-CC Excited, Ionized, Electron Attached,... States,
  $[e^{-T}He^{T}R_k]_C|0\rangle = \omega_k R_k|0\rangle$ (1989-1995)

- Excited state density matrices,
  $\gamma^k_{pq} = \langle 0|L_k \exp(-T)\{p^\tau q\}\exp(T)R_k|0\rangle$ (1993)

- Second-order properties, (1993-1994)
  $\boldsymbol{\alpha(r,r)} = \sum_k \langle 0|(1+\Lambda)e^{(-T)}(\mathbf{r}- \langle \mathbf{r}\rangle)e^{(T)}R_k|0\rangle\langle 0|L_k\, e^{(-T)}(\mathbf{r}- \langle \mathbf{r}\rangle)e^{(T)}|0\rangle/\ \omega_k$

ALL THE ABOVE GRADIENT, DENSITY MATRICES, PROPERTIES, EXCITED STATE CAPABILITIES WERE WRITTEN INTO ACES II, 1991-1995, BY MANY OUTSTANDING POSTDOCS AND GRADUATE STUDENTS,

J. STANTON, J. GAUSS, J. WATTS, P. SZALAY, M. NOOIJEN, A. PERERA, D. BERNHOLDT, W. LAUDERDALE, H. SEKINO, S. GWALTNEY, K. BAECK. A. BALKOVA, M. MUSIAL, and others.

ACES I: G. Purvis,B. Laidig,L. Adamowicz, S.Kucharski, Y. S. Lee, A. Salter, G. Trucks, H. Sekino, R. Harrison, G. Fitzgerald, M. Rittby, S. Cole, D. Magers, and others.

ACES III: V. Lotrich, M. Ponton, N. Flocke, A, Yau, A. Perera, E. Deumens (architect).

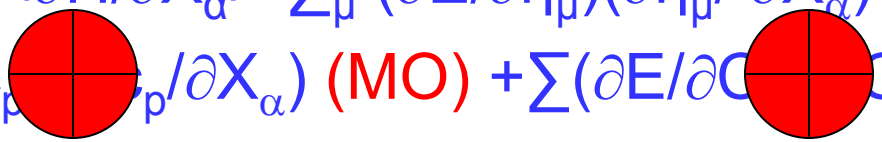
ANALYTICAL GRADIENTS IN CC THEORY

PROBLEMS:

- Before CC theory all quantum chemical methods depended upon their being variational 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.

SOLUTION:

$$\hat{H}=e^{-T}He^{T}=(He^{T})_C$$

$$E_{CC}=P\hat{H}P,\ P=|0\rangle\langle 0|$$
$$Q\hat{H}P=0$$

$$\partial E/\partial X_\alpha P= P(\partial\hat{H}/\partial X_\alpha)P + P(\hat{H}\partial T/\partial X_\alpha)P$$
$$E^\alpha = P(\hat{H}^\alpha)P + P(\hat{H}T^\alpha)P$$

Problem: ~3N $\partial T/\partial X_\alpha$ for forces, but only 1 T for energy, E_{CC}, which would make gradients ~3N times longer to compute than the energy?

But if we differentiate amplitude equation have

$$QT^\alpha P=(E_{CC}- \hat{H})^{-1}Q\ \hat{H}^\alpha P$$
$$E^\alpha P= P[(\ \hat{H}^\alpha) + \hat{H}Q(E_{CC}- \hat{H})^{-1}Q\ \hat{H}^\alpha P$$

Define $\Lambda= P\hat{H}Q(E_{CC}- \hat{H})^{-1}Q$

First time that $Q\hat{H}Q$ appears.

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

$$E^{\alpha}P=P(1+\Lambda)\hat{H}^{\alpha}P$$

👍 is *independent of the ~3N perturbations,*
means we can evaluate Λ just once,
and dot it into $Q(\partial\hat{H}/\partial X_{\alpha})P$ for any X_{α}!

Integral form defines the CC functional

$$E=P(1+\Lambda)\hat{H}P$$

Stationarity wrt to Λ gives CC equations,

$$Q\hat{H}P=0$$

Stationarity wrt to T gives Λ eqns.

$$P\Lambda\hat{H}Q+P\hat{H}Q-E_{CC}P\Lambda Q=0$$

(Notice E dependence and CI form)

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).

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

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

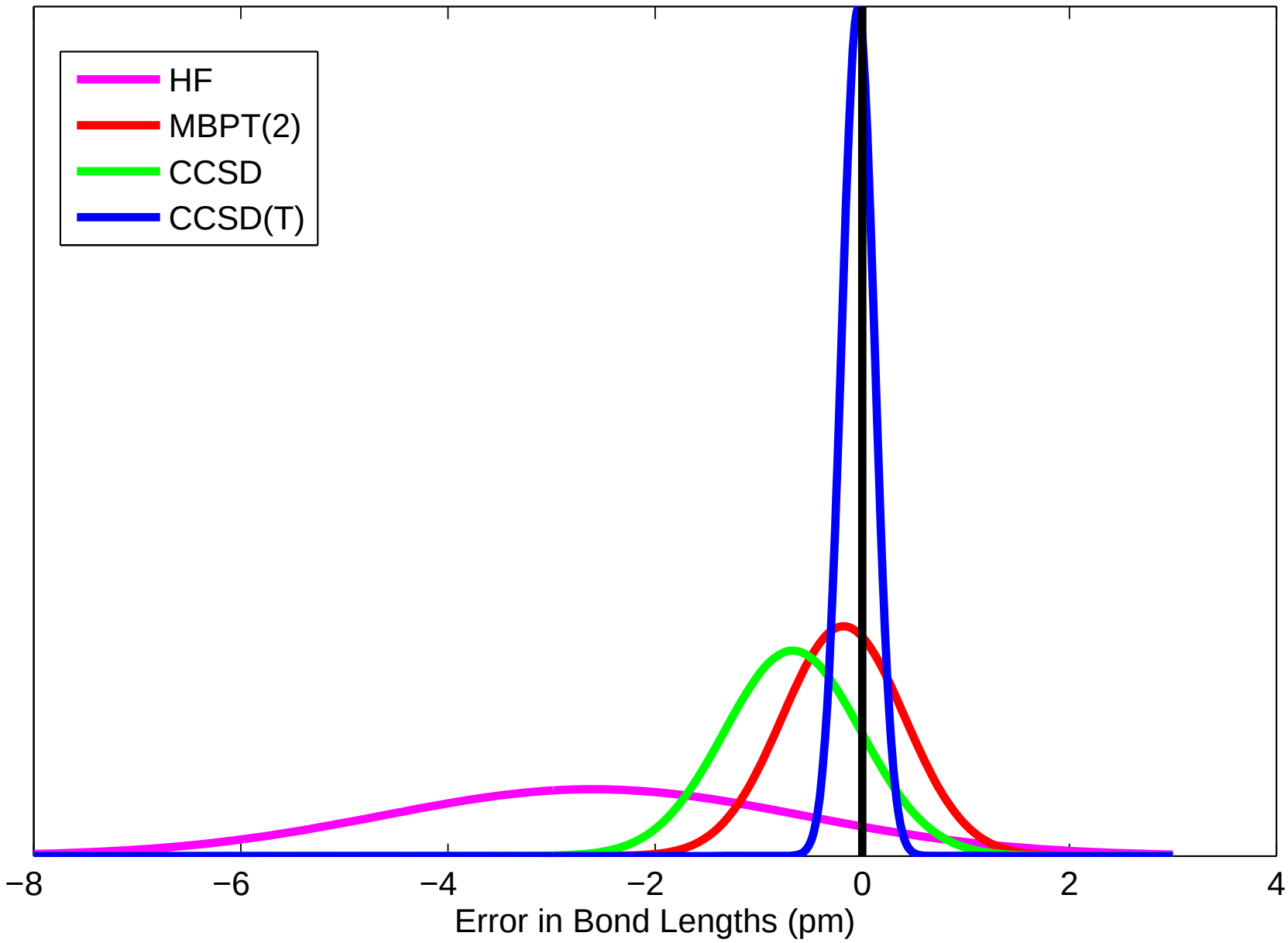
These density matrices enable CC theory to handle all first-order properties, including analytical gradients.

STRUCTURE AND FREQUENCY CALIBRATION

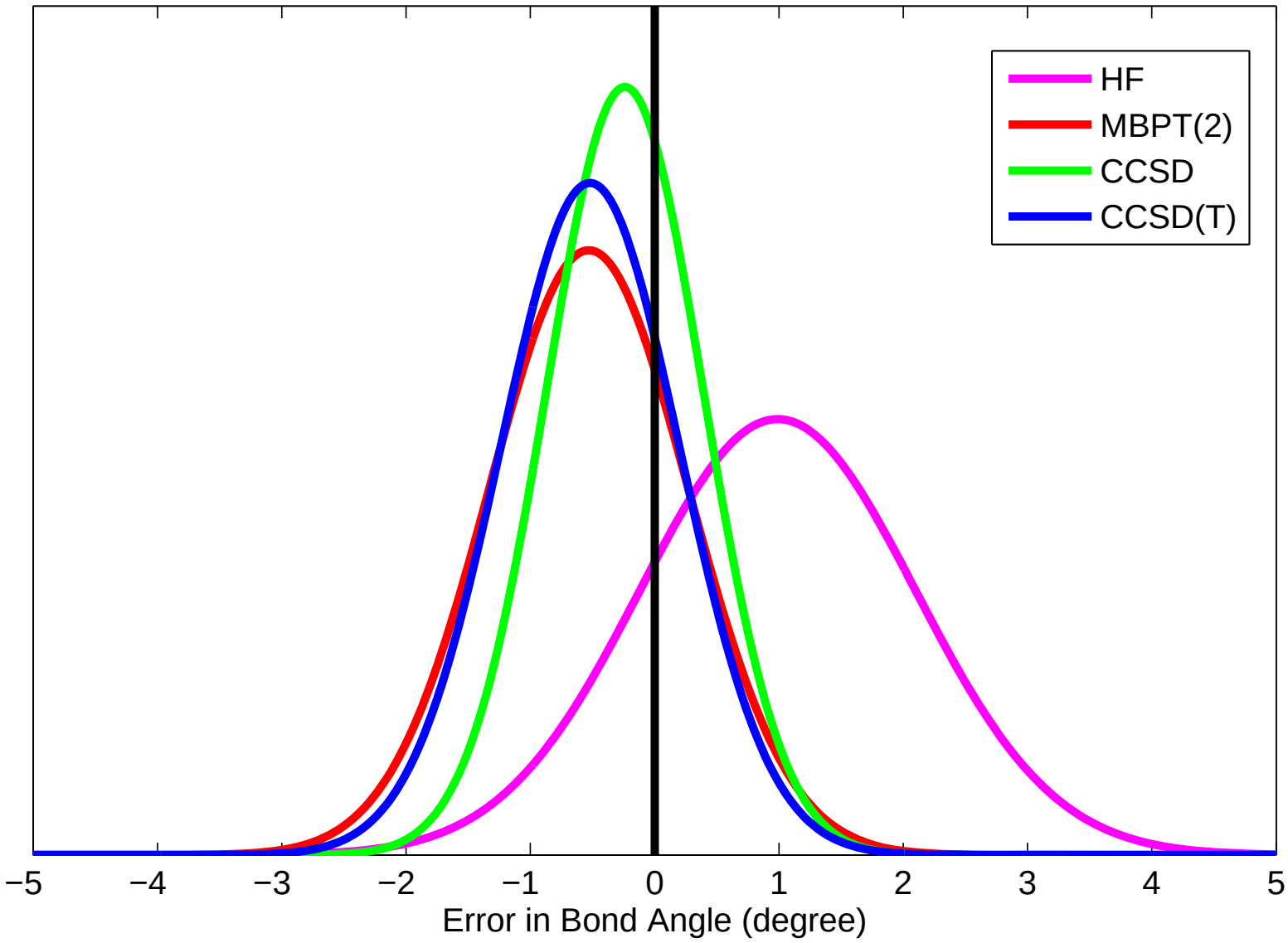
For many molecules with good basis sets, pVTZ and beyond, the CCSD(T) MAD for bond lengths are accurate to ~1 pm and angles to ~ 2 degrees.

Harmonic vibrational frequencies tend to be accurate to ~ <5 % with basis sets of pVTZ quality.

Distribution of Equilibrium Bond Length Errors for 19 Small Molecules in a cc-pCVQZ basis – ACES II results from Bak, et.al. JCP, v.114, p. 6548 (2001)

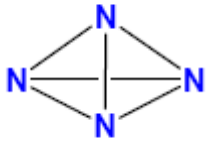


Distribution of Equilibrium Bond Angle Errors for 19 Small Molecules in a cc-pCVQZ basis – from Bak, et.al. op. cit.

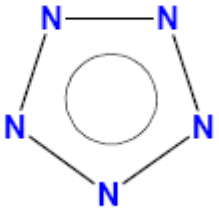


SOME OF MY FAVORITE MOLECULES, THAT DON'T EXIST BUT SHOULD.

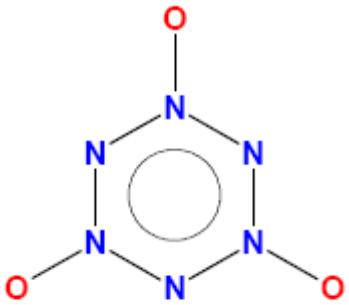
If we are to argue
that these exist and provide
spectroscopic
fingerprints to identify them, we
require a
PREDICTIVE THEORY!



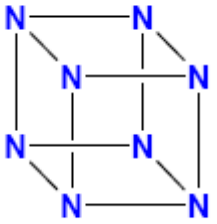
Tetrahedral N4



Pentazole Anion

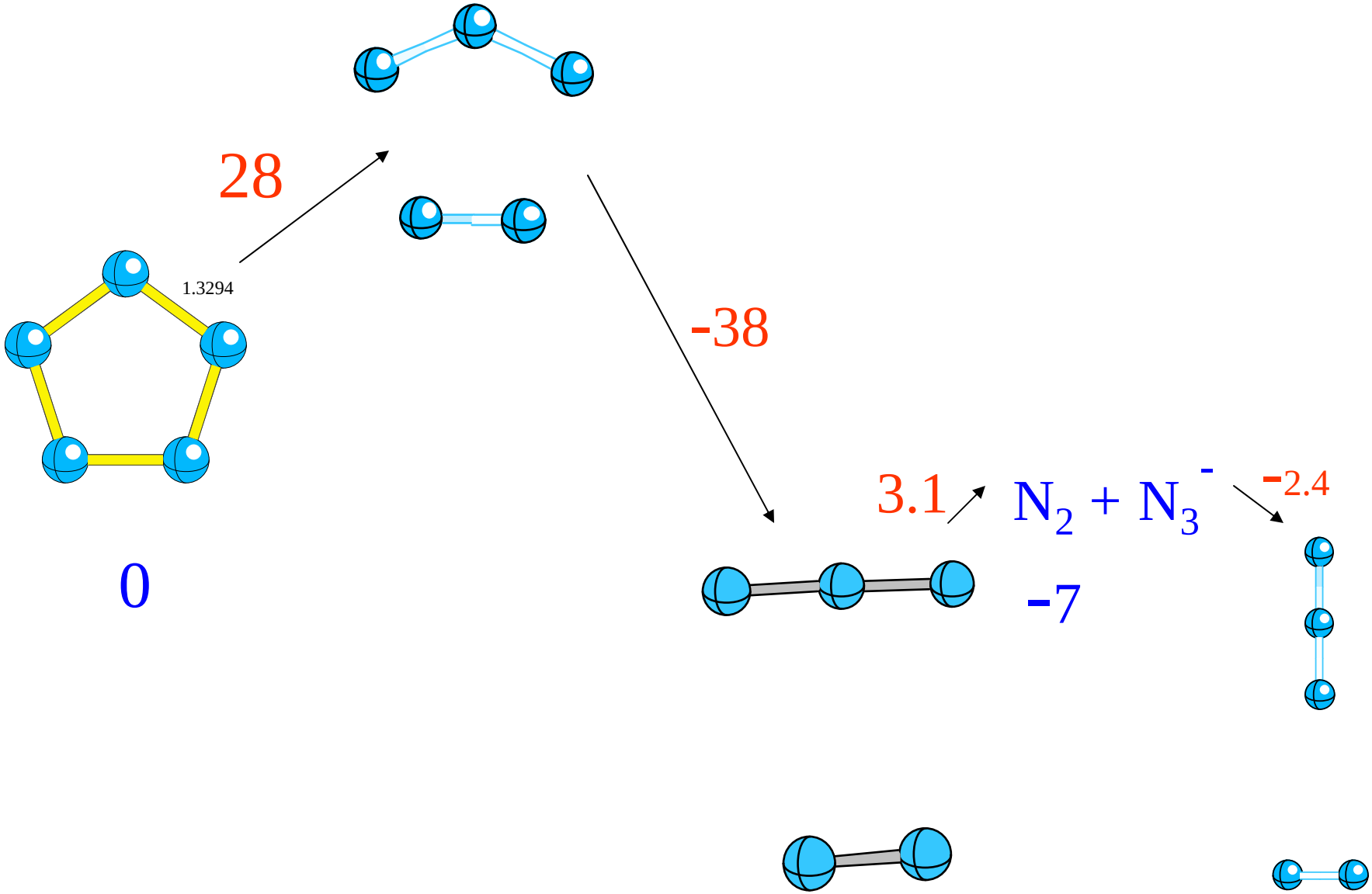


N_6 Benzene-like Ring
+3NO



Octaazacubane

Dissociation of N_5^-: Energy differences in kcal/mol



FUNDAMENTAL IDEA OF 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

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

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

CALIBRATION OF EXCITED STATES USING EOM-CCSD, -CCSDT, -CCSDTQ

Compared to Full CI (Ne, HF, CH_2,H_2O,N_2,C_2)

	Singlet States		*Triplet States*
EOM-CCSD	0.25 eV	(0.08S)	0.06 eV
EOM-CCSDT	0.05		0.02
EOM-CCSDTQ	0.01		0.01

Compared to experiment at the Complete Basis Set limit.

EOM-CCSD 0.24 (Singly excited, ~0.1)

EOM-CCSDT 0.09 (Singly and doubly excited)

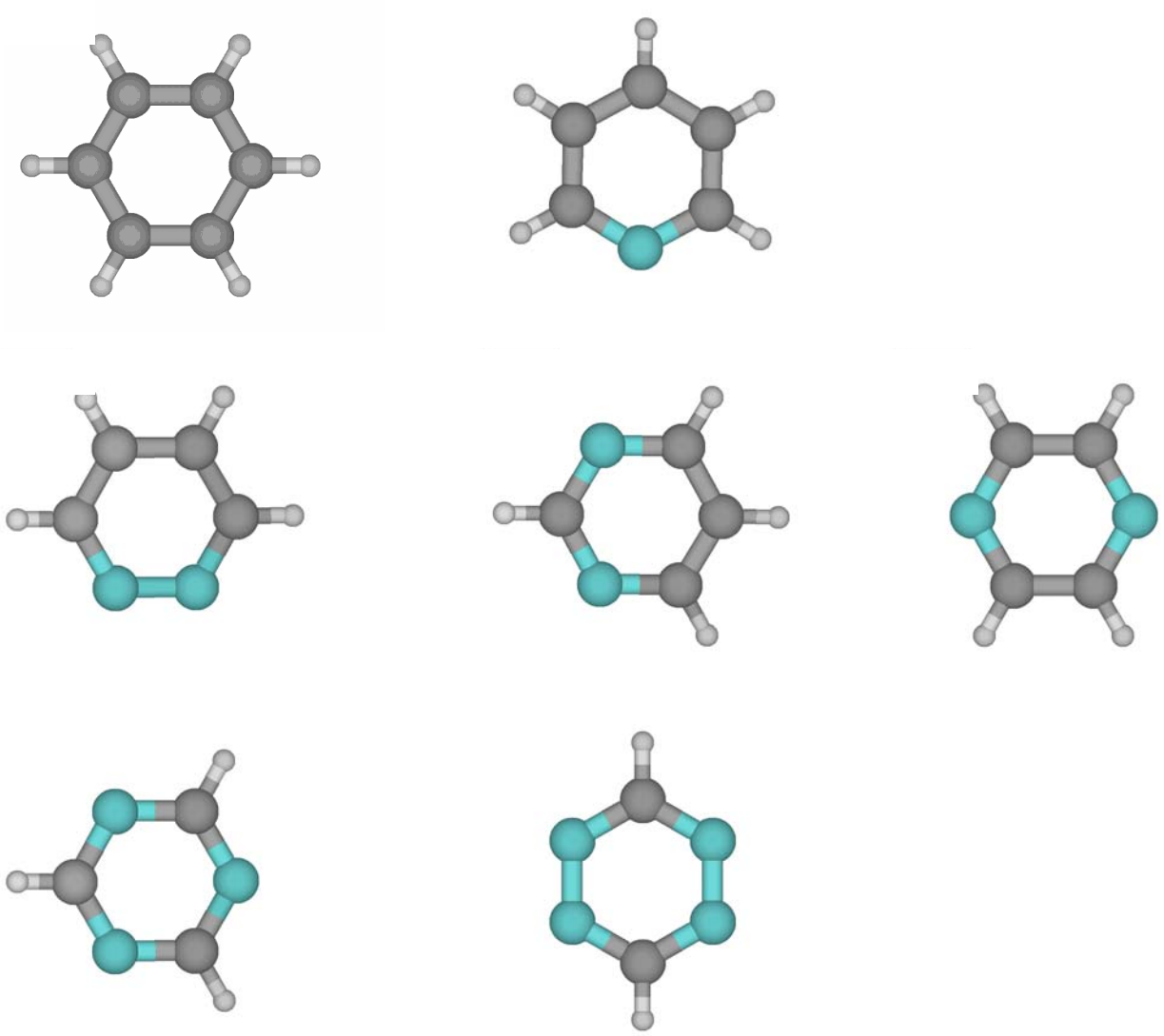
EOM-CCSD and CCSDT Basis set limit valence orbital vertical ionization potentials (N_2, CO, C_2, C_2H_2, C_2H_4, H_2CO)

EOM-CCSD 0.30 eV

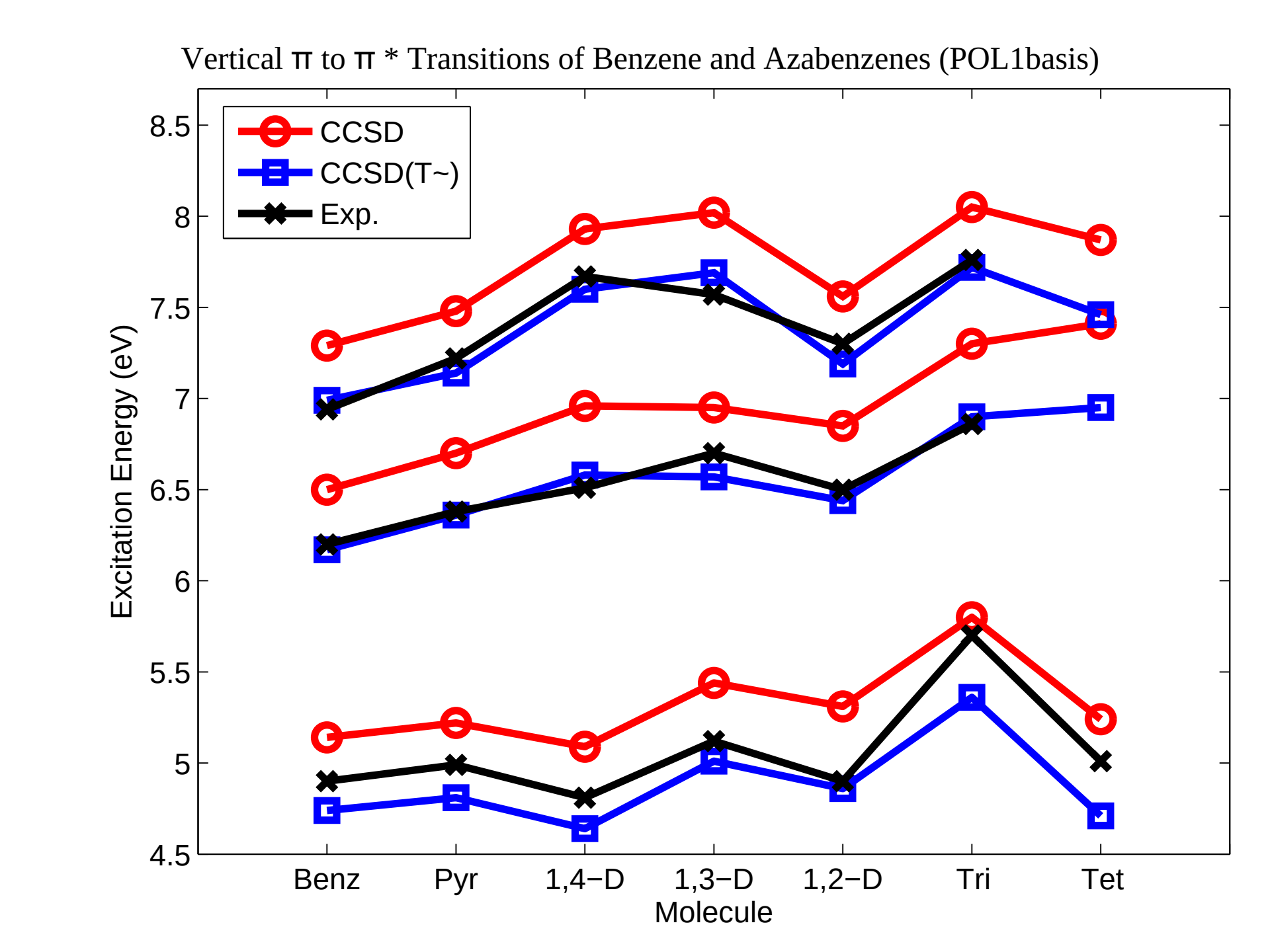
EOM-CCSDT 0.16 eV

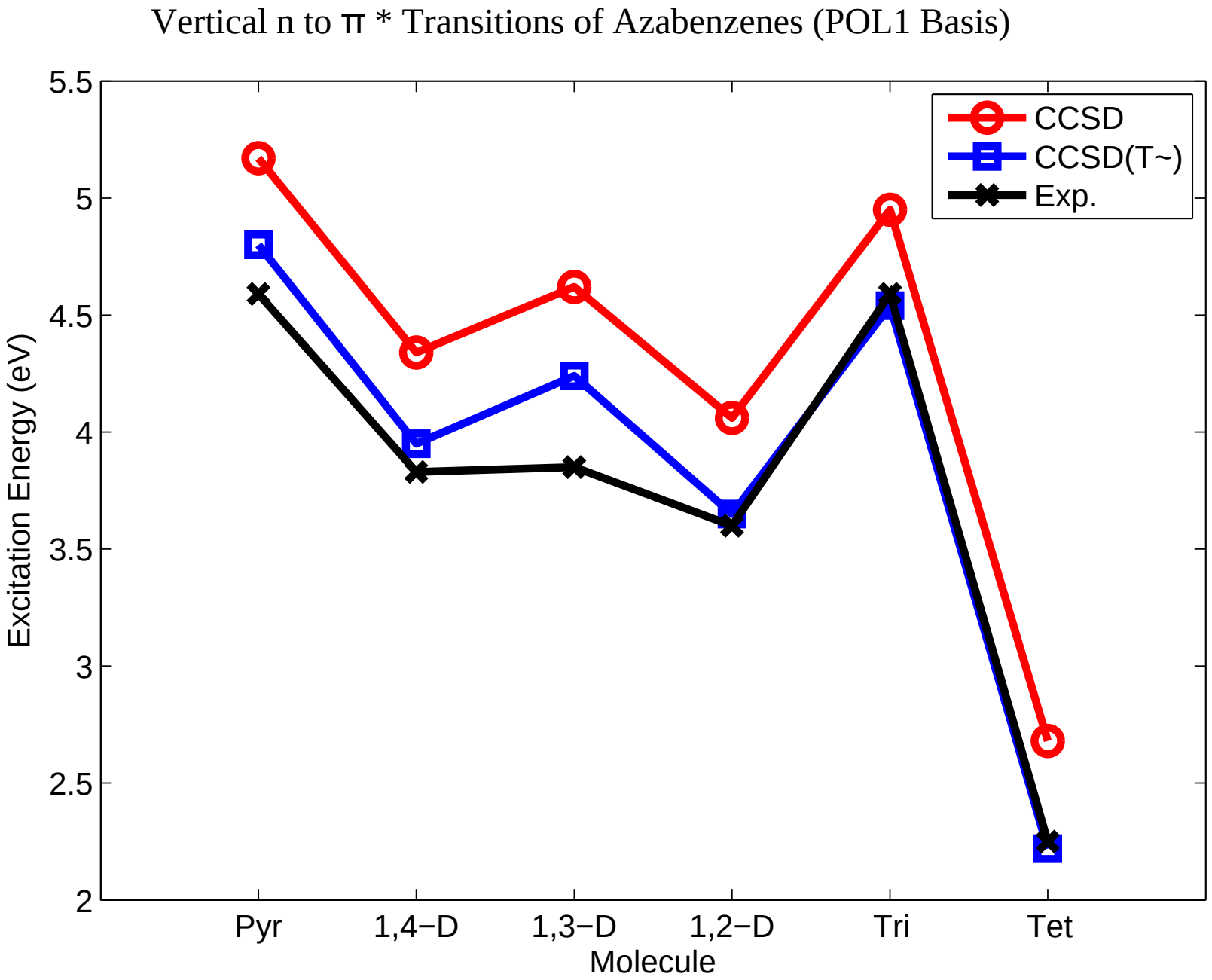
There are four out of 22 ‘experimental’ numbers whose extraction of **vertical** values looks questionable. Without those, the MAD at CCSDT is 0.08 eV.

Benzene and azabenzenes



J. DelBene, J. Watts, RJB, JCP (1997)


Vertical π to π * Transitions of Benzene and Azabenzenes (POL1basis)
CCSD
CCSD(T~)
Exp.
Excitation Energy (eV)
8.5
8
7.5
7
6.5
6
5.5
5
4.5
Benz
Pyr
1,4−D
1,3−D
1,2−D
Tri
Tet
Molecule


Vertical n to π * Transitions of Azabenzenes (POL1 Basis)
CCSD
CCSD(T~)
Exp.
Excitation Energy (eV)
5.5
5
4.5
4
3.5
3
2.5
2
Pyr
1,4−D
1,3−D
1,2−D
Tri
Tet
Molecule

So we now have ground and excited states. with analytical gradients on excited state surfaces, which has also been done (Stanton, Gauss), rather complete characterization can be made and spectra even simulated (Stanton, Nooijen).

What else is left?

Second and higher-order properties!

HIGHER-ORDER PROPERTIES IN EOM-CC

The resolvent operator,

$R_0 = (E_{CC} - \hat{H})^{-1} Q$

introduced in the gradient theory, whose matrix is diagonalized to provide the biorthogonal left- and right-hand eigenstates for EOM-CC, can be used to provide the first-order *right-hand* wfxn,

$|\Psi_R^{(1)}\rangle = R_0 e^{-T}(V - E^{(1)}) e^{T} |0\rangle$

and with the *left-hand* unperturbed solution,

$\langle \mathbf{\Psi}_L^{(0)}| = \langle 0|(1+\Lambda)$, any second-order property can be obtained from the perturbed second-order energy,

$E^{(2)} = \langle \mathbf{\Psi}_L^{(0)}| e^{-T}(V - E^{(1)}) e^{T} |\Psi_R^{(1)}\rangle$.

Problem: Inverse matrix has rank >10^6.

Solution: Solve linear equation,

$(E_{CC} - \hat{H})|\Psi_R^{(1)} = Q e^{-T}(V - E^{(1)}) e^{T} |0\rangle$.

John Stanton, rjb, dynamic polarizabilities, 1991.

CALIBRATION OF EOM-CCSD FOR NMR COUPLING CONSTANTS

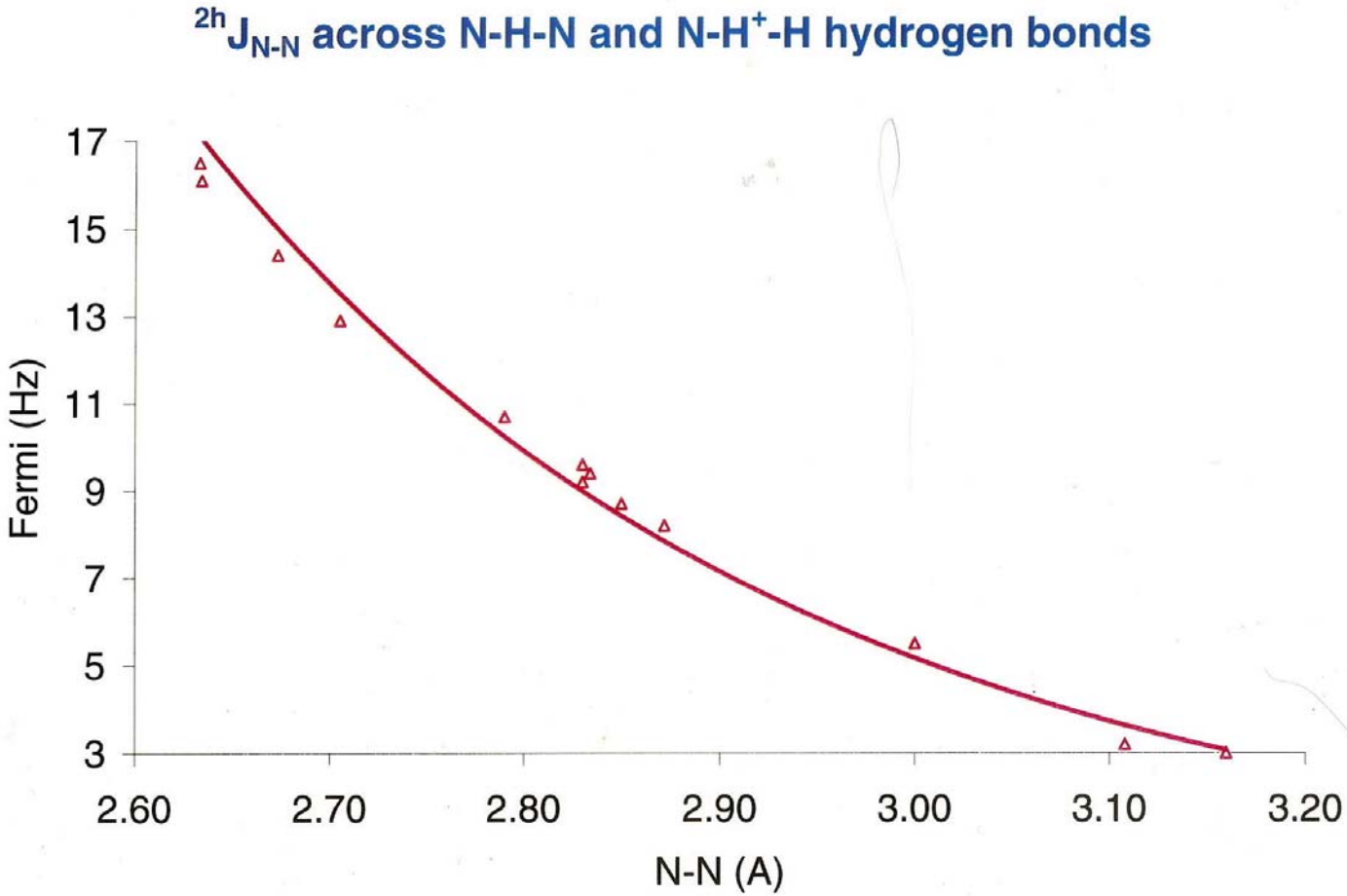
For many molecules containing, C, N, O, F, H, Cl, S, P, the MAD from experiment is 3.5 Hz, with a maximum of 12 Hz for $J^1(^{13}C^{10}F)$ (~8%, error)

This provided a predictive tool that did not exist until 1994.

Ajith Perera

In our opinion, coupling-constants of this sort tend to have predictable behavior as a function of R_{NN}, and they are only a weak function of the actual molecules containing N, which makes their behavior rather universal.

If so, then since H cannot be seen in Xray studies, such general curves of $J^{2h}(NN)$ can be used to identify them and say how far apart the N atoms are.



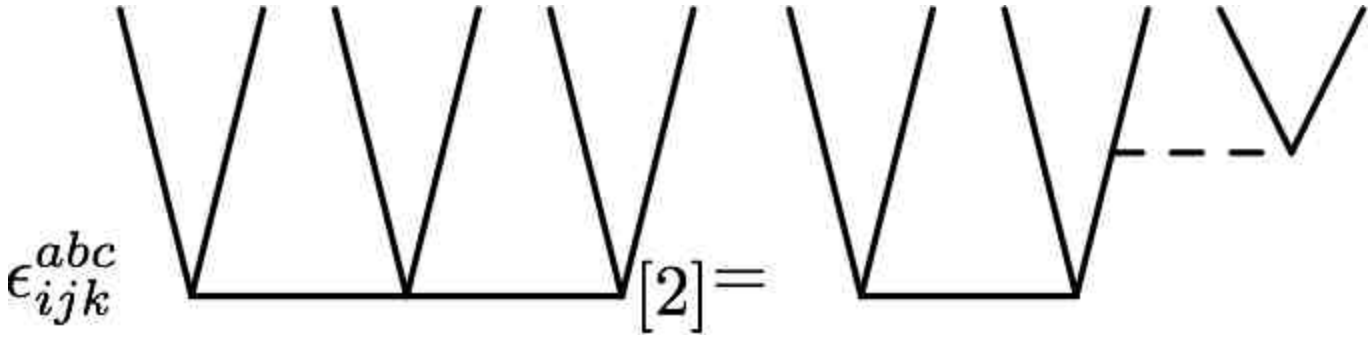
J. DelBene, S. A. Perera, RJB, Mag. Res. In Chem. (2001)
J. Am. Chem. Soc. (2000).

NOW FOR SOMETHING **NEW**, THAT IS A FURTHER MANIPULATION ON THE CC FUNCTIONAL---

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

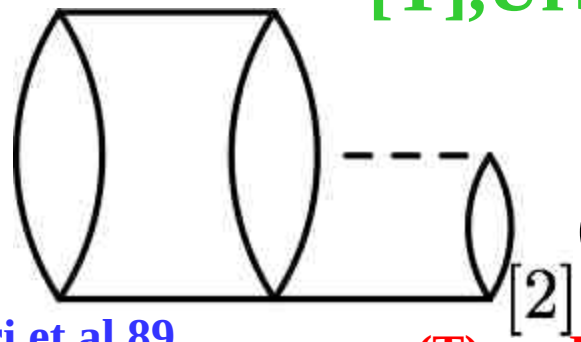
Assuming the CCSD solution has been obtained, then one can derive all the non-iterative triple excitation corrections from this expression, like CCSD[T], CCSD(T), etc.

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

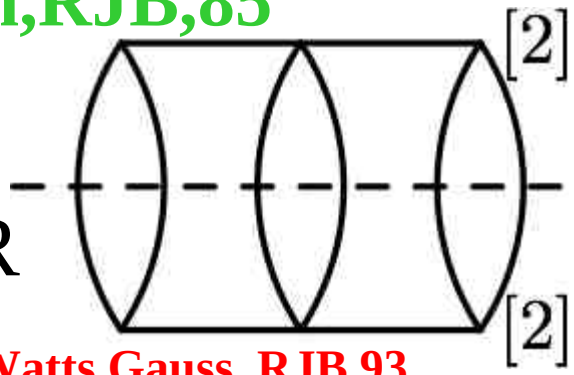


[T],Urban,RJB,85

$E_T^{[4]}$ =



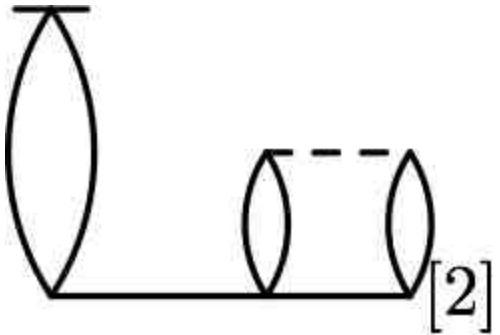
OR



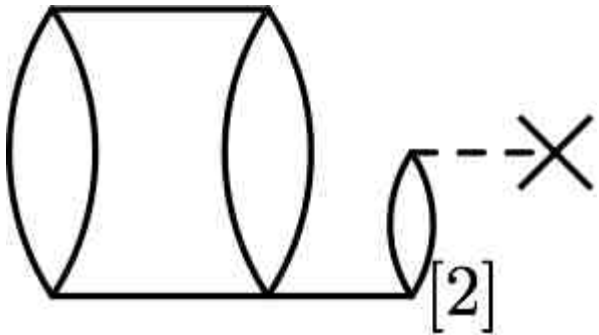
(T)Raghavachari,et al,89

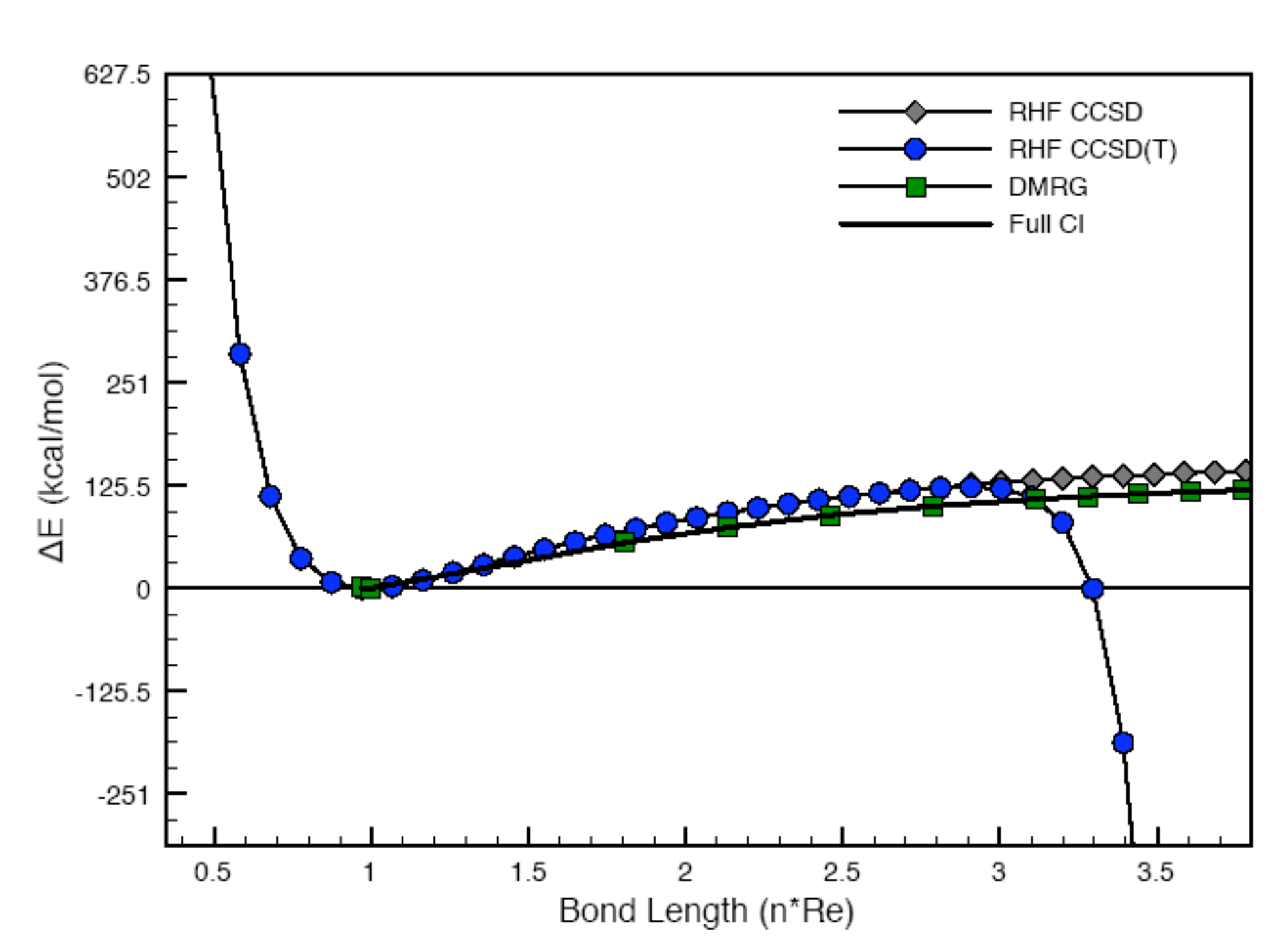
(T)non HF,Watts,Gauss, RJB,93

\+



\+




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

CC functional, $E=P(1+\Lambda)\hat{H}P$

CCSD(T) and ΛCCSD(T)

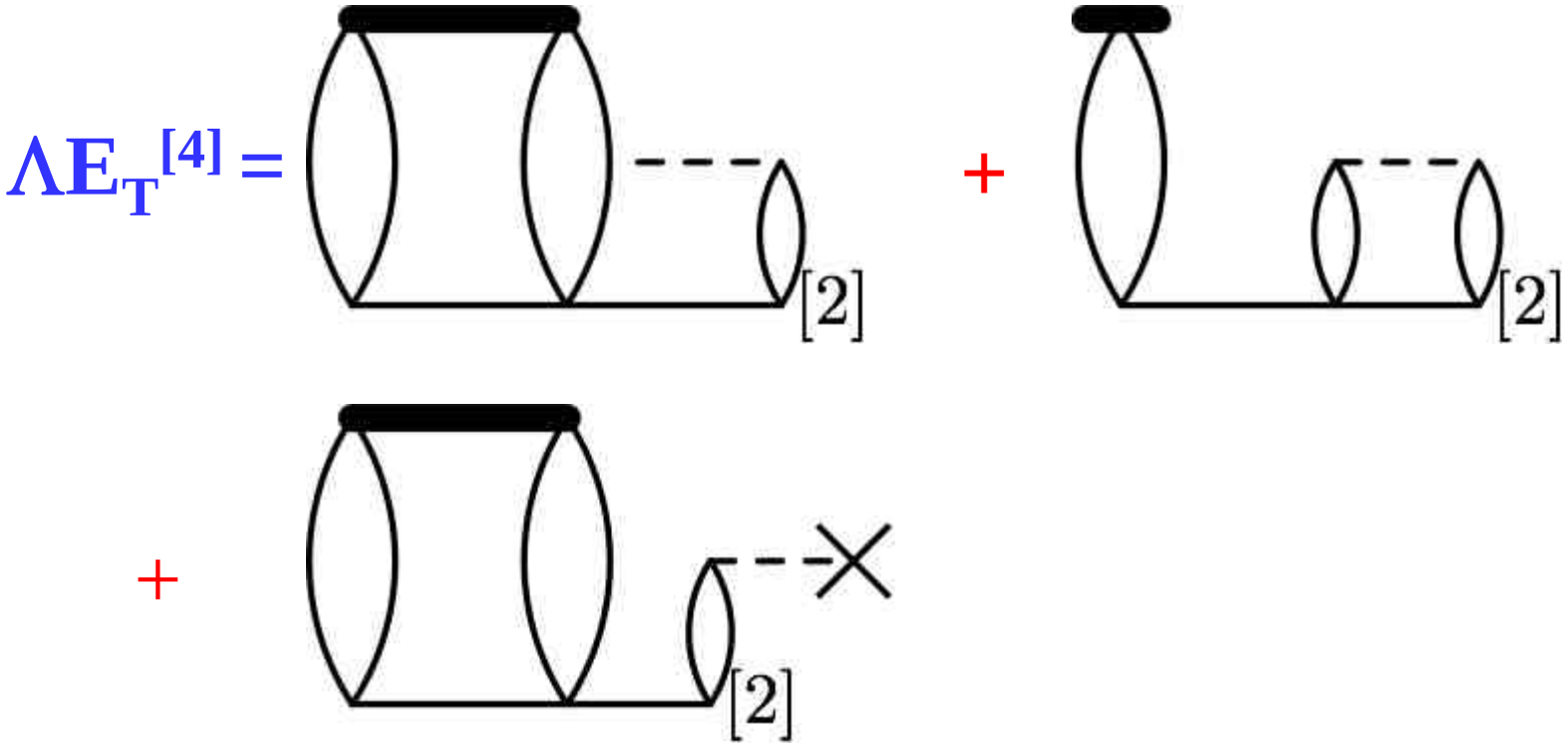
ΛCCSD(T) is the "minimal" formal improvement of CCSD(T)

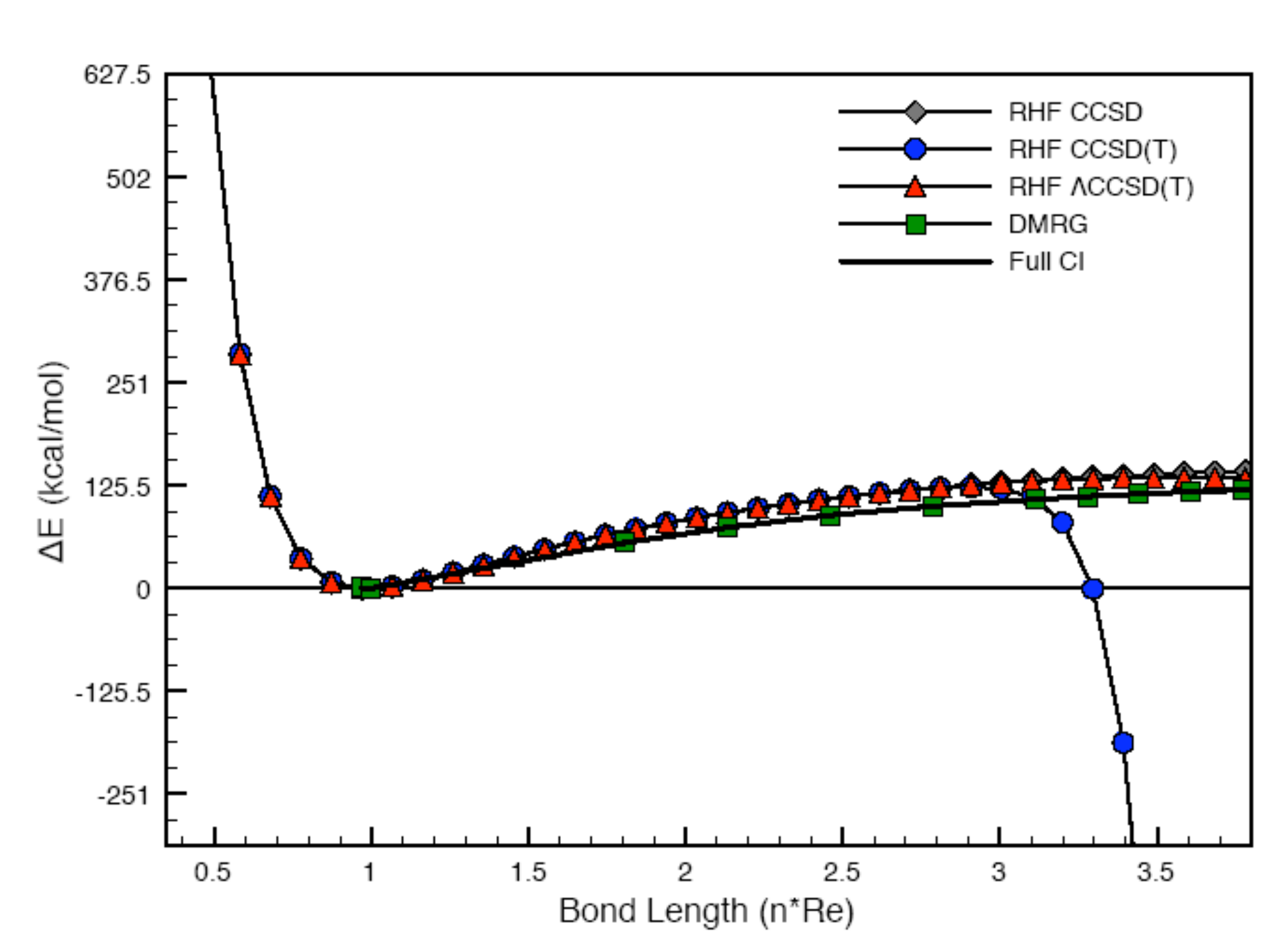
$$\Delta E_{(T)} = \langle 0 | T^{\dagger} \left(F_{ov} + W \right) | T \rangle D_3 \langle T | \left(W T_2 \right)_C | 0 \rangle$$

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

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 recently implemented gradients.

Λ- based fourth-order triples approximation, from CC functional, $\langle 0|(1+\Lambda)e^{-T}He^{T}|0\rangle$, defines ΛCCSD(T)

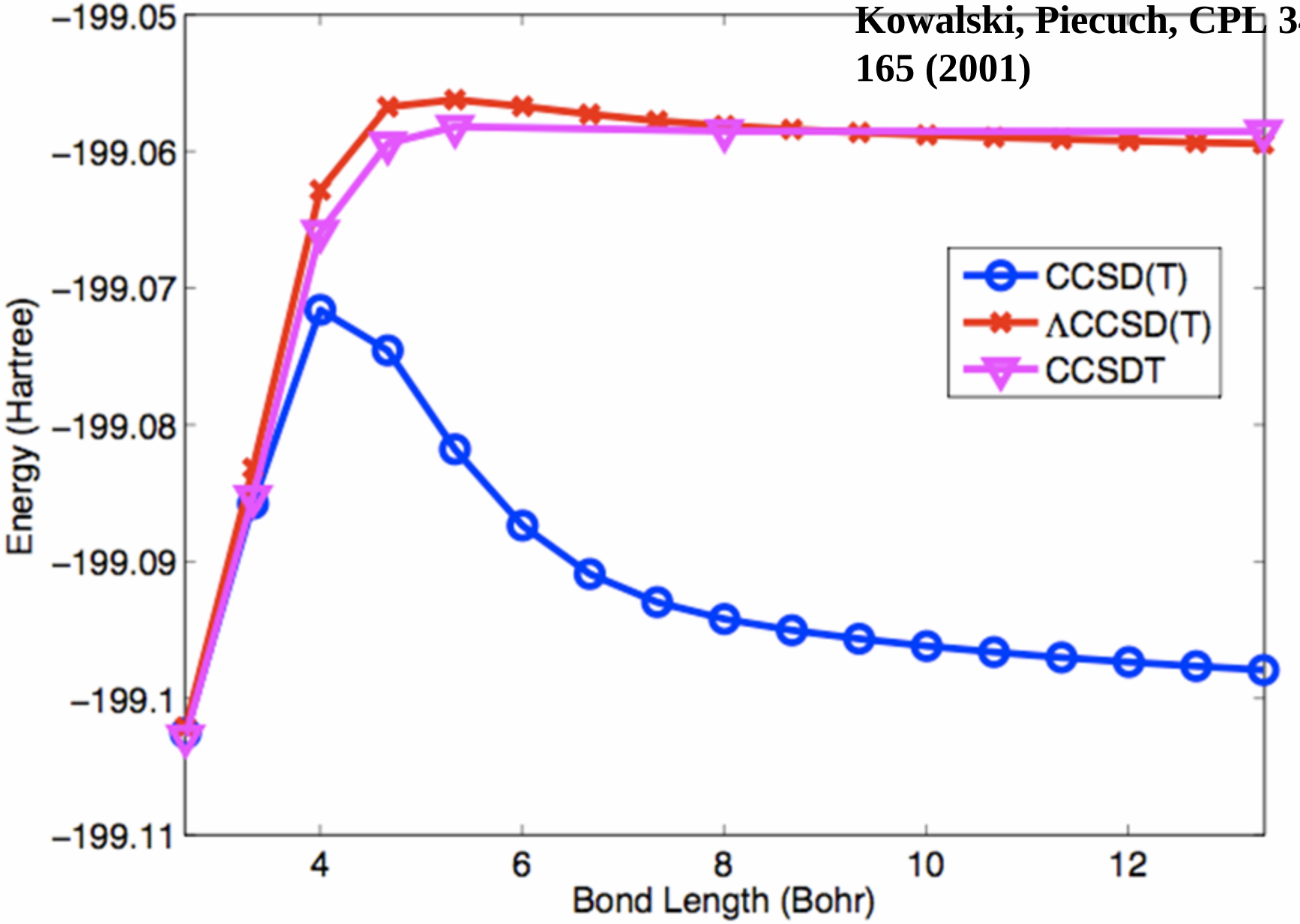



627.5
502
376.5
251
125.5
0
-125.5
-251
ΔE (kcal/mol)
0.5
1
1.5
2
2.5
3
3.5
Bond Length (n*Re)
RHF CCSD
RHF CCSD(T)
RHF ΛCCSD(T)
DMRG
Full CI

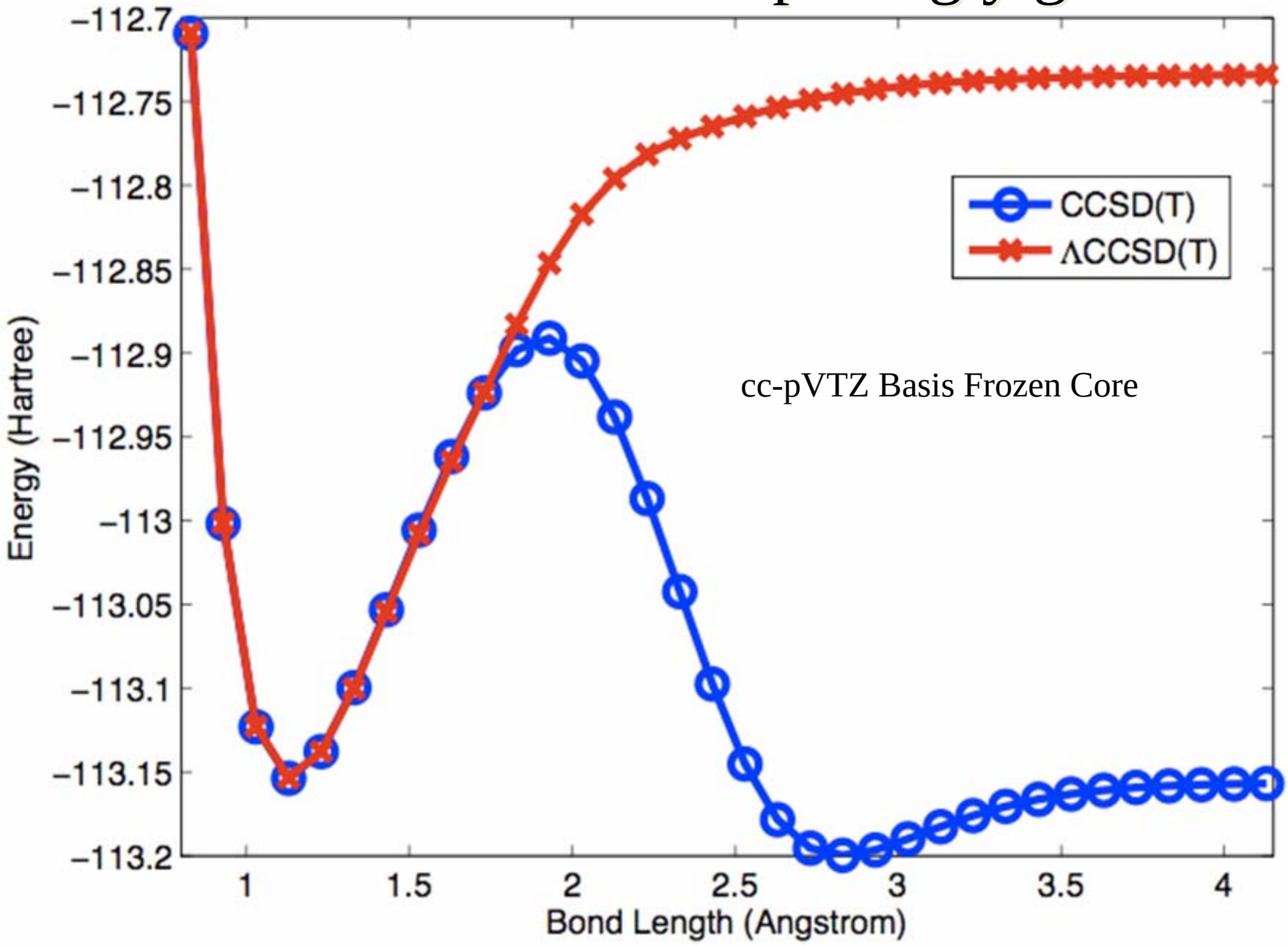
Fluorine

cc-pVDZ Basis Frozen Core

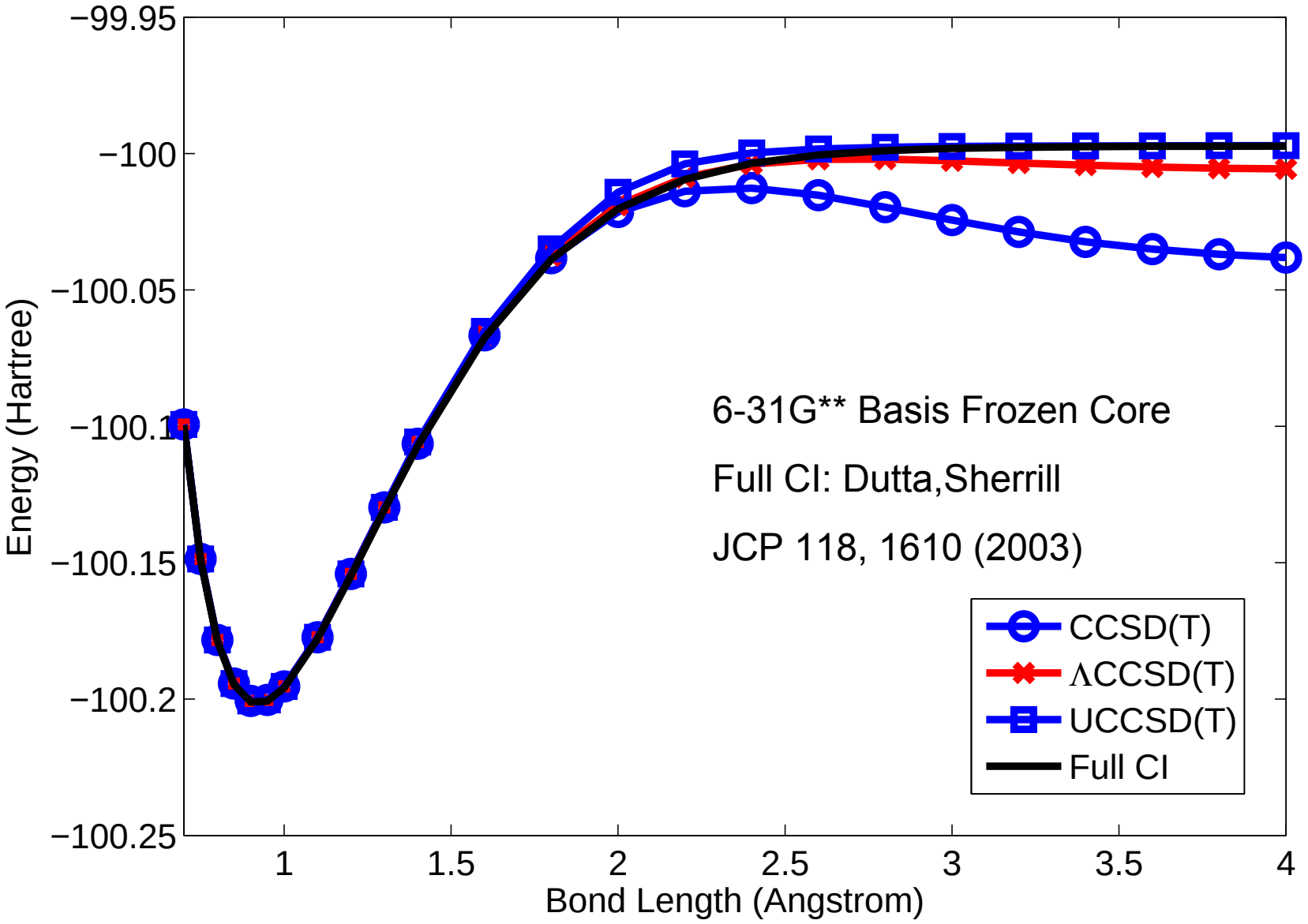
CCSDT Results from Kowalski, Piecuch, CPL 344, 165 (2001)



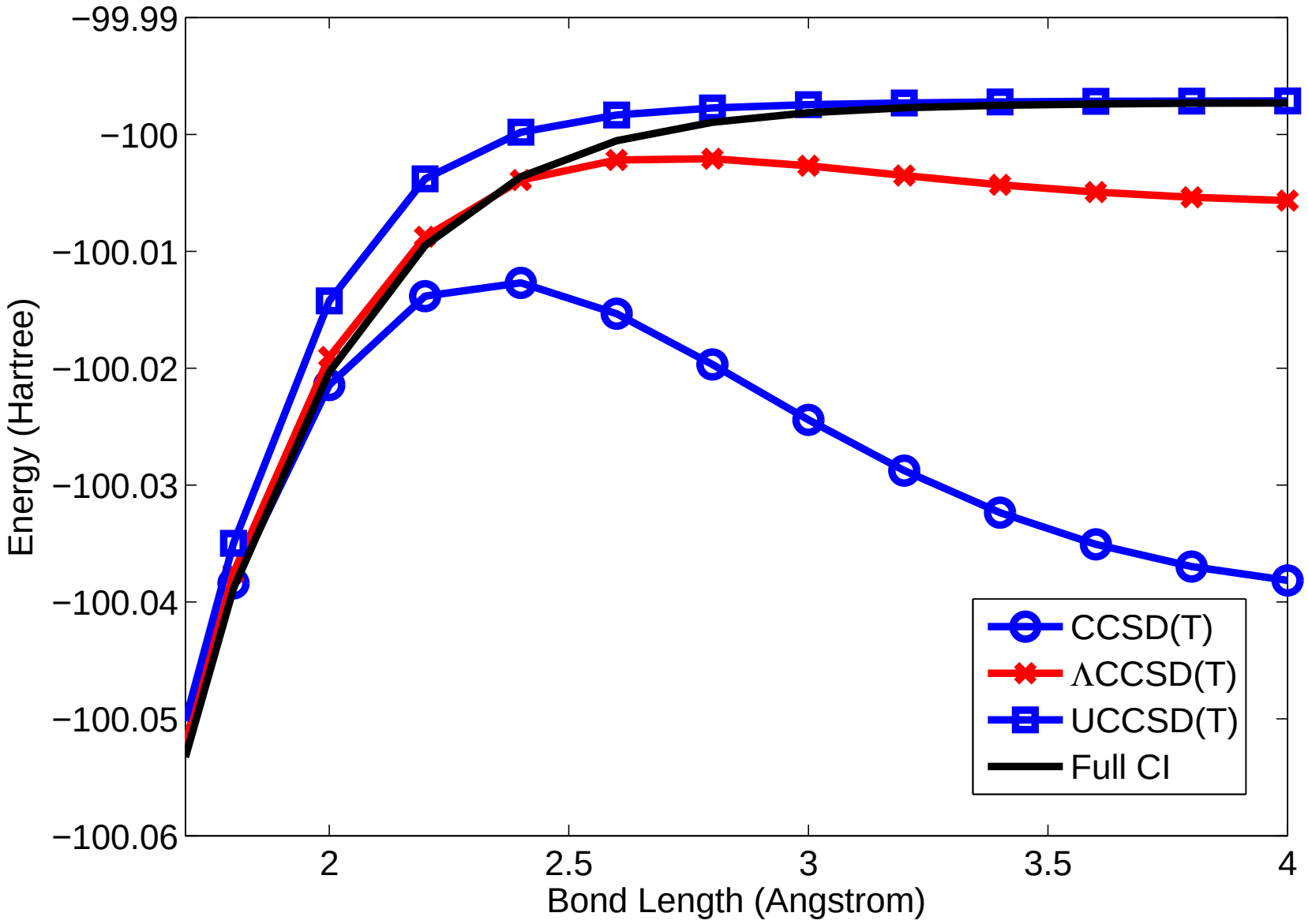
Carbon Monoxide: Surprisingly good



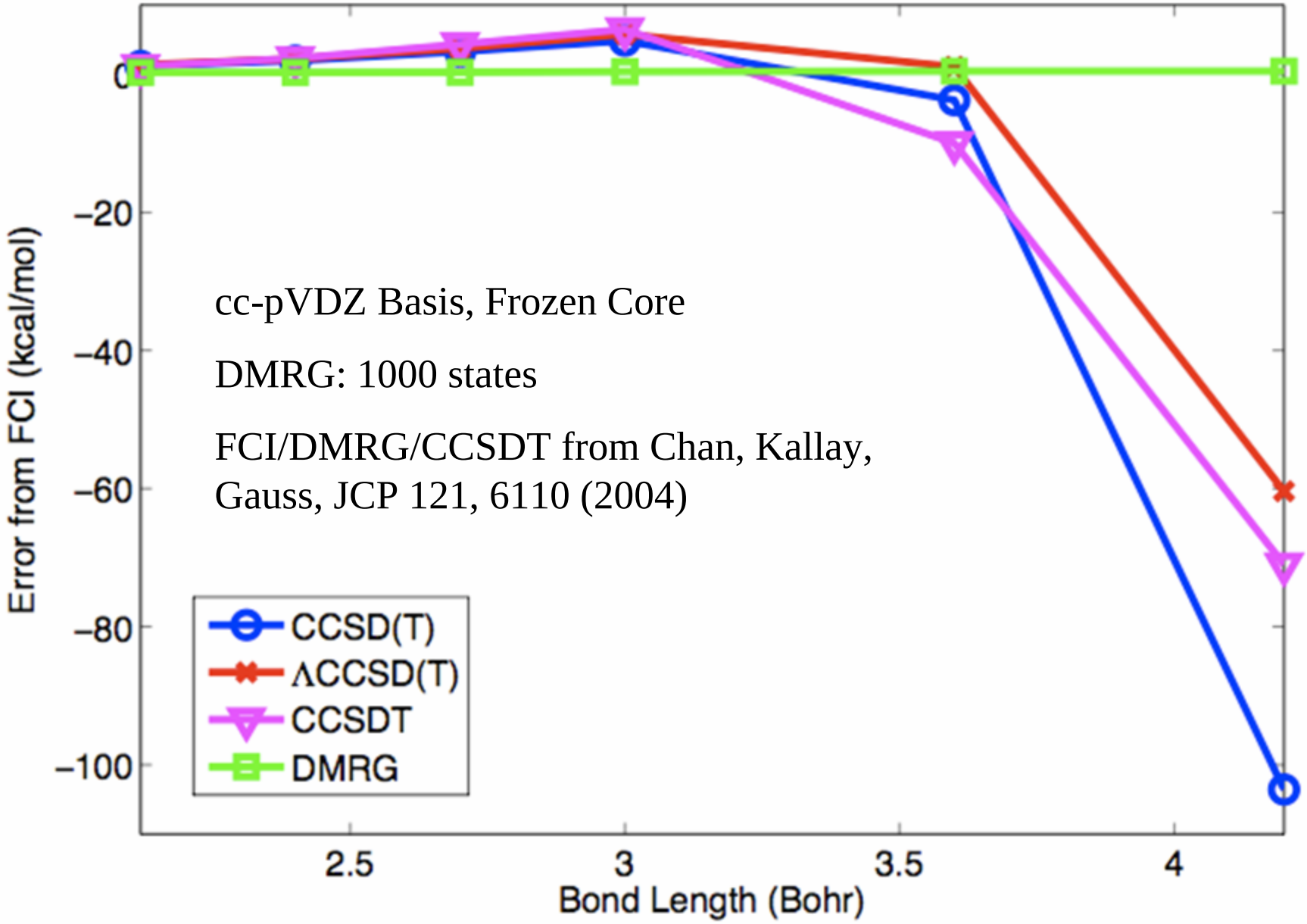
UHF HF Bond-breaking



Spin-recoupling Region (Zooming in)



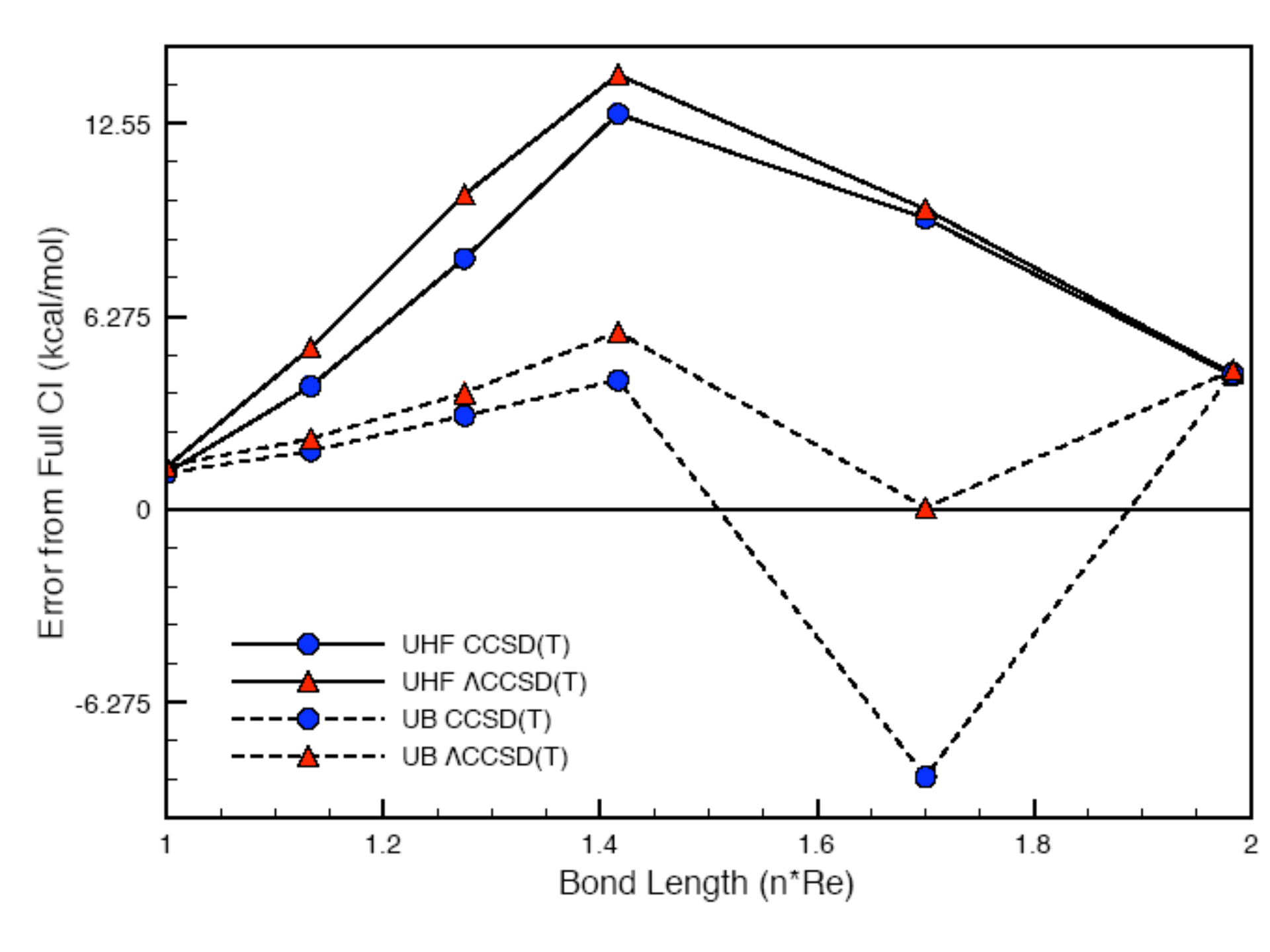
Nitrogen: As challenging as ever



cc-pVDZ Basis, Frozen Core

DMRG: 1000 states

FCI/DMRG/CCSDT from Chan, Kallay, Gauss, JCP 121, 6110 (2004)


12.55
6.275
0
-6.275
Error from Full CI (kcal/mol)
1
1.2
1.4
1.6
1.8
2
Bond Length (n*Re)
UHF CCSD(T)
UHF ΛCCSD(T)
UB CCSD(T)
UB ΛCCSD(T)

CONCLUSIONS

•CC theory now provides the 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 featurre is very different than density functional methods (DFT).

•It is used in 1,2 and 4 component forms for solutions of the Dirac equation.

•It is used with explicit consideration of interelectronic interactions, R12, which improves the basis set for some problems.

•With the recent developments, it now offers solutions for essentially all problems encountered for molecules.

•It has been applied to polymers, but cannot yet be used for 2 and 3 dim systems subject to periodic boundary conditions for the wavefunction.

•Recent work has applied the quantum chemical CC theory to nuclei, the subject of an INT Workshop this summer at the Univ. of Washington.

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 Quantum Chemistry,” Cambridge Press, to be available, 2007.

THANK YOU VERY MUCH!

Coupled-cluster theory provides a synthesis of
Cluster Expansions, Brueckner Theory,
the Gell-Mann-Brueckner theory of the Electron Gas
and an infinite-order generalization of MBPT!

Coupled-Cluster Doubles (CCD) Equations
J. Čížek (1966)

First ab initio application was to BH_3
in a minimum basis of 8 functions. Full
CI had 196 configurations!
J. Paldus, J. Čížek. I Shavitt (1972).

CORRELATION PROBLEM

"The interaction of electrons with antiparallel spins, contains, in addition to the interaction of uniformly distributed space charges, another term. This term is due to the fact that electrons repel each other and try to stay as far apart as possible. The total energy of the system will be decreased through the corresponding modifications of the wavefunction. In the present paper it is attempted to calculate this "correlation energy".

E. P. Wigner, On the Interaction of Electrons In Metals, Phys. Rev 1934.