Approaching Multi-reference (and Open-Shell Problems) in Electronic Structure Theory from the Equation-of-Motion Coupled-Cluster Perspective

INT Workshop on Advances in Many-Body Theory: From Nuclei to Molecules

April 3, 2013

RODNEY J. BARTLETT

Co-Workers

Ajith Perera, Victor Lotrich, Tom Watson, Robert Molt
Monika Musiał , Stan Kucharski, Dimitri Lyakh

$ ARO $

This workshop seeks to develop ab initio methods to address---

- Open shells and deformed nuclei
- 3 body forces
- Pairing in nuclei
- Structure and reactions
- Constraining (creating) EDF (DFT) methods
- Error estimates for calculation

The obvious parallel with similar issues In chemistry, allows for many of the same tools, notably coupled-cluster theory and its computational implementation, to be used for molecules, nuclei, and solids.

SOME PRELIMINARIES

To communicate successfully and facilitate cross-fertilization of our respective disciplines, we need to address the following:

- **Hamiltonian**
- **Basis set**
- **Mean-field**
- **Symmetry**

- **Hamiltonian**

The normal ordered H relative to the mean-field soln, Φ_0, is

$H = \langle 0|H|0\rangle + \sum_{p,q} f_{pq}\{p^{\dagger}q\} + \sum_{pqrs}\langle pq||rs\rangle\{p^{\dagger}q^{\dagger}sr\}$

f = h + J – K, is the usual Fock Operator,

with J the Coulomb and K the exchange Operator.

$\langle pq||rs\rangle = \int dx_1 \int dx_2 \varphi_p (x_1)\, \varphi_q (x_2)(1-P_{12})(\mathbf{r_1} - \mathbf{r_2})^{-1}\, \varphi_r(x_1)\, \varphi_s(x_2).$

So $(J-K)_{pq} = \sum_j \langle pj||qj\rangle$, $h_{pq} = \langle p|h|q\rangle$

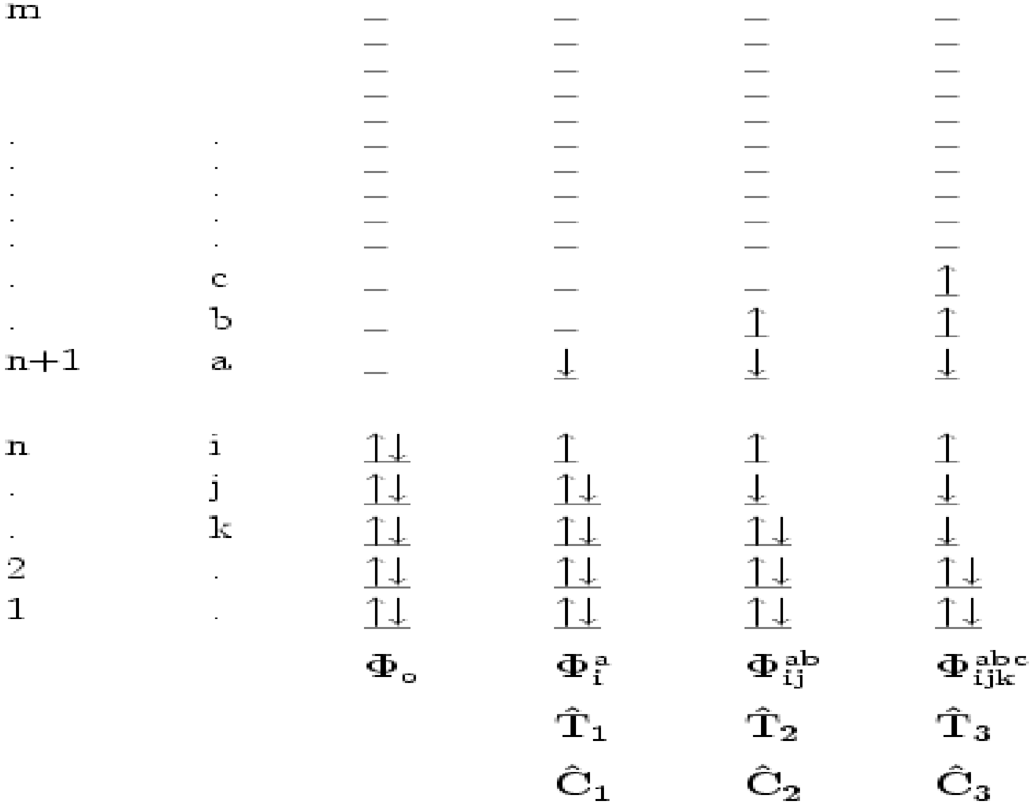
• Basis Set

Sets of gaussian ‘atomic’ orbitals, $|\chi\rangle$ located on all atoms in the molecule, square integrable, finite. # is m>>>n, # of electrons. Gaussians make it easy to evaluate the four-center integrals that occur for molecules.

‘Molecular’ orbitals $|\varphi\rangle=|\chi\rangle\mathbf{C}$, where the **C** might be taken from HF, or Brueckner, or Natural Orbitals, or Kohn-Sham or any other choice. This is the one-particle basis.

Best possible answer in $|\chi\rangle$ is the Full CI where all possible excitations (replacements of occupied orbitals by virtual ones) are taken. This is the n-particle basis. Calculation scales as $\sim n^{m}$ FCI is impossible except for very small molecules and basis sets, so practical methods will be limited to CCSD, CCSDT, CCSD(T), etc.

Fig. 2



CID, CISD, CISDT, CISDTQ, …. Full CI

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

CCD, CCSD, CCSDT, CCSDTQ…Full CI

- **Symmetry**

Most relevant for atoms and molecules is spin-symmetry, $S^2\psi = S(S+1)\psi$ and $S_Z\psi = M_Z\psi$. For closed shells with doubly occupied orbitals the ψ's will always be spin-eigenfunctions. For open-shells, as long as all orbitals are pure spin orbitals, meaning they correspond to α or β spin, then the determinants are eigenfxns of S_Z. However, if broken symmetry solns are used, like in Unrestricted Hartree-Fock (UHF), $S^2\Phi_{\mathrm{UHF}} \neq S(S+1)\,\Phi_{\mathrm{UHF}}$.
If we use ROHF solns for open shells, $S^2\Phi_{\mathrm{ROHF}} = S(S+1)\Phi_{\mathrm{ROHF}}$
SR-CC starting from Φ_{ROHF}, will not guarantee ψ is an eigenfxn of S^2.The determinants can be combined together into specific combinations, ie configurations which are eigenfxns of spin in CI, and this can be used in EOM-CC for target states.

Now that we have the basis sets, what is the best way to introduce them into the wavefunction?

Answer: Coupled-Cluster Theory

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)**

CORRECT WAVEFUNCTION HAS TO BE AN EXPONENTIAL OF CONNECTED OPERATORS!

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

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

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), …**

$$\Psi^{(1)}=[T_1^{(1)}+T_2^{(1)}]|0\rangle$$

$$\Psi^{(2)}=[T_1^{(2)}+T_2^{(2)}+T_3^{(2)}+(T_2^{(1)})^2/2+\ldots]|0\rangle$$

EXAMPLE I: Correlated Energies

The CC energy is

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

The similarity transformed Hamiltonian is

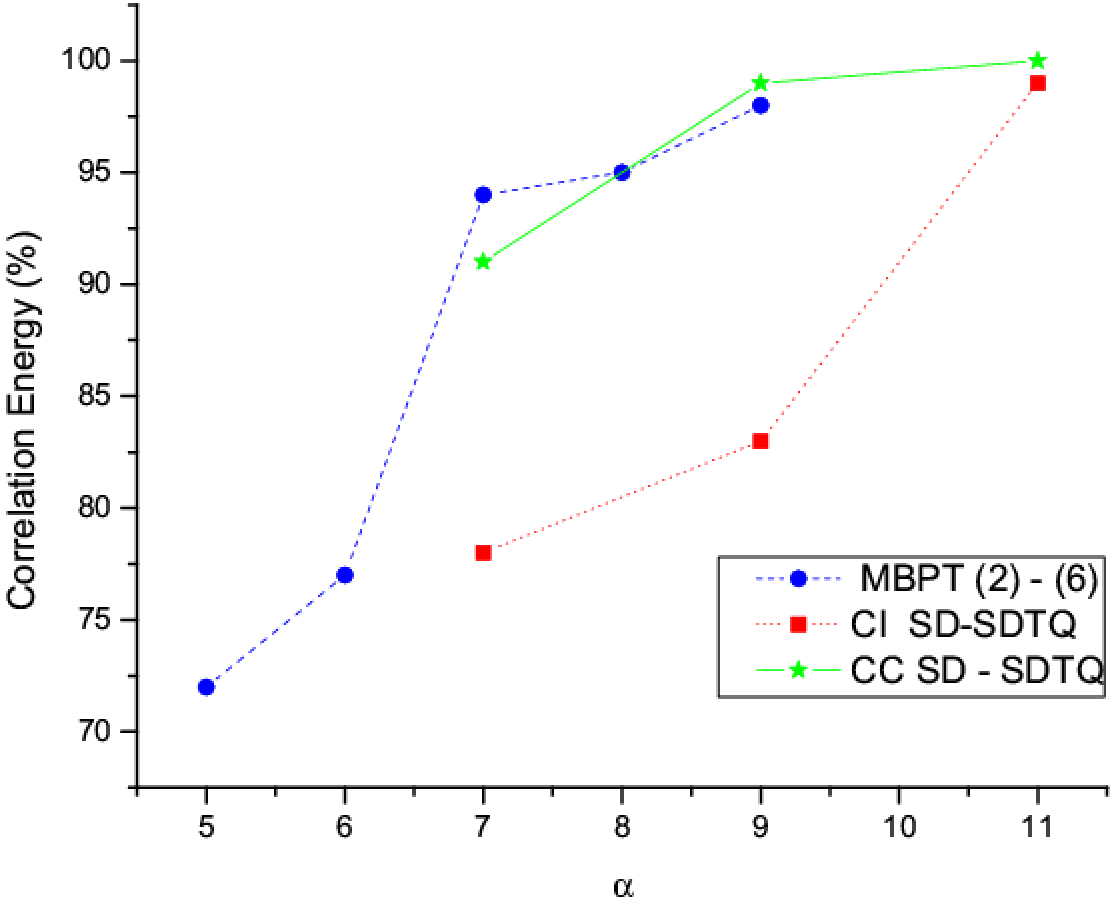
$\bar{H} = \exp(-T)H\exp(T)$ **$= I + II + III + IV + \ldots$**

and the wavefunction equations are

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

It doesn’t get much simpler than that!

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



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,

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

That's pretty simple too!

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

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

That derivation, which makes it possible to do analytical gradients in non-variational CC theory depends only upon the interchange theorem, long used in double perturbation theory.

And we don’t need a time-dependent theory to treat properties of time-independent states, or those from periodic, time-dependent perturbations, like the dynamic polarizability.

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.

Example III: Non-iterative Triple Excitation Corrections

ΛCCSD(T) Derivation (1998) Kucharski, RJB

$$E = \langle 0|(1+\Lambda)\bar{H}|0\rangle$$

Triples excitation contributions on top of CCSD are

$$E_T = \langle 0|\Lambda_3 H_0 T_3 | 0\rangle + \langle 0|\Lambda_3(W + f_{ov})(T_2 + T_1)|0\rangle$$
$$+ \langle 0|(\Lambda_1 + \Lambda_2)(W + f_{ov})T_3 |0\rangle$$

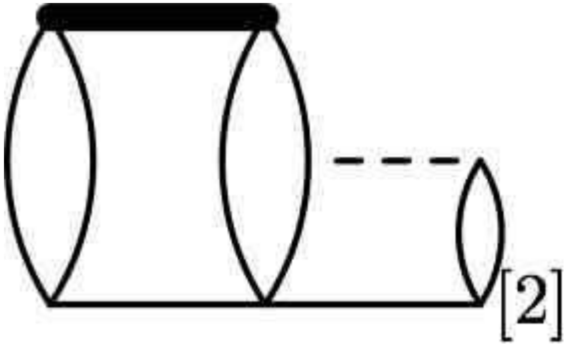
Since, $Q_3 H_0 T_3|0\rangle + Q_3[(W + f_{ov})(T_2 + T_1)]_C|0\rangle = 0$,
defines $T_3^{[2]}$

$$\mathbf{E_T^{[4]} = \langle 0|(\Lambda_1 + \Lambda_2)(W + f_{ov})T_3^{[2]} |0\rangle}$$

These are all possible fourth-order triples terms.

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

$E_T^{[4]} =$



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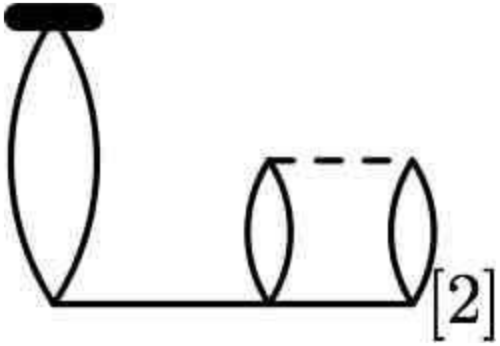

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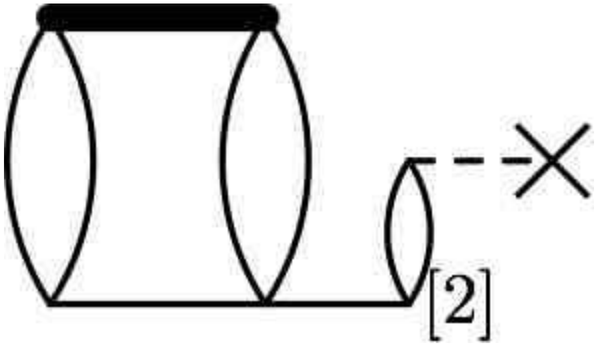


When Λ is replaced by $T^{\dagger}$ get ordinary (T).

Example IV: Excited states and any sector of Fock Space: **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, doubly ionized, etc. (these offer many attractive routes to open-shell states)-

$[T, R_k] = 0$

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

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

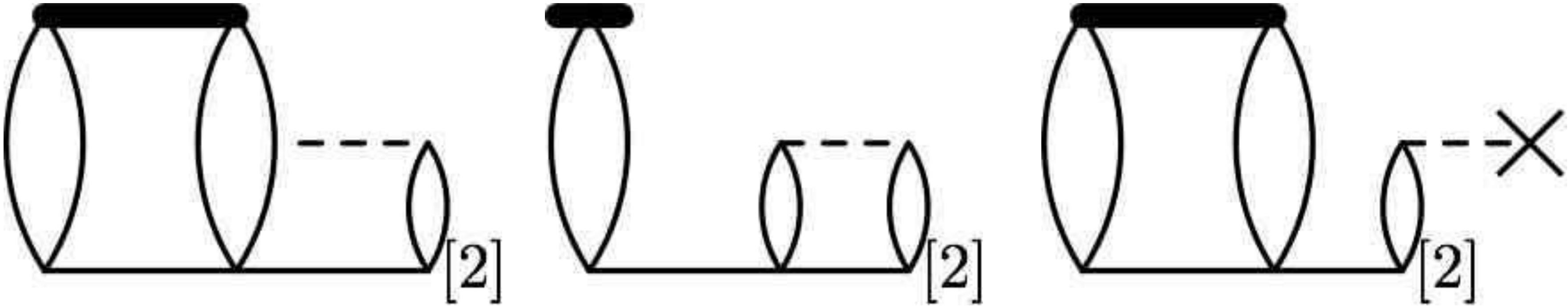
$$\langle 0|(L_k \bar{H}) = \langle 0|L_k\,\omega_K$$

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

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

Following exactly the same strategy, triples effect in EOM-CC can be readily derived….

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



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)

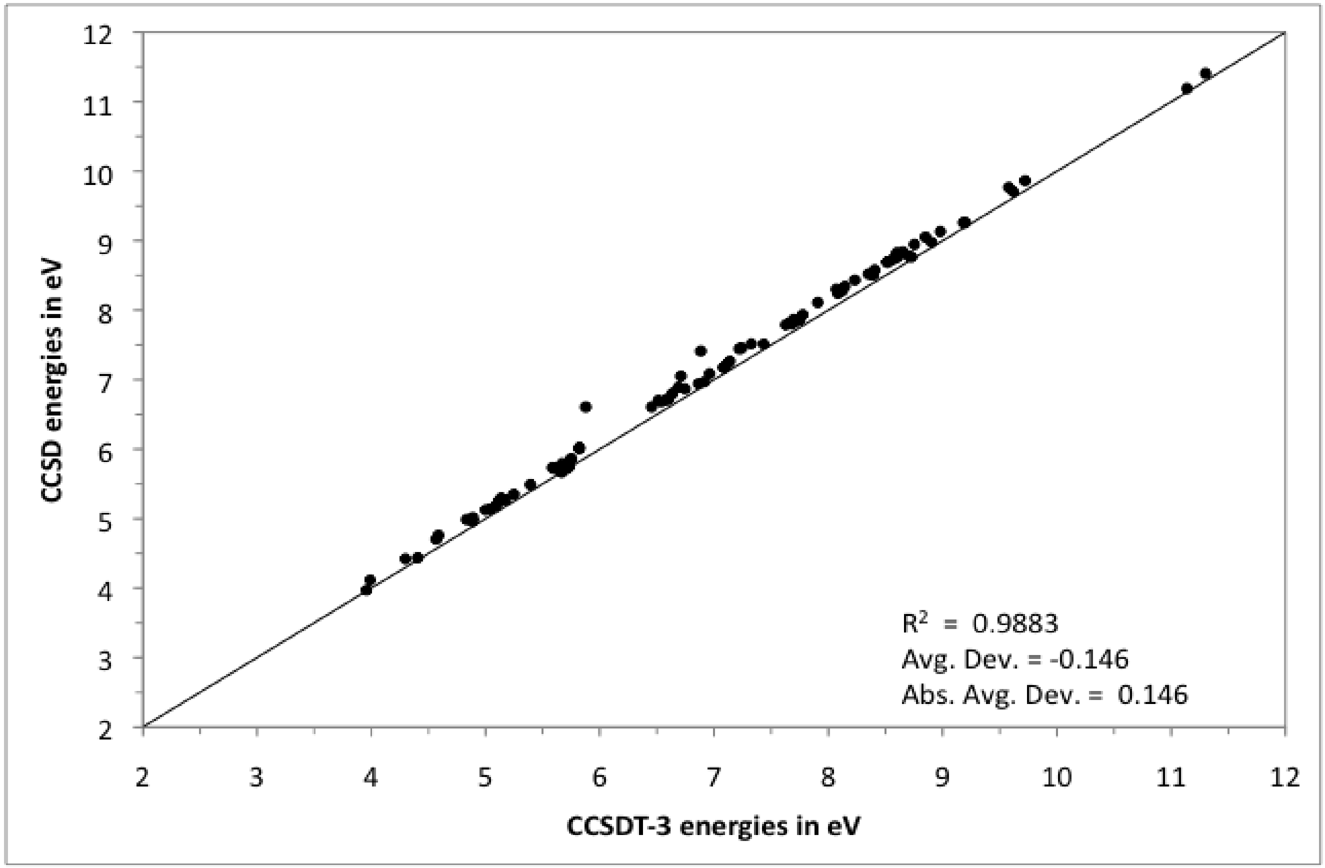
(Tom Watson's ACES III implementation)

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
$\pi \rightarrow 2\pi^*$ $n_{O+N} \rightarrow R$ $\pi_N \rightarrow 2\pi^*$	6.50 6.70 6.88	6.38 6.57 6.72	6.30 6.43 6.62	6.35 6.57 6.69

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

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

EOM-CCSD vs. EOM-CCSDT-3



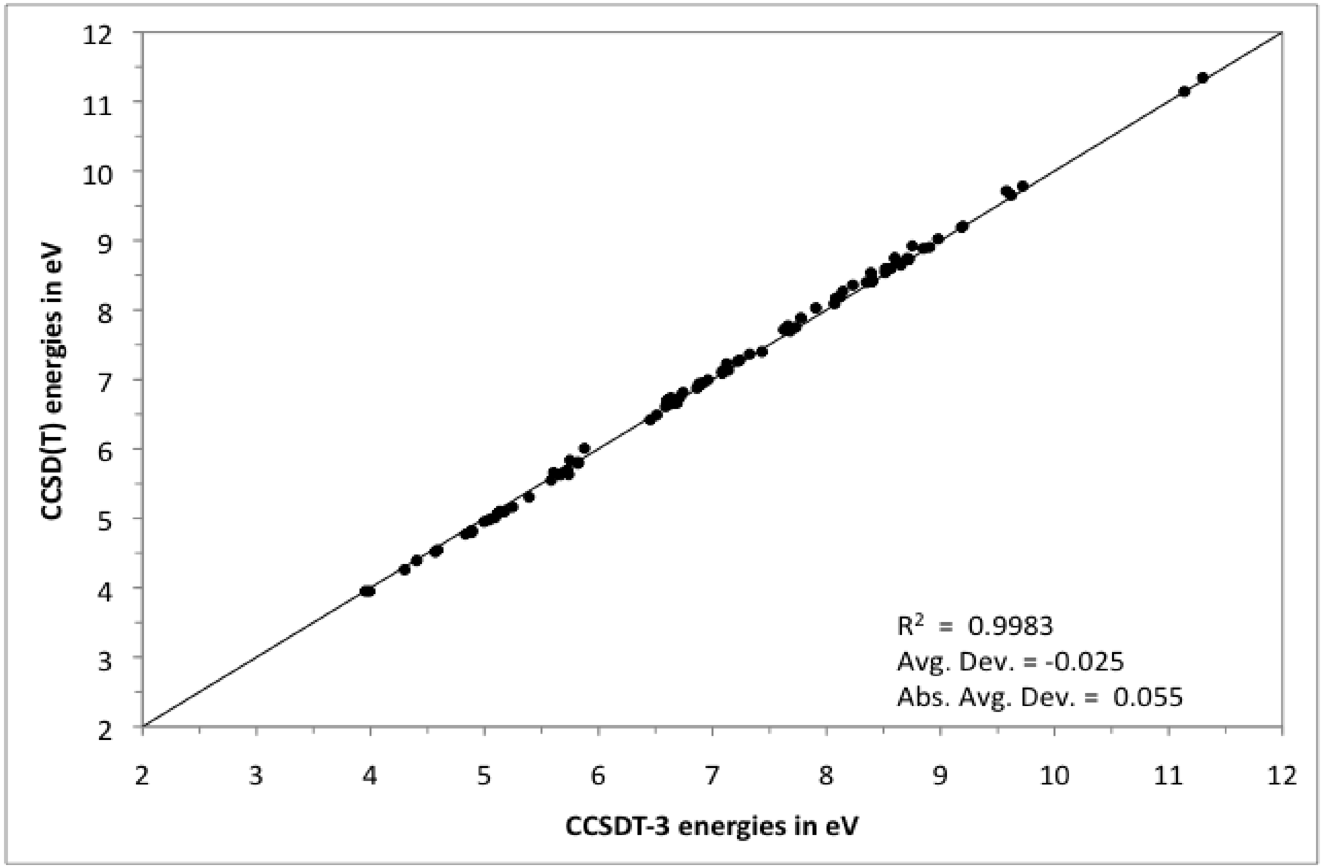
Comparative computational dependence

CC3 and EOM-CCSDT-3 scale as $\sim n^3N^4$, plus require Iterative diagonalization of a matrix that has rank $\sim n^3N^3$

EOM-CCSD scales as $\sim n^2N^4$ with matrices of rank $\sim n^2N^2$.

EOM-CCSD(T) scales as $\sim n^2N^4$ + one n^3N^4 step, but matrices are only $\sim n^2N^2$. It is tremendously faster than CC3/CCSDT-3.

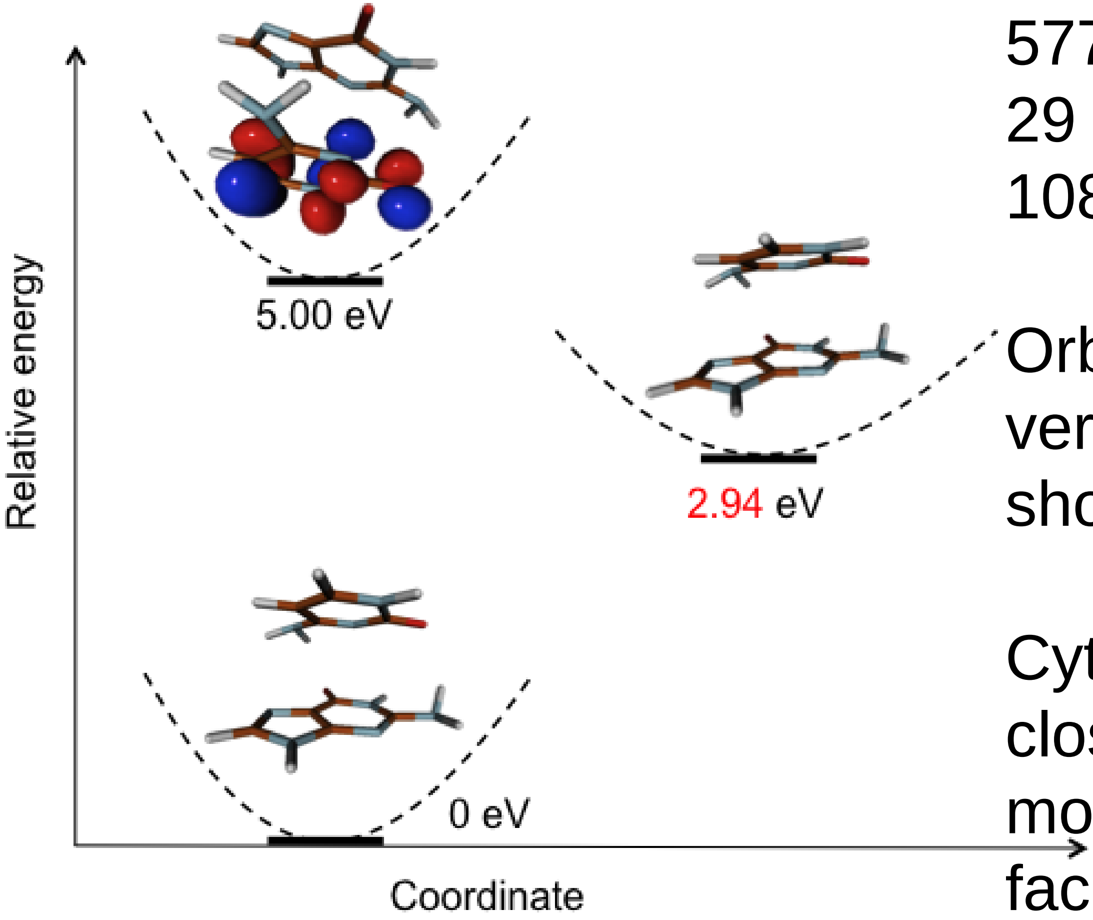
EOM-CCSD(T) vs. EOM-CCSDT-3



So we put together those four simple examples and
Add a little parallelization (ACES III) and …

EOM-CCSD gradients for geometry optimization in excited states

EOM-CCSD gradient on Cytosine – Guanine stack

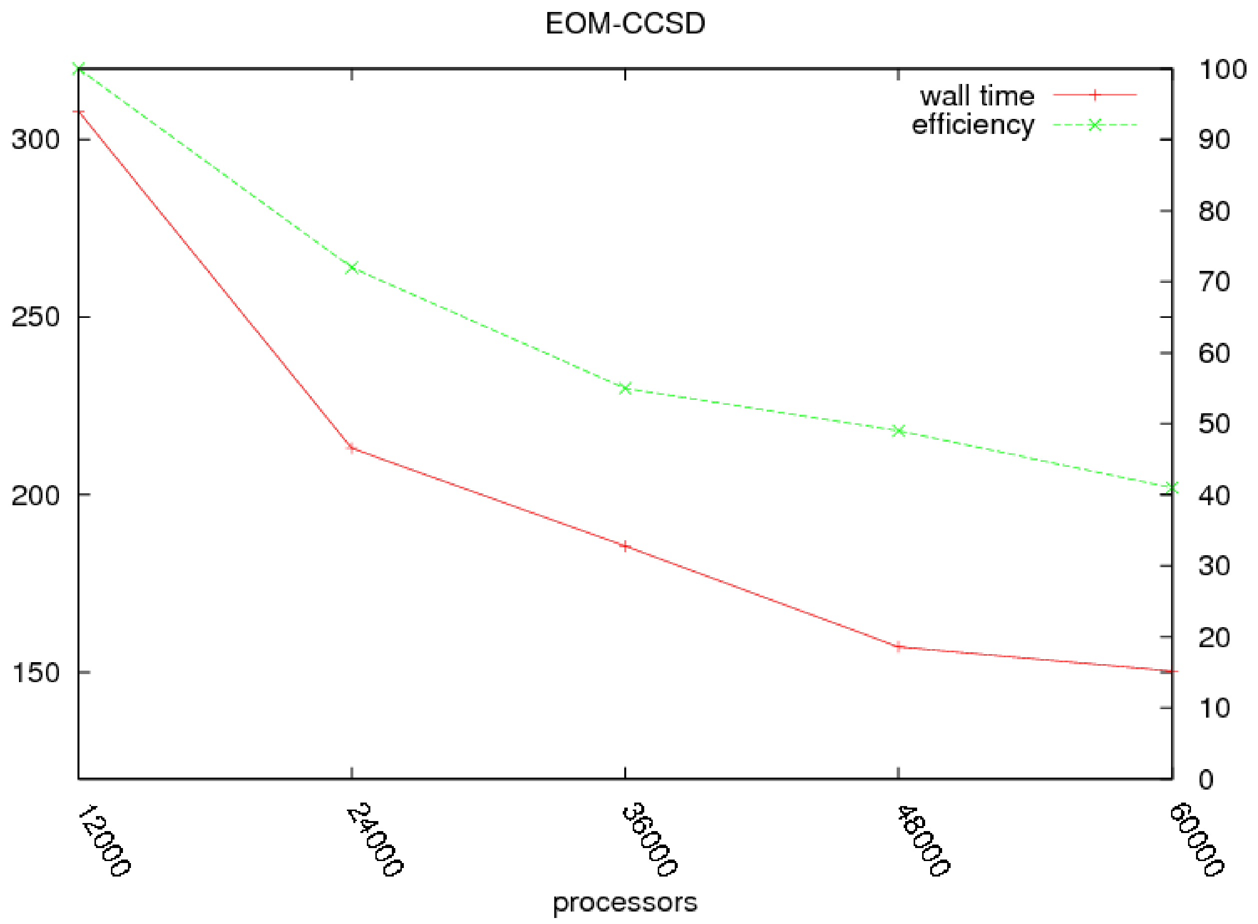


577 basis functions
29 atoms
108 electrons

Orbitals involved in vertical excitation are shown

Cytosine is pushed closer to the guanine molecule, possibly facilitating some relaxation mechanism from the excited state

Cytosine-Guanine Watson-Crick stacked dimer



1154 basis functions
58 atoms
216 electrons

Single-reference CC theory (and its EOM-CC extensions) gives the best answers for the largest number of CC accessible problems encountered in molecular-quantum mechanics…and with no decisions for the user except basis set and level of CC

When SR-CC fails the reason is most likely due to the limitations of the single determinant reference (RHF, UHF, ROHF, KS, B, N, QRHF….)

Hence, multi-reference coupled-cluster methods...

SOME COMMON EXAMPLES of MR Problems

- Open-shell transition metal atoms, multiplets, and role in catalysis.
- Correct description of equivalent (valence-bond) structures, like allyl radical, •NO_2, formic acid dimer.
- Vibrational frequencies of O_3, etc.
- Reaction paths like the insertion of Be into H_2.
- Biradicals and associated singlet-triplet energy differences.
- Transition states like Cope rearrangement, Diels-Alder, etc.
- Bond-breaking with incorrectly separating RHF references.
- The spin-recouplIng region with correctly separating UHF refs.
- Low-spin eigenstates, open-shell singlets, low-spin doublets, etc

SRCC has to give exact answer in the limit (Full CI), so the real issue is whether SRCC has enough in it at a reasonable level or needs a MR boost. This also strongly recommends that MR-CC have SR-CC as a special case.

CURRENT MR-CC METHODS

•Valence Universal, Fock-Space

Lindgren, Mukherjee, Pal, RJB, Kaldor, Meissner, Musial

•State Universal, Hilbert-Space

Kucharski, RJB, Meissner, Balkova, Paldus, Piecuch, Li

•State-Specific Hilbert Space

- **TD-CC. Open-shell Singlets. A Balkova, P. Szalay, RJB**

- **BW-CC. I. Hubač, J. Pittner, and P. Čársky,**
  J. Chem. Phys., 2000, 112, 8779.

- **Mk-CC. Mukherjee, Evangelista, Allen, Schaefer, Gauss**

- **Internally contracted. Köhn, Hanrath**

D. Lyakh, M. Musial, V. Lotrich, RJB, Chem. Rev. 2012.

Problems Encountered …

- Intruder States
- No analytical forces
- Not extensive
- Fails to satisfy projected Schrodinger Eqn.
- Not invariant to rotations among active orbitals
- Not spin eigenfunctions.

But EOM-CC accommodates many MR problems, too, and can be further generalized to describe many more.

Continuing with simple theory, the next step….

MR-MI/MA-EOM-CC,

(multi-reference, multi-ionized/attached, equation-of-motion CC)

… the simplest conceptually but least developed and tested for most MR problems, but its MANY attractive properties drive its development…

DESIDERATA IN MULTI-REFERENCE CC METHODS

RJB, “To Multireference or Not to Multireference: That is the Question?”
Int. J. Mol. Sci. 3, 579-603 (2002).

•Method should be

1. size-extensive, ie completely linked.
2. size-intensive for energy differences.
3. spin-symmetry eigenfunctions (‘static’ correlation in open-shell atoms)
4. invariant to orbital transformations among occupied/virtual/ and active orbitals.

•If active orbitals are a necessary evil, then they should be unambiguously defined for any molecular geometry while potential energy surfaces remain smooth.

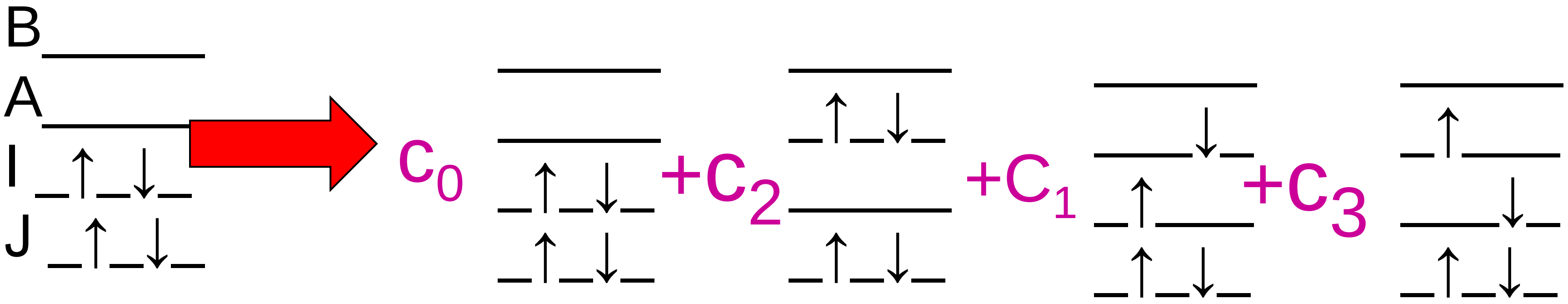
Desiderata continued….

- Calculations should be as easy to run as **single reference CC** theory.
- When MR character is encountered, theory should 'dynamically' add the other important determinants to the wavefunction in an **unbiased** way.
- **Theory should naturally reduce to SRCC in the absence of MR/quasi-degeneracy effects.**

Paradoxically this doesn't happen in most current MR-CC methods!

SR-CC, $\Psi=\exp(T)\Phi$

BASIC MR PROBLEM: Occurs when orbs like I and A become equally important.



Ref. Detm.

$C_0 \approx$ 90% Defines SRCC problem.

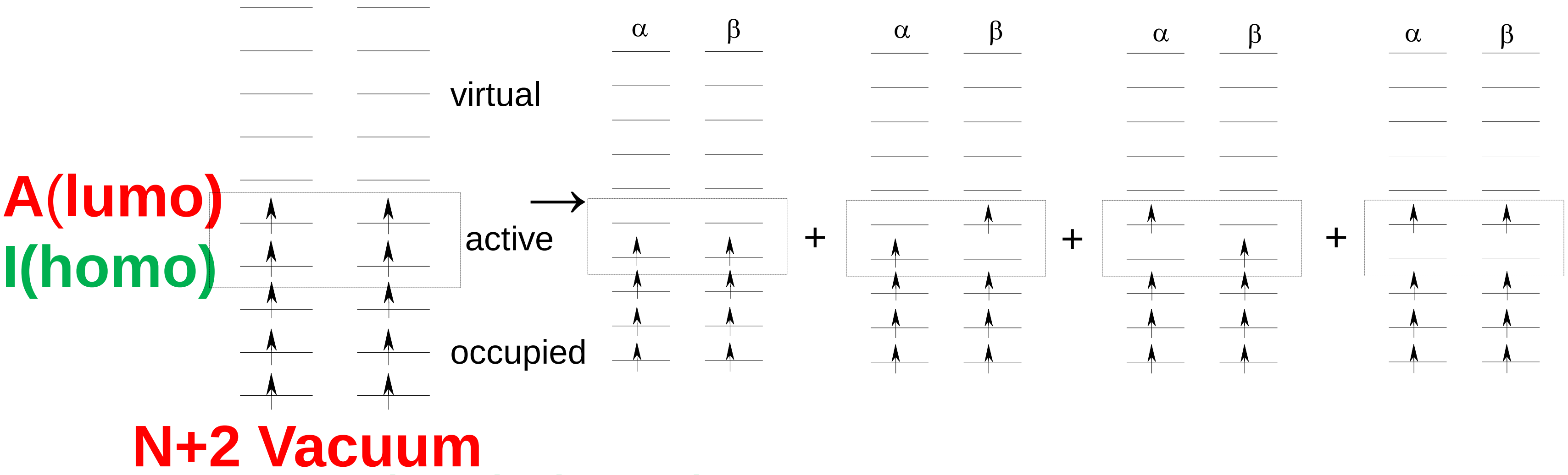
$C_2 \approx T_{II}^{AA}$, $C_1 \approx T_I^A$, $C_3 = -T_I^A$

When the C's are too large to achieve this value via T in an applicable SRCC method, we encounter a MR-CC problem. We need a way to obtain the C's without the SR bias.

MR-MI/MA-CC

Multi-reference Multi-ionization (attachment) coupled-cluster theory

Ansatz: Given a vacuum with N+2 electrons, we kick out two electrons to provide the four determinant, multi-reference space ----



MA works similarly but on an N-2 electron vacuum.

EOM-CC STRATEGY

Ħ=exp(-$T^{n\pm2}$)Hexp($T^{n\pm2}$) comes from SR-CC

Then by building the matrix **Ħ,** which consists of the complete active space of these four determinants {*IJ*} and all single excitations from them, {$A^{T}IJK$}, and diagonalizing

$$ĦR_k = R_k\omega_k$$

$$R_k = [C_k, S_k]$$

The coefficients, C_0 C_1, C_2, C_3 assume any value, enabling MR or quasi-degenerate character to be introduced. $\mathbf{S}_k$ corresponds to additional single excitations from the four determinants. These include weighted triple excitations from the SRCC viewpoint. Could add doubles, etc.

(MR-DI/DA-CC)

Illustrations

- Normal double ion cases
- Use of DI/DA to describe MR problems, like the autoisomerization of cyclobutadiene, or the twisting of ethylene.
- Singlet-triplet separations of biradicals
- Single bond breaking subject to RHF reference functions
- Choose to limit to molecules composed of units whose corresponding cations/anions are closed shell to automatically ensure spin-eigenfunction character of target state.

- **Conclusions, problems, and prospects for development**

Normal Case (Ilustration of Role of S)

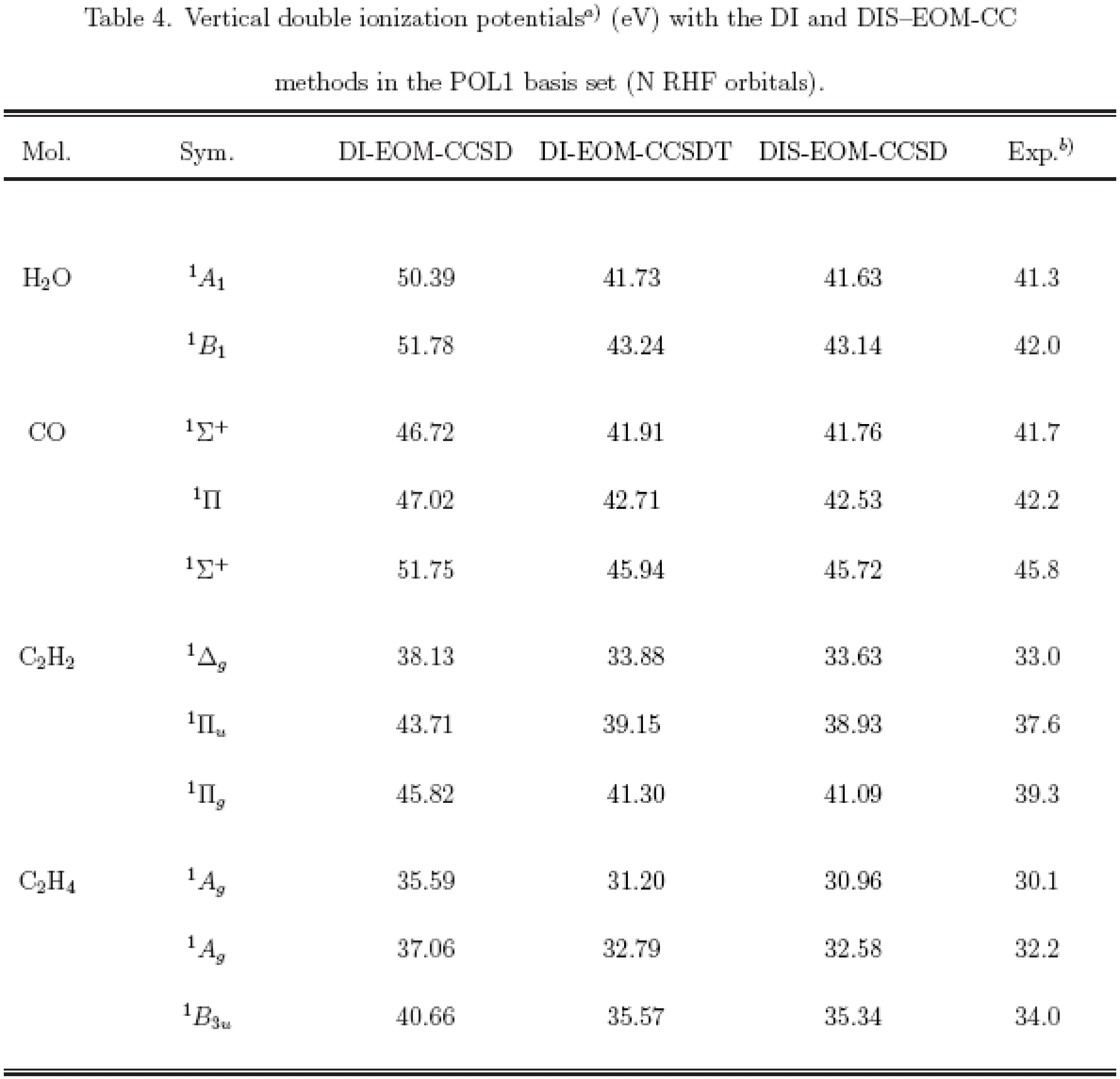


Table 4. Vertical double ionization potentials[a] (eV) with the DI and DIS–EOM-CC methods in the POL1 basis set (N RHF orbitals).

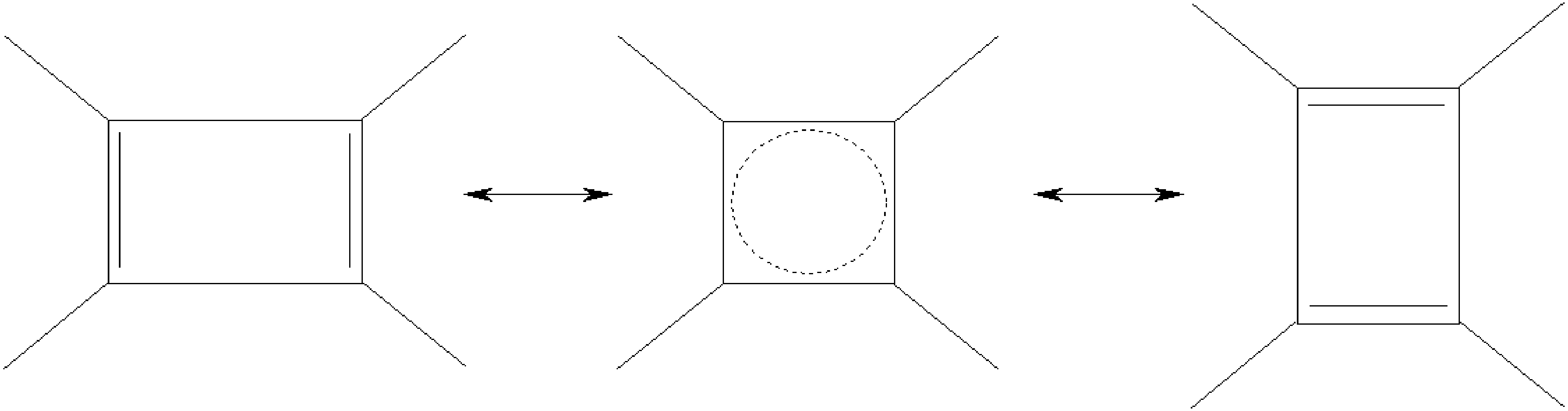
Mol.	Sym.	DI-EOM-CCSD	DI-EOM-CCSDT	DIS-EOM-CCSD	Exp.[b]
H_2O	$^1A_1$	50.39	41.73	41.63	41.3
	$^1B_1$	51.78	43.24	43.14	42.0
CO	$^1\Sigma^+$	46.72	41.91	41.76	41.7
	$^1\Pi$	47.02	42.71	42.53	42.2
	$^1\Sigma^+$	51.75	45.94	45.72	45.8
C_2H_2	$^1\Delta_g$	38.13	33.88	33.63	33.0
	$^1\Pi_u$	43.71	39.15	38.93	37.6
	$^1\Pi_g$	45.82	41.30	41.09	39.3
C_2H_4	^1A_g	35.59	31.20	30.96	30.1
	^1A_g	37.06	32.79	32.58	32.2
	$^1B_{3u}$	40.66	35.57	35.34	34.0

6.2 0.9 0.7 MAD, ~2%

As good as full triples!

Now for a MR-DI-CCSD Example…

Autoisomerization of Cyclobutadiene



A. Balkova and RJB, 1994 observed very large MR effect on barrier in early SU-CCSD calculation.

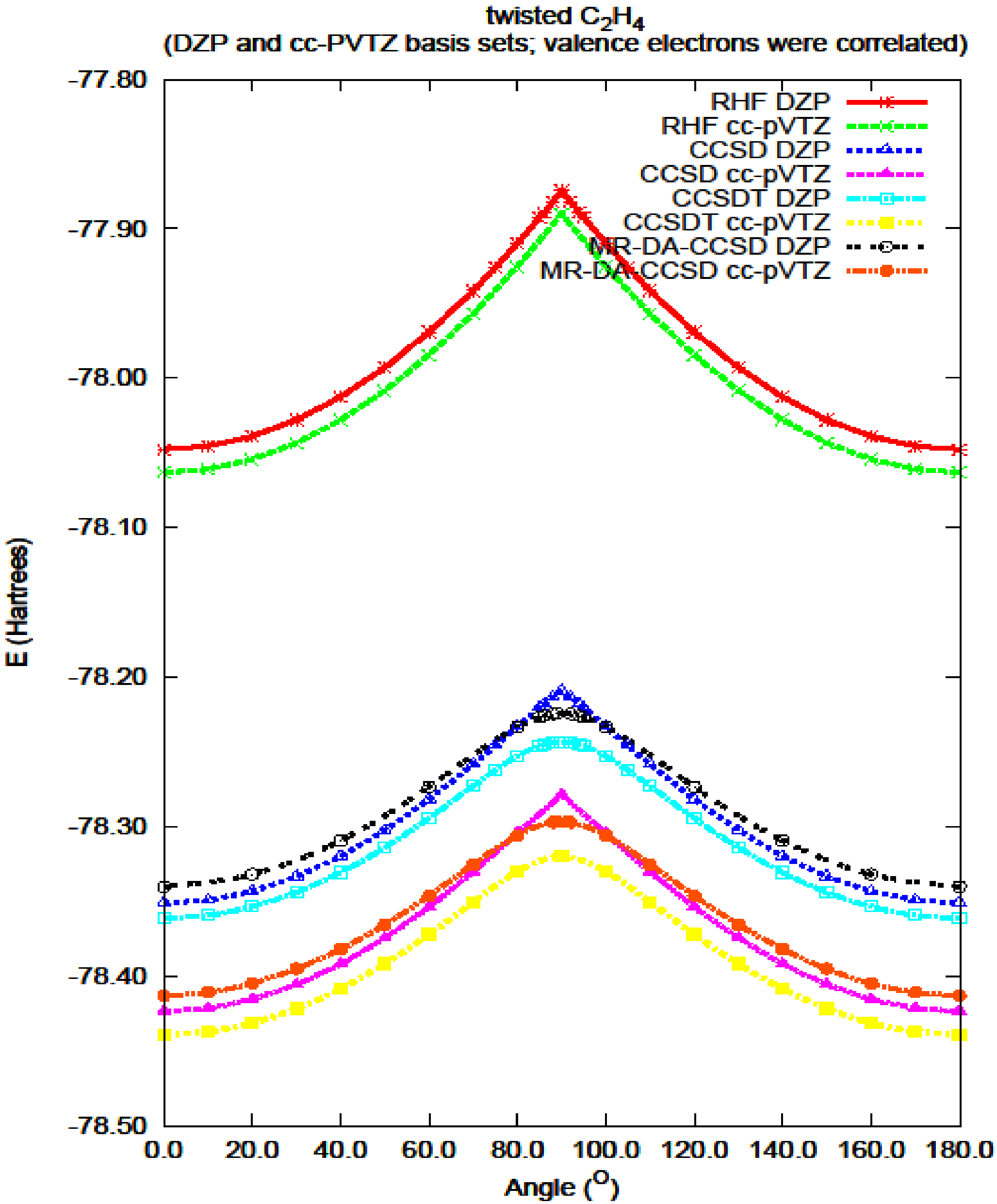
----- lumo
-↑–↓- homo

--↑--   --↓--
degenerate

----- lumo
-↑--↓- homo

TD-CCSD (~1990) works fine!

Method	cc-pVDZ, kcal/mol	cc-pVTZ, kcal/mol
CCSD	21.0	23.2
CCSD(T)	15.8	18.3
CR-CCSD(T)	18.3	21.5
ΛCCSD(T)	16.8	19.2
TCCSD	9.4	12.9
TCCSD(T)	4.6	7.0
2D-MRCCSD(T)	6.6	-----
SUCCSD(T)	4.8	5.9
BWCCSD(T)(a.c.)	6.1	7.0
BWCCSD(T)(i.c.)	5.7	6.8
MkCCSD(T)	7.8	8.9
RMRCCSD(T)	7.2	9.5
SUCCSD	7.0	8.7
BWCCSD(a.c.)	6.5	7.6
BWCCSD(i.c.)	6.2	7.4
MkCCSD	7.8	9.1
RMRCCSD	10.4	13.0
MRCISD	7.3	8.4
MRCISD+Q	7.6	8.8
MR-AQCC	7.7	8.9
DI-CCSD	8.3	10.4
DI-CCSDT-3	9.00 EXP 1.6-10	10.1
DI- CCSDT	8.86	------



twisted C_2H_4
(DZP and cc-PVTZ basis sets; valence electrons were correlated)

The DI-CC method will fail …

1. When the double anion vacuum is a bad initial approximation, even in an L^2 basis, because of its likely residual continuum nature. (CAP, complex rotation, constraining potentials.)

2. If manage (1) then the right choice of MO basis has to be made. **Formally any set of MO's can be used, but in practive need good choice.** Generally do not use dianion orbitals!

3. But even for (2), in the limit the underlying SR-CC solution $\exp[T(n+2)|n+2\rangle$ has to be invariant to MO choice and converge to the full CI for a dianion, likely found in the continuum in a complete basis..

4. So application depends upon each step being successful, so that the final wavefunction, $\psi(n)=R^{\{n-2]}\exp[T^{[n+2]}]|n+2\rangle$ makes sense.

DA-CC does not have these problems!

We explored many different choices of orbitals.
Musial, Perera, RJB JCP (2011).

n-particle HF
n+2, dianion
Brueckner
Kohn-Sham
Triplet
Fractional occupation

Results were comparable, so no clear choice.
Fractional occupation was particularly well-behaved.

Now for bond breaking…

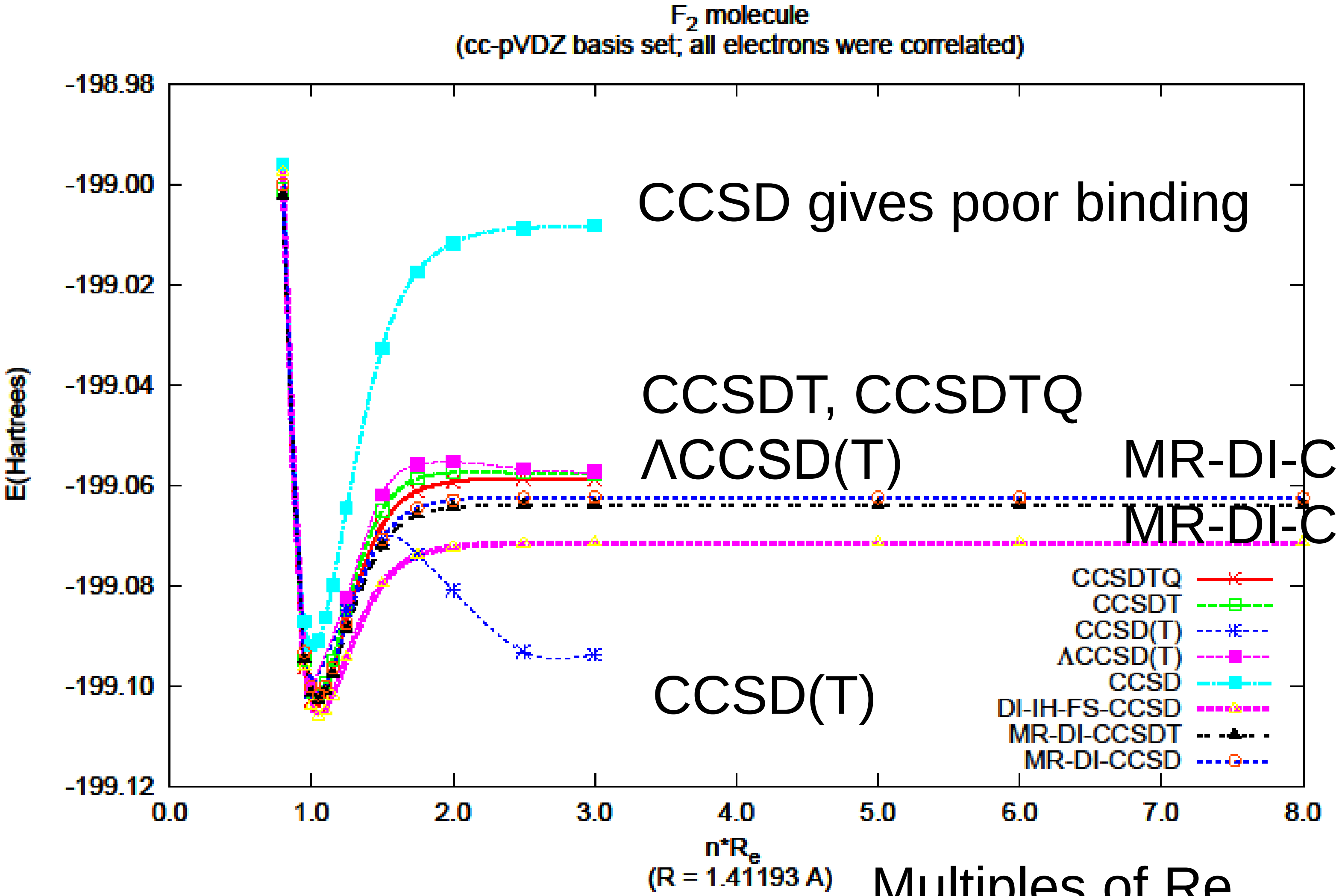
AB$\rightarrow \boldsymbol{A}\cdot + \boldsymbol{B}\cdot$ Objective

$AB^{\pm 2} \rightarrow A^{\pm 1} + B^{\pm 1}$ Computational Structure

As long as the cations and anions are closed shell,
the result for the radical dissociation is a spin-eigenstate

In the following, the qualitative behavior is primary.
The intent is to separate molecules into fragments without symmetry breaking using RHF references instead of UHF, eg.

RHF based CC



CCSD gives poor binding

CCSDT, CCSDTQ

ΛCCSD(T)

MR-DI-CCSD

MR-DI-CCSDT

CCSD(T)

Multiples of Re

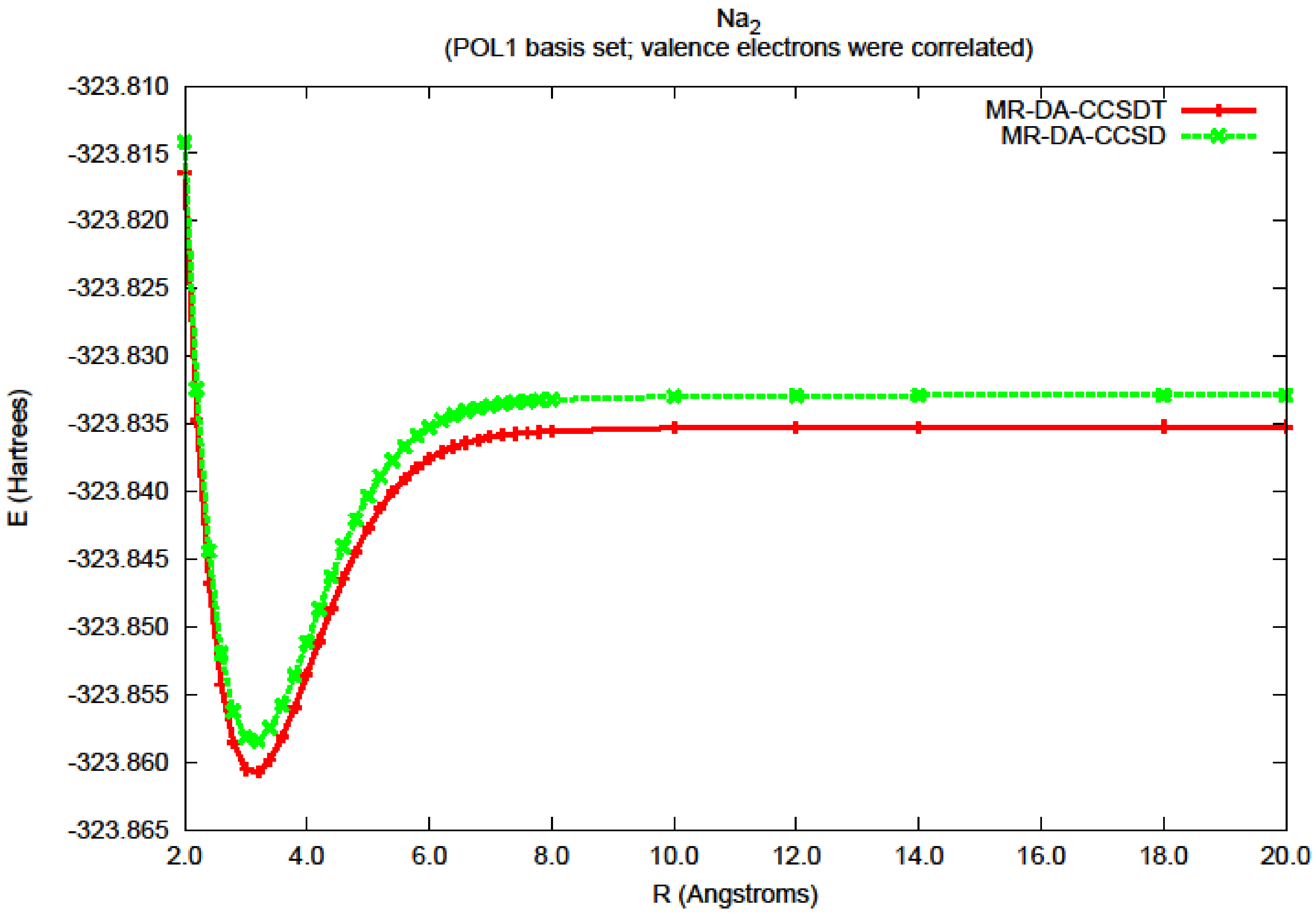
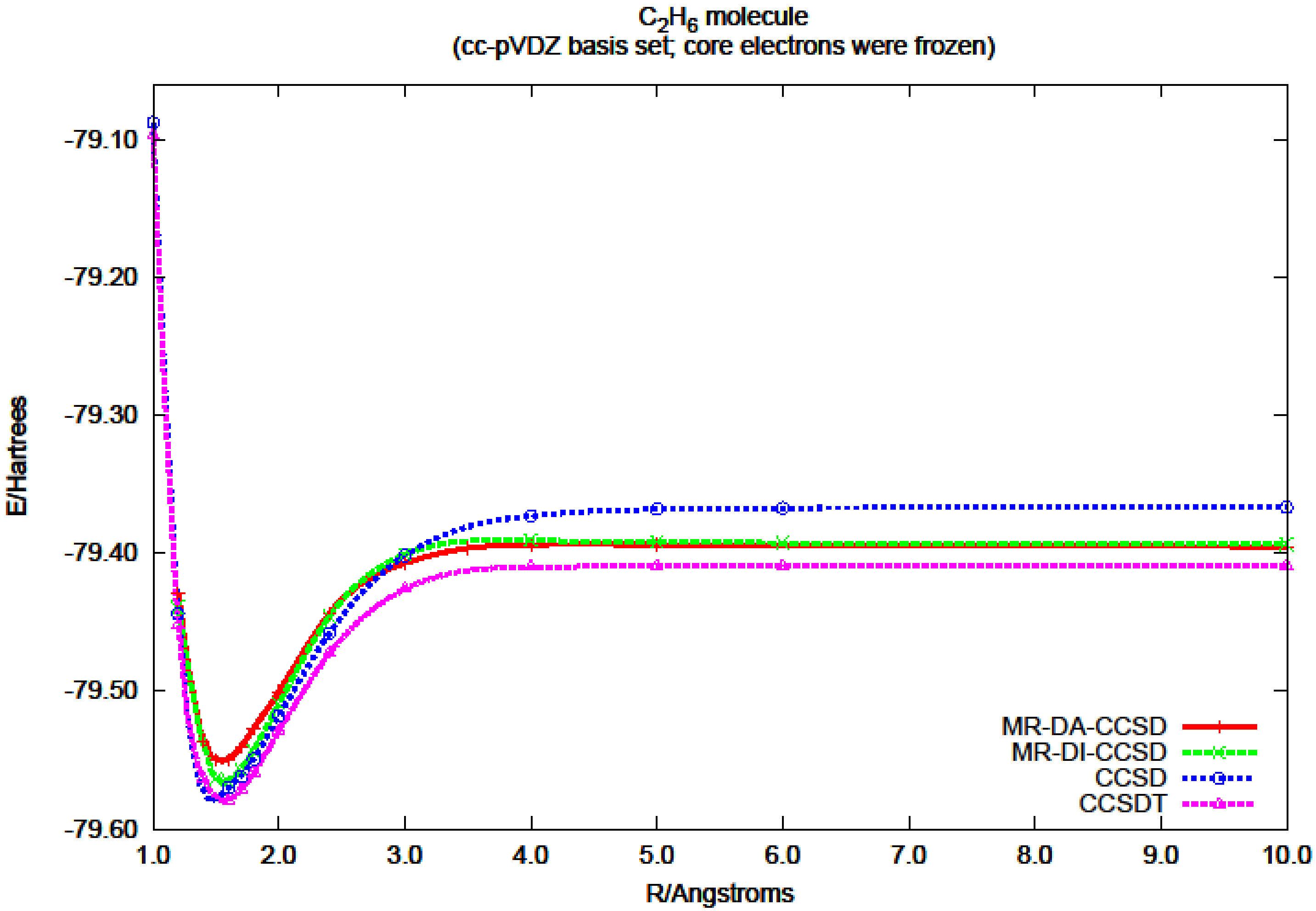


Illustration of DA Version

Comparison of DI and DA for ethane



Biradicals

“Singlet diradicals are archetypal in many classes of reactions such as ring opening and closure of strained cycloalkanes, the Cope rearrangement, bicyclobutane inversion… and they permit inter- and intramolecular coupling reactions….” Bertrand, et al Science, 2002….singlet fission chromophores for dye sensitized solar cells…NLO enhancement…”

Singlet-Triplet Splittings

The general problem is the degree of interaction between two radical centers, which is pervasive in chemistry.
This depends upon the correct description of the low-spin singlet state, which in its zeroth-order description is a two-determinant open-shell singlet. But once some bonding starts to occur between the radicals, the proper description of the singlet state depends upon all four determinants in the MR description. The triplet can be described as a SR-CC problem, but the singlet is MR.

Methylene, CH_2

Ground: $^3B_1$, C_{2v}:

$4a_1{}^1\alpha \quad b_1{}^1\beta + 4b_1{}^1\alpha \quad a_1{}^1\beta$

Excited: $^1A_1$, C_{2v}:

$3a_1{}^2$

Methylene S-T Splitting

Comparative Estimates

“Best” DEA: **-9.29**

CCSD: -10.39

CCSD(T): -9.58

SU CCSD*: -9.76

Experiment: **-9.37**

*at a different geometry, basis

Para Benzyne

Ground: ${}^1A_g$, D_{2h}

Excited: ${}^3B_{3u}$, D_{2h}:
$6a_g^{\,1}\ 5b_{3u}^{\,1}$

|n-2> State RHF Reference

CCSD(T)/6-311++G(2d,2p)
Geometries

CCSD(T) Hessian using RHF is a second-order saddle point.

DEA kcal/mol

Dunning Extrapolation: 3.4

Experiment 1: 3.8 +/- 0.3
Experiment – CCSD ZPE: 3.4 +/- 0.3

Experiment 2: 2.1 +/- 0.4
Experiment-CCSD ZPE: 1.8 +/- 0.4

Comparative Estimates

“Best” DEA: -3.4
CCSD(T): -4.2
ΛCCSD(T): -0.4

Experiment 1: -3.4 +/- 0.3
Experiment 2: -1.8 +/- 0.4

Meta Benzyne

Ground: ${}^1A_1$, C_{2v}

Excited: ${}^3B_1$, C_{2v}:
$10a_1{}^1\ 8b_1{}^1$

|n-2> State RHF Reference

CCSD(T)/6-311++G(2d,2p)
Geometries

MBPT(2) Hessian

DEA kcal/mol

Pople Extrapolation: 18.5
MBPT(2) ZPE Included: 19.1

Dunning Extrapolation: 18.5
MBPT(2) ZPE Included: 19.1

Experiment: 21 +/- 0.3

Comparative Estimates

“Best” DEA: -19.1

CCSD: -7.2

CCSD(T): -20.3

ΛCCSD(T): -18.7

Experiment: -21 +/- 0.3

- The generalization to the three-electron, TI/TA, four-electron, QI/QA, and beyond methods will enable several orbitals to be involved in MR character.
- These methods are computationally similar, with low-scaling. I-CCSD, is $\sim n^2N^3$, DI-CCSD, $\sim n^3 N^3$. TI-CCSD is $\sim n^4N^3$, compared to $\sim n^2N^4$ for CCSD.
- The A-CCSD is $\sim nN^4$, DA-CCSD, $\sim nN^5$. (FNO)
- We propose a new CC-like 2×2, 3×3, 4×4, ... quasi-degenerate generalization of SR-CC theory.
- Just as CC theory generalizes CI by introducing repeated clusters, thereby making it size-extensive, MR-MI/MA-CC generalizes SR-CC to 2, 3, 4,... electron quasi-degenerate variants.

WHAT ARE THE REMAINING ISSUES?

- **Optimum choice of orbitals**?

1. N-particle RHF (lumo virtual plays role of second orbital).
2. N±2 particle RHF (Can be unphysical for DI, core for DA).
3. Brueckner analogs (to rotate away large singles amplitudes).
4. Fractionally occupied (Useful when degeneracies encountered).
5. Use constraining potential, $h^{eff} = h + V^{HF} + U\ (Kus, Krylov)$
6. Complex scaling and CAP to address multi-anion states?
7. MCSCF/GVB (Good for MR part, but poor for global exp part)
8. Optimized?

- **Sometime poor convergence of ref. $T^{n\pm2}$ amplitudes.**

Need a natural transition from $R^{n\mp2}\, T^{n\pm2}$ to T^{n} when appropriate?

- **Iterations to convergence**

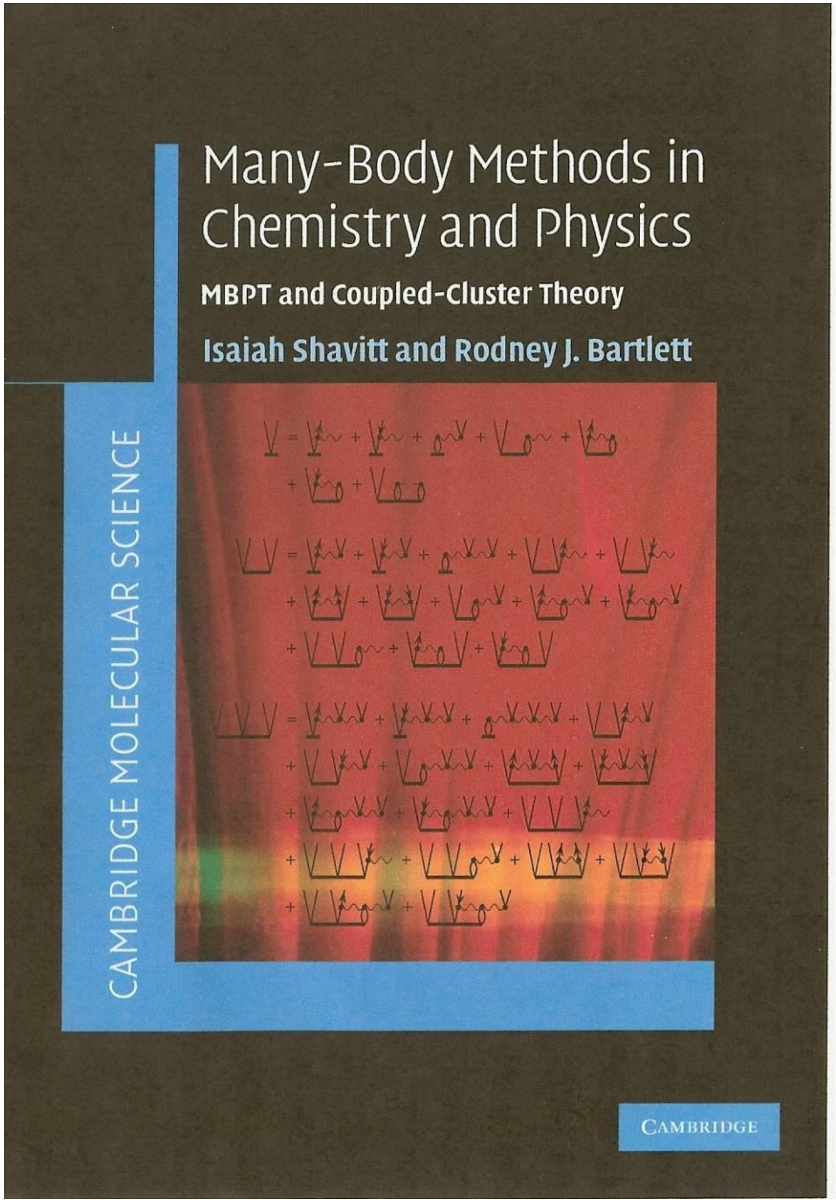
Build a new $\bar{H}$ from MR-DI/DA-CC state and repeat to provide a state-specific variant

- **Generalization to TI/TA and QI/QA**

ATTRACTIVE PROPERTIES OF MR-DI/DA-CC

- Black-box applications like SRCC.
- Only new decision is the **one** spatial orbital chosen to be active (2x2). For TI/TA, 3x3, QI/QA, 4x4.
- MR for target state.
- No intruder state problem.
- Automatic spin-eigenfunction when start with SRCC for closed shell.
- Size-intensive. Intensive part is CI-like and local. AB*→ A* + B.
- Extensive part is global, exp($T^{n\pm2}$)$|n \pm 2>$
- Active + occupied or virtual orbitals are rotationally invariant.
- MR answer seems to properly reduce (numerically) to SR, when it should.
- Excited states emerge as other solutions of the EOM Hamiltonian.
- Analytic derivatives and properties same as for EOM-CC (Alex Bazante is putting these into ACES III)

No other current MR-CC method satisfies all the above!



Many-Body Methods in Chemistry and Physics

MBPT and Coupled-Cluster Theory

Isaiah Shavitt and Rodney J. Bartlett

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