



**Approaching Near-Degeneracies in Electronic
Structure Theory from the Single Reference and
Equation-of-Motion Coupled-Cluster Perspective**



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OUTLINE

- **Some Essential Preliminaries**
- **Single reference CC theory for energies, properties**
- **EOM-CC for excited/ionized/attached states.**
- **Greens' Functions from CC**
- **Origin of problems with SR-CC**
- **Some results for near degeneracies**
- **Addition by subtraction in SR-CC**
- **EOM-DIP/DEA as an easy MR-CC**

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.

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

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

- **Basis Set**

Sets of gaussian 'atomic' orbitals, $|\chi\rangle$ located on all atoms in the molecule, square integrable, finite. # is $m \gg n$, # 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 \mathbf{C} might be taken from HF, or Brueckner, or Natural Orbitals, or Kohn-Sham or any other choice of 'Mean-Field', meaning any single Determinant composed of n occupied MO's.

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

m		—	—	—	—
.	.	—	—	—	—
.	.	—	—	—	—
.	.	—	—	—	—
.	c	—	—	—	↑
.	b	—	—	↑	↑
n+1	a	—	↓	↓	↓
n	i	↑↓	↑	↑	↑
.	j	↑↓	↑↓	↓	↓
.	k	↑↓	↑↓	↑↓	↓
2	.	↑↓	↑↓	↑↓	↑↓
1	.	↑↓	↑↓	↑↓	↑↓
		Φ_o	Φ_i^a	Φ_{ij}^{ab}	Φ_{ijk}^{abc}
			\hat{T}_1	\hat{T}_2	\hat{T}_3
			\hat{C}_1	\hat{C}_2	\hat{C}_3

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) mean fields, $S^2\Phi_{\text{UHF}} \neq S(S+1)\Phi_{\text{UHF}}$. If we use ROHF mean fields for open shells, $S^2\Phi_{\text{ROHF}} = S(S+1)\Phi_{\text{ROHF}}$. 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, but not generally in CC theory because prdts of T introduce reducible spin representations.

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

Answer: Coupled-Cluster Theory

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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!

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

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

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 DIAGRAM**
 - **ITERATIONS GIVE MBPT(2), (3), (4), ...**

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

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

EXAMPLE I: Correlated Energies

The CC energy is

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

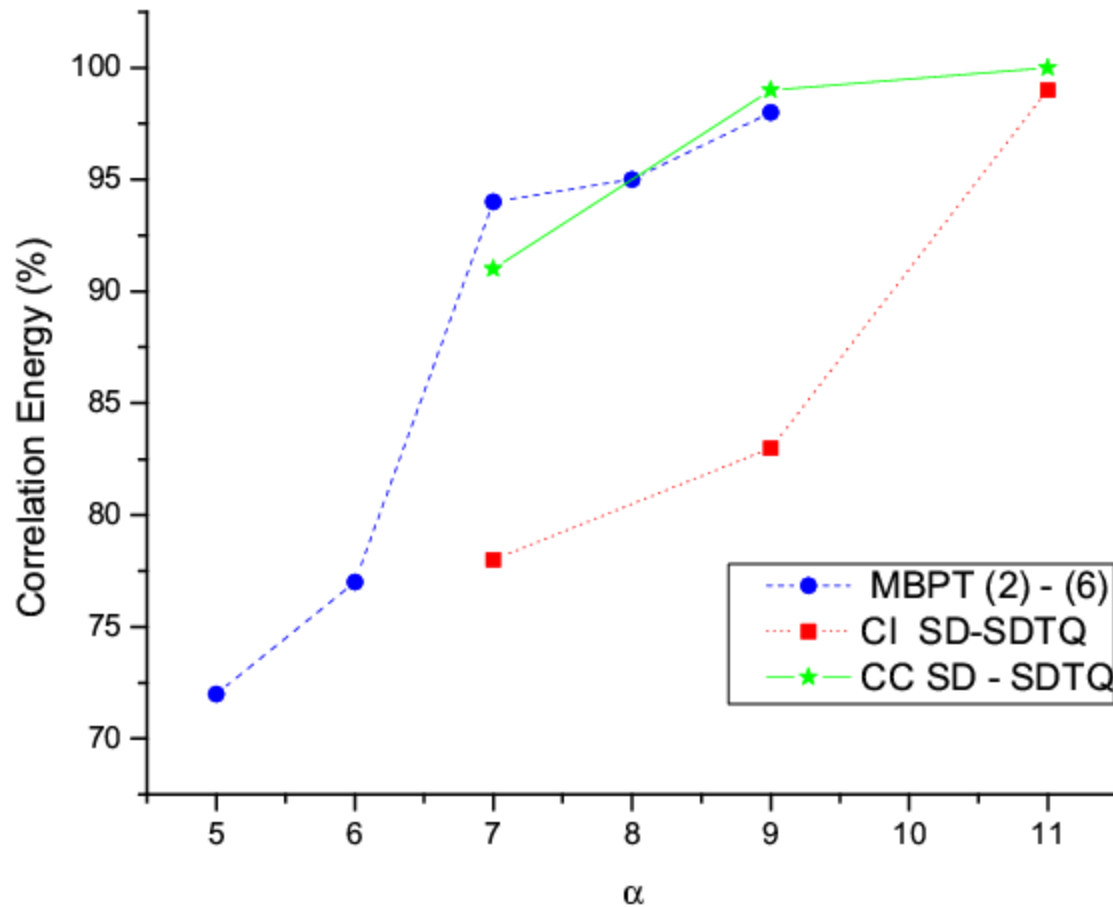
The similarity transformed Hamiltonian is

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

and the wavefunction equations are

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

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 $\partial E / \partial X_\alpha = E^\alpha$,

$$EP = PHP,$$

$$E^\alpha P = P(H^\alpha)P + P(HT^\alpha)P$$

And the wavefunction,

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

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

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

$E^\alpha P = P(1 + \Lambda)H^\alpha P$. And
 $E = P(1 + \Lambda)HP$, 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).

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

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

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

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

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 $T_3^{[2]}$

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

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 Λ CCSD(T)

$$E_T^{[4]} =$$

The diagram illustrates the fourth-order energy correction $E_T^{[4]}$ in Λ CCSD(T). It consists of three terms:

- The first term is a diagram with a thick black bar at the top, two large ovals on the left, and a dashed line connecting to a small oval on the right labeled [2].
- The second term is a diagram with a thick black bar at the top, a large oval on the left, and a dashed line connecting to two small ovals on the right labeled [2].
- The third term is a diagram with a thick black bar at the top, two large ovals on the left, and a dashed line connecting to a small oval on the right labeled [2], with a red 'X' over the dashed line indicating it is excluded.

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

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Example IV: Excited states and any sector of Fock Space: **EOM-CC**

$$(E_0 - H)\Psi_0 = 0 \quad \text{GROUND STATE}$$

$$(E_0 - H)\Psi_K = \omega_K \Psi_K \quad \text{EXCITED STATE}$$

$\Psi_K = R_k \exp(T)|0\rangle$ 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

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

$$\langle 0|(L_k \mathbb{H}) = \langle 0|L_k \omega_K \quad \text{This is the analogous functional for excited states that can be differentiated to get properties.}$$

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

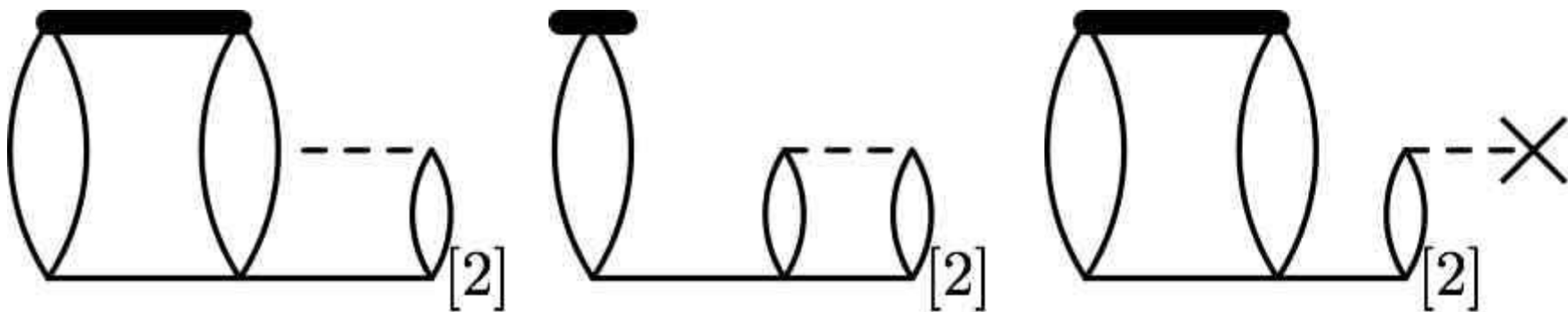
Following exactly the same strategy, triples effect in EOM-CC can be readily derived....

$$\omega_k = \langle 0 | L_K \hat{H} R_K | 0 \rangle, \langle L_K | R_L \rangle = \delta_{KL}$$

$$\omega_T = \langle 0 | (L_1 + L_2) (\hat{H} R_3)_C | 0 \rangle$$

$$Q_3 \hat{H}_0 R_3 | 0 \rangle = Q_3 [\hat{H} (R_2 + R_1)]_C | 0 \rangle \simeq$$

$$Q_3 H_0 R_3 | 0 \rangle = Q_3 W R_2 | 0 \rangle$$



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)

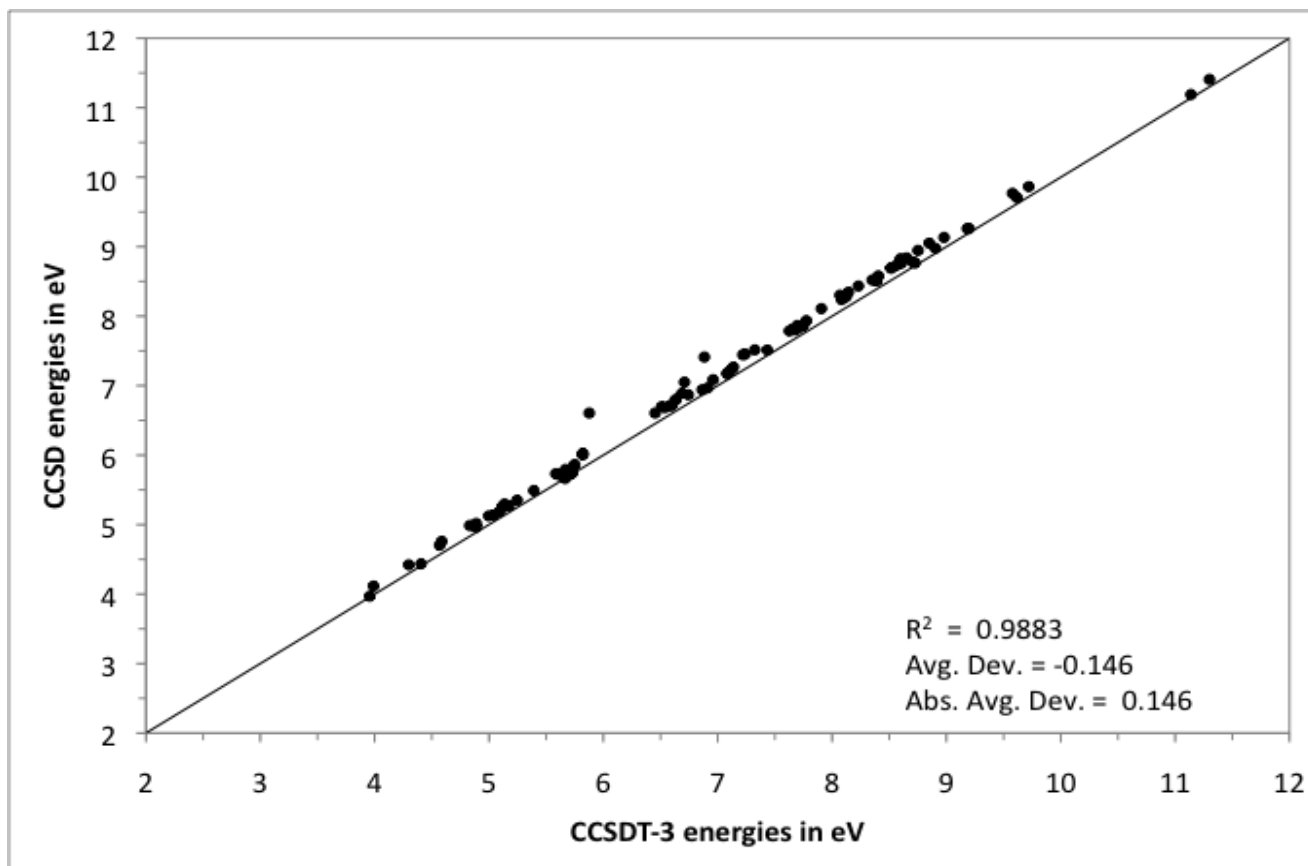
(Tom Watson's ACES III implementation)

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



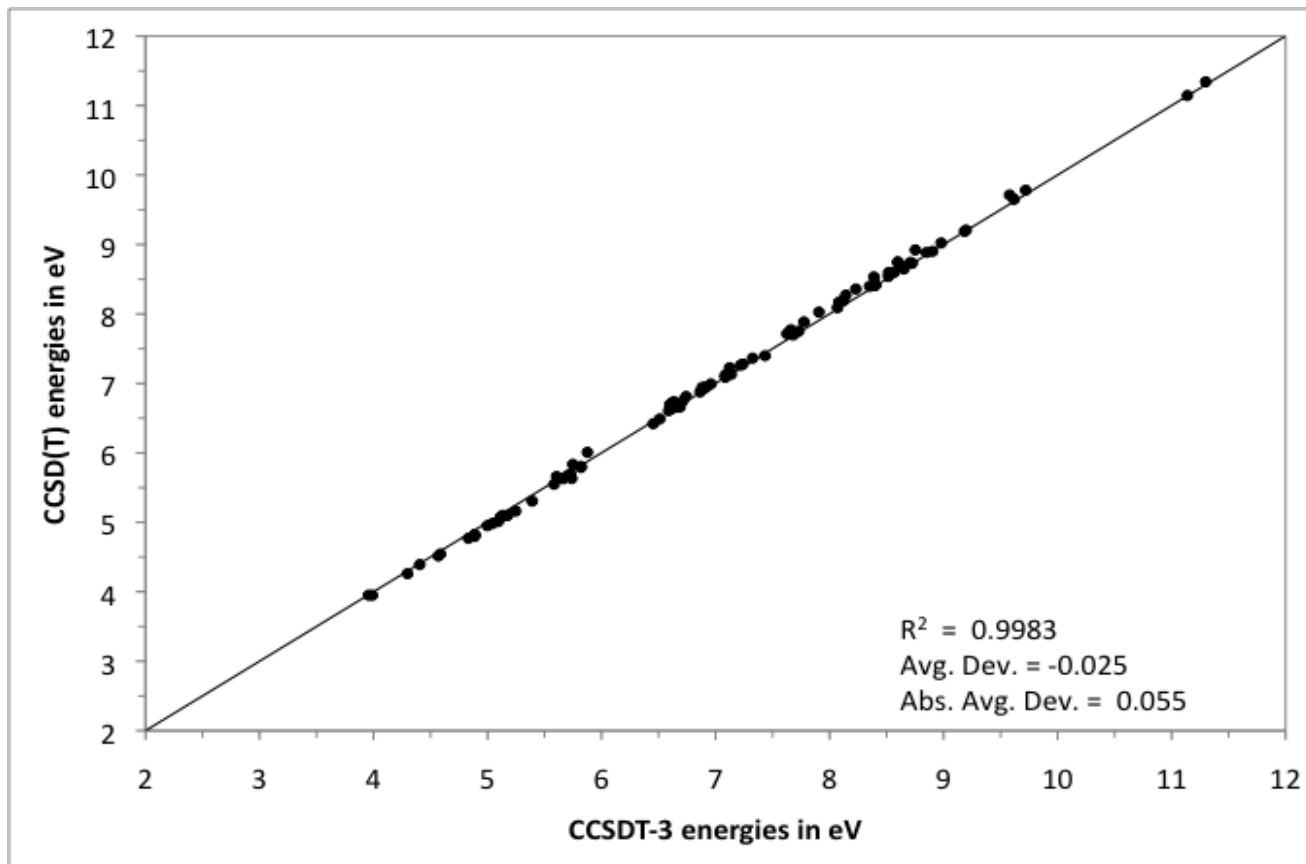
Comparative computational dependence

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

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

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

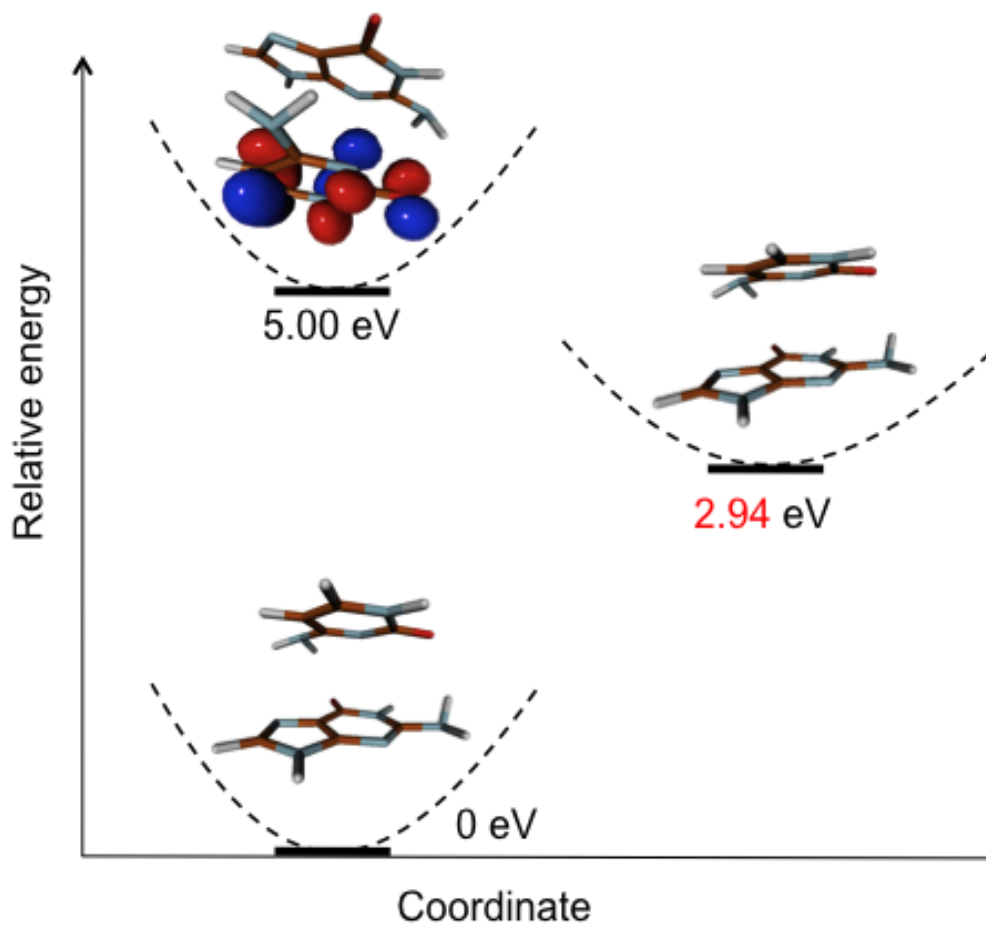
EOM-CCSD(T) vs. EOM-CCSDT-3



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

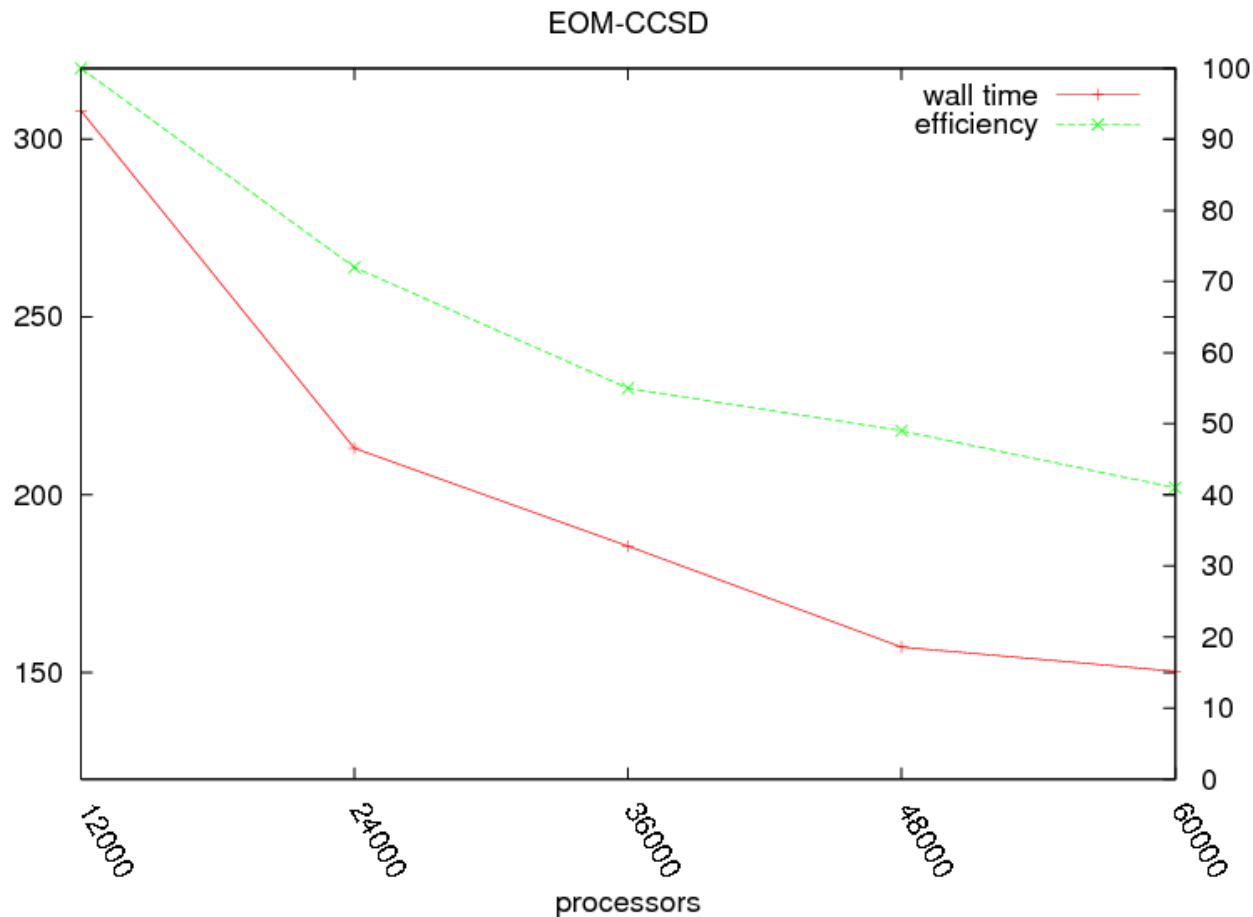


577 basis functions
29 atoms
108 electrons

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

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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 ω , as the solutions, ϕ_p , are only obtained when $\omega = \omega_p$.
- (2) This also causes the self-energy, correlation potential, $\Sigma(1,\omega)$ to be evaluated at ω_p for every orbital as in Hartree-theory, making the (Dyson) orbitals non-orthogonal and over determined.
- (3) When used to evaluate the Greens' Fxn the Ip and Ea parts are determined. The good thing is that some of the ω_p 's have to be exactly the ionization potentials and electron affinities for the 1h and 1p states,

The bad thing is those Ip's and Ea's also include 2h1p, 2p1h, etc. resonances, too. This is great for interpretation of PES, but bad for generating n-orbitals to define a correlated orbital single determinant approximation.

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

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

L. Meissner, RJB (1993)

M. Nooijen J. Snidjers (1993)

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.

$$\mathbb{H}R_k^\dagger \Phi_0 = \omega_k^\dagger R_k^\dagger \Phi_0 \quad \mathbb{H} = \exp(-\mathbf{T})H\exp(\mathbf{T})$$

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Single-reference CC theory (and its EOM-CC extensions) give 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....)

Why?

Mean-Field for Bond Breaking

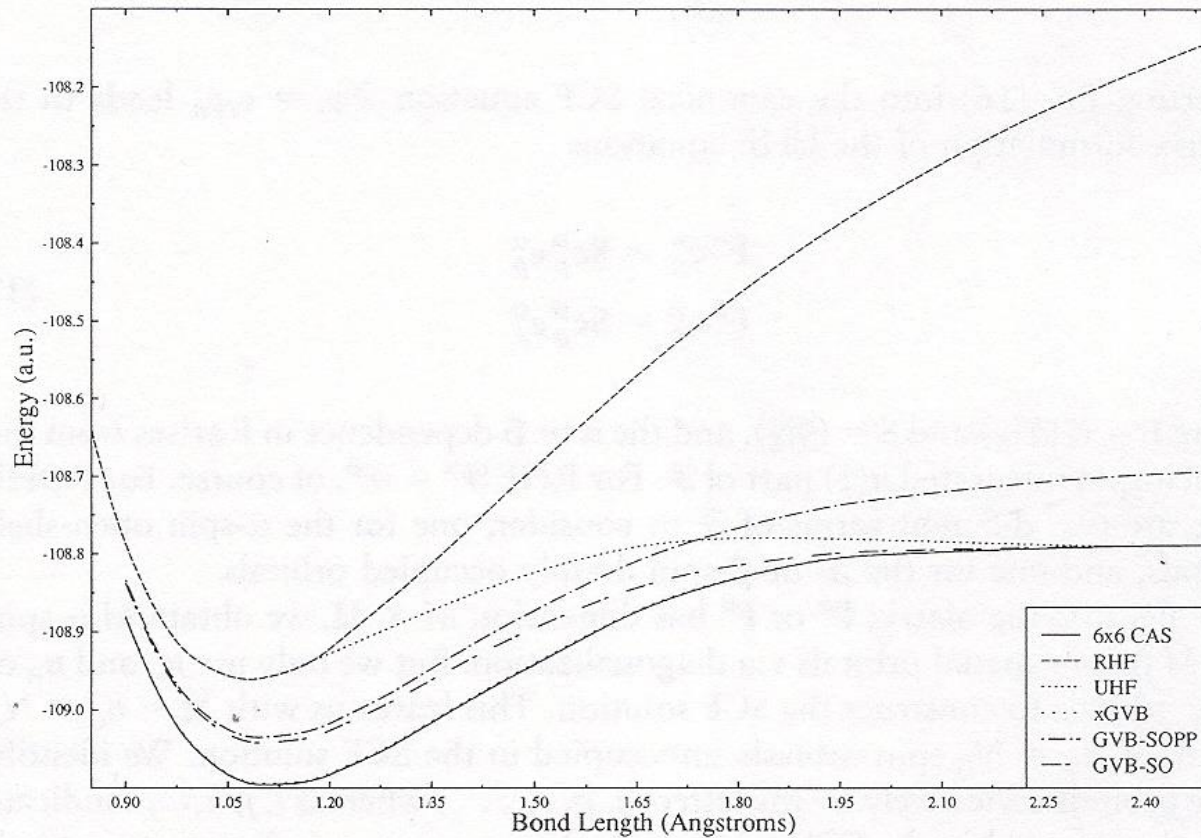


Figure 6 SCF, GVB, and CASSCF potential curves for N₂.

Mean-Field for Bond Breaking

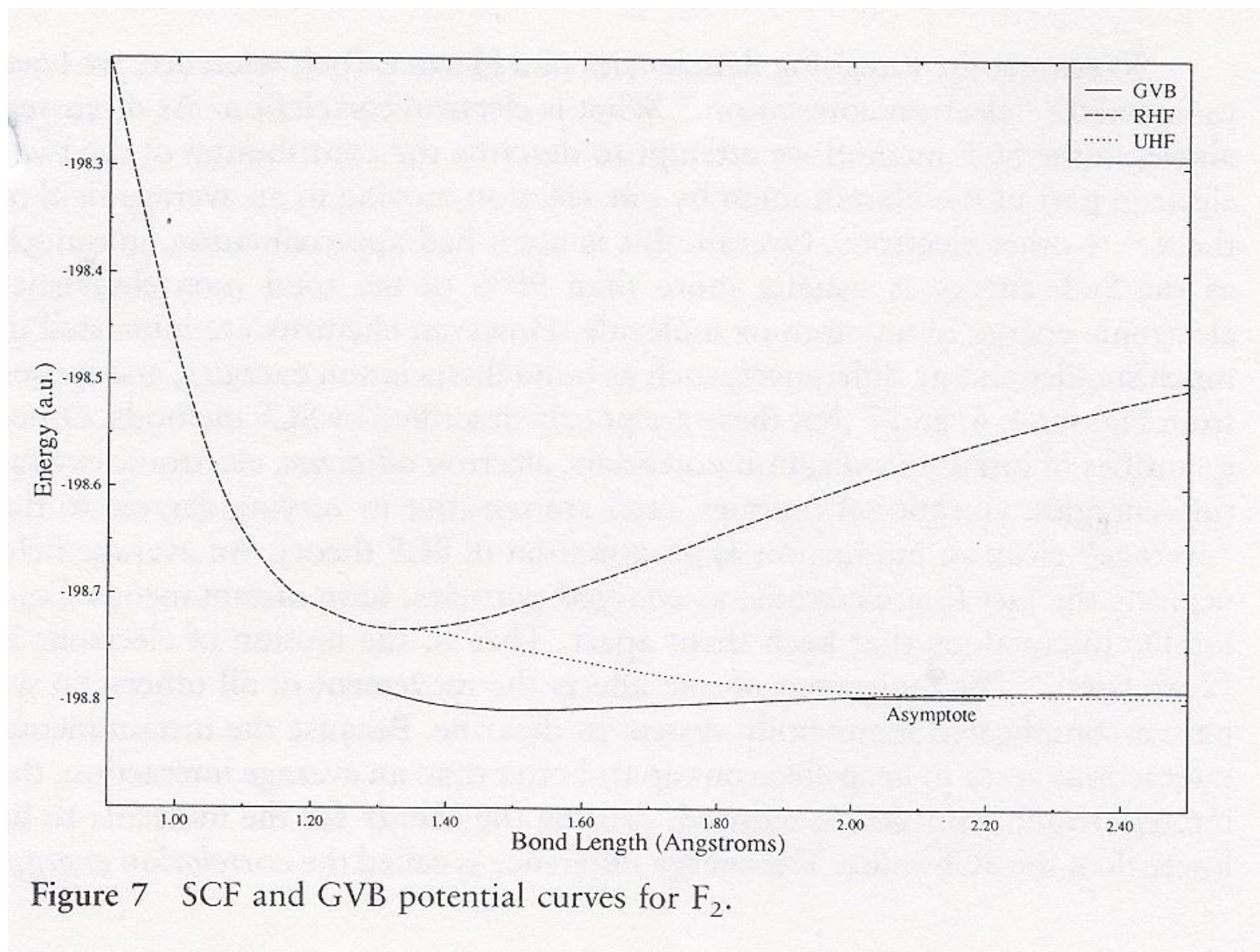


Figure 7 SCF and GVB potential curves for F₂.

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.

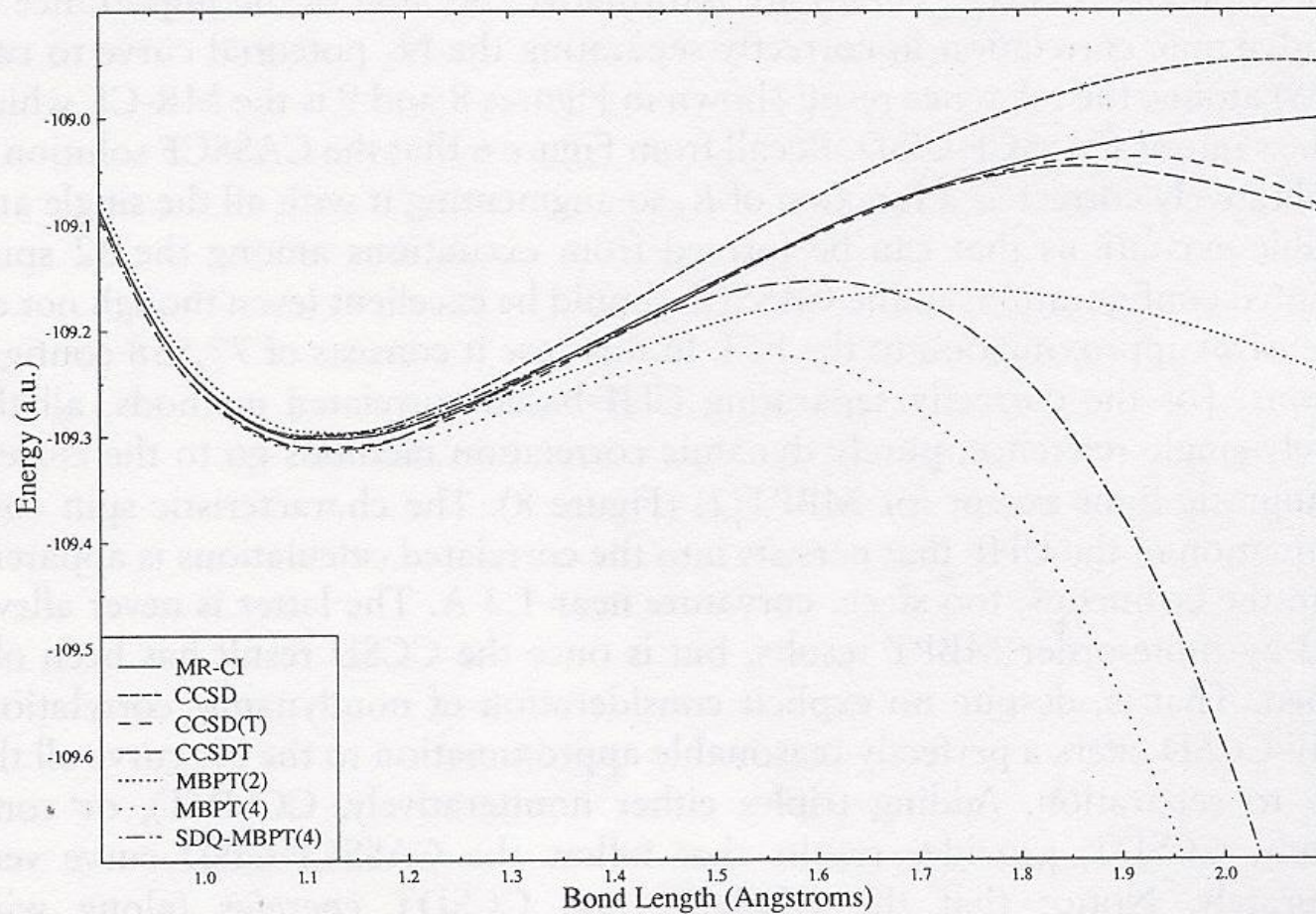


Figure 9 Correlated potential curves for N_2 using an RHF reference.

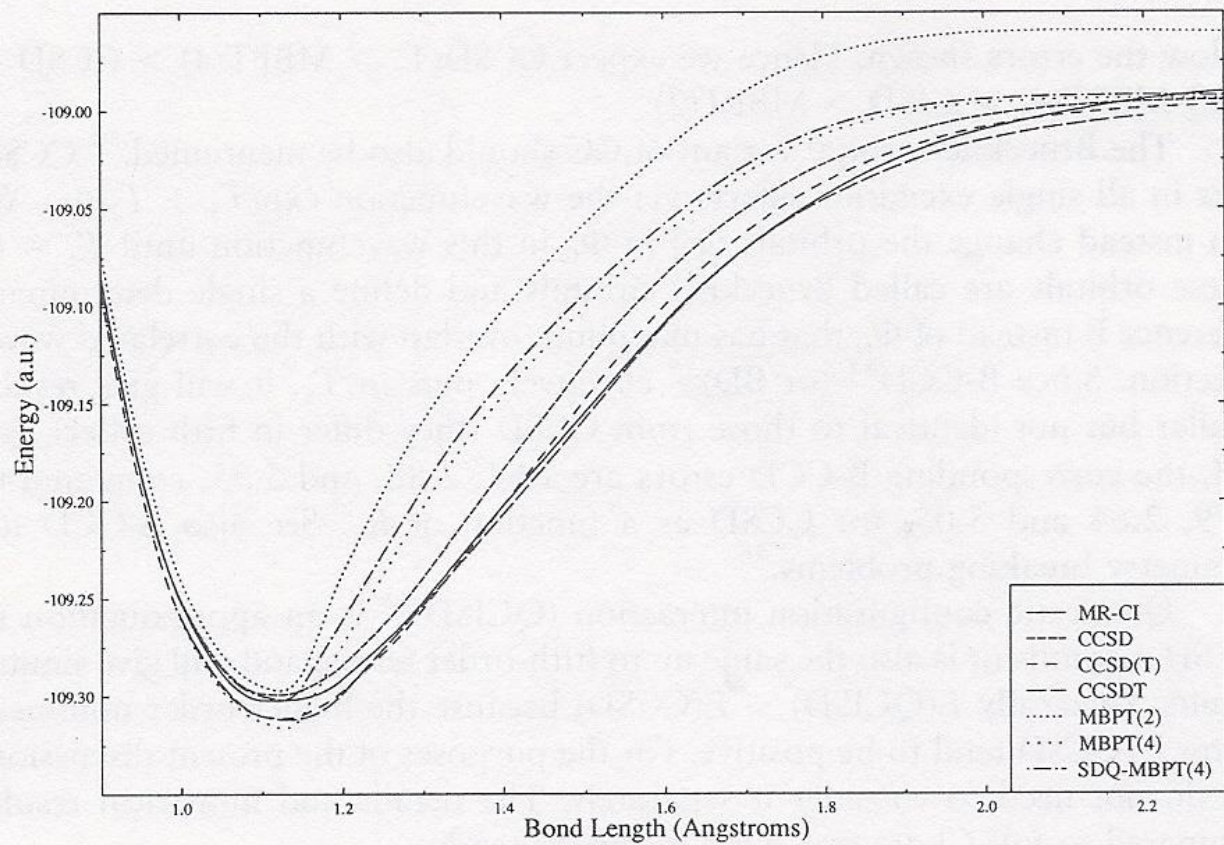


Figure 8 Correlated potential curves for N_2 using a UHF reference.

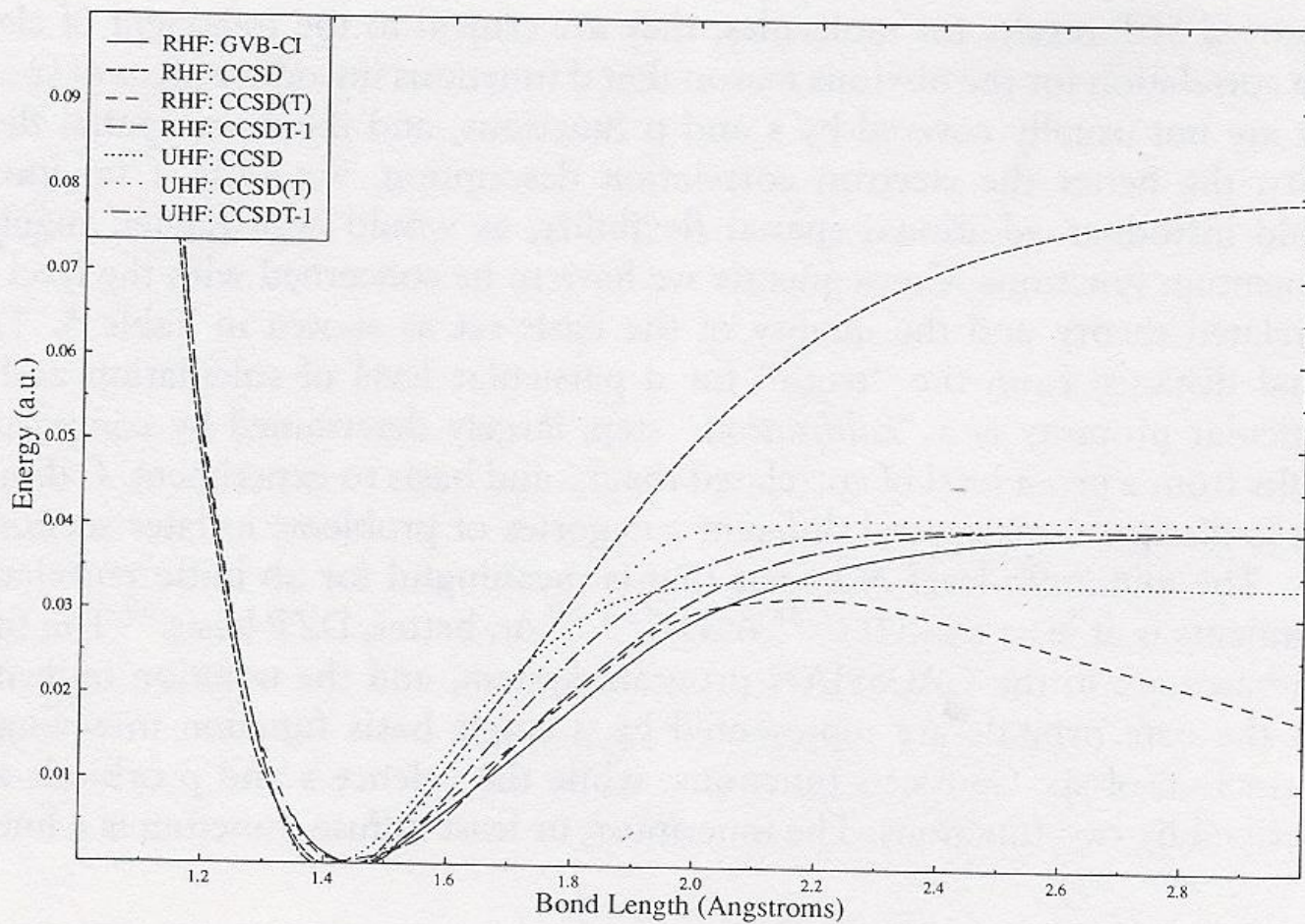


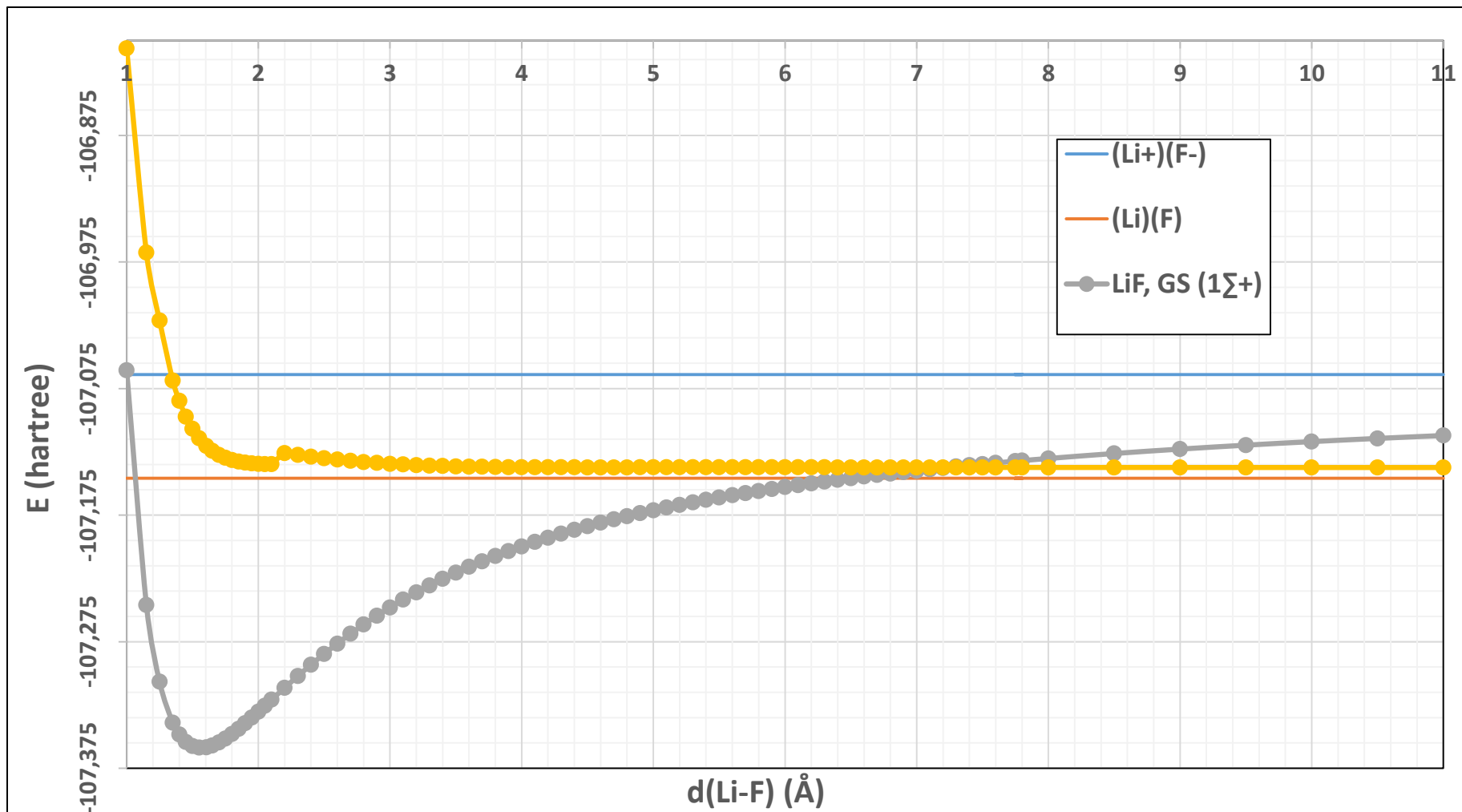
Figure 12 Correlated potential curves for F_2 .

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Lithium fluoride

EOM-CCSD method, WMR basis



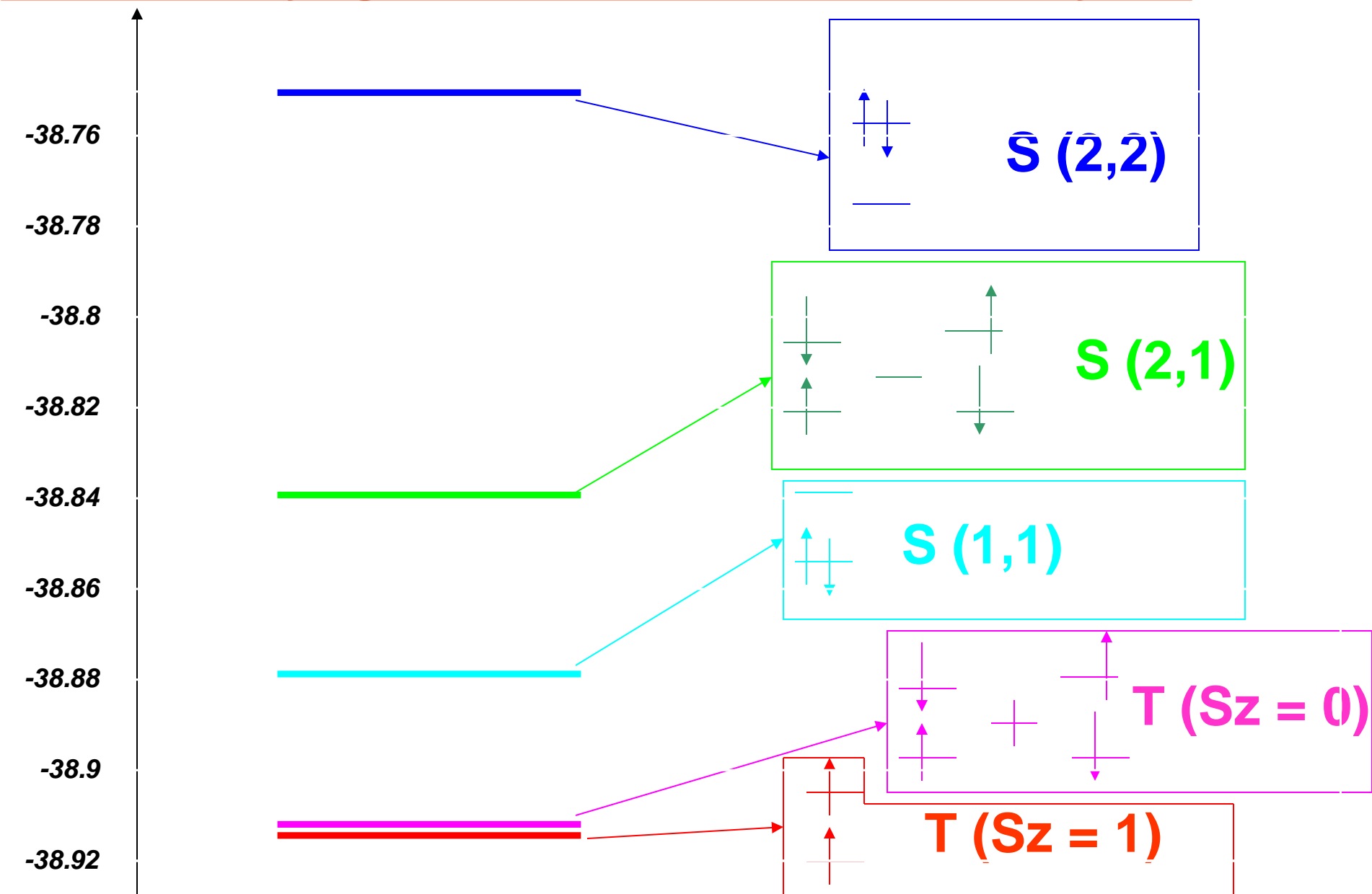
Other types of quasi-degeneracy.

Low-spin states.

Multiplet splittings in transition metals.

Degeneracies among excited states, like in very high Rydberg series.

Four lowest lying states of the two-electron methylene



E
(a.u.)

Near Degeneracy in Transition Metal Multiplets

	Excitation	SCF	CCSD	CCSD(T)	ACCSD(T)	CCSDT-3	Exp (eV)
Fe	${}^5F(d^6s^2) - {}^5D(d^7s^1)$	2.106	1.103	0.993	0.975	0.954	0.87
Co	${}^4F(d^7s^2) - {}^4F(d^8s^1)$	1.864	0.680	0.532	0.505	0.479	0.42
Ni	${}^3F(d^8s^2) - {}^3D(d^9s^1)$	1.201	-0.044	-0.168	-0.210	-0.135	-0.03
	${}^3F(d^8s^2) - {}^1S(d^{10})$	5.694	2.180	1.658	1.487	1.299	1.71
Cu	${}^2D(d^9s^2) - {}^2S(d^{10}s^1)$	0.153	-1.208	-1.383	-1.434	-1.459	-1.49

Table 2a: Relativistic ROHF-CC (DKH5) calculations on multiplet states of Fe, Co, Ni and Cu in cc-pwCVQZ-DK basis set

Near Degeneracy in Transition Metal Multiplets

	FON	CCSD	CCSD(T)	ACCS(D(T)	CCSDT-3	EXP
Fe	⁵ D(d ⁶ s ²)	0.00	0.00	0.00	0.00	0.00
	⁵ F(d ⁷ s ¹)	0.972 (0.131)	1.068 (-0.075)	1.019 (-0.044)	0.949 (0.005)	0.87
Fe ⁺	⁶ D(d ⁶ s ¹)	7.673 (0.018)	7.846 (-0.006)	7.841 (-0.013)	7.839 (-0.001)	7.90
	⁴ F(d ⁷)	8.103 (0.071)	8.365 (-0.156)	8.336 (-0.144)	8.194 (-0.001)	8.15
Co	⁴ F(d ⁷ s ²)	0.00	0.00	0.00	0.00	0.00
	⁴ F(d ⁸ s ¹)	0.480 (0.201)	0.688 (-0.154)	0.616 (-0.111)	0.493 (-0.014)	0.42
Co ⁺	⁵ F(d ⁷ s ¹)	8.066 (0.01)	8.316 (-0.087)	8.325 (-0.107)	8.230 (-0.002)	8.28
	³ F(d ⁸)	8.055 (-0.158)	8.210 (-0.305)	8.167 (-0.283)	8.023 (-0.138)	7.85
Ni	³ D(d ⁹ s ¹)	-0.319 (0.2751)	0.110 (-0.278)	0.001 (-0.211)	-0.076 (-0.059)	-0.03
	³ F(d ⁸ s ²)	0.00	0.00	0.00	0.00	0.00
Ni ⁺	⁴ F(sd ⁸)	8.143 (-0.006)	8.349 (0.001)	8.346 (-0.009)	8.460 (-0.009)	8.67
	² D(d ⁹)	7.149 (0.162)	7.504 (-0.151)	7.437 (-0.115)	7.455 (-0.028)	7.59
Cu	² S(d ¹⁰ s ¹)	-1.554 (0.346)	-0.966 (-0.417)	-1.112 (-0.322)	-1.355 (-0.104)	-1.49
	² D(d ⁹ s ²)	0.000	0.000	0.000	0.000	0.000
	² P(d ¹⁰ p ¹)	2.277 (0.261)	2.711 (-0.274)	2.625 (-0.227)	2.315 (0.00)	2.295
Cu ⁺	³ D(d ⁹ s ¹)	8.828 (-0.013)	8.963 (0.011)	8.967 (0.00)	8.975 (0.001)	9.04
	¹ S(d ¹⁰)	6.036 (0.213)	6.476 (-0.239)	6.392 (-0.19)	6.255 (-0.049)	6.23

Table 3c: QRHF-CC calculations based on reference wave functions composed of orbitals obtained from ‘fractional occupation’ HF calculations (FON). Neutral and cationic states of Fe, Co, Ni, Zn and Cu in the cc-pwCVQZ-DK basis set are studied. Relative energies (in eV) are calculated w.r.t neutral states (dⁿs²) of Fe, Co, Ni, Cu and Zn atom. The numerical difference of these results with the variationally optimal ROHF reference CC results are indicated in ‘()’.

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Quadratic terms in CCD amplitude equation

$$A = -\frac{1}{2} \sum_{k,l,c,d} v_{cd}^{kl} (t_{ik}^a t_{jl}^{cd} + t_{jl}^a t_{ik}^{cd})$$

$$B = \frac{1}{4} \sum_{k,l,c,d} v_{cd}^{kl} t_{kl}^a t_{ij}^{cd}$$

$$C = -\frac{1}{2} \sum_{k,l,c,d} v_{cd}^{kl} (t_{ij}^a t_{kl}^{bd} + t_{kl}^a t_{ij}^{bd})$$

$$D = \sum_{k,l,c,d} v_{cd}^{kl} (t_{ik}^a t_{jl}^{bd} + t_{jl}^a t_{ik}^{bd})$$

For a two electron system,

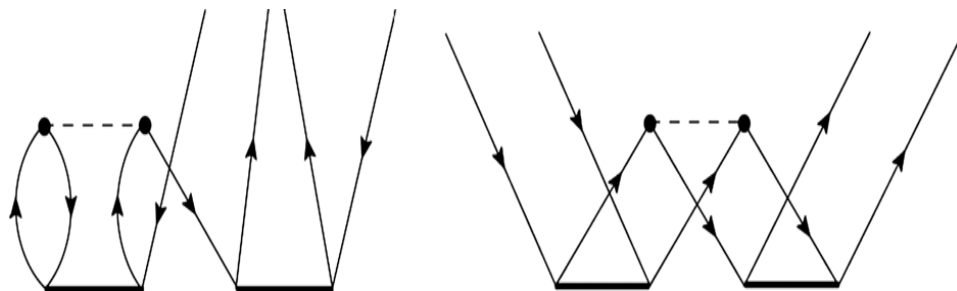
$$\frac{A}{2} + B = 0, \quad C + D = 0$$

2-CC (N-CC Family)

Quadratic terms in 2-CC :

$$A + B = \frac{A}{2} + \left(\frac{A}{2} + B \right)$$

2-CC = p-CCSD (1,0)



R. J. Bartlett and M. Musiał, JCP, 125, 2 (2006)

M. Musiał and R. J. Bartlett, JCP, 127, (2007)

Parameterized-CCSD

Quadratic terms in T_2 amplitude equation in P-CCSD(α, β)

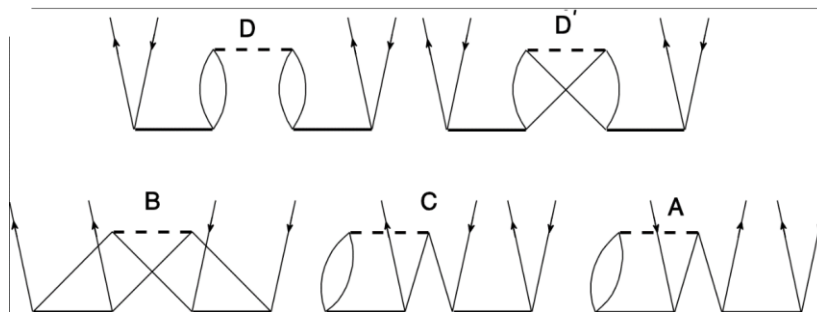
$$\frac{A}{2} + \alpha \left(\frac{A}{2} + B \right) + \beta(C + D)$$

$$p - CCSD(1,1) = \frac{A}{2} + \left(\frac{A}{2} + B \right) + (C + D) = A + B + C + D = CCSD$$

$$p - CCSD(-1,1) = \frac{A}{2} - \left(\frac{A}{2} + B \right) + (C + D) = -B + C + D$$

L. Huntington and M. Nooijen, JCP, 133,
184109 (2010)

Distinguished cluster approximation



Nonantisymmetri-
zed Goldstone
diagrams (with
Coulomb
integrals)

Quadratic terms in CCD

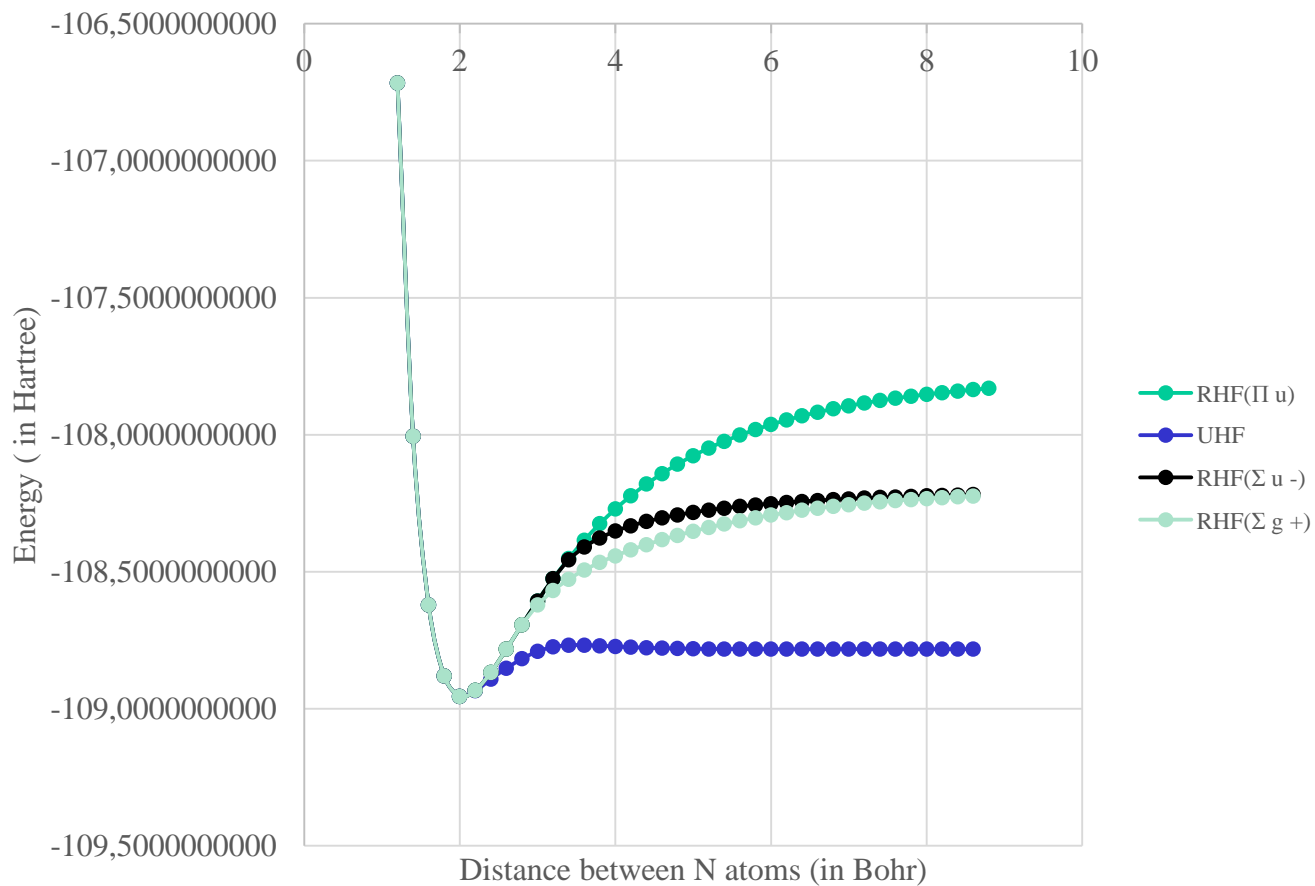
$$D + D' + B + C + A$$

Quadratic terms in DCD

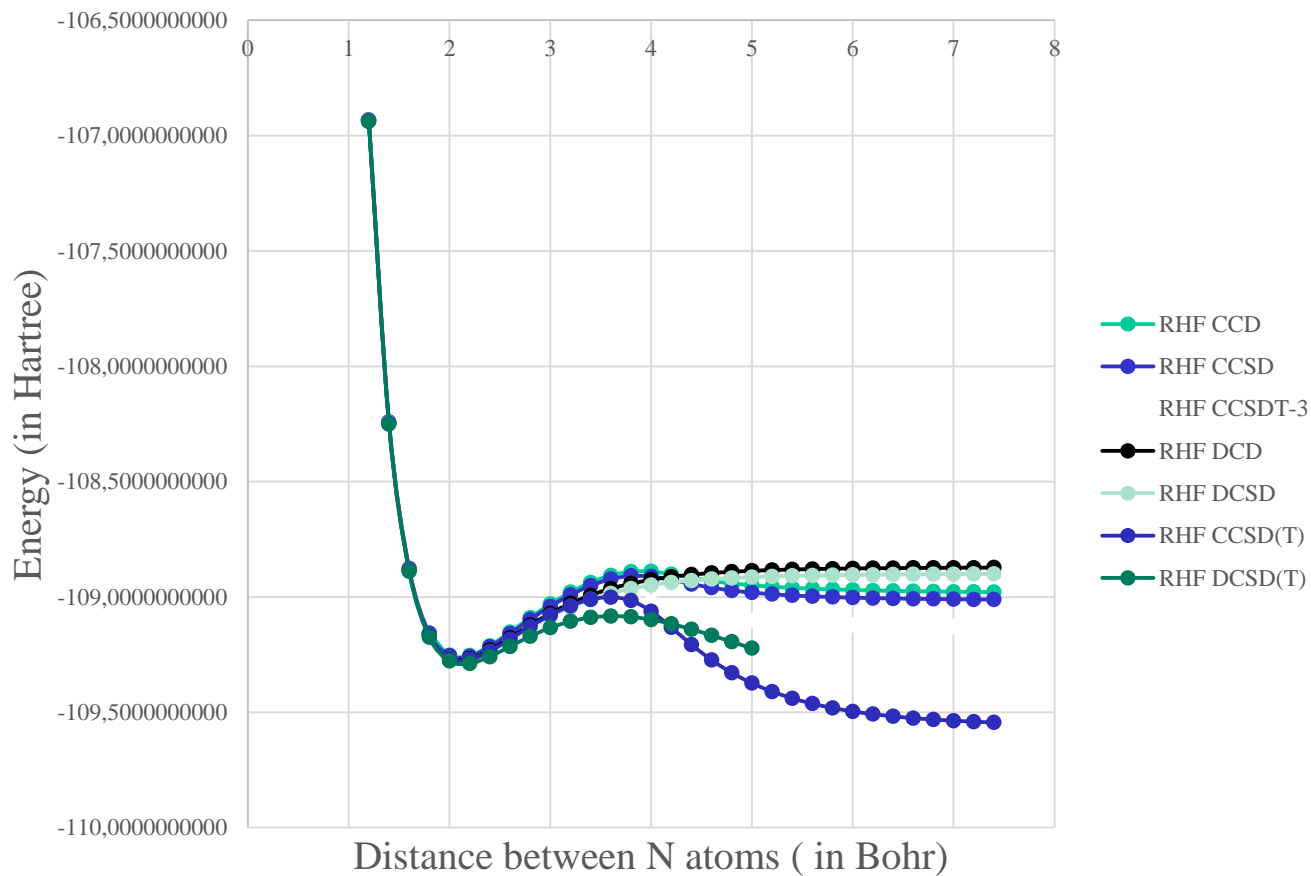
$$D + \frac{1}{2}(C + A)$$

$$= D + D' + B + C + A + \alpha(2D' + C) + \beta(2B + A) \text{ [Put } \alpha = -\frac{1}{2}, \beta = -\frac{1}{2} \text{]}$$

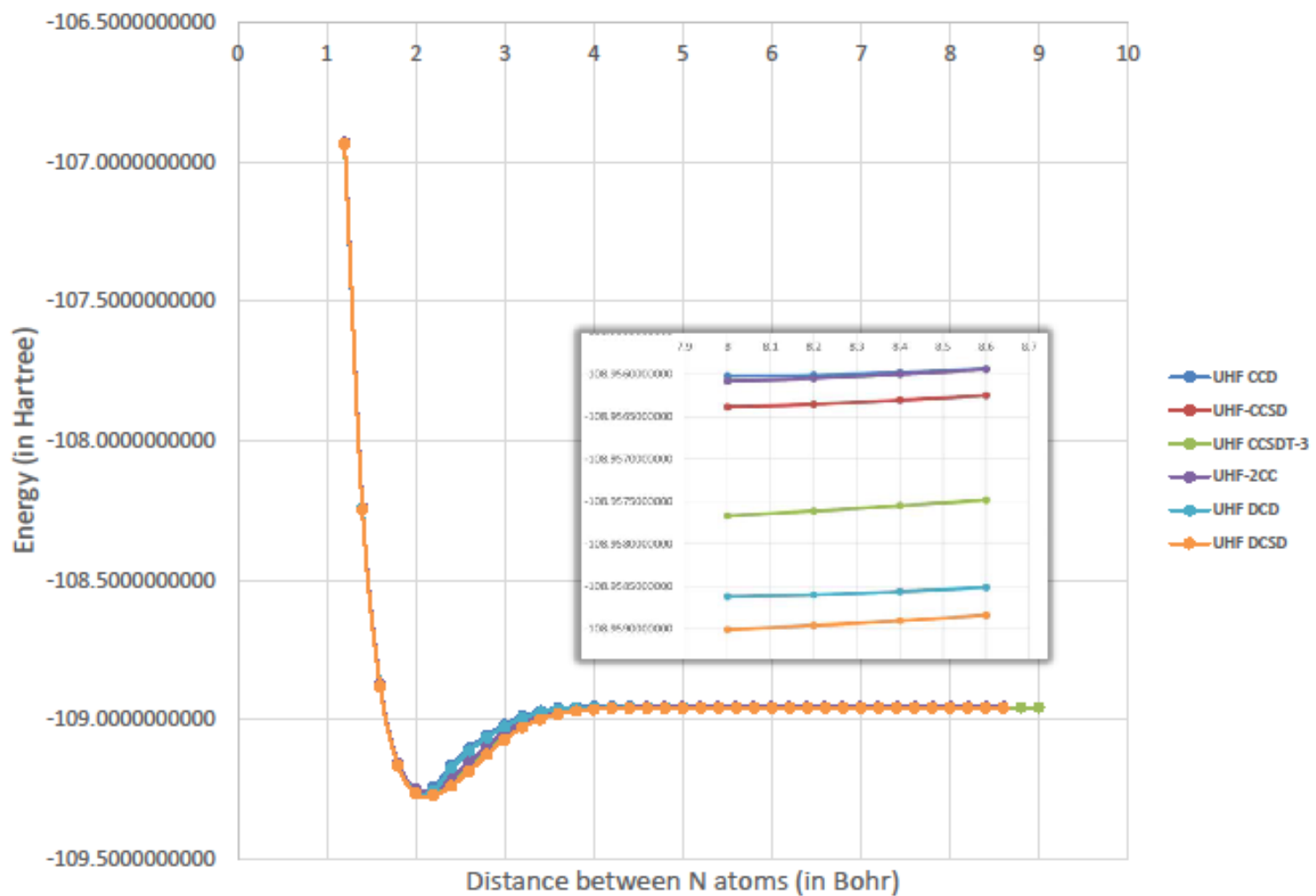
HF : bond dissociation of N₂



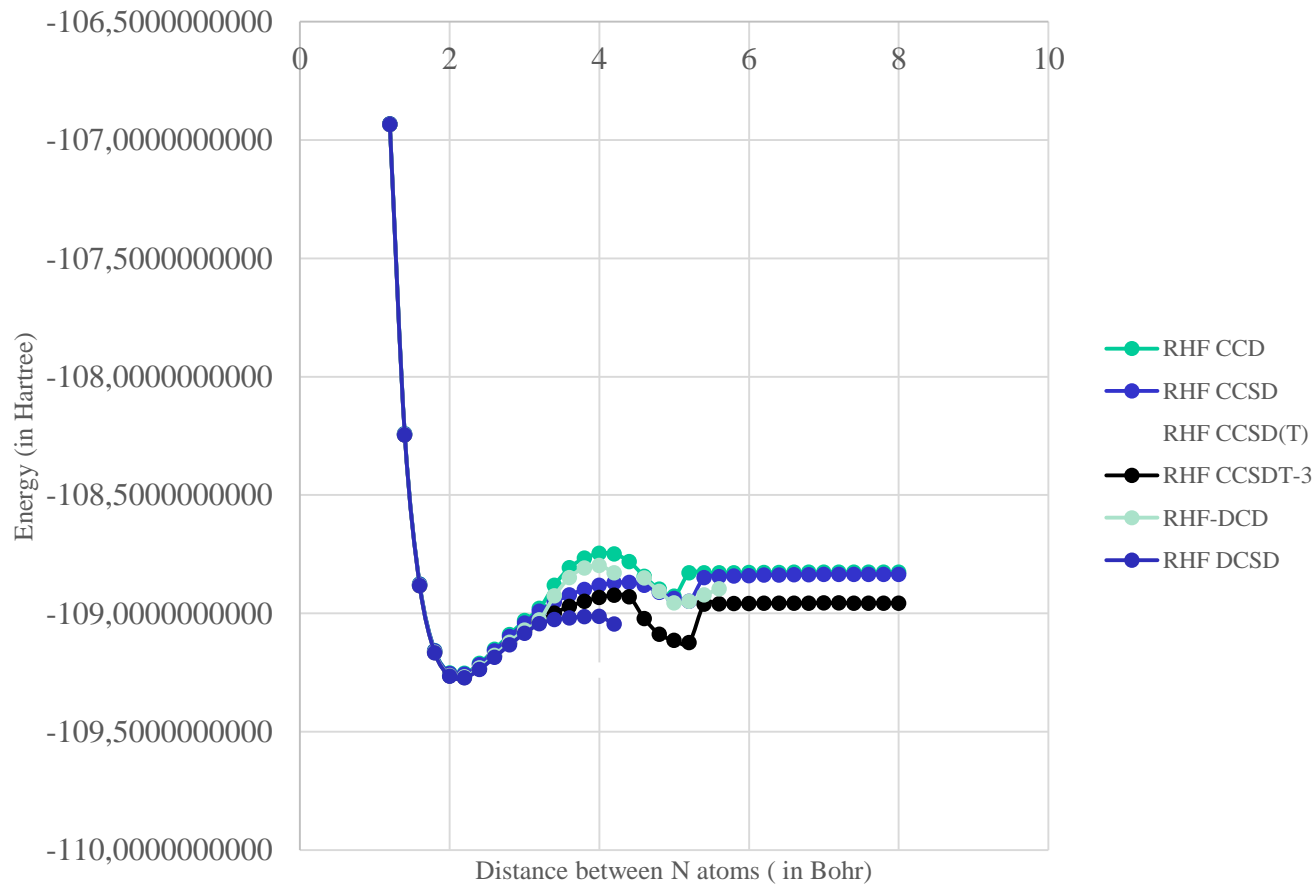
RHF based Bond dissociation of Nitrogen molecule ($\text{HOMO} - \Pi_u$)



UHF reference based bond dissociation : N₂



RHF reference based bond Dissociation of N_2 (Homo Σ_u^-)



OUTLINE

- **Some Essential Preliminaries**
- **Single reference CC theory for energies, properties**
- **EOM-CC for excited/ionized/attached states.**
- **Greens' Functions from CC**
- **Origin of problems with SR-CC**
- **Some results for near degeneracies**
- **Addition by subtraction in SR-CC**
- **EOM-DIP/DEA as an easy MR-CC**

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,

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

- Internally contracted. Köhn, Hanrath

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

Many-Body Methods in Chemistry and Physics

MBPT and Coupled-Cluster Theory

Isaiah Shavitt and Rodney J. Bartlett

CAMBRIDGE MOLECULAR SCIENCE

$$\begin{aligned} V &= V_1 + V_2 + \dots + V_{n-1} + V_n \\ &+ V_{n+1} + V_{n+2} \end{aligned}$$
$$\begin{aligned} VV &= V_1V_1 + V_1V_2 + \dots + V_1V_{n-1} + V_1V_n \\ &+ V_2V_1 + V_2V_2 + \dots + V_2V_{n-1} + V_2V_n \\ &+ \dots + V_{n-1}V_1 + V_{n-1}V_2 + \dots + V_{n-1}V_{n-1} \\ &+ V_{n-1}V_n + V_nV_1 + V_nV_2 + \dots + V_nV_{n-1} \end{aligned}$$
$$\begin{aligned} VVV &= V_1V_1V_1 + V_1V_1V_2 + \dots + V_1V_1V_{n-1} + V_1V_1V_n \\ &+ V_1V_2V_1 + V_1V_2V_2 + \dots + V_1V_2V_{n-1} + V_1V_2V_n \\ &+ \dots + V_1V_{n-1}V_1 + V_1V_{n-1}V_2 + \dots + V_1V_{n-1}V_{n-1} \\ &+ V_1V_{n-1}V_n + V_2V_1V_1 + V_2V_1V_2 + \dots + V_2V_1V_{n-1} \\ &+ V_2V_1V_n + V_2V_2V_1 + V_2V_2V_2 + \dots + V_2V_2V_{n-1} \\ &+ V_2V_2V_n + \dots + V_{n-1}V_1V_1 + V_{n-1}V_1V_2 + \dots + V_{n-1}V_1V_{n-1} \\ &+ V_{n-1}V_1V_n + V_{n-1}V_2V_1 + V_{n-1}V_2V_2 + \dots + V_{n-1}V_2V_{n-1} \\ &+ V_{n-1}V_2V_n + \dots + V_nV_1V_1 + V_nV_1V_2 + \dots + V_nV_1V_{n-1} \\ &+ V_nV_1V_n + V_nV_2V_1 + V_nV_2V_2 + \dots + V_nV_2V_{n-1} \\ &+ V_nV_2V_n + \dots + V_nV_{n-1}V_1 + V_nV_{n-1}V_2 + \dots + V_nV_{n-1}V_{n-1} \\ &+ V_nV_{n-1}V_n \end{aligned}$$

CAMBRIDGE