

Coupled-Cluster theory

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- p. 1/c

- p. 3/c

Coupled Cluster Theory

Finally the Coupled-Cluster

- Wavefunction $|\Psi\rangle = e^{\hat{S}}|\Phi_0\rangle$

- \hat{S} excitation operator

$$\hat{T}_1 = \sum_{i,a} t_i^a \hat{a}_a^\dagger \hat{a}_i$$

$$\hat{T}_2 = \sum_{i,j,ab} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j \quad \text{etc.}$$

- Schrödinger's equation $\hat{H}|\Psi\rangle = E|\Psi\rangle$

- Energy through projection against $\langle\Phi_0|$ or $\langle\Phi_0|e^{-\hat{S}}$

$$\begin{aligned} \langle\Phi_0|e^{-\hat{S}}\hat{H}e^{\hat{S}}|\Phi_0\rangle &= \langle\Phi_0|\hat{H}e^{\hat{S}}|\Phi_0\rangle \\ &= \langle\Phi_0|e^{-\hat{S}}Ee^{\hat{S}}|\Phi_0\rangle = E = E_{HF} + E_{Corr} \end{aligned}$$

- p. 2/c

- p. 4/c

General approach

Projection of $e^{-\hat{S}} \hat{H} e^{\hat{S}}$:

$$\begin{aligned} \langle \Phi_i^a | e^{-\hat{S}} \hat{H} e^{\hat{S}} | \Phi_0 \rangle &= 0 \\ \langle \Phi_{ij}^{ab} | e^{-\hat{S}} \hat{H} e^{\hat{S}} | \Phi_0 \rangle &= 0 \end{aligned} \quad (1)$$

Exponential

$$e^{\hat{S}} = 1 + \hat{S} + \frac{1}{2} \hat{S}^2 + \frac{1}{6} \hat{S}^3 + \dots$$

leads to the (exact) Baker-Campbell-Hausdorff expansion

$$e^{-\hat{S}} \hat{H} e^{\hat{S}} = \hat{H} + [\hat{H}, \hat{S}] + \frac{1}{2} [[\hat{H}, \hat{S}], \hat{S}] + \frac{1}{6} [[[\hat{H}, \hat{S}], \hat{S}], \hat{S}] + \frac{1}{24} [[[[\hat{H}, \hat{S}], \hat{S}], \hat{S}], \hat{S}], \hat{S}]$$

Remains to insert $\hat{S} = \hat{T}_1 + \hat{T}_2$, regroup and evaluate.
We may use

$$e^{-\hat{S}} \hat{H} e^{\hat{S}} = e^{-\hat{T}_1 - \hat{T}_2} \hat{H} e^{\hat{T}_1 + \hat{T}_2} = e^{-\hat{T}_2} \left(e^{-\hat{T}_1} \hat{H} e^{\hat{T}_1} \right) e^{\hat{T}_2} = e^{-\hat{T}_2} \hat{H}_e e^{\hat{T}_2}$$

General approach

Projection of $\hat{H} e^{\hat{S}}$:

$$\langle \Phi_i^a | \hat{H} e^{\hat{T}_1 + \hat{T}_2} | \Phi_0 \rangle = \langle \Phi_i^a | \hat{H} \left(\hat{T}_1 + \hat{T}_2 + \hat{T}_1 \hat{T}_2 + \frac{1}{2} \hat{T}_1^2 + \frac{1}{6} \hat{T}_1^3 \right) | \Phi_0 \rangle$$

$$\langle \Phi_{ij}^{ab} | \hat{H} e^{\hat{T}_1 + \hat{T}_2} | \Phi_0 \rangle = \langle \Phi_{ij}^{ab} | \hat{H} \left(1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_1 \hat{T}_2 + \right.$$

$$\left. + \frac{1}{2} \hat{T}_1^2 + \frac{1}{2} \hat{T}_1^2 \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 + \frac{1}{6} \hat{T}_1^3 + \frac{1}{24} \hat{T}_1^4 \right) | \Phi_0 \rangle$$

Equation of degree 4 to solve, via iterative methods.

Continuing

Take only diexcitations ($t_{ij}^{ab} = c_{ij}^{ab}$):

$$E = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle + \langle \Phi_0 | \hat{H} \hat{T}_2 | \Phi_0 \rangle = E_{HF} + \sum_I c_I \langle \Phi_0 | \hat{H} | \Phi_I \rangle$$

$$\langle \Phi_{ij}^{ab} | \hat{H} \left(1 + \hat{T}_2 + \frac{1}{2} \hat{T}_2^2 \right) | \Phi_0 \rangle = E \underbrace{\langle \Phi_{ij}^{ab} | \hat{T}_2 | \Phi_0 \rangle}_{= c_{ij}^{ab}}$$

$$\text{Contributions only from } \hat{T}_2 \hat{T}_2 | \Phi_0 \rangle = 2 \sum_{kIcd} \langle c_{ij}^{ab} * c_{kl}^{cd} | \Phi_{ijkl}^{abcd} \rangle$$

with all the possibilities

$$\begin{aligned} c_{ij}^{ab} * c_{kl}^{cd} &= c_{ij}^{ab} c_{kl}^{cd} - \langle c_{ij}^{ab} * c_{kl}^{cd} \rangle \\ &= c_{ij}^{ab} c_{kl}^{cd} - c_{ik}^{ab} c_{jl}^{cd} + c_{il}^{ab} c_{jk}^{cd} - c_{ij}^{ac} c_{kl}^{bd} + c_{ik}^{ac} c_{jl}^{bd} - c_{il}^{ac} c_{jk}^{bd} \\ &\quad + c_{ij}^{ad} c_{kl}^{bc} - c_{ik}^{ad} c_{jl}^{bc} + c_{il}^{ad} c_{jk}^{bc} + c_{ij}^{cd} c_{kl}^{ab} - c_{ik}^{cd} c_{jl}^{ab} + c_{il}^{cd} c_{jk}^{ab} \\ &\quad - c_{ij}^{bd} c_{kl}^{ac} - c_{ik}^{bd} c_{jl}^{ac} - c_{il}^{bd} c_{jk}^{ac} + c_{ij}^{bc} c_{kl}^{ad} - c_{ik}^{bc} c_{jl}^{ad} + c_{il}^{bc} c_{jk}^{ad} \end{aligned}$$

- p. 80

- p. 90

Continuing

Assembly :

$$\begin{aligned} &\hat{H}_{0I} + \sum_J \hat{H}_{IJ} c_J + \\ &+ \sum_J \langle \Phi_I | \hat{H} | \Phi_{I+J} \rangle (c_I c_J - \langle c_I * c_J \rangle) \\ &- \underbrace{\left(E_{HF} c_I + \sum_J \hat{H}_{0J} c_I c_J \right)}_{E c_I} = 0 \end{aligned}$$

With $\langle \Phi_I | \hat{H} | \Phi_{I+J} \rangle = \langle \Phi_0 | \hat{H} | \Phi_J \rangle$

$$\sum_J \langle \Phi_I | \hat{H} | \Phi_{I+J} \rangle c_I c_J - \sum_J \hat{H}_{0J} c_I c_J = 0$$

- p. 80

- p. 100

Continuing

Finally the equations to determine the coefficients :

$$\hat{H}_{0I} + \langle \Phi_I | \hat{H} - E_{HF} | \Phi_I \rangle c_I + \sum_{J \neq I} \hat{H}_{IJ} c_J = \sum_J \hat{H}_{0J} \langle c_I * c_J \rangle$$

- Still quadratic in the coefficients
- Only di-excited determinants to consider
- We had for the variational CISD correlation energy:

$$E_{Corr} = \sum_I c_I \langle \Phi_0 | \hat{H} | \Phi_I \rangle$$

- Equations resemble the CISD equations !
- To be solved iteratively

-p. 11/2

-p. 13/2

Dressing of a CISD matrix

First approximation (1st iteration) :

$$\sum_J \hat{H}_{0J} \langle c_I * c_J \rangle = 0$$

Equations CEPA-0 (DMBPT- ∞ , LCC(S)D) :

$$\sum_I \langle \Phi_0 | \hat{H} | \Phi_I \rangle c_I = E_{Corr}$$
$$\hat{H}_{0I} + \langle \Phi_I | \hat{H} - E_{HF} | \Phi_I \rangle c_I + \sum_{J \neq I} \hat{H}_{IJ} c_J = 0$$

Diagonal approximation: $\hat{H}_{IJ} = 0$ pour $I \neq J$:

$$E_{Corr} = \sum_I c_I \hat{H}_{0I} = - \sum_I \frac{\hat{H}_{0I}^2}{\langle \Phi_I | \hat{H} - E_{HF} | \Phi_I \rangle}$$

Epstein-Nesbet perturbation theory

-p. 12/2

-p. 14/2

Including triple excitations

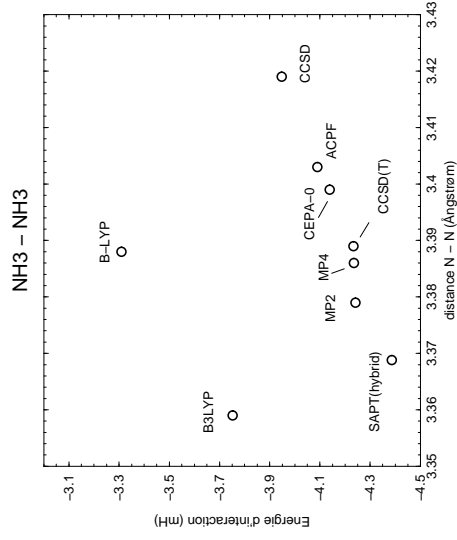
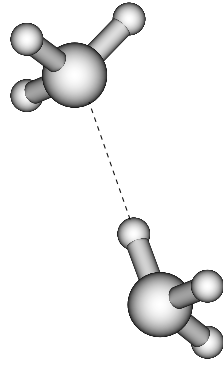
- CCSD: only di-excited determinants needed
- Cost as CISD or MP4 (SDQ): $\sim N^6$
- Triples may be important:
 - Orbital corrections for di-excitations
 - Much better performance for intermolecular interactions
- Full triples step costs $\sim N^8$:

$$\langle ij k a b c | \hat{H} | l m n d e f \rangle$$
- 6 indices $ij k a b c$ and 2 differences $\longrightarrow N^8$
- Needs much more memory for coefficients $t_{ij,k}^{abc}$, etc.
- Perturbative treatment: straightforward, no need for iterations \longrightarrow CCSD(T) as triples in MP4: $\sim N^7$
- Nowadays reference method for closed-shell systems

-p. 168

-p. 172

Example: $\text{NH}_3 \cdots \text{NH}_3$



-p. 168

-p. 172

Performance

Geometry parameters

molecule	Hartree-Fock		MP2		CCSD(T)	
	Δr (pm)	Δang ($^\circ$)	Δr (pm)	Δang ($^\circ$)	Δr (pm)	Δang ($^\circ$)
H ₂ O	-1.7	+1.8	+0.1	-0.4	-0.1	-0.3
N ₂	-3.1		+1.6		+0.6	
CH ₄	-0.5		-0.1		+0.3	
CO	-2.4		+1.1		+0.8	
HF	-1.8		+0.5		+0.4	
NH ₃	-1.4	+1.5	0.0	+0.5	+2.3	-0.3
P ₂	-3.6		+3.4		+2.3	
SO ₂	-2.7	-1.3	+2.7	-1.1	+0.3	-1.1

Source: NIST database <http://www.nist.org>

- p. 19/C

- p. 20/C

Performance

Vibrational constants, atomization energies

molecule	2nd order Møller-Plesset		CCSD(T)		Experiment	
	ν (cm^{-1})	at.ener. (kJ/mol)	ν (cm^{-1})	at.ener. (kJ/mol)	ν (cm^{-1})	at.ener. (kJ/mol)
H ₂ O	3821	917	3811	899	3657	918
N ₂	2187	952	2339	897	2359	942
CH ₄	3069	1607	3028	1617	2917	1642
CO	2110	1099	2144	1040	2170	1072
HF	4125	576	4128	557	4138	567
NH ₃	3503	1128	3464	1131	3337	1158
P ₂	726	451	768	437	781	486
SO ₂	1106	—	1136	968	1151	1063

Source: NIST database <http://www.nist.org>

- p. 19/C

- p. 20/C

Bond breaking

- General problem in (quantum) chemistry: chemical reactivity
- Closed shells \rightarrow open shells:
 - Nightmare: $\text{Cr}_2 \rightarrow 2 \text{Cr}$ (12 open shells $3d^5 4s^1$)
 - But already $\text{Be}_2 \rightarrow 2 \text{Be}$ difficult

Accepted binding energy: 2.5 kcal/mol, $r_e = 2.4 \text{ \AA}$

method	r_e (\AA)	E_B (kcal/mol)
RHF	—	—
MP2	2.74	-1.15
MP4	2.54	-2.18
CCSD(T)	2.50	-1.61
LDA	2.39	-12.95
PBE	2.43	-9.81
B3LYP	2.49	-4.14

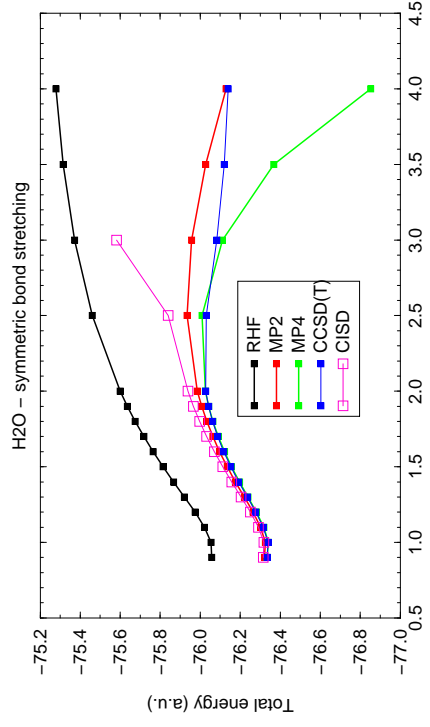
Basis: aug-cc-pvqz, 160 functions,
 BERYLLIUM (1s, 7p, 4d, 3f, 2g) \rightarrow [6s, 5p, 4d, 3f, 2g]

-p. 220c

Bond breaking

- General problem in (quantum) chemistry: chemical reactivity
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Symmetric dissociation of water



-p. 220c

-p. 220c

-p. 220c

Bond breaking

- General problem in (quantum) chemistry: chemical reactivity
- Closed shells \rightarrow open shells:
 - Nightmare: $\text{Cr}_2 \rightarrow 2 \text{Cr}$ (12 open shells $3d^5 4s^1$)
 - But already $\text{Be}_2 \rightarrow 2 \text{Be}$ difficult
- Most simple case: dissociation of H_2 in a minimal basis
 - Orbitals σ and σ^* become degenerate
 - HF occupies always the σ
 - Electrons should localize on the atoms
 - Denominator in perturbation theory vanishes
 - CCSD(T) ? There are no coupled di-excitations !
 - CISD is already the Full CI, the best description of all possible in that basis set
 - The 2 determinants will have equal weight in the final wave function

-p. 260c

T1 diagnostics

- Importance of mono-excitations:

$$\langle \Phi_0 | H | \Phi_i^a \rangle = F_{ia}$$

- Hartree-Fock orbitals $\leftrightarrow F_{ia} = 0$ (Brillouin theorem)
- Amplitudes of single excitations important \rightarrow HF orbitals are not suited for describing the wavefunction, diexcited determinants better expressed in different orbitals
- HF wavefunction: best single determinants wavefunction

Conclusion: multi-determinantal wavefunction needed.

Decision via T1 diagnostics

$$T1 = \frac{\|t_1\|}{\sqrt{N}}$$

T.J.Lee, P.R. Taylor, Int.J.Quant.Chem., S23 (1989) 199; T.J.Lee, J.E.Rice, G.E. Scuseria, H.F.Schaefer III, Theor.Chim.Acta, 75 (1989) 81

-p. 270c

T1 diagnostics

Examples (closed-shell molecules)

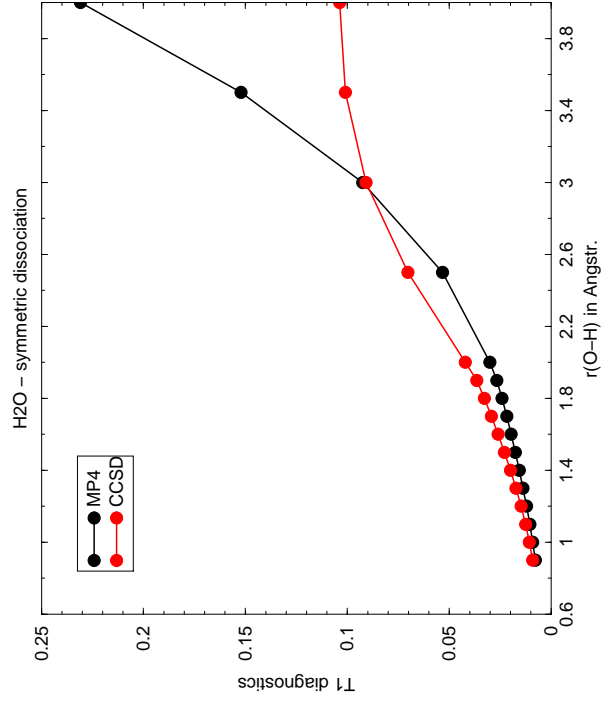
molecule	T1 term	$E_{\text{Corr}}(\text{CCSD})$	Triples (T)
CH_4	0.0075	-0.22070	-0.00653
NH_3	0.0082	-0.25150	-0.00828
H_2O	0.0101	-0.27337	-0.00867
HF	0.0102	-0.28120	-0.00755
N_2	0.0136	-0.38002	-0.01981
P_2	0.0179	-0.30139	-0.02301
CO	0.0188	-0.36440	-0.01789
N_2O	0.0200	-0.63760	-0.03829
O_3	0.0289	-0.76253	-0.05059
SO_2	0.0225	-0.66872	-0.03753

-p. 260c

-p. 270c

T1 diagnostics

The symmetric dissociation of H₂O



Example

Symmetric dissociation of water: the correct solution

