Amplitude Screening in Local Coupled Cluster Approaches - Accurate and Expensive ?

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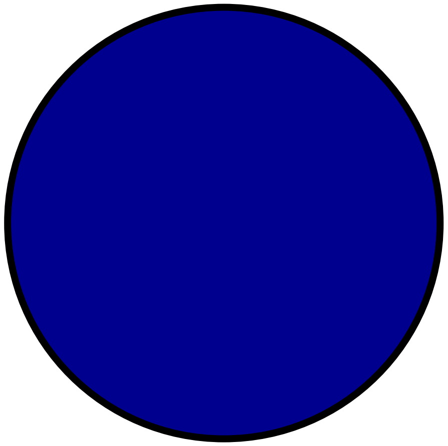
Advantages of Coupled Cluster Methods

- robust black box method
- well known limitations
- high accuracy
- systematic hierarchy of methods
- fast convergence towards FCI

Aim for an Alternative CC-Approximation

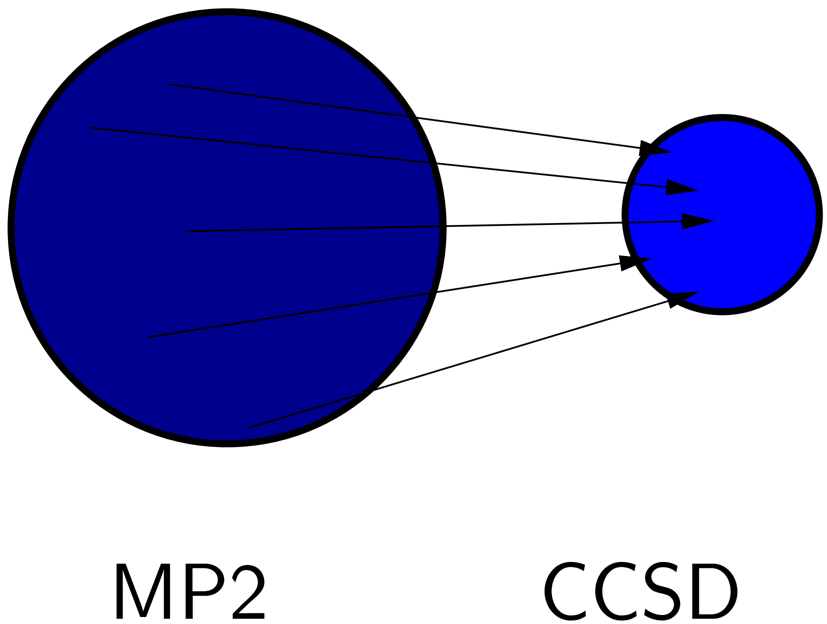
- make CC feasible for $\sim$ 50 atoms
- focus on accuracy, not efficiency
- one parameter to go from full to truncated CC
- controllable error, "fine grained" approximation
- open choice of orbitals (ideal : system independent)

Screening for CC-amplitudes

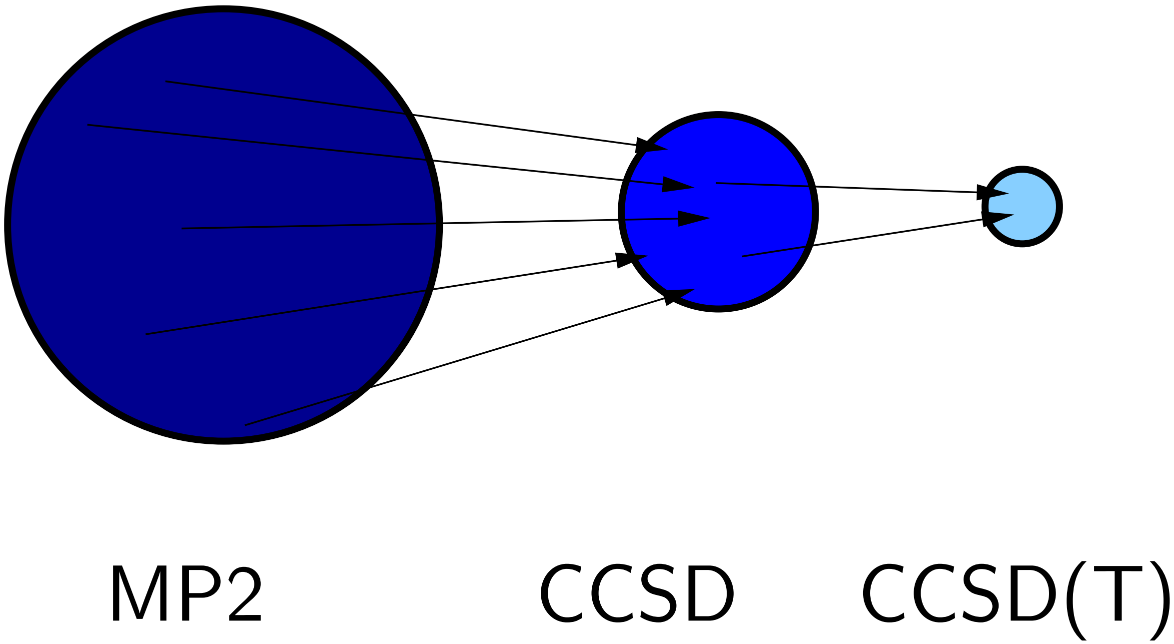


MP2

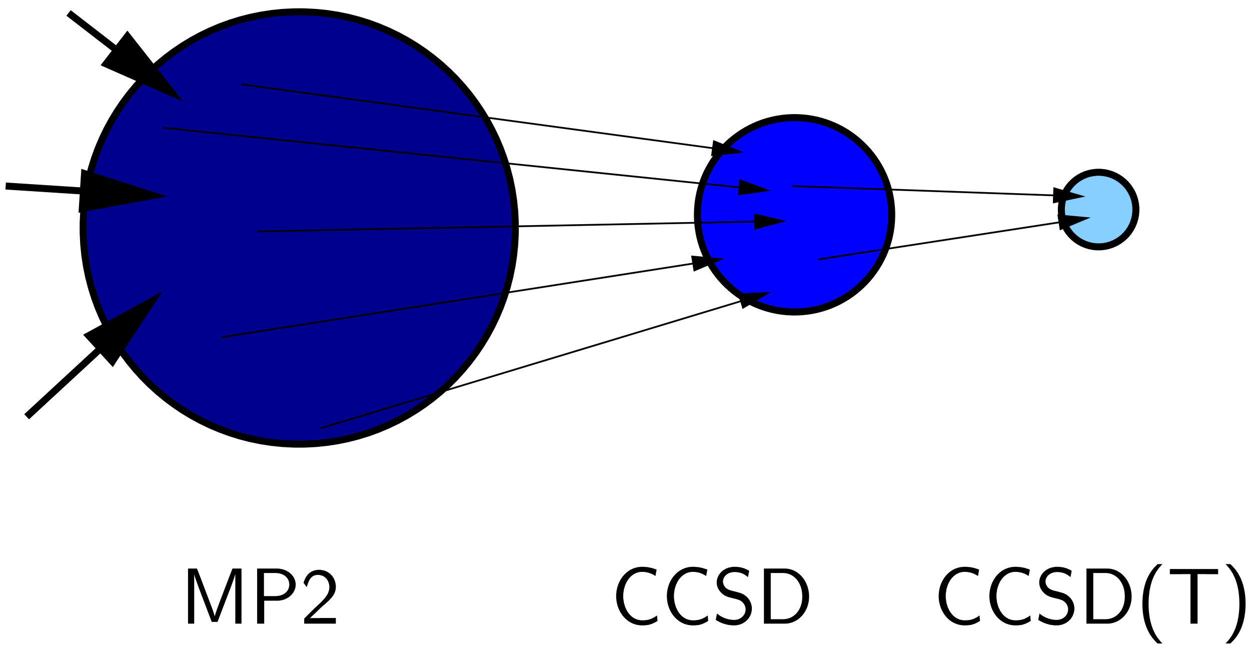
Screening for CC-amplitudes



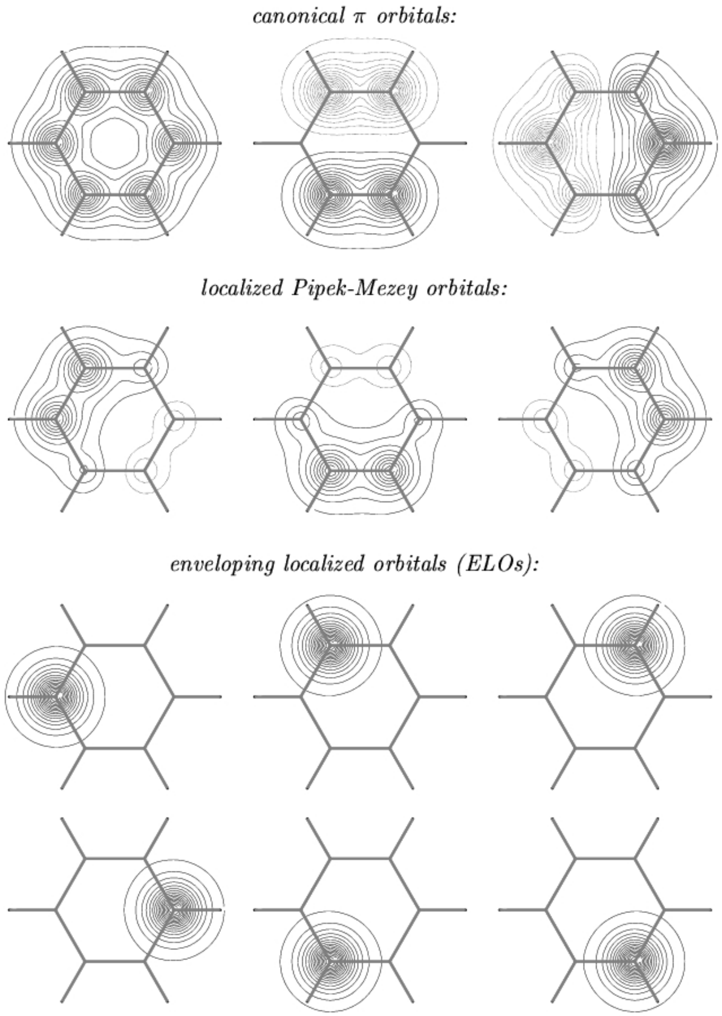
Screening for CC-amplitudes



Screening for CC-amplitudes



Choice of Orbitals: Enveloping Localized Orbitals



- strictly atom centered
- shape ao-like
- non orthogonal
- have to span occupied space
- dimension $\sim$ minimal basis
- nr. occ $<$ nr. ELOs $<$ nr. AOs

Current Dynamical Thresholding Algorithm

calculate full MP2 amplitudes

$\downarrow$

screening procedure

$\downarrow$

calculate new CC residual from old CC amplitudes

or

calculate new CC residual from all old amplitudes

$\downarrow$

for MP2 part of amplitudes : $< Q_{MP2}| \; [H_0, T] + V \; |0 >= 0$

$\downarrow$

transform to MO basis and weight by denominator

AAA and M. Nooijen, JCP 125, 024104 (2006)

Aim for an Alternative CC-Approximation

conventional CC

Aim for an Alternative CC-Approximation

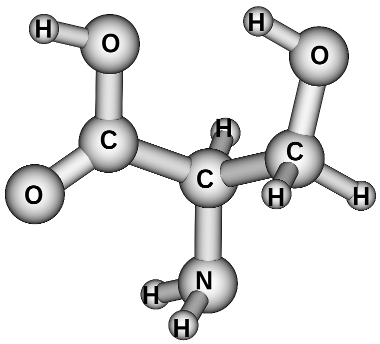
conventional CC

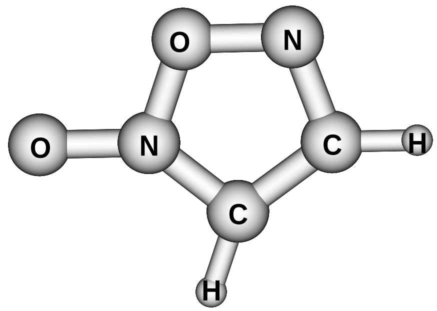
LCC approximations

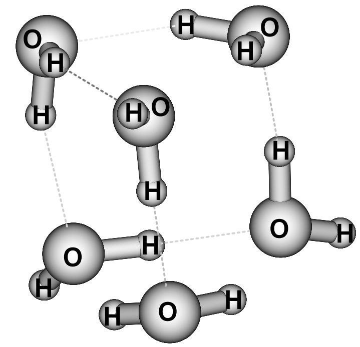
Aim for an Alternative CC-Approximation

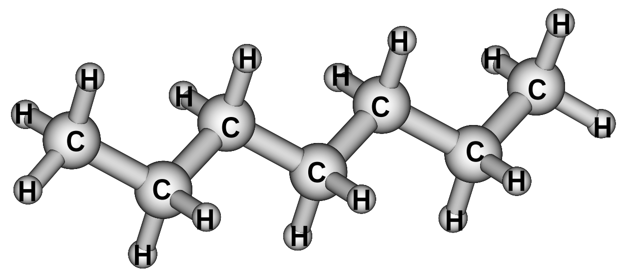
conventional CC   dynamical thresholding   LCC approximations

Test Systems

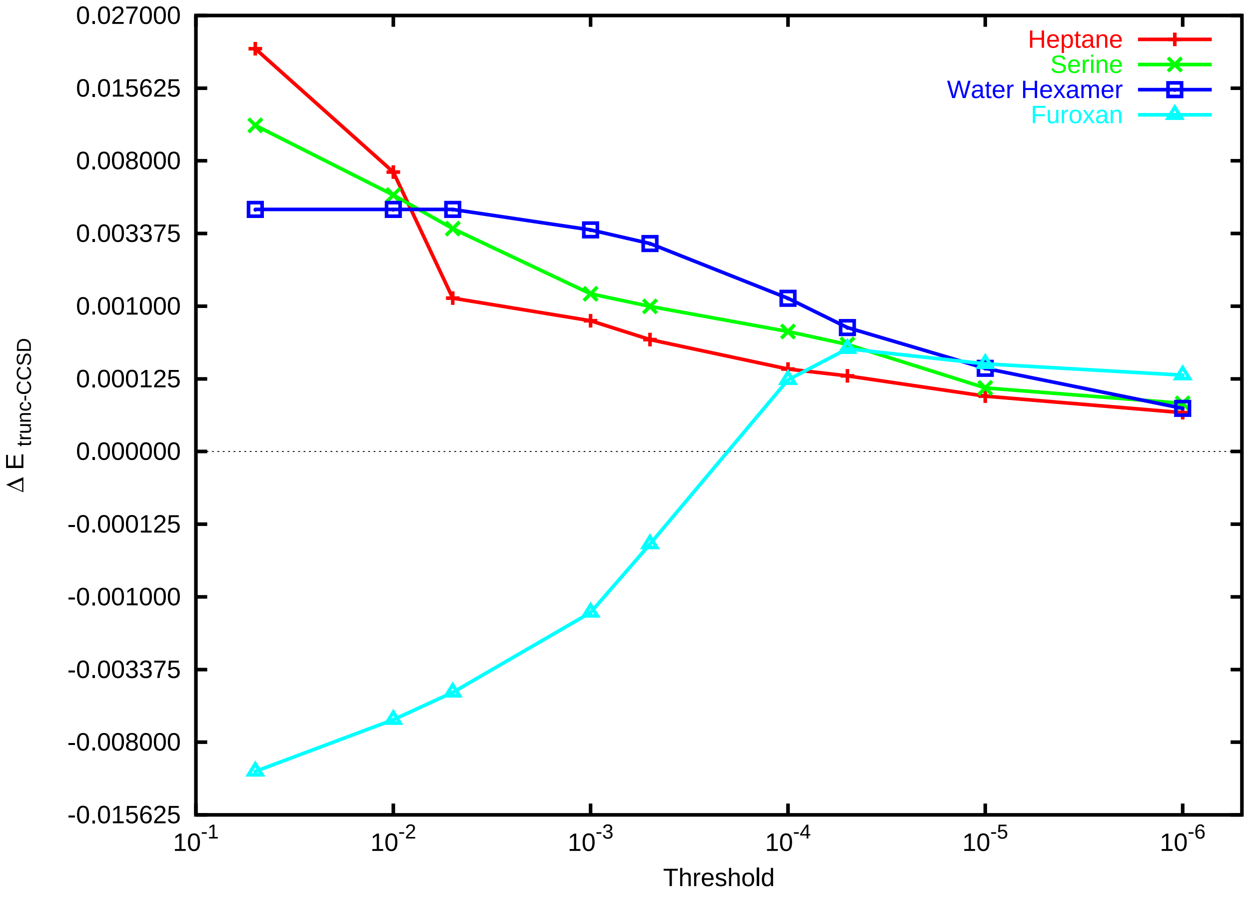




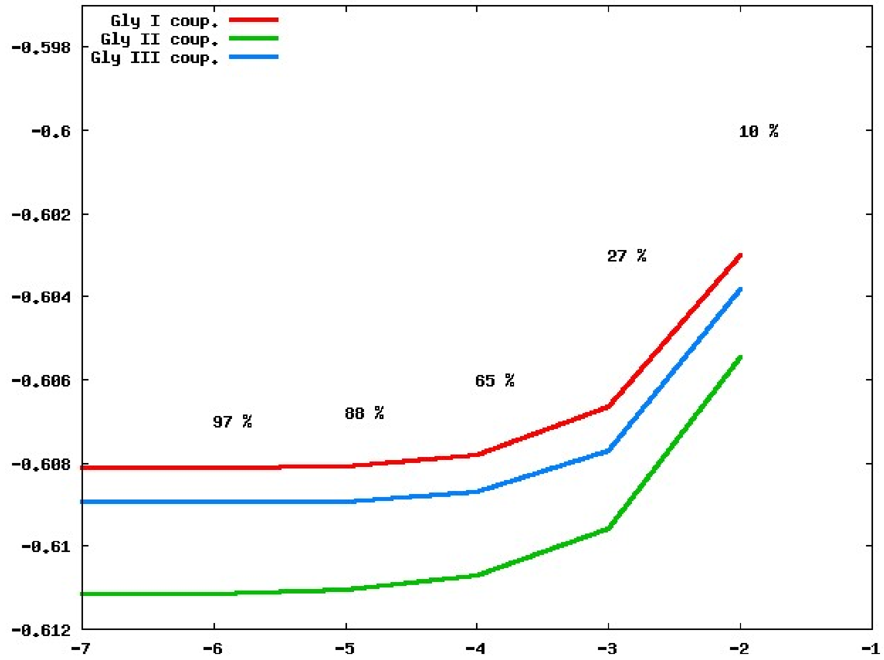


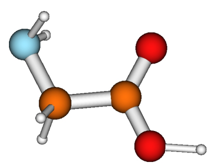


Convergence Towards Full CCSD in TZ Basis

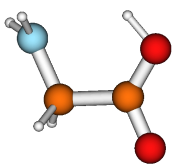


CCSD Energy for Glycine Conformers in DZ Basis

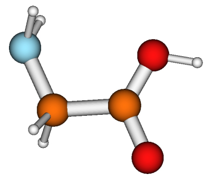




Conformer I



Conformer II

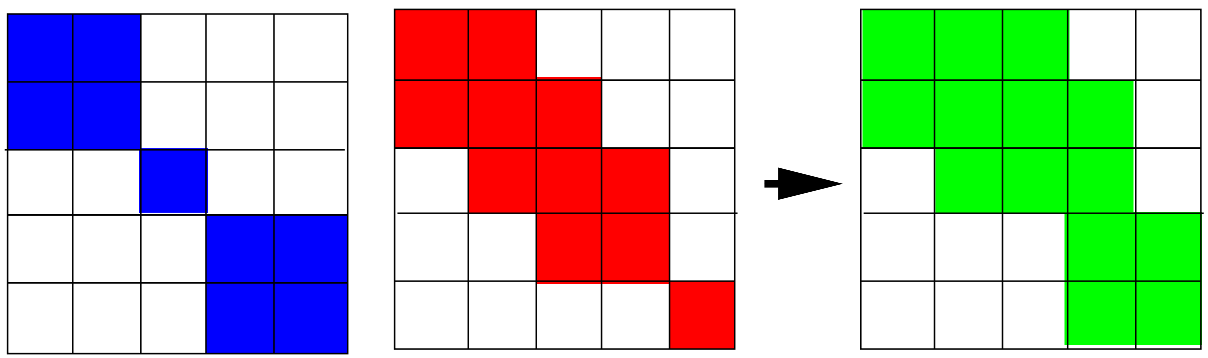


Conformer III

CCSD Doubles Equations

$$
\begin{aligned}
& t_{ij}^{ab} \leftarrow \\
& v_{ij}^{ab} - t_m^a v_{ij}^{mb} + t_j^e v_{ie}^{ab} - f_i^m t_{mj}^{ab} - f_e^b t_{ij}^{ea} + \frac{1}{2} t_{mn}^{ab} v_{ij}^{mn} \\
+ \quad & t_{nj}^{ea} v_{ie}^{nb} + \frac{1}{2} t_{ij}^{ef} v_{ef}^{ab} + t_m^a t_n^b v_{ij}^{mn} - t_j^e t_n^a v_{ie}^{nb} + t_i^e t_j^f v_{ef}^{ab} \\
- \quad & f_f^m t_{mj}^{ab} t_i^f + f_f^m t_{ij}^{fa} t_m^b + \frac{1}{2} t_{mn}^{ab} t_j^f v_{if}^{mn} - t_{nj}^{ea} t_m^b v_{ie}^{nm} \\
- \quad & t_{mj}^{ab} t_n^f v_{if}^{mn} - t_{nj}^{ea} t_i^f v_{ef}^{nb} - \frac{1}{2} t_{ij}^{ef} t_m^a v_{ef}^{mb} + t_{ij}^{ea} t_m^f v_{ef}^{mb} \\
+ \quad & \frac{1}{2} t_{ij}^{eb} t_{mn}^{fa} v_{ef}^{mn} + \frac{1}{4} t_{ij}^{ef} t_{mn}^{ab} v_{ef}^{mn} - \frac{1}{2} t_{mi}^{ab} t_{nj}^{ff} v_{ff}^{mn} \\
- \quad & t_{ni}^{eb} t_{mj}^{fa} v_{ef}^{nm} + t_j^e t_n^a t_m^b v_{ie}^{nm} - t_i^e t_j^f t_m^a v_{ef}^{mb} \\
+ \quad & \frac{1}{2} t_i^e t_j^f t_{mn}^{ab} v_{ef}^{mn} + t_i^e t_n^b t_{mj}^{fa} v_{ef}^{nm} + t_i^e t_m^f t_{nj}^{ab} v_{ef}^{mn} \\
+ \quad & \frac{1}{2} t_m^a t_n^b t_{ij}^{fe} v_{fe}^{mn} - t_m^b t_n^f t_{ij}^{ea} v_{fe}^{mn} + t_i^e t_j^f t_m^a t_n^b v_{ef}^{mn}
\end{aligned}
$$

Sparsity in T_2 is Not Enough !



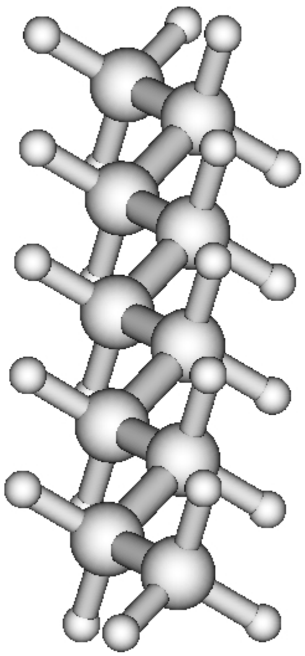
$$\sum_{\gamma\delta} \mathsf{T}_{\mu\nu}^{\gamma\delta} \quad \mathsf{V}(\gamma\delta\alpha\beta) \;\rightarrow\; \mathsf{R}_{\mu\nu}^{\alpha\beta}$$

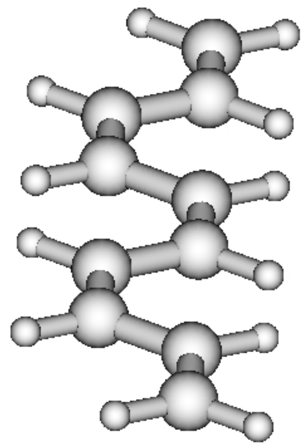
CCD / B-CCD Doubles Equations

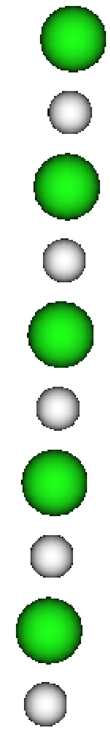
$$
\begin{aligned}
& {t_2}_{ij}^{ab} \leftarrow \\
& v_{ij}^{ab} - f_i^m t_{mj}^{ab} - f_e^b t_{ij}^{ea} + \frac{1}{2} t_{mn}^{ab} v_{ij}^{mn} + t_{nj}^{ea} v_{ie}^{nb} + \frac{1}{2} t_{ij}^{ef} v_{ef}^{ab} \\
+ \quad & t_{ij}^{ea} t_m^f v_{ef}^{mb} + \frac{1}{2} t_{ij}^{eb} t_{mn}^{fa} v_{ef}^{mn} + \frac{1}{4} t_{ij}^{ef} t_{mn}^{ab} v_{ef}^{mn} - \frac{1}{2} t_{mi}^{ab} t_{nj}^{ff} v_{ff}^{mn} \\
- \quad & t_{ni}^{eb} t_{mj}^{fa} v_{ef}^{nm}
\end{aligned}
$$

- At most quadratic terms
- Only Integrals and T_2 Amplitudes
- Algebraic simplicity

Molecular Chain Test



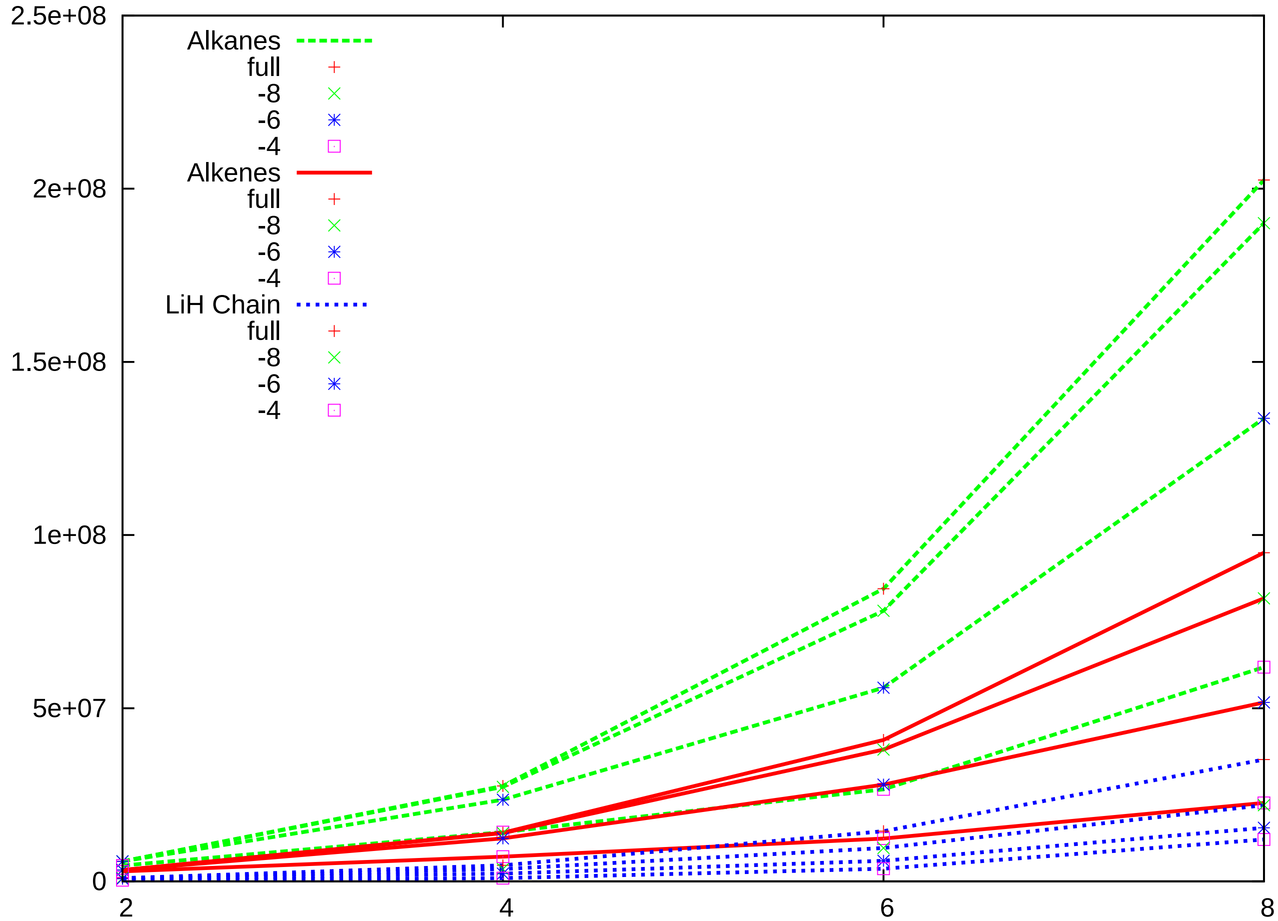




CH_3-$(CH_2)_n$-CH_3 CH_2-$(CH)_n$-CH_2 LiH-$(LiH)_n$-LiH

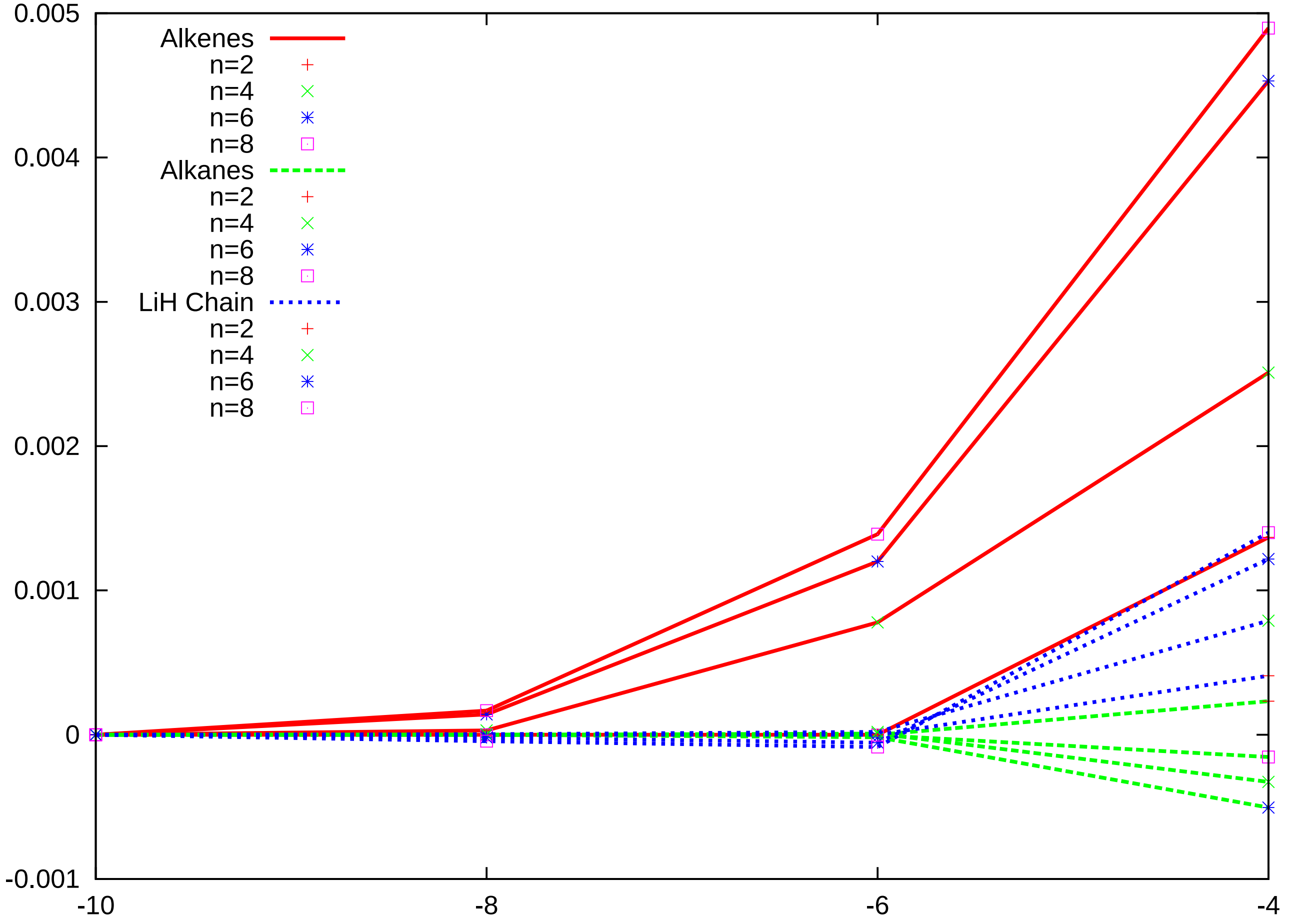
CCD energy and amplitudes in DZ basis for n=2,4,6,8

Number of T_2 Amplitudes



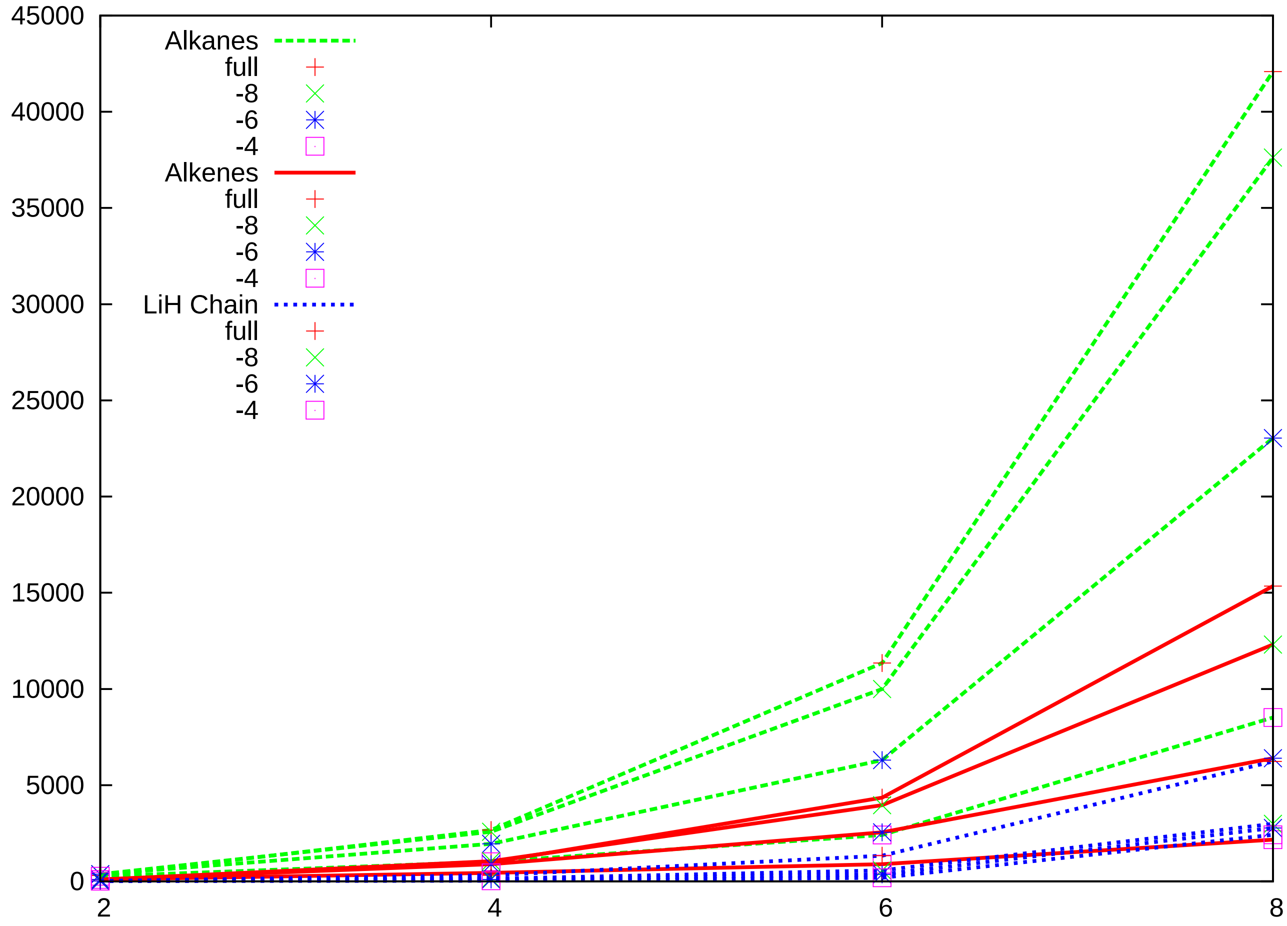
chain length vs. number of amplitudes (different plots for log(thrs))

Truncation Error vs. Threshold



log(thrs) vs. truncation error [Hartree]

Walltime for T_2 Equations



chain length vs. time for T_2 (different plots for log(thrs))

Summary

- dynamical thresholding algorithm : a posteriori scheme
- use ao-like orbital to ensure system independence
- screening works well, error correlates with threshold
- physics of the system decides on amplitude truncation
- in new DT-CCD implementation time decreases with amplitudes

Outlook : Parallelization of CC Methods

first parallel implementation of second derivatives for CC methods
replicated-T_2 algorithm tailored to PC clusters in ACES II MAB

molecule	basis set	#bf	number of CPUs	execution time [h]
benzene (NMR)	cc-pCVTZ	342	16	5
benzene (E-fc)	cc-pV5Z	876	16	4
benzene (E-fc)	cc-pV6Z	1386	16	21
cyclohexene (E-fc)	aug-cc-pVQZ	940	16	40
adamantyl cation				
(geometry 1 step)	cc-pVTZ	510	9	90

M. E. Harding, T. Metzroth, AAA and J. Gauss, submitted to JCTC

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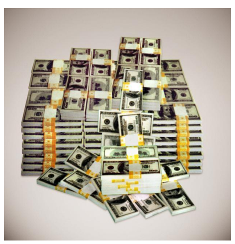

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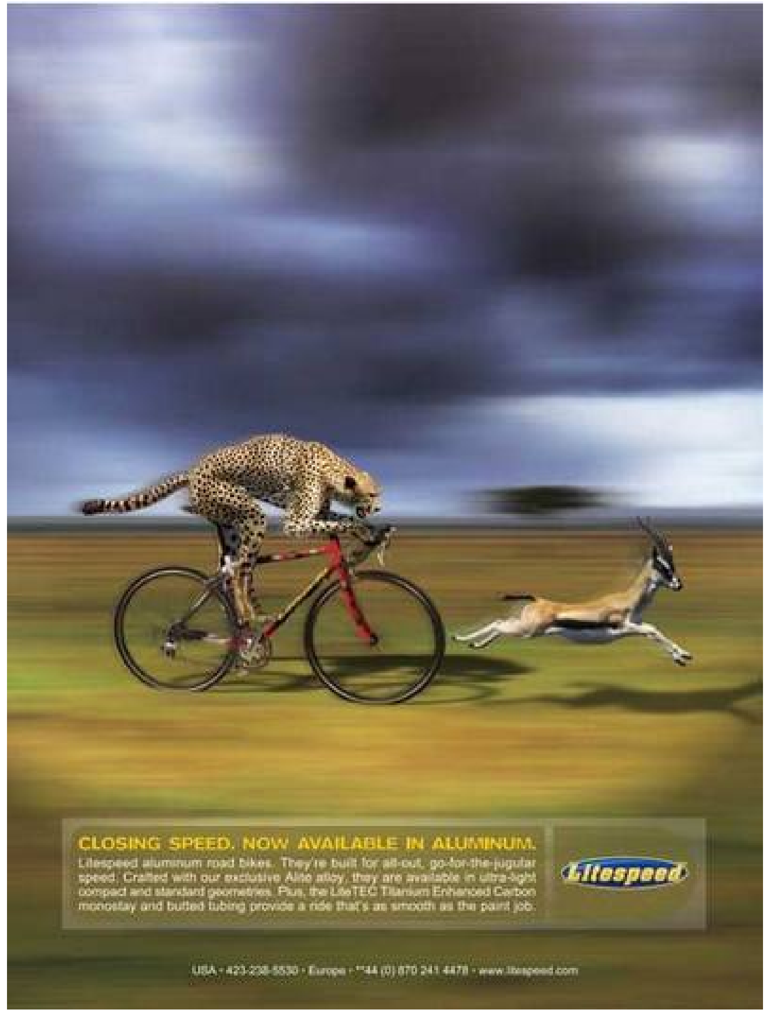
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