Implementation of the incremental scheme and application to CCSD energies

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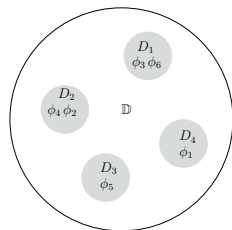
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Outline

The Incremental Scheme
(A General Local Correlation Approach)

- Introduced by Nesbet (1967) and Stoll (1992)
- Solve the Hartree-Fock problem
- Divide the system into localized orbital domains
- Calculate the correlation energies for single domains, pairs, ... up to a given order
- Expand the correlation energy as

$$E_{corr} = \sum_i \Delta\varepsilon_i + \frac{1}{2!}\sum_{ij}\Delta\varepsilon_{ij} + \frac{1}{3!}\sum_{ijk}\Delta\varepsilon_{ijk} + ...$$

$$\Delta\varepsilon_i = \varepsilon_i \qquad \Delta\varepsilon_{ij} = \varepsilon_{ij} - \Delta\varepsilon_i - \Delta\varepsilon_j$$

$$\Delta\varepsilon_{ijk} = \varepsilon_{ijk} - \Delta\varepsilon_{ij} - \Delta\varepsilon_{ik} - \Delta\varepsilon_{jk} - \Delta\varepsilon_i - \Delta\varepsilon_j - \Delta\varepsilon_k$$

$\vdots$

## Automatic generation of the domains

- Construct the centers of charge according to the dipole integrals in AO-basis
- Construct the connectivity matrix C

$$
C_{ij} = \begin{cases} 10^8, & \text{if } D_{ij} \leq t_{con} \wedge \frac{q}{D_{ij}} \geq 10^8 \\ \frac{q}{D_{ij}}, & \text{if } D_{ij} \leq t_{con} \wedge \frac{q}{D_{ij}} < 10^8 \\ 0, & \text{if } D_{ij} > t_{con} \end{cases}
$$

- Use METIS-Graphpartitioning to divide the set of orbitals into disjoint subsets
- Generate all necessary orbital sets for higher order terms

Domains for Naphtalen
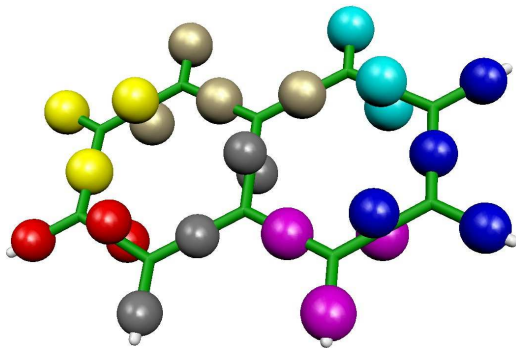
- $t_{con} = 3$, in C1-Symmetry

Energy Screening[1]

- If the energy of an increment is lower than a given threshold, we can neglect it in the summation

$$E_{\text{corr}} = \sum_{\substack{\mathbb{X} \\ \mathbb{X} \in \mathcal{P}(\mathbb{D}) \\ |\mathbb{X}| \leq \mathcal{O} \wedge |\Delta\tilde{\varepsilon}_{\mathbb{X}}| > E_{thres}}} \Delta\varepsilon_{\mathbb{X}}$$

- The goal is to obtain $\Delta\tilde{\varepsilon}_{\mathbb{X}}$ before the increment $\Delta\varepsilon_{\mathbb{X}}$ is explicitly calculated

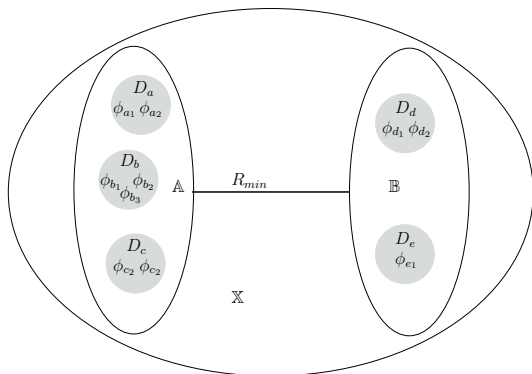- Low level correlation methods (MP2)

- Small basis set calculations

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[1]J. Friedrich, M. Hanrath, M. Dolg, J. Chem. Phys. **126**, 154110 (2007).

Distance Screening[2]

- If two parts of a given *n*-site domain are far apart, we can neglect the incremental energy (eg.: $\varepsilon_{ij} \approx \varepsilon_i + \varepsilon_j$)

- Simple and efficient

[2]J. Friedrich, M. Hanrath, M. Dolg, J. Phys. Chem. A (2007), accepted.

Contribution of Low Order Summations

$$p_{s,t} = \binom{(|\mathbb{D}| - t)}{(s - t)} \text{ with } s > t$$
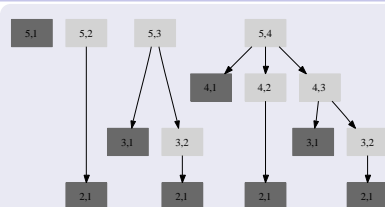
$$F(s,t) = -\sum_{i=t}^{s-1} p_{s,i} \cdot F(i,t)$$

$$F(t,t) = 1$$

All possibilities to include the 1st order summation in the 5th order summation

Example:

$$F(5,2) = (-p_{5,2}) + (-p_{5,3}) \cdot (-p_{3,2}) + (-p_{5,4}) \cdot [(-p_{4,2}) + (-p_{4,3}) \cdot (-p_{3,2})]$$

order $\mathcal{O}$	1	2	3
$F(4,\mathcal{O})$	-969	153	-17

(20 domains)

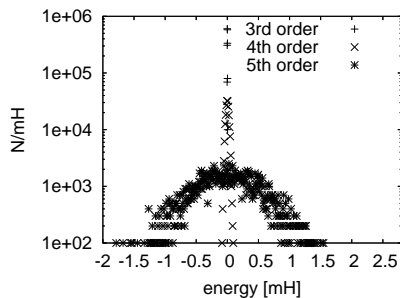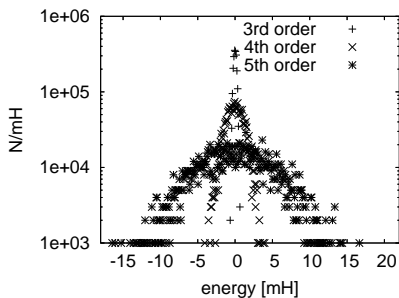- Adapt convergence thresholds according to the desired accuracy

Error Propagation - Simulation by Random Numbers

- Limited accuracy of the correlation calculations

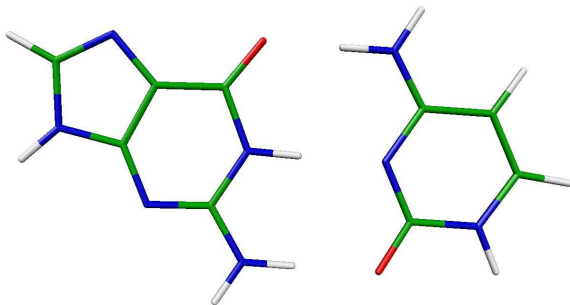$$\varepsilon_{\mathbb{X}} = X \cdot 10^{-6} \qquad\qquad \varepsilon_{\mathbb{X}} = X \cdot 10^{-10} \cdot 10^{\mathcal{O}}$$

- Results based on 2000 sets of uniformly distributed random numbers X

Example: DNA Base-Pair I

- RI-BP86/SVP optimized structure of the guanine-cytosine base pair.

Example: DNA Base-Pair II

order i	i-th order correction [au]	$E_{corr}(i)$ [au]	error [kcal/mol]	% E_{corr}
1	-1.916622	-1.916622	592.65	66.99
2	-0.979382	-2.896004	-21.92	101.22
3	0.031816	-2.864189	-1.96	100.11
4	0.002382	-2.861807	-0.46	100.03
exact CCSD		-2.861067		

- Comparison of the incremental energies with the full CCSD/6-31G** calculations for the guanine-cytosine dimer. (dsp=3, 16 domains, core=19)
- The canonical CCSD calculation is already impossible on a Pentium IV (1.35 GB RAM) PC
- 421 of 2516 CCSD calculations where necessary for $t_{dist} = \frac{16}{\mathcal{O}_i}$

Performance of the Incremental Scheme I
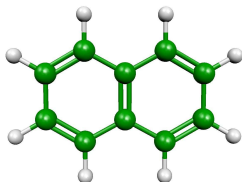
Naphtaline		
order	error	% E_{corr}
1	278.87	67.11
2	-10.65	101.26
3	-0.14	100.02
4	0.15	99.98

Alkyne		
order	error	% E_{corr}
1	395.63	68.93
2	-12.28	100.96
3	-0.52	100.04
4	-0.04	100.00

- Errors with respect to the exact CCSD calculation [kcal/mol]

Alkyne

energy threshold	E_{corr}	error	n calc
[au]	[au]	[kcal/mol]	
total number of calculations			561
10^{-8}	-2.029578	-0.04	555
10^{-7}	-2.029578	-0.04	506
10^{-6}	-2.029565	-0.03	299
10^{-5}	-2.029656	-0.09	135
10^{-4}	-2.030857	-0.85	71

- Simulated energy screening

Performance of the Incremental Scheme II
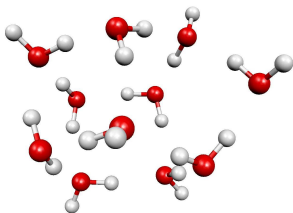
$(H_2O)_{11}$		
order	error	% E_{corr}
1	33.35	97.68
2	0.18	99.99
3	0.01	100.00
4	0.00	100.00
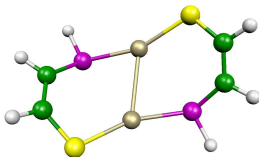
$Au_2(PH\text{-}C_2H_2\text{-}S)_2$		
order	error	% E_{corr}
1	317.17	64.14
2	-30.13	103.41
3	1.98	99.78
4	-0.07	100.01

- Errors with respect to the exact CCSD calculation [kcal/mol]

Performance of the Incremental Scheme III
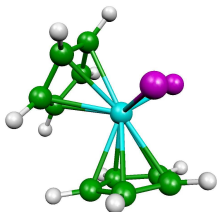
	$TiCp_2Cl_2$	
order	error	% E_{corr}
1	305.25	73.66
2	-34.64	102.99
3	7.60	99.34
4	0.08	99.99
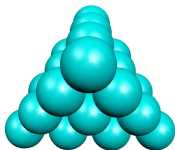
	Hg_{20}	
order	error	% E_{corr}
1	88.00	78.02
2	-6.03	101.51
3	0.32	99.92
4	-0.03	100.01

- Errors with respect to the exact CCSD calculation [kcal/mol]

Potential Energy Surfaces I[3]
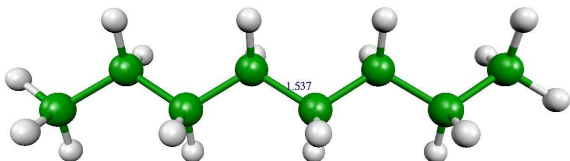
- DFT (RI-BP86/SVP) relaxed scan along the C4–C5-bond
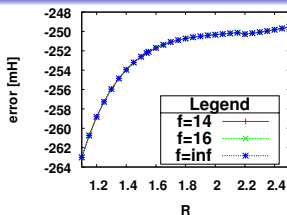
- Incremental CCSD/6-31G** energy

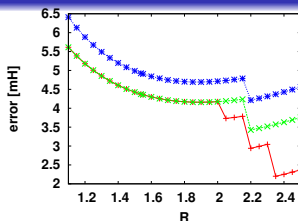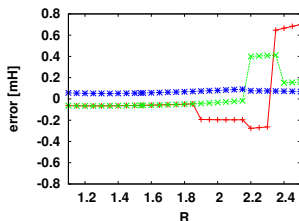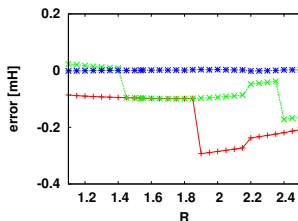[3] J. Friedrich, M. Hanrath, M. Dolg, Chem. Phys. **338**, 33 (2007).

Potential Energy Surfaces II

first order

second order

third order

fourth order

R[Å], $R_e = 1.537$ Å

Conclusions

- Fully automatized implementation to arbitrary order
- Chemical accuracy for a wide variety of systems
- Truncation at low order possible
- The CCSD correlation energy can be obtained in a parallel manner
- The number of calculations can be reduced by distance or energy thresholds
- Costly higher order increments require a lower accuracy then cheaper low order ones
- Disk space and RAM requirements are reduced

Outlook

- Use different correlation methods within the framework of the incremental scheme (CC2, CCSD(T), CCSDT)
- Extend the incremental expansion to molecular properties
- Interface to a periodic Hartree-Fock code (WANNIER)
- Formulation and Implementation of energy-difference dedicated and spatially restricted incremental expansions
- Account for the core and core-valence correlation in an efficient way
- Implement a gradient
- Design of a CCSD code adapted to the Incremental Scheme (in order to obtain a linear scaling method)

Acknowledgments

Thank you for attention!