Local explicit correlation methods

Hans-Joachim Werner

Institute for Theoretical Chemistry
University of Stuttgart
Pfaffenwaldring 55
D-70569 Stuttgart

Fred Manby (Bristol, UK)

Outline:

1.) Overview of local correlation methods

2.) Preliminary work on local explicit correlation methods

3.) Proposal

Motivation

- Steep scaling of computational cost with molecular size:
  - MP2: $\mathcal{O}(\mathcal{N}^5)$, CCSD(T): $\mathcal{O}(\mathcal{N}^7)$.
- Steep scaling of computational cost with basis set size:
  - For given molecule, CPU scales (at least) with $\mathcal{O}(N_{\mathrm{AO}}^4)$.
- Slow convergence of correlation energy with basis set size:
  - Slow convergence with angular momentum l_{max}:
    $E(l_{max}) \approx E_{CBS} + Al_{max}^{-3}$.
- Three remedies:
  - Local approximations lead to linear scaling: $\mathcal{O}(\mathcal{N}^7) \rightarrow \mathcal{O}(\mathcal{N})$.
  - Density fitting approximations reduce scaling with basis size as well as the prefactor: $\mathcal{O}(N_{\mathrm{AO}}^4) \rightarrow \mathcal{O}(N_{\mathrm{AO}}^3)$.
  - Explicitly correlated wavefunctions improve basis set convergence (e.g., R_{12}-methods, Gaussian Geminals . . .)

The Local Basis (P. Pulay, 1983)

Occupied Space: **Localized Molecular Orbitals (LMOs):**

- generated from *occupied* Hartree-Fock orbitals by a *unitary Transformation*
  - Orthonormality is preserved
  - Non-diagonal fock matrix
- Various localization procedures, e.g.: Boys, Pipek-Mezey

Virtual Space: **Projected AOs (PAOs):**

- generated by projecting AOs onto virtual space:

$$|\Phi_r^{\mathrm{PAO}}> = \sum_a^{virt} |\phi_a >< \phi_a|\phi_r^{\mathrm{AO}} >$$

- mutual orthogonality lost, but orthogonality to occupied space maintained.

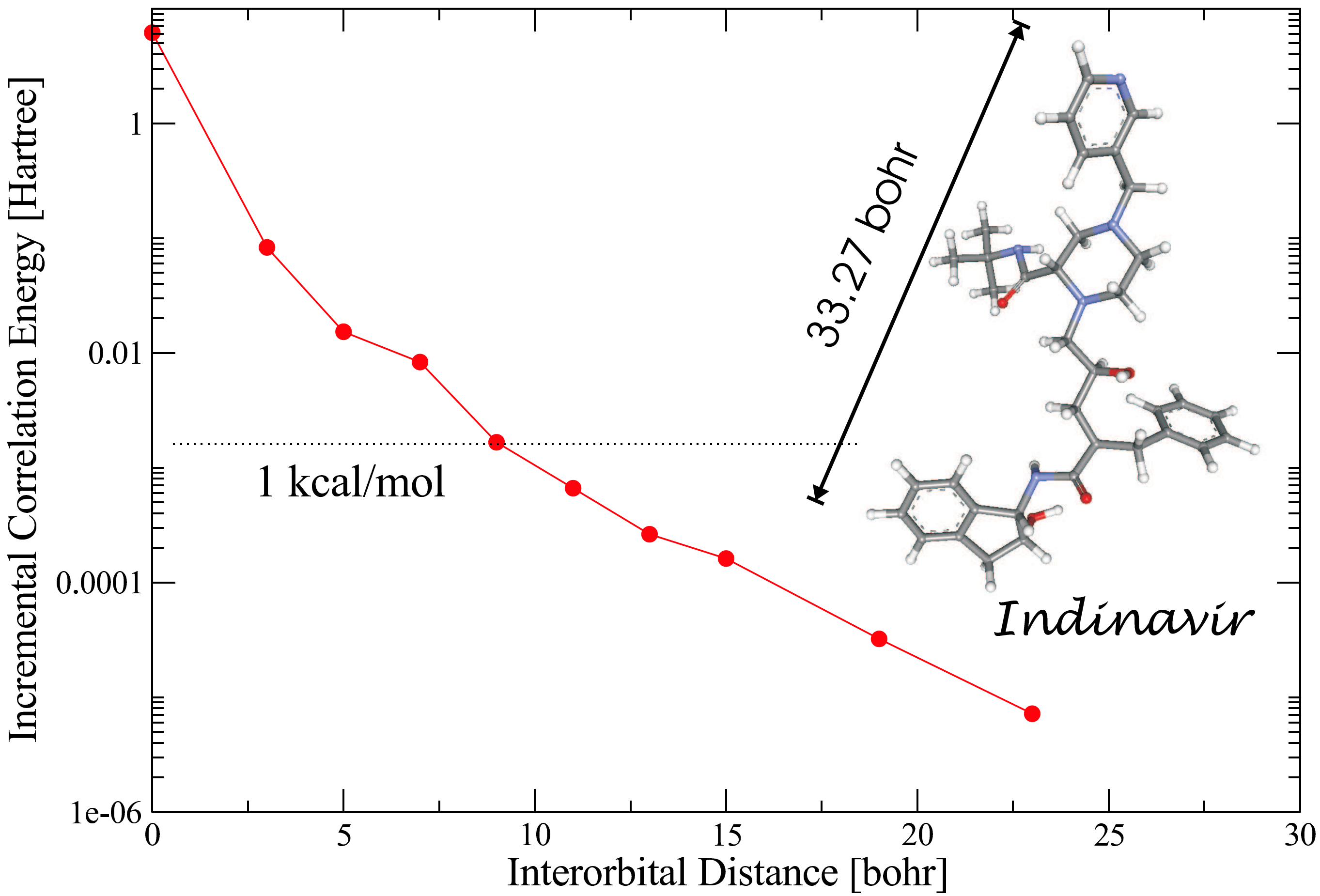
The PAOs are atom-centered and inherently local!

Local Approximations

- Excitation domains:
  - Excitations can be restricted to subsets of PAOs:
    Orbital domains, pair domains, triples domains...
- Hierarchical treatment of electron pairs:
  - Strong pairs: LCCSD(T)
  - Weak pairs: LMP2
  - Distant pairs: LMP2 with multipole approximations
  - Very distant pairs: neglected
- The number of pairs in each class scales linearly with molecular size!

  Various strategies are possible to select the domains and pair classes (distance or energy criteria). Accurary can be controlled.
- The local approximations lead to linear scaling for all methods from LMP2 to LCCSD(T)

Correlation energy as function of orbital distance



For $R = 0$ (strong pairs) 98.26 % of the correlation energy is obtained!

Linear scaling LMP2 and LCCSD(T) (M. Schütz and HJW)

- Consequences of pair selection and domains:
  - Each occupied orbital label i is connected only to a finite number of j (independent of molecular size)
  - All integral labels are automatically restricted to domains, e.g.,

    $$\begin{aligned} &(ri|sj), && r,s \in [ij]_{\mathrm{K}} \\ &(rs|ij), && r,s \in [ij]_{\mathrm{J}} \\ &(rs|tu), && r,s,t,u \in [ij]_{\mathrm{P}} \end{aligned}$$
  - The same holds for all intermediates.
- The number of integrals scales linearly with molecular size.
- Linear cost scaling results (almost) automatically.
- The total number of integrals, memory, and disk requirements depend on the pair domain sizes and the number of strong pairs.
- A compromise between accuracy and efficiency must be found.

Bottlenecks of LMP2 and LCCSD(T) calculations

Most time spent in the direct integral transformations

$$
\begin{aligned}
(ri|sj) &= \sum_{\mu} P_{\mu r} \sum_{\nu} P_{\nu s} \sum_{\rho} L_{\rho i} \sum_{\sigma} L_{\sigma j} \ \ (\mu\rho|\nu\sigma) \\
(rt|su) &= \sum_{\mu} P_{\mu r} \sum_{\nu} P_{\nu s} \sum_{\rho} P_{\rho t} \sum_{\sigma} P_{\sigma u} \ \ (\mu\rho|\nu\sigma)
\end{aligned}
$$

and similar ones for other integral types.

- CPU-times increase with the 4th power of the basis set size per atom.
- Disk space for transformed integrals scales with the 4th power of the basis set size per atom.
- Generation of 4-external integrals takes most time in LCCSD calculations.

Density-fitting approximations

Baerends (1973), Whitten (1973), Dunlap et al. (1977,1979)

Approximate density in KS calculations in an auxiliary basis $\{\chi_A\}$

$$\check{\rho}(\mathbf{r}) \quad = \quad \sum_A D_A \, \chi_A(\mathbf{r})$$

Determine the fitting coefficients D_A by minimizing (Dunlap)

$$\Delta = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \frac{(\rho(\mathbf{r}_1) - \check{\rho}(\mathbf{r}_1))\,(\rho(\mathbf{r}_2) - \check{\rho}(\mathbf{r}_2))}{r_{12}}.$$

Generalization for MP2 by Vahtras, Almlöf and Feyereisen (1993)

$$\phi_r(\mathbf{r})\phi_i(\mathbf{r}) \quad \approx \quad \check{\rho}_{ri}(\mathbf{r}) = \sum_A D_A^{ri} \, \chi_A(\mathbf{r})$$

Optimized fitting basis sets for HF (Coulomb and exchange) and MP2:

Ahlrichs, Weigend, Hättig et al. (1997-2004)

Density fitting in DF-LMP2

The fitting coefficients D_A^{ri} are obtained by solving the linear equations

$$\sum_A D_A^{ri} J_{AB} \quad = \quad R_B^{ri} \ ,$$

The 4-index integrals are then obtained by simple matrix multiplications

$$(ri|sj) \quad \approx \quad \sum_A D_A^{ri} R_A^{sj} \ .$$

where

$$\begin{aligned} J_{AB} \ \equiv \ (A|B) \quad &= \quad \int d\mathbf{r}_1 \int d\mathbf{r}_2 \, \frac{\chi_A(\mathbf{r}_1)\chi_B(\mathbf{r}_2)}{r_{12}} \ , \\ R_A^{ri} \ \equiv \ (ri|A) \quad &= \quad \int d\mathbf{r}_1 \int d\mathbf{r}_2 \, \frac{\chi_r(\mathbf{r}_1)\chi_i(\mathbf{r}_1)\chi_A(\mathbf{r}_2)}{r_{12}} \ . \end{aligned}$$

Scaling with molecular size: canonical $\mathcal{O}(\mathcal{N}^5)$, local $\mathcal{O}(\mathcal{N}^2)$

Scaling with basis size: $\mathcal{O}[(N_{\mathrm{AO}}/N_{\mathrm{atom}})^3]$.

Local approximations in density fitting

- The PAOs ϕ_r are close to LMO ϕ_i (”Orbital domains”).
- Only fitting functions close to i and r needed (”Fitting domains”).

  The fitting domains can be determined for each pair ij

  $$(ri|sj) \quad = \quad \sum_{A \in [ij]_{\rm fit}} D_A^{ri} R_A^{sj}$$

  or for each orbital (robust fitting)

  $$(ri|sj) \quad = \quad \sum_{A \in [i]_{\rm fit}} D_A^{ri} R_A^{sj} + \sum_{B \in [j]_{\rm fit}} \tilde{R}_B^{ri} D_B^{sj}$$

  This leads to best balance between accuracy and cost.
- Linear scaling can be obtained in either case.
- Local fitting also for exchange in HF/KS and in DF-LMP2 gradients.

CPU-times^a for indinavir (92 atoms, 240 val. el., cc-pVTZ, 2008 BF).

	LMP2	DF-LMP2
Integrals $(ri\|sj)$	1369	70
Iteration	63	63
Total MP2	1436	137

a) In minutes for HP ZX6000 Itanium2/900 MHz.

Total times in minutes:

	conventional	density fitted
HF	3257	337
LMP2	1436	137

Largest DF-LMP2 calculation so far: Indinavir with full cc-pVQZ basis (3885 basis functions): 11 h CPU (AMD Opteron 2.0 GHZ)

Density fitting in DF-LCCSD (M. Schütz and HJW)

- Similar local density fitting approximations have been implemented for all types of integrals needed in LCCSD(T).
- 0-2 external $(ik|lj)$, $(rk|lj)$, $(rk|ls)$, $(rs|kl)$ stored on disk.
- 3,4 external $(rs|ti)$, $(rs|tu)$: two options:
  - 4-index integrals precomputed and stored on disk.
  - 3-index integrals precomputed and stored, 4-index integrals assembled on the fly in each iteration: More CPU, less disk.

Example: Pregandiol, cc-pVTZ(f/p), 59 atoms, 1014 basis functions:

	3-ext.	4-ext.
3-index	9.7 GB	4.3 GB
4-index	15.4 GB	6.2 GB

Fitting basis sets for DF-LCCSD

- Optimized fitting basis sets are only available for HF and MP2 (Weigend, Hättig)
- For the 0-3 external integrals the cc-pVnZ MP2 sets work well with cc-pVnZ orbital bases.
- For the 4 external integrals the cc-pV(n+1)Z sets are required for high accuracy.

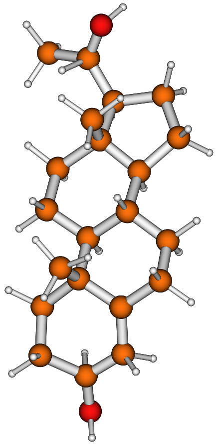
Example: Glycine, DF-LCCSD/cc-pVTZ (Fitting bases of C. Hättig)

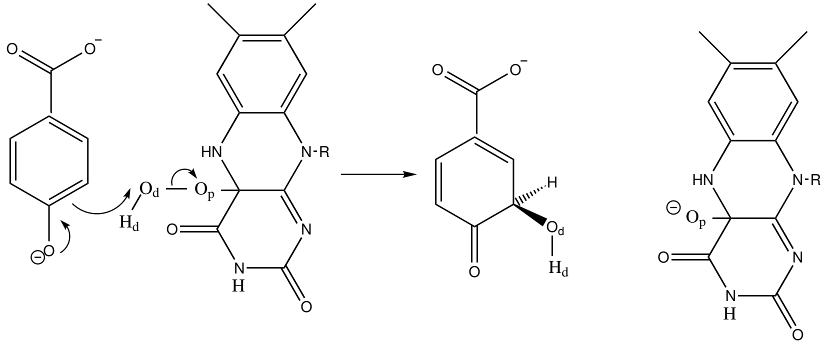
0-3 ext.	4-ext.	Error(LMP2)	Error(LCCSD)
cc-pVTZ	cc-pVTZ	0.000056	-0.000598
cc-pVTZ	cc-pVQZ	0.000056	-0.000022
cc-pVQZ	cc-pVQZ	0.000031	-0.000040

CPU times (min) for LCCSD calculations[a] using cc-pVTZ basis

Molecule	basis functions	Disk 3,4 ext.	CPU DF-LCCSD	CPU DF-HF
Pregnandiol	1014	22 GB	418	98
PHPB	1182	63 GB	1294	129
PHPB (TS)	1182	88 GB	1485	166

a) cc-pVTZ/MP2 fitting basis for 0-3 ext. integrals;
cc-pVQZ/MP2 fitting basis for 4-ext. integrals.



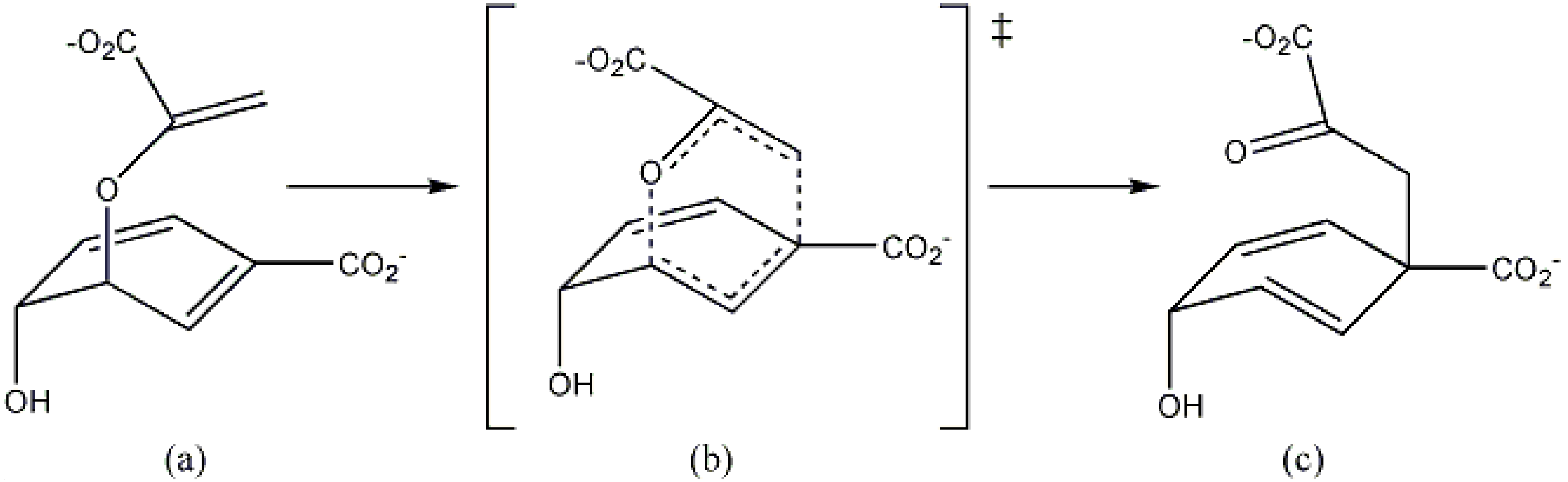


Hydroxilation Step in *p*-Hydroxybenzoate Hydroxilase

Chorismate Mutase Claisen Rearrangement

Multiple high-level QM/MM reaction paths demonstrate transition state stabilization in chorismate mutase: correlation of barrier height with transition state stabilization.

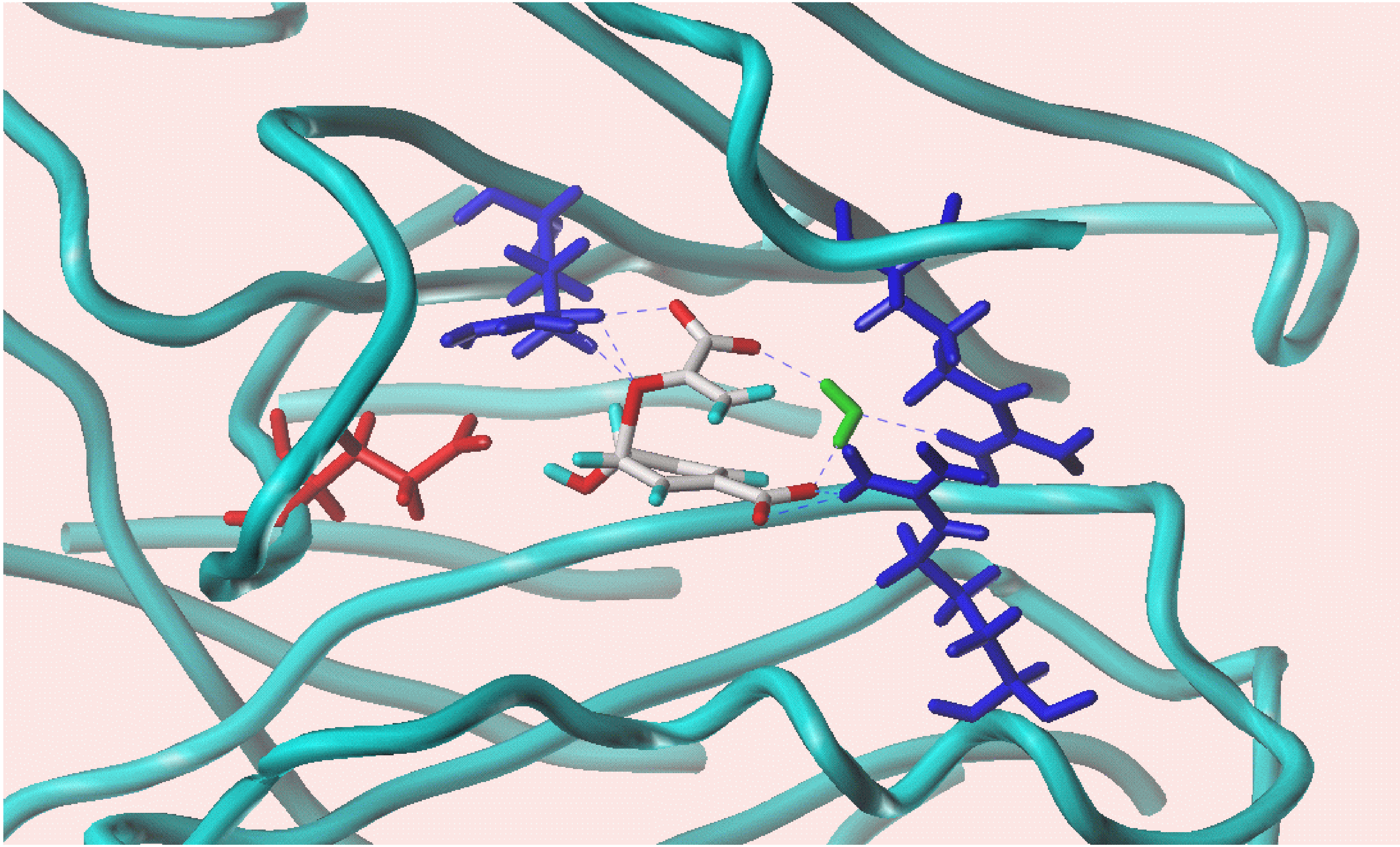
Frederik Claeyssens, Kara E. Ranaghan, Frederick R. Manby, Jeremy N. Harvey
and Adrian J. Mulholland*
School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.



21 atoms in QM region, MM region 25 Å (7033 atoms, electronic embedding)

MOLPRO - Tinker - CHARMM27

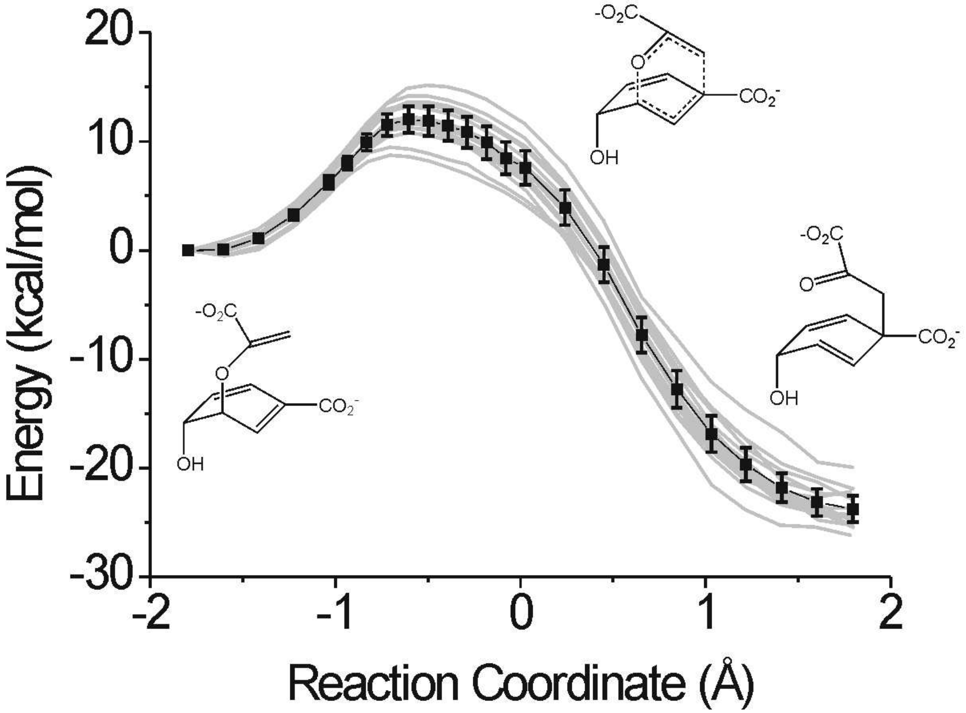
Chorismate Mutase Active Site



Chorismate Mutase Reaction Path

Multiple high-level QM/MM reaction paths demonstrate transition state stabilization in chorismate mutase: correlation of barrier height with transition state stabilization.

Frederik Claeyssens, Kara E. Ranaghan, Frederick R. Manby, Jeremy N. Harvey
and Adrian J. Mulholland*
School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K.



Activation energy $\Delta H^\dagger = 12.7$ kcal/mol (20.7 kcal in aqueous solution)

Basis set dependence of chorismate mutase reaction

Basis	DF-HF	DF-MP2	DF-LMP2^a
Barrier height (kcal/mol):			
VTZ	30.84	11.97	12.96
VTZ,O=AVTZ	30.62	11.22	11.22
AVTZ	30.46	10.71	
AVQZ	30.55	10.78	
Exothermicity (kcal/mol):			
VTZ	-21.08	-21.28	-20.65
VTZ,O=AVTZ	-21.11	-20.31	-19.98
AVTZ	-21.04	-20.89	
AVQZ	-21.24	-20.69	

a) Using domains from TS

Chorismate Mutase Reaction Barrier Height (kcal/mol)

16 trajectories averaged

Method	ΔE_A
DF-HF/[aug]-cc-pVTZ	29.3
DF-LMP2/[aug]-cc-pVTZ	10.4
DF-LCCSD/[aug]-cc-pVTZ	19.7
DF-LCCSD(T0)/[aug]-cc-pVTZ	15.3

Further corrections

MM energy contribution:	$\approx$ -2 kcal/mol
Zero point correction:	$\approx$ -1 kcal/mol
Best LCCSD(T) estimate:	12.3 kcal/mol
Experiment	12.7 kcal/mol

Explicitly correlated wavefunctions: MP2-R12

Kutzelnigg (1985), Klopper, Kutzelnigg (1987,1991)
W. Klopper, C. Samson, JCP **116**, 6397 (2002)

The basis set convergence can be much improved by including in the pair functions terms that depend explicitly on the interelectronic distance r_{12}:

$$|u_{ij}> \quad = \quad \sum_{ab} t^{ij}_{ab}|ab> + \sum_{kl} c^{ij}_{kl}\ \hat{Q}_{12} f_{12}(r_{12})|kl>$$

where the projector $\hat{Q}_{12}$ ensures stong orthogonality of the pair function to the occupied space.

- ”Ansätze” 1 and 2 differ in the choice of the projectors $\hat{Q}_{12}$.
- ”Versions” A, A*, A’, B etc differ in integral approximations.
- ”Methods” (R_{12}, F_{12}) differ in the choice of the correlation factors.

In the original work of Kutzelnigg and Klopper, $f_{12}(r_{12}) = r_{12}$ was used.

Ansätze in MP2-R12

Different choices of the projection operators have been proposed:

Ansatz 1: $\hat{Q}_{12}^{P} = (1 - \hat{P}_1)(1 - \hat{P}_2)$

Ansatz 2: $\hat{Q}_{12}^{O} = (1 - \hat{O}_1)(1 - \hat{O}_2)$

or $\hat{Q}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2)(1 - \hat{V}_1\hat{V}_2)$

$$= 1 - \hat{O}_1 - \hat{O}_2 + \hat{O}_1\hat{O}_2 - \hat{V}_1\hat{V}_2$$

where $\hat{O}_i$, $\hat{V}_i$, and $\hat{P}_i$ are one-electron projection operators onto the occupied occupied, virtual and full MO spaces, respectively.

If the RI is done in the MO basis, all three forms are equivalent.

In the absence of further approximations the the operators $\hat{Q}_{12}^{O}$ and $\hat{Q}_{12}$ lead to equivalent Ansätze.

Differences may arise, however, if further approximations of the integrals are made. $\hat{Q}_{12}$ is used in this work.

RI-approximation in MP2-R12

The one-electron projection operators in $\hat{Q}_{12}$ lead to 3-electron integrals:

$$< ij|r_{12}\hat{O}_1 g_{12}|kl > \quad = \quad \sum_m < ijm|r_{12}g_{32}|mkl >$$

Introducing a resolution of the identity $P' = \sum_{p'} |p' >< p'|$ and making the approximation

$$\hat{O}_1 \rightarrow \hat{O}_1 \hat{P}'_2$$

leads to a factorization of the 3-electron integrals:

$$\begin{aligned} < ij|r_{12}\hat{O}_1 g_{12}|kl > \quad &\approx \quad < ij|r_{12}\hat{O}_1 \hat{P}'_2 g_{12}|kl > \\ &= \quad \sum_{mp'} < ij|r_{12}|mp' >< mp'|g_{12}|kl > \end{aligned}$$

The RI-basis $\{p'\}$ should be larger than the MO basis
(*auxiliary basis set (ABS)-approximation*).

Further approximations in MP2-R12

The following approximations are commonly used:

The generalized Brillouin condition (GBC):

$$\hat{f}|i>=\sum_j f_{ji}|j>$$

allows to delete commutators of the form $[\hat{f}_1+\hat{f}_2,Q^O_{12}]$.

The extended Brillouin condition (EBC):

$$\hat{f}|r>=\sum_s f_{sr}|s>$$

allows to delete commutators of the form $[\hat{f}_1+\hat{f}_2,Q^P_{12}]$.
Avoiding the EBC leads to $\mathcal{O}(m^6N^2)$ scaling.

The EBC leads to a decoupling of the conventional and R12 parts.

Versions of MP2-R12

$$[\hat{f}_1, r_{12}] \quad = \quad [\hat{t}_1 - \hat{k}_1, r_{12}] \approx [\hat{t}_1, r_{12}]$$

Neglect of exchange terms in version A.

Including the exchange terms leads to Version B.

Method	GBC	EBC	$[\hat{k}_1, r_{12}] = 0$	Projector
R12/1A’	+	+	+	$\hat{Q}_{12}^P$
R12/2*A’	+	+	+	$\hat{Q}_{12}^O$
R12/2A’	+	-	+	$\hat{Q}_{12}^O$
R12/2B	+	-	-	$\hat{Q}_{12}^O$

In our preliminary work we used MP2-R12/2*A with projector $\hat{Q}_{12}$

Working equations for MP2-R12

W. Klopper, C. Samson, JCP **116**, 6397 (2002)

Integrals needed ($g_{12} = 1/r_{12}$):

$$\begin{aligned} K^{ij}_{pq} &= (pi|g_{12}|qj) \\ R^{ij}_{pq} &= (pi|r_{12}|qj) \\ U^{ij}_{pq} &= (pi|[\hat{f}_1 + \hat{f}_2, r_{12}]|qj) \end{aligned}$$

In approximation 2*A the energy correction is a simple function of

$$\begin{aligned} V^{ij}_{kl} &= \delta_{ik}\delta_{jl} - \sum_{pq} R^{kl}_{pq} K^{ij}_{pq} - \sum_{mp'} R^{kl}_{mp'} K^{ij}_{mp'} + \sum_{mp} R^{kl}_{mp} K^{ij}_{mp} + \ldots \\ T^{ij}_{kl} &= \delta_{ik}\delta_{jl} - \sum_{pq} R^{kl}_{pq} U^{ij}_{pq} - \sum_{mp'} R^{kl}_{mp'} U^{ij}_{mp'} + \sum_{mp} R^{kl}_{mp} U^{ij}_{mp} + \ldots \end{aligned}$$

p, q : orbital basis, p': RI-basis, m : occupied

Density fitting approximations in MP2-R12

F. R. Manby, JCP **119**, 4607 (2003)

The fitting coeffcients are determined by minimizing (Whitten, 1973)

$$\Delta_{pq} = (pq - \tilde{pq}|g_{12}|pq - \tilde{pq})$$

In order to obtain accurate integrals over operators other than g_{12} *robust fitting approximations* (Dunlap, 2000) must be used, e.g.,

$$(pi|r_{12}|qj)_{\mathrm{robust}} = \bar{J}^A_{pi} R^A_{qj} + R^B_{pi} \bar{J}^B_{qj} - \bar{J}^A_{pi} R_{AB} \bar{J}^B_{qj}$$

with

$$\begin{aligned} J_{AB} &= (A|g_{12}|B) & \qquad R_{AB} &= (A|r_{12}|B) \\ J^A_{pi} &= (A|g_{12}|pi) & R^A_{pi} &= (A|r_{12}|pi) \\ \bar{J}^A_{pi} &= [\mathbf{J}^{-1}]_{AB} J^B_{pi} \end{aligned}$$

The error of $(pi|r_{12}|qj)_{\mathrm{robust}}$ is quadratic in the fitting error $(pq - \tilde{pq})$.

Local approximations in MP2-R12

Restrict excitations to *domains*:

$$|u_{ij}> \quad = \quad \sum_{rs\in[ij]_{\rm ext}} t^{ij}_{rs}|rs> + \sum_{kl\in[ij]_{\rm int}} c^{ij}_{kl}\,\hat{Q}_{12}r_{12}|kl>$$

So far, we have only implemented $k, l \in \{i, j\}$. This leads to strong simplifications, since the r12-equations decouple.

The following further approximations can be made in a local orbital basis:

- Compute the r_{12} correction only for *strong pairs*.
- Neglect distant pairs.
- Use local approximations in the density fitting.
- Use local approximations in the RI-approximations.

Density fitted local MP2-R12 (DF-LMP2-R12)

F. R. Manby, HJW

The following (optional) approximations are possible:

- Compute the r_{12} correction only for *strong pairs*
- Use a local AO basis for the RI-approximation:

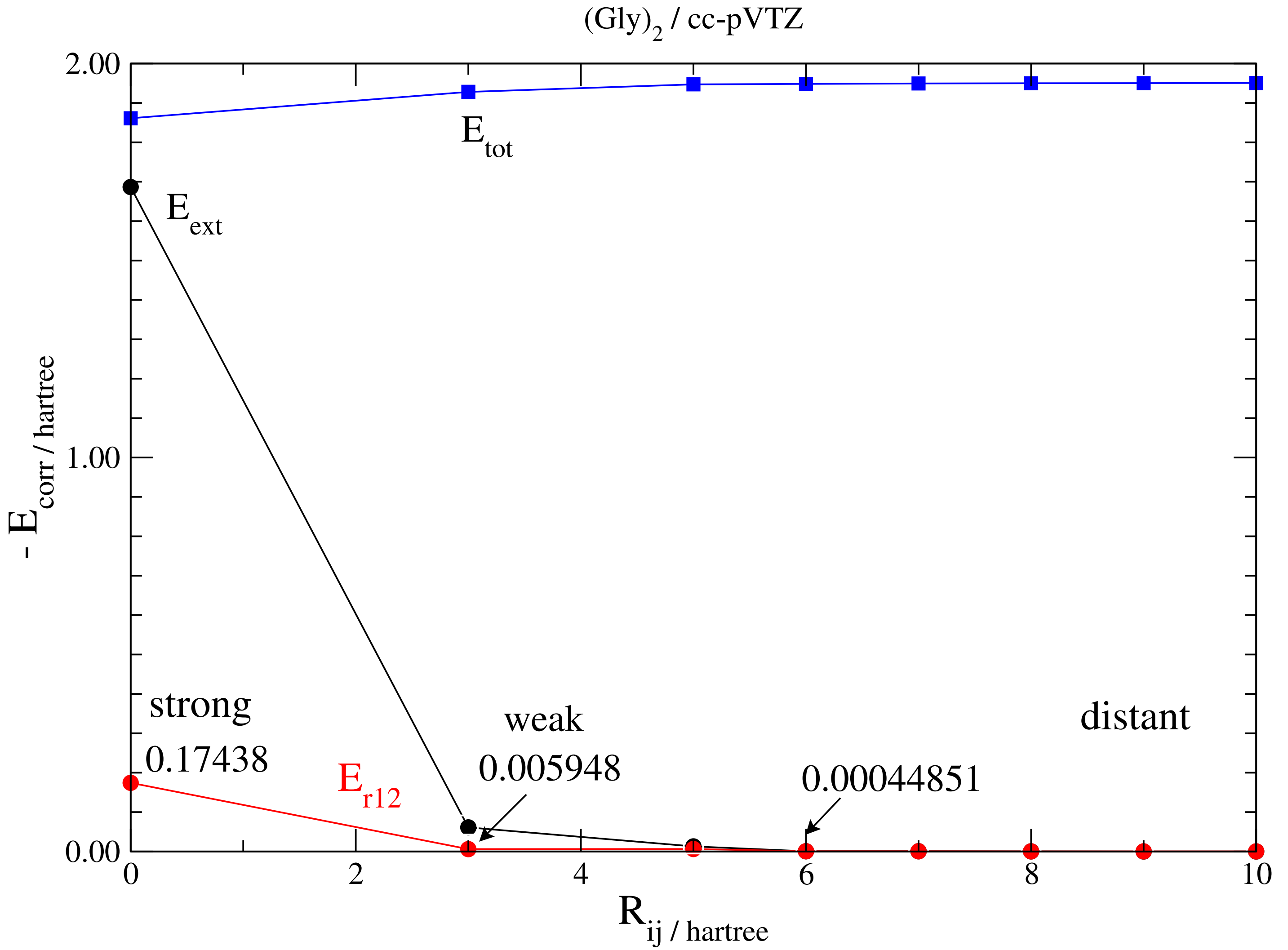
$$\sum_{pq} R^{kl}_{pq} K^{ij}_{pq} \quad \approx \quad \sum_{\mu\nu\rho\sigma\in[ij]_{\mathrm{RI}}} R^{kl}_{\mu\nu} [S^{-1}]_{\nu\rho} K^{ij}_{\rho\sigma} [S^{-1}]_{\sigma\mu}$$

- Use a local fitting basis:

$$R^{ij}_{\mu\nu} \quad \approx \quad \sum_{A\in[i]_{\mathrm{fit}}} \bar{J}^{A}_{\mu i} R^{A}_{\nu j} + \sum_{B\in[j]_{\mathrm{fit}}} R^{B}_{\mu i} \bar{J}^{B}_{\nu j} - \sum_{A\in[i]_{\mathrm{fit}}} \sum_{B\in[j]_{\mathrm{fit}}} \bar{J}^{A}_{\mu i} R_{AB} \bar{J}^{B}_{\nu j}$$

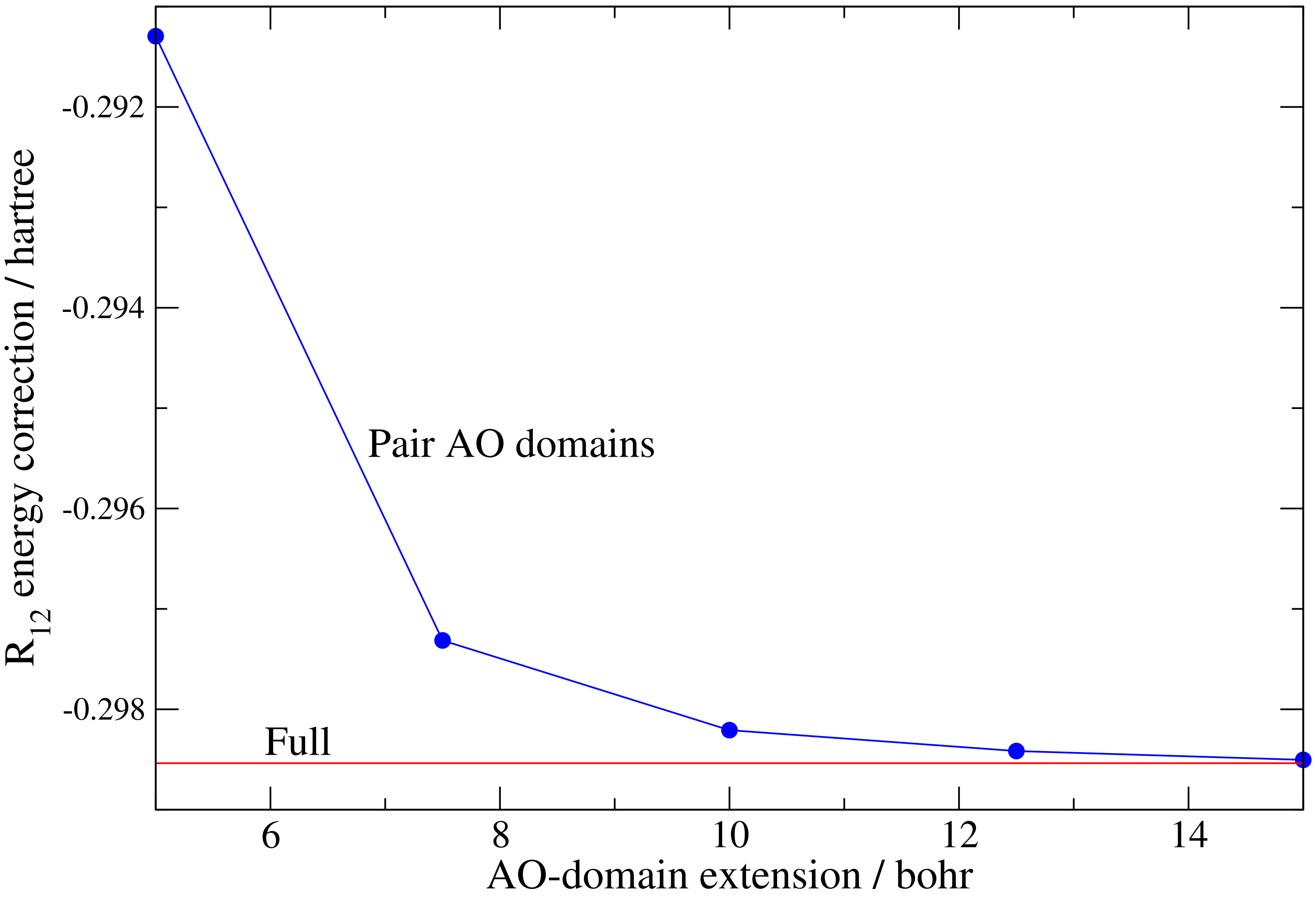
If all three approximations are possible, linear scaling can be achieved.

Pair correlation energies as function of orbital distance



Convergence of R_{12}-correction with AO domain size

$(Gly)_4$ cc-pVTZ (uncontracted)



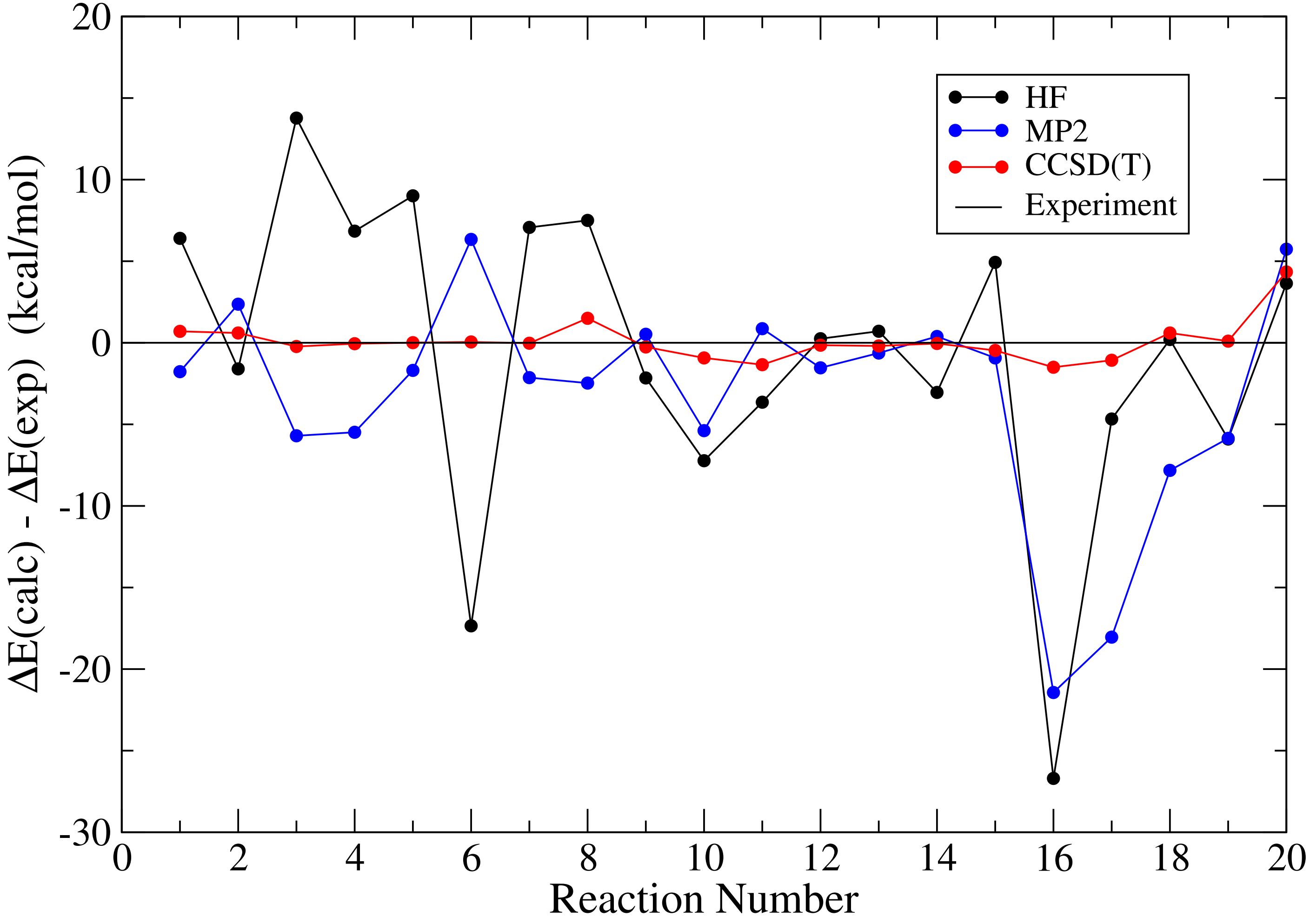
Benchmark reactions for DF-LMP2-R12

Nr.	Reaction	Nr	Reaction
1	$CO + SO_3 \rightarrow CO_2 + SO_2$	11	$C_2H_2 + H_2 \rightarrow C_2H_4$
2	$C_2H_2 + H_2O \rightarrow CH_3CHO$	12	$C_2H_4 + H_2 \rightarrow C_2H_6$
3	$CO + Cl_2 \rightarrow COCl_2$	13	$HCHO + H_2 \rightarrow CH_3OH$
4	FURAN + $H_2S \rightarrow$ THIOPHEN + H_2O	14	$C_2H_6 + H_2 \rightarrow 2\ CH_4$
5	$CO + CH_3OH \rightarrow HCOOCH_3$	15	$CO + H_2 \rightarrow HCHO$
6	$CO + NH_3 \rightarrow HCONH_2$	16	$CH_4 + 4\ H_2O_2 \rightarrow CO_2 + 6H_2O$
7	$CO + H_2O \rightarrow CO_2 + H_2$	17	$NH_3 + 4\ H_2O_2 \rightarrow HNO_3 + 5\ H_2O$
8	$CS_2 + 2\ H_2O \rightarrow CO_2 + 2\ H_2S$	18	$CO + H_2O_2 \rightarrow CO_2 + H_2O$
9	$H2CCO + HCHO \rightarrow C_2H_4O + CO$	19	$SO_2 + H_2O_2 \rightarrow SO_3 + H_2O$
10	$H_2O_2 + H_2 \rightarrow 2\ H_2O$	20	$HNCO + NH_3 \rightarrow NH_2CONH_2$

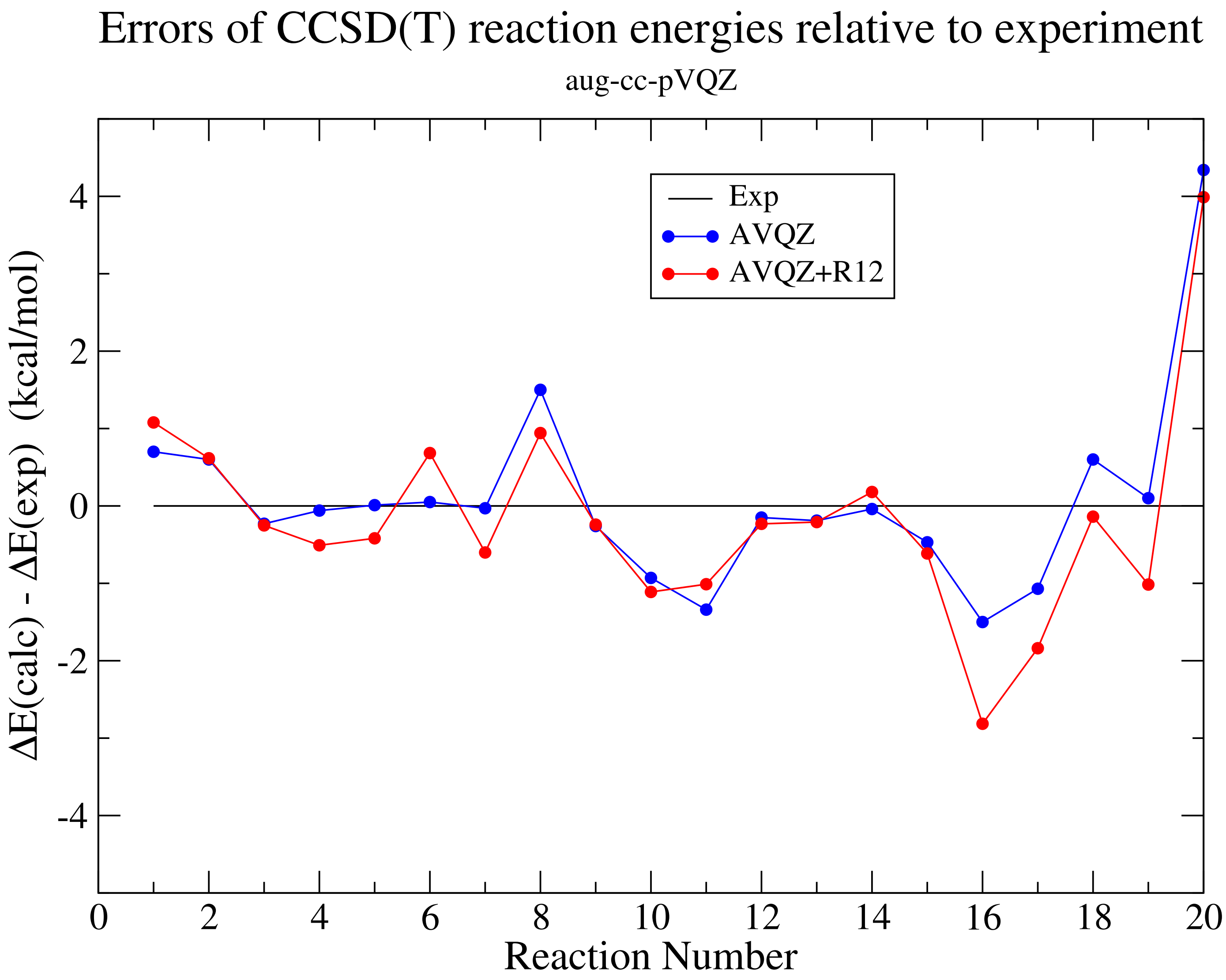
Geometries optimized at MP2/AVTZ level, cc-pVQZ fitting basis

Errors of reaction energies relative to experiment

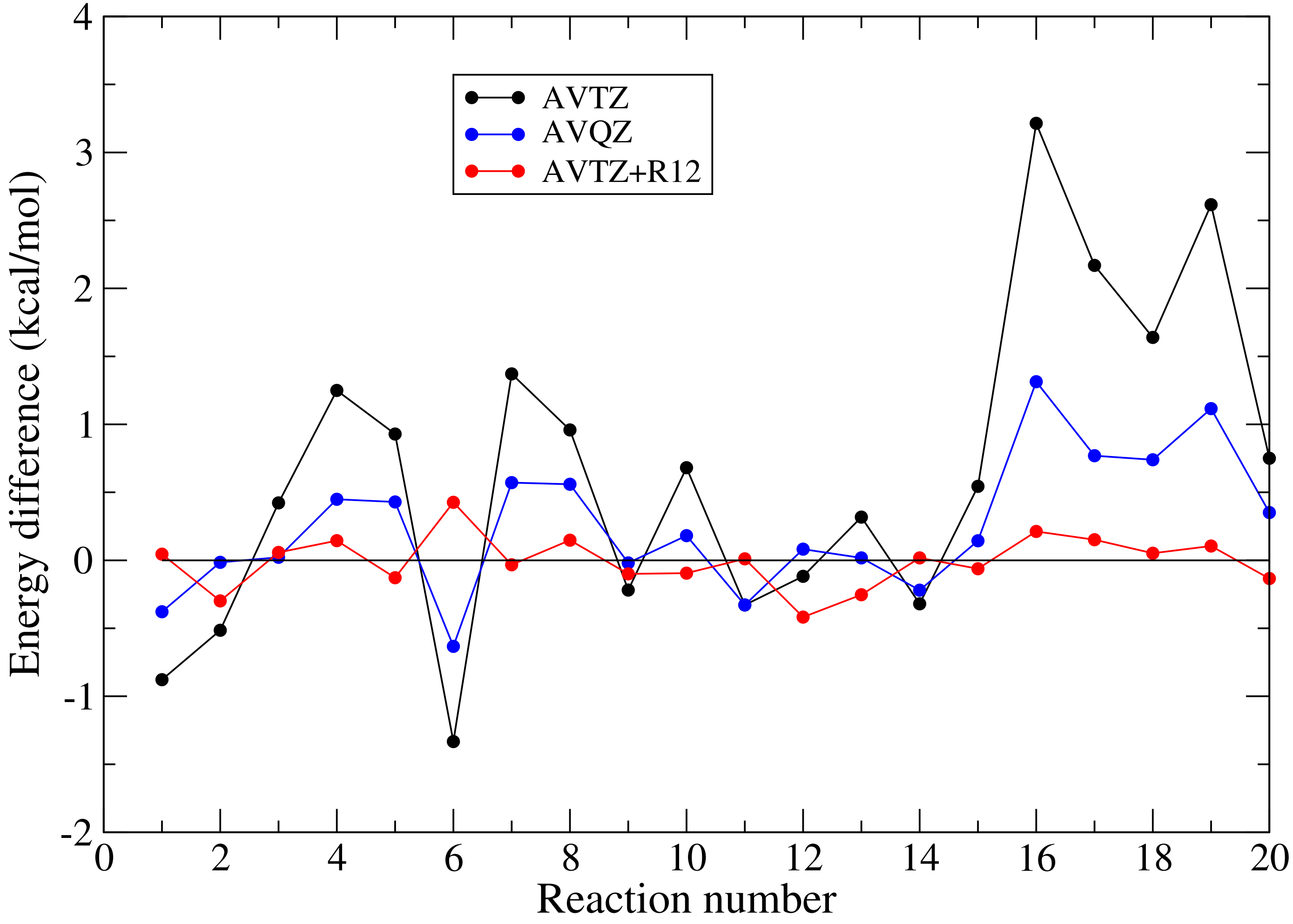
aug-cc-pVQZ



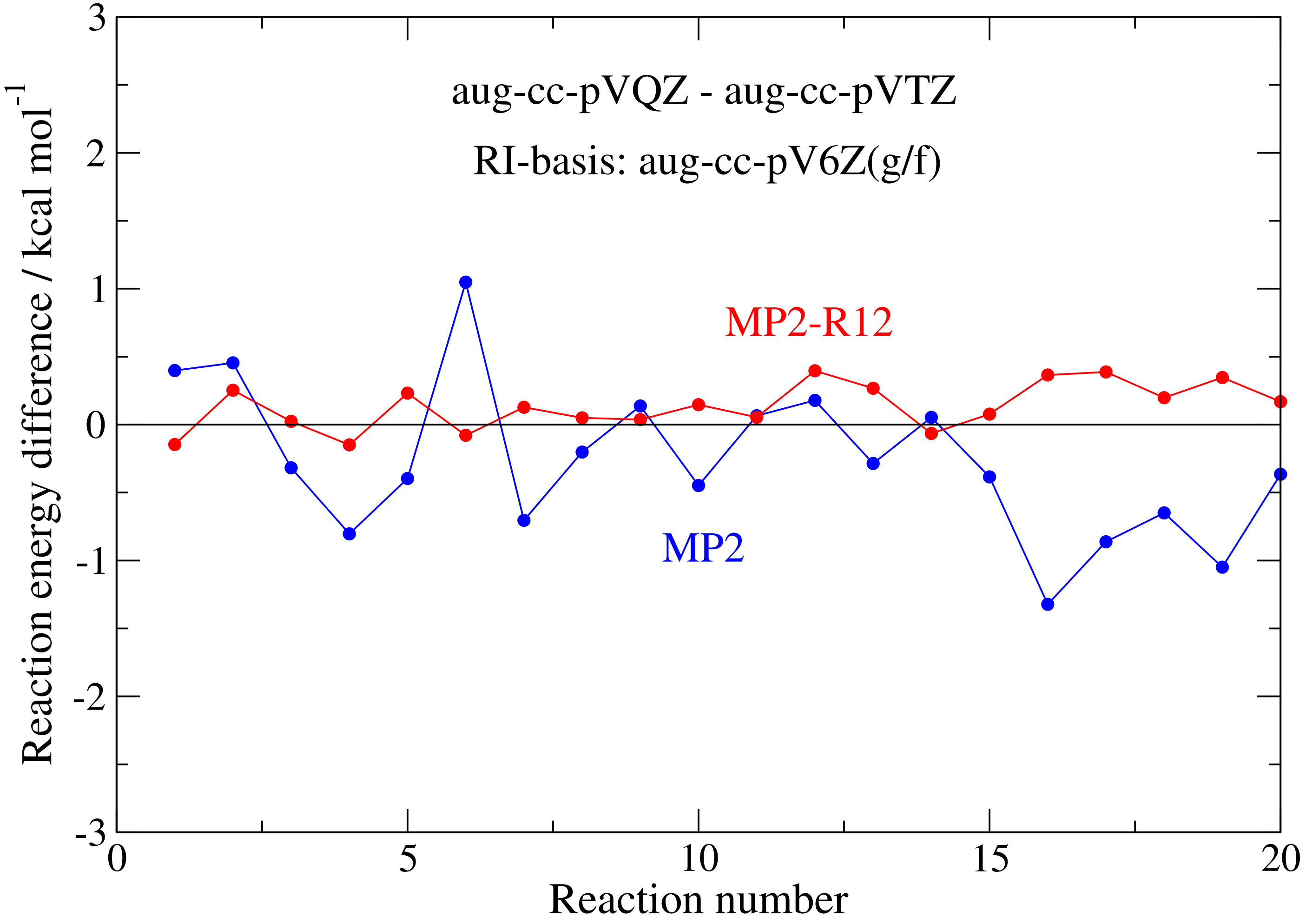
Errors of CCSD(T) reaction energies relative to experiment



CCSD(T) correlation energy contributions relative to AVQZ+R12



Basis set effect on MP2-R12 correlation energies



Conclusions about preliminary DF-LMP2-R12

- Very efficient local MP2-R12 implementation with density fitting.
- Treating the strong pairs only accounts for $> 95\%$ of the R_{12}-correction.
- For full fitting domains, formally $\mathcal{O}(\mathcal{N}^3)$ scaling.
- Energy correction converges from above with increasing RI domain size, but quite large domains are needed.
- Significant errors if fitting domains are used, unless these very large.
  - A local correlation factor may be useful
- Need at least aug-cc-pVTZ basis to get reasonably converged HF values and sufficiently accurate R12-correction.
- Stable results only with rather large RI-Basis basis sets (at least u-AVQZ).

Recent developments

Recent work of May, Valeev, Polly, and Manby (PCCP, in press) show that:

- RI-approximations leads to sufficiently small errors if the RI-basis is at least of (uncontracted) VQZ quality.
- Errors due to the GBC are negligible.
- EBC and version A should be avoided (errors are a few mH for small molecules).
- Errors due to the R12-ansatz itself strongly dominate.

They found that much better results can be obtained by replacing r_{12} by a fixed linear combination of Gaussian Geminals

$$f_{12}(r_{12}) \quad = \quad \sum_i c_i \exp(\gamma_i r_{12}^2) \; \approx \; \exp(-\alpha r_{12})$$

which is fitted to a simple Slater function with exponent $\alpha = 1$.

Proposed project

- Implement DF-LMP2-F12 with local correlation factor $f_{12}(r_{12})$.
  Test if this improves local fitting approximations.
- Avoid EBC approximation and implement DF-LMP2-F12/B.
  This leads to a coupling of conventional and R12 contributions.
  Avoid $\mathcal{O}(m^6 N^2)$ scaling using local approximations.
- Increase internal domains $[kl]_{\mathrm{int}}$ and investigate how many terms are needed to get converged results

$$|u_{ij} > \quad = \quad \sum_{rs\in[ij]_{\mathrm{ext}}} t_{rs}^{ij} |rs > + \sum_{kl\in[ij]_{\mathrm{int}}} c_{kl}^{ij} \hat{Q}_{12} r_{12} |kl >$$

- Test modified local RI approximations (include all occupied orbitals).
- Test accuracy of all approximations for larger molecules.
- Applications, e.g. in QM/MM studies.