

The PARI Approximation Much Ado About Nothing?

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Limitations of pure KS-DFT for large molecules

Large/Protein-like molecules:

- self-interaction error increases with system size
> **error on properties increases with system size**
- vanishing HUMO-LUMO gap
> **fail to converge** (e.g. Insulin)
- Required starting-points: HF or Hybrid-DFT
> **Bottleneck: exact exchange contribution!**

How to construct the Fock/KS matrix efficiently?

The RI approximation

- Four-center two-electron integrals in AO basis (Mulliken notation)

$$\int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \psi_a(\mathbf{r}_1) \psi_b(\mathbf{r}_1) \frac{1}{r_{12}} \psi_c(\mathbf{r}_2) \psi_d(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = (ab|cd)$$

- Approximate AO-product functions: $|cd) \approx |\widetilde{cd}) = \sum_{\gamma} C_{\gamma}^{cd} |\gamma)$
- Robust integral approximation (Dunlap)

$$(ab|cd) \approx (\widetilde{ab}|\widetilde{cd}) = (\widetilde{ab}|cd) + (ab|\widetilde{cd}) - (\widetilde{ab}|\widetilde{cd})$$

- Error on integrals bounded with $\Delta_{ab} = |cd) - |\widetilde{cd})$

$$|(ab|cd) - (\widetilde{ab}|\widetilde{cd})| \leq \sqrt{(\Delta_{ab}|\Delta_{ab})(\Delta_{cd}|\Delta_{cd})}$$

- Find fitting coefficients C_{α}^{ab} for each AO-product $|ab)$

$$\min_{\mathbf{C}} (\Delta_{ab}|\Delta_{ab}) \iff (\Delta_{ab}|\alpha) = 0 \quad \forall \alpha$$

The RI approximation

The **Resolution-of-the-Identity (RI)**, or the **density-fitting (DF)** approximation:

- Speed up calculations (**typically by factor 3-30**) at little loss of chemical accuracy
- Highly successful for **approximating the Coulomb contribution** (in particular in DFT)
- Also used for small- to medium-sized systems for **approximation of the exact exchange** and in correlated treatment
 - > **Scaling wall** about 1000 AO basis-functions

RI for the exact exchange (RI-K)

- The (regular) exchange contribution

$$K_{ab} = \sum_{cd} (ac|bd) D_{cd} = \sum_i^{\text{occ}} (ai|bi)$$

Weigend (2002), Polly *et.al* (2004)

- in RI-K, each pair is fitted over the whole molecule
Too expensive, not even needed: “contaminants”!
the **Scaling wall** limits the approach to about 1000 AO basis-functions
 - metric matrix $(I|J)$ non-sparse $\rightarrow \mathcal{O}(N^3)$ scaling
 - non-locality of fitting coefficients $c_i^{\mu\nu}$ (for each pair $\mu\nu$)
- Exchange and Correlation are local phenomena
Locality has to be exploited!

Methods for linear-scaling RI

Two main approaches forcing locality toward linear-scaling RI:

- **the Local Metric approach**

Obtain the fitting coefficients using (w) a local metric (e.g. the overlap metric)

Baerends *et.al* (1973), Vahtras *et.al* (1993), Jung *et.al* (2005), Reine *et.al* (2008)

- **the Partitioning approach**

Partition the density and fit each density in a local region

Gallant and St-Amant (1996), Sodt *et.al* (2006), Sodt and Head-Gordon (2008)

- e.g. The Atomic RI (ARI)

Methods for linear-scaling RI

Atomic RI (ARI): an elegant and balanced partitioning approach:

- In the ARI approach of Sodt *et.al* each charge distribution $|\mu\nu\rangle$ is first associated with a center C , and is fitted using auxiliary functions $|I\rangle$ centered on the atoms in some buffer zone $[C]$ around C

$$|\mu\nu\rangle = \sum_I c_I^{\mu\nu} |I\rangle, \quad |I\rangle \in [C]$$

- fixed buffer-zone size - **system dependent**
- the set $|I\rangle$ includes the **auxiliary functions centered on several atoms**

The PARI approach

We propose the pair-atomic resolution-of-the-identity (PARI):

- fit each charge distribution $|\mu\nu\rangle$ with auxiliary functions $|I\rangle$ centered on the two parent atoms A and B of the basis functions $|\mu\rangle$ and $|\nu\rangle$

$$|\widetilde{\mu\nu}\rangle = \sum_{I \in A \cup B} c_I^{\mu\nu} |I\rangle, \quad c_I^{\mu\nu} = \sum_{J \in A \cup B} (I|J)^{-1} (J|\mu\nu)$$

instead of the (regular) RI approx.

$$|\widetilde{\mu\nu}\rangle = \sum_{I \in \mathcal{M}} c_I^{\mu\nu} |I\rangle, \quad c_I^{\mu\nu} = \sum_{J \in \mathcal{M}} (I|J)^{-1} (J|\mu\nu)$$

- Pros/Cons:
 - Highly local : **removes scaling bottleneck**
 - Straightforwardly linear scaling using screening and FMM
 - decreases accuracy** \rightarrow larger auxiliary basis sets
 - some unpredictable & spectacular diverging cases!!!**

PARI Accuracy

G2/G3 Benchmark set (480 molecules),
B3LYP, 6-31G/df-def2, in μE_H

Development version of LSDalton, www.daltonprogram.org

		RI-J	PARI-J	RI-K	PARI-K
6-31G/df-def2	μ	-21	-74	8	21
	σ	9	48	3	10
cc-pVTZ/cc-pVTZdenfit	μ	-18	-22	9	14
	σ	4	11	3	7

- PARI errors: factor 2-3 bigger than RI
- 4 molecules out of 480 with diverging negative energies!

Problem Analysis:

Attractive forces between the electrons....

- Two-electron contribution to the total energy becomes negative (**attractive interaction!**)
- The robust integral representation,

$$(ab|cd) \approx \widetilde{(ab|cd)} = \widetilde{(ab|cd)} + (ab|\widetilde{cd}) - (\widetilde{ab}|\widetilde{cd})$$

though accurate to second order in the fitting error
not inherently positive-definite ($(ab|ab) < 0$) **sometimes**
NEGATIVE SHIFT OF THE EIGENVALUES

- The SCF solver does what it is supposed to: minimize the energy.

Problem Analysis:

H₂ already infected by PARI

		exact	RI	PARI	PARI+diag(exact)
H ₂	mad(eri)	-	2.7	8.9	0.36
	min(eigV)	4.4e-2	1.5e-2	-1.1	5.85e-2
	eigV < 0	0/11	0/11	2 / 11	0 / 11
C ₂ H ₄	mad(eri)	-	5.6	10.9	0.48
	min(eigV)	0	0	-3.9	-1.45
	eigV < 0	0/352	0/352	63 / 352	17 / 352

PARI operator:

- non-positive definite!!

- “unbalanced”:

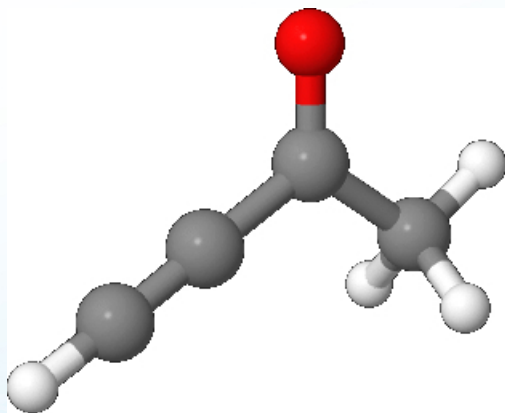
$(ab|cd)$ with $a \in A$, $b \in B$, $c \in C$ and $d \in D$

$(ab|cd)$ with $a \in A$, $b \in A$, $c \in B$ and $d \in B$

not treated with the same basis set, not the same accuracy

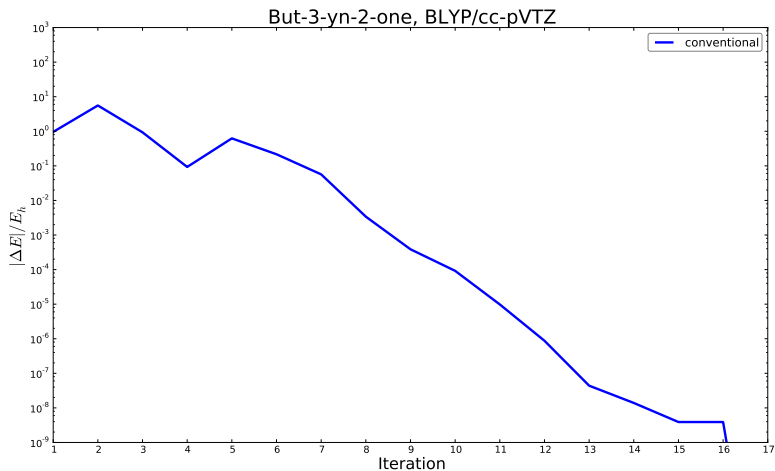
UNBALANCED negative shift between the blocks $(AB|CD)$

One failing case: but-3-yn-2-one



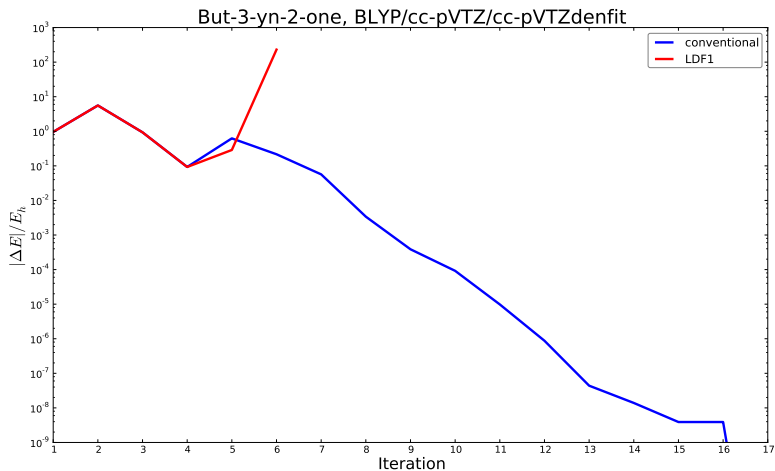
BLYP cc-pVTZ SCF iterations

Development version of Molcas, www.molcas.org



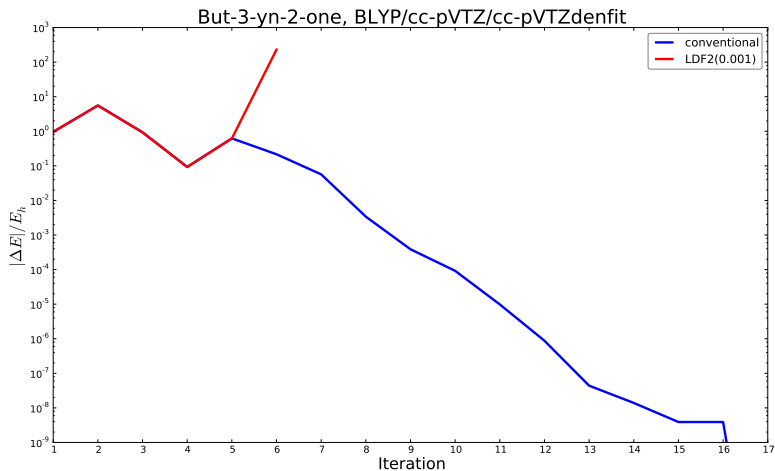
BLYP cc-pVTZ/cc-pVTZdenfit SCF iterations

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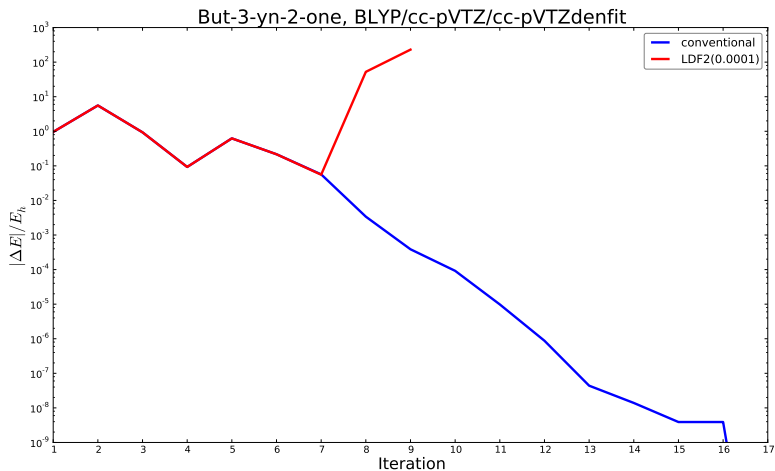
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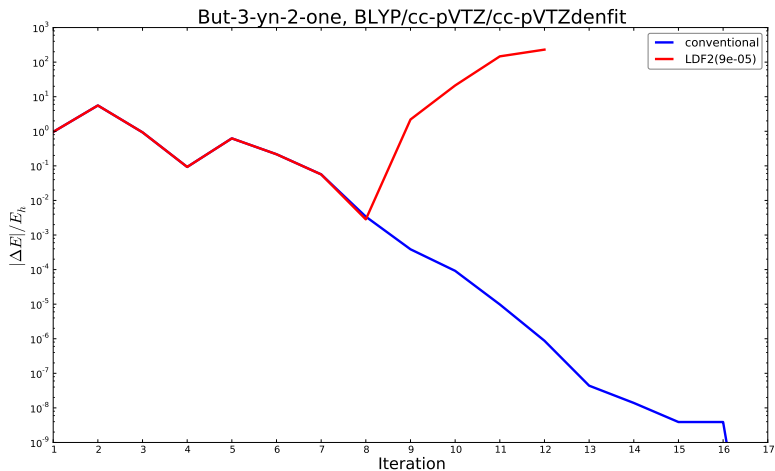
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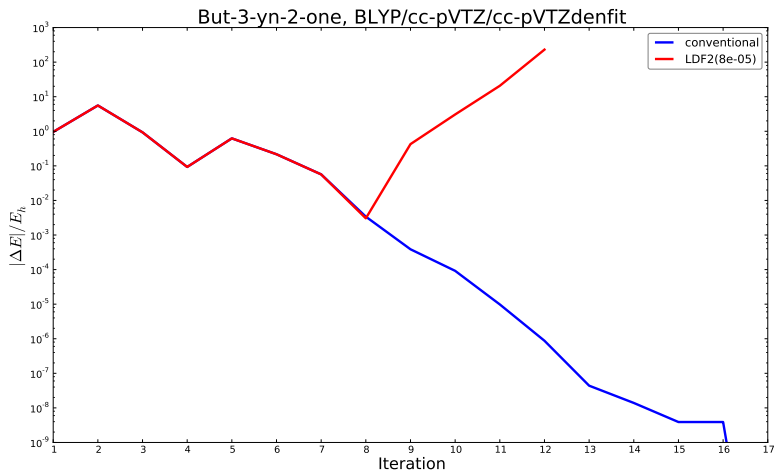
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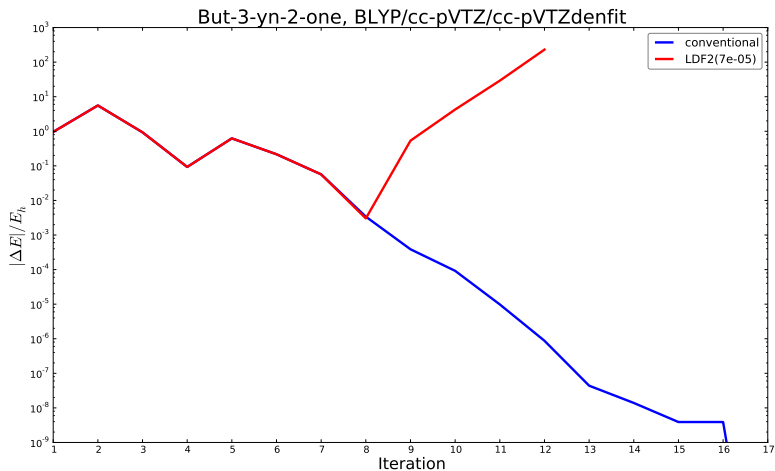
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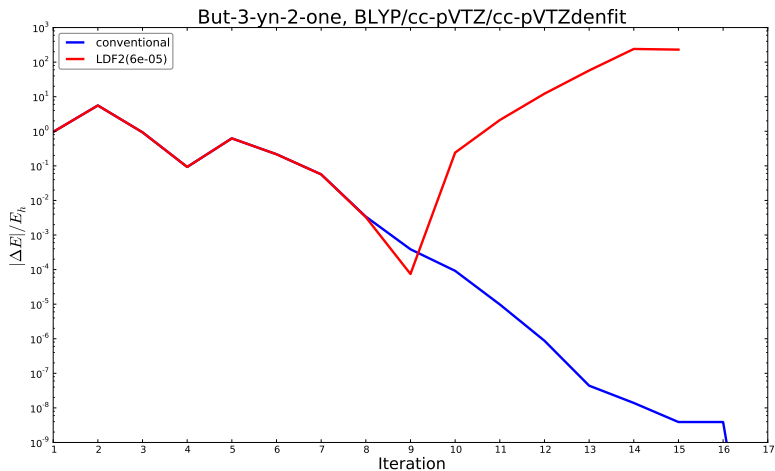
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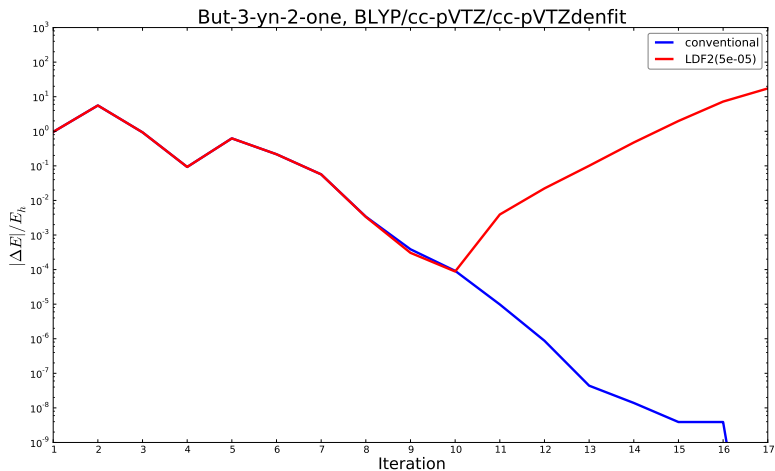
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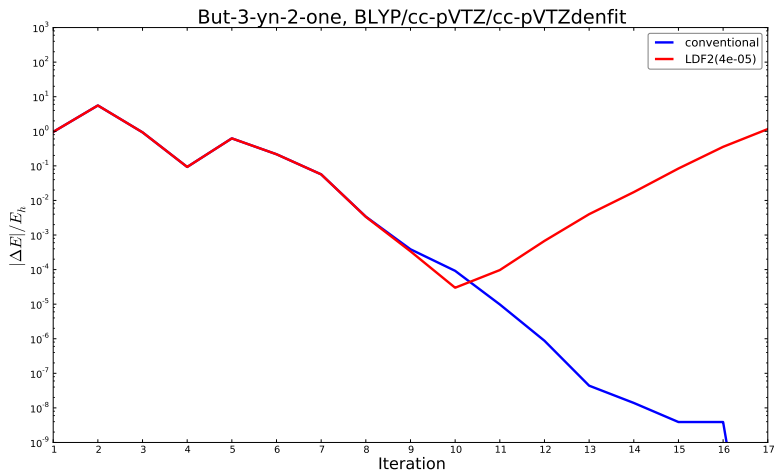
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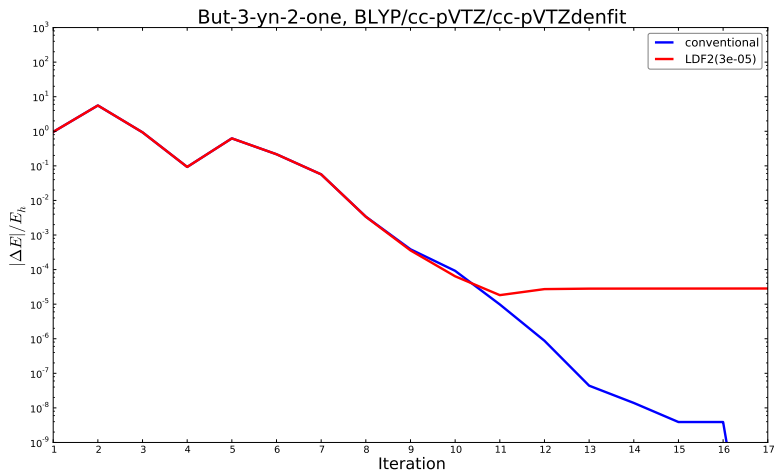
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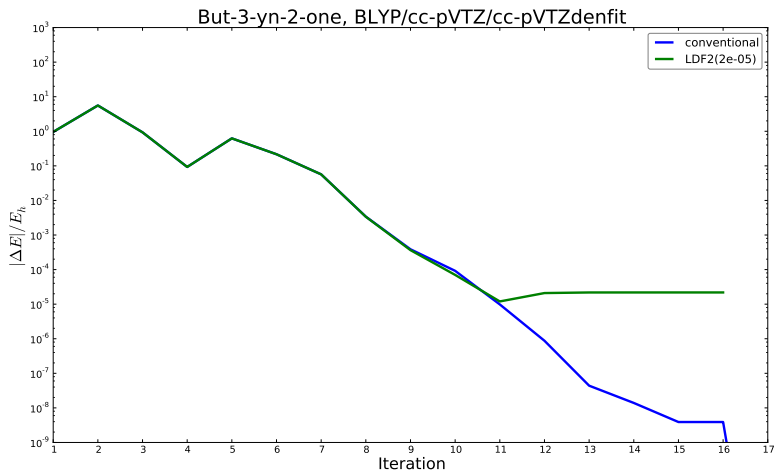
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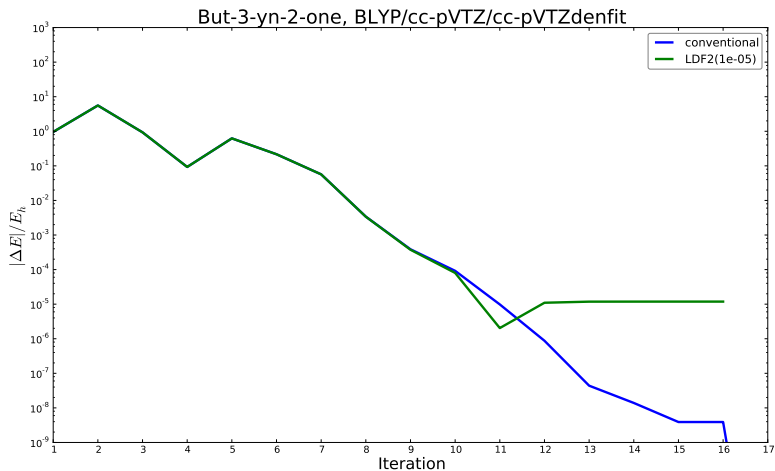
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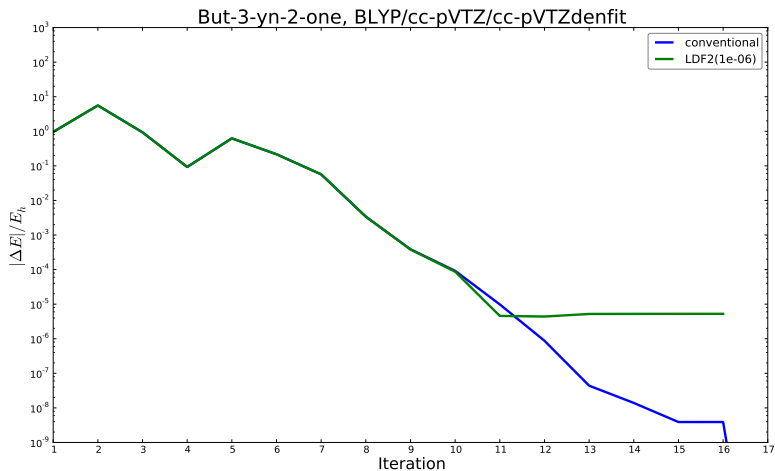
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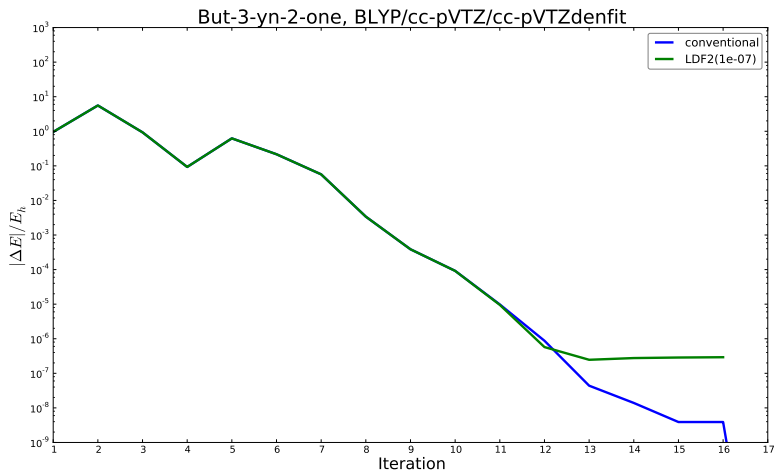
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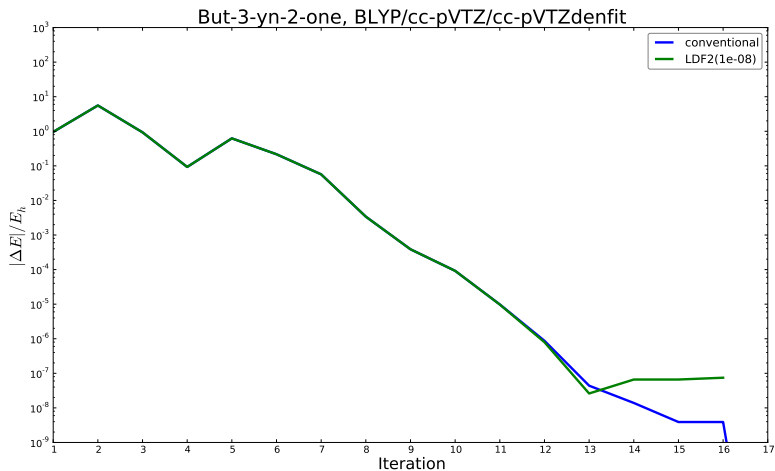
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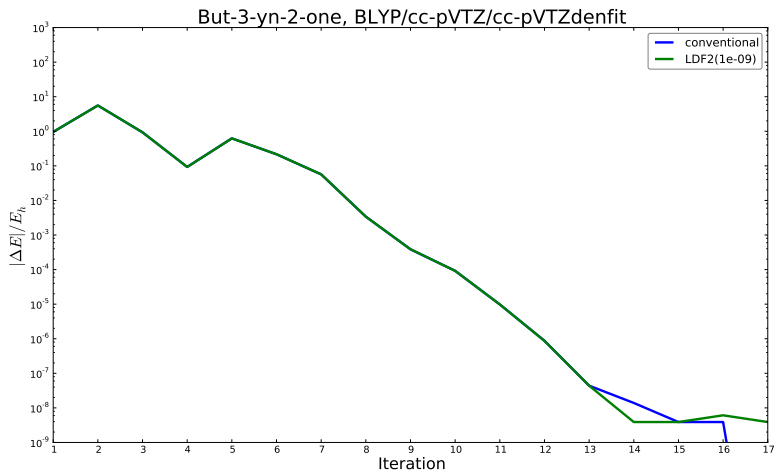
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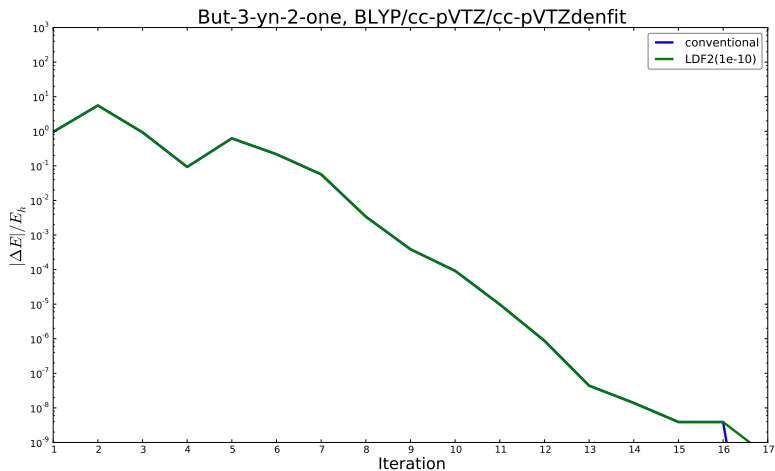
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Conclusions

- PARI is promising
- When it fails, it fails spectacularly!
- Reason: small attractive forces between the electrons.
- Present in all local domain fitting schemes (using robust or similar integral representations).
- Only known solution: locally complete fitting basis.
- We use two-center functions selected by Cholesky decomposition of the fitting error matrix for each atom pair.
- Problems:
 - Slows down the calculation, even compared to conventional (up to a factor of 2 slow-down has been observed for smallish molecules).
 - Fitting basis becomes geometry-dependent \implies discontinuities.

- Organizers for the invitation
- Collaborators
 - Prof. Trygve Helgaker
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 - Dr. Thomas Bondo Pedersen
 - Dr. Thomas Kjærgaard
- Funding

