

Supplementary Material for “A density-fitting implementation of the density-based basis-set correction method”

Andreas Heßelmann,^{1,*} Emmanuel Giner,^{2,†} Peter Reinhardt,^{2,‡} Peter
J. Knowles,^{3,§} Hans-Joachim Werner,^{1,¶} and Julien Toulouse^{2,4,**}

¹*Institute for Theoretical Chemistry, University of Stuttgart, 70569, Stuttgart, Germany*

²*Laboratoire de Chimie Théorique, Sorbonne Université and CNRS, F-75005 Paris, France*

³*School of Chemistry, Cardiff University, Cardiff CF10 3AT, United Kingdom*

⁴*Institut Universitaire de France, F-75005 Paris, France*

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I. COMPUTATION TIMES FOR THE DFT-BASED BASIS-SET CORRECTION

Table I reports computation times for calculating the PBE-based basis-set correction for four molecules. Three methods for dealing with the two-electron integrals are compared: conventional (when possible), integral-direct, and density fitting. The integral-direct integral transformation used is from the CCSD program described in Ref. 1. This also computes the integrals ($ijklab$) as well as a Fock matrix, which are not needed for the basis-set correction. The 3-index integrals in the density-fitting calculations are computed without symmetry. Only valence orbitals have been included in the basis-set correction calculations. The spatial grid threshold is 1d-6 (default).

The density-fitting algorithm scales formally as $O(N^4)$, while the conventional and integral-direct methods scale as $O(N^5)$, where N is a measure of the molecular size (e.g. the number of electrons N_{el} or the number of basis functions N_{basis} - not the spatial size). Taking the number of basis functions as measure of size, the scaling exponents obtained from the timings of last 2 molecules are:

density fitting (parallel) : 1.84,

density fitting (serial) : 3.45,

integral-direct (parallel) : 4.56,

integral-direct (serial) : 5.13,

quite as expected. In the last integral-direct calculation the computation of the integrals took 771 seconds and the assembly of the basis-set correction 247 seconds (using 16 cores).

*Electronic address: andreas.hesselmann@theochem.uni-stuttgart.de

†Electronic address: emmanuel.giner@lct.jussieu.fr

‡Electronic address: peter.reinhardt@lct.jussieu.fr

§Electronic address: KnowlesPJ@Cardiff.ac.uk

¶Electronic address: werner@theochem.uni-stuttgart.de

**Electronic address: toulouse@lct.jussieu.fr

TABLE I: Elapsed times (in seconds) for computing the PBE-based basis-set correction with the aug-cc-pVTZ basis set. The number of basis functions N_{basis} is reported. The calculations were performed on an Intel Xeon CPU E5-2660 v3@2.60GHz.

Molecule (symmetry)	N_{basis}	method	serial	parallel ^a
urea (C_2)	276	conventional	11.0	2.6
		integral-direct	38.3	4.3
		density fitting	5.9	2.5
benzene (D_{2h})	414	conventional	7.7	1.4
		integral-direct	96.7	12.6
		density fitting	10.3	6.3
n-hexane (C_1)	598	integral-direct	1615.5	145.4
		density fitting	86.8	22.2
tetramethylpentane (C_1)	874	integral-direct	9128.8	1020.4
		density fitting	321.1	44.6

^aUsing 16 MPI processes.

II. FURTHER STATISTICAL MEASURES ON THE FH51 SET

Table II reports mean errors, standard deviations and maximal absolute errors in reaction energies of the FH51 set with respect to MP2/CBS with *avnz* basis sets. For all the different density-functional approximations except for LYP, the main effect of the basis-set correction is to systematically reduce the standard deviation and maximal absolute error obtained at the uncorrected MP2 level.

TABLE II: Mean error (ME), standard deviation (SD), and maximal absolute error (MAX) (in kcal/mol) in reaction energies of the FH51 set with respect to MP2/CBS with *avnz* basis sets. The MP2/CBS reference is estimated as MP2-F12/av5z.

	ME				SD				MAX			
	avdz	avtz	avqz	av5z	avdz	avtz	avqz	av5z	avdz	avtz	avqz	av5z
MP2	-0.52	0.09	0.01	0.01	3.11	1.03	0.40	0.20	12.61	3.82	1.59	0.73
MP2+CABS	0.09	0.02	0.01	0.01	1.27	0.74	0.32	0.17	3.42	2.20	0.98	0.54
MP2+PBE	-0.93	-0.07	-0.08	-0.03	2.32	0.50	0.17	0.06	8.43	1.88	0.59	0.19
MP2+CABS+PBE	-0.32	-0.14	-0.08	-0.03	0.87	0.25	0.11	0.05	3.00	1.05	0.35	0.17
MP2+CABS+LDA	-0.12	-0.10	-0.07	-0.03	0.89	0.24	0.10	0.05	2.53	0.96	0.34	0.16
MP2+CABS+LYP	-0.38	-0.18	-0.12	-0.14	2.85	0.70	0.52	0.62	19.06	2.39	3.43	3.24
MP2+CABS+TPSS	-0.33	-0.14	-0.08	-0.03	0.88	0.25	0.11	0.05	3.05	1.06	0.35	0.17
MP2+CABS+SCAN	-0.43	-0.15	-0.08	0.03	0.94	0.28	0.11	0.05	3.83	1.18	0.37	0.17
MP2+CABS+PBE-CS ($q = 1.88$)	-0.24	-0.21	-0.07	-0.03	0.88	0.28	0.12	0.05	2.78	1.06	0.42	0.21
MP2+CABS+PBE-HP ($q = 2.05$)	-0.26	-0.12	-0.07	-0.03	0.90	0.29	0.12	0.06	2.88	1.07	0.44	0.23
MP2-F12	-0.28	-0.10	-0.03	0.00	0.31	0.13	0.03	0.00	1.38	0.54	0.09	0.00

[1] M. Schütz, R. Lindh and H.-J. Werner, Mol. Phys. **96**, 719 (1999).