Title
Note: The performance of new density functionals for a recent blind test of non-covalent interactions

Journal
The Journal of Chemical Physics, 145(18)

ISSN
0021-9606

Authors
Mardirossian, Narbe
Head-Gordon, Martin

Publication Date
2016-11-14

DOI
10.1063/1.4967424

Peer reviewed

Note: The performance of new density functionals for a recent blind test of non-covalent interactions

Narbe Mardirossian[1] and Martin Head-Gordon[1, 2, a)]
[1)] *Kenneth S. Pitzer Center for Theoretical Chemistry, Department of Chemistry, University of California, Berkeley, California 94720, USA*
[2)] *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

Benchmark datasets of non-covalent interactions are essential for assessing the performance of density functionals and other quantum chemistry approaches. In a recent blind test[1], Taylor et al. benchmarked 14 methods on a new dataset consisting of 10 dimer potential energy curves calculated at the CCSD(T)/CBS level (80 data points in total). The dataset is particularly interesting because compressed, near-equilibrium, and stretched regions of the potential energy surface are extensively sampled. The dimers included in the study were 1) water dimer, 2) ethanol dimer, 3) nitromethane dimer, 4) methylformate dimer, 5) benzene-methane, 6) benzene-water, 7) imidazole dimer, 8) nitrobenzene dimer, 9) FOX-7 dimer $(C_2N_4O_4H_4)_2$, and 10) EDNA dimer $(C_2O_4N_4H_6)_2$. The 14 methods benchmarked in the original work are M06[2], M11[3], DCACP[4], dlDF+D[5], B3LYP-D3[6], LC-ωPBE-D3[7], LC-BOP12+LRD[8], LCgau-BOP+LRD[8], vdW-DF2[9], SAPT(DFT)[10], RSH+lrMP2[11], RSH+lrRPAx-SO2[12], MP2 at the complete basis set (CBS) limit, and counterpoise-corrected, augmented triple-zeta CCSD(T).

In the present note, 14 density functionals developed between the years 2012 and 2016 are benchmarked on this dataset. The 14 selected functionals (summarized in Table I) include three combinatorially-optimized density functionals (ωB97X-V[13], B97M-V[14], and ωB97M-V[15]), two Minnesota density functionals (MN15-L[16] and MN15[17]), two Bayesian error estimation density functionals (BEEF-vdW[18] and mBEEF[19]), two systematically-optimized density functionals (ωB97X-D3[20] and ωM06-D3[20]), four non-empirical density functionals (MS2-D3[21], MS2h-D3[21], SCAN-D3(BJ)[22], and TM[23]), and one "low-cost" electronic structure approach (PBEh-3c[24]). For all of the functionals except PBEh-3c, the def2-QZVPPD basis set is used without counterpoise corrections (CP), a (99,590) grid is used for local exchange-correlation functionals, and the SG-1 grid is used for nonlocal correlation functionals. For PBEh-3c, the def2-mSVP basis set is used without CP, along with a (99,590) grid. All of the calculations are performed with a development version of the Q-Chem 4 package[25]. The methods from the original work are treated as indicated in Table I of Ref 1.

Functional	#	%	Class	Year	Ref
ωB97X-V	10	16.7-100	RSH GGA VV10	2014	13
B97M-V	12	0	L meta-GGA VV10	2015	14
ωB97M-V	12	15-100	RSH meta-GGA VV10	2016	15
MN15-L	58	0	L meta-NGA	2016	16
MN15	59	44	GH meta-NGA	2016	17
BEEF-vdW	31	0	L GGA vdW-DF2	2012	18
mBEEF	64	0	L meta-GGA	2014	19
ωB97X-D3	16	19.6-100	RSH GGA D3(0)	2013	20
ωM06-D3	25	27.2-100	RSH meta-GGA D3(0)	2013	20
MS2-D3	3	0	L meta-GGA D3(0)	2013	21
MS2h-D3	4	9	GH meta-GGA D3(0)	2013	21
TM	0	0	L meta-GGA	2016	23
SCAN-D3(BJ)	2	0	L meta-GGA D3(BJ)	2016	22
PBEh-3c	7	42	GH GGA D3(BJ) gCP	2015	24

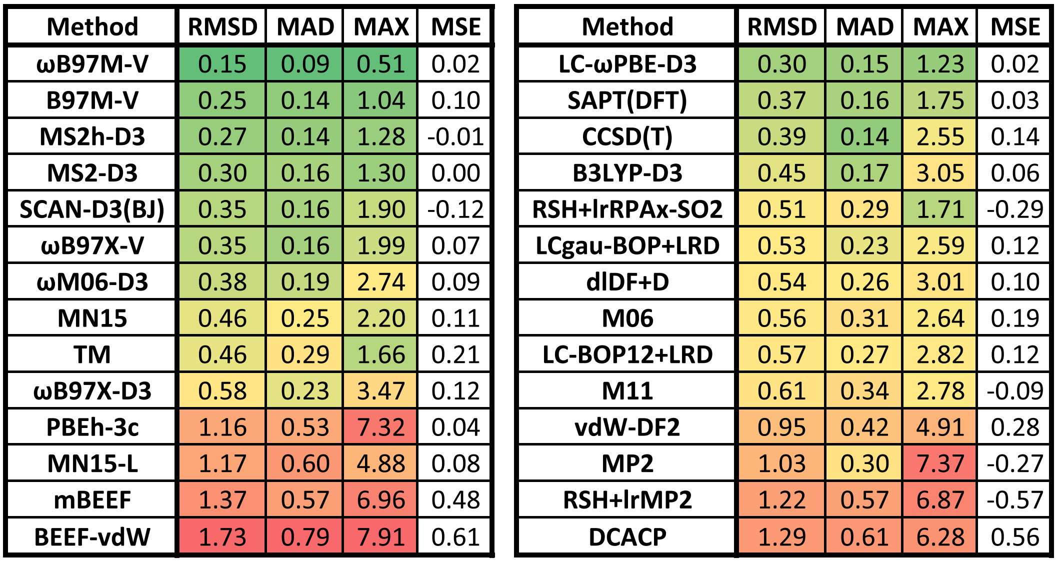
TABLE I. Details for the 14 density functionals benchmarked in the present work. L stands for local, GH stands for global hybrid, and RSH stands for range-separated hybrid. The second column lists the number of parameters that were optimized on a training set. The third column lists the percentage of exact exchange.

The 28 methods are compared using the root-mean-square deviation (RMSD), mean absolute deviation (MAD), maximum absolute error (MAX), and mean signed error (MSE). The results (ranked according to RMSD) are presented in Figure 1, and are separated into the density functionals new to the present work (left) and the methods from the original work (right). Overall, ωB97M-V is by far the most accurate method, with an RMSD of 0.15 kcal/mol, an MAD of 0.09 kcal/mol, and a MAX of 0.51 kcal/mol. ωB97M-V is 40% more accurate than the next best method overall (B97M-V), and two times more accurate than the best method from the original work (LC-ωPBE-D3). The best functional that has no exact exchange is B97M-V, followed by MS2-D3 and SCAN-D3(BJ), while the best hybrid functional is ωB97M-V, followed by MS2h-D3 and LC-ωPBE-D3.

Considering the new data, six density functionals besides ωB97M-V have RMSDs that are smaller than that of counterpoise-corrected, augmented triple-zeta CCSD(T): B97M-V, MS2h-D3, MS2-D3, SCAN-D3(BJ), ωB97X-V, and ωM06-D3. These functionals perform quite well, with RMSDs between 0.25 kcal/mol and 0.38 kcal/mol. On the other hand, PBEh-3c, MN15-L, mBEEF, and BEEF-vdW perform poorly, with RMSDs in excess of 1 kcal/mol. The errors of PBEh-3c and MN15-L are not systematic, while the mBEEF and BEEF-vdW binding energies appear to be consistently underestimated. While MN15 outperforms MN15-L and the two Minnesota functionals from the original work, its performance is lackluster compared to that of the best density functionals. Despite the lack of exact exchange, the TM functional performs very sim-

---

[a)] Electronic mail: mhg@cchem.berkeley.edu



Method	RMSD	MAD	MAX	MSE
ωB97M-V	0.15	0.09	0.51	0.02
B97M-V	0.25	0.14	1.04	0.10
MS2h-D3	0.27	0.14	1.28	-0.01
MS2-D3	0.30	0.16	1.30	0.00
SCAN-D3(BJ)	0.35	0.16	1.90	-0.12
ωB97X-V	0.35	0.16	1.99	0.07
ωM06-D3	0.38	0.19	2.74	0.09
MN15	0.46	0.25	2.20	0.11
TM	0.46	0.29	1.66	0.21
ωB97X-D3	0.58	0.23	3.47	0.12
PBEh-3c	1.16	0.53	7.32	0.04
MN15-L	1.17	0.60	4.88	0.08
mBEEF	1.37	0.57	6.96	0.48
BEEF-vdW	1.73	0.79	7.91	0.61

Method	RMSD	MAD	MAX	MSE
LC-ωPBE-D3	0.30	0.15	1.23	0.02
SAPT(DFT)	0.37	0.16	1.75	0.03
CCSD(T)	0.39	0.14	2.55	0.14
B3LYP-D3	0.45	0.17	3.05	0.06
RSH+lrRPAx-SO2	0.51	0.29	1.71	-0.29
LCgau-BOP+LRD	0.53	0.23	2.59	0.12
dlDF+D	0.54	0.26	3.01	0.10
M06	0.56	0.31	2.64	0.19
LC-BOP12+LRD	0.57	0.27	2.82	0.12
M11	0.61	0.34	2.78	-0.09
vdW-DF2	0.95	0.42	4.91	0.28
MP2	1.03	0.30	7.37	-0.27
RSH+lrMP2	1.22	0.57	6.87	-0.57
DCACP	1.29	0.61	6.28	0.56

FIG. 1. Statistics in kcal/mol for the dataset (80 data points) reported in Ref 1. The 14 density functionals benchmarked in the present work are on the left, while the 14 methods benchmarked in the original work are on the right. The methods are ranked with respect to the root-mean-square deviation (RMSD).

ilarly to MN15, yet performs 30% worse than SCAN-D3(BJ), 50% worse than MS2-D3, and 85% worse than B97M-V. The fact that ωB97X-V performs 40% better than ωB97X-D3 is an indication of the accuracy that nonlocal correlation functionals can offer over damped atom-atom potentials, since the functionals differ primarily in the utilized dispersion correction. Finally, it is noteworthy that the five most accurate functionals new to the present work are dispersion-corrected meta-GGAs.

Considering all 28 benchmarked methods, it is remarkable (although not surprising) that MP2/CBS performs worse than most of the density functionals considered (by up to a factor of 7 relative to the best-performing functional, ωB97M-V). Additionally, LC-ωPBE-D3 performs exceptionally well for a functional with only a few empirical parameters. The performance of B3LYP-D3 is certainly worth mentioning, since it manages to outperform 7 of the 14 recently-developed density functionals benchmarked in the present work. In summary, seven density functionals developed in the past five years either match or outperform counterpoise-corrected, augmented triple-zeta CCSD(T) (by up to a factor of 2.5). These results are very encouraging for the application of modern density functionals to intermolecular interactions, including compressed configurations. In particular, the exceptional performance of ωB97M-V makes it a very promising choice for calculations involving non-covalent interactions.

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The authors thank Yuezhi Mao, Susi Lehtola, and Jon Witte for helpful comments.

[1] D. E. Taylor *et al.*, J. Chem. Phys. **145**, 124105 (2016).

[2] Y. Zhao and D. Truhlar, Theor. Chem. Acc. **120**, 215 (2008).

[3] R. Peverati and D. G. Truhlar, J. Phys. Chem. Lett. **2**, 2810 (2011).

[4] O. A. von Lilienfeld, I. Tavernelli, U. Rothlisberger, and D. Sebastiani, Phys. Rev. Lett. **93**, 153004 (2004).

[5] K. Pernal, R. Podeszwa, K. Patkowski, and K. Szalewicz, Phys. Rev. Lett. **103**, 263201 (2009).

[6] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, J. Chem. Phys. **132**, 154104 (2010).

[7] O. A. Vydrov, J. Heyd, A. V. Krukau, and G. E. Scuseria, J. Chem. Phys. **125**, 074106 (2006).

[8] J.-W. Song and K. Hirao, Chem. Phys. Lett. **563**, 15 (2013).

[9] K. Lee, E. D. Murray, L. Kong, B. I. Lundqvist, and D. C. Langreth, Phys. Rev. B **82**, 081101 (2010).

[10] G. Jansen, WIREs Comput Mol Sci **4**, 127 (2014).

[11] J. G. Ángyán, I. C. Gerber, A. Savin, and J. Toulouse, Phys. Rev. A **72**, 012510 (2005).

[12] J. Toulouse, W. Zhu, A. Savin, G. Jansen, and J. G. Ángyán, J. Chem. Phys. **135**, 084119 (2011).

[13] N. Mardirossian and M. Head-Gordon, Phys. Chem. Chem. Phys. **16**, 9904 (2014).

[14] N. Mardirossian and M. Head-Gordon, J. Chem. Phys. **142**, 074111 (2015).

[15] N. Mardirossian and M. Head-Gordon, J. Chem. Phys. **144**, 214110 (2016).

[16] H. S. Yu, X. He, and D. G. Truhlar, J. Chem. Theory Comput. **12**, 1280 (2016).

[17] H. S. Yu, X. He, S. L. Li, and D. G. Truhlar, Chem. Sci. **7**, 5032 (2016).

[18] J. Wellendorff *et al.*, Phys. Rev. B **85**, 235149 (2012).

[19] J. Wellendorff, K. T. Lundgaard, K. W. Jacobsen, and T. Bligaard, J. Chem. Phys. **140**, 144107 (2014).

[20] Y.-S. Lin, G.-D. Li, S.-P. Mao, and J.-D. Chai, J. Chem. Theory Comput. **9**, 263 (2013).

[21] J. Sun, R. Haunschild, B. Xiao, I. W. Bulik, G. E. Scuseria, and J. P. Perdew, J. Chem. Phys. **138**, 044113 (2013).

[22] J. G. Brandenburg, J. E. Bates, J. Sun, and J. P. Perdew, Phys. Rev. B **94**, 115144 (2016).

[23] J. Tao and Y. Mo, Phys. Rev. Lett. **117**, 073001 (2016).

[24] S. Grimme, J. G. Brandenburg, C. Bannwarth, and A. Hansen, J. Chem. Phys. **143**, 054107 (2015).

[25] Y. Shao *et al.*, Mol. Phys. **113**, 184 (2015).