10.1071/CH19023_AC

Australian Journal of Chemistry 2019, 72(8), 563-573

Supplementary material for:

A trip to the Density Functional Theory zoo: warnings and recommendations for the user

Lars Goerigk* and Nisha Mehta

School of Chemistry, The University of Melbourne, Parkville, Australia. ; Tel: +61-(0)3-83446784

E-mail: lars.goerigk@unimelb.edu.au

Contents

SI.1 Analysis of the first-division DFAs for each year of the DFT poll

We performed additional calculations with SVWN (LDA),[S1,S2] B3LYP*,[S3] and CAM-B3LYP[S4] for the GMTKN55 database, as they had appeared in the first division in some years. All molecular geometries of the GMTKN55 database and reference values were taken from Ref. S5. All calculations were performed using ORCA 4.0.1.[S6,S7] The large Ahlrichs-type quadruple-ζ atomic-orbital (AO) basis set def2-QZVP[S8] was used. For the G21EA, AHB21, and IL16 test sets we applied diffuse s and p functions from aug-cc-pVQZ[S9] to all non-hydrogen atoms, and diffuse s functions to H atoms in accordance with the previous GMTKN studies.[S5,S10–S14] Diffuse s and p functions were added to oxygen in the WATER27 test set. def2-ECP[S8] effective-core potentials were used to define the core-electrons of heavy elements in some molecules in the HEAVY28, HEAVYSB11, HAL59, and RG18 sets. All SCF calculations were carried out as a multi-grid procedure with ORCA's quadrature grid '3' until convergence, followed by a non-iterative step with the larger grid '4'. With the exception of CAM-B3LYP, all functionals were treated with the resolution-of-the-identity (RI) approximation and chain-of-sphere approximation (COSX)[S15] to speed up the evaluation of Coulomb and exchange integrals, respectively. All calculations were set to the SCF convergence criterion of $10^{-7} E_h$.

Our analysis of the DFT-poll results is based on the assessment of 216 dispersion-corrected and -uncorrected DFAs with GMTKN55. Dispersion-corrected DFAs only refer to the recommended DFT-D3(BJ) correction with Becke-Johnson damping. In some cases, where this damping functional turned out to be incompatible due to short range double counting effects, we considered the zero-damping version:[S5,S12] M052X-D3(0), M062X-D3(0), M08HX-D3(0), M06-D3(0), M05-D3(0), PW1PW-D3(0), MPW1LYP-D3(0), M06L-D3(0), M11L-D3(0), N12-D3(0), PKZB-D3(0), MN15L-D3(0), and PW91P86-D3(0). We also considered ωB97X-D3(0), DSD-PBEP86-NL, DSD-BLYP-NL, PWPB95-NL, SOS1-PBE-QIDH-NL, PBE-QIDH-NL, PW6B95-NL, B3LYP-NL, and revPBE-NL.
In addition to just listing each year's first-division DFAs, the authors of the DFT poll also reported weight factors for each functional based on the number of votes for that DFA to be used for a composite DFT method based on popularity. We will come back to that idea shortly as an additional investigation that complements our analysis in the main manuscript. For that purpose, we used the weight factors as reported in Ref. S16. Some functionals were excluded from our analysis, therefore, weight factors of the remaining DFAs needed to be adjusted so that the overall weight of first-division DFAs remained the same ($\sim$1). We added the weights of functionals that were excluded from our study, and then evenly distributed that number among the remaining first-division DFAs of the corresponding year.

Tabs. S1-S8 show the first-division DFAs in each year, how they rank and the weight factors. Tab. S9 refers to the composite method of each year based on the aforementioned weight factors. Table S9 shows the final WTMAD-2 numbers, and how they rank compared with the individual DFAs tested with the GMTKN55 database. Again, we can confirm that the first-division DFAs exhibit very average performance.

Table S1: Overview of the "DFT-Poll 2010" first-division DFAs and their ranking among 216 dispersion-corrected and -uncorrected DFAs tested on the GMTKN55 benchmark database. The weight factors correspond to each DFA as reported in Ref. S16. The fourth column represents the adjusted weight factors after excluding the mPW1K, SAOP and SSB-D DFAs from the analysis. Whenever "DFT-D" is mentioned, we use the DFT-D3(BJ) version.[S17,S18]

Functional	ranking	weight factor	adjusted weight factor	Ref.
PBE0	154	0.0951	0.1015	S19,S20
B3LYP	197	0.094	0.1004	S21,S22
PBE	185	0.0877	0.0941	S23
BP86	205	0.0647	0.0711	S24–S26
M06-2X	36	0.0569	0.0633	S27
B2PLYP	121	0.0522	0.0586	S28
B3PW91	198	0.0503	0.0567	S21
B97-D	213	0.0483	0.0547	S29
M06-L	119	0.0472	0.0536	S30
CAM-B3LYP	159	0.0472	0.0536	S4
TPSSh	190	0.0452	0.0516	S31
OLYP	215	0.0366	0.0430	S32–S34
mPW1K	–	0.0366	–	S35
SAOP	–	0.0363	–	S36
SSB-D	–	0.0355	–	S37
BLYP	211	0.0347	0.0411	S24,S32,S33
LDA	214	0.0331	0.0395	S1,S2,S38,S39
revTPSS-D	116	0.0331	0.0395	S5,S40
M05-2X	41	0.0327	0.0391	S41
B3LYP*	209	0.0324	0.0388	S3

Table S2: Overview of the "DFT-Poll 2011" first-division DFAs and their ranking among 216 dispersion-corrected and -uncorrected DFAs tested on the GMTKN55 benchmark database. The weight factors correspond to each DFA as reported in Ref. S16. The fourth column represents the adjusted weight factors after excluding the mPW1K, SAOP and SSB-D DFAs from the analysis. Whenever "DFT-D" is mentioned, we use the DFT-D3(BJ) version.[S17,S18]

Functional	ranking	weight factor	adjusted weight factor	Ref.
PBE0	154	0.1143	0.1176	S19,S20
B3LYP	197	0.0993	0.1026	S21,S22
PBE	185	0.0936	0.0969	S23
BP86	205	0.0861	0.0894	S24–S26
B97-D	213	0.0645	0.0678	S29
B2PLYP	121	0.0587	0.0620	S28
B3PW91	198	0.0517	0.0550	S21
CAM-B3LYP	159	0.0503	0.0536	S4
M06-2X	36	0.0494	0.0527	S27
revTPSS-D	116	0.0468	0.0501	S5,S40
BLYP	211	0.0464	0.0497	S24,S32,S33
TPSSh	190	0.0397	0.0430	S31
M06-L	119	0.0366	0.0399	S30
SSB-D	–	0.0331	–	S37
B3LYP*	209	0.0305	0.0338	S3
OLYP	215	0.0296	0.0329	S32–S34
SAOP	–	0.0000	–	S36
LDA	214	0.0234	0.0267	S1,S2,S38,S39
M05-2X	41	0.0234	0.0267	S41
mPW1K	–	0.0225	–	S35

Table S3: Overview of the "DFT-Poll 2012" first-division DFAs and their ranking among 216 dispersion-corrected and -uncorrected DFAs tested on the GMTKN55 benchmark database. The weight factors correspond to each DFA as reported in Ref. S16. The fourth column represents the adjusted weight factors after excluding the SSB-D DFA from the analysis. Whenever "DFT-D" is mentioned, we use the DFT-D3(BJ) version.[S17,S18]

Functional	ranking	weight factor	adjusted weight factor	Ref.
PBE	185	0.115	0.1169	S23
PBE0	154	0.1044	0.1063	S19,S20
B3LYP	197	0.0882	0.0901	S21,S22
PW91	181	0.073	0.0749	S42
BP86	205	0.0651	0.0670	S24–S26
B97-D	213	0.0537	0.0556	S29
B3LYP-D	72	0.0507	0.0526	S18,S21,S22
M06-2X	36	0.0502	0.0521	S27
BLYP	211	0.0498	0.0517	S24,S32,S33
revPBE	210	0.0472	0.0491	S43
CAM-B3LYP	159	0.045	0.0469	S4
B2PLYP	121	0.0415	0.0434	S28
B3PW91	198	0.0411	0.0430	S21
SSB-D	–	0.0336	–	S37
TPSSh	190	0.0315	0.0334	S31
M06-L	119	0.0301	0.0320	S30
B3LYP*	209	0.0275	0.0294	S3
PWPB95-D3	14	0	0	S11
revTPSS-D	116	0.0271	0.0290	S5,S40
revTPSS	187	0.0253	0.0272	S40

Table S4: Overview of the "DFT-Poll 2013" first-division DFAs and their ranking among 216 dispersion-corrected and -uncorrected DFAs tested on the GMTKN55 benchmark database. The weight factors correspond to each DFA as reported in Ref. S16. The fourth column represents the adjusted weight factors after excluding the SSB-D DFA from the analysis. Whenever "DFT-D" is mentioned, we use the DFT-D3(BJ) version.[S17,S18]

Functional	ranking	weight factor	adjusted weight factor	Ref.
PBE	185	0.1229	0.1238	S23
PBE0	154	0.1045	0.1054	S19,S20
B3LYP	197	0.0709	0.0718	S21,S22
LDA	214	0.0675	0.0684	S1,S2,S38,S39
PW91	181	0.0628	0.0637	S42
BP86	205	0.0534	0.0543	S24–S26
HSE[a]	144	0.0524	0.0533	S44,S45
revPBE	210	0.049	0.0499	S43
ωB97X-D	24	0.0484	0.0493	S46
B3LYP-D	72	0.044	0.0449	S18,S21,S22
CAM-B3LYP	159	0.043	0.0439	S4
M06-2X	36	0.04	0.0409	S27
B97-D	213	0.0376	0.0385	S29
B2PLYP	121	0.0349	0.0358	S28
B3PW91	198	0.0346	0.0355	S21
M06	64	0.0329	0.0338	S27
TPSSh	190	0.0326	0.0335	S31
BLYP	211	0.0309	0.0318	S24,S32,S33
OLYP	215	0.0208	0.0217	S32–S34
SSB-D	–	0.0168	–	S37

[a] HSE06 version.

Table S5: Overview of the "DFT-Poll 2014" first-division DFAs and their ranking among 216 dispersion-corrected and -uncorrected DFAs tested on the GMTKN55 benchmark database. The weight factors correspond to each DFA as reported in Ref. S16. The fourth column represents the adjusted weight factors after excluding RPA and the LC-ωPBE DFA from the analysis. Whenever "DFT-D" is mentioned, we use the DFT-D3(BJ) version.[S17,S18]

Functional	ranking	weight factor	adjusted weight factor	Ref.
PBE	185	0.1299	0.1315	S23
PBE0	154	0.1108	0.1124	S19,S20
B3LYP	197	0.0724	0.0740	S21,S22
PW91	181	0.0599	0.0615	S42
B3LYP-D	72	0.0595	0.0611	S18,S21,S22
LDA	214	0.0591	0.0607	S1,S2,S38,S39
M06-2X	36	0.0542	0.0558	S27
CAM-B3LYP	159	0.0534	0.0550	S4
BP86	205	0.0494	0.0510	S24–S26
HSE[a]	144	0.0494	0.0510	S44,S45
B97-D	213	0.0421	0.0437	S29
B2PLYP	121	0.0352	0.0368	S28
RPA	–	0	–	S47
B3PW91	198	0.034	0.0356	S21
revPBE	210	0.0332	0.0348	S43
RPBE	206	0.0283	0.0299	S48
LC-ωPBE	–	0.0279	–	S49
B3LYP*	209	0.0235	0.0251	S3
BHandHLYP	187	0.015	0.0166	S50

[a] HSE06 version.

Table S6: Overview of the "DFT-Poll 2015" first-division DFAs and their ranking among 216 dispersion-corrected and -uncorrected DFAs tested on the GMTKN55 benchmark database. The weight factors correspond to each DFA as reported in Ref. S16. The fourth column represents the adjusted weight factors after excluding RPA. Whenever "DFT-D" is mentioned, we use the DFT-D3(BJ) version.[S17,S18]

Functional	ranking	weight factor	adjusted weight factor	Ref.
PBE	185	0.1104	0.1119	S23
PBE0	154	0.1068	0.1083	S19,S20
B3LYP	197	0.0673	0.0688	S21,S22
ωB97X-D	24	0.0655	0.0670	S46
B3LYP-D	72	0.0601	0.0616	S18,S21,S22
LDA	214	0.0548	0.0563	S1,S2,S38,S39
PW91	181	0.0530	0.0545	S42
B97-D	213	0.0512	0.0527	S29
M06-2X	36	0.0512	0.0527	S27
B2PLYP	121	0.0503	0.0518	S28
CAM-B3LYP	159	0.0449	0.0464	S4
HSE[a]	144	0.0449	0.0464	S44,S45
BP86	205	0.0422	0.0437	S24–S26
M06	64	0.0359	0.0374	S27
B3PW91	198	0.0350	0.0365	S21
revTPSS	187	0.0314	0.0329	S40
RPA	–	0.0287	–	S47
TPSSh	190	0.0278	0.0293	S31
M06-L	119	0.0215	0.0230	S30
BLYP	211	0.0171	0.0186	S24,S32,S33

[a] HSE06 version.

Table S7: Overview of the "DFT-Poll 2016" first-division DFAs and their ranking among 216 dispersion-corrected and -uncorrected DFAs tested on the GMTKN55 benchmark database. The weight factors correspond to each DFA as reported in Ref. S16. The fourth column represents the adjusted weight factors after excluding the LC-ωPBE DFA from the analysis. Whenever "DFT-D" is mentioned, we use the DFT-D3(BJ) version.[S17,S18]

Functional	ranking	weight factor	adjusted weight factor	Ref.
PBE	185	0.1176	0.1195	S23
PBE0	154	0.1003	0.1022	S19,S20
B3LYP	197	0.0743	0.0762	S21,S22
ωB97X-D	24	0.0736	0.0755	S46
B3LYP-D	72	0.0584	0.0603	S18,S21,S22
CAM-B3LYP	159	0.0563	0.0582	S4
BP86	205	0.0527	0.0546	S24–S26
LDA	214	0.0498	0.0517	S1,S2,S38,S39
M06-2X	36	0.0476	0.0495	S27
B97-D	213	0.0462	0.0481	S29
PW91	181	0.0418	0.0437	S42
HSE[a]	144	0.0390	0.0409	S44,S45
B2PLYP	121	0.0382	0.0401	S28
revPBE	210	0.0368	0.0387	S43
LC-ωPBE	–	0.0346	–	S49
M06	64	0.0332	0.0351	S27
PWPB95-D3	14	0.0303	0.0322	S11
RPBE	206	0.0303	0.0322	S48
B3PW91	198	0.0224	0.0243	S21

[a] HSE06 version.

Table S8: Overview of the "DFT-Poll 2017" first-division DFAs and their ranking among 216 dispersion-corrected and -uncorrected DFAs tested on the GMTKN55 benchmark database. The weight factors correspond to each DFA as reported in Ref. S16. The fourth column represents the adjusted weight factors after excluding RPA and the LC-ωPBE DFA from the analysis. Whenever "DFT-D" is mentioned, we use the DFT-D3(BJ) version.[S17,S18]

Functional	ranking	weight factor	adjusted weight factor	Ref.
PBE0	154	0.1014	0.1049	S19,S20
PBE	185	0.0971	0.1006	S23
ωB97X-D	24	0.0917	0.0952	S46
B3LYP-D	72	0.0787	0.0822	S18,S21,S22
CAM-B3LYP	159	0.0723	0.0758	S4
B97-D	213	0.0712	0.0747	S29
B3LYP	197	0.0701	0.0736	S21,S22
TPSSh	190	0.0496	0.0531	S31
BP86	205	0.0453	0.0488	S24–S26
B2PLYP	121	0.0442	0.0477	S28
PW91	181	0.0378	0.0413	S42
HSE[a]	144	0.0367	0.0402	S44,S45
LC-ωPBE	–	0.0356	–	S49
M06-2X	36	0.0324	0.0359	S27
revPBE	210	0.0324	0.0359	S43
BLYP	211	0.0270	0.0305	S24,S32,S33
RPA	–	0.0270	–	S47
OLYP	215	0.0205	0.0240	S32–S34
LDA	214	0.0162	0.0197	S1,S2,S38,S39
BHandHLYP	187	0.0129	0.0164	S50

[a] HSE06 version.

Table S9: Analysis of the performance of the first-division DFAs on the GMTKN55 database. The second column represents a linear combination of their individually weighted WTMAD-2 values (kcal/mol), with all weight factors being reported in Tabs. S1-S8. The last column shows how such a combined method ranks compared with the individual DFAs tested with the GMTKN55 database.

	WTMAD-2	rank
2010	14.39	192
2011	14.51	192
2012	14.01	187
2013	13.95	186
2014	13.14	178
2015	12.56	171
2016	12.41	171
2017	13.15	178

SI.2 Citation analysis of the first-division DFAs that appear in the DFT polls

Table S10: Overview of the citations of the unique first-division exchange-correlation DFAs featured in the DFT polls. The results were obtained by searching for the original publication (in superscript) on Web of Science Core Collection[S51] accessed on 1 January 2019.

DFA	number of citations
B2PLYP	1417[S28]
B3LYP	69562;[S21] 11511[S22]
B3LYP*	884[S3]
B3PW91	69562[S21]
B97-D	12200[S29]
BHandHLYP	10041[S50]
BLYP	36101;[S24] 66019;[S32] 4816[S33]
BP86	36101;[S24] 13671;[S25] 2735[S26]
CAM-B3LYP	5458[S4]
HSE	5489;[S44] 2318[S45]
LC-ωPBE	991[S49]
LDA	1052;[S38] 3402;[S1] 15716;[S2] 17018[S39]
M05-2X	2275[S41]
M06	11440[S27]
M06-2X	11440[S27]
M06-L	2403[S30]
mPW1K	1214[S35]
OLYP	66019;[S32] 4816;[S33] 1007[S34]
PBE	74606[S23]
PBE0	7215;[S19] 1726[S20]
PW91	69562[S21]
PWPB95	481[S11]
revPBE	1300[S43]
revTPSS	272[S40]
RPA	161[S47]
RPBE	3515[S48]
SAOP	627[S36]
SSB-D	89[S37]
TPSSh	1118[S31]
ωB97X-D	121[S46]

SI.3 Statistical results for all test sets of GMTKN55 and the new DFAs

Table S11: Statistical analysis of the CAM-B3LYP DFA for all 55 test sets of the GMTKN55 database. The statistical key data are: mean deviation (MD), mean absolute deviation (MAD), root-mean-square deviation (RMSD), normalised MAD (NMAD), deviation span (Δ_{error}), maximum (max) and minimum deviation (min). The NMAD is defined as the ratio between the MAD for a set and its average absolute reaction energy. For all test sets, the def2-QZVP atomic-orbital basis set was used, with additional diffuse functions for the G21EA, WATER27, AHB21, and IL16 sets. All values are in kcal/mol, except for the dimensionless NMAD.

set	MD	MAD	RMSD	NMAD	Δ_{error}	max	min
SIE4x4	13.53	13.53	16.11	0.40	32.17	34.07	1.90
ACONF	0.70	0.70	0.78	0.38	1.03	1.29	0.26
ADIM6	−3.54	3.54	3.89	1.05	4.70	−1.30	−6.00
AHB21	−0.35	0.72	0.89	0.03	2.82	1.10	−1.72
AL2X6	−6.01	6.01	6.45	0.17	6.68	−2.85	−9.53
ALK8	−4.68	4.84	7.87	0.08	17.36	0.63	−16.73
ALKBDE10	−1.34	4.57	6.13	0.05	17.75	5.12	−12.63
AMINO20x4	0.02	0.51	0.65	0.21	3.21	2.00	−1.21
BH76	−2.92	3.18	3.76	0.17	9.71	1.76	−7.95
BHDIV10	0.46	1.93	2.19	0.04	6.21	3.83	−2.38
BHPERI	4.56	4.61	5.22	0.22	10.74	10.09	−0.64
BHROT27	0.35	0.42	0.66	0.07	1.82	1.65	−0.17
BSR36	−8.09	8.09	9.31	0.50	18.17	−2.82	−20.99
BUT14DIOL	0.14	0.19	0.26	0.07	0.85	0.61	−0.25
C60ISO	10.31	10.31	11.09	0.10	11.96	16.28	4.32
CARBHB12	0.02	0.43	0.55	0.07	1.94	1.09	−0.86
CDIE20	0.44	0.66	0.89	0.16	2.89	2.12	−0.77
CHB6	−1.04	1.62	1.80	0.06	4.30	1.74	−2.56
DARC	7.39	7.39	7.83	0.23	8.77	9.64	0.87
DC13	1.34	10.58	13.59	0.19	54.83	26.42	−28.41
DIPCS10	2.12	4.36	5.39	0.01	17.88	12.23	−5.65
FH51	0.53	2.16	2.93	0.07	16.88	7.79	−9.09
G21EA	1.38	2.28	3.01	0.07	9.96	7.25	−2.71
G21IP	1.97	3.80	4.91	0.01	16.05	11.18	−4.87
G2RC	−1.45	3.04	3.34	0.06	11.40	4.96	−6.45
HAL59	−1.18	1.22	1.62	0.27	6.82	1.08	−5.74
HEAVY28	−0.93	0.93	1.01	0.75	1.51	−0.23	−1.74
HEAVYSB11	−7.31	7.31	7.55	0.13	6.34	−4.42	−10.76
ICONF	0.15	0.52	0.68	0.16	3.04	1.67	−1.37
IDISP	1.64	11.09	12.24	0.78	33.42	18.76	−14.66
IL16	2.55	2.55	2.65	0.02	2.71	4.14	1.42
INV24	−0.78	1.79	2.32	0.06	10.34	5.08	−5.26
ISO34	−0.35	1.32	2.10	0.09	14.54	7.52	−7.03
ISOL24	−2.47	5.50	8.33	0.25	42.30	11.63	−30.66
MB16-43	−47.86	48.06	55.91	0.12	149.41	4.17	−145.24
MCONF	−1.67	1.75	2.00	0.35	3.72	0.53	−3.19
NBPRC	2.28	3.33	4.45	0.12	13.31	9.77	−3.54
PA26	0.37	1.29	1.81	0.01	7.65	5.15	−2.50
PArel	0.12	0.72	1.17	0.16	5.88	3.87	−2.01
PCONF21	−0.19	2.84	3.24	1.75	9.21	5.14	−4.07
PNICO23	−1.18	1.18	1.35	0.28	2.70	−0.24	−2.94
PX13	−4.50	4.50	4.80	0.13	5.45	−1.56	−7.01
RC21	0.95	2.01	2.23	0.06	6.41	3.59	−2.82
RG18	−0.42	0.43	0.62	0.74	1.64	0.10	−1.54
RSE43	−1.38	1.38	1.56	0.18	3.00	−0.54	−3.54
S22	−2.39	2.51	3.51	0.34	10.23	0.84	−9.39
S66	−2.00	2.09	2.64	0.38	7.21	0.87	−6.34
SCONF	−0.10	0.30	0.40	0.07	1.73	1.15	−0.58
TAUT15	0.10	0.89	1.12	0.29	3.70	2.04	−1.65
UPU23	1.82	2.01	2.92	0.35	7.82	7.11	−0.71
W4-11	−1.09	3.54	6.06	0.01	43.19	7.23	−35.95
WATER27	2.88	3.31	3.99	0.04	17.28	11.49	−5.79
WCPT18	−0.65	1.90	2.27	0.05	8.41	5.03	−3.38
YBDE18	−5.38	5.38	6.28	0.11	10.49	−0.82	−11.30
BH76RC	−0.76	1.92	2.45	0.09	9.20	2.68	−6.52

Table S12: Statistical analysis of the B3LYP* DFA for all 55 test sets of the GMTKN55 database. The statistical key data are: mean deviation (MD), mean absolute deviation (MAD), root-mean-square deviation (RMSD), normalised MAD (NMAD), deviation span (Δ_{error}), maximum (max) and minimum deviation (min). The NMAD is defined as the ratio between the MAD for a set and its average absolute reaction energy. For all test sets, the def2-QZVP atomic-orbital basis set was used, with additional diffuse functions for the G21EA, WATER27, AHB21, and IL16 sets. All values are in kcal/mol, except for the dimensionless NMAD.

set	MD	MAD	RMSD	NMAD	Δ_{error}	max	min
SIE4x4	19.16	19.16	22.08	0.57	39.94	43.59	3.65
ACONF	1.10	1.10	1.23	0.60	1.78	2.17	0.39
ADIM6	−5.96	5.96	6.51	1.77	7.62	−2.38	−9.99
AHB21	1.77	1.77	1.90	0.08	2.84	3.34	0.50
AL2X6	−11.40	11.40	11.89	0.32	10.25	−6.68	−16.93
ALK8	−7.92	7.92	10.89	0.13	20.24	−0.23	−20.47
ALKBDE10	−1.79	4.62	5.44	0.05	18.59	8.29	−10.30
AMINO20x4	−0.20	0.78	0.99	0.32	4.99	2.68	−2.30
BH76	−4.84	4.90	5.72	0.26	13.30	1.24	−12.06
BHDIV10	−0.66	3.08	3.85	0.07	12.24	5.48	−6.76
BHPERI	4.77	5.67	6.62	0.27	18.30	11.54	−6.76
BHROT27	0.18	0.33	0.48	0.05	1.42	1.11	−0.31
BSR36	−12.41	12.41	14.06	0.77	28.64	−3.19	−31.82
BUT14DIOL	−0.46	0.63	0.68	0.23	2.12	0.93	−1.19
C60ISO	−2.49	2.90	4.11	0.03	9.25	0.93	−8.32
CARBHB12	−1.01	1.03	1.25	0.17	2.69	0.14	−2.56
CDIE20	1.34	1.34	1.53	0.33	2.87	2.83	−0.04
CHB6	1.18	1.54	2.08	0.06	5.25	4.42	−0.83
DARC	20.72	20.72	21.03	0.64	11.86	24.32	12.46
DC13	6.80	19.03	24.31	0.35	83.21	39.71	−43.50
DIPCS10	−1.11	4.78	5.92	0.01	20.69	10.80	−9.89
FH51	4.24	5.41	7.04	0.17	41.10	20.51	−20.58
G21EA	1.45	2.27	3.08	0.07	11.54	9.26	−2.28
G21IP	0.13	3.64	4.65	0.01	18.79	11.86	−6.93
G2RC	3.15	4.03	5.01	0.08	15.08	9.89	−5.18
HAL59	−2.27	2.32	2.76	0.51	10.37	1.31	−9.06
HEAVY28	−1.63	1.63	1.71	1.31	2.05	−0.66	−2.71
HEAVYSB11	−9.68	9.68	10.22	0.17	10.02	−5.70	−15.73
ICONF	−0.03	0.65	0.98	0.20	4.87	2.47	−2.39
IDISP	5.42	19.17	22.33	1.35	60.76	41.61	−19.15
IL16	5.24	5.24	5.31	0.05	3.28	7.36	4.08
INV24	−2.11	2.17	2.52	0.07	5.60	0.66	−4.94
ISO34	−0.63	2.91	4.16	0.20	24.08	13.03	−11.05
ISOL24	−6.41	11.75	18.35	0.54	98.68	35.44	−63.24
MB16-43	−73.12	73.12	76.81	0.18	105.60	−28.38	−133.98
MCONF	−2.90	2.94	3.34	0.59	5.32	0.34	−4.97
NBPRC	5.87	7.16	9.63	0.26	28.14	24.05	−4.08
PA26	2.95	3.03	3.93	0.02	10.55	9.76	−0.79
PArel	−0.20	1.42	2.06	0.31	10.72	5.66	−5.06
PCONF21	−0.51	4.32	4.95	2.67	14.85	8.11	−6.74
PNICO23	−2.41	2.41	2.53	0.56	2.87	−1.44	−4.31
PX13	−2.60	2.60	2.73	0.08	2.72	−1.21	−3.93
RC21	−2.45	3.44	4.94	0.10	20.65	4.93	−15.71
RG18	−1.01	1.01	1.26	1.74	2.53	−0.17	−2.70
RSE43	−2.04	2.04	2.29	0.27	4.42	−0.71	−5.13
S22	−4.72	4.72	5.89	0.65	14.34	−0.73	−15.08
S66	−4.04	4.04	4.59	0.74	9.93	−0.68	−10.61
SCONF	−0.60	1.10	1.27	0.24	4.56	2.53	−2.03
TAUT15	−0.28	1.11	1.30	0.36	3.65	1.69	−1.96
UPU23	2.32	2.89	4.20	0.51	13.03	11.26	−1.78
W4-11	−4.88	5.81	7.99	0.02	36.12	7.84	−28.27
WATER27	−11.53	11.56	17.59	0.14	46.61	0.29	−46.32
WCPT18	−0.34	1.02	1.20	0.03	4.07	1.85	−2.22
YBDE18	−10.92	10.98	12.60	0.22	22.60	0.55	−22.05
BH76RC	−0.16	2.74	3.31	0.13	12.36	5.87	−6.49

Table S13: Statistical analysis of the LDA DFA for all 55 test sets of the GMTKN55 database. The statistical key data are: mean deviation (MD), mean absolute deviation (MAD), root-mean-square deviation (RMSD), normalised MAD (NMAD), deviation span (Δ_{error}), maximum (max) and minimum deviation (min). The NMAD is defined as the ratio between the MAD for a set and its average absolute reaction energy. For all test sets, the def2-QZVP atomic-orbital basis set was used, with additional diffuse functions for the G21EA, WATER27, AHB21, and IL16 sets. All values are in kcal/mol, except for the dimensionless NMAD.

set	MD	MAD	RMSD	NMAD	Δ_{error}	max	min
SIE4x4	27.64	27.64	30.76	0.82	49.71	51.32	1.61
ACONF	−0.36	0.36	0.41	0.20	0.67	−0.08	−0.76
ADIM6	1.05	1.05	1.10	0.31	0.88	1.48	0.60
AHB21	−5.54	5.54	5.73	0.25	5.36	−2.96	−8.32
AL2X6	6.08	6.08	6.30	0.17	4.66	8.22	3.57
ALK8	6.38	7.22	8.98	0.12	18.54	15.54	−3.00
ALKBDE10	22.77	22.77	25.50	0.23	38.55	49.40	10.85
AMINO20x4	0.56	1.04	1.37	0.43	5.60	3.91	−1.69
BH76	−15.29	15.39	17.54	0.83	53.72	3.29	−50.43
BHDIV10	−13.11	13.61	15.71	0.30	28.75	2.37	−26.38
BHPERI	−12.64	12.64	13.29	0.61	16.64	−1.47	−18.11
BHROT27	0.97	1.05	1.40	0.17	4.01	3.20	−0.82
BSR36	0.41	1.60	2.04	0.10	10.52	3.97	−6.55
BUT14DIOL	2.10	2.11	2.19	0.75	3.04	2.85	−0.20
C60ISO	−10.00	10.00	12.34	0.10	21.21	−0.80	−22.01
CARBHB12	4.35	4.35	4.99	0.72	7.35	8.56	1.21
CDIE20	1.74	1.75	1.97	0.43	3.21	3.06	−0.15
CHB6	−2.91	2.91	2.97	0.11	1.87	−2.11	−3.98
DARC	−11.48	11.48	12.18	0.35	12.94	−6.78	−19.72
DC13	−6.44	18.65	23.63	0.34	82.81	31.23	−51.58
DIPCS10	−0.51	6.63	7.94	0.01	25.84	9.81	−16.03
FH51	−3.67	6.61	8.94	0.21	42.16	17.30	−24.86
G21EA	7.46	7.46	8.52	0.22	16.56	16.73	0.17
G21IP	3.09	5.18	6.29	0.02	26.74	12.18	−14.56
G2RC	−6.16	12.88	16.41	0.25	62.79	22.75	−40.05
HAL59	3.26	3.28	4.40	0.71	12.33	11.94	−0.39
HEAVY28	1.11	1.11	1.28	0.90	2.21	2.59	0.37
HEAVYSB11	12.93	12.93	14.93	0.22	21.63	23.59	1.97
ICONF	0.53	0.70	0.89	0.21	2.46	1.67	−0.79
IDISP	−0.18	2.98	3.82	0.21	12.32	7.07	−5.25
IL16	−5.60	5.60	5.62	0.05	2.05	−4.50	−6.55
INV24	−2.65	2.91	4.01	0.09	12.46	1.24	−11.22
ISO34	−0.28	2.18	2.99	0.15	14.15	7.86	−6.29
ISOL24	2.38	5.31	7.29	0.24	30.31	15.75	−14.56
MB16-43	72.39	72.81	80.90	0.18	163.80	156.68	−7.13
MCONF	0.70	1.05	1.33	0.21	3.65	2.57	−1.08
NBPRC	−6.73	9.60	11.26	0.35	32.23	9.46	−22.77
PA26	−4.93	4.93	5.58	0.03	10.87	−0.42	−11.29
PArel	1.02	3.25	4.25	0.70	19.22	9.10	−10.12
PCONF21	−0.63	1.67	2.31	1.03	7.37	2.63	−4.74
PNICO23	3.49	3.49	4.38	0.82	12.16	12.67	0.52
PX13	−24.69	24.69	25.23	0.74	19.75	−17.82	−37.57
RC21	15.49	16.63	18.93	0.47	37.87	32.35	−5.53
RG18	0.47	0.47	0.60	0.81	1.36	1.54	0.17
RSE43	−5.02	5.02	5.59	0.66	10.42	−1.31	−11.74
S22	2.19	2.21	3.27	0.30	8.62	8.44	−0.18
S66	1.94	1.97	2.66	0.36	8.87	8.52	−0.35
SCONF	1.74	3.11	3.40	0.68	10.69	4.18	−6.51
TAUT15	1.69	3.22	5.28	1.06	16.69	12.15	−4.54
UPU23	0.24	0.54	0.70	0.09	2.50	1.62	−0.88
W4-11	59.01	59.01	66.73	0.19	131.82	135.47	3.65
WATER27	38.49	40.08	55.36	0.49	151.08	129.66	−21.42
WCPT18	−17.56	17.56	18.82	0.50	20.81	−9.33	−30.13
YBDE18	13.32	13.36	16.27	0.27	30.60	30.23	−0.36
BH76RC	−0.63	8.24	10.79	0.39	51.92	35.52	−16.40

References

(S1) Slater, J. C. *Phys. Rev.* **1951**, *81*, 385–390.

(S2) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200–1211.

(S3) Reiher, M.; Salomon, O.; Hess, B. A. *Theor. Chem. Acc.* **2001**, *107*, 48–55.

(S4) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51–57.

(S5) Goerigk, L.; Hansen, A.; Bauer, C.; Ehrlich, S.; Najibi, A.; Grimme, S. *Phys. Chem. Chem. Phys.* **2017**, *19*, 32184–32215.

(S6) Neese, F. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012**, *2*, 73–78.

(S7) ORCA – an ab initio, density functional and semiempirical program package, V. 4.0.1, F. Neese, MPI für Chemische Energiekonversion, Mülheim a. d. Ruhr (Germany), 2017.

(S8) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(S9) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

(S10) Goerigk, L.; Grimme, S. *J. Chem. Theory Comput.* **2010**, *6*, 107–126.

(S11) Goerigk, L.; Grimme, S. *J. Chem. Theory Comput.* **2011**, *7*, 291–309.

(S12) Goerigk, L.; Grimme, S. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6670–6688.

(S13) Mehta, N.; Casanova-Páez, M.; Goerigk, L. *Phys. Chem. Chem. Phys.* **2018**, *20*, 23175–23194.

(S14) Najibi, A.; Goerigk, L. *J. Chem. Theory Comput.* **2018**, *14*, 5725–5738.

(S15) Izsak, R.; Neese, F. *J. Chem. Phys.* **2011**, *135*, 144105.

(S16) http://www.marcelswart.eu/dft-poll/paco_coefficients.html.

(S17) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

(S18) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456–1465.

(S19) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158–6170.

(S20) Ernzerhof, M.; Scuseria, G. E. *J. Chem. Phys.* **1999**, *110*, 5029–5036.

(S21) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

(S22) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.

(S23) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(S24) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.

(S25) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822–8824.

(S26) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.

(S27) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(S28) Grimme, S. *J. Chem. Phys.* **2006**, *124*, 034108.

(S29) Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787–1799.

(S30) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101.

(S31) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003**, *119*, 12129–12137.

(S32) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

(S33) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem Phys. Lett.* **1989**, *157*, 200–206.

(S34) Handy, N. C.; Cohen, A. J. *Mol. Phys.* **2001**, *99*, 403–412.

(S35) Lynch, B. J.; Fast, P. L.; Harris, M.; Truhlar, D. G. *J. Phys. Chem. A* **2000**, *104*, 4811–4815.

(S36) Schipper, P.; Gritsenko, O.; Van Gisbergen, S.; Baerends, E. *J. Chem. Phys.* **2000**, *112*, 1344–1352.

(S37) Swart, M.; Solà, M.; Bickelhaupt, F. M. *J. Chem. Phys.* **2009**, *131*, 094103.

(S38) Dirac, P. A. M. *Proc. R. Soc. Lond. A* **1929**, *123*, 714–733.

(S39) Perdew, J. P. *Phys. Rev. B* **1992**, *45*, 13244–13249.

(S40) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Constantin, L. A.; Sun, J. *Phys. Rev. Lett.* **2009**, *103*, 026403.

(S41) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364–382.

(S42) Perdew, J. P. *in Proceedings of the 21st Annual International Symposium on the Electronic Structure of Solids (P. Ziesche and H. Eschrig, Eds.)*; Akademie Verlag: Berlin, 1991; p 11.

(S43) Zhang, Y.; Yang, W. *Phys. Rev. Lett.* **1998**, *80*, 890–890.

(S44) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. *J. Chem. Phys.* **2003**, *118*, 8207–8215.

(S45) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. *J. Chem. Phys* **2006**, *124*, 219906.

(S46) Lin, Y.-S.; Li, G.-D.; Mao, S.-P.; Chai, J.-D. *J. Chem. Theory Comput. Chem.* **2013**, *9*, 263–272.

(S47) Furche, F. *J. Chem. Phys.* **2008**, *129*, 114105.

(S48) Hammer, B.; Hansen, L. B.; Norskov, J. K. *Phys. Rev. B* **1999**, *59*, 7413–7421.

(S49) Vydrov, O. A.; Scuseria, G. E. *J. Chem. Phys.* **2006**, *125*, 234109.

(S50) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372–1377.

(S51) Web of Science Core Collection, see http://www.webofscience.com.