Supporting Information: Benchmarking London dispersion corrected density functional theory for noncovalent ion-π interactions

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Availability of program packages

The *xtb*[S1] and *crest*[S2] program packages are available free of charge for academic use. Collected atomic Cartesian coordinates (XYZ format) of all benchmark structures are available as additional supplementary material (geometries.zip). The nomenclature of the benchmark set is the following. For systems **1-17** the complex is termed AB and A/B are the respective fragments of which B is the ion. For systems **18** and **19**, A and B are the respective conformers. The CHRG files contain the molecular charge.

Statistical measures

For statistical analysis of a set $\{x_1, \ldots, x_n\}$ of data points with references $\{r_1, \ldots, r_n\}$ we use the following measures:

- Average : $\overline{x} = \frac{1}{n} \sum_i x_i$
- Mean deviation (MD): $MD = \frac{1}{n} \sum_i (\mathrm{x}_i - \mathrm{r}_i)$
- Mean absolute deviation (MAD): $MAD = \frac{1}{n} \sum_i |\mathrm{x}_i - \mathrm{r}_i|$
- Standard deviation (SD) : $\mathrm{SD} = \sqrt{\frac{\sum_i (x_i - \overline{x})^2}{n}}$
- relative MAD (*rel*MAD): $relMAD = \frac{1}{n} \sum_i \frac{|\mathrm{x}_i - \mathrm{r}_i|}{\mathrm{r}_i}$

Detailed results

Results of the tested methods

For all DFAs and HF, a large def2-QZVPP basis set was employed. The composite 3c methods have their own adjusted basis set. For MP2, a CBS extrapolation was performed. For all systems including alkali metals (**1-6**), a counterpoise (CP) correction was additionally applied.

Table S1: Interaction energies in kcal mol^{-1} for the IONPI19 benchmark calculated with the listed WFT methods and different LD corrections.

System	Ref.	HF			MP2/CBS
		D3	D4	NL	–
1	-39.09	-42.30	-37.36	-41.64	-39.36
2	-25.63	-27.00	-27.00	-26.99	-25.71
3	-19.90	-14.78	-16.85	-19.79	-20.49
4	-14.81	-14.85	-14.51	-13.35	-15.31
5	-25.65	-34.19	-23.13	-25.94	-25.11
6	-19.74	-25.18	-18.62	-19.67	-19.84
7	-21.51	-22.40	-20.21	-19.36	-24.92
8	-14.57	-13.82	-15.56	-14.60	-15.08
9	-10.41	-10.23	-12.72	-11.04	-10.89
10	-1.93	0.33	-2.40	-0.83	-2.81
11	-5.70	-4.21	-6.86	-5.36	-6.48
12	-18.56	-17.38	-19.18	-17.61	-19.07
13	-33.66	-32.41	-34.69	-32.91	-35.59
14	-45.03	-44.38	-46.92	-45.45	-48.49
15	-29.43	-28.84	-30.62	-30.33	-32.54
16	-26.27	-25.25	-27.80	-25.72	-29.83
17	-37.17	-39.57	-40.86	-43.73	-52.40
18	-5.01	-5.66	-4.89	-5.59	-6.22
19	-2.42	-2.87	-2.81	-2.86	-2.66

Table S2: Interaction energies in kcal mol^{-1} for the IONPI19 benchmark calculated with the listed double hybrid functionals and different LD corrections.

System	Ref.	PWPB95			revDSD-BLYP	revDSD-PBEP86	B2PLYP		
		D3	D4	NL	D4	D4	D3	D4	NL
1	-39.09	-41.86	-40.56	-41.49	-38.39	-38.53	-40.30	-39.09	-39.96
2	-25.63	-27.47	-26.31	-26.78	-25.37	-25.15	-26.33	-25.63	-25.80
3	-19.90	-20.34	-18.52	-19.66	-17.84	-18.14	-19.15	-18.18	-19.06
4	-14.81	-16.80	-15.75	-16.03	-14.95	-14.75	-15.83	-15.15	-15.11
5	-25.65	-28.67	-27.14	-27.82	-24.97	-25.03	-27.58	-25.74	-26.32
6	-19.74	-21.66	-20.00	-20.67	-19.23	-19.25	-21.24	-19.76	-20.10
7	-21.51	-22.55	-22.22	-22.18	-21.41	-21.49	-22.64	-21.99	-21.69
8	-14.57	-14.30	-14.51	-14.58	-14.86	-14.49	-14.39	-14.65	-14.70
9	-10.41	-10.61	-11.02	-10.87	-11.29	-11.00	-10.77	-11.18	-11.05
10	-1.93	-1.74	-2.14	-1.99	-2.57	-2.36	-2.04	-2.55	-2.36
11	-5.70	-5.55	-5.94	-5.85	-6.37	-6.09	-5.88	-6.37	-6.25
12	-18.56	-18.00	-18.47	-18.44	-18.8	-18.36	-17.88	-18.17	-18.35
13	-33.66	-33.05	-33.74	-33.85	-34.39	-33.72	-33.03	-33.33	-33.84
14	-45.03	-45.29	-45.86	-46.41	-46.08	-45.21	-44.78	-45.10	-45.88
15	-29.43	-28.41	-29.39	-29.70	-30.58	-29.99	-30.08	-30.92	-31.56
16	-26.27	-25.90	-26.28	-26.27	-27.3	-26.71	-27.11	-27.66	-27.42
17	-37.17	-40.62	-37.69	-40.31	-37.19	-37.09	-42.53	-42.25	-42.06
18	-5.01	-5.49	-5.12	-5.48	-4.58	-4.75	-5.28	-5.00	-5.16
19	-2.42	-2.48	-2.45	-2.49	-2.31	-2.36	-2.31	-2.31	-2.30

Table S3: Interaction energies in kcal mol^{-1} for the IONPI19 benchmark calculated with the listed range-separated hybrid functionals and different LD corrections as well as two Minnesota-type hybrid functionals.

System	Ref.	ωB97M			ωB97X			M06-2x	MN15
		D3	D4	NL	D3	D4	NL	–	–
1	-39.09	-40.71	-39.52	-41.33	-37.22	-37.30	-41.21	-42.20	-39.88
2	-25.63	-25.73	-25.57	-26.72	-23.89	-24.42	-26.55	-27.23	-25.53
3	-19.90	-17.51	-17.34	-19.78	-17.71	-18.63	-19.58	-20.30	-19.20
4	-14.81	-14.66	-14.56	-15.38	-13.37	-13.28	-15.06	-15.87	-14.71
5	-25.65	-28.11	-25.89	-27.24	-23.91	-23.47	-26.75	-28.06	-26.23
6	-19.74	-20.83	-19.43	-20.84	-18.62	-18.47	-20.46	-21.04	-19.50
7	-21.51	-22.38	-21.23	-21.62	-20.46	-19.79	-20.65	-22.02	-21.85
8	-14.57	-13.76	-14.24	-14.79	-13.34	-14.29	-14.34	-15.07	-15.38
9	-10.41	-10.55	-11.35	-11.55	-10.24	-11.30	-11.11	-11.45	-11.75
10	-1.93	-1.42	-2.33	-2.39	-1.37	-2.34	-2.02	-1.96	-2.64
11	-5.70	-5.34	-6.21	-6.46	-5.13	-6.19	-6.02	-6.15	-6.61
12	-18.56	-17.13	-17.66	-18.40	-16.30	-17.78	-17.95	-19.07	-18.77
13	-33.66	-31.70	-32.30	-34.00	-30.32	-33.09	-33.22	-35.09	-34.52
14	-45.03	-43.16	-43.78	-46.47	-41.69	-44.88	-45.35	-48.77	-47.99
15	-29.43	-28.87	-30.07	-31.01	-29.08	-30.31	-30.34	-29.38	-29.22
16	-26.27	-25.69	-26.61	-27.14	-25.16	-26.48	-26.24	-26.40	-26.47
17	-37.17	-40.72	-40.10	-42.27	-41.18	-37.05	-40.49	-35.96	-38.89
18	-5.01	-5.70	-5.19	-5.67	-5.64	-5.11	-5.48	-5.53	-5.88
19	-2.42	-2.59	-2.57	-2.62	-2.52	-2.38	-2.63	-2.47	-2.60

Table S4: Interaction energies in kcal mol^{-1} for the IONPI19 benchmark calculated with the listed hybrid functionals and different LD corrections.

System	Ref.	B3LYP			PW6B95			PBE0		
		D3	D4	NL	D3	D4	NL	D3	D4	NL
1	-39.09	-40.45	-38.18	-40.25	-42.53	-41.38	-42.34	-42.07	-40.97	-42.14
2	-25.63	-26.57	-25.98	-26.17	-27.86	-27.34	-27.54	-27.07	-26.85	-27.21
3	-19.90	-18.47	-17.55	-19.24	-20.06	-18.84	-20.00	-19.34	-18.95	-20.25
4	-14.81	-16.18	-15.67	-15.35	-17.03	-16.62	-16.58	-16.31	-16.15	-16.25
5	-25.65	-28.97	-25.40	-26.79	-29.61	-28.14	-28.79	-29.16	-27.40	-28.22
6	-19.74	-22.19	-19.88	-20.46	-21.91	-20.69	-21.16	-21.88	-20.80	-21.3
7	-21.51	-23.55	-22.34	-21.80	-22.61	-22.36	-22.18	-23.48	-22.84	-23.02
8	-14.57	-14.03	-14.75	-14.78	-14.22	-14.65	-14.70	-13.52	-13.99	-14.37
9	-10.41	-10.59	-11.63	-11.34	-10.60	-11.19	-11.05	-10.18	-10.81	-11.01
10	-1.93	-1.67	-2.85	-2.40	-1.62	-2.18	-2.01	-1.22	-1.93	-1.95
11	-5.70	-5.56	-6.72	-6.42	-5.44	-6.01	-5.92	-5.04	-5.74	-5.93
12	-18.56	-17.00	-17.90	-18.22	-17.65	-18.44	-18.41	-17.09	-17.66	-18.36
13	-33.66	-31.48	-32.60	-33.54	-32.40	-33.61	-33.76	-31.37	-32.15	-33.64
14	-45.03	-42.78	-44.08	-45.59	-44.21	-45.50	-46.12	-42.14	-43.13	-45.33
15	-29.43	-29.09	-30.65	-31.52	-27.79	-28.82	-29.38	-28.27	-29.37	-30.53
16	-26.27	-26.57	-27.83	-27.06	-25.34	-25.91	-25.89	-25.74	-26.63	-26.86
17	-37.17	-42.48	-41.96	-39.58	-38.81	-35.86	-37.74	-38.92	-38.66	-38.44
18	-5.01	-5.33	-4.80	-5.07	-5.32	-4.90	-5.28	-5.35	-5.03	-5.35
19	-2.42	-2.23	-2.23	-2.23	-2.36	-2.35	-2.38	-2.41	-2.42	-2.45

Table S5: Interaction energies in kcal mol^{-1} for the IONPI19 benchmark calculated with the listed meta GGA functionals and different LD corrections.

System	Ref.	B97M			r^2SCAN			TPSS			M06-L
		D3	D4	NL	D3	D4	NL	D3	D4	NL	–
1	-39.09	-39.63	-35.58	-37.42	-38.98	-38.65	-39.05	-40.50	-38.82	-40.69	-35.37
2	-25.63	-27.03	-24.02	-24.30	-26.15	-26.04	-26.35	-25.93	-25.77	-26.22	-22.63
3	-19.90	-19.35	-16.57	-18.19	-18.89	-18.72	-19.40	-18.08	-17.64	-19.49	-16.78
4	-14.81	-17.36	-14.52	-14.35	-15-98	-15.88	-16.19	-16.21	-16.17	-16.20	-13.58
5	-25.65	-29.09	-24.02	-25.26	-26.20	-25.63	-26.00	-29.03	-26.45	-27.75	-24.10
6	-19.74	-23.54	-18.93	-19.64	-21.11	-20.72	-21.15	-21.60	-20.14	-20.91	-18.43
7	-21.51	-22.73	-22.14	-21.57	-23.49	-23.03	-23.08	-24.81	-24.27	-24.38	-21.26
8	-14.57	-13.41	-14.14	-14.02	-13.51	-13.61	-13.92	-13.33	-14.16	-14.54	-12.52
9	-10.41	-10.91	-11.99	-11.54	-10.77	-10.91	-11.13	-10.27	-11.38	-11.46	-10.22
10	-1.93	-1.95	-3.15	-2.67	-2.02	-2.20	-2.32	-1.60	-2.77	-2.63	-1.77
11	-5.70	-5.74	-6.89	-6.51	-5.80	-5.97	-6.17	-5.28	-6.46	-6.54	-5.29
12	-18.56	-17.31	-18.06	-17.88	-17.57	-17.70	-18.15	-16.87	-17.96	-18.72	-16.19
13	-33.66	-31.95	-32.93	-32.99	-32.27	-32.41	-33.33	-30.77	-32.33	-34.00	-30.35
14	-45.03	-43.35	-44.43	-44.94	-43.54	-43.74	-45.03	-41.11	-43.09	-45.66	-43.61
15	-29.43	-28.89	-30.85	-31.25	-30.16	-30.57	-31.01	-27.63	-29.35	-30.71	-29.66
16	-26.27	-26.09	-27.78	-27.11	-26.28	-26.46	-26.58	-25.57	-27.14	-27.18	-25.70
17	-37.17	-37.60	-38.95	-39.27	-38.85	-37.97	-36.52	-39.64	-39.96	-39.50	-34.67
18	-5.01	-4.98	-4.73	-5.07	-5.23	-5.04	-5.01	-5.17	-4.82	-5.28	-5.17
19	-2.42	-1.96	-1.97	-1.99	-2.08	-2.07	-2.06	-2.05	-2.08	-2.14	-1.86

Table S6: Interaction energies in kcal mol^{-1} for the IONPI19 benchmark calculated with the listed GGA functional and different LD corrections.

System	Ref.	PBE		
		D3	D4	NL
1	-39.09	-40.43	-39.25	-40.60
2	-25.63	-26.06	-26.06	-26.39
3	-19.90	-18.32	-18.20	-19.58
4	-14.81	-16.38	-16.47	-16.51
5	-25.65	-28.71	-26.83	-27.77
6	-19.74	-21.62	-20.64	-21.24
7	-21.51	-24.54	-24.08	-24.23
8	-14.57	-13.44	-14.09	-14.51
9	-10.41	-10.57	-11.42	-11.61
10	-1.93	-2.08	-3.00	-3.03
11	-5.70	-5.72	-6.64	-6.84
12	-18.56	-16.95	-17.74	-18.38
13	-33.66	-30.86	-32.01	-33.42
14	-45.03	-40.88	-42.34	-44.48
15	-29.43	-28.60	-29.9	-31.29
16	-26.27	-25.79	-27.06	-27.41
17	-37.17	-37.16	-37.61	-38.45
18	-5.01	-5.06	-4.76	-5.19
19	-2.42	-2.04	-2.06	-2.10

Table S7: **Interaction energies in kcal mol^{-1} for the IONPI19 benchmark calculated with the listed composite (3C) DFT methods.**

System	Ref.	PBEh-3c	B97-3c	r^2SCAN-3c
1	-39.09	-39.95	-37.34	-37.87
2	-25.63	-27.43	-24.94	-24.95
3	-19.9 0	-20.32	-15.82	-16.77
4	-14.81	-16.94	-15.82	-16.60
5	-25.65	-27.75	-26.90	-26.52
6	-19.74	-23.47	-21.97	-21.69
7	-21.51	-23.66	-25.51	-23.86
8	-14.57	-16.84	-15.56	-15.43
9	-10.41	-13.35	-11.45	-12.15
10	-1.93	-2.68	-2.52	-3.07
11	-5.70	-7.56	-6.30	-7.16
12	-18.56	-25.35	-18.58	-18.75
13	-33.66	-46.57	-35.02	-35.27
14	-45.03	-62.26	-46.49	-46.71
15	-29.43	-32.81	-27.75	-30.83
16	-26.27	-29.24	-26.39	-26.28
17	-37.17	-39.74	-39.76	-39.07
18	-5.01	-5.13	-5.20	-5.37
19	-2.42	-2.85	-2.22	-2.29

Table S8: Interaction energies in kcal mol^{-1} for the IONPI19 benchmark calculated with the listed SQM and FF methods.

System	Ref.	PM6-D3H4X	PM7	GFN2-xTB	GFN1-xTB	GFN-FF
1	-39.09	-12.23	-36.61	-36.55	-40.77	–
2	-25.63	-29.04	-15.42	-28.48	-14.76	-30.84
3	-19.90	-20.35	-6.62	-24.72	-20.47	-60.7
4	-14.81	-26.78	-19.74	-23.60	-15.16	-17.98
5	-25.65	4.15	-23.89	-30.44	-41.87	–
6	-19.74	-33.71	-16.73	-29.43	-21.41	-12.13
7	-21.51	-14.63	-3.03	-20.11	-13.69	-7.31
8	-14.57	-9.63	-5.49	-19.75	-16.65	-14.14
9	-10.41	-8.45	-6.03	-9.60	-7.53	-1.9
10	-1.93	-0.17	-5.43	-1.12	2.37	3.54
11	-5.70	-3.55	-6.54	-4.76	-1.58	0.81
12	-18.56	-19.15	-6.54	-23.77	-10.73	-8.77
13	-33.66	-35.59	-13.16	-43.85	-20.47	-17.76
14	-45.03	-49.41	-19.08	-61.93	-29.31	-26.39
15	-29.43	-22.93	56.84	-26.20	-18.27	-11.09
16	-26.27	-20.40	-1.59	-24.90	-22.17	-10.73
17	-37.17	-37.15	11.39	-29.60	-27.24	-23.02
18	-5.01	-5.03	-3.88	-2.43	-1.73	0.86
19	-2.42	-4.01	0.10	-1.61	-0.58	0.30

Table S9: **CP uncorrected interaction energies in kcal mol^{-1} for systems 1-6 of the IONPI19 benchmark calculated with the listed methods. The MAD for the entire test set is also given.**

Method	1	2	3	4	5	6	MAD
HF-NL	-41.66	-27.01	-19.82	-13.42	-26.02	-19.75	1.12
double hybrids							
PWPB95-D4	-40.79	-27.08	-18.93	-16.59	-27.43	-20.89	0.65
revDSD-BLYP-D4	-38.79	-26.97	-18.61	-16.68	-25.45	-21.06	0.72
revDSD-PBEP86-D4	-38.95	-26.72	-18.91	-16.44	-25.52	-21.04	0.45
B2PLYP-D4	-39.32	-26.63	-18.66	-16.25	-26.04	-20.93	0.89
hybrids							
ωB97M-D4	39.54	-25.62	-17.41	-14.69	-25.99	-19.56	0.73
ωB97X-V	-41.23	-26.60	-19.65	-15.18	-26.83	-20.58	0.75
B3LYP-NL	-40.29	-26.26	-19.34	-15.51	-26.89	-20.62	0.76
PW6B95-D4	-41.41	-27.43	-18.94	-16.76	-28.22	-20.83	0.85
PBE0-D4	-41.01	-26.92	-19.03	-16.27	-27.48	-20.92	0.90
MN15	-39.90	-25.73	-19.40	-14.97	-26.29	-19.78	0.71
M06-2x	-42.22	-27.26	-20.35	-15.96	-28.14	-21.13	1.07
(meta-) GGAs							
B97M-V	-37.44	-24.33	-18.24	-14.45	-25.35	-19.75	0.80
r^2SCAN-D4	-38.67	-26.08	-18.77	-15.98	-25.71	-20.82	0.72
TPSS-D4	-38.90	-25.88	-17.76	-16.33	-26.57	-20.30	1.02
M06-L	-35.51	-22.81	-16.93	-13.76	-24.26	-18.64	1.43
PBE-D4	-39.31	-26.17	-18.33	-16.65	-26.95	-20.83	1.06

Table S10: DLPNO-CCSD(T)/*TightPNO*/def2-SVP diagnostic for nondynamical correlation and multi-reference character for the systems of the IONPI19 set.

System	T1 diagnostic			max. T2 amplitudes		
	AB	A	B	AB	A	B
1	0.0101	0.0106	0.0005	0.0386	0.0430	0.0446
2	0.0093	0.0105	0.0004	0.0388	0.0191	0.0667
3	0.0092	0.0104	0.0016	0.0385	0.0389	0.0409
4	0.0157	0.0172	0.0004	0.0513	0.0439	0.0667
5	0.0152	0.0151	0.0005	0.0430	0.0491	0.0446
6	0.0146	0.0155	0.0004	0.0340	0.0468	0.0667
7	0.0103	0.0106	0.0092	0.0106	0.0672	0.0031
8	0.0111	0.0120	0.0043	0.0409	0.0365	0.0354
9	0.0150	0.0159	0.0043	0.0510	0.0465	0.0354
10	0.0144	0.0151	0.0043	0.0528	0.0513	0.0354
11	0.0148	0.0155	0.0043	0.0437	0.0430	0.0354
12	0.0148	0.0155	0.0043	0.0465	0.0468	0.0354
13	0.0152	0.0155	0.0043	0.0466	0.0468	0.0354
14	0.0153	0.0156	0.0043	0.0495	0.0464	0.0354
15	0.0150	0.0144	0.0167	0.0622	0.0622	0.0500
16	0.0147	0.0144	0.0155	0.0622	0.0622	0.0608
17	0.0125	0.0126	0.0132	0.0125	0.0126	0.0362
18	–	0.0114	0.0114	–	0.0494	0.0507
19	–	0.0106	0.0106	–	0.0405	0.0398

IONPI17 subset statistics

Table S11: Statistical evaluation of all tested low-cost DFT, SQM, and FF methods on the IONPI17 subset. The MD, MAD and SD are given in kcal mol^{-1}, the *rel*MAD is given in %.

Method	MD	MAD	SD	*rel*MAD
composite (3c) DFT				
PBEh-3c	-3.93	3.93	4.49	18.88
B97-3c	-0.53	1.50	1.86	8.69
r^2SCAN-3c	-0.82	1.41	1.41	10.86
SQM				
PM6-D3H4X	3.44	7.77	11.21	40.05
PM7	16.46	17.46	22.21	75.93
GFN2-xTB	-2.93	5.12	6.14	24.10
GFN1-xTB	4.58	7.26	7.76	42.87
FF				
GFN-FF*	6.07	11.86	14.07	80.28

Table S12: Statistical evaluation of all tested WFT and DFT methods on the IONPI17 subset. The MD, MAD and SD are given in kcal mol^{-1}, the *rel*MAD is given in %.

Method	LD	MD	MAD	SD	*rel*MAD
MP2/CBS	–	-2.05	2.11	3.65	10.26
	D3	-0.44	2.14	3.13	16.38
HF	D4	-0.37	1.55	1.80	8.99
	NL	-0.31	1.19	1.95	7.88
double hybrids					
	D3	-0.81	1.18	1.41	5.42
PWPB95	D4	-0.38	0.57	0.67	3.27
	NL	-0.81	0.86	0.99	3.54
revDSD-BLYP	D4	-0.15	0.66	0.83	5.23
revDSD-PBEP86	D4	0.10	0.41	0.58	3.43
	D3	-0.74	1.03	1.43	4.49
B2PLYP	D4	-0.51	0.80	1.38	5.45
	NL	-0.73	0.86	1.24	4.81
hybrids					
	D3	0.05	1.20	1.58	6.34
ωB97M	D4	0.05	0.81	1.17	4.92
	NL	-1.08	1.11	1.23	6.11
	D3	1.18	1.65	1.62	8.50
ωB97X	D4	0.59	0.93	0.97	5.86
	NL	-0.49	0.78	1.03	3.55
	D3	-0.50	1.53	2.01	6.84
B3LYP	D4	-0.41	1.13	1.54	8.07
	NL	-0.67	0.81	0.77	5.23
	D3	-0.66	1.39	1.70	6.69
PW6B95	D4	-0.50	0.91	1.10	4.93
	NL	-0.85	0.92	1.10	4.26
	D3	-0.22	1.58	1.87	8.79
PBE0	D4	-0.29	0.99	1.17	4.08
	NL	-0.93	0.98	0.95	4.37
MN15	–	-0.59	0.75	0.87	5.84
M06-2x	–	-1.00	1.15	1.22	4.93
(meta-) GGAs					
	D3	-0.40	1.24	1.65	5.82
B97M	D4	0.24	1.34	1.64	10.07
	NL	0.01	0.89	1.12	6.56
	D3	-0.15	0.86	1.07	4.15
r^2SCAN	D4	-0.07	0.77	0.91	4.47
	NL	0.13	1.06	1.58	7.66
	D3	0.05	1.71	2.11	8.07
TPSS	D4	-0.28	1.09	1.39	7.73
	NL	-1.03	1.08	0.86	7.29
M06-L	–	1.58	1.61	1.26	7.40
	D3	0.06	1.43	1.92	6.32
PBE	D4	-0.25	1.12	1.34	8.76
	NL	-0.98	1.14	0.95	9.08

IONPI19 statistics

Table S13: Statistical evaluation of all tested low-cost DFT, SQM, and FF methods on the IONPI19 set. The MD, MAD and SD are given in kcal mol^{-1}, the *rel*MAD is given in %.

Method	MD	MAD	SD	*rel*MAD
composite (3c) DFT				
PBEh-3c	-3.55	3.55	4.39	17.96
B97-3c	-0.48	1.36	1.76	8.41
r^2SCAN-3c	-0.75	1.29	1.35	10.37
SQM				
PM6-D3H4X	3.00	7.04	10.66	39.32
PM7	14.92	15.82	21.45	74.61
GFN2-xTB	-2.44	4.76	5.98	26.03
GFN1-xTB	4.37	6.76	7.34	45.82
FF				
GFN-FF*	6.06	11.86	14.07	80.28

Table S14: Functional mean deviation from the reference values calculated as the average of all tested DFAs (3c methods excluded). For system 1-6 the values are given with and without CP correction.

System	Functional MD	
	CP	w/o CP
1	-0.38	-0.49
2	-0.15	-0.52
3	1.21	1.07
4	-0.53	-0.97
5	-0.63	-0.80
6	-0.27	-0.74
7	-0.62	–
8	0.23	–
9	-0.78	–
10	-0.41	–
11	-0.47	–
12	0.49	–
13	0.55	–
14	0.03	–
15	-0.59	–
16	-0.40	–
17	-1.16	–
18	-0.08	–
19	0.12	–

Table S15: Statistical evaluation of all tested WFT and DFT methods on the IONPI19 set. The MD, MAD and SD are given in kcal mol^{-1}, the *rel*MAD is given in %.

Method	LD	MD	MAD	SD	*rel*MAD
MP2/CBS	–	-1.91	1.97	3.47	10.98
HF	D3	-0.45	1.97	2.95	16.32
	D4	-0.34	1.41	1.70	9.01
	NL	-0.33	1.12	1.84	8.62
double hybrids					
PWPB95	D3	-0.75	1.09	1.35	5.48
	D4	-0.35	0.51	0.64	3.11
	NL	-0.76	0.80	0.95	3.82
revDSD-BLYP	D4	-0.11	0.62	0.79	5.37
revDSD-PBEP86	D4	0.10	0.39	0.55	3.47
B2PLYP	D3	-0.67	0.94	1.36	4.32
	D4	-0.45	0.72	1.32	5.13
	NL	-0.66	0.78	1.19	4.72
hybrids					
ωB97M	D3	0.00	1.12	1.50	6.76
	D4	0.03	0.74	1.10	4.92
	NL	-1.01	1.04	1.18	5.59
ωB97X	D3	-1.02	1.52	1.61	9.48
	D4	0.52	0.84	0.94	5.43
	NL	-0.47	0.73	0.98	4.12
B3LYP	D3	-0.46	1.39	1.90	6.87
	D4	-0.34	1.04	1.46	7.85
	NL	-0.60	0.73	0.76	5.15
PW6B95	D3	-0.57	1.26	1.61	6.44
	D4	-0.44	0.83	1.05	4.68
	NL	-0.78	0.84	1.07	4.19
PBE0	D3	-0.21	1.43	1.77	8.25
	D4	-0.26	0.88	1.10	3.68
	NL	-0.85	0.90	0.93	4.32
MN15	–	-0.59	0.73	0.83	6.53
M06-2x	–	-0.92	1.06	1.17	5.07
(meta-) GGAs					
B97M	D3	-0.34	1.13	1.57	6.24
	D4	0.26	1.24	1.55	10.28
	NL	0.03	0.82	1.06	6.87
r^2SCAN	D3	-0.13	0.80	1.01	4.68
	D4	-0.04	0.71	0.87	4.79
	NL	0.13	0.97	1.49	7.63
TPSS	D3	0.06	1.56	1.99	8.20
	D4	-0.23	1.00	1.32	7.85
	NL	-0.92	1.00	0.88	7.42
M06-L	–	1.44	1.48	1.27	8.01
PBE	D3	0.07	1.30	1.81	6.54
	D4	-0.19	1.03	1.27	8.89
	NL	-0.87	1.05	0.96	9.01

References

(S1) "Semiempirical Extended Tight-Binding Program Package `xtb`", https://github.com/grimme-lab/xtb. Accessed: 2020-06-20.

(S2) Pracht, P.; Bohle, F.; Grimme, S. Automated exploration of the low-energy chemical space with fast quantum chemical methods. *Phys. Chem. Chem. Phys.* **2020**, *22*, 7169–7192.