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

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.

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

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	5	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.		$\omega B97M$			$\omega B97X$		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	ó		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

System	Ref.		B97M			r^2 SCAN			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 S5: Interaction energies in kcal mol^{-1} for the IONPI19 benchmark calculated with the listed meta GGA functionals and different LD corrections.

Table S6:	Interaction	n energies in	kcal mol⁻	$^{-1}$ for the	IONPI19	benchmark	calcu-
lated with	the listed	GGA functio	onal and o	different 1	LD correc	tions.	

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

System	Ref.	PBEh-3c	B97-3c	r^2 SCAN-3c
1	-39.09	-39.95	-37.34	-37.87
2	-25.63	-27.43	-24.94	-24.95
3	-19.90	-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 S7: Interaction energies in kcal mol^{-1} for the IONPI19 benchmark calculated with the listed composite (3C) DFT methods.

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

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							
$\omega B97M-D4$	39.54	-25.62	-17.41	-14.69	-25.99	-19.56	0.73
$\omega B97X-V$	-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^2 SCAN-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 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.

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

System	T	l diagnos	tic	max. T2 amplitudes				
	AB	А	В	AB	А	В		
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 relMAD is given in %.

Method	MD	MAD	SD	relMAD
composite (3c) DFT				
PBEh-3c	-3.93	3.93	4.49	18.88
B97-3c	-0.53	1.50	1.86	8.69
r^2 SCAN-3c	-0.82	1.41	1.41	10.86
\mathbf{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 kcalmol⁻¹, the relMAD is given in %.

MethodLDMADMADSDrel/MADMP2/CBS2.052.113.6510.26MP2/CBS-03-0.442.143.1316.38HF0.4-0.371.551.808.99NU-0.311.191.957.88 double hybrids 3.27PWPB95D3-0.811.181.415.42PWPB95D4-0.380.570.52revDSD-BLYPD4-0.150.660.835.23revDSD-BEP8D4-0.150.801.384.49B2PLYPD4-0.510.801.385.45MB97MD30.051.201.586.34\u00e4-0.730.861.244.81\u00e4D40.050.811.174.92\u00e4NL-1.081.111.236.11\u00e4MA0.590.930.975.86\u00e4NL-0.490.781.033.55\u00e4D40.500.811.174.92\u00e4NL-0.490.781.033.55\u00e4D40.500.911.104.93\u00e4D40.500.911.104.93\u00e4NL-0.670.810.775.23\u00e4NL-0.670.911.104.93\u00e4-0.700.911.10 <td< th=""><th></th><th></th><th></th><th></th><th></th><th></th></td<>						
MP2/CBS2.052.113.6510.26HFD3-0.442.143.1316.38HFD4-0.371.551.808.99NL-0.311.191.957.88double hybridsD3-0.811.181.415.42PWPB95D4-0.380.570.673.27NL-0.810.860.993.54revDSD-BLYPD4-0.150.660.835.23revDSD-PBEP86D40.100.410.583.43B2PLYPD4-0.510.801.385.45M2-0.730.861.244.81b3-0.741.031.434.49B2PLYPD4-0.510.801.385.45M2D4-0.510.801.385.45M2D40.050.811.174.92M31.181.651.628.50M40.050.811.174.92M31.181.651.628.50M40.590.930.975.86NL-0.490.781.033.55B3LYPD40.500.911.104.93M40.550.921.104.26PB6D4-0.290.981.774.92M151.581.611.22M151.001.151.224.37<	Method	LD	MD	MAD	SD	relMAD
HFD3 PA	MP2/CBS	_	-2.05	2.11	3.65	10.26
HFD4-0.371.551.808.99NL-0.311.191.957.88double hybridsD3-0.811.181.415.42PWPB95D4-0.380.570.673.27NL-0.810.860.993.54revDSD-BLYPD4-0.150.660.835.23revDSD-PBEP86D4-0.110.410.583.43B2PLYPD4-0.730.861.244.81B2PLYPD4-0.730.861.244.81mbyridsD3-0.741.031.434.49B2PLYPD4-0.510.801.385.45MB30.051.201.586.34mbyridsD40.050.811.174.92MB40.050.811.174.92MB7D40.590.930.975.86ML-1.081.111.236.11MB7D40.590.930.975.86MD40.590.930.975.86MD40.590.911.104.93MB40.411.131.548.07MB40.411.131.548.07MD40.661.391.706.69PW6B95D4-0.500.911.104.93MD40.930.921.104.26MD40.930.940.951.224.93		D3	-0.44	2.14	3.13	16.38
NL-0.311.191.957.88double hybridsD3-0.811.181.415.42PWPB95D4-0.380.570.673.27NL-0.810.860.993.54revDSD-BLYPD4-0.150.660.835.23revDSD-PBEP86D40.100.410.583.43B2PLYPD4-0.510.801.385.45b3-0.741.031.434.49B2PLYPD4-0.510.801.385.45b4-0.510.801.201.586.34b30.051.201.586.34b30.051.201.586.34b40.590.811.174.92b5D40.050.811.174.92b40.590.930.975.86b31.181.651.628.50b3D4-0.500.911.034.81b3-0.670.810.775.23b3D4-0.500.911.104.93b4-0.500.911.104.93b5D4-0.500.911.104.93b3-0.661.391.704.66b3-0.670.810.775.84b3-0.660.991.114.93b3-0.620.991.114.93b3-0.661.391.65 </td <td>HF</td> <td>D4</td> <td>-0.37</td> <td>1.55</td> <td>1.80</td> <td>8.99</td>	HF	D4	-0.37	1.55	1.80	8.99
double hybridsD30.811.181.415.42PWPB95D40.380.570.673.27NL0.810.860.993.54revDSD-BLYPD40.100.410.583.43revDSD-PBEP86D40.100.410.583.43B2PLYPD3-0.741.031.434.49B2PLYPD40.510.801.385.45wB97MD40.050.811.174.92M20.051.201.586.34wB97MD40.050.811.174.92M40.050.811.174.92M40.050.811.174.92M30.651.201.586.34WB97MD40.590.930.975.86M30.651.201.586.34WB97XD40.590.930.975.86M30.440.590.930.975.86M40.590.931.076.52M40.590.931.075.23PW6B95D3-0.670.811.706.69M4-0.490.781.004.37M40.500.911.104.93M40.590.991.174.08M1-0.830.921.104.26M40.290.991.174.08M1-0.930.98 <td></td> <td>\mathbf{NL}</td> <td>-0.31</td> <td>1.19</td> <td>1.95</td> <td>7.88</td>		\mathbf{NL}	-0.31	1.19	1.95	7.88
D3 -0.81 1.18 1.41 5.42 PWPB95D4 -0.38 0.57 0.67 3.27 NL -0.81 0.86 0.99 3.54 revDSD-BLYPD4 -0.15 0.66 0.83 5.23 revDSD-PBEP86D4 0.10 0.41 0.58 3.43 B2PLYPD4 -0.51 0.80 1.38 5.45 NL -0.73 0.86 1.24 4.81 hybrids u -0.73 0.86 1.24 4.81 ω B97MD4 0.05 0.81 1.17 4.92 ML -1.08 1.11 1.23 6.11 ω B97MD4 0.05 0.81 1.17 4.92 ML -1.08 1.11 1.23 6.11 ω B97XD4 0.59 0.93 0.97 5.86 ML -0.49 0.78 1.03 3.55 B3LYPD4 -0.59 0.81 0.77 5.23 PW6B95D4 -0.67 0.81 0.77 5.23 PBE0D3 -0.22 1.58 1.87 8.79 PBE0D4 0.22 1.58 1.87 8.79 PBE0D3 0.40 1.24 1.65 5.82 B97MD4 0.24 1.34 1.64 10.07 MN15 $ -0.59$ 0.75 0.87 5.84 M06-2x $ -1.00$ 1.24 1.65 5.82 B97M<	double hybrids					
PWPB95D4-0.380.570.673.27NL-0.810.860.993.54revDSD-BLYPD4-0.150.660.835.23revDSD-PBEP86D40.100.410.583.43B2PLYPD4-0.510.801.385.45NL-0.730.861.244.81b30.051.201.586.34ωB97MD40.050.811.174.92M40.050.811.174.92M40.590.930.975.86M597XD40.590.930.975.86M20.40.590.930.975.86M3-0.590.781.033.55M40.490.781.033.55M512PD4-0.411.131.548.07M40.590.930.975.86M51M1-0.490.781.033.55M530.401.532.016.84M512M2-0.490.810.775.23M530.501.532.016.84M530.661.391.706.69PW6B95D4-0.290.911.104.93M54-0.250.911.104.93M55M2-0.590.750.875.82PB6D3-0.401.241.655.82B97MD4 <t< td=""><td></td><td>D3</td><td>-0.81</td><td>1.18</td><td>1.41</td><td>5.42</td></t<>		D3	-0.81	1.18	1.41	5.42
NL-0.810.860.993.54revDSD-BLYPD4-0.150.660.835.23revDSD-PBEP86D40.100.410.583.43B2PLYPD4-0.510.801.385.45D3-0.730.861.244.81 hybrids D30.051.201.586.34 ω B97MD40.050.811.174.92D40.050.811.174.92MB97MD40.590.930.975.86 ω B97MD40.590.930.975.86MB97XD31.181.651.628.50MB97XD40.590.930.975.86B3LYPD4-0.411.131.548.07ML-0.490.781.033.55PW6B95D4-0.670.810.775.23PW6B95D4-0.670.810.775.23MN150.991.174.08M06-2x0.991.174.08M06-2x0.991.174.08PBE0D3-0.221.581.878.79MM150.590.750.875.84M06-2x1.001.151.224.93M06-2x0.010.891.126.56B97MD3-0.941.24<	PWPB95	D4	-0.38	0.57	0.67	3.27
revDSD-BLYP D4 -0.15 0.66 0.83 5.23 revDSD-PBEP86 D4 0.10 0.41 0.58 3.43 B2PLYP D3 -0.74 1.03 1.43 4.49 B2PLYP D4 -0.51 0.80 1.38 5.45 bybrids NL -0.73 0.86 1.24 4.81 ωB97M D4 0.05 0.81 1.17 4.92 ωB97M D4 0.05 0.81 1.17 4.92 ωB97X D4 0.59 0.93 0.97 5.86 NL -0.49 0.78 1.03 3.55 B3LYP D4 0.51 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 PB60 D4 -0.29 0.99 1.10 4.93 NL -0.85 0.92 1.10 4.93 </td <td></td> <td>NL</td> <td>-0.81</td> <td>0.86</td> <td>0.99</td> <td>3.54</td>		NL	-0.81	0.86	0.99	3.54
revDSD-PBEP86 D4 0.10 0.41 0.58 3.43 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 ML -1.08 1.11 1.23 6.11 ωB97M D4 0.59 0.93 0.97 5.86 ML -0.49 0.78 1.03 3.55 ωB97X D4 0.59 0.93 0.97 5.86 NL -0.49 0.78 1.03 3.55 B3LYP D4 -0.41 1.13 1.54 8.07 NL -0.67 0.81 0.77 5.23 PB60 D4 -0.50 0.91 1.10 4.93 NL -0.85 0.92 1.10 4.26 PB60 D4 <td< td=""><td>revDSD-BLYP</td><td>D4</td><td>-0.15</td><td>0.66</td><td>0.83</td><td>5.23</td></td<>	revDSD-BLYP	D4	-0.15	0.66	0.83	5.23
B2PLYP 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 ML -1.08 1.11 1.23 6.11 MB97M D4 0.59 0.93 0.97 5.86 MB97X D4 0.59 0.93 0.97 5.86 ML -0.49 0.78 1.03 3.55 B3LYP D3 -0.60 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 PW6B95 D4 -0.50 0.91 1.10 4.93 NL -0.85 0.92 1.10 4.26 PBE0	revDSD-PBEP86	D4	0.10	0.41	0.58	3.43
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 ML -1.08 1.11 1.23 6.11 ωB97M D4 0.59 0.93 0.97 5.86 ωB97X D4 0.59 0.93 0.97 5.86 ML -0.49 0.78 1.03 3.55 B3LYP D4 -0.49 0.78 1.03 3.55 B3LYP D4 -0.41 1.13 1.54 8.07 ML -0.67 0.81 0.77 5.23 PW6B95 D4 -0.67 0.81 0.77 5.23 M15 - - 0.50 0.91 1.10 4.93 MN15 - - 0.59 0.75 0.87 5.84		D3	-0.74	1.03	1.43	4.49
NL -0.73 0.86 1.24 4.81 hybridsD3 0.05 1.20 1.58 6.34 ω B97MD4 0.05 0.81 1.17 4.92 ML -1.08 1.11 1.23 6.11 ω B97XD4 0.59 0.93 0.97 5.86 ω B97XD4 0.59 0.93 0.97 5.86 ML -0.49 0.78 1.03 3.55 $B3LYP$ D4 -0.41 1.13 1.54 8.07 ML -0.67 0.81 0.77 5.23 $PW6B95$ D4 -0.66 1.39 1.70 6.69 $PW6B95$ D4 -0.66 1.39 1.70 4.93 ML -0.85 0.92 1.10 4.26 $PBE0$ D4 -0.29 0.99 1.17 4.08 $M06-2x$ $ 0.59$ 0.75 0.87 5.84 $M06-2x$ $ 0.59$ 0.75 0.87 5.84 $B97M$ D4 0.24 1.34 1.64 10.07 ML 0.01 0.89 1.12 6.56 r^2SCAN D3 -0.45 0.86 1.07 4.47 ML 0.13 1.06 1.58 7.66 r^2SCAN D4 -0.28 1.09 1.39 7.73 $M06-L$ $ 1.58$ 1.61 1.26 7.40 PBE D4 -0.28 1.09 1.39 <	B2PLYP	D4	-0.51	0.80	1.38	5.45
hybridsD3 0.05 1.20 1.58 6.34 ω B97MD4 0.05 0.81 1.17 4.92 NL -1.08 1.11 1.23 6.11 ω B97XD3 1.18 1.65 1.62 8.50 ω B97XD4 0.59 0.93 0.97 5.86 NL -0.49 0.78 1.03 3.55 B3LYPD3 -0.50 1.53 2.01 6.84 B3LYPD4 -0.41 1.13 1.54 8.07 NL -0.67 0.81 0.77 5.23 PW6B95D4 -0.50 0.91 1.10 4.93 NL -0.85 0.92 1.10 4.26 PBE0D4 -0.29 0.99 1.17 4.08 NL -0.85 0.92 1.10 4.26 PBE0D4 0.29 0.99 1.17 4.08 NL -0.93 0.98 0.95 4.37 MN15 $ 0.99$ 1.12 MD6-2x $ 0.59$ 0.75 0.87 SED3 -0.40 1.24 1.65 5.82 B97MD4 0.24 1.34 1.64 10.07 NL 0.11 0.89 1.12 6.56 r^2 SCAND3 -0.15 0.86 1.07 4.15 r^2 SCAND4 -0.28 1.09 1.39 7.73 M06-L $ 1.58$		NL	-0.73	0.86	1.24	4.81
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	hybrids					
		D3	0.05	1.20	1.58	6.34
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\omega B97M$	D4	0.05	0.81	1.17	4.92
$ \begin{split} & \begin{array}{ccccccccccccccccccccccccccccccccccc$		NL	-1.08	1.11	1.23	6.11
		D3	1 18	1.65	1.62	8 50
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\omega B97X$	D_{0}	$1.10 \\ 0.59$	1.00	1.02 0.97	5.86
ALL 0.15 0.16 1.66 0.66 $B3LYP$ $D3$ -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 $PW6B95$ $D4$ -0.50 0.91 1.10 4.93 NL -0.85 0.92 1.10 4.26 $PBE0$ $D4$ -0.29 0.99 1.17 4.08 NL -0.85 0.92 1.10 4.26 $PBE0$ $D4$ -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 $P3$ -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 PBE	wbbtt	NL	-0.49	0.50 0.78	1.03	3 55
B3LYPD3 -0.30 1.33 2.01 6.84 B3LYPD4 -0.41 1.13 1.54 8.07 NL -0.67 0.81 0.77 5.23 PW6B95D4 -0.66 1.39 1.70 6.69 PW6B95D4 -0.50 0.91 1.10 4.93 NL -0.85 0.92 1.10 4.26 PBE0D4 -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-) GGAsD3 -0.40 1.24 1.65 5.82 B97MD4 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 TPSSD4 -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 PBED4 -0.25 1.12 1.34 8.76 NL -0.98 1.14 0.95 9.08		D9	0.10	1 5 9	0.01	6.94
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	BAIND	D3 D4	-0.50	1.55	2.01 1.54	0.84
NL -0.01 0.81 0.77 5.23 PW6B95D3 -0.66 1.39 1.70 6.69 D4 -0.50 0.91 1.10 4.93 NL -0.85 0.92 1.10 4.26 PBE0D4 -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 $ -1.00$ 1.24 1.65 5.82 B97MD4 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^2 SCAND4 -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 TPSSD4 -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 PBED4 -0.25 1.12 1.34 8.76 NL -0.98 1.14 0.95 9.08	DJLIF	D4 NI	-0.41	1.13	1.04 0.77	0.07 5.22
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			-0.07	1.00	1 =0	0.20
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	DWCDOF	D_3	-0.66	1.39	1.70	6.69
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	PW6B95	D4 NI	-0.50	0.91	1.10	4.93
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		NL Da	-0.85	0.92	1.10	4.20
PBE0D4 -0.29 0.99 1.17 4.08 NLNL -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 $ -1.00$ 1.15 1.22 4.93 (meta-) GGAs $ -0.40$ 1.24 1.65 5.82 B97MD4 0.24 1.34 1.64 10.07 NL 0.01 0.89 1.12 6.56 r^2 SCAND4 -0.15 0.86 1.07 4.15 r^2 SCAND4 -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 TPSSD4 -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 PBED4 -0.25 1.12 1.34 8.76 NL -0.98 1.14 0.95 9.08	DDD0	D3	-0.22	1.58	1.87	8.79
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	PBE0	D4 NI	-0.29	0.99	1.17	4.08
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$		NL	-0.93	0.98	0.95	4.37
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	MN15	_	-0.59	0.75	0.87	5.84
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	M06-2x	—	-1.00	1.15	1.22	4.93
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(meta-) GGAs					
B97MD4 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^2 SCAND4 -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 TPSSD4 -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 PBED4 -0.25 1.12 1.34 8.76 NL -0.98 1.14 0.95 9.08		D3	-0.40	1.24	1.65	5.82
NL 0.01 0.89 1.12 6.56 D3 -0.15 0.86 1.07 4.15 r^2 SCAND4 -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 TPSSD4 -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 PBED4 -0.25 1.12 1.34 8.76 NL -0.98 1.14 0.95 9.08	B97M	D4	0.24	1.34	1.64	10.07
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		\mathbf{NL}	0.01	0.89	1.12	6.56
$\begin{array}{cccccccc} r^2 {\rm SCAN} & {\rm D4} & -0.07 & 0.77 & 0.91 & 4.47 \\ {\rm NL} & 0.13 & 1.06 & 1.58 & 7.66 \\ \\ {\rm D3} & 0.05 & 1.71 & 2.11 & 8.07 \\ \\ {\rm TPSS} & {\rm D4} & -0.28 & 1.09 & 1.39 & 7.73 \\ {\rm NL} & -1.03 & 1.08 & 0.86 & 7.29 \\ \\ {\rm M06-L} & - & 1.58 & 1.61 & 1.26 & 7.40 \\ \\ {\rm D3} & 0.06 & 1.43 & 1.92 & 6.32 \\ \\ {\rm PBE} & {\rm D4} & -0.25 & 1.12 & 1.34 & 8.76 \\ \\ {\rm NL} & -0.98 & 1.14 & 0.95 & 9.08 \\ \end{array}$		D3	-0.15	0.86	1.07	4.15
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	r^2 SCAN	D4	-0.07	0.77	0.91	4.47
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		\mathbf{NL}	0.13	1.06	1.58	7.66
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		D3	0.05	1.71	2.11	8.07
$\begin{array}{cccccccc} \mathrm{NL} & -1.03 & 1.08 & 0.86 & 7.29 \\ \mathrm{M06\text{-L}} & - & 1.58 & 1.61 & 1.26 & 7.40 \\ \mathrm{D3} & 0.06 & 1.43 & 1.92 & 6.32 \\ \mathrm{PBE} & \mathrm{D4} & -0.25 & 1.12 & 1.34 & 8.76 \\ \mathrm{NL} & -0.98 & 1.14 & 0.95 & 9.08 \end{array}$	TPSS	D4	-0.28	1.09	1.39	7.73
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		NL	-1.03	1.08	0.86	7.29
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	M06-L	_	1.58	1.61	1.26	7.40
PBE D4 -0.25 1.12 1.34 8.76 NL -0.98 1.14 0.95 9.08		D3	0.06	1.43	1.92	6.32
NL -0.98 1.14 0.95 9.08	PBE	$\tilde{\rm D4}$	-0.25	1.12	1.34	8.76
		NL	-0.98	1.14	0.95	9.08

IONPI19 statistics

Method	MD	MAD	SD	relMAD
composite (3c) DFT				
PBEh-3c	-3.55	3.55	4.39	17.96
B97-3c	-0.48	1.36	1.76	8.41
r^2 SCAN-3c	-0.75	1.29	1.35	10.37
\mathbf{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 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 relMAD is given in %.

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 kcalmol⁻¹, the relMAD is given in %.

Method	LD	MD	MAD	SD	relMAD
MP2/CBS	_	-1.91	1.97	3.47	10.98
	D3	-0.45	1.97	2.95	16.32
$_{ m HF}$	D4	-0.34	1.41	1.70	9.01
	\mathbf{NL}	-0.33	1.12	1.84	8.62
double hybrids					
	D3	-0.75	1.09	1.35	5.48
PWPB95	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
	D3	-0.67	0.94	1.36	4.32
B2PLYP	D4	-0.45	0.72	1.32	5.13
	NL	-0.66	0.78	1.19	4.72
hybrids					
	D3	0.00	1.12	1.50	6.76
$\omega B97M$	D4	0.03	0.74	1.10	4.92
	\mathbf{NL}	-1.01	1.04	1.18	5.59
	D3	-1.02	1.52	1.61	9.48
$\omega B97X$	D4	0.52	0.84	0.94	5.43
	\mathbf{NL}	-0.47	0.73	0.98	4.12
	D3	-0.46	1.39	1.90	6.87
B3LYP	D4	-0.34	1.04	1.46	7.85
	\mathbf{NL}	-0.60	0.73	0.76	5.15
	D3	-0.57	1.26	1.61	6.44
PW6B95	D4	-0.44	0.83	1.05	4.68
	\mathbf{NL}	-0.78	0.84	1.07	4.19
	D3	-0.21	1.43	1.77	8.25
PBE0	D4	-0.26	0.88	1.10	3.68
	\mathbf{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					
· · · · · ·	D3	-0.34	1.13	1.57	6.24
B97M	D4	0.26	1.24	1.55	10.28
	\mathbf{NL}	0.03	0.82	1.06	6.87
	D3	-0.13	0.80	1.01	4.68
r^2 SCAN	D4	-0.04	0.71	0.87	4.79
	\mathbf{NL}	0.13	0.97	1.49	7.63
	D3	0.06	1.56	1.99	8.20
TPSS	D4	-0.23	1.00	1.32	7.85
	\mathbf{NL}	-0.92	1.00	0.88	7.42
M06-L	—	1.44	1.48	1.27	8.01
	D3	0.07	1.30	1.81	6.54
PBE	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.