Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplemental Information for

Performance of Conventional and Dispersion-Corrected Density-Functional Theory Methods for Hydrogen Bonding Interaction Energies.

Gino A. DiLabio,[a,b,*] Erin R. Johnson,[c,*] Alberto Otero-de-la-Roza[c]

[a]National Institute for Nanotechnology, National Research Council of Canada, 11421 Saskatchewan Drive, Edmonton, Alberta, Canada T6G 2M9. [b]Department of Physics, University of Alberta, Edmonton, Alberta Canada T6G 2E1 [c]Chemistry and Chemical Biology, School of Natural Sciences, University of California, Merced, 5200 North Lake Road, Merced, CA, 95343.

Figure S1. Sample Gaussian-09 input file demonstrating the calculations required to obtain the component energies of the composite method described in reference S1 (reference 18 of the manuscript).

```
%chk=Water.chk
#CCSD(T,SaveAmplitudes) aug-cc-pVDZ

Water composite calculation: CCSD(T)/aDZ step

0 1
O   -0.702196054  -0.056060256   0.009942262
H   -1.022193224   0.846775782  -0.011488714
H    0.257521062   0.042121496   0.005218999

--Link1--
%chk=Water.chk
#CCSD(ReadAmplitudes,SaveAmplitudes) aug-cc-pVTZ Geom=CheckPoint Guess=Read

Water composite calculation: CCSD/aTZ step

0 1

--Link1--
%chk=Water.chk
#MP2 aug-cc-pVQZ Geom=CheckPoint Guess=Read

Water composite calculation: MP2/aQZ step

0 1
```

Table S1. List of XDM parameters used with selected functionals and the aug-cc-pVTZ basis set. The a_1 and a_2 parameters are used in definition of the van der Waals radius. Values were fit to minimize the RMS percent error for the 65-dimer set of Kannemann and Becke or the 49-dimer set resulting from omitting those complexes involving noble-gas atoms.

Method	a_1	a_2 (Å)	MAPE	n_{set}
BLYP	0.7738	0.8395	9.8	49
PW86	0.7891	1.3794	11.3	65
PBE	0.4879	2.4683	14.3	49
B3LYP	0.6722	1.4257	6.7	49
B971	0.2800	3.3315	12.3	49
PBE0	0.4993	2.4660	10.2	49
LC-wPBE	1.0875	0.4850	7.8	49

Table S2. Binding energies (kcal/mol) for the HB23 set of hydrogen bonded dimers calculated using the CCSD(T)-based composite approach described in the main paper, with counterpoise (CP) corrections, without CP corrections, and with half-CP corrections. All values are in kcal/mol. Values obtained using equation 1 of the text. Values in parentheses were obtained using CCSD(T)/aug-cc-pV(Q-T)Z.[a] Also shown are the Ave-MP2/aug-cc-pV(Q-T)Z binding energies calculated as part of this work. Counterpoise-corrected SCS-MP2/CBS and SCS-MI-MP2/CBS binding energies listed on www.begdb.com are also listed.

HB Dimer[b]	CCSD(T)			MP2/CBS		
	CP	No-CP	Ave	Ave[d]	SCS[e]	SCS-MI[f]
water – water	4.94 (5.01)	5.11 (5.04)	5.03 (5.03)	5.005	4.508	4.906
water – methanol	5.61 (5.69)	5.79 (5.73)	5.70 (5.71)	5.750	5.095	5.53
water – methylamine	6.91 (7.00)	7.08 (7.03)	6.99 (7.02)	7.124	6.391	6.822
water – peptide[c]	8.10	8.32	8.21	8.137	7.26	8.003
methanol – methanol	5.76	5.94	5.85	5.892	5.15	5.637
methanol – methylamine	7.52	7.69	7.61	7.757	6.779	7.33
methanol – peptide[c]	8.22	8.06	8.14	8.057	7.195	8.029
methanol – water	5.018 (5.089)	5.182 (5.113)	5.100 (5.101)	5.079	4.516	4.954
methylamine – methanol	3.04	3.13	3.09	3.075	2.505	2.78
methylamine – methylamine	4.115	4.200	4.158	4.299	3.472	3.798
methylamine – peptide[c]	5.360	5.563	5.462	5.576	4.454	5.038
methylamine – water	7.26 (7.36)	7.43 (7.38)	7.34 (7.37)	7.551	6.704	7.176
peptide[c] – methanol	6.175	6.308	6.241	6.349	5.459	5.958
peptide[c] – methylamine	7.415	7.523	7.469	7.681	6.614	7.113
peptide[c] – peptide[c]	8.597	8.789	8.693	8.708	7.51	8.266
peptide[c] – water	5.148	5.255	5.202	5.181	4.61	5.016
uracil – uracil (base pair)	17.259	17.563	17.411	17.255	15.281	17.406
water – pyridine	6.855	7.084	6.970	7.136	6.384	6.735
methanol – pyridine	7.381	7.590	7.486	8.057	6.782	7.24
formic acid – formic acid	19.184	19.695	19.439	19.162	17.309	19.396
formamide – formamide	16.577	16.592	16.585	16.330	14.706	16.075
formic acid – uracil	19.575	19.963	19.769	19.517	17.625	19.772
formamide – uracil	19.266	19.535	19.400	19.169	17.392	19.364

[a] See text for additional details. [b]All dimers are named in the form *donor-acceptor*. [c]"Peptide" is the nomenclature used in Ref. 9 for methylamide. The MAD and MaxAD values associated with the MP2 methods, in kcal/mol, relative to our revised BE data, are: d) 0.14, 0.57; e) 1.02, 2.04; f) 0.22, 0.51.

Table S3. Binding energies (kcal/mol) for the HB23 set of hydrogen bonded dimers, calculated in the present work using B3LYP-DCP/6-31+G(2d,2p) and DFT-XDM/aug-cc-pVTZ. All values are in kcal/mol.

	DCP	XDM						
HB Dimer[a]	B3LYP	B3LYP	PBE0	PBE	BLYP	PW86	LC-ωPBE	B971
water – water	5.35	5.15	5.20	5.19	5.02	5.17	4.86	5.09
water – methanol	5.81	5.78	5.70	5.68	5.70	5.72	5.48	5.54
water – methylamine	7.64	7.46	7.57	7.73	7.60	7.70	7.21	7.30
water – peptide[b]	8.19	8.31	8.24	8.06	8.23	8.13	8.10	7.97
methanol – methanol	5.89	5.95	5.86	5.85	5.89	5.89	5.62	5.66
methanol – methylamine	8.17	8.06	8.10	8.27	8.25	8.23	7.75	7.76
methanol – peptide[b]	8.26	8.59	8.48	8.38	8.61	8.49	8.27	8.12
methanol – water	5.38	5.21	5.25	5.25	5.05	5.22	4.87	5.12
methylamine – methanol	3.16	3.16	3.07	3.16	3.14	3.19	2.83	3.07
methylamine – methylamine	4.23	4.14	4.07	4.18	4.37	4.29	3.91	3.96
methylamine – peptide[b]	5.35	5.37	5.14	5.06	5.54	5.31	5.15	4.96
methylamine – water	7.82	7.61	7.69	7.80	7.74	7.76	7.42	7.39
Peptide[b] – methanol	6.03	6.15	6.05	5.90	6.03	6.03	5.94	5.88
Peptide[b] – methylamine	7.74	7.64	7.69	7.73	7.80	7.81	7.42	7.40
Peptide[b] – peptide[b]	8.44	8.74	8.62	8.40	8.69	8.60	8.48	8.32
Peptide[b] – water	5.28	5.08	5.18	5.06	4.79	5.03	4.83	5.11
uracil – uracil (base pair)	17.13	17.97	17.97	17.52	17.66	17.54	16.90	17.20
water – pyridine	7.40	7.41	7.36	7.55	7.63	7.60	7.08	7.14
methanol – pyridine	7.84	7.94	7.87	8.08	8.19	8.12	7.55	7.58
formic acid – formic acid	19.34	20.43	20.70	20.08	20.00	19.83	20.18	19.55
formamide – formamide	16.32	16.86	16.93	16.50	16.62	16.57	16.08	16.20
formic acid – uracil	19.58	20.51	20.65	20.02	20.08	19.91	19.83	19.66
formamide – uracil	19.30	19.91	20.01	19.41	19.49	19.37	19.02	19.18
MAD	0.23	0.29	0.33	0.28	0.27	0.25	0.25	0.18

[a]All indicated dimers have a hydrogen-bonded interaction are named in the form *donor-acceptor*.
[b]"Peptide" is the nomenclature used in reference 9 and refers to methylamide.

Table S4. Mean absolute (signed) deviations, mean absolute (signed) percent deviations, and maximum mean absolute deviation and maximum mean percent error of the counterpoise-corrected binding energies of dimers of the HB23 set relative to the revised binding energies calculated in this work and listed in column 3 of Table 1 obtained using non-dispersion-corrected DFT methods. All data but percent values are in kcal/mol.

Method	MAD[a]	MSD[b]	MAPD[c]	MSPD[d]	MAX AD[e]	MAX APD[f]
Pure DFT Methods						
BLYP	2.53	-2.53	32.83	-32.83	4.26	72.45
HCTH407	2.54	-2.54	29.72	-29.72	4.86	62.22
PBE	0.93	-0.91	12.22	-11.98	2.23	37.29
Hybrid DFT Methods						
B3LYP	1.67	-1.67	22.53	-22.53	3.16	55.28
BMK	1.47	-1.47	20.66	-20.66	2.32	59.02
mPW1PW91	1.46	-1.46	20.60	-20.60	2.33	58.91
B98	1.44	-1.44	20.16	-20.16	2.84	51.15
B971	1.20	-1.20	15.75	-15.75	2.35	40.41
BHandHLYP	0.92	-0.92	11.78	-11.78	1.93	32.34
PBE0PBE	0.90	-0.90	13.32	-13.32	2.13	38.95
Long-Range Corrected DFT Methods						
LC-ωPBE	1.58	-1.58	20.85	-20.85	2.87	46.19
LC-BLYP	0.95	0.93	10.73	10.42	3.08	22.86
LC-PBE	0.62	0.22	7.52	0.20	2.64	20.91
HSEh1PBE	0.66	-0.62	9.79	-9.45	1.85	33.34
CAM-B3LYP	0.63	-0.57	9.22	-8.67	1.85	32.30
ωB97X	0.35	0.33	4.46	4.30	1.09	11.03

[a]Mean absolute deviation. [b]Mean signed deviation. A negative value indicates that the DFT number is lower than the reference number. [c]Mean absolute percent deviation. [d]Mean signed percent deviation. A negative value indicates that the DFT number is lower than the reference number. [e]Maximum absolute deviation. [f]Maximum absolute percent deviation.

Table S5. Mean absolute (signed) deviations, mean absolute (signed) percent deviations, and maximum mean absolute deviation and maximum mean percent error of the non-counterpoise-corrected binding energies of dimers of the HB23 set relative to the binding energies reported in reference 9 obtained using non-dispersion-corrected DFT methods. All data but percent values are in kcal/mol.

Method	MAD[a]	MSD[b]	MAPD[c]	MSPD[d]	MAX AD[e]	MAX APD[f]
Pure DFT Methods						
BLYP	2.35	-2.35	31.18	-31.18	4.09	71.51
HCTH407	2.36	-2.36	28.15	-28.15	4.47	61.21
PBE	0.77	-0.73	10.68	-10.15	2.07	36.15
Hybrid DFT Methods						
B3LYP	1.49	-1.49	20.83	-20.83	3.01	54.28
BMK	1.26	-1.26	18.49	-18.49	2.10	56.88
mPW1PW91	1.26	-1.26	18.33	-18.33	2.71	50.10
B98	1.02	-1.02	14.02	-14.02	2.20	39.36
B971	0.74	-0.74	10.06	-10.00	1.78	31.20
BHandHLYP	0.77	-0.73	11.87	-11.53	2.05	37.84
PBE0PBE	0.66	-0.60	9.96	-9.47	1.85	34.06
Long-Range Corrected DFT Methods						
LC-ωPBE	1.39	-1.39	19.09	-19.09	2.50	44.90
LC-BLYP	1.11	1.11	12.53	12.53	3.55	26.01
LC-PBE	0.74	0.41	8.57	2.19	3.13	19.39
HSEh1PBE	0.57	-0.45	8.73	-7.62	1.74	32.20
CAM-B3LYP	0.55	-0.39	8.41	-6.81	1.69	31.11
ωB97X	0.52	0.52	6.46	6.46	1.60	13.94

[a]Mean absolute deviation. [b]Mean signed deviation. A negative value indicates that the DFT number is lower than the reference number. [c]Mean absolute percent deviation. [d]Mean signed percent deviation. A negative value indicates that the DFT number is lower than the reference number. [e]Maximum absolute deviation. [f]Maximum absolute percent deviation.

Table S6. Mean absolute (signed) deviations, mean absolute (signed) percent deviations, and maximum mean absolute deviation and maximum mean percent error of the counterpoise-corrected binding energies of dimers of the HB23 set relative to the binding energies reported in reference 9 obtained using non-dispersion-corrected DFT methods. All data but percent values are in kcal/mol.

Method	MAD[a]	MSD[b]	MAPD[c]	MSPD[d]	MAX AD[e]	MAX APD[f]
Pure DFT Methods						
BLYP	2.42	-2.42	31.99	-31.99	4.19	72.23
HCTH407	2.42	-2.42	28.86	-28.86	4.63	61.92
PBE	0.83	-0.80	11.34	-10.91	2.17	36.80
Hybrid DFT Methods						
B3LYP	1.56	-1.56	21.57	-21.57	3.10	54.92
BMK	1.36	-1.36	19.69	-19.69	2.26	58.65
mPW1PW91	1.33	-1.33	19.17	-19.17	2.78	50.76
B98	1.09	-1.09	14.73	-14.73	2.28	39.94
B971	0.81	-0.81	10.73	-10.71	1.87	31.80
BHandHLYP	0.82	-0.79	12.50	-12.26	2.08	38.46
PBE0PBE	0.71	-0.67	10.53	-10.20	1.91	34.64
Long-Range Corrected DFT Methods						
LC-wPBE	1.46	-1.46	19.88	-19.88	2.64	45.69
LC-BLYP	1.05	1.04	11.91	11.74	3.42	25.54
LC-PBE	0.70	0.34	8.35	1.41	2.99	20.19
HSEh1PBE	0.61	-0.52	9.20	-8.38	1.78	32.81
CAM-B3LYP	0.58	-0.46	8.79	-7.55	1.79	31.76
wB97X	0.45	0.44	5.60	5.53	1.44	13.45

[a]Mean absolute deviation. [b]Mean signed deviation. A negative value indicates that the DFT number is lower than the reference number. [c]Mean absolute percent deviation. [d]Mean signed percent deviation. A negative value indicates that the DFT number is lower than the reference number. [e]Maximum absolute deviation. [f]Maximum absolute percent deviation.

Table S7. Deviations of the XDM-corrected binding energies of the HB23 set relative to both the revised binding energies calculated in this work and the original reference data of Řezáč et al. All data (except percent values) are in kcal/mol.

Method	Present reference data				Řezáč et al. reference data			
	MAD[a]	MSD[b]	MAPD[c]	MSPD[d]	MAD[a]	MSD[b]	MAPD[c]	MSPD[d]
PBE0PBE	0.33	0.26	3.32	2.20	0.42	0.37	4.21	3.37
B3LYP	0.29	0.26	3.06	2.55	0.39	0.37	3.96	3.72
PBE	0.28	0.15	3.64	1.77	0.35	0.26	4.29	2.93
BLYP	0.27	0.21	3.46	2.38	0.36	0.32	4.32	3.54
PW86	0.25	0.18	3.39	2.38	0.32	0.29	4.12	3.54
LC-wPBE	0.25	-0.11	3.23	-1.99	0.22	0.00	2.80	-0.88
B971	0.18	-0.09	2.37	-1.25	0.17	0.01	2.37	-0.13

[a]Mean absolute deviation. [b]Mean signed deviation. A negative value indicates that the DFT number is lower than the reference number. [c]Mean absolute percent deviation. [d]Mean signed percent deviation. A negative value indicates that the DFT number is lower than the reference number.