Geometrical Correction for the Inter- and Intramolecular Basis Set Superposition Error in Periodic Density Functional Theory Calculations

Supporting information for: A Geometrical Correction for the Inter- and Intra-Molecular Basis Set Superposition Error in Periodic Density Functional Theory Calculations

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Table 1: Theoretic sublimation energies for the X23 benchmark set on the PBE/CBS, PBE-D3/CBS, PBE-D3/CBS+$E^{(3)}$, PBE/SVP, PBE-D3/SVP, PBE-D3-gCP/SVP, PBE-D3-gCP+$E^{(3)}$, B3LYP-D3/SVP, B3LYP-D3-gCP/SVP, and B3LYP-D3-gCP/SVP+$E^{(3)}$ level. Only electronic energy contributions are given. The experimental value is thermodynamically back-corrected as provided by Tkatchenko *et al.*. All values are given per molecule and in kcal/mol.

Func/basis:	PBE/CBS			PBE/SVP			B3LYP/CBS			Exp
Disp-Corr:	-	-D3	-D3	-	-D3	-D3	-D3	-D3	-D3	-D3	
BSSE-Corr:	-	-	-	-	-	-gCP	-gCP	-	-gCP	-gCP	
3-body:	-	-	$+E^{(3)}$	-	-	-	$+E^{(3)}$	-	-	$+E^{(3)}$	
C1	6.9	21.6	20.4	16.8	31.8	20.8	19,6	33.2	22.3	21.2	21.2
C2	9.7	17.2	16.7	18.9	26.7	16.6	16.1	26.6	16.7	16.2	17.4
C3	−1.5	17.1	15.4	2.0	20.4	14.4	12.7	20.5	14.6	13.6	16.6
C4	6.6	10.3	10.1	13.1	16.5	13.0	12.8	15.3	11.8	11.6	8.9
C5	−1.4	25.4	23.1	3.4	31.5	24.3	22.0	37.8	30.6	28.3	26.9
C6	0.3	13.1	12.2	4.1	16.6	12.9	12.1	17.4	13.7	12.8	12.4
C7	1.9	6.0	5.8	5.7	9.9	2.6	2.4	11.0	3.7	3.5	6.5
C8	15.2	22.4	22.0	21.3	28.4	22.8	22.4	27.9	22.4	21.8	19.1
C9	21.1	37.8	36.5	34.2	50.5	37.3	36.1	51.8	38.9	37.6	40.6
C10	10.9	21.4	20.7	20.0	30.4	20.1	19.4	31.1	21.0	20.3	20.6
C11	13.4	20.1	19.7	20.7	27.4	18.9	18.4	27.6	19.1	18.7	18.9
C12	11.8	22.0	21.3	18.2	28.1	22.6	21.9	28.4	22.9	22.2	20.8
C13	−1.2	19.1	17.5	2.4	21.9	16.2	14.6	26.1	20.5	18.9	19.5
C14	13.1	23.0	22.2	24.4	34.4	15.3	14.6	41.3	21.0	20.3	23.0
C15	13.9	23.6	23.0	24.9	35.3	15.9	15.2	41.4	20.8	20.1	23.0
C16	3.3	15.7	14.9	8.9	20.9	15.9	15.1	21.9	17.0	16.2	14.7
C17	9.2	19.4	18.7	15.3	25.6	19.7	19.0	25.7	19.9	19.1	18.6
C18	3.2	14.6	13.7	9.6	21.1	15.0	14.3	23.3	17.3	16.5	14.8
C19	4.1	14.1	13.3	14.4	25.8	12.8	12.0	27.8	15.1	14.3	15.9
C20	18.9	33.5	32.4	29.5	44.8	30.8	29.7	47.0	33.6	32.5	32.4
C21	19.0	27.3	26.8	28.5	36.8	25.5	25.0	37.0	25.9	25.4	24.5
R22	3.0	20.7	19.1	11.8	30.6	22.1	19.9	32.9	24.6	22.9	20.6
R23	17.7	32.0	30.8	33.3	47.6	26.9	26.1	47.6	27.2	26.0	31.1

Table 2: Mean absolute deviation (MAD), mean deviation (MD), and standard deviation (SD) of the sublimation energy for the X23 test set and for the subset X12/Hydrogen dominated by hydrogen bonds. We calculate the energy with different combinations of functionals (PBE and B3LYP), dispersion correction D3, and geometric counterpoise correction gCP and compare with thermodynamically back-corrected experimental sublimation energies. On the PBE/SVP level, we give values based on deviations to the corresponding large plane-wave basis set values in parentheses. All values are in kcal/mol.

	X23			X12/Hydrogen	
Method	MAD	MD	SD	MAD	MD
PBE/CBS	11.7	−11.7	6.1	9.7	−9.7
PBE-D3/CBS	1.1	0.4	1.3	1.3	0.8
PBE-D3/CBS+$E^{(3)a}$	1.2	−0.5	1.7	1.1	0.1
PBE/SVP	5.4 (7.7)	−3.8 (7.7)	7.0 (3.3)	2.6 (9.5)	−0.1 (9.5)
PBE-D3/SVP	8.5 (8.1)	8.5 (8.1)	3.5 (3.4)	10.5 (9.7)	10.5 (9.7)
PBE-D3-gCP/SVP	2.5 (2.1)	−1.1 (−1.5)	3.0 (2.6)	2.8 (2.5)	−1.4 (−2.3)
PBE-D3-gCP/SVP+$E^{(3)a}$	2.9 (2.0)	−2.0 (−1.5)	3.2 (2.5)	3.1 (2.4)	−2.2 (−2.2)
B3LYP-D3/SVP	10.1	10.1	4.1	12.0	12.0
B3LYP-D3-gCP/SVP	2.0	0.6	2.2	1.7	−0.1
B3LYP-D3-gCP/SVP+$E^{(3)a}$	1.7	−0.3	2.2	1.8	−0.8

[a] Three-body dispersion single-point energy $E^{(3)}$ on optimized structures.

Table 3: Crystal structures of a subgroub of the X23 benchmark set. We calculate the geometries on the PBE-D3/CBS, PBE-D3/SVP, PBE-D3-$\frac{1}{2}$gCP/SVP, PBE-D3-gCP/SVP, B3LYP-D3/SVP, and B3LYP-D3-$\frac{1}{2}$gCP/SVP levels. Cell length are in Åand volumes in Å^3. All systems are orthorhombic.

Func/bais:		PBE/CBS	PBE/SVP			B3LYP/CBS		Exp
Disp-Corr:		-D3	-D3	-D3	-D3	-D3	-D3	
BSSE-Corr:		-	-	-$\frac{1}{2}$gCP	-gCP	-	-$\frac{1}{2}$gCP	
C2	*a*	12.12	13.04	13.20	13.25	13.01	13.15	13.15
	b	4.07	3.83	3.99	4.13	3.75	3.90	3.92
	c	6.09	5.64	5.82	5.93	5.60	5.74	5.76
	Vol	300.2	281.5	306.5	324.8	272.9	294.0	297.3
C3	*a*	6.62	6.58	6.71	6.83	6.51	6.61	6.64
	c	8.88	8.86	8.98	9.04	8.69	8.85	8.92
	Vol	389.4	383.3	403.7	422.3	368.1	387.4	393.1
C4	*a*	5.01	4.91	5.04	5.13	4.91	5.01	5.12
	Vol	126.0	118.3	128.2	135.1	118.6	125.9	135.0
C6	*a*	7.35	7.13	7.29	7.49	−−	−−	7.39
	b	9.39	9.09	9.23	9.43	−−	−−	9.42
	c	6.77	6.96	7.01	7.02	−−	−−	6.81
	Vol	467.5	451.3	471.4	324.8	−−	−−	474.1
C7	*a*	5.68	5.52	5.74	5.94	5.40	5.60	5.62
	Vol	183.3	168.1	189.5	209.6	157.4	176.0	177.9
C8	*a*	6.86	6.75	6.91	7.07	6.66	6.79	6.86
	b	6.69	6.50	6.61	6.76	6.44	6.56	6.63
	c	8.94	8.90	8.94	9.00	8.99	9.07	9.15
	Vol	410.4	390.4	408.3	430.5	396.0	404.0	415.7
C14	*a*	6.69	6.59	6.97	7.38	6.41	6.66	6.55
	b	7.64	7.45	7.64	7.71	7.50	7.66	7.84
	c	6.15	5.96	6.25	6.35	5.94	6.09	6.09
	Vol	314.6	292.6	332.9	361.4	285.2	310.5	312.6
C16	*a*	9.23	9.17	9.21	9.31	9.14	9.27	9.33
	b	5.80	5.64	5.70	5.84	5.53	5.58	5.85
	c	3.71	3.65	3.80	3.86	3.57	3.69	3.73
	Vol	198.4	188.7	199.6	209.8	180.8	190.8	203.6
C17	*a*	8.20	8.05	8.04	8.25	−−	−−	8.19
	b	12.16	12.22	12.46	12.68	−−	−−	12.59
	c	6.80	6.74	6.99	7.10	−−	−−	6.77
	Vol	702.5	662.9	700.3	742.2	−−	−−	698.3
C21	*a*	5.56	5.41	5.56	5.67	5.39	5.54	5.57
	c	4.67	4.66	4.70	4.78	4.64	4.67	4.68
	Vol	144.4	136.5	145.0	153.6	134.9	143.6	145.1