

# Supporting Information for “Accurate and Efficient *ab Initio* Calculations for Supramolecular Complexes: Symmetry-Adapted Perturbation Theory with Many-Body Dispersion”

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## 1. DEFORMATION ENERGIES AND BINDING ENERGIES OF S30L COMPLEXES

In the study of noncovalent interactions, the effect of geometric deformation can sometimes be neglected in small systems. In systems as large as those in S30L, however, the energetic penalty due to geometry changes during non-covalent association becomes significant and must be considered. Table S1 reports deformation energies for S30L computed at the SCS-MP2/CBS level. The CBS limit is approximated here using a two-point cc-pVDZ/cc-pVTZ extrapolation outlined in Ref. 1. Deformation energies  $\Delta E_{\text{def}}$  are computed as

$$\Delta E_{\text{def}} = \left( E_A^{AB} - E_A^A \right) + \left( E_B^{AB} - E_B^B \right), \quad (\text{S1})$$

where  $E_X^{XY}$  means the energy of monomer  $X$  computed at the geometry that it adopts in dimer  $XY$ .  $E_X^X$  refers to the energy of the monomer  $X$  at its geometry in dimer  $XY$ .

In Table S1, we also report XSAPT+MBD binding energies along with the corresponding energy decomposition. The MBD+esDQ energy stands in for  $E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)}$  from SAPT. The total induction energy is taken to be

$$E_{\text{ind}} = E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + \left( E_{AB}^{\text{XSAPT}} - E_{AB}^{\text{SAPT}} \right) + \delta E_{AB}^{\text{HF}}, \quad (\text{S2})$$

where  $E_{\text{ind}}^{(2)}$  and  $E_{\text{exch-ind}}^{(2)}$  are the usual pairwise induction terms. The difference between the XSAPT interaction energy ( $E_{AB}^{\text{XSAPT}}$ ) and the SAPT interaction energy ( $E_{AB}^{\text{SAPT}}$ ) yields the influence of including self-consistent polarization. The final term is the usual “ $\Delta$ (Hartree-Fock)” approximation for higher-order induction effects.

## 2. L7 INTERACTION ENERGIES AND ENERGY DECOMPOSITION

The L7 structures are likely to exhibit minimal geometric deformation upon interaction, and we assume this contribution to be small. Therefore, we report interaction energies for the L7 set alongside the XSAPT energy decomposition in Table S3. Again we report a total induction energy consistent with Eq. (S2). There is no many-body polarization contribution, because benchmark L7 interaction energies consist of two interacting fragments per system, even in the systems where there exist more than two distinct molecules.

Table S4 reports the GDD-tuned values of the range separation parameter ( $\omega_{\text{GDD}}$ ), determined at the LRC- $\omega$ PBE/aug-cc-pVTZ level. XSAPT calculations for L7 reported in this work were performed using a different basis set (LRC- $\omega$ PBE/def2-TZVPPD), however the results of the GDD tuning procedure are essentially unaffected by this change in basis, with tuned values  $\omega_{\text{GDD}}$  that differ by only  $\sim 0.001$  bohr $^{-1}$  as compared to the values reported in Table S4.

## 3. TOTAL BINDING ENERGIES AND ENERGY DECOMPOSITION OF NOBLE GAS@CB5

The total binding energies for the rare-gas $\cdots$ cucurbit[5]uril (CB5) systems are reported here using the MP2/def2-TZVP deformation energies that are reported in Ref. 2. The energy decomposition provided by XSAPT+MBD in Table S5 suggests that dispersion is the dominant attractive interaction, as the sum of electrostatics, exchange, and induction is positive for all of these systems. GDD-tuned values  $\omega_{\text{GDD}}$  for these complexes are provided in Table S6.

## 4. BENCHMARK DATA FOR THE $\pi 11 \times 8$ DATA SET

The  $\pi 11 \times 8$  data set is comprised of seven structures representative of heterocyclic  $\pi$ -stacking interactions and four substituted benzene complexes from Ref. 3. All structures exhibit either parallel-displaced or sandwich configurations, and are shown in Fig. S1. Equilibrium geometries for the  $\pi 11 \times 8$  data set were obtained via a two-step procedure. First, guess geometries were obtained at the RI-MP2/cc-pVTZ level using the RIJCOSX approximation<sup>4</sup> in the Orca v. 4.1.1 software package,<sup>5</sup> using also the corresponding cc-pVTZ/C and def2/J auxiliary basis sets. Then, the final geometries were converged at the RI-MP2/cc-pVTZ level in Q-Chem,<sup>6</sup> without the RIJCOSX approximation. To construct the  $\pi 11 \times 8$  of geometries at different intermolecular separations, the frozen-geometry potential surface is then scanned by incrementing the intermolecular separation by factors of 0.90, 0.95, 1.00, 1.05, 1.10, 1.25, 1.50, and 2.00 times the equilibrium distance. (The equilibrium distance is defined by the nearest pair of atoms that belong to different monomers.)

Benchmark-quality SAPT2+/aug-cc-pVTZ calculations were carried out on the entire  $\pi 11 \times 8$  data set (Table S7). For the substituted benzene complexes in Table S8, the higher-level SAPT2+3(CCD) approach is also tractable

(Table S8). For the heterocyclic systems where SAPT2+3(CCD) is prohibitively expensive, we present SAPT2+(3) benchmarks instead. The SAPT2+3(CCD) dispersion energy couples induction and dispersion terms and is given by

$$E_{\text{disp}}^{\text{SAPT2+3(CCD)}} = E_{\text{exch-disp}}^{(20)} + E_{\text{disp}}^{(2)}(\text{CCD}) + E_{\text{disp}}^{(22)}[\text{S(CCD)}] + E_{\text{disp}}^{(22)}[\text{T(CCD)}] \\ + E_{\text{disp}}^{(30)} + E_{\text{exch-disp}}^{(30)} + E_{\text{ind-disp}}^{(30)} + E_{\text{exch-ind-disp}}^{(30)}. \quad (\text{S3})$$

The SAPT2+(3) dispersion energy does not include induction/dispersion coupling and is given by

$$E_{\text{disp}}^{\text{SAPT2+(3)}} = E_{\text{exch-disp}}^{(20)} + E_{\text{disp}}^{(20)} + E_{\text{disp}}^{(21)} + E_{\text{disp}}^{(22)}(\text{SDQ}) + E_{\text{disp}}^{(22)}(\text{T}) + E_{\text{disp}}^{(30)} \quad (\text{S4})$$

## 5. ADDITIONAL DATA FOR 3B-69 AND A24 DATA SETS

In an effort to select the best triple- $\zeta$  basis set to pair with XSAPT+MBD, we compared XSAPT+MBD and XSAPT+*aiD3* with CCSD(T)/CBS data for the A24 data set.<sup>7</sup> Among the basis sets considered are Dunning’s aug-cc-pVTZ (aTZ),<sup>8</sup> the pruned Dunning basis sets, jun-cc-pVTZ (junTZ) and jul-cc-pVTZ (julTZ), of Papajak and coworkers,<sup>9</sup> and the Karlsruhe basis set modified with diffuse functions (def2-TZVPPD).<sup>10,11</sup>

Results in Fig. S3 demonstrate reduced errors as compared to the previous XSAPT+*aiD3* method, and also reduced as compared to SAPT(KS) calculations that use traditional second-order dispersion and gas-phase monomer wave functions. All four triple- $\zeta$  basis sets that are compared in Fig. S3 afford quite similar results but the errors are smallest when using the def2-TZVPPD basis set. Given that this basis set is slightly smaller than jun-cc-pVTZ, and is defined for more of the periodic table, we use def2-TZVPPD for the XSAPT calculations presented in this work.

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**6. TABLES**

Table S1: S30L Total binding energies and XSAPT decomposition.

System	Deformation <sup>a</sup> (kcal/mol)	XSAPT+MBD <sup>b</sup> (kcal/mol)				
		Elst	Exch	Ind <sup>c</sup>	MBD+esDQ	Total <sup>d</sup>
1	3.12	-26.76	52.15	-11.90	-56.01	-39.40
2	1.82	-16.88	35.98	-6.09	-40.20	-25.38
3	20.81	-25.30	66.24	-9.05	-73.68	-20.97
4	15.98	-18.66	38.01	-6.77	-48.22	-19.66
5	4.48	-26.74	58.79	-9.41	-64.80	-37.68
6	4.82	-27.90	67.51	-11.47	-65.11	-32.15
7	0.61	-20.52	66.30	-8.26	-84.38	-46.25
8	0.62	-20.49	69.57	-7.37	-93.45	-51.12
9	1.20	-26.54	68.38	0.62	-75.63	-31.96
10	2.54	-27.54	72.21	1.07	-79.95	-31.68
11	4.05	-33.69	87.38	-9.30	-93.16	-44.72
12	3.80	-32.83	85.96	-6.24	-93.16	-42.47
13	0.26	-12.40	25.96	42.45	-41.59	-31.45
14	0.27	-15.25	34.04	49.73	-49.06	-34.59
15	2.50	-52.39	78.21	-15.49	-31.67	-18.84
16	3.09	-47.48	80.51	-16.28	-42.66	-22.83
17	7.18	-48.22	69.23	-20.60	-48.11	-40.52
18	5.63	-33.20	54.46	-12.60	-41.51	-27.22
19	1.38	-14.46	26.46	-4.22	-26.49	-17.34
20	1.91	-17.36	38.27	-4.83	-39.57	-21.58
21	0.26	-9.96	29.17	-2.94	-47.68	-31.15
22	7.67	-63.31	82.62	-30.97	-34.40	-38.39
23	4.72	-72.76	69.07	-42.15	-26.00	-67.12
24	2.83	-111.55	79.84	-38.17	-85.34	-152.39
25	2.92	-13.45	29.60	-3.75	-50.05	-34.74
26	2.94	-13.16	29.28	-5.02	-49.95	-35.92
27	4.26	-67.71	38.76	-25.44	-34.60	-84.72
28	4.77	-65.32	33.08	-25.40	-28.37	-81.24
29	24.92	-83.53	95.11	-52.14	-45.03	-60.68
30	28.05	-78.14	94.97	-50.81	-52.10	-58.02

<sup>a</sup>Calculated at the SCS-MP2/CBS level<sup>b</sup>Using def2-TZVPPD basis.<sup>c</sup>Includes XPol polarization and  $\delta E_{\text{HF}}$  correction.<sup>d</sup>Includes geometric deformation energy.

Table S2: Tuned values of the range separation parameter  $\omega$  for S30L complexes.

System <sup>a</sup>	$\omega_{\text{GDD}}$ (bohr <sup>-1</sup> ) <sup>b</sup>
1a	0.248
1b	0.297
2a	0.248
2b	0.314
3a	0.250
3b	0.296
4a	0.250
4b	0.316
5a	0.243
5b	0.296
6a	0.243
6b	0.296
7a	0.224
7b	0.242
8a	0.220
8b	0.235
9a	0.236
9b	0.243
10a	0.236
10b	0.238
11a	0.234
11b	0.242
12a	0.234
12b	0.237
13a	0.238
13b	0.332
14a	0.238
14b	0.321
15a	0.234
15b	0.296
16a	0.224
16b	0.291
17a	0.236
17b	0.332
18a	0.234
18b	0.336
19a	0.247
19b	0.327
20a	0.247
20b	0.309
21a	0.248
21b	0.304
22a	0.257
22b	0.263
23a	0.254
23b	0.278
24a	0.248
24b	0.290
25a	0.241
25b	0.278
26a	0.241
26b	0.278
27a	0.256
27b	0.339
28a	0.256
28b	0.360
29a	0.251
29b	0.348
30a	0.248
30b	0.303

<sup>a</sup>Host is labeled as *a*,  
 guest is labeled as *b*.

<sup>b</sup>LRC- $\omega$ PBE/def2-TZVPPD.

Table S3: L7 Total interaction energies and XSAPT decomposition.

System	XSAPT+MBD <sup>a</sup> (kcal/mol)				
	Elst	Exch	Ind <sup>b</sup>	MBD+esDQ	Total
C2C2PD	-7.37	25.63	-2.55	-36.87	-21.17
C3A	-7.07	19.05	-2.14	-26.83	-16.99
C3GC	-12.31	36.12	-4.05	-47.64	-27.89
CBH	-3.30	13.88	-1.23	-22.18	-12.83
GCGC	-8.26	23.30	-2.06	-27.52	-14.55
GGG	2.87	6.13	-1.33	-9.80	-2.13
PHE	-27.38	31.64	-11.39	-18.52	-25.64

<sup>a</sup>Using def2-TZVPPD basis.<sup>b</sup>Includes XPol polarization and  $\delta E_{\text{HF}}$  correction.Table S4: Tuned values of the range separation parameter  $\omega$  for L7 complexes.

System	$\omega_{\text{GDD}}$ (bohr <sup>-1</sup> ) <sup>a</sup>
adenine	0.316
circumcoronene	0.242
GC Base-pair	0.288
coronene	0.271
guanine	0.316
guanine dimer	0.286
octadecane	0.314
phenylalanine	0.314
phenylalanine dimer	0.268

<sup>a</sup>LRC- $\omega$ PBE/aug-cc-pVTZ.

Table S5: Rare gas@CB5 total binding energies and XSAPT decomposition

System	XSAPT+MBD <sup>a</sup> (kcal/mol)				
	Elst	Exch	Ind <sup>b</sup>	MBD+esDQ	Total
He	-0.05	0.21	-0.02	-1.28	-1.01
Ne	-0.21	0.73	-0.02	-2.56	-2.01
Ar	-1.20	3.49	-0.19	-8.49	-6.73
Kr	-2.43	6.99	-0.40	-12.06	-8.93
Xe	-41.42	53.51	-2.30	-19.46	-13.88

<sup>a</sup>Using def2-TZVPPD basis.<sup>b</sup>Includes XPol polarization and  $\delta E_{\text{HF}}$  correction.

Table S6: Tuned values of range-separation parameter for rare gas@CB5 complexes.

System	$\omega_{\text{GDD}}$ (bohr <sup>-1</sup> ) <sup>a</sup>
He	0.803
Ne	0.661
Ar	0.513
Kr	0.455
Xe	0.279
CB5	0.265

<sup>a</sup>LRC- $\omega$ PBE/def2-TZVPPD

Table S7: Energy decomposition for heterocyclic systems in  $\pi 11 \times 8$ .

System	Distance <sup>a</sup>	SAPT2+(3) <sup>b</sup> (kcal/mol)				
		Elst	Exch	Ind	Disp	Total
benzene···naphthaline	0.90	-8.26	24.51	-2.17	-16.73	-2.66
benzene···naphthaline	0.95	-4.60	15.05	-1.40	-13.26	-4.22
benzene···naphthaline	1.00	-2.40	9.18	-0.92	-10.56	-4.69
benzene···naphthaline	1.05	-1.09	5.58	-0.62	-8.43	-4.56
benzene···naphthaline	1.10	-0.33	3.37	-0.43	-6.75	-4.14
benzene···naphthaline	1.25	0.45	0.73	-0.17	-3.56	-2.54
benzene···naphthaline	1.50	0.44	0.05	-0.05	-1.34	-0.89
benzene···naphthaline	2.00	0.19	0.00	-0.01	-0.27	-0.09
benzene···pteridine	0.90	-19.77	47.91	-4.51	-23.48	0.15
benzene···pteridine	0.95	-12.51	30.00	-2.86	-18.57	-3.94
benzene···pteridine	1.00	-7.96	18.68	-1.82	-14.75	-5.85
benzene···pteridine	1.05	-5.11	11.58	-1.17	-11.76	-6.47
benzene···pteridine	1.10	-3.33	7.14	-0.77	-9.41	-6.36
benzene···pteridine	1.25	-1.05	1.64	-0.24	-4.92	-4.58
benzene···pteridine	1.50	-0.28	0.13	-0.06	-1.83	-2.03
benzene···pteridine	2.00	-0.07	0.00	-0.01	-0.36	-0.43
benzene···quinazoline	0.90	-18.26	46.16	-4.41	-23.11	0.39
benzene···quinazoline	0.95	-11.48	29.44	-2.84	-18.47	-3.34
benzene···quinazoline	1.00	-7.17	18.68	-1.84	-14.81	-5.14
benzene···quinazoline	1.05	-4.45	11.79	-1.20	-11.92	-5.78
benzene···quinazoline	1.10	-2.74	7.41	-0.79	-9.62	-5.74
benzene···quinazoline	1.25	-0.57	1.79	-0.26	-5.16	-4.20
benzene···quinazoline	1.50	0.04	0.16	-0.06	-1.97	-1.84
benzene···quinazoline	2.00	0.06	0.00	-0.01	-0.40	-0.35
pyrazine···naphthaline	0.90	-19.33	49.70	-5.32	-24.35	0.69
pyrazine···naphthaline	0.95	-12.04	31.28	-3.41	-19.33	-3.50
pyrazine···naphthaline	1.00	-7.47	19.56	-2.18	-15.40	-5.50
pyrazine···naphthaline	1.05	-4.63	12.17	-1.40	-12.32	-6.19
pyrazine···naphthaline	1.10	-2.87	7.53	-0.91	-9.89	-6.13
pyrazine···naphthaline	1.25	-0.68	1.74	-0.27	-5.22	-4.43
pyrazine···naphthaline	1.50	-0.05	0.14	-0.06	-1.95	-1.92
pyrazine···naphthaline	2.00	0.02	0.00	-0.01	-0.38	-0.37
pyrazine···pteridine	0.90	-19.93	49.12	-5.39	-24.27	-0.48
pyrazine···pteridine	0.95	-12.70	30.74	-3.38	-19.21	-4.56
pyrazine···pteridine	1.00	-8.18	19.12	-2.13	-15.26	-6.45
pyrazine···pteridine	1.05	-5.35	11.83	-1.35	-12.17	-7.04
pyrazine···pteridine	1.10	-3.58	7.28	-0.86	-9.74	-6.90
pyrazine···pteridine	1.25	-1.28	1.65	-0.24	-5.11	-4.98
pyrazine···pteridine	1.50	-0.44	0.13	-0.04	-1.90	-2.26
pyrazine···pteridine	2.00	-0.14	0.00	-0.01	-0.38	-0.52
pyrazine···quinazoline	0.90	-18.15	46.50	-4.65	-23.56	0.14
pyrazine···quinazoline	0.95	-11.46	29.44	-2.96	-18.78	-3.75
pyrazine···quinazoline	1.00	-7.24	18.53	-1.87	-15.01	-5.60
pyrazine···quinazoline	1.05	-4.59	11.60	-1.19	-12.05	-6.22
pyrazine···quinazoline	1.10	-2.92	7.23	-0.76	-9.70	-6.15
pyrazine···quinazoline	1.25	-0.80	1.71	-0.21	-5.18	-4.48
pyrazine···quinazoline	1.50	-0.13	0.14	-0.04	-1.97	-2.00
pyrazine···quinazoline	2.00	-0.01	0.00	-0.01	-0.40	-0.42
pyridine···pteridine	0.90	-20.03	46.64	-4.98	-23.50	-1.87
pyridine···pteridine	0.95	-13.28	29.95	-3.24	-18.85	-5.42
pyridine···pteridine	1.00	-8.93	19.13	-2.12	-15.16	-7.08
pyridine···pteridine	1.05	-6.11	12.16	-1.40	-12.24	-7.59
pyridine···pteridine	1.10	-4.29	7.70	-0.94	-9.91	-7.44
pyridine···pteridine	1.25	-1.78	1.91	-0.32	-5.37	-5.55
pyridine···pteridine	1.50	-0.74	0.18	-0.08	-2.09	-2.73
pyridine···pteridine	2.00	-0.30	0.00	-0.02	-0.43	-0.75

<sup>a</sup>Distances given as fraction of the equilibrium distance.<sup>b</sup>All SAPT calculations done using aug-cc-pVTZ basis set.



Table S8: Energy decomposition of substituted benzene systems in  $\pi 11 \times 8$ .

System	Distance <sup>a</sup>	SAPT2+3(CCD) <sup>b</sup> (kcal/mol)				
		Elst	Exch	Ind	Disp	Total
benzene...benzotrile	0.90	-8.26	24.51	-2.17	-16.73	-2.66
benzene...benzotrile	0.95	-4.60	15.05	-1.40	-13.26	-4.22
benzene...benzotrile	1.00	-2.40	9.18	-0.92	-10.56	-4.69
benzene...benzotrile	1.05	-1.09	5.58	-0.62	-8.43	-4.56
benzene...benzotrile	1.10	-0.33	3.37	-0.43	-6.75	-4.14
benzene...benzotrile	1.25	0.45	0.73	-0.17	-3.56	-2.54
benzene...benzotrile	1.50	0.44	0.05	-0.05	-1.34	-0.89
benzene...benzotrile	2.00	0.19	0.00	-0.01	-0.27	-0.09
benzene...fluorobenzene	0.90	-19.77	47.91	-4.51	-23.48	0.15
benzene...fluorobenzene	0.95	-12.51	30.00	-2.86	-18.57	-3.94
benzene...fluorobenzene	1.00	-7.96	18.68	-1.82	-14.75	-5.85
benzene...fluorobenzene	1.05	-5.11	11.58	-1.17	-11.76	-6.47
benzene...fluorobenzene	1.10	-3.33	7.14	-0.77	-9.41	-6.36
benzene...fluorobenzene	1.25	-1.05	1.64	-0.24	-4.92	-4.58
benzene...fluorobenzene	1.50	-0.28	0.13	-0.06	-1.83	-2.03
benzene...fluorobenzene	2.00	-0.07	0.00	-0.01	-0.36	-0.43
benzene...phenol	0.90	-18.26	46.16	-4.41	-23.11	0.39
benzene...phenol	0.95	-11.48	29.44	-2.84	-18.47	-3.34
benzene...phenol	1.00	-7.17	18.68	-1.84	-14.81	-5.14
benzene...phenol	1.05	-4.45	11.79	-1.20	-11.92	-5.78
benzene...phenol	1.10	-2.74	7.41	-0.79	-9.62	-5.74
benzene...phenol	1.25	-0.57	1.79	-0.26	-5.16	-4.20
benzene...phenol	1.50	0.04	0.16	-0.06	-1.97	-1.84
benzene...phenol	2.00	0.06	0.00	-0.01	-0.40	-0.35
benzene...toluene	0.90	-19.33	49.70	-5.32	-24.35	0.69
benzene...toluene	0.95	-12.04	31.28	-3.41	-19.33	-3.50
benzene...toluene	1.00	-7.47	19.56	-2.18	-15.40	-5.50
benzene...toluene	1.05	-4.63	12.17	-1.40	-12.32	-6.19
benzene...toluene	1.10	-2.87	7.53	-0.91	-9.89	-6.13
benzene...toluene	1.25	-0.68	1.74	-0.27	-5.22	-4.43
benzene...toluene	1.50	-0.05	0.14	-0.06	-1.95	-1.92
benzene...toluene	2.00	0.02	0.00	-0.01	-0.38	-0.37

<sup>a</sup>Distances given in fraction of equilibrium distance.<sup>b</sup>All SAPT calculations done using aug-cc-pVTZ basis set.

**7. FIGURES**

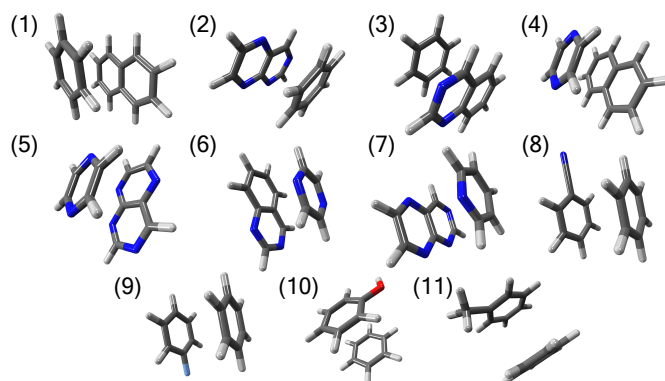


Figure S1: Equilibrium structures of the  $\pi 11 \times 8$  data set. (1) benzene...naphthalene, (2) benzene...pteridine, (3) benzene...quinazoline, (4) pyrazine...naphthalene, (5) pyrazine...pteridine, (6) pyrazine...quinazoline, (7) pyridine...pteridine, (8) benzene...benzonitrile, (9) benzene...fluorobenzene, (10) benzene...phenol, (11) benzene...toluene.

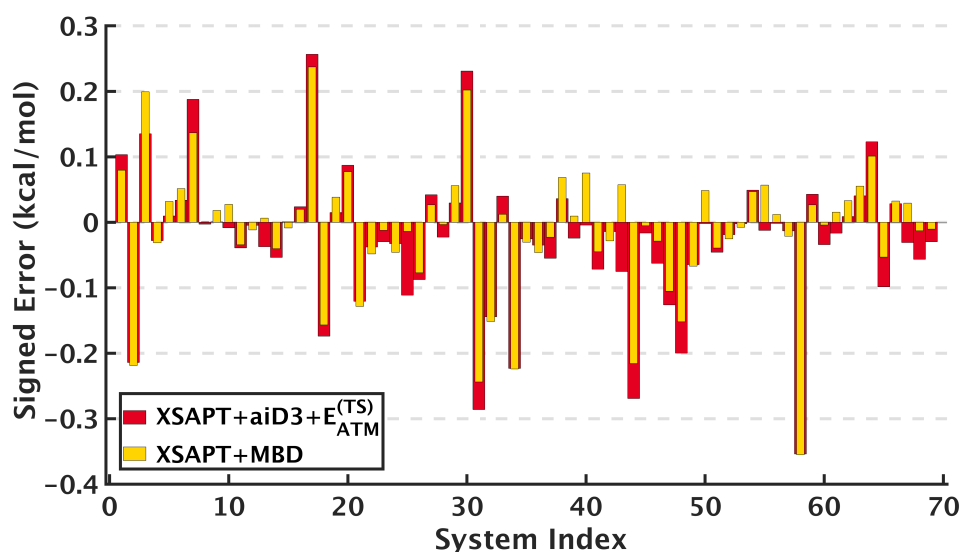


Figure S2: Errors in the three-body interaction energies for the 3B-69 data set, relative to CCSD(T)/CBS results. Negative values correspond to an overestimation of the three-body contribution to the interaction energy.

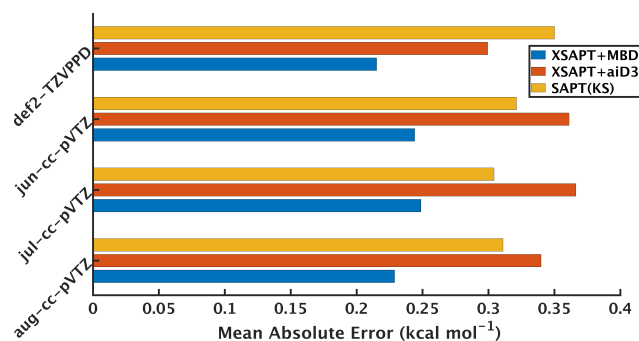


Figure S3: Comparison of mean absolute errors in total interaction energies versus CCSD(T)/CBS benchmarks for the A24 data set, using the  $+aiD3$  correction versus the new MBD correction. The jun-cc-pVTZ and jul-cc-pVTZ basis sets are taken from Ref. 9 and def2-TZVPPD is the updated basis set from Ref. 11.