

Supporting Information for “Comprehensive Basis-Set Testing of Extended Symmetry-Adapted Perturbation Theory and Assessment of Mixed-Basis Combinations to Reduce Cost”

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Table S1: Range-separation parameters for the monomers A and B in the S66 dimers $A \cdots B$.

index	Dimer $A \cdots B$			ω_{GDD} (bohr $^{-1}$)	
	A	B	(notes)	A	B
1	water	water		0.505	0.503
2	water	MeOH		0.505	0.430
3	water	MeNH ₂		0.504	0.412
4	water	peptide		0.505	0.351
5	MeOH	MeOH		0.429	0.430
6	MeOH	MeNH ₂		0.428	0.412
7	MeOH	peptide		0.429	0.352
8	MeOH	water		0.429	0.503
9	MeNH ₂	MeOH		0.411	0.427
10	MeNH ₂	MeNH ₂		0.413	0.411
11	MeNH ₂	peptide		0.413	0.352
12	MeNH ₂	water		0.412	0.505
13	peptide	MeOH		0.352	0.429
14	peptide	MeNH ₂		0.351	0.410
15	peptide	peptide		0.350	0.350
16	peptide	water		0.351	0.507
17	uracil	uracil	(base pair)	0.341	0.342
18	water	pyridine		0.502	0.354
19	MeOH	pyridine		0.428	0.355
20	AcOH	AcOH		0.391	0.391
21	AcNH ₂	AcNH ₂		0.377	0.377
22	AcOH	uracil		0.392	0.342
23	AcNH ₂	uracil		0.378	0.342
24	benzene	benzene	(π - π)	0.344	0.344
25	pyridine	pyridine	(π - π)	0.352	0.351
26	uracil	uracil	(π - π)	0.343	0.343
27	benzene	pyridine	(π - π)	0.339	0.353
28	benzene	uracil	(π - π)	0.345	0.343
29	pyridine	uracil		0.354	0.343
30	benzene	ethene		0.341	0.425
31	uracil	ethene		0.342	0.423
32	uracil	ethyne		0.342	0.438
33	pyridine	ethene		0.348	0.418
34	pentane	pentane		0.323	0.323
35	neopentane	pentane		0.323	0.328
36	neopentane	neopentane		0.329	0.329
37	cyclopentane	neopentane		0.338	0.327
38	cyclopentane	cyclopentane		0.337	0.338
39	benzene	cyclopentane		0.341	0.336
40	benzene	neopentane		0.342	0.328
41	uracil	pentane		0.341	0.322
42	uracil	cyclopentane		0.343	0.338
43	uracil	neopentane		0.343	0.327
44	ethene	pentane		0.424	0.324
45	ethyne	pentane		0.435	0.324
46	peptide	pentane		0.351	0.323

Continued on next page

Table S1 – continued from previous page

index	Dimer $A \cdots B$			ω_{GDD} (bohr $^{-1}$)	
	A	B	(notes)	A	B
47	benzene	benzene	(T-shaped)	0.338	0.340
48	pyridine	pyridine	(T-shaped)	0.350	0.353
49	benzene	pyridine	(T-shaped)	0.338	0.349
50	benzene	ethyne	(CH $\cdots\pi$)	0.342	0.437
51	ethyne	ethyne	(T-shaped)	0.435	0.437
52	benzene	AcOH		0.337	0.391
53	benzene	AcNH $_2$		0.339	0.379
54	benzene	water	(OH $\cdots\pi$)	0.341	0.502
55	benzene	MeOH	(OH $\cdots\pi$)	0.343	0.429
56	benzene	MeNH $_2$	(NH $\cdots\pi$)	0.343	0.411
57	benzene	peptide	(NH $\cdots\pi$)	0.344	0.351
58	pyridine	pyridine	(CH $\cdots\text{N}$)	0.355	0.355
59	ethyne	water	(CH $\cdots\text{O}$)	0.436	0.504
60	ethyne	AcOH	(OH $\cdots\pi$)	0.437	0.391
61	pentane	AcOH		0.322	0.394
62	pentane	AcNH $_2$		0.323	0.377
63	benzene	AcOH		0.340	0.391
64	peptide	ethene		0.350	0.424
65	pyridine	ethyne		0.353	0.437
66	MeNH $_2$	pyridine		0.412	0.349

Table S2: Range-separation parameters for the monomers A and B in the S22 dimers $A \cdots B$.

index	Dimer $A \cdots B$			ω_{GDD} (bohr $^{-1}$)	
	A	B	(notes)	A	B
1	NH ₃	NH ₃		0.463	0.463
2	H ₂ O	H ₂ O		0.506	0.505
3	H ₂ CO ₂	H ₂ CO ₂		0.435	0.435
4	formamide	formamide		0.415	0.415
5	uracil	uracil	(H-bonded)	0.342	0.342
6	2-pyridoxine	2-aminopyridine		0.339	0.333
7	adenine	thymine	(base pair)	0.322	0.332
8	CH ₄	CH ₄		0.445	0.445
9	C ₂ H ₄	C ₂ H ₄		0.422	0.422
10	C ₆ H ₆	CH ₄		0.341	0.446
11	C ₆ H ₆	C ₆ H ₆	(parallel-displaced)	0.342	0.342
12	pyrazine	pyrazine		0.365	0.360
13	uracil	uracil	(stacked)	0.343	0.343
14	indole	C ₆ H ₆	(stacked)	0.343	0.310
15	adenine	thymine	(stacked)	0.321	0.331
16	C ₂ H ₄	C ₂ H ₂		0.424	0.435
17	C ₆ H ₆	H ₂ O		0.341	0.506
18	C ₆ H ₆	NH ₃		0.341	0.463
19	C ₆ H ₆	HCN		0.344	0.477
20	C ₆ H ₆	C ₆ H ₆	(T-shaped)	0.337	0.337
21	indole	C ₆ H ₆	(T-shaped)	0.341	0.309
22	phenol	phenol		0.332	0.331

Table S3: Range-separation parameters for the monomers A and B in the AHB21 dimers $A \cdots B$.

index	Dimer $A \cdots B$		ω_{GDD} (bohr $^{-1}$)	
	A	B	A	B
1	F $^{-}$	NH $_3$	0.548	0.459
2	F $^{-}$	H $_2$ O	0.548	0.495
3	F $^{-}$	HF	0.548	0.550
4	Cl $^{-}$	NH $_3$	0.407	0.461
5	Cl $^{-}$	H $_2$ O	0.407	0.502
6	Cl $^{-}$	HF	0.407	0.573
7	Cl $^{-}$	H $_2$ S	0.407	0.404
8	Cl $^{-}$	HCl	0.407	0.433
9	OH $^{-}$	NH $_3$	0.462	0.459
10	OH $^{-}$	H $_2$ O	0.454	0.491
11	N $_3^{-}$	NH $_3$	0.421	0.462
12	N $_3^{-}$	H $_2$ O	0.418	0.502
13	N $_3^{-}$	HF	0.459	0.572
14	N $_3^{-}$	H $_2$ S	0.421	0.405
15	SH $^{-}$	NH $_3$	0.365	0.462
16	SH $^{-}$	H $_2$ O	0.365	0.499
17	SH $^{-}$	HF	0.365	0.568
18	HCO $_2^{-}$	CH $_3$ NH $_2$	0.404	0.410
19	HCO $_2^{-}$	CH $_3$ OH	0.404	0.425
20	HCO $_2^{-}$	H $_2$ O	0.401	0.502
21	HCO $_2^{-}$	HF	0.406	0.566

Table S4: Range-separation parameters for the monomers A and B in the CHB6 dimers $A \cdots B$.

index	Dimer $A \cdots B$		ω_{GDD} (bohr $^{-1}$)	
	A	B	A	B
22	Li $^{+}$	H $_2$ O	1.305	0.502
23	Na $^{+}$	H $_2$ O	0.839	0.504
24	K $^{+}$	H $_2$ O	0.589	0.505
25	Li $^{+}$	C $_6$ H $_6$	1.305	0.341
26	Na $^{+}$	C $_6$ H $_6$	0.839	0.340
27	K $^{+}$	C $_6$ H $_6$	0.589	0.340

Table S5: Range-separation parameters for the monomers A and B in the A24 dataset, $A \cdots B$.

Complex	Dimer ^a $A \cdots B$	ω_{GDD} (bohr ⁻¹)	
		A	B
01	Water-Water	0.505	0.463
02	Water-Water	0.506	0.504
03	HCN-HCN	0.479	0.479
04	HF-HF	0.583	0.579
05	Ammonia-Ammonia	0.464	0.464
06	HF-Methane	0.445	0.582
07	Ammonia-Methane	0.462	0.446
08	Water-Methane	0.507	0.446
09	Formaldehyde-Formaldehyde	0.458	0.46
10	Water-Ethene	0.504	0.419
11	Formaldehyde-Ethene	0.459	0.419
12	Ethyne-Ethyne	0.435	0.435
13	Ammonia-Ethene	0.463	0.421
14	Ethene-Ethene	0.424	0.425
15	Methane-Ethene	0.445	0.419
16	Borane-Methane	0.442	0.446
17	Methane-Ethane	0.445	0.405
18	Methane-Ethane	0.445	0.408
19	Methane-Methane	0.446	0.446
20	Ar-Methane	0.522	0.446
21	Ar-Ethene	0.522	0.424
22	Ethene-Ethyne	0.425	0.435
23	Ethene-Ethene	0.425	0.425
24	Ethyne-Ethyne	0.435	0.435

^aFrom *J. Chem. Theory Comput.* **9**, 2151 (2013).

Table S6: Range-separation parameters for the monomers A and B in the IL16 dimers $A \cdots B$.

index	Dimer ^a $A \cdots B$	ω_{GDD} (bohr ⁻¹)	
		A	B
1	IL-008	0.337	0.407
2	IL-144	0.389	0.381
3	IL-147	0.389	0.384
4	IL-148	0.354	0.407
5	IL-150	0.355	0.407
6	IL-152	0.359	0.375
7	IL-187	0.340	0.407
8	IL-202	0.352	0.407
9	IL-212	0.362	0.407
10	IL-213	0.362	0.409
11	IL-214	0.364	0.374
12	IL-227	0.391	0.407
13	IL-228	0.387	0.409
14	IL-229	0.391	0.375
15	IL-230	0.392	0.349
16	IL-231	0.391	0.370

^aFrom *Phys. Chem. Chem. Phys.* **15**, 13664 (2013).

Table S7: Range-separation parameters for monomers in the $F^-(H_2O)_6$ complex.

Monomer	ω_{GDD} (bohr $^{-1}$)
F $^-$	0.548
water1	0.502
water2	0.503
water3	0.502
water4	0.501
water5	0.503
water6	0.502

Table S8: Range-separation parameters for large complexes.

Monomer	ω_{GDD} (bohr $^{-1}$)
DNA double strand	0.242
ellipticene	0.282
coronene	0.273

Table S9: XSAPT + MBD error statistics for interaction energies in the A24 data set, as compared to CCSD(T)/CBS benchmarks.^a

Basis Set	Error (kcal/mol)							
	All A24		H-Bonded ^b		Mixed ^c		Disp.-Bound ^d	
	MAE	Max	MAE	Max	MAE	Max	MAE	Max
aug-cc-pVDZ	0.35	1.30	0.41	1.15	0.37	0.78	0.28	1.30
aug-cc-pVTZ	0.27	1.56	0.33	0.73	0.28	0.66	0.22	1.56
aug-cc-pVQZ	0.26	1.59	0.26	0.75	0.25	0.69	0.27	1.59
aug-cc-pV5Z	0.26	1.62	0.23	0.67	0.27	0.83	0.26	1.62

^aBenchmarks from *J. Chem. Theory Comput.* **9**, 2151 (2013)

^bComplexes 1–5 of A24.

^cComplexes 6–15.

^dComplexes 16–24.

Table S10: Error statistics for SAPT0(KS) + MBD applied to the S66 data set.^a (Values in parenthesis exclude the δE_{HF} correction.)

Method	Error (kcal/mol)							
	H-Bonded		Dispersion		Mixed		All S66	
	MAE	Max	MAE	Max	MAE	Max	MAE	Max
def2-SVP	3.56 (1.68)	7.38 (2.62)	2.39 (2.09)	5.37 (4.98)	1.84 (1.43)	2.52 (2.01)	2.60 (1.75)	7.38 (4.98)
def2-SVPD	0.67 (1.25)	1.92 (4.22)	1.66 (1.32)	3.47 (2.96)	1.19 (0.75)	2.25 (1.65)	1.17 (1.12)	3.47 (4.22)
def2-TZVP	0.40 (1.68)	0.95 (6.71)	0.58 (0.30)	2.02 (1.49)	0.79 (0.34)	1.35 (0.87)	0.58 (0.79)	2.02 (6.71)
def2-TZVPD	0.50 (2.49)	1.62 (8.06)	0.43 (0.18)	1.51 (0.93)	0.48 (0.23)	0.95 (0.58)	0.47 (1.00)	1.62 (8.06)
def2-QZVP	0.22 (2.22)	0.77 (6.71)	0.38 (0.18)	1.30 (0.72)	0.53 (0.23)	1.11 (0.60)	0.37 (0.90)	1.30 (6.71)
def2-QZVPD	0.43 (2.47)	0.98 (7.13)	0.32 (0.14)	1.00 (0.46)	0.46 (0.30)	1.10 (0.70)	0.40 (1.00)	1.10 (7.13)
cc-pVDZ	3.13 (1.29)	6.90 (2.03)	2.45 (2.12)	5.37 (4.94)	1.89 (1.46)	2.61 (2.07)	2.52 (1.63)	6.90 (4.94)
jun-cc-pVDZ	0.81 (1.12)	1.96 (4.20)	0.72 (0.43)	2.06 (1.56)	0.67 (0.39)	1.32 (0.81)	0.74 (0.66)	2.06 (4.20)
jul-cc-pVDZ	0.31 (2.16)	1.01 (5.82)	0.76 (0.41)	2.06 (1.50)	0.62 (0.43)	1.27 (0.91)	0.56 (1.03)	2.06 (5.82)
aug-cc-pVDZ	0.19 (1.85)	0.81 (5.90)	0.77 (0.45)	2.02 (1.47)	0.68 (0.38)	1.45 (0.96)	0.54 (0.91)	2.02 (5.90)
cc-pVTZ	1.74 (0.78)	3.55 (2.96)	1.17 (0.80)	3.20 (2.66)	1.19 (0.70)	1.73 (1.15)	1.38 (0.76)	3.55 (2.96)
jun-cc-pVTZ	0.17 (2.10)	0.60 (6.42)	0.55 (0.22)	1.79 (1.22)	0.49 (0.24)	1.00 (0.63)	0.40 (0.88)	1.79 (6.42)
jul-cc-pVTZ	0.16 (2.11)	0.60 (6.49)	0.53 (0.20)	1.65 (1.07)	0.49 (0.23)	1.01 (0.58)	0.39 (0.88)	1.65 (6.49)
aug-cc-pVTZ	0.21 (2.21)	0.67 (6.80)	0.42 (0.17)	1.53 (0.95)	0.41 (0.22)	1.00 (0.62)	0.34 (0.90)	1.53 (6.80)
cc-pVQZ	0.36 (1.74)	0.66 (6.29)	0.59 (0.26)	2.10 (1.53)	0.76 (0.31)	1.40 (0.66)	0.56 (0.79)	2.10 (6.30)
jun-cc-pVQZ	0.39 (0.39)	1.01 (7.43)	0.31 (0.18)	1.04 (0.52)	0.42 (0.24)	0.95 (0.62)	0.37 (0.98)	1.04 (7.43)
jul-cc-pVQZ	0.34 (2.38)	0.92 (7.23)	0.31 (0.18)	1.10 (0.53)	0.40 (0.24)	0.91 (0.61)	0.35 (0.96)	1.10 (7.23)
aug-cc-pVQZ	0.42 (2.46)	0.87 (7.19)	0.28 (0.19)	1.05 (0.51)	0.38 (0.24)	0.95 (0.64)	0.36 (0.99)	1.05 (7.19)
6-311+G(3df,2pd)	0.56 (1.50)	2.05 (4.45)	0.86 (0.50)	2.41 (1.84)	0.79 (0.41)	1.41 (0.98)	0.73 (0.82)	2.41 (4.45)
6-311++G(3df,2pd)	0.50 (1.58)	1.95 (4.55)	0.81 (0.45)	2.34 (1.77)	0.74 (0.39)	1.40 (0.97)	0.68 (0.82)	2.34 (4.55)

^aValues with the δE_{HF} correction are the same as those given in Table 6.

Table S11: Error Statistics for XSAPT Methods Applied to the IL16 Data Set.

Basis Set	Error (kcal/mol)					
	XSAPT + <i>aiD3</i>		SAPT0(HF) + <i>aiD3</i>		SAPT0(KS) + <i>aiD3</i>	
	MAE	Max	MAE	Max	MAE	Max
jun-cc-pVDZ	1.09 (1.0%)	3.18	3.50 (3.1%)	9.55	5.48 (5.0%)	9.86
jul-cc-pVDZ	2.53 (2.3%)	5.75	1.89 (1.7%)	4.82	3.46 (3.2%)	5.05
aug-cc-pVDZ	1.29 (1.2%)	3.54	1.68 (1.5%)	4.11	3.00 (2.7%)	4.17
def2-SVPD	1.23 (1.1%)	2.60	1.36 (1.2%)	3.11	2.52 (2.3%)	5.02
jun-cc-pVTZ	0.80 (0.8%)	3.07	1.77 (1.6%)	4.28	2.53 (2.3%)	4.79
jul-cc-pVTZ	1.28 (1.2%)	3.46	1.45 (1.3%)	3.39	2.62 (2.4%)	3.83
aug-cc-pVTZ	1.71 (1.6%)	3.83	1.34 (1.2%)	3.07	2.31 (2.1%)	3.49
def2-TZVPD	1.08 (1.0%)	2.29	2.10 (1.9%)	4.49	3.35 (3.0%)	5.24
def2-TZVPPD	0.85 (0.8%)	2.16	1.71 (1.5%)	3.93	2.97 (2.7%)	4.62
jun-cc-pVDZ	1.17 (1.1%)	2.79	1.29 (1.2%)	2.94	2.98 (2.7%)	4.23
jul-cc-pVQZ	1.44 (1.3%)	3.38	1.15 (1.0%)	2.47	2.27 (2.1%)	3.92
aug-cc-pVQZ	1.72 (1.6%)	3.69	1.06 (1.0%)	2.64	1.95 (1.8%)	3.54
def2-QZVPD	1.24 (1.1%)	2.63	1.38 (1.2%)	3.15	2.55 (2.3%)	4.28
def2-QZVPPD	1.24 (1.1%)	2.63	1.38 (1.2%)	3.15	2.55 (2.3%)	4.28
6-311+G(3df,2pd)	8.33 (8.1%)	18.12	2.47 (2.3%)	4.89	2.52 (2.3%)	4.78
6-311++G(3df,2pd)	8.32 (8.1%)	18.09	2.47 (2.3%)	4.89	2.53 (2.3%)	4.79

Table S12: Error Statistics for XSAPT Methods Applied to the AHB21 Data Set.

Basis Set	Error (kcal/mol)								
	XSAPT + <i>aiD3</i>			SAPT0(HF) + <i>aiD3</i>			SAPT0(KS) + <i>aiD3</i>		
	MAE		Max	MAE		Max	MAE		Max
jun-cc-pVDZ	3.12	(13%)	13.12	3.17	(13%)	20.81	4.85	(18%)	18.85
jul-cc-pVDZ	2.26	(11%)	7.69	2.26	(9.9%)	15.23	3.93	(16%)	14.56
aug-cc-pVDZ	1.86	(8.0%)	7.36	2.15	(9.3%)	13.85	4.08	(16%)	13.38
def2-SVPD	2.49	(11%)	8.14	2.42	(11%)	14.18	4.05	(16%)	13.68
jun-cc-pVTZ	1.76	(8.4%)	6.44	2.25	(10%)	14.44	3.72	(16%)	13.49
jul-cc-pVTZ	1.48	(7.0%)	5.69	2.07	(9.4%)	12.08	3.17	(14%)	11.08
aug-cc-pVTZ	1.27	(5.8%)	5.70	1.82	(8.5%)	9.06	3.06	(14%)	8.30
def2-TZVPD	2.54	(11%)	8.36	2.80	(12%)	15.76	4.50	(19%)	14.76
def2-TZVPPD	1.89	(8.9%)	6.09	2.38	(11%)	12.78	4.03	(17%)	12.81
jun-cc-pVDZ	1.43	(6.9%)	6.18	2.05	(9.6%)	10.84	3.13	(14%)	9.72
jul-cc-pVQZ	1.28	(6.2%)	7.80	1.92	(8.9%)	9.32	2.84	(13%)	8.18
aug-cc-pVQZ	1.23	(5.5%)	8.18	1.75	(8.2%)	6.66	2.41	(12%)	5.73
def2-QZVPD	1.46	(7.3%)	3.06	2.10	(10%)	10.87	3.53	(15%)	9.71
def2-QZVPPD	1.46	(7.3%)	3.06	2.10	(10%)	10.87	3.53	(15%)	9.71
6-311+G(3df,2pd)	1.76	(8.2%)	8.28	2.55	(11.7%)	16.38	3.37	(14.6%)	15.34
6-311++G(3df,2pd)	1.74	(8.1%)	8.09	2.51	(12%)	16.06	3.37	(15%)	15.10

Table S13: Error Statistics for XSAPT Methods Applied to the CHB6 Data Set.

Basis Set	Error (kcal/mol)					
	XSAPT + <i>aiD3</i>		SAPT0(HF) + <i>aiD3</i>		SAPT0(KS) + <i>aiD3</i>	
	MAE ^a	Max ^b	MAE ^a	Max ^b	MAE ^a	Max ^b
jun-cc-pVDZ	1.46 (5.0%)	3.11	0.37 (1.6%)	0.90	0.51 (2.0%)	1.17
jul-cc-pVDZ	2.05 (6.4%)	6.19	1.73 (6.0%)	4.69	1.52 (5.4%)	4.35
aug-cc-pVDZ	2.01 (6.2%)	6.50	1.80 (6.2%)	4.98	1.56 (5.5%)	4.60
def2-SVPD	1.52 (5.3%)	2.89	1.92 (7.1%)	3.66	1.09 (3.8%)	3.40
jun-cc-pVTZ	2.09 (6.4%)	7.21	1.54 (5.0%)	5.17	1.68 (5.6%)	5.89
jul-cc-pVTZ	2.32 (7.1%)	7.57	1.68 (5.4%)	5.52	1.66 (5.5%)	6.22
aug-cc-pVTZ	2.09 (6.3%)	7.06	1.72 (5.6%)	5.68	1.73 (5.7%)	6.33
def2-TZVPD	1.26 (4.0%)	3.65	1.82 (6.0%)	5.73	1.76 (5.8%)	6.39
def2-TZVPPD	1.63 (5.0%)	5.78	1.88 (6.2%)	6.11	1.88 (6.2%)	6.69
jun-cc-pVDZ	1.53 (4.8%)	4.40	1.87 (6.0%)	6.14	1.91 (6.4%)	6.85
jul-cc-pVQZ	1.69 (5.1%)	5.53	1.84 (5.9%)	6.09	1.87 (6.2%)	6.74
aug-cc-pVQZ	1.31 (3.8%)	7.74	1.82 (5.8%)	6.11	1.88 (6.3%)	6.69
def2-QZVPD	1.20 (3.8%)	3.96	1.88 (6.2%)	6.05	1.98 (6.6%)	7.05
def2-QZVPPD	1.20 (3.8%)	3.96	1.90 (6.2%)	6.05	1.98 (6.6%)	7.05
6-311+G(3df,2pd)	2.98 (8.8%)	10.38	1.80 (5.9%)	5.85	1.89 (6.4%)	5.56
6-311++G(3df,2pd)	2.94 (8.7%)	10.26	1.83 (6.0%)	5.89	1.91 (6.4%)	6.58

Table S14: SAPT0(KS)+MBD Results for Large Supramolecular Complexes.

Basis Set ^a	E_{int} (kcal/mol)			
	DNA/ellipticine		coronene dimer	
	sans δE_{HF}	with δE_{HF}^b	sans δE_{HF}	with δE_{HF}^b
6-311+G(3df,2pd)	-43.4	-46.3	-26.1	-27.9
6-311++G(3df,2pd)	-42.6	-45.7	-25.9	-27.7
def2-SVP	-61.2	-64.2		
def2-ma-SVP	-62.2	-65.1	-31.5	-33.4
def2-ha-SVP	-54.4	-57.3	-32.5	-34.3
def2-SVPD	-54.3	-46.4	-32.5	-34.3
def2-TZVP	-41.6	-46.4		
def2-ma-TZVP	-41.6	-44.5	-20.9	-22.7
def2-ha-TZVP	-40.6	-43.5	-20.9	-22.8
def2-TZVPD	-40.4	-43.3	-21.0	-22.8
jun-cc-pVDZ	-44.0	-46.9	-27.4	-29.2
jul-cc-pVDZ	-43.5	-46.4	-27.0	-28.9
aug-cc-pVDZ	-43.3	-46.2	-27.5	-29.3
jun-cc-pVTZ	-40.5	-44.5	-22.6	-24.5
jul-cc-pVTZ			-22.6	-24.4
aug-cc-pVTZ			-22.4	-24.3
CCSD(T)/CBS ^c	-38.6 ± 2.2		-20.93 ± 0.44	
QMC ^c	-33.6 ± 0.9		-18.1 ± 0.8	

^aCalculations performed at SAPT0(KS)+MBD level (except for the benchmarks), using the indicated basis set for all parts of the calculation except δE_{HF} . ^bThe δE_{HF} calculation is performed using 6-31+G(d). ^cSee Tables 10 and 11 for literature references for the benchmark calculations.

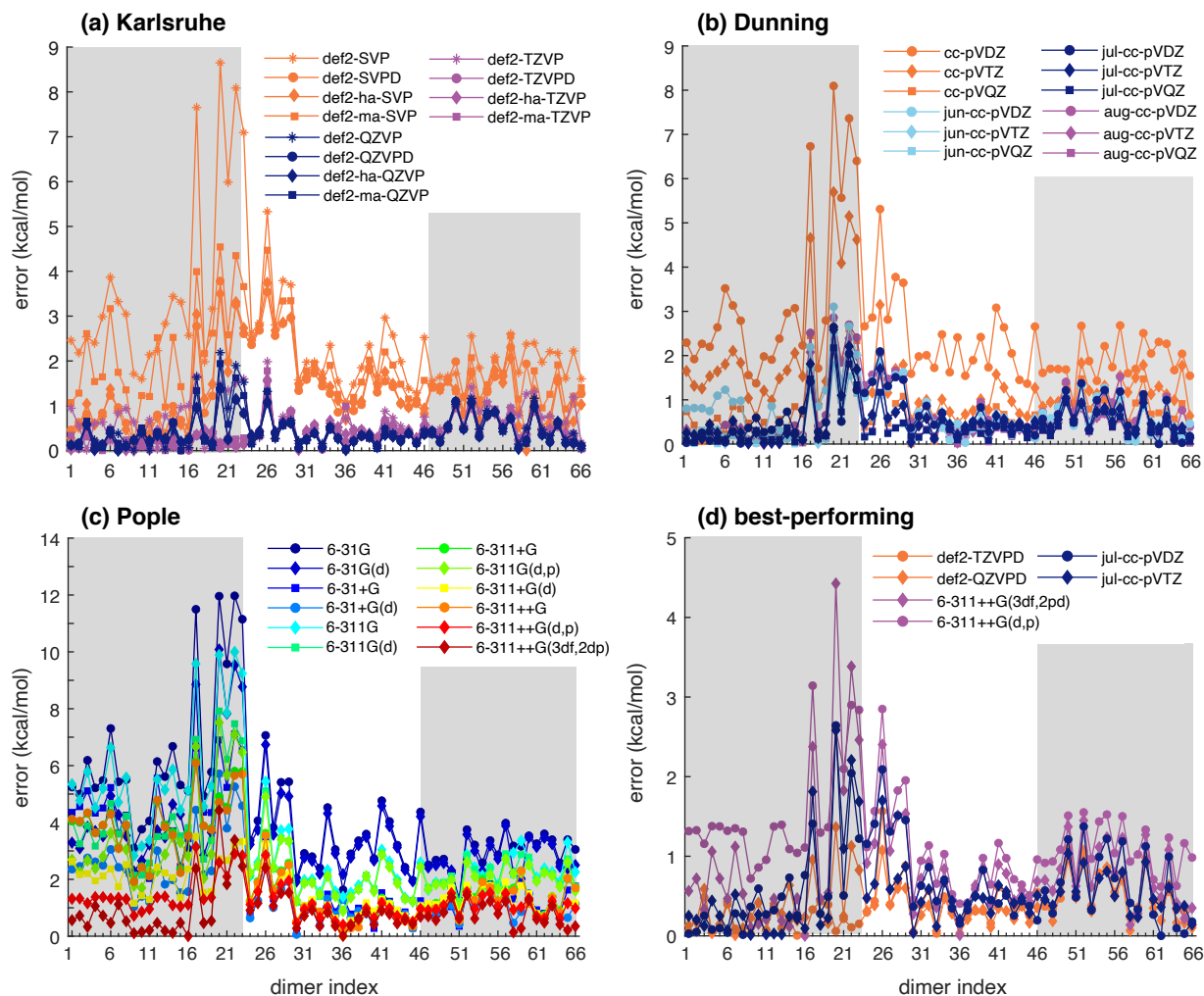


Fig. S1: Absolute errors in XSAPT + MBD total interaction energies for the S66 dimers, using (a) Karlsruhe basis sets, (b) Dunning correlation-consistent basis sets, (c) Pople basis sets, and (d) the best-performing basis sets from amongst these three categories. Indices along the horizontal axis refer to the ordering of the S66 dimers as described in the manuscript and the three regions delineated by shading indicate the hydrogen-bonded subset (dimers 1–23), the dispersion-dominated subset (24–46), and the subset of mixed-influence dimers (47–66). Errors are defined with respect to the CCSD(T)/CBS benchmarks as described in the manuscript. Panel (d) plots the same data as Fig. 2.

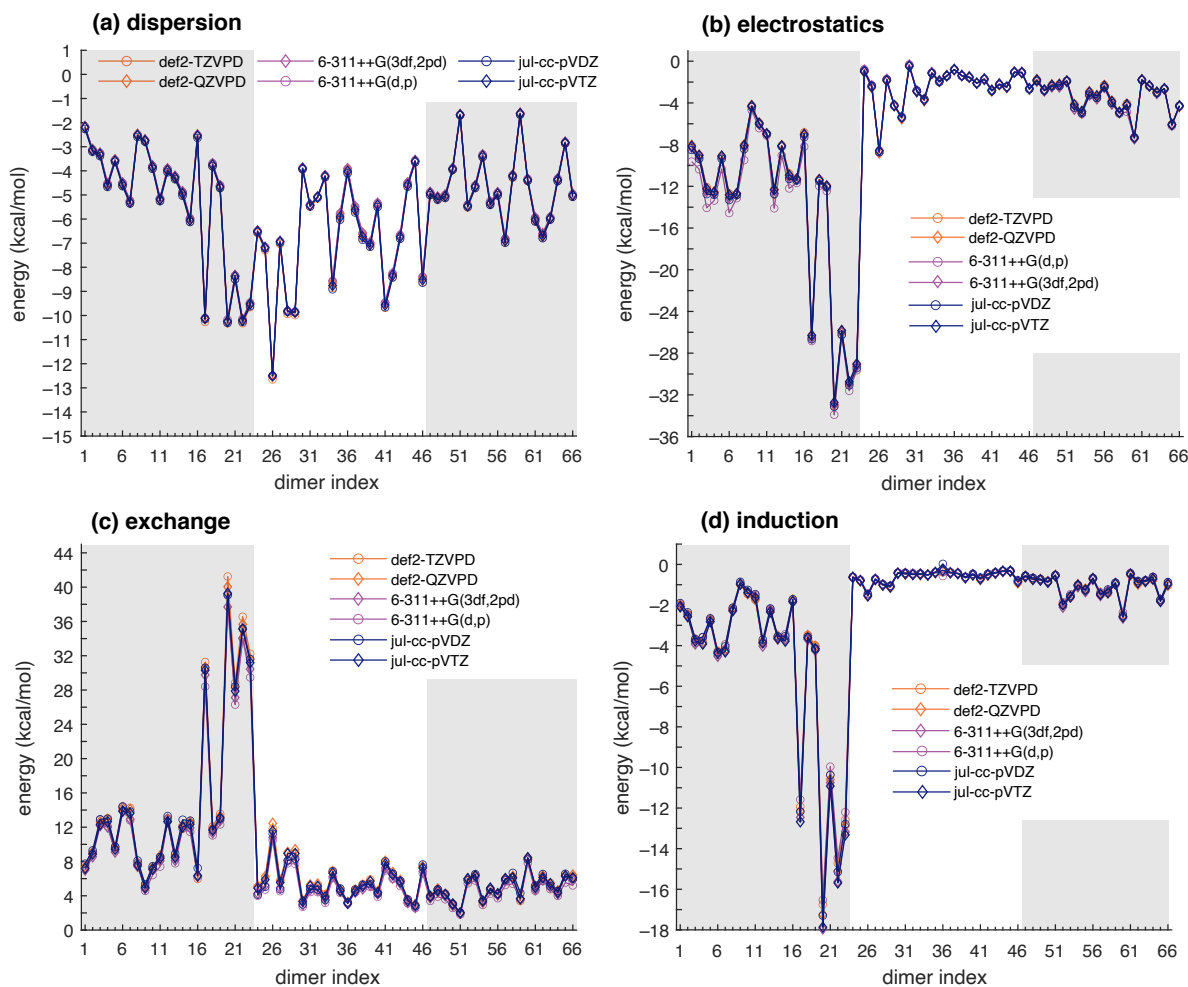


Fig. S2: XSAPT + MBD energy components for S66, evaluated using the best-performing basis sets. The energy components are (a) dispersion energy computed from the MBD model, which depends on the SCF monomer charge densities; (b) electrostatic energy, equal to the Coulomb interaction between isolated-monomer SCF charge densities; (c) exchange energy (*i.e.*, Pauli repulsion); and (d) induction energy, including the δE_{HF} correction. Shaded regions delineate the three subsets of S66: hydrogen-bonded dimers (1–23), dispersion-dominated complexes (24–46), and dimers with mixed-influence interactions (47–66).

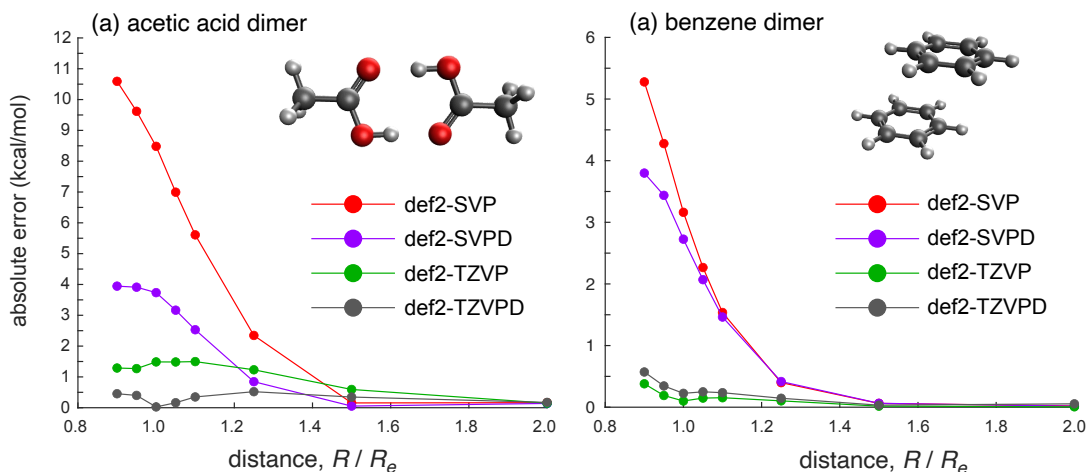


Fig. S3: Absolute error in the XSAPT + MBD interaction energy, as compared to the CCSD(T)/CBS benchmark, for (a) acetic acid dimer and (b) parallel-displaced benzene dimer, as a function of intermolecular separation. Geometries and benchmark values of E_{int} come from the S66 \times 8 data set. Panel (a) is the same as Fig. 4.

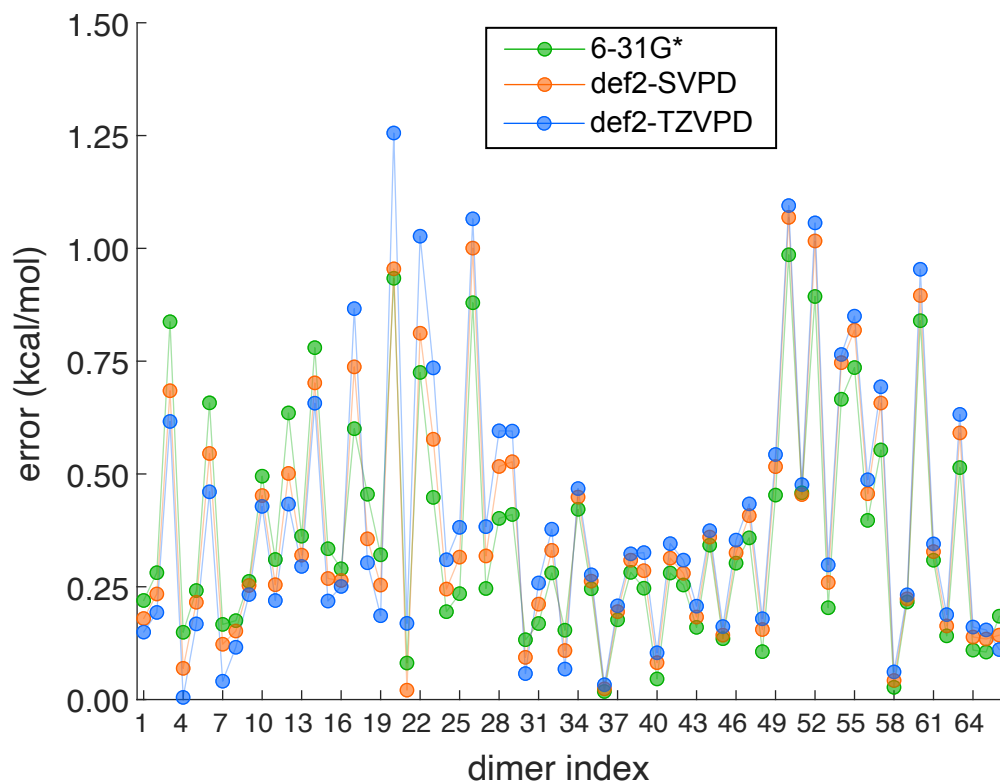


Fig. S4: Errors in XSAPT + MBD interaction energies for the S66 data set, computed using a hybrid scheme in which def2-QZVPD is used to evaluate all terms except δE_{HF} , which is computed in one of the smaller basis sets that is indicated. Errors are computed with respect to CCSD(T)/CBS benchmarks.