Supporting Information for "Systematic Evaluation of Counterpoise Correction in Density Functional Theory"

Montgomery Gray,[1] Paige E. Bowling,[1,2] and John M. Herbert[1,2*]

[1] *Department of Chemistry and Biochemistry*
[2] *Biophysics Graduate Program*

The Ohio State University, Columbus, Ohio 43210 USA

October 7, 2022

List of Figures

*herbert@chemistry.ohio-state.edu

List of Tables

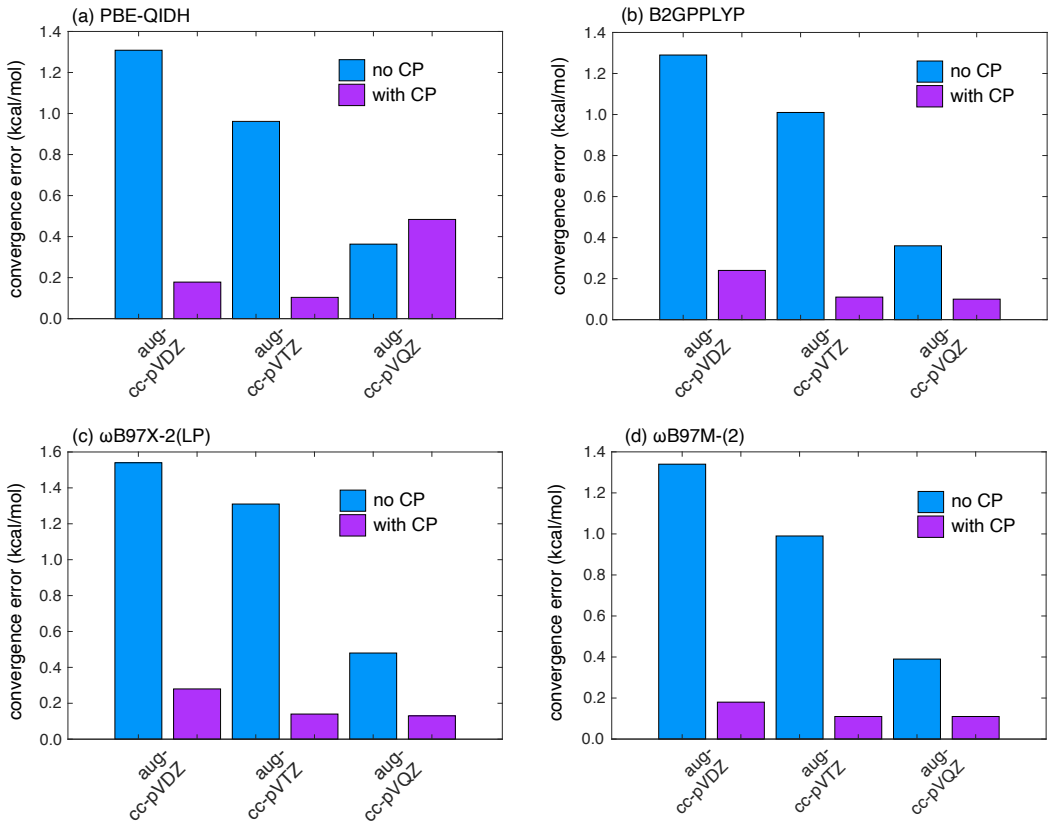

Fig. S1: Mean absolute convergence errors with respect to the DH-DFT/CBS limit, for ΔE_{int} in the S66 data, set using double-hybrid functionals in various Dunning basis sets.

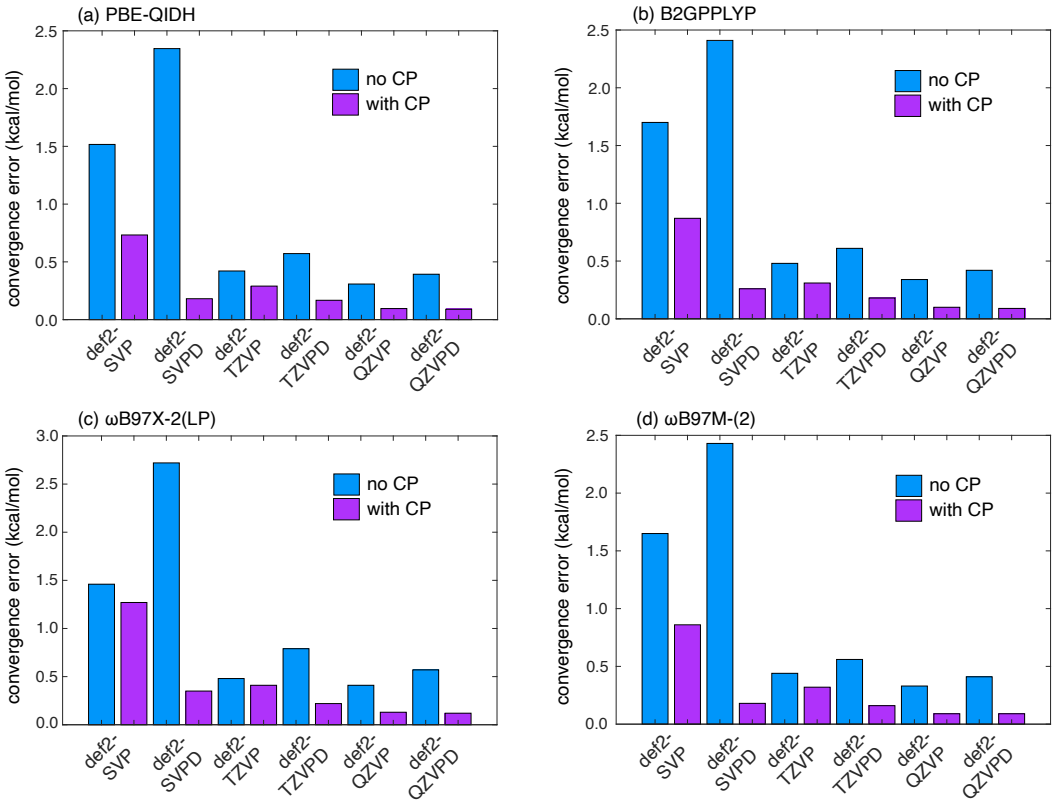

Fig. S2: Mean absolute convergence errors with respect to the DH-DFT/CBS limit, for $\Delta E_{\rm int}$ in the S66 data, set using double-hybrid functionals in various Karlsruhe basis sets. Panel (d) is the same as Fig. 1.

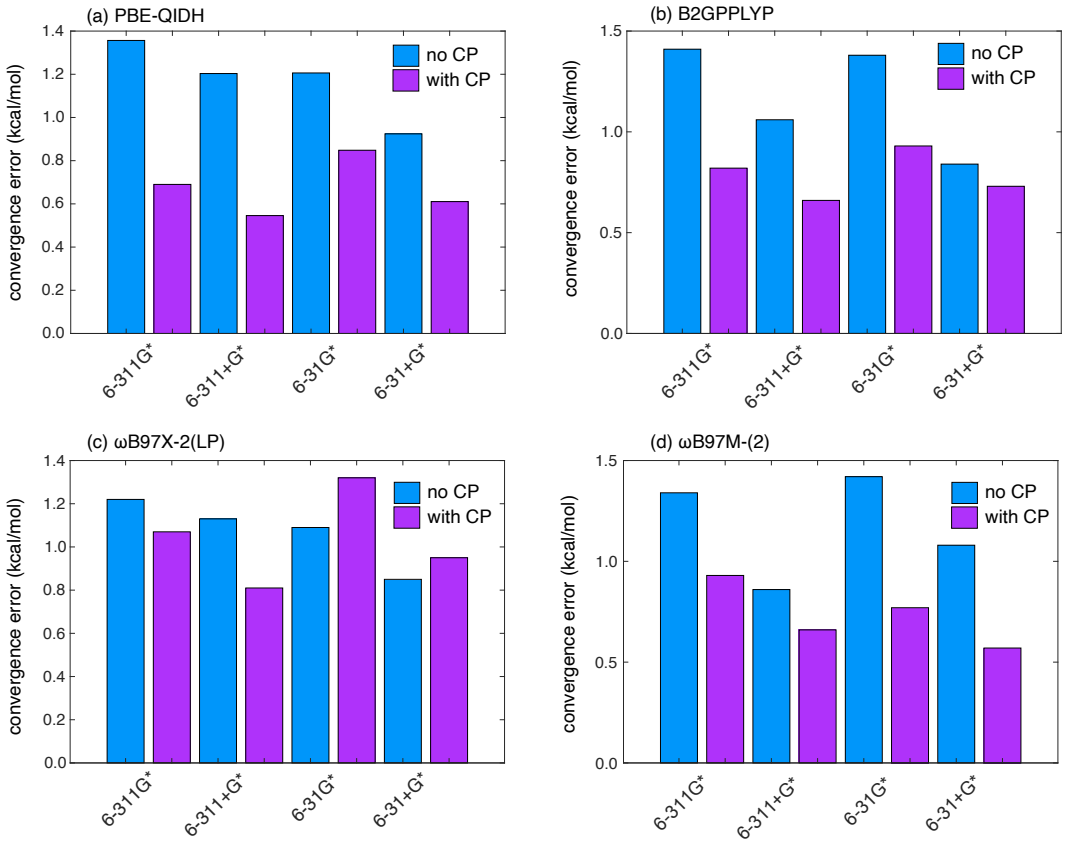

Fig. S3: Mean absolute convergence errors with respect to the DH-DFT/CBS limit, for ΔE_{int} in the S66 data, set using double-hybrid functionals in various Pople basis sets.

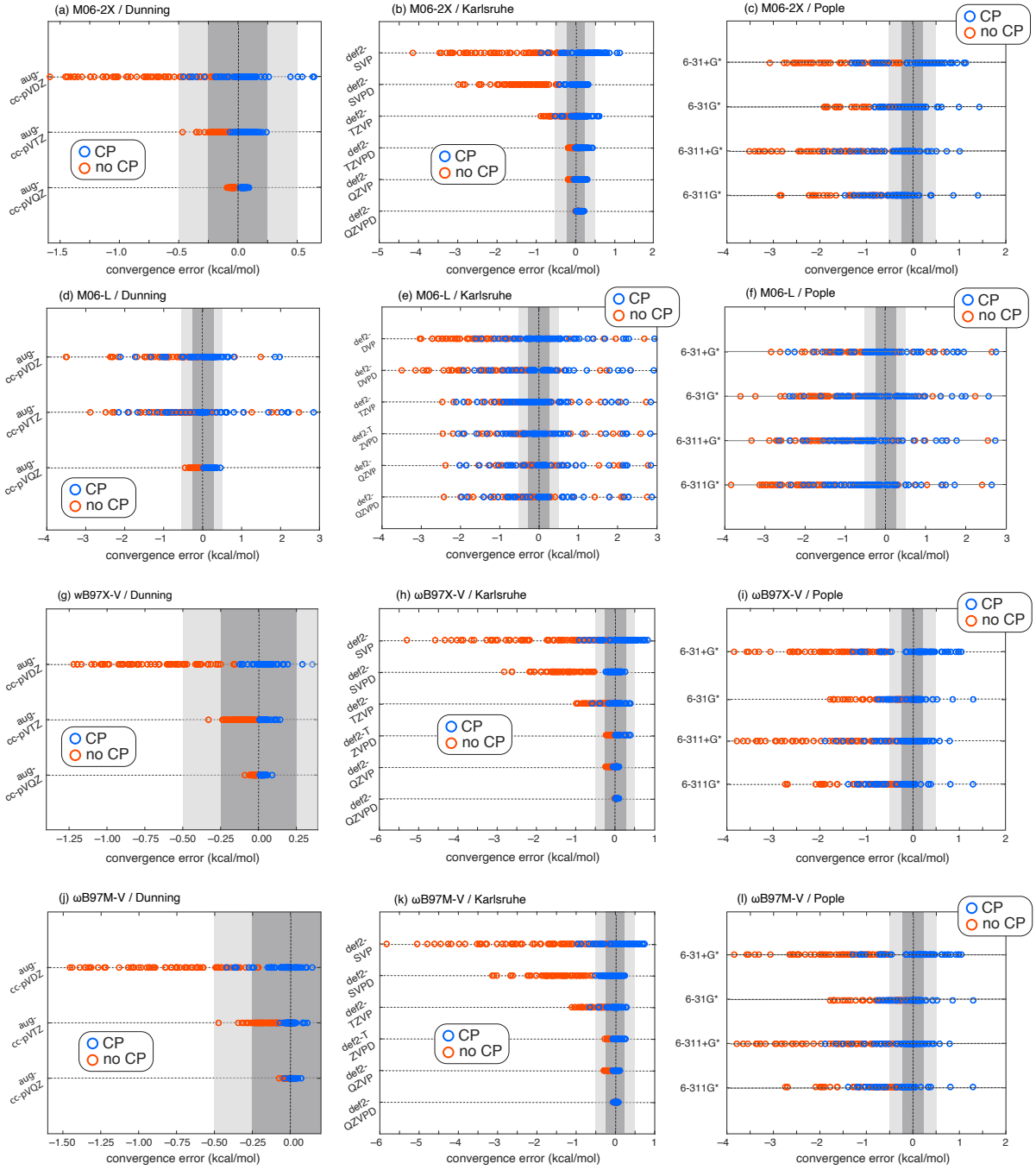

Fig. S4: Distributions of signed convergence errors in interactions energies for the S66 data set, using various functionals and basis sets. Gray rectangles delineate errors of ±0.25 and ±0.50 kcal/mol. The corresponding data for BLYP+D3(BJ) can be found in Fig. 2.

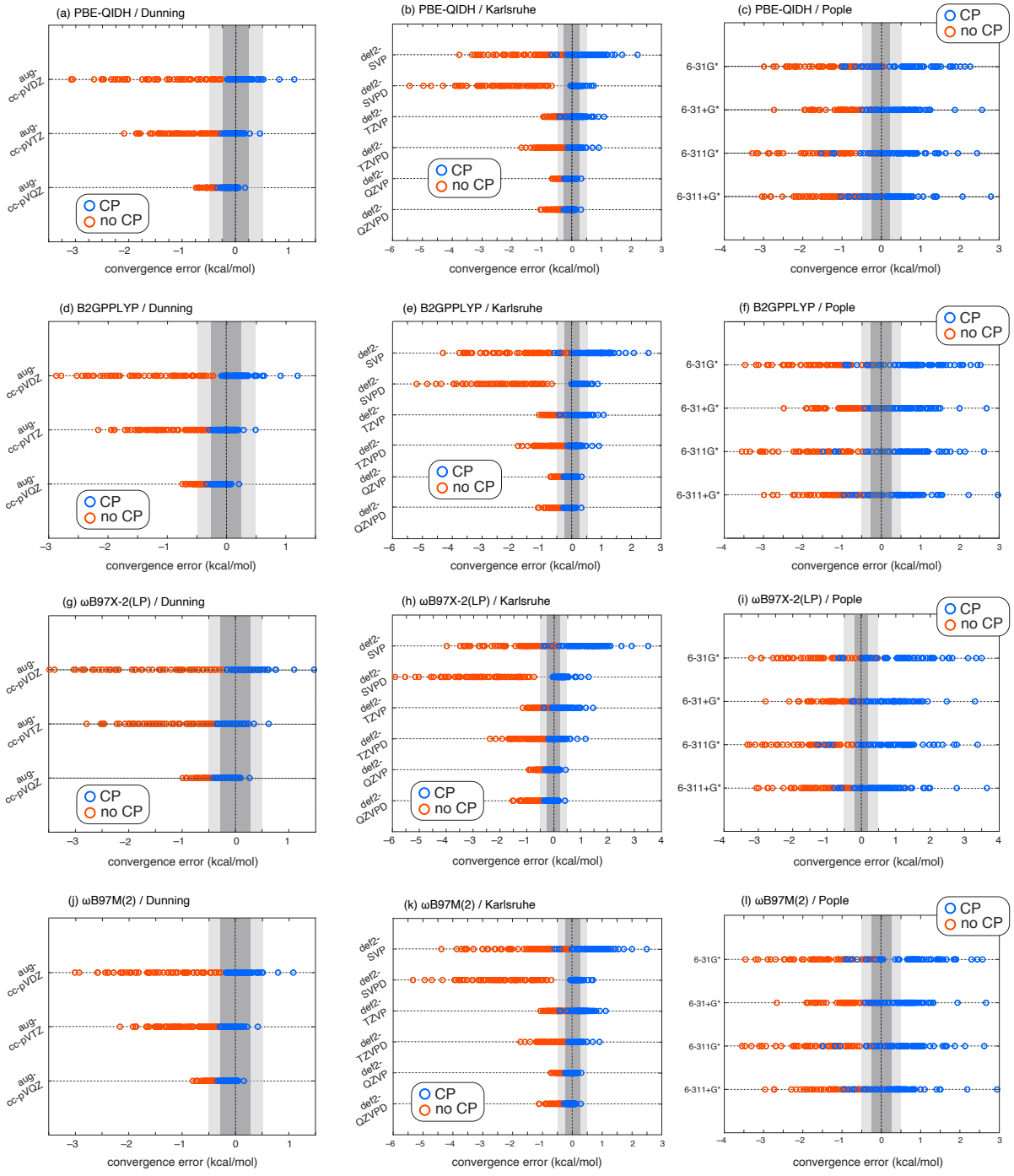

Fig. S5: Distributions of signed convergence errors in interactions energies for the S66 data set, using various double hybrid functionals and basis sets. Gray rectangles delineate errors of ±0.25 and ±0.50 kcal/mol.

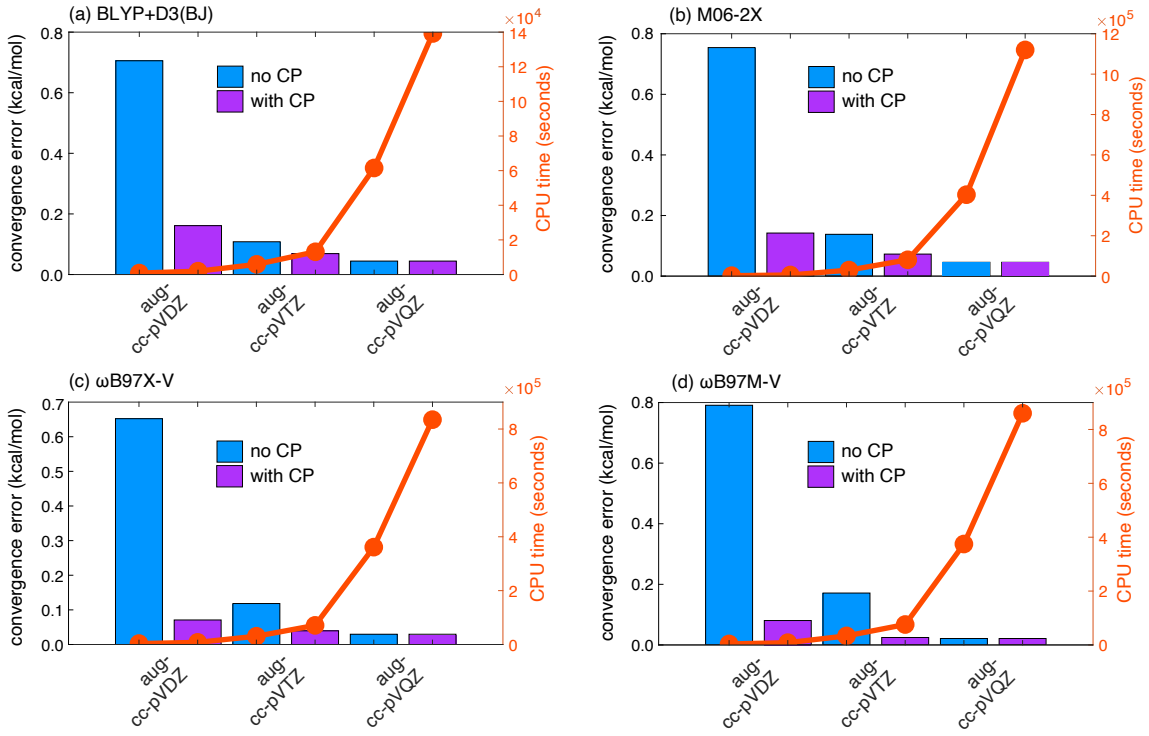

Fig. S6: Mean absolute convergence errors with respect to the DFT/CBS limit (bar graphs, to be read from the scale on the left), for ΔE_{int} in the S66 data set, using four different functionals and a variety of Dunning basis sets. Also shown are timing data for pentane dimer (points, to be read from the scale on the right). Timings represent aggregate CPU time on 14 processors of a single compute note (Dell Intel Xeon E5-2680 v4).

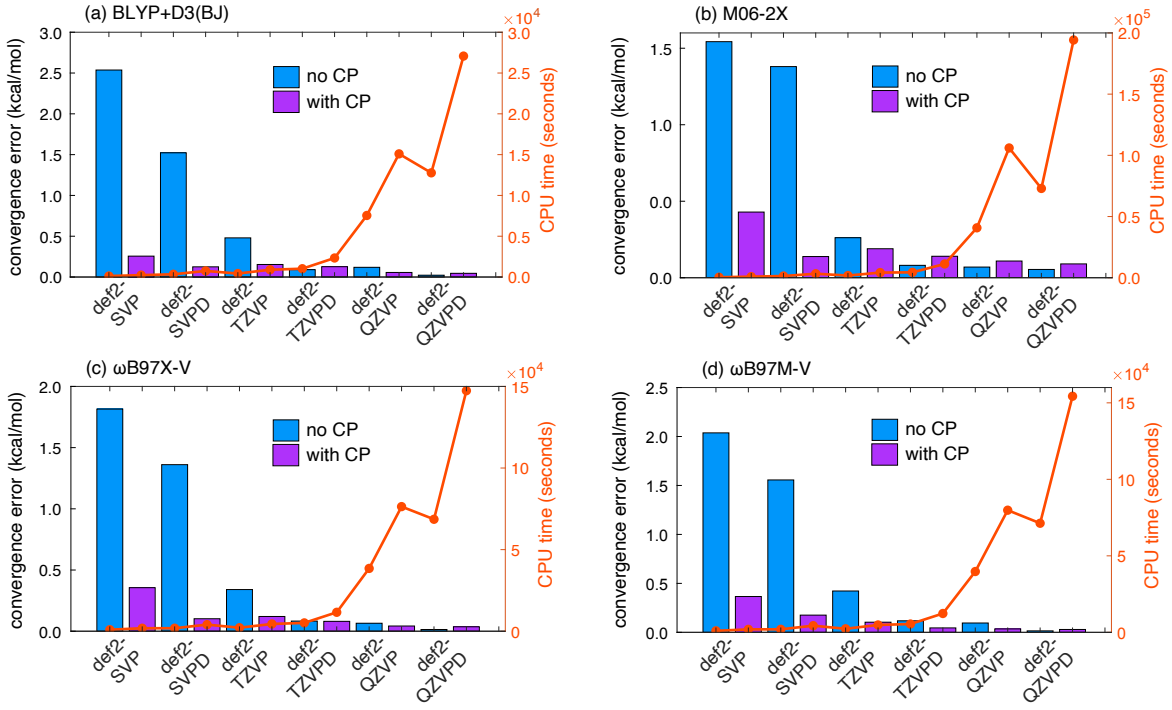

Fig. S7: Mean absolute convergence errors with respect to the DFT/CBS limit (bar graphs, to be read from the scale on the left), for ΔE_{int} in the S66 data set, using four different functionals and a variety of Karlsruhe basis sets. Also shown are timing data for pentane dimer (points, to be read from the scale on the right). Timings represent aggregate CPU time on 14 processors of a single compute note (Dell Intel Xeon E5-2680 v4). Panel (a) is the same as Fig. 3.

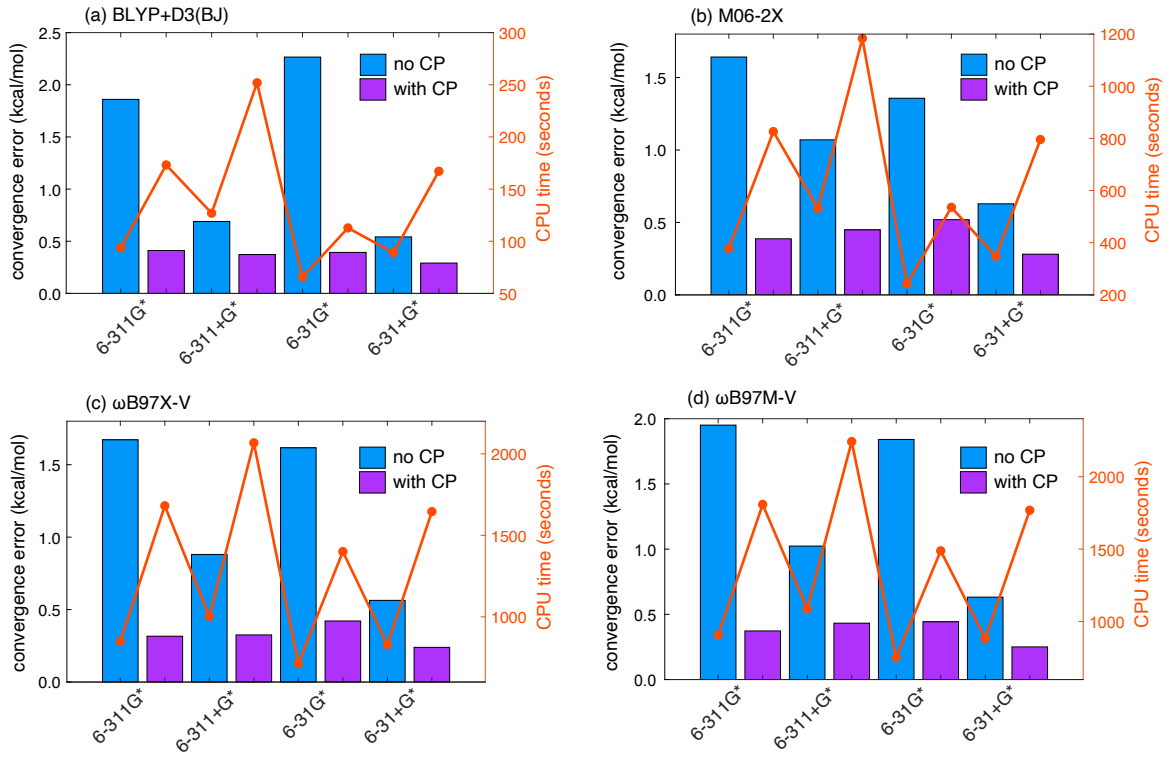

Fig. S8: Mean absolute convergence errors with respect to the DFT/CBS limit (bar graphs, to be read from the scale on the left), for ΔE_{int} in the S66 data set, using four different functionals and a variety of Pople basis sets. Also shown are timing data for pentane dimer (points, to be read from the scale on the right). Timings represent aggregate CPU time on 14 processors of a single compute note (Dell Intel Xeon E5-2680 v4).

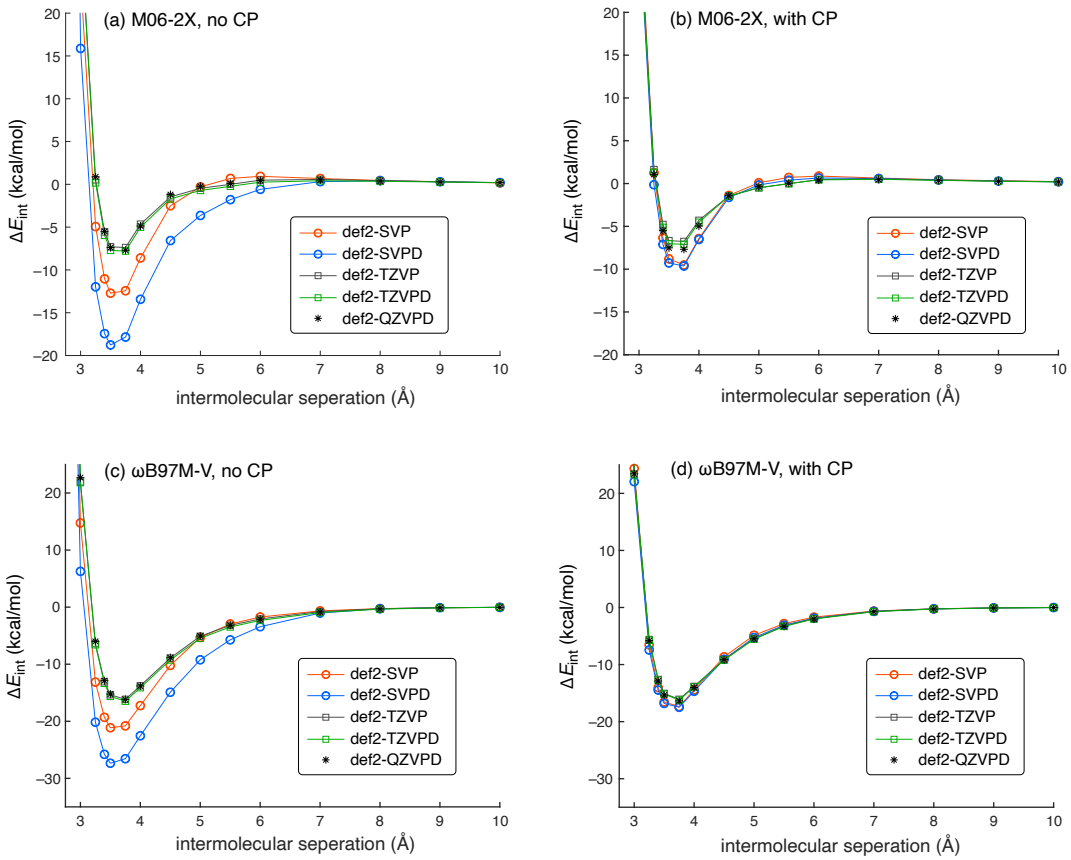

Fig. S9: Potential energy profiles of coronene dimer as a function of the center-to-center intermolecular separation, using two different functionals and Karlsruhe basis sets.

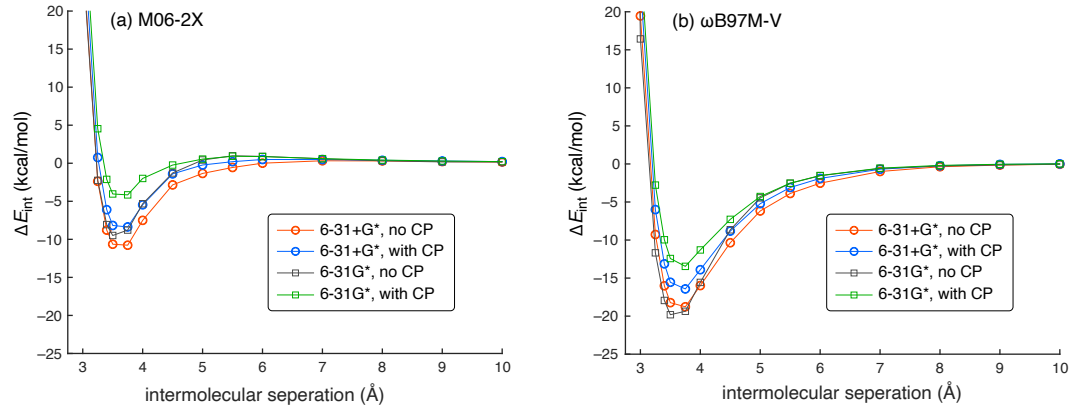

Fig. S10: Potential energy profiles of coronene dimer as a function of the center-to-center intermolecular separation, using two different functionals and Pople basis sets.

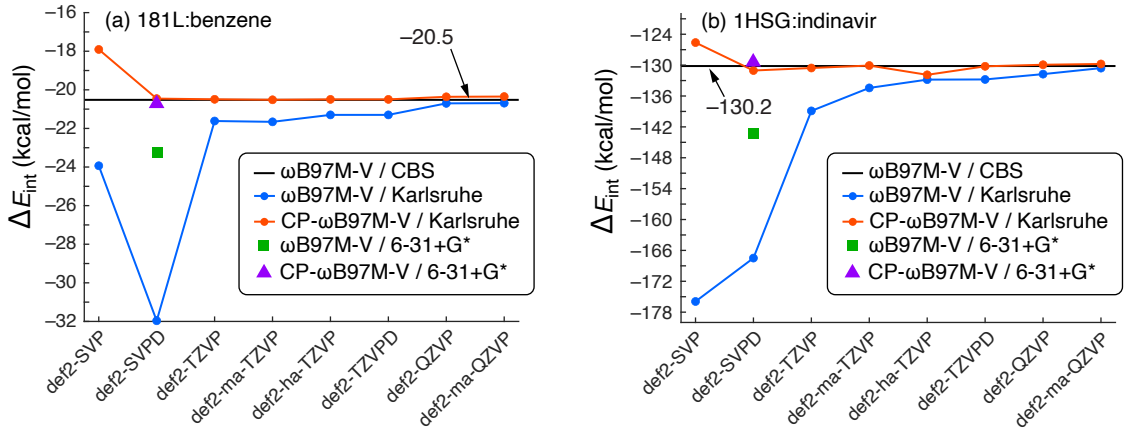

Fig. S11: Interaction energies for (a) 181L:benzene and (b) 1HSG:indinavir computed using ωB97M-V in various basis sets. Connected points illustrate convergence of ΔE_{int} in Karlsruhe basis sets, both with and without CP correction. For comparison, values of ΔE_{int} in the 6-31+G* basis set are also shown. The ωB97M-V/CBS limit, obtained by averaging def2-ma-QZVP interaction energies with and without CP correction, is indicated by the horizontal line and its numerical value is also indicated. These plots are complementary to the ones for ligand–protein complexes 1LI2:phenol and 1O44:RU85052 that are shown in Fig. 6.

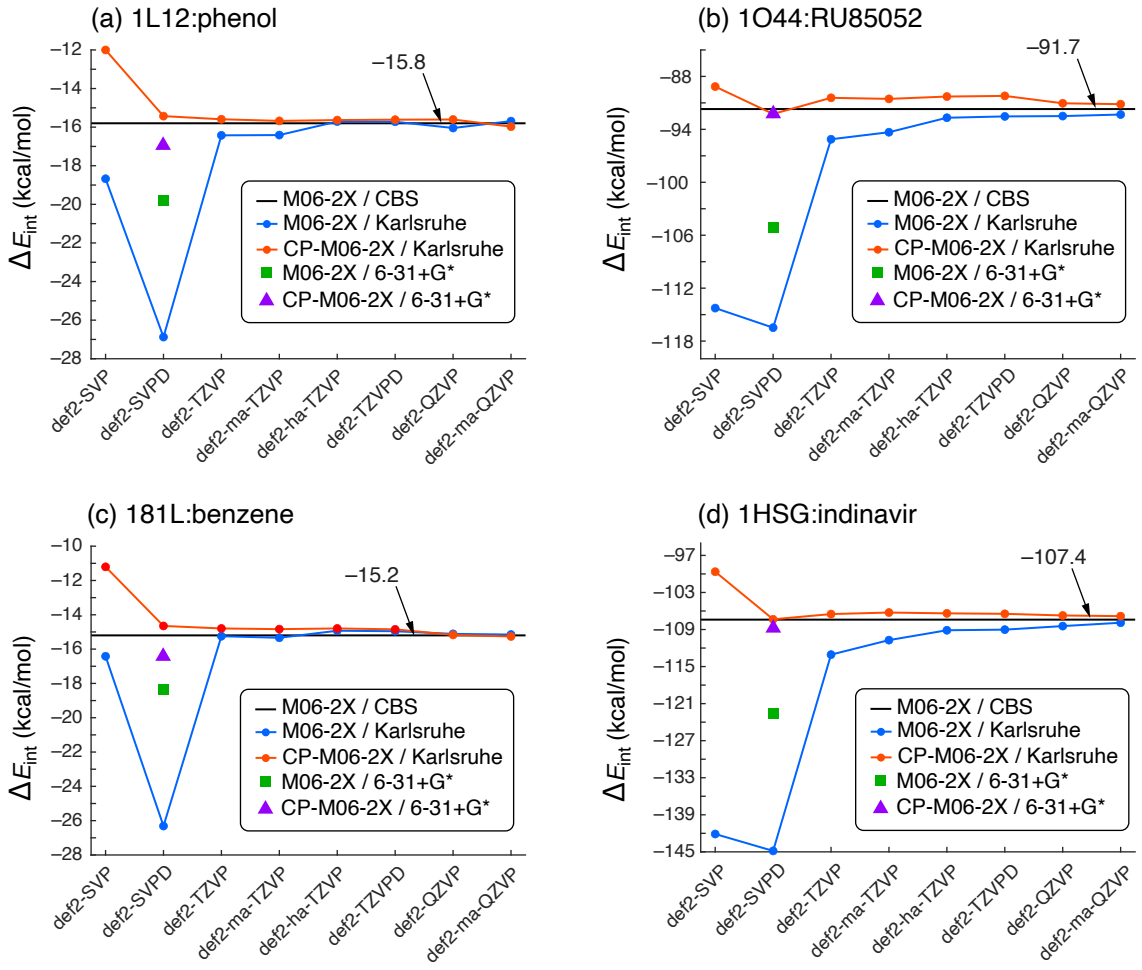

Fig. S12: Interaction energies for the indicated protein–ligand complexes, computed using M06-2X in various basis sets. Connected points illustrate convergence of ΔE_{int} in Karlsruhe basis sets, both with and without CP correction. For comparison, values of ΔE_{int} in the 6-31+G* basis set are also shown. The ωB97M-V/CBS limit, obtained by averaging def2-ma-QZVP interaction energies with and without CP correction, is indicated by the horizontal line and its numerical value is also indicated.

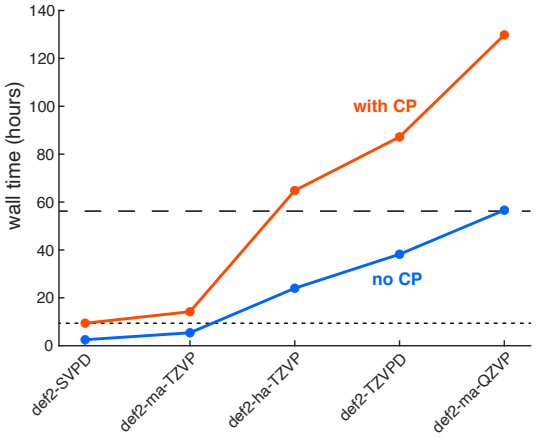

Fig. S13: Wall time required to compute ΔE_{int} for the 1HSG:indinavir complex. Calculations were performed on a single 48-core node using the ωB97M-V functional. Horizontal dashed lines indicate the time required for the CP-corrected def2-SVPD (which is a good approximation of the CBS limit) and for the uncorrected def2-ma-QZVP calculation that is used to establish the CBS limit.

Table S1: Convergence error statistics (with respect to the DFT/CBS limit) for interaction energies in the S66 data set computed using M06-2X.

Basis Set	CP?	Mean Absolute Error (kcal/mol)				Mean Signed Error (kcal/mol)				Mean Absolute Percent Error (%)			
		All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed
aug-cc-pVDZ	no	0.75	0.40	1.13	0.73	−0.75	−0.40	−1.13	−0.73	22.6	6.1	39.2	22.4
aug-cc-pVDZ	yes	0.14	0.19	0.15	0.07	0.03	0.19	−0.10	−0.00	3.5	1.8	6.3	2.2
aug-cc-pVTZ	no	0.14	0.10	0.15	0.18	−0.14	−0.10	−0.14	−0.18	3.4	1.3	4.0	5.1
aug-cc-pVTZ	yes	0.07	0.07	0.10	0.04	0.07	0.07	0.10	0.02	2.0	0.7	3.8	1.3
aug-cc-pVQZ	no	0.05	0.04	0.06	0.04	−0.05	−0.04	−0.06	−0.04	1.2	0.5	1.8	1.2
aug-cc-pVQZ	yes	0.05	0.04	0.06	0.04	0.05	0.04	0.06	0.04	1.2	0.5	1.8	1.2
def2-SVP	no	1.54	2.69	0.84	1.02	−1.50	−2.69	−0.72	−1.02	30.6	37.8	23.7	30.4
def2-SVP	yes	0.43	0.38	0.50	0.40	0.31	0.10	0.50	0.31	11.3	5.3	17.4	11.3
def2-SVPD	no	1.38	0.98	1.84	1.31	−1.38	−0.98	−1.84	−1.31	38.0	13.4	61.2	39.5
def2-SVPD	yes	0.14	0.09	0.23	0.09	0.02	0.04	−0.02	0.05	4.1	1.0	8.4	2.8
def2-TZVP	no	0.26	0.46	0.11	0.20	−0.21	−0.43	−0.01	−0.20	5.8	7.9	3.9	5.7
def2-TZVP	yes	0.19	0.23	0.21	0.11	0.12	0.08	0.21	0.07	4.5	2.8	7.4	3.4
def2-TZVPD	no	0.08	0.09	0.08	0.07	−0.02	0.02	−0.03	−0.06	1.9	0.9	2.7	2.0
def2-TZVPD	yes	0.14	0.14	0.18	0.09	0.14	0.14	0.18	0.09	3.5	1.5	6.1	2.7
def2-QZVP	no	0.07	0.07	0.09	0.05	0.01	−0.07	0.08	0.00	2.1	1.3	3.4	1.4
def2-QZVP	yes	0.11	0.09	0.15	0.09	0.11	0.09	0.15	0.08	2.9	1.2	5.0	2.6
def2-QZVPD	no	0.05	0.05	0.07	0.04	0.05	0.05	0.07	0.04	1.4	0.6	2.4	1.2
def2-QZVPD	yes	0.09	0.08	0.12	0.07	0.09	0.08	0.12	0.07	2.4	1.0	3.9	2.1
6-31G*	no	1.36	2.21	0.79	1.03	−1.36	−2.21	−0.79	−1.03	28.4	31.1	24.0	30.5
6-31G*	yes	0.52	0.59	0.64	0.29	0.20	−0.40	0.60	0.20	13.6	9.7	21.6	9.0
6-31+G*	no	0.63	1.11	0.39	0.34	−0.62	−1.10	−0.37	−0.34	13.3	18.8	10.4	10.3
6-31+G*	yes	0.28	0.57	0.13	0.12	−0.06	−0.21	0.01	0.05	5.5	8.1	4.7	3.4
6-311G*	no	1.64	2.57	1.05	1.25	−1.64	−2.57	−1.05	−1.25	35.5	39.2	30.9	36.5
6-311G*	yes	0.39	0.74	0.17	0.23	−0.27	−0.45	−0.14	−0.22	8.6	12.1	6.3	7.3
6-311+G*	no	1.07	1.47	0.90	0.81	−1.06	−1.43	−0.90	−0.81	25.4	24.9	27.1	24.0
6-311+G*	yes	0.45	0.78	0.27	0.27	−0.34	−0.49	−0.26	−0.25	9.8	12.2	9.0	8.0
6-311++G**	no	0.75	0.85	0.78	0.61	−0.56	−0.78	−0.54	−0.34	18.7	14.2	23.6	18.2
6-311++G**	yes	0.28	0.42	0.23	0.19	−0.07	−0.16	−0.06	0.03	6.6	6.1	7.9	5.7

Table S2: Convergence error statistics (with respect to the DFT/CBS limit) for interaction energies in the S66 data set computed using M06-2X+D3(0).

Basis Set	CP?	Mean Absolute Error (kcal/mol)				Mean Signed Error (kcal/mol)				Mean Absolute Percent Error (%)			
		All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed
aug-cc-pVDZ	no	0.75	0.40	1.13	0.73	−0.75	−0.40	−1.13	−0.73	19.4	5.9	32.2	20.4
aug-cc-pVDZ	yes	0.14	0.19	0.15	0.07	0.03	0.19	−0.10	0.00	3.0	1.8	5.2	2.0
aug-cc-pVTZ	no	0.14	0.10	0.15	0.18	−0.14	−0.10	−0.14	−0.18	3.1	1.2	3.4	4.7
aug-cc-pVTZ	yes	0.07	0.07	0.10	0.04	0.07	0.07	0.10	0.02	1.7	0.7	3.1	1.2
aug-cc-pVQZ	no	0.05	0.04	0.06	0.04	−0.05	−0.04	−0.06	−0.04	1.0	0.5	1.5	1.1
aug-cc-pVQZ	yes	0.05	0.04	0.06	0.04	0.05	0.04	0.06	0.04	1.0	0.5	1.5	1.1
def2-SVP	no	1.54	2.69	0.84	1.02	−1.50	−2.69	−0.72	−1.02	28.4	36.8	20.3	28.2
def2-SVP	yes	0.43	0.38	0.50	0.40	0.31	0.10	0.50	0.31	9.9	5.2	14.1	10.4
def2-SVPD	no	1.38	0.98	1.84	1.31	−1.38	−0.98	−1.84	−1.31	33.2	13.0	50.8	36.1
def2-SVPD	yes	0.14	0.09	0.23	0.09	0.02	0.04	−0.02	0.05	3.5	1.0	6.9	2.6
def2-TZVP	no	0.26	0.46	0.11	0.20	−0.21	−0.43	−0.01	−0.20	5.4	7.7	3.2	5.3
def2-TZVP	yes	0.19	0.23	0.21	0.11	0.12	0.08	0.21	0.07	4.0	2.7	6.0	3.1
def2-TZVPD	no	0.08	0.09	0.08	0.07	−0.02	0.02	−0.03	−0.06	1.6	0.9	2.3	1.9
def2-TZVPD	yes	0.14	0.14	0.18	0.09	0.14	0.14	0.18	0.09	3.0	1.5	5.0	2.5
def2-QZVP	no	0.07	0.07	0.09	0.05	0.01	−0.07	0.08	0.00	1.8	1.2	2.7	1.3
def2-QZVP	yes	0.11	0.09	0.15	0.09	0.11	0.09	0.15	0.08	2.5	1.1	4.1	2.3
def2-QZVPD	no	0.05	0.05	0.07	0.04	0.05	0.05	0.07	0.04	1.2	0.6	2.0	1.1
def2-QZVPD	yes	0.09	0.08	0.12	0.07	0.09	0.08	0.12	0.07	2.0	1.0	3.2	1.9
6-31G*	no	1.36	2.21	0.79	1.03	−1.36	−2.21	−0.79	−1.03	26.2	30.3	20.4	28.2
6-31G*	yes	0.52	0.59	0.64	0.29	0.16	−0.36	0.64	0.18	12.1	9.5	18.2	8.3
6-31+G*	no	0.63	1.11	0.39	0.34	−0.62	−1.10	−0.37	−0.34	12.4	18.3	9.0	9.6
6-31+G*	yes	0.28	0.57	0.13	0.12	−0.06	−0.21	0.01	0.05	5.1	7.9	3.8	3.2
6-311G*	no	1.64	2.57	1.05	1.25	−1.64	−2.57	−1.05	−1.25	32.8	38.2	26.5	33.7
6-311G*	yes	0.39	0.74	0.17	0.23	−0.27	−0.45	−0.14	−0.22	8.0	11.8	5.2	6.9
6-311+G*	no	1.07	1.47	0.90	0.81	−1.06	−1.43	−0.90	−0.81	23.2	24.3	23.1	22.1
6-311+G*	yes	0.45	0.78	0.27	0.27	−0.34	−0.49	−0.26	−0.25	9.1	11.9	7.7	7.4
6-311++G**	no	0.75	0.85	0.78	0.61	−0.75	−0.85	−0.78	−0.61	16.9	13.9	20.0	16.7
6-311++G**	yes	0.28	0.42	0.23	0.19	−0.20	−0.19	−0.23	−0.17	6.0	5.9	6.7	5.3

Table S3: Convergence error statistics (with respect to the DFT/CBS limit) for interaction energies in the S66 data set computed using M06-L.

Basis Set	CP?	Mean Absolute Error (kcal/mol)				Mean Signed Error (kcal/mol)				Mean Absolute Percent Error (%)			
		All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed
aug-cc-pVDZ	no	0.79	0.17	1.52	0.65	−0.69	−0.10	−1.32	−0.63	34.8	2.6	71.3	29.8
aug-cc-pVDZ	yes	0.43	0.35	0.71	0.21	0.04	0.35	−0.29	0.05	16.3	4.8	32.8	10.6
aug-cc-pVTZ	no	0.85	0.37	1.12	1.10	−0.56	−0.37	−0.85	−0.45	32.5	5.1	50.2	43.8
aug-cc-pVTZ	yes	0.49	0.05	0.58	0.88	0.01	0.03	−0.11	0.13	18.5	0.6	25.4	31.1
aug-cc-pVQZ	no	0.20	0.20	0.22	0.19	−0.20	−0.20	−0.22	−0.19	6.1	2.9	8.7	7.0
aug-cc-pVQZ	yes	0.20	0.20	0.22	0.19	0.20	0.20	0.22	0.19	6.1	2.9	8.7	7.0
def2-SVP	no	1.48	2.02	1.25	1.14	−1.19	−2.02	−0.82	−0.67	42.4	30.8	51.4	45.3
def2-SVP	yes	0.60	0.38	0.61	0.85	0.21	0.21	0.06	0.39	19.3	5.6	24.7	28.8
def2-SVPD	no	1.24	0.56	1.84	1.34	−1.02	−0.56	−1.66	−0.82	48.3	7.8	82.1	55.9
def2-SVPD	yes	0.57	0.19	0.67	0.88	0.08	0.19	−0.17	0.24	20.7	3.0	29.6	30.7
def2-TZVP	no	0.82	0.77	0.78	0.93	−0.46	−0.77	−0.38	−0.21	27.1	11.9	35.1	35.4
def2-TZVP	yes	0.58	0.31	0.62	0.86	−0.08	−0.31	−0.02	0.12	20.1	4.8	26.4	30.4
def2-TZVPD	no	0.75	0.45	0.85	0.97	−0.39	−0.45	−0.49	−0.22	27.1	6.3	39.0	37.3
def2-TZVPD	yes	0.54	0.17	0.64	0.86	0.002	−0.17	0.02	0.18	19.1	2.1	26.8	29.8
def2-QZVP	no	0.59	0.22	0.67	0.91	−0.17	−0.22	−0.25	−0.004	21.7	3.2	30.2	33.2
def2-QZVP	yes	0.51	0.10	0.60	0.86	0.11	0.10	0.01	0.22	18.4	1.5	25.5	29.7
def2-QZVPD	no	0.59	0.12	0.76	0.93	−0.18	−0.12	−0.35	−0.05	22.7	1.7	33.4	34.4
def2-QZVPD	yes	0.52	0.14	0.59	0.86	0.13	0.14	0.03	0.24	18.5	2.0	25.2	29.7
6-31G*	no	1.42	1.68	1.24	1.32	−1.21	−1.68	−1.00	−0.92	44.7	26.8	55.0	53.4
6-31G*	yes	0.75	0.58	0.80	0.89	−0.11	−0.21	−0.07	−0.04	26.0	9.6	35.9	33.6
6-31+G*	no	0.96	0.85	1.07	0.98	−0.63	−0.71	−0.75	−0.40	33.4	15.3	46.4	39.3
6-31+G*	yes	0.68	0.47	0.70	0.88	−0.11	0.02	−0.33	−0.001	23.3	6.1	32.1	33.0
6-311G*	no	1.76	2.35	1.46	1.43	−1.57	−2.35	−1.22	−1.10	53.1	38.4	63.7	58.0
6-311G*	yes	0.78	0.64	0.80	0.91	−0.42	−0.54	−0.48	−0.23	28.0	12.2	37.5	35.3
6-311+G*	no	1.35	1.41	1.43	1.18	−1.14	−1.39	−1.20	−0.79	45.7	25.5	63.0	48.9
6-311+G*	yes	0.82	0.67	0.86	0.94	−0.45	−0.55	−0.54	−0.25	29.0	11.8	39.8	36.3
6-311++G**	no	1.08	0.84	1.33	1.09	−0.82	−0.84	−1.06	−0.53	38.7	14.4	58.3	44.0
6-311++G**	yes	0.70	0.36	0.86	0.93	−0.33	−0.30	−0.53	−0.13	26.6	6.1	39.8	35.0

Table S4: Convergence error statistics (with respect to the DFT/CBS limit) for interaction energies in the S66 data set computed using BLYP+D3(BJ).

Basis Set	CP?	Mean Absolute Error (kcal/mol)				Mean Signed Error (kcal/mol)				Mean Absolute Percent Error (%)			
		All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed
aug-cc-pVDZ	no	0.71	0.52	0.96	0.63	−0.71	−0.52	−0.96	−0.63	18.4	6.9	29.5	18.9
aug-cc-pVDZ	yes	0.16	0.17	0.18	0.12	0.16	0.17	0.18	0.12	3.6	2.1	5.1	3.6
aug-cc-pVTZ	no	0.11	0.07	0.15	0.11	−0.11	−0.07	−0.15	−0.11	2.6	0.8	4.0	3.1
aug-cc-pVTZ	yes	0.07	0.08	0.09	0.04	0.07	0.08	0.09	0.04	1.5	0.9	2.5	1.1
aug-cc-pVQZ	no	0.04	0.03	0.07	0.03	−0.04	−0.03	−0.07	−0.03	1.1	0.4	2.0	0.8
aug-cc-pVQZ	yes	0.04	0.03	0.07	0.03	0.04	0.03	0.07	0.03	1.1	0.4	2.0	0.8
def2-SVP	no	2.54	4.11	1.54	1.88	−2.54	−4.11	−1.54	−1.88	51.2	57.1	42.0	55.0
def2-SVP	yes	0.26	0.38	0.25	0.12	0.07	−0.05	0.23	0.04	5.6	6.0	6.8	3.8
def2-SVPD	no	1.52	1.25	1.90	1.40	−1.52	−1.25	−1.90	−1.40	38.4	16.4	57.5	41.6
def2-SVPD	yes	0.13	0.07	0.18	0.13	0.09	−0.03	0.17	0.13	3.2	0.9	5.0	3.8
def2-TZVP	no	0.48	0.82	0.21	0.40	−0.47	−0.82	−0.19	−0.40	9.9	12.9	5.4	11.8
def2-TZVP	yes	0.15	0.20	0.18	0.08	0.06	−0.03	0.18	0.01	3.7	3.0	5.3	2.5
def2-TZVPD	no	0.09	0.08	0.13	0.06	−0.07	−0.04	−0.12	−0.06	2.1	1.1	3.5	1.8
def2-TZVPD	yes	0.13	0.11	0.17	0.10	0.13	0.11	0.17	0.10	3.0	1.1	5.0	3.0
def2-QZVP	no	0.12	0.21	0.05	0.09	−0.12	−0.21	−0.04	−0.09	2.5	3.4	1.4	2.7
def2-QZVP	yes	0.06	0.05	0.09	0.03	0.05	.04	0.08	0.02	1.3	0.7	2.4	0.9
def2-QZVPD	no	0.02	0.01	0.04	0.01	−0.01	0.01	−0.03	−0.00	0.6	0.2	1.3	0.3
def2-QZVPD	yes	0.05	0.03	0.07	0.03	0.04	0.03	0.07	0.02	1.1	0.4	2.1	0.8
6-31G*	no	2.27	3.19	1.67	1.89	−2.27	−3.19	−1.67	−1.89	48.4	43.2	47.6	55.2
6-31G*	yes	0.39	0.54	0.39	0.23	−0.07	−0.41	0.37	−0.20	9.4	9.5	11.2	7.3
6-31+G*	no	0.54	0.97	0.22	0.41	−0.54	−0.97	−0.22	−0.41	11.2	16.3	5.0	12.4
6-31+G*	yes	0.29	0.43	0.31	0.11	0.10	−0.06	0.31	0.04	6.3	5.5	9.6	3.5
6-311G*	no	1.86	3.30	0.79	1.44	−1.85	−3.30	−0.77	−1.44	36.4	48.9	19.1	42.0
6-311G*	yes	0.41	0.64	0.36	0.20	−0.03	−0.35	0.36	−0.13	9.6	10.9	11.0	6.7
6-311+G*	no	0.69	1.26	0.28	0.51	−0.66	−1.22	−0.23	−0.51	14.4	21.7	6.3	15.4
6-311+G*	yes	0.37	0.62	0.33	0.14	0.00	−0.31	0.33	−0.02	8.1	9.2	10.2	4.5
6-311++G**	no	0.43	0.72	0.23	0.33	−0.42	−0.72	−0.20	−0.33	9.1	12.1	5.4	9.9
6-311++G**	yes	0.23	0.29	0.27	0.11	0.07	−0.10	0.27	0.04	5.2	4.1	7.9	3.4

Table S5: Convergence error statistics (with respect to the DFT/CBS limit) for interaction energies in the S66 data set computed using PBE0+D4.

Basis Set	CP?	Mean Absolute Error (kcal/mol)				Mean Signed Error (kcal/mol)				Mean Absolute Percent Error (%)			
		All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed
aug-cc-pVDZ	no	0.66	0.44	0.90	0.63	−0.66	−0.44	−0.90	−0.63	16.9	5.7	27.2	18.0
aug-cc-pVDZ	yes	0.06	0.09	0.04	0.05	0.06	0.09	0.03	0.05	1.1	0.8	1.2	1.3
aug-cc-pVTZ	no	0.10	0.07	0.14	0.10	−0.10	−0.07	−0.14	−0.10	2.5	0.7	3.9	2.9
aug-cc-pVTZ	yes	0.05	0.07	0.06	0.03	0.05	0.07	0.06	0.03	1.1	0.7	1.7	0.8
aug-cc-pVQZ	no	0.04	0.03	0.05	0.02	−0.04	−0.03	−0.05	−0.02	0.9	0.3	1.5	0.7
aug-cc-pVQZ	yes	0.04	0.03	0.05	0.02	0.04	0.03	0.05	0.02	0.9	0.3	1.5	0.7
def2-SVP	no	1.85	3.15	1.06	1.27	−1.85	−3.15	−1.06	−1.27	35.1	40.8	29.2	35.2
def2-SVP	yes	0.28	0.35	0.24	0.23	0.05	−0.22	0.24	0.13	6.1	5.1	7.0	6.2
def2-SVPD	no	1.37	1.12	1.72	1.25	−1.37	−1.12	−1.72	−1.25	33.3	13.8	51.4	35.1
def2-SVPD	yes	0.09	0.13	0.06	0.07	−0.01	−0.13	0.05	0.07	1.8	1.5	1.7	2.1
def2-TZVP	no	0.35	0.58	0.16	0.31	−0.35	−0.58	−0.15	−0.31	7.2	9.0	4.2	8.7
def2-TZVP	yes	0.13	0.20	0.12	0.06	0.04	0.00	0.12	−0.01	2.8	2.6	3.6	1.9
def2-TZVPD	no	0.09	0.07	0.12	0.07	−0.06	0.00	−0.12	−0.06	2.0	0.8	3.4	1.9
def2-TZVPD	yes	0.09	0.12	0.10	0.06	0.09	0.12	0.10	0.06	1.9	1.1	2.9	1.7
def2-QZVP	no	0.08	0.13	0.05	0.06	−0.08	−0.13	−0.04	−0.06	1.7	2.0	1.3	1.8
def2-QZVP	yes	0.04	0.04	0.06	0.02	0.04	0.04	0.06	0.02	1.0	0.5	1.7	0.7
def2-QZVPD	no	0.02	0.01	0.03	0.01	−0.01	0.01	−0.03	−0.01	0.5	0.1	1.1	0.3
def2-QZVPD	yes	0.04	0.03	0.06	0.02	0.04	0.03	0.06	0.02	0.9	0.3	1.7	0.7
6-31G*	no	1.62	2.46	1.07	1.29	−1.62	−2.46	−1.07	−1.29	32.9	31.8	31.4	36.0
6-31G*	yes	0.39	0.56	0.43	0.14	−0.02	−0.46	0.43	−0.04	9.0	9.0	12.8	4.4
6-31+G*	no	0.62	1.10	0.31	0.42	−0.62	−1.10	−0.31	−0.42	11.9	16.9	7.2	11.6
6-31+G*	yes	0.24	0.49	0.13	0.08	−0.01	−0.17	0.13	−0.01	4.5	6.3	4.5	2.4
6-311G*	no	1.63	2.72	0.88	1.26	−1.63	−2.72	−0.88	−1.26	32.1	38.1	23.6	34.8
6-311G*	yes	0.34	0.68	0.13	0.19	−0.16	−0.44	0.11	−0.16	6.8	10.6	4.3	5.5
6-311+G*	no	0.93	1.40	0.64	0.71	−0.92	−1.38	−0.64	−0.71	19.7	22.2	17.0	20.0
6-311+G*	yes	0.32	0.69	0.08	0.17	−0.16	−0.40	0.05	−0.12	5.8	9.9	2.6	4.8
6-311++G**	no	0.96	1.42	0.69	0.75	−0.95	−1.39	−0.69	−0.75	20.7	22.3	18.7	21.0
6-311++G**	yes	0.32	0.68	0.08	0.17	−0.15	−0.40	0.06	−0.12	5.8	9.8	2.7	4.7

Table S6: Convergence error statistics (with respect to the DFT/CBS limit) for interaction energies in the S66 data set computed using ωB97X-V.

Basis Set	CP?	Mean Absolute Error (kcal/mol)				Mean Signed Error (kcal/mol)				Mean Absolute Percent Error (%)			
		All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed
aug-cc-pVDZ	no	0.65	0.45	0.88	0.63	−0.65	−0.45	−0.88	−0.63	17.0	6.1	26.7	18.2
aug-cc-pVDZ	yes	0.07	0.09	0.06	0.05	0.05	0.09	0.01	0.05	1.6	1.0	2.2	1.5
aug-cc-pVTZ	no	0.12	0.08	0.14	0.13	−0.12	−0.08	−0.14	−0.13	2.9	0.9	4.0	3.7
aug-cc-pVTZ	yes	0.04	0.06	0.03	0.03	0.04	0.06	0.03	0.03	0.8	0.7	0.9	0.8
aug-cc-pVQZ	no	0.03	0.03	0.04	0.03	−0.03	−0.03	−0.04	−0.03	0.7	0.3	0.9	0.8
aug-cc-pVQZ	yes	0.03	0.03	0.04	0.03	0.03	0.03	0.04	0.03	0.7	0.3	0.9	0.8
def2-SVP	no	1.82	3.24	0.93	1.20	−1.82	−3.24	−0.93	−1.20	34.3	43.7	25.0	34.0
def2-SVP	yes	0.36	0.34	0.36	0.36	0.19	−0.07	0.36	0.27	8.4	5.1	10.3	10.0
def2-SVPD	no	1.36	1.12	1.70	1.25	−1.36	−1.12	−1.70	−1.25	33.7	14.6	50.9	35.9
def2-SVPD	yes	0.10	0.12	0.10	0.09	−0.00	−0.12	0.05	0.08	2.4	1.5	3.1	2.5
def2-TZVP	no	0.34	0.58	0.14	0.29	−0.34	−0.58	−0.14	−0.29	7.0	9.4	3.3	8.3
def2-TZVP	yes	0.12	0.20	0.09	0.06	0.04	0.02	0.09	0.02	2.4	2.7	2.5	1.9
def2-TZVPD	no	0.08	0.07	0.10	0.07	−0.05	0.01	−0.10	−0.07	1.9	0.8	3.0	2.0
def2-TZVPD	yes	0.08	0.12	0.06	0.06	0.08	0.12	0.06	0.06	1.5	1.2	1.7	1.6
def2-QZVP	no	0.07	0.12	0.02	0.05	−0.06	−0.12	−0.01	−0.05	1.3	2.0	0.5	1.4
def2-QZVP	yes	0.04	0.04	0.05	0.04	0.04	0.04	0.05	0.03	1.0	0.6	1.3	1.0
def2-QZVPD	no	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.01	0.3	0.2	0.3	0.3
def2-QZVPD	yes	0.04	0.03	0.04	0.03	0.04	0.03	0.04	0.03	0.8	0.4	1.2	0.9
6-31G*	no	1.62	2.53	1.05	1.23	−1.62	−2.53	−1.05	−1.23	33.0	34.0	30.2	34.9
6-31G*	yes	0.42	0.52	0.51	0.21	0.08	−0.38	0.51	0.11	10.4	8.7	15.6	6.5
6-31+G*	no	0.56	1.06	0.27	0.33	−0.56	−1.06	−0.27	−0.33	11.1	17.3	6.2	9.5
6-31+G*	yes	0.24	0.49	0.10	0.11	−0.01	−0.18	0.10	0.06	4.5	6.8	3.6	3.0
6-311G*	no	1.67	2.82	0.91	1.24	−1.67	−2.82	−0.91	−1.24	33.5	41.2	24.6	34.9
6-311G*	yes	0.32	0.66	0.11	0.16	−0.16	−0.39	0.03	−0.12	6.4	10.8	3.2	5.0
6-311+G*	no	0.88	1.36	0.62	0.63	−0.87	−1.33	−0.62	−0.63	19.3	22.7	16.9	18.2
6-311+G*	yes	0.33	0.71	0.09	0.16	−0.21	−0.44	−0.06	−0.13	6.1	10.9	2.7	4.6
6-311++G**	no	0.61	0.82	0.55	0.44	−0.61	−0.82	−0.55	0.44	13.7	13.0	15.1	12.8
6-311++G**	yes	0.18	0.35	0.07	0.11	−0.12	−0.22	−0.06	−0.06	3.7	5.4	2.4	3.1

Table S7: Convergence error statistics (with respect to the DFT/CBS limit) for interaction energies in the S66 data set computed using ωB97M-V.

Basis Set	CP?	Mean Absolute Error (kcal/mol)				Mean Signed Error (kcal/mol)				Mean Absolute Percent Error (%)			
		All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed
aug-cc-pVDZ	no	0.79	0.55	1.07	0.74	−0.79	−0.55	−1.07	−0.74	20.6	7.5	32.9	21.4
aug-cc-pVDZ	yes	0.08	0.04	0.15	0.06	−0.05	0.001	−0.11	−0.04	2.4	0.4	5.3	1.5
aug-cc-pVTZ	no	0.17	0.13	0.21	0.18	−0.17	−0.13	−0.21	−0.18	4.1	1.5	5.9	5.1
aug-cc-pVTZ	yes	0.02	0.04	0.02	0.02	0.005	0.04	−0.02	−0.01	0.5	0.4	0.8	0.4
aug-cc-pVQZ	no	0.02	0.03	0.02	0.02	−0.02	−0.03	−0.02	−0.02	0.5	0.3	0.6	0.4
aug-cc-pVQZ	yes	0.02	0.03	0.02	0.02	0.02	0.03	0.02	0.02	0.5	0.3	0.6	0.4
def2-SVP	no	2.04	3.55	1.10	1.37	−2.04	−3.55	−1.10	−1.37	38.8	48.1	29.2	39.0
def2-SVP	yes	0.37	0.38	0.36	0.35	0.15	−0.14	0.36	0.25	8.5	5.4	10.6	9.6
def2-SVPD	no	1.56	1.26	1.96	1.43	−1.56	−1.26	−1.96	−1.43	38.7	16.4	58.9	41.3
def2-SVPD	yes	0.18	0.23	0.20	0.08	−0.11	−0.23	−0.07	−0.00	3.9	2.8	6.5	2.3
def2-TZVP	no	0.42	0.70	0.21	0.35	−0.42	−0.70	−0.21	−0.35	8.7	11.1	5.4	9.9
def2-TZVP	yes	0.10	0.20	0.05	0.05	−0.00	−0.03	0.03	−0.01	2.0	3.0	1.4	1.6
def2-TZVPD	no	0.12	0.09	0.16	0.11	−0.11	−0.06	−0.16	−0.11	3.0	1.4	4.6	3.1
def2-TZVPD	yes	0.05	0.06	0.04	0.03	0.03	0.06	0.02	0.02	0.9	0.5	1.3	0.7
def2-QZVP	no	0.10	0.17	0.04	0.07	−0.09	−0.17	−0.03	−0.07	1.9	2.6	1.0	2.1
def2-QZVP	yes	0.03	0.04	0.03	0.02	0.03	0.04	0.02	0.02	0.8	0.6	1.1	0.7
def2-QZVPD	no	0.02	0.01	0.02	0.01	−0.00	0.01	−0.01	−0.01	0.4	0.2	0.5	0.4
def2-QZVPD	yes	0.03	0.03	0.03	0.02	0.03	0.03	0.02	0.02	0.7	0.4	1.0	0.6
6-31G*	no	1.84	2.76	1.30	1.41	−1.84	−2.76	−1.30	−1.41	38.2	37.0	37.4	40.3
6-31G*	yes	0.44	0.52	0.55	0.23	0.08	−0.41	0.55	0.11	11.1	8.9	16.6	7.2
6-31+G*	no	0.63	1.14	0.37	0.35	−0.63	−1.14	−0.35	−0.35	12.6	18.5	8.7	10.3
6-31+G*	yes	0.25	0.50	0.13	0.10	−0.06	−0.24	0.02	0.04	4.7	7.2	3.9	2.8
6-311G*	no	1.95	3.10	1.22	1.47	−1.95	−3.10	−1.22	−1.47	40.2	45.4	33.6	41.7
6-311G*	yes	0.37	0.67	0.19	0.25	−0.29	−0.46	−0.17	−0.24	8.4	11.4	6.2	7.6
6-311+G*	no	1.02	1.46	0.83	0.75	−1.02	−1.44	−0.83	−0.75	23.1	24.5	22.9	21.6
6-311+G*	yes	0.43	0.75	0.27	0.25	−0.36	−0.53	−0.27	−0.25	9.3	11.9	8.4	7.4
6-311++G**	no	0.75	0.94	0.74	0.56	−0.75	−0.94	−0.74	−0.56	17.4	14.8	20.8	16.3
6-311++G**	yes	0.29	0.39	0.27	0.20	−0.26	−0.33	−0.27	−0.18	7.0	6.5	8.7	5.8

Table S8: Error statistics in S66 interaction energies as compared to CCSD(T)/CBS benchmarks.

Basis Set	Mean Absolute Error (kcal/mol)											
	M06-2X		M06-L		BLYP+D3(BJ)		PBE0+D4		ωB97X-V		ωB97M-V	
	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP
aug-cc-pVDZ	0.62	0.28	0.66	0.87	0.71	0.24	0.84	0.27	0.64	0.13	0.80	0.18
aug-cc-pVTZ	0.27	0.32	0.28	0.71	0.25	0.21	0.34	0.28	0.18	0.14	0.24	0.16
aug-cc-pVQZ	0.26	0.29	0.85	1.11	0.23	0.21	0.31	0.29	0.15	0.14	0.16	0.16
def2-SVP	1.48	0.54	0.79	0.92	2.53	0.24	2.03	0.46	1.81	0.37	2.04	0.37
def2-SVPD	1.24	0.32	0.45	0.78	1.52	0.23	1.56	0.35	1.35	0.17	1.56	0.24
def2-TZVP	0.37	0.36	0.43	0.66	0.49	0.18	0.58	0.32	0.36	0.15	0.44	0.15
def2-TZVPD	0.28	0.34	0.38	0.73	0.23	0.23	0.31	0.28	0.13	0.15	0.18	0.14
def2-QZVP	0.30	0.33	0.56	0.81	0.22	0.19	0.35	0.29	0.15	0.14	0.18	0.16
def2-QZVPD	0.30	0.32	0.54	0.83	0.22	0.20	0.30	0.29	0.14	0.14	0.16	0.16
6-31G*	1.25	0.60	0.64	0.67	2.26	0.29	1.81	0.59	1.61	0.41	1.85	0.41
6-31+G*	0.61	0.38	0.38	0.60	0.56	0.26	0.83	0.37	0.56	0.22	0.65	0.25
6-311G*	1.54	0.39	0.94	0.46	1.86	0.31	1.82	0.49	1.66	0.26	1.96	0.33
6-311+G*	0.96	0.43	0.56	0.39	0.69	0.33	1.10	0.48	0.86	0.28	1.02	0.39
6-311++G**	0.64	0.27	0.31	0.40	0.45	0.22	1.14	0.48	0.60	0.16	0.76	0.27

Table S9: Convergence error data (in kcal/mol) for MP2 calculations in the S66 data set, with respect to the MP2/CBS limit.

Dimer	6-31G*		6-31+G*		6-311G*		6-311+G*		6-311++G**		def2-SVP		def2-SVPD		def2-TZVP		def2-TZVPD		def2-QZVP		def2-QZVPD	
Index	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP
1	−1.95	−0.23	−1.83	0.16	−2.84	−0.35	−2.63	−0.24	−1.27	−0.51	−2.26	0.66	−0.71	0.66	−0.58	0.23	0.05	0.52	−0.11	0.28	0.06	0.28
2	−1.55	0.73	−1.55	0.58	−2.19	0.84	−1.91	0.47	−1.03	−0.32	−1.91	1.44	−1.13	0.72	−0.37	0.72	0.08	0.63	−0.05	0.37	0.06	0.33
3	−1.33	0.70	−1.36	0.83	−2.06	1.25	−1.33	0.69	−0.98	−0.28	−1.58	1.71	−1.28	0.82	−0.30	0.86	0.07	0.68	−0.01	0.43	0.09	0.33
4	−1.01	2.09	−0.47	1.41	−0.95	2.34	−0.41	1.58	−0.81	−0.38	−1.28	2.71	−1.56	1.15	0.09	1.24	0.16	0.91	0.03	0.52	0.11	0.46
5	−1.77	0.65	−1.61	0.80	−2.52	0.77	−1.88	0.68	−1.00	−0.20	−2.49	1.13	−1.52	0.73	−0.50	0.72	−0.04	0.63	−0.13	0.35	0.03	0.31
6	−1.64	0.76	−1.27	1.33	−2.45	1.20	−1.24	1.09	−0.86	−0.12	−2.22	1.44	−1.78	0.97	−0.45	0.85	−0.14	0.74	−0.06	0.40	0.03	0.34
7	−1.97	2.08	−0.57	1.86	−2.06	2.38	−0.29	2.04	−0.70	−0.16	−2.74	2.42	−2.05	1.18	−0.26	1.28	−0.01	0.92	−0.10	0.50	0.03	0.44
8	−2.08	−0.28	−1.90	0.38	−3.05	−0.41	−2.70	−0.01	−1.25	−0.39	−2.70	0.35	−1.00	0.67	−0.63	0.26	−0.04	0.53	−0.14	0.27	0.03	0.27
9	−1.21	0.72	−0.80	0.71	−1.34	0.68	−0.92	0.61	−0.68	−0.27	−1.66	1.03	−1.48	0.56	−0.25	0.52	−0.23	0.41	−0.08	0.21	−0.03	0.18
10	−0.89	1.18	−0.49	1.15	−1.44	1.07	−0.49	0.98	−0.56	−0.19	−1.53	1.57	−1.61	0.81	−0.31	0.69	−0.29	0.54	−0.07	0.25	−0.01	0.21
11	−1.07	2.16	−0.31	1.86	−1.27	2.04	−0.26	1.80	−0.45	−0.13	−1.74	2.43	−2.44	1.10	−0.10	1.12	−0.41	0.76	−0.02	0.41	−0.04	0.36
12	−1.25	1.00	−1.21	0.96	−2.17	1.36	−1.38	0.84	−0.90	−0.22	−1.55	1.87	−1.39	0.94	−0.38	0.88	0.04	0.73	0.01	0.44	0.09	0.35
13	−1.65	1.07	−1.33	0.98	−2.34	0.82	−1.74	0.71	−0.92	−0.37	−2.57	1.36	−2.41	0.84	−0.39	0.73	−0.35	0.64	−0.13	0.31	−0.07	0.28
14	−1.76	1.02	−1.18	1.37	−2.35	0.98	−1.25	1.14	−0.72	−0.12	−2.30	1.43	−2.48	0.94	−0.62	0.75	−0.52	0.62	−0.14	0.30	−0.10	0.25
15	−1.36	2.43	−0.47	2.05	−1.19	2.47	−0.39	2.07	−0.49	−0.08	−1.91	2.65	−3.28	1.14	−0.12	1.27	−0.55	0.81	−0.10	0.44	−0.16	0.37
16	−1.98	−0.10	−1.76	0.36	−2.80	−0.59	−3.02	−0.03	−1.28	−0.48	−2.73	0.32	−1.66	0.65	−0.66	0.11	−0.24	0.48	−0.16	0.20	−0.03	0.22
17	−1.53	3.42	−0.02	3.55	0.05	4.34	0.77	3.98	−0.63	0.08	−1.74	3.77	−3.49	2.13	0.71	2.11	−0.05	1.52	−0.09	0.71	−0.15	0.64
18	−0.46	1.80	−0.90	1.23	−0.59	2.14	−0.68	1.28	−0.48	0.02	−0.76	2.17	−2.20	0.82	0.12	1.16	0.03	0.71	0.04	0.49	0.09	0.37
19	−0.84	1.80	−1.01	1.53	−1.02	2.06	−0.66	1.51	−0.42	0.18	−1.47	1.92	−2.76	0.89	−0.08	1.11	−0.15	0.73	0.00	0.45	0.03	0.37
20	−1.18	4.42	1.30	5.10	0.22	5.60	2.38	5.79	−0.59	0.15	−2.57	4.03	−2.06	2.85	0.88	2.51	0.71	2.11	0.12	1.05	0.16	1.01
21	−2.02	3.15	0.60	3.43	−0.39	4.05	1.31	3.86	−0.31	0.16	−1.98	3.76	−2.21	2.16	0.77	2.12	0.32	1.56	0.00	0.76	0.05	0.71
22	−1.28	3.92	0.55	4.30	0.17	4.96	1.56	4.89	−0.60	0.12	−2.01	3.92	−2.64	2.58	0.83	2.32	0.41	1.87	0.03	0.90	0.04	0.85
23	−1.63	3.44	0.30	3.56	−0.03	4.35	1.08	4.05	−0.53	0.05	−1.72	3.88	−2.70	2.32	0.73	2.13	0.22	1.63	−0.05	0.76	−0.02	0.72
24	1.52	4.17	−1.14	2.67	0.57	2.75	−2.02	1.95	0.82	1.35	0.23	2.82	−5.45	0.80	−0.41	0.86	−1.73	0.33	−0.31	0.19	−0.76	0.09
25	1.37	4.15	−0.76	2.78	0.41	2.83	−1.52	2.09	1.13	1.70	0.19	3.13	−5.26	0.99	−0.26	1.05	−1.60	0.48	−0.20	0.33	−0.60	0.22
26	0.06	5.58	−2.88	3.97	−0.43	4.89	−3.33	3.81	−0.46	0.83	−0.94	5.73	−7.76	2.04	−0.79	2.00	−2.51	1.10	−0.36	0.80	−0.91	0.60
27	1.44	4.19	−1.04	2.72	0.43	2.79	−1.86	2.01	0.89	1.50	0.17	2.99	−5.39	0.88	−0.37	0.94	−1.71	0.40	−0.28	0.25	−0.70	0.14
28	1.07	5.17	−2.22	3.43	−0.04	3.95	−2.80	2.86	0.43	1.32	−0.24	4.46	−7.15	1.35	−0.61	1.45	−2.27	0.68	−0.39	0.48	−0.88	0.32
29	1.08	5.21	−1.90	3.42	0.14	4.20	−2.20	3.04	0.56	1.48	−0.08	4.73	−6.80	1.47	−0.41	1.61	−2.10	0.78	−0.26	0.60	−0.73	0.42
30	1.10	2.96	0.12	2.04	0.76	2.14	−0.28	1.60	0.51	0.64	0.40	2.07	−2.65	0.64	0.05	0.77	−0.85	0.34	−0.03	0.23	−0.31	0.14
31	0.73	3.16	−0.39	2.26	0.28	2.47	−0.63	1.93	0.06	0.45	0.02	2.63	−3.34	0.98	0.00	1.02	−0.99	0.53	−0.02	0.38	−0.30	0.28
32	0.94	3.10	−0.49	2.10	0.57	2.44	−0.60	1.81	0.06	0.41	0.46	2.73	−2.71	1.03	0.14	0.98	−0.76	0.50	0.04	0.40	−0.23	0.29
33	1.00	2.91	−0.03	2.01	0.58	2.09	−0.36	1.59	0.53	0.72	0.30	2.11	−2.65	0.69	0.06	0.81	−0.83	0.37	−0.03	0.25	−0.29	0.17
34	1.53	3.25	0.59	2.91	1.32	2.63	0.22	2.43	−0.70	−0.35	0.76	2.50	−4.82	0.81	−0.07	1.18	−1.40	0.53	−0.23	0.15	−0.45	0.09
35	0.69	2.18	0.13	1.97	0.67	1.82	−0.13	1.65	−0.52	−0.31	0.15	1.67	−4.16	0.53	−0.05	0.81	−1.06	0.34	−0.19	0.08	−0.36	0.04
36	0.12	1.37	−0.28	1.27	0.27	1.21	−0.29	1.07	−0.37	−0.26	−0.06	1.06	−3.44	0.32	0.01	0.55	−1.00	0.22	−0.12	0.06	−0.27	0.03
37	0.60	2.04	0.12	1.86	0.63	1.68	−0.25	1.52	−0.58	−0.29	0.11	1.55	−3.87	0.49	−0.02	0.72	−1.13	0.31	−0.19	0.07	−0.37	0.03
38	0.87	2.44	0.40	2.26	0.96	2.02	−0.27	1.86	−0.64	−0.20	0.36	1.87	−3.73	0.62	0.04	0.88	−1.09	0.41	−0.19	0.11	−0.38	0.07
39	0.47	3.20	−0.39	2.59	−0.12	2.20	−1.37	1.92	−0.07	0.44	−0.55	2.33	−5.76	0.76	−0.36	0.83	−1.68	0.39	−0.35	0.11	−0.67	0.05
40	0.11	2.50	−0.67	2.02	−0.35	1.73	−1.25	1.52	−0.11	0.21	−0.66	1.87	−5.28	0.58	−0.30	0.65	−1.54	0.31	−0.28	0.09	−0.57	0.04
41	0.27	4.11	−0.68	3.44	−0.19	3.51	−1.09	3.06	−0.36	0.38	−0.82	3.67	−6.57	1.34	−0.40	1.53	−1.84	0.79	−0.26	0.49	−0.59	0.36
42	0.31	3.51	−0.74	2.89	−0.08	2.96	−1.20	2.54	−0.35	0.38	−0.77	3.08	−6.01	1.09	−0.32	1.27	−1.71	0.65	−0.26	0.40	−0.61	0.29
43	0.30	2.99	−0.69	2.41	−0.10	2.43	−0.94	2.09	−0.41	0.14	−0.55	2.56	−5.28	0.88	−0.29	1.03	−1.50	0.52	−0.21	0.32	−0.51	0.23
44	0.69	2.02	0.32	1.81	0.60	1.69	0.01	1.52	−0.05	0.07	0.43	1.64	−2.25	0.61	0.14	0.78	−0.59	0.40	−0.04	0.17	−0.16	0.13
45	0.56	1.95	0.39	1.68	0.51	1.46	0.03	1.30	0.05	0.21	0.50	1.61	−1.67	0.59	0.15	0.68	−0.48	0.36	0.01	0.21	−0.12	0.16
46	0.43	3.59	0.16	3.08	0.06	3.01	−0.21	2.69	−0.48	−0.04	−0.60	3.12	−4.88	1.14	−0.21	1.36	−1.36	0.71	−0.20	0.35	−0.41	0.26
47	0.26	2.25	−1.25	1.76	−0.23	1.61	−1.66	1.32	0.27	0.66	−0.34	1.83	−4.59	0.65	−0.33	0.60	−1.30	0.31	−0.25	0.11	−0.47	0.06
48	0.02	2.32	−0.71	1.88	−0.31	1.83	−1.04	1.52	0.34	0.78	−0.43	2.15	−4.28	0.83	−0.12	0.79	−0.95	0.46	−0.12	0.25	−0.32	0.19
49	0.19	2.22	−1.08	1.80	−0.25	1.62	−1.59	1.35	0.22	0.62	−0.29	1.93	−4.53	0.72	−0.27	0.63	−1.23	0.36	−0.22	0.15	−0.44	0.10
50	−0.08	1.70	−0.68	1.61	−0.17	1.33	−1.05	1.23	0.18	0.47	−0.35	1.66	−3.16	0.75	−0.12	0.54	−0.66	0.38	−0.06	0.20	−0.26	0.16
51	−0.38	0.58	−0.26	0.73	−0.02	0.61	−0.27	0.66	0.04	0.13	−0.08	0.83	−1.08	0.53	0.11	0.36	−0.17	0.24	0.04	0.14	−0.03	0.12
52	−0.65	2.20	−0.91	2.21	−0.81	2.15	−1.24	1.93	0.04	0.54	−0.55	2.68	−4.39	1.14	−0.27	0.94	−1.03	0.58	−0.16	0.34	−0.34	0.27
53	−0.81	2.16	−0.79	1.69	−0.84	1.81	−0.91	1.46	−0.09	0.24	−0.61	2.41	−3.30	0.93	−0.21	0.85	−0.77	0.50	−0.10	0.30	−0.23	0.23
54	−0.51	1.36	−0.79	1.37	−0.74	1.30	−1.18	1.10	−0.38	0.13	−0.36	1.75	−2.49	0.71	−0.66	0.68	−0.50	0.45	−0.24	0.25	−0.17	0.20
55	−0.24	2.25	−0.58	2.19	−0.50	2.05	−0.97	1.82	−0.04	0.50	−0.32	2.43	−3.83	1.00	−0.43	0.92	−0.89	0.56	−0.21	0.28	−0.29	0.22
56	0.20	2.39	−0.27	2.09	−0.02	1.94	−0.63	1.68	0.10	0.41	−0.17	2.17	−3.77	0.81	−0.26	0.83	−0.99	0.45	−0.18	0.20	−0.35	0.14
57	−0.21	2.83	−0.82	2.55	−0.50	2.24	−1.47	1.99	0.15	0.62	−0.47	2.75	−5.47	0.98	−0.46	0.92	−1.56	0.50	−0.32	0.21	−0.56	0.15
58	−0.87	1.31	−0.30	1.19	−1.10	1.13	−0.29	1.07	−0.04	0.26	−1.64	1.40	−3.44	0.80	0.02	0.73	−0.43	0.48	0.00	0.27	−0.06	0.22
59	−1.21	−0.08	−1.32	0.26	−1.73	−0.57	−2.17	−0.08	−1.02	−0.45	−1.94	0.17	−0.98	0.61	−0.49	0.03	−0.11	0.33	−0.08	0.13	0.01	0.16
60	−0.82	1.81	0.12	1.91	−0.17	2.04	0.31	1.89	−0.11	0.09	−0.12	2.46	−1.10	1.46	0.45	1.09	0.10	0.80	0.13	0.43	0.07	0.38
61	−0.06	2.56	0.07	2.32	−0.26	2.33	−0.22	2.11	−0.37	0.10	−0.71	2.34	−3.41	0.94	−0.09	1.12	−0.89	0.61	−0.07	0.36	−0.24	0.29
62	−0.31	3.03	0.14	2.60	−0.49	2.65	−0.24	2.35	−0.41	−0.01	−1.27	2.72	−4.00	1.04	−0.18	1.25	−1.02	0.67	−0.13	0.37	−0.27	0.29
63	0.33	2.87	−0.61	2.33	−0.27	2.33	−1.12	1.94	−0.14	0.39	−0.35	2.65	−4.38	0.98	−0.18	1.01	−1.22	0.53	−0.16	0.31	−0.45	0.22
64	−0.24	2.20	−0.13	1.79	−0.36	1.87	−0.41	1.58	−0.10	0.09	−0.61	2.11	−2.21	0.89	0.04	0.90	−0.54	0.54	0.02	0.32	−0.11	0.27
65	−0.91	0.77	−0.45	0.84	−0.79	0.77	−0.27	0.76	−0.31	−0.01	−1.31	0.93	−2.21	0.77	0.01	0.52	−0.23	0.38	0.04	0.21	−0.03	0.18
66	0.06	2.41	−0.31	1.90	−0.25	2.09	−0.39	1.70	0.06	0.44	−0.41	2.35	−3.17	0.86	−0.01	1.00	−0.64	0.55	−0.07	0.31	−0.19	0.23

Table S10: Convergence error statistics (with respect to the MP2/CBS limit) for interaction energies in the S66 data set computed using MP2.

Basis Set	CP?	Mean Absolute Error (kcal/mol)				Mean Signed Error (kcal/mol)				Mean Absolute Percent Error (%)			
		All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed
aug-cc-pVDZ	no	1.70	0.66	2.69	1.77	−1.70	−0.65	−2.69	−1.77	39.8	9.1	66.8	44.1
aug-cc-pVDZ	yes	0.80	1.13	0.61	0.63	0.80	1.13	0.61	0.63	14.2	12.7	14.3	15.7
aug-cc-pVTZ	no	0.78	0.40	1.13	0.80	−0.78	−0.40	−1.13	−0.80	17.4	5.0	27.9	19.6
aug-cc-pVTZ	yes	0.32	0.52	0.20	0.22	0.32	0.52	0.20	0.22	5.1	5.9	4.1	5.5
aug-cc-pVQZ	no	0.28	0.14	0.42	0.28	−0.28	−0.14	−0.42	−0.28	6.4	1.8	10.5	6.9
aug-cc-pVQZ	yes	0.16	0.28	0.10	0.10	0.15	0.28	0.08	0.10	2.7	3.1	2.2	2.6
def2-SVP	no	1.02	1.97	0.41	0.62	−0.89	−1.97	−0.05	−0.62	18.2	27.8	10.4	16.2
def2-SVP	yes	2.27	2.09	2.69	1.99	2.27	2.09	2.69	1.99	45.1	23.6	63.5	48.8
def2-SVPD	no	3.31	1.99	4.65	3.29	−3.31	−1.99	−4.65	−3.29	73.0	25.5	113.8	80.7
def2-SVPD	yes	0.99	1.20	0.90	0.87	0.99	1.20	0.90	0.87	18.7	13.5	21.1	21.9
def2-TZVP	no	0.31	0.44	0.24	0.23	−0.15	−0.08	−0.19	−0.17	5.4	5.5	4.8	5.9
def2-TZVP	yes	0.99	1.12	1.03	0.79	0.99	1.12	1.03	0.79	19.0	12.2	25.5	19.5
def2-TZVPD	no	0.79	0.22	1.38	0.76	−0.72	−0.04	−1.38	−0.75	18.2	2.8	33.3	18.5
def2-TZVPD	yes	0.63	0.90	0.50	0.48	0.63	0.90	0.50	0.48	11.5	10.2	12.1	12.2
def2-QZVP	no	0.13	0.07	0.19	0.13	−0.12	−0.05	−0.19	−0.11	2.9	1.1	4.5	3.1
def2-QZVP	yes	0.34	0.47	0.28	0.26	0.34	0.47	0.28	0.26	6.0	5.4	6.2	6.5
def2-QZVPD	no	0.27	0.07	0.49	0.24	−0.24	0.01	−0.49	−0.24	6.0	0.8	11.4	5.8
def2-QZVPD	yes	0.28	0.42	0.19	0.20	0.28	0.42	0.19	0.20	4.7	4.8	4.2	5.2
6-31G*	no	0.89	1.45	0.75	0.42	−0.34	−1.45	0.75	−0.31	17.4	20.4	19.9	11.0
6-31G*	yes	2.34	1.70	3.29	1.97	2.32	1.65	3.29	1.96	48.7	18.0	79.8	48.3
6-31+G*	no	0.77	0.99	0.72	0.58	−0.61	−0.75	−0.52	−0.55	14.7	15.2	14.1	14.8
6-31+G*	yes	2.00	1.72	2.50	1.75	2.00	1.72	2.50	1.75	41.1	17.7	62.7	43.4
6-311G*	no	0.84	1.54	0.44	0.49	−0.56	−1.50	0.32	−0.49	17.3	25.3	13.6	12.4
6-311G*	yes	2.12	2.05	2.56	1.71	2.07	1.93	2.56	1.66	41.8	20.9	62.1	42.4
6-311+G*	no	1.07	1.32	0.99	0.87	−0.84	−0.70	−0.97	−0.84	20.0	19.1	19.0	22.2
6-311+G*	yes	1.78	1.75	2.08	1.48	1.77	1.73	2.08	1.47	34.9	16.8	51.5	36.6
6-311++G**	no	0.48	0.76	0.44	0.22	−0.29	−0.76	−0.002	−0.08	9.8	11.4	11.4	6.1
6-311++G**	yes	0.39	0.22	0.59	0.35	0.20	−0.15	0.47	0.30	8.4	3.5	13.2	8.5

Table S11: Convergence error statistics (with respect to DH-DFT/CBS limit) for interaction energies in the S66 data set computed using PBE-QIDH.

Basis Set	CP?	Mean Absolute Error (kcal/mol)				Mean Signed Error (kcal/mol)				Mean Absolute Percent Error (%)			
		All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed
aug-cc-pVDZ	no	1.31	0.68	1.87	1.38	−1.31	−0.68	−1.87	−1.38	67.3	9.7	132.0	59.3
aug-cc-pVDZ	yes	0.18	0.33	0.09	0.10	0.15	0.33	0.04	0.05	4.6	3.9	5.7	4.1
aug-cc-pVTZ	no	0.96	0.67	1.19	1.03	−0.96	−0.67	−1.19	−1.03	45.1	8.4	83.5	43.2
aug-cc-pVTZ	yes	0.10	0.12	0.09	0.10	0.00	0.12	−0.05	−0.08	4.5	1.5	8.0	4.0
aug-cc-pVQZ	no	0.36	0.25	0.45	0.39	−0.36	−0.25	−0.45	−0.39	17.2	3.2	32.1	16.3
aug-cc-pVQZ	yes	0.11	0.06	0.11	0.15	−0.08	−0.01	−0.11	−0.14	5.4	0.8	9.5	6.0
def2-SVP	no	1.52	2.59	0.80	1.10	−1.52	−2.59	−0.80	−1.10	42.7	37.5	46.2	44.5
def2-SVP	yes	0.73	0.57	0.93	0.68	0.67	0.45	0.93	0.62	32.5	7.2	61.6	28.1
def2-SVPD	no	2.35	1.62	3.12	2.30	−2.35	−1.62	−3.12	−2.30	112.2	21.9	216.4	96.2
def2-SVPD	yes	0.18	0.21	0.17	0.16	0.18	0.21	0.16	0.16	6.6	2.5	10.7	6.6
def2-TZVP	no	0.42	0.46	0.36	0.44	−0.41	−0.45	−0.36	−0.44	15.7	8.2	21.4	17.7
def2-TZVP	yes	0.29	0.39	0.30	0.17	0.25	0.32	0.30	0.12	10.9	4.4	20.5	7.3
def2-TZVPD	no	0.57	0.20	0.91	0.61	−0.56	−0.18	−0.91	−0.61	31.0	3.1	63.2	25.9
def2-TZVPD	yes	0.17	0.30	0.11	0.08	0.14	0.30	0.08	0.04	5.1	3.6	8.0	3.5
def2-QZVP	no	0.31	0.25	0.36	0.32	−0.31	−0.25	−0.36	−0.32	13.8	3.4	24.8	13.1
def2-QZVP	yes	0.10	0.10	0.09	0.10	0.01	0.09	−0.01	−0.06	4.3	1.4	7.5	4.0
def2-QZVPD	no	0.39	0.17	0.60	0.41	−0.39	−0.17	−0.60	−0.41	20.5	2.1	41.5	17.5
def2-QZVPD	yes	0.09	0.08	0.08	0.10	−0.01	0.07	−0.04	−0.08	4.3	1.1	7.6	4.1
6-31G*	no	1.21	2.07	0.50	1.02	−1.20	−2.07	−0.49	−1.02	33.2	30.0	30.1	40.5
6-31G*	yes	0.85	0.65	1.27	0.59	0.66	0.17	1.27	0.51	41.5	8.2	88.7	25.5
6-31+G*	no	0.92	1.25	0.76	0.75	−0.92	−1.24	−0.75	−0.75	30.3	20.6	40.1	30.1
6-31+G*	yes	0.61	0.56	0.78	0.48	0.54	0.38	0.78	0.45	28.1	5.3	57.4	20.5
6-311G*	no	1.36	2.24	0.67	1.13	−1.36	−2.24	−0.67	−1.13	38.9	35.8	36.5	45.0
6-311G*	yes	0.69	0.82	0.77	0.44	0.47	0.29	0.77	0.32	27.8	9.9	53.6	18.7
6-311+G*	no	1.20	1.41	1.13	1.05	−1.18	−1.34	−1.13	−1.05	45.4	24.4	68.7	42.9
6-311+G*	yes	0.55	0.72	0.56	0.33	0.36	0.24	0.56	0.26	21.1	8.0	40.3	14.3
6-311++G**	no	0.99	0.83	1.20	0.93	−0.98	−0.82	−1.20	−0.93	43.6	13.9	77.2	39.1
6-311++G**	yes	0.39	0.45	0.41	0.30	0.36	0.40	0.41	0.26	14.2	4.0	26.1	12.1

Table S12: Convergence error statistics (with respect to DH-DFT/CBS limit) for interaction energies in the S66 data set computed using B2GPPLYP.

Basis Set	CP?	Mean Absolute Error (kcal/mol)				Mean Signed Error (kcal/mol)				Mean Absolute Percent Error (%)			
		All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed
aug-cc-pVDZ	no	1.29	0.70	1.84	1.34	−1.29	−0.70	−1.84	−1.34	103.7	10.4	223.4	73.3
aug-cc-pVDZ	yes	0.24	0.40	0.17	0.12	0.23	0.40	0.16	0.10	11.3	5.1	22.5	5.7
aug-cc-pVTZ	no	1.01	0.71	1.24	1.09	−1.01	−0.71	−1.24	−1.09	71.8	9.2	146.5	57.8
aug-cc-pVTZ	yes	0.11	0.13	0.08	0.11	0.01	0.13	−0.03	−0.09	6.8	1.7	13.0	5.5
aug-cc-pVQZ	no	0.36	0.25	0.44	0.39	−0.36	−0.25	−0.44	−0.39	25.5	3.3	52.0	20.7
aug-cc-pVQZ	yes	0.10	0.07	0.09	0.14	−0.06	0.01	−0.08	−0.13	7.2	0.9	13.8	7.1
def2-SVP	no	1.70	2.90	0.85	1.29	−1.70	−2.90	−0.85	−1.29	62.5	43.8	80.1	63.9
def2-SVP	yes	0.87	0.74	1.13	0.73	0.83	0.66	1.13	0.69	62.9	9.7	137.8	37.9
def2-SVPD	no	2.41	1.66	3.19	2.37	−2.41	−1.66	−3.19	−2.37	184.0	23.7	395.1	125.6
def2-SVPD	yes	0.26	0.30	0.27	0.20	0.26	0.30	0.27	0.20	16.2	3.8	34.4	9.6
def2-TZVP	no	0.48	0.54	0.40	0.50	−0.48	−0.54	−0.40	−0.49	24.1	9.9	37.6	25.0
def2-TZVP	yes	0.31	0.40	0.34	0.18	0.28	0.34	0.34	0.13	20.4	4.9	45.4	9.7
def2-TZVPD	no	0.61	0.23	0.96	0.65	−0.61	−0.21	−0.96	−0.65	52.4	3.6	116.0	35.2
def2-TZVPD	yes	0.18	0.31	0.12	0.09	0.16	0.31	0.10	0.04	8.5	3.9	16.2	4.9
def2-QZVP	no	0.34	0.29	0.38	0.35	−0.34	−0.29	−0.38	−0.35	21.4	4.1	41.4	18.2
def2-QZVP	yes	0.10	0.11	0.09	0.11	0.01	0.09	0.01	−0.07	7.2	1.5	14.4	5.4
def2-QZVPD	no	0.42	0.19	0.62	0.45	−0.42	−0.19	−0.62	−0.45	34.6	2.4	75.8	24.0
def2-QZVPD	yes	0.09	0.09	0.08	0.11	−0.01	0.07	−0.03	−0.09	6.7	1.2	13.2	5.8
6-31G*	no	1.38	2.29	0.62	1.22	−1.38	−2.29	−0.61	−1.22	49.5	34.1	56.2	59.5
6-31G*	yes	0.93	0.66	1.46	0.62	0.79	0.31	1.46	0.56	81.6	8.2	195.9	34.6
6-31+G*	no	0.84	1.16	0.62	0.71	−0.83	−1.14	−0.61	−0.71	34.3	20.0	48.0	35.2
6-31+G*	yes	0.73	0.60	1.00	0.56	0.68	0.49	1.00	0.54	59.3	5.9	137.4	30.8
6-311G*	no	1.41	2.44	0.58	1.18	−1.39	−2.44	−0.53	−1.18	45.8	40.3	41.7	56.9
6-311G*	yes	0.82	0.87	1.03	0.52	0.64	0.44	1.03	0.41	60.1	10.4	137.5	28.0
6-311+G*	no	1.06	1.33	0.90	0.94	−1.03	−1.22	−0.90	−0.94	52.4	24.0	85.1	47.5
6-311+G*	yes	0.66	0.73	0.79	0.43	0.51	0.36	0.79	0.36	46.7	8.0	105.8	23.3
6-311++G**	no	0.86	0.76	0.99	0.84	−0.85	−0.73	−0.99	−0.84	54.8	13.3	105.2	44.4
6-311++G**	yes	0.51	0.53	0.61	0.38	0.49	0.50	0.61	0.35	34.0	5.1	75.3	19.8

Table S13: Convergence error statistics (with respect to DH-DFT/CBS limit) for interaction energies in the S66 data set computed using ωB97X-2(LP).

Basis Set	CP?	Mean Absolute Error (kcal/mol)				Mean Signed Error (kcal/mol)				Mean Absolute Percent Error (%)			
		All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed
aug-cc-pVDZ	no	1.54	0.82	2.22	1.59	−1.54	−0.82	−2.22	−1.59	38.0	10.1	61.0	43.6
aug-cc-pVDZ	yes	0.28	0.50	0.17	0.16	0.26	0.50	0.13	0.12	4.6	5.5	4.2	4.1
aug-cc-pVTZ	no	1.31	0.92	1.61	1.42	−1.31	−0.92	−1.61	−1.42	30.6	10.2	43.9	38.6
aug-cc-pVTZ	yes	0.14	0.16	0.11	0.14	0.00	0.16	−0.07	−0.11	3.0	1.9	3.5	3.8
aug-cc-pVQZ	no	0.48	0.33	0.59	0.52	−0.48	−0.33	−0.59	−0.52	11.2	3.7	16.1	14.2
aug-cc-pVQZ	yes	0.13	0.09	0.13	0.18	−0.09	0.01	−0.13	−0.17	3.2	1.0	4.0	4.9
def2-SVP	no	1.46	2.62	0.62	1.09	−1.45	−2.62	−0.59	−1.09	25.7	33.5	14.5	29.4
def2-SVP	yes	1.27	1.17	1.54	1.09	1.25	1.14	1.54	1.05	27.2	13.2	40.1	28.6
def2-SVPD	no	2.72	1.82	3.65	2.70	−2.72	−1.82	−3.65	−2.70	64.6	21.9	100.0	72.9
def2-SVPD	yes	0.35	0.47	0.31	0.27	0.35	0.47	0.30	0.27	6.7	5.2	7.9	7.0
def2-TZVP	no	0.48	0.47	0.46	0.52	−0.46	−0.44	−0.46	−0.50	10.6	7.2	11.2	13.9
def2-TZVP	yes	0.41	0.55	0.41	0.26	0.38	0.51	0.41	0.21	7.9	5.8	10.9	6.9
def2-TZVPD	no	0.79	0.27	1.26	0.85	−0.78	−0.25	−1.26	−0.85	20.0	3.6	33.7	23.1
def2-TZVPD	yes	0.22	0.40	0.13	0.12	0.19	0.40	0.09	0.05	3.7	4.4	3.5	3.2
def2-QZVP	no	0.41	0.32	0.48	0.43	−0.41	−0.32	−0.48	−0.43	9.3	3.9	12.7	11.6
def2-QZVP	yes	0.13	0.14	0.11	0.13	0.02	0.12	0.00	−0.08	2.8	1.7	3.3	3.6
def2-QZVPD	no	0.57	0.26	0.84	0.60	−0.57	−0.26	−0.84	−0.60	13.7	2.8	22.4	16.3
def2-QZVPD	yes	0.12	0.11	0.11	0.14	−0.02	0.09	−0.06	−0.11	2.8	1.3	3.3	3.9
6-31G*	no	1.09	2.01	0.35	0.90	−1.03	−2.01	−0.17	−0.90	19.3	25.4	9.1	24.1
6-31G*	yes	1.32	0.91	1.96	1.04	1.25	0.75	1.96	0.99	30.2	9.5	53.0	27.8
6-31+G*	no	0.85	1.08	0.73	0.73	−0.83	−1.03	−0.71	−0.73	17.5	16.0	16.4	20.4
6-31+G*	yes	0.95	0.80	1.24	0.79	0.93	0.75	1.24	0.77	20.9	7.1	34.7	21.0
6-311G*	no	1.22	2.15	0.47	1.01	−1.18	−2.15	−0.37	−1.01	22.7	30.7	11.0	27.0
6-311G*	yes	1.07	1.10	1.29	0.79	0.94	0.82	1.29	0.68	22.2	11.0	34.5	21.0
6-311+G*	no	1.13	1.31	1.06	1.01	−1.07	−1.14	−1.06	−1.01	24.4	20.0	25.6	28.1
6-311+G*	yes	0.81	0.86	0.95	0.59	0.71	0.64	0.95	0.53	16.5	7.7	25.9	15.8
6-311++G**	no	0.96	0.73	1.19	0.96	−0.94	−0.68	−1.19	−0.94	22.5	11.0	30.6	26.3
6-311++G**	yes	0.66	0.74	0.73	0.50	0.65	0.73	0.73	0.48	12.9	6.7	18.8	12.3

Table S14: Convergence error statistics (with respect to DH-DFT/CBS limit) for interaction energies in the S66 data set computed using ωB97M-(2).

Basis Set	CP?	Mean Absolute Error (kcal/mol)				Mean Signed Error (kcal/mol)				Mean Absolute Percent Error (%)			
		All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed	All	H-Bond	Dispersion	Mixed
aug-cc-pVDZ	no	1.34	0.74	1.91	1.37	−1.34	−0.74	−1.91	−1.37	39.9	10.1	66.5	43.5
auv-cc-pVDZ	yes	0.18	0.33	0.09	0.11	0.14	0.33	0.03	0.05	3.2	3.8	2.8	3.1
aug-cc-pVTZ	no	0.99	0.69	1.23	1.07	−0.99	−0.69	−1.23	−1.07	27.7	8.3	41.8	33.7
aug-cc-pVTZ	yes	0.11	0.11	0.10	0.12	−0.03	0.09	−0.09	−0.11	2.9	1.3	3.7	3.8
aug-cc-pVQZ	no	0.39	0.28	0.47	0.41	−0.39	−0.28	−0.47	−0.41	10.7	3.3	16.2	12.9
aug-cc-pVQZ	yes	0.11	0.06	0.13	0.15	−0.09	−0.02	−0.13	−0.15	3.3	0.7	4.6	4.7
def2-SVP	no	1.65	2.88	0.82	1.19	−1.65	−2.88	−0.81	−1.19	33.5	39.9	24.1	36.8
def2-SVP	yes	0.86	0.71	1.08	0.78	0.81	0.62	1.08	0.72	22.8	8.8	36.0	23.6
def2-SVPD	no	2.43	1.69	3.22	2.36	−2.43	−1.69	−3.22	−2.36	69.0	22.2	111.7	73.6
def2-SVPD	yes	0.18	0.21	0.16	0.17	0.17	0.21	0.15	0.16	4.2	2.4	5.3	5.1
def2-TZVP	no	0.44	0.52	0.35	0.46	−0.44	−0.51	−0.35	−0.45	10.8	8.7	10.0	14.1
def2-TZVP	yes	0.32	0.43	0.32	0.20	0.29	0.37	0.32	0.15	7.5	4.9	11.3	6.2
def2-TZVPD	no	0.56	0.19	0.90	0.61	−0.55	−0.17	−0.90	−0.61	17.2	2.7	30.2	19.0
def2-TZVPD	yes	0.16	0.31	0.09	0.09	0.14	0.31	0.06	0.03	3.1	3.6	3.1	2.6
def2-QZVP	no	0.33	0.28	0.36	0.33	−0.33	−0.28	−0.36	−0.33	8.6	3.7	11.8	10.4
def2-QZVP	yes	0.09	0.10	0.07	0.10	0.00	0.08	−0.02	−0.07	2.4	1.3	2.8	3.2
def2-QZVPD	no	0.41	0.20	0.61	0.43	−0.41	−0.20	−0.61	−0.43	12.0	2.3	20.5	13.6
def2-QZVPD	yes	0.09	0.08	0.08	0.11	−0.04	0.05	−0.07	−0.10	2.5	0.9	3.2	3.6
6-31G*	no	1.34	2.25	0.62	1.13	−1.34	−2.25	−0.62	−1.13	28.1	30.9	19.4	34.8
6-31G*	yes	0.93	0.65	1.41	0.70	0.80	0.33	1.41	0.63	26.3	7.6	49.2	21.5
6-31+G*	no	0.86	1.18	0.70	0.68	−0.85	−1.16	−0.70	−0.68	19.8	18.9	19.4	21.4
6-31+G*	yes	0.66	0.57	0.83	0.55	0.60	0.44	0.83	0.52	17.5	5.2	30.2	16.9
6-311G*	no	1.42	2.44	0.64	1.16	−1.41	−2.44	−0.61	−1.16	29.8	37.2	17.5	35.4
6-311G*	yes	0.77	0.88	0.87	0.52	0.58	0.45	0.87	0.39	18.7	9.9	30.0	16.0
6-311+G*	no	1.08	1.33	0.98	0.92	−1.04	−1.20	−0.98	−0.92	27.0	22.3	29.7	29.2
6-311+G*	yes	0.57	0.73	0.59	0.37	0.41	0.32	0.59	0.30	13.6	7.6	21.1	11.7
6-311++G**	no	0.88	0.77	1.03	0.82	−0.87	−0.75	−1.03	−0.81	23.8	12.7	33.0	26.0
6-311++G**	yes	0.43	0.47	0.46	0.30	0.40	0.43	0.46	0.30	9.9	4.1	15.3	10.2

Table S15: Distribution of errors in ΔE_{int} predictions (in kcal/mol) for the S66 data set.

Basis Set	RMSD vs. CCSD(T)/CBS											
	M06-2X		M06-L		BLYP+D3(BJ)		PBE0+D4		ωB97X-V		ωB97M-V	
	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP
aug-cc-pVDZ	0.86	0.21	1.10	0.63	0.79	0.18	0.95	0.44	0.71	0.09	0.86	0.12
aug-cc-pVTZ	0.17	0.09	1.08	0.85	0.13	0.08	0.56	0.46	0.13	0.05	0.19	0.03
aug-cc-pVQZ	0.05	0.05	0.21	0.21	0.06	0.06	0.52	0.49	0.03	0.03	0.02	0.02
def2-SVP	1.86	0.50	1.67	0.86	2.92	0.36	2.53	0.67	2.22	0.41	2.46	0.43
def2-SVPD	1.49	0.18	1.50	0.85	1.59	0.16	1.69	0.57	1.11	1.44	1.66	0.21
def2-TZVP	0.36	0.24	1.00	0.85	0.59	0.19	0.77	0.46	0.44	0.17	0.51	0.16
def2-TZVPD	0.10	0.17	0.95	0.85	0.11	0.15	0.48	0.43	0.10	0.11	0.29	0.13
def2-QZVP	0.10	0.13	0.88	0.84	0.16	0.07	0.55	0.48	0.09	0.05	0.12	0.04
def2-QZVPD	0.07	0.10	0.89	0.84	0.04	0.06	0.50	0.48	0.02	0.04	0.02	0.03
6-31G*	1.54	0.85	0.58	0.80	2.48	0.52	2.14	0.76	1.87	0.67	2.10	0.64
6-31+G*	0.87	0.57	0.93	0.94	0.73	0.37	1.09	0.49	0.81	0.43	0.86	0.40
6-311G*	1.84	0.70	1.28	0.71	2.24	0.56	2.19	0.70	1.99	0.63	2.24	0.64
6-311+G*	1.25	0.66	0.82	0.61	0.99	0.48	1.37	0.64	1.13	0.56	1.25	0.60
6-311++G**	0.78	0.34	0.39	0.49	0.60	0.25	1.38	0.63	0.69	0.21	0.86	0.34

Table S16: Distribution of errors in ΔE_{int} predictions (in kcal/mol) for the S66 data set.

Basis Set	RMSD vs. CCSD(T)/CBS									
	MP2		PBE-QIDH		B2GP-PLYP		ωB97X-2(LP)		ωB97M(2)	
	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP
aug-cc-pVDZ	2.66	0.80	0.54	1.32	0.34	1.80	1.99	0.19	1.23	0.14
aug-cc-pVTZ	1.54	0.64	0.64	1.22	0.72	1.61	1.70	0.32	0.84	0.14
aug-cc-pVQZ	1.00	0.67	0.94	1.17	1.27	1.56	0.81	0.41	0.25	0.14
def2-SVP	1.63	1.98	1.69	1.99	1.76	2.54	2.09	1.13	1.86	0.14
def2-SVPD	4.33	0.85	1.55	1.39	1.14	1.87	3.24	0.19	2.37	0.14
def2-TZVP	0.96	0.82	0.98	1.48	1.27	1.90	0.81	0.27	0.40	0.14
def2-TZVPD	1.67	0.70	0.63	1.33	0.93	1.74	1.20	0.20	0.46	0.14
def2-QZVP	0.86	0.58	1.00	1.25	1.31	1.63	0.75	0.30	0.24	0.14
def2-QZVPD	1.06	0.62	0.86	1.22	1.17	1.60	0.94	0.34	0.31	0.14
6-31G*	1.15	2.09	1.47	2.12	1.53	2.64	1.64	1.28	1.44	0.17
6-31+G*	1.53	1.76	1.03	1.84	1.25	2.40	1.29	0.87	0.88	0.15
6-311G*	1.41	1.93	1.49	1.85	1.64	2.43	1.77	1.00	1.56	0.19
6-311+G*	1.89	1.67	1.05	1.70	1.21	2.27	1.58	0.79	1.10	0.18
6-311++G**	0.86	0.34	0.67	1.59	0.93	2.15	1.34	0.57	0.77	0.78

Table S17: Timing data for pentane dimer.

Functional	Wall Time (min)[a]									
	M06-2X		PBE0+D4		BLYP+D3(BJ)		ωB97X-V		ωB97M-V	
	no CP	CP	no CP	CP	no CP	CP	no CP	CP	no CP	CP
aug-cc-pVDZ	2.7	7.0	1.8	4.8	1.2	2.7	4.4	10.4	4.8	10.9
aug-cc-pVTZ	37.9	102.8	34.0	94.7	7.3	16.4	37.4	87.0	41.0	92.9
aug-cc-pVQZ	486.1	1351.1	417.8	1093.8	75.0	169.3	434.0	1001.6	450.0	1032.7
def2-SVP	0.5	1.1	0.2	0.4	0.2	0.3	1.2	2.2	1.2	2.4
def2-SVPD	1.8	4.0	0.9	2.4	0.5	1.0	2.5	5.1	2.6	5.4
def2-TZVP	2.2	5.2	1.4	3.5	0.5	1.1	2.6	5.4	2.8	5.9
def2-TZVPD	5.6	14.1	4.3	11.3	1.5	3.0	6.5	14.5	6.8	15.3
def2-QZV	49.5	129.1	45.0	110.9	9.3	18.5	46.5	92.6	48.0	96.8
def2-QZVPD	91.0	243.4	78.6	207.0	15.7	33.3	84.5	182.8	87.7	191.1
6-31G*	0.3	0.7	0.1	0.2	0.1	0.1	0.9	1.7	0.9	1.8
6-31+G*	0.4	1.0	0.1	0.3	0.1	0.2	1.0	2.0	1.1	2.1
6-311G*	0.4	1.0	0.2	0.4	0.1	0.2	1.0	2.0	1.1	2.2
6-311+G*	0.6	1.4	0.2	0.6	0.2	0.3	1.2	2.5	1.4	2.7
6-311++G**	1.3	2.9	0.6	1.5	0.3	0.6	1.8	3.8	2.1	4.1

[a] Using 14 processors on a single compute node (Dell Intel Xeon E5-2680 v4)