Supporting Information for *Acta Phys. -Chim. Sin.* 2017, *33* (6), 1149−1159
doi: 10.3866/PKU.WHXB201703291

B972-PFD：一种高精度的色散校正密度泛函方法

何　禹 [1,2]　　王一波 [1,2,*]

([1] 贵州省高性能计算化学重点实验室，贵阳 550025；[2] 贵州大学网络与信息中心，贵阳 550025)

B972-PFD: A High Accuracy Density Functional Method for Dispersion Correction

HE Yu[1,2]　　WANG Yi-Bo[1,2,*]

([1]*Key Laboratory of High Performance Computational Chemistry, Guiyang 550025, P. R. China*;
[2]*Network and Information Center of Guizhou University, Guiyang 550025, P. R. China*)

[*]Corresponding author.　Email: ybw@gzu.edu.cn; Tel: +86-851-88292009.

Part 1

表 S1　S66 测试集各类泛函以 CCSD(T)/CBS 为基准的计算精度范围比较

Table S1　The calculated errors of different DFT methods with respect to the benchmark CCSD(T)/CBS calculations on the S66 data set.

Method	Basis set	Counterpoise correction	RMSD /(kJ•mol^{-1})	Ref.
ωB97X-V	def2-QZVPPD	NCP	0.55	14
ωB97M-V	def3-QZVPPD	NCP	0.63	14
B97M-V	def4-QZVPPD	NCP	0.76	14
ωB97X-D3	6-311++G(3df,3pd)	CP	1.24	this work
ωB97X-D	6-311++G(3df,3pd)	CP	1.88	this work
B3PW91-D3(BJ)	6-311++G(2d,p)	CP	1.34	this work
B3LYP-D3(BJ)	Def2QZVP	CP	1.5	this work
TPSS-D3(BJ)	6-311++G(2d,p)	CP	1.6	this work
PBE0-D3(BJ)	6-311++G(2d,p)	CP	1.73	this work
APF-PFD*	6-311++G(2d,p)	CP	1.76	12
APF-PFD	6-311++G(2d,p)	CP	3.27	12
M06-2X	def2-QZVPPD	NCP	1.38	3
M11	def2-QZVPPD	NCP	2.55	3
MN15	def2-QZVPPD	NCP	2.68	3
M05-2X	def2-QZVPPD	NCP	2.92	3
XYG3	6-311+G(3df,2p)	NCP	1.61	this work
ωB97X-2	cc-VT(Q)Z	CP	1.77	this work
XYGJ-OS	6-311+G(3df,2p)	NCP	1.79	this work
PBE0-2	6-311++G(3df,3pd)	CP	3.40	this work
B2PLYP	aug-cc-pVTZ	NCP	5.75	this work

表 S2 使用 PFD 校正的各类密度泛函方法与 CCSD(T)/CBS 参考基准计算数据

Table S2 Binding energies in kJ ꞏmol^{-1} for the S66 data set for the DFT-PFD/6-311++G(2*d*,*p*) and CCSD(T)/CBS methods.

S66 data set	**Ref**[1]	APF-PF	BLYB-PF	B3LYB-PF	B3PW91-PF	PBE-PF	PBE0-PF	TPSS-PF	X3LYP-PF	B972-PF	B97-PF	B971-PF	B973-PF	B97K-PF	ωB97-PF	ωB97x-PF
01_Water-Water	**-20.5**	-22.93	-20.71	-22.80	-20.59	-24.48	-24.56	-22.43	-24.43	-20.63	-23.64	-24.39	-21.21	-22.22	-27.70	-27.49
02_Water-MeOH	**-23.4**	-25.73	-23.14	-25.61	-22.97	-27.53	-27.70	-25.19	-27.53	-23.05	-26.61	-27.49	-23.59	-25.10	-31.84	-31.55
03_Water-MeNH2	**-28.9**	-32.72	-29.87	-31.71	-30.21	-35.10	-34.43	-32.80	-33.38	-29.87	-33.01	-33.85	-29.71	-30.42	-36.86	-36.82
04_Water-Peptide	**-33.9**	-37.24	-32.84	-36.61	-33.64	-38.87	-39.75	-35.69	-39.03	-33.51	-38.12	-39.29	-34.72	-38.33	-46.32	-45.48
05_MeOH-MeOH	**-24.0**	-26.23	-23.39	-25.94	-23.30	-28.20	-28.28	-25.69	-27.98	-23.56	-27.15	-28.07	-23.91	-24.94	-32.30	-32.17
06_MeOH-MeNH2	**-31.6**	-35.56	-31.38	-33.93	-32.17	-38.49	-37.91	-35.40	-36.12	-32.38	-36.28	-37.45	-32.23	-32.64	-41.71	-41.71
07_MeOH-Peptide	**-34.4**	-37.95	-33.26	-36.94	-34.14	-40.08	-40.63	-36.53	-39.45	-34.18	-38.87	-40.17	-35.16	-37.99	-47.07	-46.40
08_MeOH-Water	**-20.9**	-22.84	-20.42	-22.59	-20.33	-24.52	-24.60	-22.34	-24.30	-20.50	-23.60	-24.39	-21.02	-21.76	-27.74	-27.61
09_MeNH2-MeOH	**-12.8**	-14.27	-11.55	-13.77	-11.21	-16.65	-16.44	-14.02	-15.68	-12.59	-15.98	-17.11	-12.97	-12.05	-20.63	-20.67
10_MeNH2-MeNH2	**-17.4**	-18.54	-14.43	-17.15	-14.90	-21.34	-21.09	-17.74	-19.38	-15.82	-20.04	-21.51	-17.00	-18.41	-27.82	-27.15
11_MeNH2-Peptide	**-22.6**	-24.39	-18.66	-22.72	-19.87	-26.90	-27.53	-22.51	-25.49	-20.92	-26.19	-27.99	-22.94	-26.48	-37.36	-36.07
12_MeNH2-Water	**-30.4**	-34.18	-30.63	-33.05	-31.17	-36.69	-36.28	-33.85	-35.09	-30.92	-34.64	-35.65	-30.93	-32.55	-40.17	-39.92
13_Peptide-MeOH	**-25.8**	-27.49	-22.84	-26.57	-23.68	-29.41	-30.21	-25.98	-29.04	-24.52	-29.00	-30.38	-25.84	-27.91	-37.24	-36.69
14_Peptide-MeNH2	**-31.1**	-34.18	-28.62	-31.97	-30.29	-36.90	-36.90	-33.18	-34.41	-30.96	-35.31	-36.78	-31.65	-33.01	-43.01	-42.72
15_Peptide-Peptide	**-36.1**	-38.99	-32.38	-37.11	-34.43	-41.00	-42.17	-36.94	-39.96	-35.31	-40.54	-42.22	-37.03	-40.38	-51.00	-50.12
16_Peptide-Water	**-21.4**	-22.51	-19.08	-21.92	-19.58	-23.89	-24.56	-21.42	-23.85	-20.33	-23.68	-24.64	-21.14	-21.76	-28.79	-28.62
17_Uracil-Uracil_BP	**-71.8**	-76.99	-69.08	-75.23	-72.22	-78.28	-80.29	-74.56	-78.55	-70.71	-77.03	-78.37	-71.75	-76.32	-85.65	-85.69
18_Water-Pyridine	**-28.6**	-31.34	-29.16	-30.88	-28.83	-33.89	-33.10	-31.67	-32.63	-28.62	-32.01	-32.80	-28.53	-29.16	-35.94	-35.94
19_MeOH-Pyridine	**-31.0**	-33.81	-30.96	-32.93	-30.92	-36.69	-35.82	-34.02	-34.90	-30.92	-34.56	-35.48	-30.67	-31.17	-39.04	-39.12
20_AcOH-AcOH	**-79.8**	-89.12	-79.37	-86.32	-84.56	-89.75	-92.26	-86.73	-89.65	-81.88	-87.82	-88.74	-81.38	-87.78	-97.91	-97.36
21_AcNH2-AcNH2	**-68.0**	-72.26	-64.35	-70.25	-67.78	-73.51	-75.44	-69.83	-73.35	-66.27	-72.17	-73.51	-67.52	-72.05	-81.76	-81.42
22_AcOH-Uracil	**-81.5**	-88.49	-79.50	-86.27	-83.85	-89.08	-91.71	-85.77	-89.66	-81.63	-87.82	-88.91	-82.00	-87.78	-97.24	-96.99
23_AcNH2-Uracil	**-80.2**	-85.60	-76.78	-83.43	-80.92	-86.23	-88.91	-82.63	-86.75	-79.29	-85.40	-86.61	-80.24	-85.06	-94.39	-94.35
24_Benzene-Benzene_pi-pi	**-11.8**	-14.64	-6.86	-10.71	-9.87	-17.87	-17.99	-13.60	-13.38	-12.26	-17.24	-19.54	-14.31	-18.74	-32.51	-30.42
25_Pyridine-Pyridine_pi-pi	**-16.3**	-19.46	-10.79	-15.27	-14.35	-22.47	-23.05	-17.95	-18.14	-16.53	-21.88	-24.27	-18.82	-24.52	-38.45	-36.02
26_Uracil-Uracil_pi-pi	**-41.1**	-49.54	-36.28	-44.85	-41.30	-52.63	-55.31	-45.10	-49.74	-43.18	-52.43	-56.02	-48.04	-60.79	-79.12	-74.64
27_Benzene-Pyridine_pi-pi	**-14.3**	-17.41	-9.12	-13.35	-12.43	-20.54	-20.88	-16.07	-16.12	-14.69	-19.87	-22.22	-16.84	-21.92	-35.98	-33.68
28_Benzene-Uracil_pi-pi	**-23.9**	-28.49	-17.36	-23.68	-21.80	-31.80	-33.18	-25.82	-27.48	-23.77	-31.00	-34.14	-27.34	-37.07	-54.02	-50.00
29_Pyridine-Uracil_pi-pi	**-28.5**	-32.68	-21.84	-28.33	-25.90	-35.82	-37.36	-29.87	-32.25	-27.87	-35.35	-38.45	-31.71	-41.97	-58.45	-54.43
30_Benzene-Ethene	**-5.99**	-6.69	-1.46	-4.02	-3.18	-9.41	-9.16	-6.32	-6.02	-5.10	-8.74	-10.42	-6.21	-8.45	-18.91	-17.70
31_Uracil-Ethene	**-14.1**	-15.40	-8.62	-12.72	-10.88	-17.87	-18.62	-13.89	-15.35	-12.76	-17.61	-19.66	-14.77	-18.79	-30.71	-28.87

32_Uracil-Ethyne	**-15.6**	-16.65	-10.29	-14.23	-12.43	-18.74	-19.62	-15.15	-16.73	-14.14	-18.79	-20.63	-16.11	-19.92	-30.92	-29.29
33_Pyridine-Ethene	**-7.83**	-8.49	-3.10	-5.86	-4.81	-11.25	-11.09	-7.95	-8.00	-6.65	-10.54	-12.30	-8.00	-10.75	-21.25	-19.87
34_Pentane-Pentane	**-15.8**	-19.20	-10.29	-16.11	-11.88	-24.10	-24.31	-17.03	-20.22	-15.15	-23.56	-26.94	-20.19	-25.73	-43.93	-40.96
35_Neopentane-Pentane	**-10.9**	-12.89	-6.53	-10.59	-7.66	-16.61	-16.57	-11.67	-13.56	-10.38	-16.15	-18.49	-13.22	-15.48	-29.25	-27.66
36_Neopentane-Neopentane	**-7.43**	-8.66	-4.10	-6.95	-4.69	-11.80	-11.42	-8.28	-9.17	-7.28	-11.51	-13.22	-8.91	-8.62	-19.79	-19.20
37_Cyclopentane-Neopentane	**-10.0**	-12.18	-6.28	-10.04	-7.28	-15.73	-15.65	-11.05	-12.83	-9.79	-15.27	-17.49	-12.49	-14.43	-27.49	-26.02
38_Cyclopentane-Cyclopenta	**-12.5**	-15.19	-9.00	-13.18	-9.54	-19.29	-19.12	-13.81	-16.38	-12.22	-18.66	-21.25	-15.75	-18.45	-33.01	-31.09
39_Benzene-Cyclopentane	**-14.9**	-18.66	-10.42	-15.02	-13.26	-21.88	-22.43	-17.11	-18.06	-15.48	-21.25	-23.77	-18.17	-23.14	-37.40	-34.98
40_Benzene-Neopentane	**-12.1**	-14.56	-7.45	-11.34	-10.00	-17.28	-17.70	-13.35	-13.91	-12.30	-16.99	-19.04	-14.22	-16.99	-29.58	-28.03
41_Uracil-Pentane	**-20.2**	-24.43	-14.02	-20.54	-17.07	-28.49	-29.58	-21.67	-24.76	-19.62	-27.82	-31.25	-24.21	-32.47	-50.25	-46.61
42_Uracil-Cyclopentane	**-17.3**	-20.96	-12.43	-17.91	-14.52	-24.81	-25.48	-18.87	-21.62	-17.03	-24.23	-27.15	-20.82	-27.15	-42.93	-40.04
43_Uracil-Neopentane	**-15.5**	-18.07	-10.63	-15.40	-12.59	-21.25	-21.92	-16.36	-18.55	-15.02	-20.92	-23.39	-17.79	-21.84	-35.94	-33.89
44_Ethene-Pentane	**-8.39**	-9.33	-4.18	-7.49	-4.94	-12.43	-12.38	-8.37	-10.01	-7.24	-12.05	-14.02	-9.51	-11.17	-22.43	-21.30
45_Ethyne-Pentane	**-7.31**	-8.24	-3.64	-6.36	-4.56	-10.92	-10.79	-7.70	-8.48	-6.86	-10.71	-12.26	-8.14	-8.41	-18.62	-18.12
46_Peptide-Pentane	**-17.8**	-21.13	-12.13	-18.07	-14.06	-25.44	-26.11	-18.70	-22.12	-16.78	-24.81	-28.07	-21.42	-28.16	-45.10	-41.97
47_Benzene-Benzene_TS	**-12.0**	-14.02	-7.66	-11.21	-10.13	-16.07	-16.78	-12.80	-13.43	-11.88	-15.77	-17.49	-13.31	-15.52	-26.11	-24.89
48_Pyridine-Pyridine_TS	**-14.7**	-16.53	-9.96	-13.89	-12.38	-18.49	-19.41	-14.81	-16.28	-13.93	-18.37	-20.13	-15.97	-19.25	-29.54	-28.12
49_Benzene-Pyridine_TS	**-13.9**	-16.32	-9.54	-13.35	-12.34	-18.16	-19.12	-14.85	-15.62	-13.97	-17.95	-19.66	-15.43	-18.03	-28.62	-27.28
50_Benzene-Ethyne_CH-pi	**-12.0**	-14.14	-8.49	-11.67	-10.96	-15.40	-16.40	-12.89	-13.51	-12.26	-15.44	-16.74	-13.36	-14.90	-22.64	-21.88
51_Ethyne-Ethyne_TS	**-6.38**	-7.28	-4.98	-6.40	-5.40	-8.54	-8.58	-7.11	-7.51	-6.61	-8.45	-9.16	-6.78	-5.73	-10.59	-10.71
52_Benzene-AcOH_OH-pi	**-19.6**	-24.18	-16.48	-20.88	-20.08	-25.69	-27.07	-22.30	-23.29	-21.21	-25.23	-26.86	-22.18	-25.15	-35.02	-33.64
53_Benzene-AcNH2_NH-pi	**-18.2**	-21.00	-14.60	-18.62	-17.07	-22.68	-23.81	-19.08	-20.94	-18.41	-22.55	-24.14	-19.94	-22.22	-31.55	-30.46
54_Benzene-Water_OH-pi	**-13.7**	-16.95	-11.63	-14.73	-13.77	-18.41	-19.16	-15.61	-16.57	-14.94	-18.12	-19.37	-15.62	-16.90	-24.73	-24.02
55_Benzene-MeOH_OH-pi	**-17.5**	-21.17	-14.31	-18.20	-16.86	-23.51	-24.23	-19.66	-20.68	-18.33	-22.76	-24.60	-19.75	-22.59	-33.22	-31.80
56_Benzene-MeNH2_NH-pi	**-13.5**	-15.56	-9.00	-12.68	-11.34	-17.91	-18.49	-14.27	-15.09	-13.05	-17.36	-19.20	-14.56	-17.41	-28.20	-26.86
57_Benzene-Peptide_NH-pi	**-22.1**	-26.02	-16.61	-21.80	-20.79	-28.28	-29.71	-23.85	-24.76	-22.64	-27.82	-30.12	-24.74	-29.33	-42.47	-40.46
58_Pyridine-Pyridine_CH-N	**-17.3**	-16.86	-12.38	-15.52	-13.51	-18.70	-19.20	-15.65	-17.57	-14.39	-18.37	-19.66	-15.92	-17.41	-26.02	-25.23
59_Ethyne-Water_CH-O	**-11.9**	-13.14	-10.96	-12.89	-11.05	-14.18	-14.60	-12.59	-14.24	-11.84	-14.27	-14.94	-12.42	-12.26	-16.82	-16.86
60_Ethyne-AcOH_OH-pi	**-20.3**	-23.85	-18.66	-22.01	-20.50	-25.48	-26.23	-22.64	-18.32	-21.09	-24.94	-26.23	-16.45	-24.14	-31.59	-30.75
61_Pentane-AcOH	**-12.1**	-15.02	-8.62	-13.01	-9.50	-18.66	-18.87	-13.56	-16.21	-12.22	-18.24	-20.67	-14.95	-17.24	-31.46	-29.87
62_Pentane-AcNH2	**-14.7**	-17.45	-10.21	-15.02	-11.51	-21.34	-21.63	-15.61	-18.47	-14.02	-20.75	-23.43	-17.50	-21.67	-36.40	-34.23
63_Benzene-AcOH	**-15.9**	-19.12	-11.17	-15.86	-14.27	-21.38	-22.55	-17.32	-18.68	-16.19	-21.21	-23.30	-18.04	-22.18	-35.02	-33.01
64_Peptide-Ethene	**-12.5**	-13.97	-8.70	-12.30	-9.67	-16.57	-16.99	-12.59	-14.82	-11.72	-16.40	-18.20	-13.61	-15.23	-26.23	-25.23
65_Pyridine-Ethyne	**-16.7**	-17.99	-15.31	-17.20	-15.77	-19.50	-19.54	-17.82	-18.61	-16.36	-19.12	-19.92	-16.79	-16.53	-21.76	-21.97
66_MeNH2-Pyridine	**-16.6**	-17.28	-12.01	-15.31	-13.05	-20.17	-20.21	-16.02	-17.85	-14.43	-19.20	-21.00	-16.22	-19.41	-30.12	-28.83

Ref[1]: Rezac, J.; Riley, K. E.; Hobza, P. *J. Chem. Theory Comput.* **2011**, 7, 2427. doi: 10.1021/ct200294

表 S3 使用 PFD 校正的各类密度泛函方法与 CCSD(T)/CBS 参考基准的结合能误差数据

Table S3 $\Delta E_{\text{DFT-PFD}} - \Delta E_{\text{CCSD(T)/CBS}}$ in kJ mol^{-1} for the DFT-PFD methods for the S66 data set using 6-311++G(2*d*,*p*) basis sets.

S66 data set	**Ref**[1]	APF-PF	BLYB-PF	B3LYB-PF	B3PW91-PF	PBEPBE-PF	PBE1PBE-PF	TPSS-PF	X3LYP-PF	B972-PF	B97-PF	B971-PF	B973-PF	B97-K-PF	ωB97-PF	ωB97x-PF
01 Water-Water	**-20.5**	-2.35	-0.13	-2.23	-0.01	-3.90	-3.98	-1.85	-3.86	-0.05	-3.06	-3.82	-0.63	-1.64	-7.12	-6.91
02_Water-MeOH	**-23.4**	-2.33	0.26	-2.21	0.43	-4.13	-4.30	-1.79	-4.13	0.34	-3.21	-4.09	-0.19	-1.71	-8.44	-8.15
03_Water-MeNH2	**-28.9**	-3.82	-0.97	-2.81	-1.31	-6.20	-5.53	-3.90	-4.48	-0.97	-4.11	-4.95	-0.81	-1.51	-7.96	-7.92
04_Water-Peptide	**-33.9**	-3.33	1.06	-2.71	0.26	-4.97	-5.85	-1.79	-5.13	0.39	-4.21	-5.38	-0.82	-4.42	-12.41	-11.58
05_MeOH-MeOH	**-24.0**	-2.15	0.70	-1.85	0.78	-4.11	-4.20	-1.60	-3.89	0.53	-3.07	-3.99	0.18	-0.85	-8.21	-8.09
06_MeOH-MeNH2	**-31.6**	-3.96	0.23	-2.33	-0.57	-6.89	-6.30	-3.79	-4.51	-0.78	-4.67	-5.84	-0.62	-1.03	-10.11	-10.11
07_MeOH-Peptide	**-34.4**	-3.51	1.17	-2.51	0.29	-5.65	-6.19	-2.09	-5.02	0.25	-4.44	-5.73	-0.72	-3.56	-12.64	-11.97
08_MeOH-Water	**-20.9**	-1.89	0.54	-1.64	0.62	-3.56	-3.64	-1.38	-3.34	0.46	-2.64	-3.44	-0.06	-0.80	-6.78	-6.66
09_MeNH2-MeOH	**-12.8**	-1.47	1.25	-0.97	1.59	-3.85	-3.64	-1.22	-2.88	0.21	-3.18	-4.31	-0.17	0.75	-7.83	-7.87
10_MeNH2-MeNH2	**-17.4**	-1.13	2.97	0.25	2.51	-3.93	-3.68	-0.33	-1.98	1.59	-2.64	-4.10	0.40	-1.00	-10.42	-9.75
11_MeNH2-Peptide	**-22.6**	-1.72	4.01	-0.05	2.80	-4.23	-4.86	0.16	-2.81	1.75	-3.52	-5.32	-0.27	-3.81	-14.69	-13.39
12_MeNH2-Water	**-30.4**	-3.78	-0.23	-2.65	-0.77	-6.29	-5.87	-3.45	-4.69	-0.52	-4.24	-5.25	-0.53	-2.15	-9.77	-9.51
13_Peptide-MeOH	**-25.8**	-1.60	3.04	-0.68	2.20	-3.53	-4.32	-0.10	-3.15	1.37	-3.11	-4.49	0.05	-2.02	-11.35	-10.81
14_Peptide-MeNH2	**-31.1**	-3.00	2.57	-0.78	0.90	-5.72	-5.72	-1.99	-3.22	0.23	-4.13	-5.59	-0.46	-1.82	-11.82	-11.53
15_Peptide-Peptide	**-36.1**	-2.89	3.72	-1.00	1.67	-4.90	-6.07	-0.84	-3.85	0.79	-4.44	-6.11	-0.92	-4.27	-14.90	-14.02
16_Peptide-Water	**-21.4**	-1.07	2.36	-0.49	1.86	-2.45	-3.12	0.02	-2.41	1.10	-2.24	-3.20	0.30	-0.32	-7.35	-7.18
17_Uracil-Uracil_BP	**-71.8**	-5.10	2.81	-3.34	-0.33	-6.39	-8.40	-2.67	-6.66	1.18	-5.14	-6.48	0.14	-4.43	-13.76	-13.80
18_Water-Pyridine	**-28.6**	-2.65	-0.47	-2.19	-0.14	-5.20	-4.41	-2.98	-3.94	0.07	-3.32	-4.11	0.16	-0.47	-7.25	-7.25
19_MeOH-Pyridine	**-31.0**	-2.80	0.04	-1.92	0.08	-5.69	-4.81	-3.01	-3.89	0.08	-3.56	-4.48	0.34	-0.17	-8.03	-8.12
20_AcOH-AcOH	**-79.8**	-9.23	0.51	-6.43	-4.67	-9.86	-12.37	-6.85	-9.77	-2.00	-7.94	-8.86	-1.50	-7.90	-18.02	-17.48
21_AcNH2-AcNH2	**-68.0**	-4.20	3.70	-2.20	0.27	-5.46	-7.38	-1.78	-5.30	1.78	-4.12	-5.46	0.53	-4.00	-13.70	-13.37
22_AcOH-Uracil	**-81.5**	-6.94	2.05	-4.72	-2.30	-7.53	-10.16	-4.22	-8.11	-0.08	-6.27	-7.36	-0.45	-6.23	-15.69	-15.43
23_AcNH2-Uracil	**-80.2**	-5.32	3.51	-3.14	-0.63	-5.95	-8.62	-2.35	-6.46	1.00	-5.11	-6.32	0.04	-4.77	-14.10	-14.06
24_Benzene-Benzene_pi-pi	**-11.8**	-2.84	4.95	1.10	1.93	-6.06	-6.18	-1.79	-1.57	-0.45	-5.43	-7.73	-2.50	-6.94	-20.70	-18.61
25_Pyridine-Pyridine_pi-pi	**-16.3**	-3.16	5.50	1.03	1.95	-6.17	-6.76	-1.65	-1.84	-0.23	-5.59	-7.97	-2.53	-8.22	-22.15	-19.73
26_Uracil-Uracil_pi-pi	**-41.1**	-8.41	4.85	-3.73	-0.17	-11.51	-14.19	-3.98	-8.62	-2.05	-11.30	-14.90	-6.92	-19.67	-37.99	-33.52
27_Benzene-Pyridine_pi-pi	**-14.3**	-3.02	5.27	1.04	1.96	-6.15	-6.49	-1.68	-1.73	-0.30	-5.49	-7.83	-2.45	-7.54	-21.59	-19.29
28_Benzene-Uracil_pi-pi	**-23.9**	-4.59	6.54	0.22	2.10	-7.90	-9.28	-1.91	-3.57	0.14	-7.10	-10.24	-3.44	-13.17	-30.11	-26.10
29_Pyridine-Uracil_pi-pi	**-28.5**	-4.15	6.69	0.21	2.63	-7.28	-8.83	-1.34	-3.72	0.67	-6.82	-9.92	-3.18	-13.43	-29.92	-25.90
30_Benzene-Ethene	**-5.99**	-0.70	4.53	1.97	2.81	-3.42	-3.17	-0.33	-0.03	0.89	-2.75	-4.43	-0.22	-2.46	-12.92	-11.71
31_Uracil-Ethene	**-14.1**	-1.26	5.52	1.42	3.26	-3.72	-4.48	0.25	-1.20	1.38	-3.47	-5.52	-0.62	-4.64	-16.57	-14.73
32_Uracil-Ethyne	**-15.6**	-1.01	5.35	1.41	3.21	-3.10	-3.98	0.49	-1.09	1.50	-3.15	-4.99	-0.47	-4.28	-15.28	-13.65

33_Pyridine-Ethene	**-7.83**	-0.66	4.74	1.97	3.02	-3.42	-3.26	-0.12	-0.16	1.18	-2.71	-4.47	-0.17	-2.92	-13.42	-12.04
34_Pentane-Pentane	**-15.8**	-3.41	5.51	-0.31	3.92	-8.30	-8.51	-1.23	-4.42	0.65	-7.76	-11.15	-4.39	-9.93	-28.13	-25.16
35_Neopentane-Pentane	**-10.9**	-1.95	4.41	0.35	3.28	-5.68	-5.64	-0.74	-2.62	0.56	-5.22	-7.56	-2.28	-4.55	-18.31	-16.72
36_Neopentane-Neopentane	**-7.43**	-1.23	3.33	0.49	2.75	-4.36	-3.99	-0.85	-1.73	0.15	-4.07	-5.79	-1.47	-1.18	-12.36	-11.77
37_Cyclopentane-Neopenta	**-10.0**	-2.12	3.78	0.02	2.78	-5.67	-5.59	-0.99	-2.77	0.27	-5.21	-7.43	-2.43	-4.38	-17.43	-15.97
38_Cyclopentane-Cyclopent	**-12.5**	-2.65	3.54	-0.64	3.00	-6.75	-6.58	-1.27	-3.85	0.32	-6.12	-8.72	-3.21	-5.91	-20.47	-18.55
39_Benzene-Cyclopentane	**-14.9**	-3.70	4.54	-0.06	1.69	-6.92	-7.47	-2.15	-3.10	-0.52	-6.30	-8.81	-3.21	-8.18	-22.45	-20.02
40_Benzene-Neopentane	**-12.1**	-2.45	4.67	0.77	2.11	-5.17	-5.59	-1.23	-1.80	-0.19	-4.87	-6.92	-2.11	-4.87	-17.47	-15.92
41_Uracil-Pentane	**-20.2**	-4.15	6.27	-0.26	3.21	-8.21	-9.30	-1.39	-4.48	0.66	-7.54	-10.97	-3.92	-12.18	-29.97	-26.33
42_Uracil-Cyclopentane	**-17.3**	-3.65	4.89	-0.59	2.79	-7.50	-8.17	-1.56	-4.31	0.28	-6.91	-9.84	-3.51	-9.84	-25.61	-22.73
43_Uracil-Neopentane	**-15.5**	-2.54	4.90	0.13	2.94	-5.72	-6.39	-0.83	-3.02	0.51	-5.39	-7.86	-2.26	-6.31	-20.41	-18.36
44_Ethene-Pentane	**-8.39**	-0.94	4.20	0.90	3.45	-4.04	-4.00	0.02	-1.62	1.15	-3.66	-5.63	-1.12	-2.78	-14.04	-12.91
45_Ethyne-Pentane	**-7.31**	-0.93	3.67	0.95	2.75	-3.61	-3.48	-0.38	-1.16	0.45	-3.40	-4.95	-0.82	-1.10	-11.31	-10.80
46_Peptide-Pentane	**-17.8**	-3.29	5.71	-0.23	3.78	-7.60	-8.27	-0.86	-4.28	1.06	-6.97	-10.23	-3.58	-10.32	-27.26	-24.12
47_Benzene-Benzene_TS	**-12.0**	-1.98	4.38	0.82	1.91	-4.03	-4.74	-0.77	-1.40	0.15	-3.74	-5.46	-1.27	-3.49	-14.07	-12.86
48_Pyridine-Pyridine_TS	**-14.7**	-1.74	4.83	0.90	2.41	-3.70	-4.62	-0.02	-1.49	0.86	-3.58	-5.33	-1.18	-4.46	-14.75	-13.33
49_Benzene-Pyridine_TS	**-13.9**	-2.38	4.40	0.59	1.59	-4.22	-5.18	-0.92	-1.69	-0.04	-4.01	-5.73	-1.49	-4.10	-14.68	-13.34
50_Benzene-Ethyne_CH-pi	**-12.0**	-2.15	3.50	0.32	1.03	-3.40	-4.41	-0.89	-1.51	-0.26	-3.44	-4.74	-1.37	-2.90	-10.64	-9.89
51_Ethyne-Ethyne_TS	**-6.38**	-0.90	1.40	-0.03	0.98	-2.16	-2.20	-0.74	-1.14	-0.23	-2.08	-2.79	-0.40	0.64	-4.21	-4.33
52_Benzene-AcOH_OH-pi	**-19.6**	-4.49	3.21	-1.18	-0.39	-6.00	-7.38	-2.61	-3.60	-1.52	-5.54	-7.17	-2.49	-5.45	-15.33	-13.95
53_Benzene-AcNH2_NH-pi	**-18.2**	-2.76	3.64	-0.37	1.18	-4.43	-5.56	-0.83	-2.69	-0.16	-4.31	-5.90	-1.70	-3.97	-13.30	-12.21
54_Benzene-Water_OH-pi	**-13.7**	-3.23	2.08	-1.02	-0.05	-4.70	-5.45	-1.90	-2.86	-1.23	-4.41	-5.66	-1.91	-3.19	-11.02	-10.31
55_Benzene-MeOH_OH-pi	**-17.5**	-3.65	3.21	-0.68	0.66	-5.99	-6.70	-2.14	-3.16	-0.80	-5.24	-7.08	-2.23	-5.07	-15.70	-14.28
56_Benzene-MeNH2_NH-pi	**-13.5**	-2.05	4.52	0.84	2.18	-4.39	-4.97	-0.75	-1.57	0.46	-3.85	-5.69	-1.05	-3.89	-14.68	-13.34
57_Benzene-Peptide_NH-pi	**-22.1**	-3.92	5.49	0.30	1.31	-6.18	-7.61	-1.75	-2.66	-0.54	-5.72	-8.02	-2.64	-7.23	-20.37	-18.36
58_Pyridine-Pyridine_CH-N	**-17.3**	0.49	4.96	1.82	3.83	-1.36	-1.86	1.70	-0.22	2.95	-1.02	-2.32	1.43	-0.06	-8.68	-7.88
59_Ethyne-Water_CH-O	**-11.9**	-1.21	0.96	-0.96	0.88	-2.26	-2.68	-0.67	-2.32	0.08	-2.34	-3.01	-0.49	-0.33	-4.90	-4.94
60_Ethyne-AcOH_OH-pi	**-20.3**	-3.48	1.71	-1.64	-0.13	-5.11	-5.87	-2.27	2.05	-0.72	-4.57	-5.87	3.91	-3.77	-11.22	-10.38
61_Pentane-AcOH	**-12.1**	-2.84	3.56	-0.83	2.69	-6.48	-6.69	-1.37	-4.02	-0.03	-6.06	-8.49	-2.76	-5.05	-19.28	-17.69
62_Pentane-AcNH2	**-14.7**	-2.66	4.58	-0.23	3.28	-6.55	-6.85	-0.82	-3.69	0.77	-5.97	-8.64	-2.72	-6.89	-21.61	-19.44
63_Benzene-AcOH	**-15.9**	-3.22	4.73	0.05	1.64	-5.48	-6.65	-1.42	-2.78	-0.29	-5.31	-7.40	-2.14	-6.27	-19.12	-17.11
64_Peptide-Ethene	**-12.5**	-1.43	3.85	0.25	2.88	-4.02	-4.44	-0.05	-2.28	0.83	-3.85	-5.65	-1.06	-2.68	-13.69	-12.68
65_Pyridine-Ethyne	**-16.7**	-1.29	1.38	-0.50	0.92	-2.80	-2.84	-1.13	-1.92	0.34	-2.42	-3.22	-0.09	0.17	-5.06	-5.27
66_MeNH2-Pyridine	**-16.6**	-0.68	4.59	1.29	3.55	-3.56	-3.61	0.58	-1.25	2.17	-2.60	-4.40	0.38	-2.81	-13.52	-12.23
MD		-2.80	3.31	-0.63	1.51	-5.23	-5.82	-1.43	-3.13	0.29	-4.56	-6.28	-1.26	-4.44	-15.23	-13.97
MAD		2.80	3.39	1.26	1.84	5.23	5.82	1.52	3.19	0.71	4.56	6.28	1.51	4.52	15.23	13.97
RMSD		**3.26**	**3.85**	**1.76**	**2.22**	**5.56**	**6.23**	**1.94**	**3.7**	**0.96**	**4.85**	**6.69**	**2.05**	**5.82**	**16.65**	**15.15**
MAX		9.25	6.69	6.44	4.69	11.51	14.18	6.85	9.7	2.97	11.30	14.90	6.90	19.66	37.99	33.51

表 S4　B972-PFD 配合 13 种基函数基于 S66 数据集的计算结果（kJ mol^{-1}）

Table S4　Binding energies in kJ mol^{-1} for the B972-PFD methods for the S66 data set using 13 basis sets.

S66 data set	**Ref**[1]	BS1	BS2	BS3	BS4	BS5	BS6	BS7	BS8	BS9	BS10	BS11	BS12	BS13
01_Water-Water	**-20.58**	-20.54	-20.63	-19.66	-19.66	-20.17	-19.33	-19.58	-19.41	-19.54	-19.54	-21.3	-19.87	-19.62
02_Water-MeOH	**-23.4**	-21.55	-23.05	-22.47	-22.64	-21	-22.3	-21.51	-22.18	-21.97	-22.3	-22.84	-22.13	-22.26
03_Water-MeNH2	**-28.9**	-27.2	-29.87	-29.46	-29.58	-26.65	-29.29	-27.61	-29.29	-28.45	-29.29	-29.37	-28.66	-29.04
04_Water-Peptide	**-33.9**	-30.96	-33.51	-33.05	-33.05	-29.46	-32.64	-31.67	-32.8	-32.43	-32.93	-32.89	-32.55	-32.84
05_MeOH-MeOH	**-24.09**	-23.43	-23.56	-23.3	-23.51	-23.68	-23.22	-23.14	-23.22	-23.35	-23.35	-23.85	-23.43	-23.39
06_MeOH-MeNH2	**-31.61**	-31.8	-32.38	-32.26	-32.38	-32.17	-32.13	-31.71	-32.22	-31.97	-32.22	-32.55	-32.13	-32.13
07_MeOH-Peptide	**-34.43**	-33.68	-34.18	-34.18	-34.39	-32.84	-33.89	-33.93	-34.14	-34.18	-34.27	-34.06	-34.18	-34.23
08_MeOH-Water	**-20.96**	-21.92	-20.5	-19.96	-20.00	-22.34	-19.75	-20.67	-19.87	-20.33	-20	-21.67	-20.59	-20.17
09_MeNH2-MeOH	**-12.8**	-12.51	-12.59	-12.22	-12.13	-12.22	-12.01	-11.92	-11.92	-11.92	-12.01	-12.64	-12.09	-12.01
10_MeNH2-MeNH2	**-17.41**	-15.77	-15.82	-15.56	-15.48	-15.19	-15.27	-15.31	-15.36	-15.31	-15.36	-16.02	-15.52	-15.36
11_MeNH2-Peptide	**-22.67**	-20.79	-20.92	-20.75	-20.71	-19.66	-20.42	-20.42	-20.46	-20.46	-20.5	-20.71	-20.54	-20.5
12_MeNH2-Water	**-30.4**	-28.66	-30.92	-30.42	-30.46	-28.12	-30.21	-28.95	-30.21	-29.58	-30.21	-30.63	-29.83	-30.04
13_Peptide-MeOH	**-25.89**	-24.69	-24.52	-24.23	-23.97	-24.94	-23.72	-24.18	-23.89	-24.1	-23.97	-24.85	-24.31	-24.1
14_Peptide-MeNH2	**-31.19**	-31.67	-30.96	-30.75	-30.67	-32.01	-30.5	-30.75	-30.46	-30.59	-30.5	-31.34	-30.79	-30.54
15_Peptide-Peptide	**-36.11**	-34.81	-35.31	-35.31	-35.31	-34.14	-35.06	-34.89	-35.1	-35.15	-35.23	-35.06	-35.1	-35.19
16_Peptide-Water	**-21.44**	-22.43	-20.33	-19.75	-19.41	-22.64	-19.25	-20.63	-19.46	-20.04	-19.54	-21.92	-20.54	-19.83
17_Uracil-Uracil_BP	**-71.89**	-70.46	-70.71	-71.3	-71.80	-70.67	-71.59	-71.55	-71.92	-72.13	-72.26	-71.09	-71.88	-72.22
18_Water-Pyridine	**-28.69**	-25.52	-28.62	-28.62	-28.58	-24.27	-28.58	-26.69	-28.62	-27.78	-28.66	-27.87	-27.7	-28.37
19_MeOH-Pyridine	**-31**	-29.33	-30.92	-31.09	-31.09	-28.7	-31.09	-30.17	-31.21	-30.84	-31.25	-30.59	-30.71	-31.13
20_AcOH-AcOH	**-79.89**	-82.89	-81.88	-82.47	-83.51	-82.68	-82.8	-84.06	-83.76	-84.31	-84.18	-83.01	-84.06	-84.18
21_AcNH2-AcNH2	**-68.05**	-66.32	-66.27	-66.78	-67.15	-65.73	-66.82	-66.9	-66.86	-67.28	-67.2	-66.4	-67.15	-67.24
22_AcOH-Uracil	**-81.55**	-82.05	-81.63	-82.26	-82.97	-82.13	-82.51	-83.26	-83.22	-83.64	-83.55	-82.51	-83.43	-83.55

23_AcNH2-Uracil	**-80.29**	-79.2	-79.29	-79.79	-80.21	-79.16	-79.83	-80.08	-80.04	-80.46	-80.33	-79.54	-80.33	-80.42
24_Benzene-Benzene_pi-pi	**-11.81**	-11.59	-12.26	-12.26	-11.97	-11.8	-12.38	-12.01	-12.22	-12.01	-12.26	-11.88	-11.92	-12.18
25_Pyridine-Pyridine_pi-pi	**-16.3**	-16.07	-16.53	-16.44	-16.19	-16.11	-16.57	-16.11	-16.36	-16.15	-16.36	-16.07	-16.07	-16.32
26_Uracil-Uracil_pi-pi	**-41.12**	-42.76	-43.18	-43.1	-42.80	-41.21	-42.8	-42.63	-42.89	-42.76	-42.84	-42.63	-42.55	-42.84
27_Benzene-Pyridine_pi-pi	**-14.39**	-14.1	-14.69	-14.6	-14.35	-14.23	-14.77	-14.31	-14.56	-14.31	-14.56	-14.23	-14.27	-14.52
28_Benzene-Uracil_pi-pi	**-23.9**	-23.01	-23.77	-23.6	-23.47	-22.59	-23.77	-23.1	-23.64	-23.39	-23.64	-23.26	-23.22	-23.56
29_Pyridine-Uracil_pi-pi	**-28.53**	-26.78	-27.87	-27.82	-27.61	-25.94	-27.99	-27.2	-27.91	-27.57	-27.91	-27.41	-27.41	-27.78
30_Benzene-Ethene	**-5.99**	-4.35	-5.1	-5.15	-4.94	-4.35	-5.31	-4.9	-5.19	-4.98	-5.23	-4.85	-4.94	-5.15
31_Uracil-Ethene	**-14.14**	-12.18	-12.76	-12.8	-12.72	-11.8	-12.89	-12.55	-12.89	-12.76	-12.89	-12.59	-12.68	-12.84
32_Uracil-Ethyne	**-15.64**	-13.39	-14.14	-14.1	-13.93	-12.84	-14.14	-13.81	-14.14	-14.02	-14.18	-13.89	-13.89	-14.1
33_Pyridine-Ethene	**-7.83**	-5.98	-6.65	-6.61	-6.49	-6.02	-6.82	-6.44	-6.74	-6.53	-6.74	-6.4	-6.44	-6.65
34_Pentane-Pentane	**-15.8**	-15.36	-15.15	-15.23	-15.19	-14.69	-15.36	-15.19	-15.23	-15.23	-15.27	-14.85	-15.1	-15.27
35_Neopentane-Pentane	**-10.93**	-10.5	-10.38	-10.54	-10.54	-10.08	-10.38	-10.5	-10.54	-10.59	-10.59	-10.29	-10.54	-10.59
36_Neopentane-Neopentane	**-7.43**	-7.41	-7.28	-7.41	-7.36	-7.36	-7.36	-7.45	-7.41	-7.45	-7.45	-7.24	-7.41	-7.45
37_Cyclopentane-Neopentane	**-10.06**	-9.87	-9.79	-9.92	-9.92	-9.5	-9.83	-9.87	-9.92	-9.92	-9.96	-9.67	-9.87	-9.96
38_Cyclopentane-Cyclopentane	**-12.54**	-12.43	-12.22	-12.43	-12.43	-11.97	-12.38	-12.38	-12.43	-12.43	-12.43	-12.05	-12.34	-12.43
39_Benzene-Cyclopentane	**-14.96**	-15.69	-15.48	-15.31	-15.15	-15.27	-15.36	-15.23	-15.23	-15.27	-15.23	-15.06	-15.19	-15.23
40_Benzene-Neopentane	**-12.11**	-12.59	-12.3	-12.09	-11.97	-11.97	-11.97	-12.09	-12.05	-12.09	-12.05	-12.05	-12.05	-12.05
41_Uracil-Pentane	**-20.28**	-19.83	-19.62	-19.75	-19.71	-18.87	-19.75	-19.66	-19.79	-19.75	-19.79	-19.46	-19.62	-19.79
42_Uracil-Cyclopentane	**-17.31**	-17.24	-17.03	-17.15	-17.07	-16.57	-17.11	-17.07	-17.15	-17.15	-17.2	-16.9	-17.03	-17.15
43_Uracil-Neopentane	**-15.53**	-15.02	-15.02	-15.06	-15.02	-14.35	-15.1	-14.94	-15.1	-15.06	-15.1	-14.94	-14.94	-15.1
44_Ethene-Pentane	**-8.39**	-7.36	-7.24	-7.36	-7.36	-7.07	-7.45	-7.32	-7.36	-7.36	-7.36	-7.11	-7.28	-7.36
45_Ethyne-Pentane	**-7.31**	-6.9	-6.86	-6.82	-6.78	-6.61	-6.95	-6.82	-6.78	-6.78	-6.82	-6.69	-6.74	-6.78
46_Peptide-Pentane	**-17.84**	-16.9	-16.78	-16.86	-16.78	-15.98	-16.82	-16.78	-16.82	-16.86	-16.86	-16.53	-16.69	-16.86
47_Benzene-Benzene_TS	**-12.03**	-12.13	-11.88	-11.59	-11.55	-11.76	-11.46	-11.46	-11.42	-11.51	-11.42	-11.46	-11.51	-11.46
48_Pyridine-Pyridine_TS	**-14.79**	-14.1	-13.93	-13.68	-13.64	-13.39	-13.56	-13.43	-13.43	-13.47	-13.43	-13.39	-13.43	-13.43

49_Benzene-Pyridine_TS	**-13.94**	-14.23	-13.97	-13.68	-13.60	-13.68	-13.47	-13.51	-13.43	-13.56	-13.43	-13.56	-13.51	-13.47
50_Benzene-Ethyne_CH-pi	**-12**	-12.8	-12.26	-11.76	-11.72	-12.18	-11.34	-11.88	-11.59	-11.8	-11.59	-11.97	-11.84	-11.63
51_Ethyne-Ethyne_TS	**-6.38**	-6.99	-6.61	-6.49	-6.53	-6.95	-6.36	-6.61	-6.53	-6.61	-6.53	-6.61	-6.53	-6.53
52_Benzene-AcOH_OH-pi	**-19.69**	-21.71	-21.21	-20.92	-20.88	-19.92	-20.33	-20.84	-20.84	-21	-20.79	-21.13	-21	-20.84
53_Benzene-AcNH2_NH-pi	**-18.25**	-18.16	-18.41	-18.28	-18.33	-16.9	-17.95	-17.82	-17.95	-17.99	-17.95	-18.03	-17.95	-17.99
54_Benzene-Water_OH-pi	**-13.71**	-14.77	-14.94	-14.27	-14.23	-13.39	-13.89	-13.77	-13.97	-14.02	-13.97	-14.64	-14.1	-14.02
55_Benzene-MeOH_OH-pi	**-17.52**	-18.49	-18.33	-17.95	-17.91	-17.24	-17.57	-17.74	-17.82	-17.91	-17.82	-18.12	-17.91	-17.82
56_Benzene-MeNH2_NH-pi	**-13.52**	-13.01	-13.05	-12.72	-12.59	-12.13	-12.43	-12.47	-12.59	-12.64	-12.64	-12.76	-12.64	-12.59
57_Benzene-Peptide_NH-pi	**-22.1**	-23.1	-22.64	-22.22	-22.09	-21.8	-21.8	-22.09	-22.01	-22.18	-22.01	-22.3	-22.13	-22.01
58_Pyridine-Pyridine_CH-N	**-17.35**	-14.73	-14.39	-14.23	-14.23	-14.35	-14.23	-14.1	-14.1	-14.1	-14.1	-14.18	-14.1	-14.1
59_Ethyne-Water_CH-O	**-11.92**	-13.26	-11.84	-11.21	-11.00	-13.43	-10.88	-11.84	-11	-11.42	-11.05	-12.64	-11.8	-11.3
60_Ethyne-AcOH_OH-pi	**-20.37**	-21.3	-21.09	-21.09	-21.09	-20.21	-20.59	-21.13	-21.09	-21.21	-21.13	-20.92	-21.05	-21.13
61_Pentane-AcOH	**-12.18**	-12.38	-12.22	-12.34	-12.34	-11.88	-12.38	-12.3	-12.34	-12.34	-12.34	-12.18	-12.26	-12.38
62_Pentane-AcNH2	**-14.79**	-14.18	-14.02	-14.14	-14.10	-13.31	-14.06	-14.06	-14.1	-14.1	-14.1	-13.85	-14.02	-14.14
63_Benzene-AcOH	**-15.9**	-16.19	-16.19	-15.94	-15.98	-15.48	-15.9	-15.61	-15.77	-15.82	-15.82	-15.69	-15.69	-15.82
64_Peptide-Ethene	**-12.55**	-11.55	-11.72	-11.59	-11.59	-10.88	-11.46	-11.38	-11.46	-11.46	-11.51	-11.42	-11.38	-11.51
65_Pyridine-Ethyne	**-16.7**	-16.28	-16.36	-16.32	-16.36	-16.44	-16.4	-16.23	-16.36	-16.32	-16.4	-16.4	-16.32	-16.4
66_MeNH2-Pyridine	**-16.6**	-13.93	-14.43	-14.31	-14.27	-13.01	-14.23	-13.72	-14.14	-13.97	-14.18	-14.02	-13.93	-14.1

BS1:6-311G(2*d*,*p*); BS2:6-311++g(2*d*,*p*); BS3: 6-311++G(2*df*,2*p*); BS4: 6-311++G(3*df*3*pd*); BS5: CC-Pvdz; BS6: aug-CC-Pvdz; BS7: CC-pVTZ

BS8:aug-CC-pVTZ; BS9:cc-pVQZ; BS10::aug-cc-pVQZ; BS11:def2TZVP; BS12:def2TZVPP; BS13:def2QZVPP

表 S5　B972-PFD 配合 13 种基函数基于 S66 数据集与 CCSD(T)/CBS 标准的误差值(kJ ·mol^{-1})

Table S5　$\Delta E_{\text{B972-PFD}} - \Delta E_{\text{CCSD(T)/CBS}}$ in kJ ·mol^{-1} for the B972-PFD methods for the S66 data set using 13 basis sets.

S66 date set	Ref[1]	BS1	BS2	BS3	BS4	BS5	BS6	BS7	BS8	BS9	BS10	BS11	BS12	BS13
01_Water-Water	**-20.58**	0.03	-0.05	0.91	0.91	0.41	1.25	1	1.16	1.04	1.04	-0.72	0.7	0.95
02_Water-MeOH	**-23.4**	1.85	0.34	0.93	0.76	2.39	1.1	1.89	1.22	1.43	1.1	0.55	1.26	1.14
03_Water-MeNH2	**-28.9**	1.71	-0.97	-0.55	-0.68	2.25	-0.38	1.29	-0.38	0.45	-0.38	-0.47	0.24	-0.13
04_Water-Peptide	**-33.9**	2.94	0.39	0.85	0.85	4.45	1.27	2.23	1.1	1.48	0.97	1.02	1.35	1.06
05_MeOH-MeOH	**-24.09**	0.66	0.53	0.78	0.57	0.41	0.87	0.95	0.87	0.74	0.74	0.24	0.66	0.7
06_MeOH-MeNH2	**-31.61**	-0.19	-0.78	-0.65	-0.78	-0.57	-0.53	-0.11	-0.61	-0.36	-0.61	-0.95	-0.53	-0.53
07_MeOH-Peptide	**-34.43**	0.75	0.25	0.25	0.04	1.59	0.54	0.5	0.29	0.25	0.17	0.38	0.25	0.21
08_MeOH-Water	**-20.96**	-0.97	0.46	1	0.96	-1.38	1.21	0.29	1.08	0.62	0.96	-0.72	0.37	0.79
09_MeNH2-MeOH	**-12.8**	0.29	0.21	0.58	0.66	0.58	0.79	0.87	0.87	0.87	0.79	0.16	0.71	0.79
10_MeNH2-MeNH2	**-17.41**	1.63	1.59	1.84	1.92	2.22	2.13	2.09	2.05	2.09	2.05	1.38	1.88	2.05
11_MeNH2-Peptide	**-22.67**	1.88	1.75	1.92	1.96	3.01	2.26	2.26	2.21	2.21	2.17	1.96	2.13	2.17
12_MeNH2-Water	**-30.4**	1.74	-0.52	-0.02	-0.06	2.28	0.19	1.45	0.19	0.82	0.19	-0.23	0.57	0.36
13_Peptide-MeOH	**-25.89**	1.2	1.37	1.66	1.91	0.95	2.16	1.7	2	1.79	1.91	1.03	1.58	1.79
14_Peptide-MeNH2	**-31.19**	-0.49	0.23	0.44	0.52	-0.82	0.69	0.44	0.73	0.6	0.69	-0.15	0.39	0.64
15_Peptide-Peptide	**-36.11**	1.3	0.79	0.79	0.79	1.97	1.05	1.21	1	0.96	0.88	1.05	1	0.92
16_Peptide-Water	**-21.44**	-0.99	1.1	1.69	2.02	-1.2	2.19	0.81	1.98	1.4	1.9	-0.49	0.9	1.61
17_Uracil-Uracil_BP	**-71.89**	1.43	1.18	0.59	0.09	1.22	0.3	0.34	-0.03	-0.24	-0.37	0.8	0.01	-0.33
18_Water-Pyridine	**-28.69**	3.17	0.07	0.07	0.11	4.42	0.11	2	0.07	0.91	0.03	0.82	0.99	0.32
19_MeOH-Pyridine	**-31**	1.67	0.08	-0.08	-0.08	2.3	-0.08	0.84	-0.21	0.17	-0.25	0.42	0.29	-0.13
20_AcOH-AcOH	**-79.89**	-3	-2	-2.58	-3.62	-2.79	-2.92	-4.17	-3.88	-4.42	-4.3	-3.13	-4.17	-4.3
21_AcNH2-AcNH2	**-68.05**	1.74	1.78	1.28	0.9	2.32	1.23	1.15	1.19	0.77	0.86	1.65	0.9	0.82
22_AcOH-Uracil	**-81.55**	-0.5	-0.08	-0.71	-1.42	-0.58	-0.96	-1.71	-1.67	-2.09	-2	-0.96	-1.88	-2

23_AcNH2-Uracil	**-80.29**	1.08	1	0.5	0.08	1.13	0.46	0.21	0.25	-0.17	-0.05	0.75	-0.05	-0.13
24_Benzene-Benzene_pi-pi	**-11.81**	0.22	-0.45	-0.45	-0.16	0.01	-0.58	-0.2	-0.41	-0.2	-0.45	-0.08	-0.12	-0.37
25_Pyridine-Pyridine_pi-pi	**-16.3**	0.23	-0.23	-0.15	0.1	0.19	-0.27	0.19	-0.06	0.15	-0.06	0.23	0.23	-0.02
26_Uracil-Uracil_pi-pi	**-41.12**	-1.64	-2.05	-1.97	-1.68	-0.09	-1.68	-1.51	-1.76	-1.64	-1.72	-1.51	-1.43	-1.72
27_Benzene-Pyridine_pi-pi	**-14.39**	0.29	-0.3	-0.21	0.04	0.16	-0.38	0.08	-0.17	0.08	-0.17	0.16	0.12	-0.13
28_Benzene-Uracil_pi-pi	**-23.9**	0.89	0.14	0.31	0.43	1.31	0.14	0.81	0.26	0.51	0.26	0.64	0.68	0.35
29_Pyridine-Uracil_pi-pi	**-28.53**	1.75	0.67	0.71	0.92	2.59	0.54	1.33	0.62	0.96	0.62	1.13	1.13	0.75
30_Benzene-Ethene	**-5.99**	1.64	0.89	0.85	1.05	1.64	0.68	1.1	0.8	1.01	0.76	1.14	1.05	0.85
31_Uracil-Ethene	**-14.14**	1.97	1.38	1.34	1.42	2.34	1.26	1.59	1.26	1.38	1.26	1.55	1.46	1.3
32_Uracil-Ethyne	**-15.64**	2.25	1.5	1.54	1.71	2.79	1.5	1.83	1.5	1.62	1.46	1.75	1.75	1.54
33_Pyridine-Ethene	**-7.83**	1.85	1.18	1.22	1.35	1.81	1.01	1.39	1.1	1.31	1.1	1.43	1.39	1.18
34_Pentane-Pentane	**-15.8**	0.44	0.65	0.57	0.61	1.11	0.44	0.61	0.57	0.57	0.53	0.95	0.69	0.53
35_Neopentane-Pentane	**-10.93**	0.43	0.56	0.39	0.39	0.85	0.56	0.43	0.39	0.35	0.35	0.64	0.39	0.35
36_Neopentane-Neopentane	**-7.43**	0.03	0.15	0.03	0.07	0.07	0.07	-0.01	0.03	-0.01	-0.01	0.2	0.03	-0.01
37_Cyclopentane-Neopentane	**-10.06**	0.18	0.27	0.14	0.14	0.56	0.23	0.18	0.14	0.14	0.1	0.39	0.18	0.1
38_Cyclopentane-Cyclopentane	**-12.54**	0.11	0.32	0.11	0.11	0.57	0.15	0.15	0.11	0.11	0.11	0.49	0.2	0.11
39_Benzene-Cyclopentane	**-14.96**	-0.73	-0.52	-0.36	-0.19	-0.31	-0.4	-0.27	-0.27	-0.31	-0.27	-0.1	-0.23	-0.27
40_Benzene-Neopentane	**-12.11**	-0.48	-0.19	0.02	0.15	0.15	0.15	0.02	0.06	0.02	0.06	0.06	0.06	0.06
41_Uracil-Pentane	**-20.28**	0.45	0.66	0.54	0.58	1.41	0.54	0.62	0.49	0.54	0.49	0.83	0.66	0.49
42_Uracil-Cyclopentane	**-17.31**	0.08	0.28	0.16	0.24	0.74	0.2	0.24	0.16	0.16	0.12	0.41	0.28	0.16
43_Uracil-Neopentane	**-15.53**	0.51	0.51	0.47	0.51	1.18	0.43	0.59	0.43	0.47	0.43	0.59	0.59	0.43
44_Ethene-Pentane	**-8.39**	1.03	1.15	1.03	1.02	1.32	0.94	1.07	1.03	1.03	1.03	1.28	1.11	1.03
45_Ethyne-Pentane	**-7.31**	0.41	0.45	0.49	0.54	0.7	0.37	0.49	0.54	0.54	0.49	0.62	0.58	0.54
46_Peptide-Pentane	**-17.84**	0.94	1.06	0.98	1.06	1.86	1.02	1.06	1.02	0.98	0.98	1.31	1.15	0.98
47_Benzene-Benzene_TS	**-12.03**	-0.1	0.15	0.44	0.48	0.28	0.57	0.57	0.61	0.53	0.61	0.57	0.53	0.57
48_Pyridine-Pyridine_TS	**-14.79**	0.69	0.86	1.11	1.15	1.4	1.23	1.36	1.36	1.32	1.36	1.4	1.36	1.36

49_Benzene-Pyridine_TS	**-13.94**	-0.29	-0.04	0.26	0.34	0.26	0.46	0.42	0.51	0.38	0.51	0.38	0.42	0.46
50_Benzene-Ethyne_CH-pi	**-12**	-0.81	-0.26	0.24	0.28	-0.18	0.66	0.11	0.41	0.2	0.41	0.03	0.15	0.36
51_Ethyne-Ethyne_TS	**-6.38**	-0.61	-0.23	-0.11	-0.15	-0.57	0.02	-0.23	-0.15	-0.23	-0.15	-0.23	-0.15	-0.15
52_Benzene-AcOH_OH-pi	**-19.69**	-2.02	-1.52	-1.23	-1.18	-0.22	-0.64	-1.14	-1.14	-1.31	-1.1	-1.44	-1.31	-1.14
53_Benzene-AcNH2_NH-pi	**-18.25**	0.09	-0.16	-0.04	-0.08	1.34	0.3	0.42	0.3	0.26	0.3	0.21	0.3	0.26
54_Benzene-Water_OH-pi	**-13.71**	-1.06	-1.23	-0.56	-0.51	0.32	-0.18	-0.05	-0.26	-0.31	-0.26	-0.93	-0.39	-0.31
55_Benzene-MeOH_OH-pi	**-17.52**	-0.97	-0.8	-0.43	-0.38	0.28	-0.05	-0.22	-0.3	-0.38	-0.3	-0.59	-0.38	-0.3
56_Benzene-MeNH2_NH-pi	**-13.52**	0.51	0.46	0.8	0.92	1.38	1.09	1.05	0.92	0.88	0.88	0.76	0.88	0.92
57_Benzene-Peptide_NH-pi	**-22.1**	-1	-0.54	-0.12	0.01	0.3	0.3	0.01	0.09	-0.08	0.09	-0.2	-0.03	0.09
58_Pyridine-Pyridine_CH-N	**-17.35**	2.62	2.95	3.12	3.12	3	3.12	3.25	3.25	3.25	3.25	3.16	3.25	3.25
59_Ethyne-Water_CH-O	**-11.92**	-1.34	0.08	0.71	0.92	-1.51	1.05	0.08	0.92	0.5	0.88	-0.71	0.13	0.63
60_Ethyne-AcOH_OH-pi	**-20.37**	-0.93	-0.72	-0.72	-0.72	0.16	-0.22	-0.76	-0.72	-0.85	-0.76	-0.55	-0.68	-0.76
61_Pentane-AcOH	**-12.18**	-0.2	-0.03	-0.16	-0.16	0.3	-0.2	-0.12	-0.16	-0.16	-0.16	0.01	-0.08	-0.2
62_Pentane-AcNH2	**-14.79**	0.6	0.77	0.64	0.69	1.48	0.73	0.73	0.69	0.69	0.69	0.94	0.77	0.64
63_Benzene-AcOH	**-15.9**	-0.29	-0.29	-0.04	-0.08	0.42	0	0.3	0.13	0.09	0.09	0.21	0.21	0.09
64_Peptide-Ethene	**-12.55**	1	0.83	0.96	0.96	1.67	1.08	1.17	1.08	1.08	1.04	1.13	1.17	1.04
65_Pyridine-Ethyne	**-16.7**	0.42	0.34	0.38	0.34	0.26	0.3	0.46	0.34	0.38	0.3	0.3	0.38	0.3
66_MeNH2-Pyridine	**-16.6**	2.67	2.17	2.29	2.33	3.59	2.38	2.88	2.46	2.63	2.42	2.59	2.67	2.5
MD		**0.46**	**0.29**	**0.44**	**0.46**	**0.96**	**0.5**	**0.59**	**0.46**	**0.45**	**0.39**	**0.38**	**0.46**	**0.4**
MAD		**1.05**	**0.71**	**0.75**	**0.79**	**1.26**	**0.79**	**0.92**	**0.84**	**0.84**	**0.8**	**0.79**	**0.79**	**0.79**
RMSD		**1.3**	**0.96**	**0.99**	**1.08**	**1.63**	**1.05**	**1.26**	**1.13**	**1.16**	**1.12**	**1.05**	**1.13**	**1.12**
MAX		**3.18**	**2.97**	**3.08**	**3.75**	**4.44**	**3.14**	**4.18**	**3.89**	**4.42**	**4.3**	**3.18**	**4.18**	**4.3**

BS1: 6-311G(2*d*,*p*); BS2: 6-311++g(2*d*,*p*); BS3: 6-311++G(2*df*,*2p*); BS4: 6-311++G(3*df*3*pd*); BS5: CC-Pvdz; BS6: aug-CC-Pvdz; BS7: CC-pVTZ

BS8: aug-CC-pVTZ; BS9: cc-pVQZ; BS10: aug-cc-pVQZ; BS11: def2TZVP; BS12: def2TZVPP; BS13: def2QZVPP

表 S6　B972-PFD, APF-PFd*,ωB97XD,B3LYP-D3, ωB97X-V,B97M-V and ωB97M-V 与 CCSD(T)/CBS 标准基于 s66 数据集的比较数据

Table S6　ΔE_{DFT} - $\Delta E_{CCSD(T)/CBS}$ in kJ ▪mol^{-1} for the B972-PFD, APF-PFd*,ωB97XD,B3LYP-D3, ωB97X-V,B97M-V and ωB97M-V, methods for the S66 data set.

		ΔE_{DFT}							ΔE_{DFT} - $\Delta E_{CCSD(T)/CBS}$						
S66 date set	**Ref**[1]	B972-PF	APF-PFD*	ωb97XD	B3LY	ωB97X-V	B97M-	ωB97M	B972-PFD*	APF-PFD	ωb97X	B3LY	ωB97	B97M-	ωB97
		BS1	BS1	BS2	BS3	BS1	BS1	BS1	BS1	BS1	BS2	BS3	BS4	BS4	BS4
01_Water-Water	**-20.5**	-20.63	-22.52	-20.63	-21.59	-20.68	-20.86	-20.62	-0.05	-1.94	-0.05	-1.01	-0.10	-0.28	-0.04
02_Water-MeOH	**-23.4**	-23.05	-25.00	-23.26	-24.18	-23.16	-22.62	-23.07	0.34	-1.60	0.13	-0.79	0.23	0.78	0.32
03_Water-MeNH2	**-28.9**	-29.87	-32.09	-30.67	-31.00	-29.35	-28.63	-28.90	-0.97	-3.18	-1.77	-2.10	-0.44	0.27	0.00
04_Water-Peptide	**-33.9**	-33.51	-36.14	-34.02	-34.89	-34.25	-33.74	-34.13	0.39	-2.24	-0.11	-0.99	-0.34	0.16	-0.23
05_MeOH-MeOH	**-24.0**	-23.56	-25.29	-23.81	-24.85	-23.68	-23.26	-23.68	0.53	-1.20	0.28	-0.77	0.41	0.82	0.41
06_MeOH-MeNH2	**-31.6**	-32.38	-34.42	-33.43	-33.64	-31.70	-30.91	-31.24	-0.78	-2.81	-1.82	-2.03	-0.09	0.69	0.37
07_MeOH-Peptide	**-34.4**	-34.18	-36.52	-35.10	-35.94	-34.56	-34.59	-34.69	0.25	-2.09	-0.67	-1.51	-0.12	-0.16	-0.26
08_MeOH-Water	**-20.9**	-20.50	-22.29	-20.67	-21.80	-20.90	-21.19	-20.91	0.46	-1.33	0.29	-0.84	0.06	-0.23	0.04
09_MeNH2-MeOH	**-12.8**	-12.59	-13.31	-12.76	-13.22	-12.41	-12.30	-12.27	0.21	-0.51	0.04	-0.42	0.38	0.50	0.53
10_MeNH2-MeNH2	**-17.4**	-15.82	-17.40	-18.24	-17.53	-16.75	-16.73	-16.86	1.59	0.00	-0.84	-0.13	0.65	0.67	0.54
11_MeNH2-Peptide	**-22.6**	-20.92	-22.64	-23.18	-22.72	-22.21	-22.48	-22.63	1.75	0.03	-0.51	-0.05	0.46	0.19	0.04
12_MeNH2-Water	**-30.4**	-30.92	-33.34	-31.46	-31.80	-30.59	-29.46	-30.20	-0.52	-2.94	-1.06	-1.40	-0.19	0.94	0.20
13_Peptide-MeOH	**-25.8**	-24.52	-26.10	-25.65	-25.86	-25.17	-24.68	-25.32	1.37	-0.21	0.24	0.03	0.71	1.21	0.57
14_Peptide-MeNH2	**-31.1**	-30.96	-32.68	-33.10	-32.34	-30.56	-30.13	-30.57	0.23	-1.49	-1.91	-1.15	0.62	1.06	0.61
15_Peptide-Peptide	**-36.1**	-35.31	-36.99	-37.40	-37.15	-35.62	-35.52	-35.83	0.79	-0.88	-1.30	-1.05	0.48	0.58	0.28
16_Peptide-Water	**-21.4**	-20.33	-21.81	-20.42	-21.38	-21.05	-21.05	-21.05	1.10	-0.37	1.02	0.06	0.38	0.39	0.38
17_Uracil-Uracil_BP	**-71.8**	-70.71	-74.94	-72.22	-75.98	-71.16	-71.74	-71.72	1.18	-3.05	-0.33	-4.09	0.73	0.15	0.17
18_Water-Pyridine	**-28.6**	-28.62	-30.60	-29.54	-31.09	-28.87	-28.03	-28.41	0.07	-1.91	-0.85	-2.40	-0.18	0.66	0.28
19_MeOH-Pyridine	**-31.0**	-30.92	-32.69	-31.67	-33.47	-30.84	-30.12	-30.53	0.08	-1.69	-0.67	-2.47	0.16	0.88	0.47
20_AcOH-AcOH	**-79.8**	-81.88	-87.21	-83.01	-85.65	-82.58	-81.47	-82.08	-2.00	-7.33	-3.13	-5.76	-2.67	-1.59	-2.19
21_AcNH2-AcNH2	**-68.0**	-66.27	-70.67	-69.08	-71.21	-67.38	-67.63	-67.60	1.78	-2.62	-1.03	-3.16	0.67	0.42	0.45
22_AcOH-Uracil	**-81.5**	-81.63	-86.54	-83.14	-86.40	-82.29	-82.03	-82.36	-0.08	-4.99	-1.59	-4.85	-0.73	-0.48	-0.81
23_AcNH2-Uracil	**-80.2**	-79.29	-83.77	-81.34	-84.27	-79.78	-79.88	-80.06	1.00	-3.48	-1.05	-3.98	0.50	0.41	0.22
24_Benzene-Benzene_pi-pi	**-11.8**	-12.26	-11.45	-13.64	-12.76	-11.47	-11.43	-12.25	-0.45	0.35	-1.83	-0.95	0.33	0.37	-0.44
25_Pyridine-Pyridine_pi-pi	**-16.3**	-16.53	-16.06	-18.07	-17.45	-15.62	-15.21	-16.43	-0.23	0.24	-1.78	-1.15	0.67	1.08	-0.14
26_Uracil-Uracil_pi-pi	**-41.1**	-43.18	-43.68	-40.84	-42.72	-41.09	-40.99	-42.62	-2.05	-2.56	0.29	-1.59	0.03	0.13	-1.49
27_Benzene-Pyridine_pi-pi	**-14.3**	-14.69	-14.09	-16.15	-15.44	-13.86	-13.64	-14.69	-0.30	0.30	-1.76	-1.05	0.52	0.75	-0.30

28_Benzene-Uracil_pi-pi	**-23.9**	-23.77	-23.86	-24.23	-24.10	-23.11	-22.53	-24.47	0.14	0.04	-0.32	-0.20	0.78	1.37	-0.57
29_Pyridine-Uracil_pi-pi	**-28.5**	-27.87	-28.11	-28.49	-29.00	-27.84	-27.29	-29.06	0.67	0.42	0.04	-0.46	0.69	1.24	-0.52
30_Benzene-Ethene	**-5.99**	-5.10	-4.94	-7.15	-6.19	-5.65	-6.08	-6.15	0.89	1.05	-1.16	-0.20	0.34	-0.09	-0.16
31_Uracil-Ethene	**-14.1**	-12.76	-13.09	-14.85	-14.35	-13.81	-13.43	-14.37	1.38	1.05	-0.71	-0.21	0.32	0.71	-0.23
32_Uracil-Ethyne	**-15.6**	-14.14	-14.64	-15.61	-15.86	-15.64	-15.33	-16.23	1.50	1.00	0.03	-0.22	0.00	0.31	-0.59
33_Pyridine-Ethene	**-7.83**	-6.65	-6.67	-8.83	-8.08	-7.27	-7.69	-7.80	1.18	1.17	-1.00	-0.24	0.56	0.14	0.03
34_Pentane-Pentane	**-15.8**	-15.15	-15.56	-22.26	-16.74	-16.26	-16.22	-16.20	0.65	0.24	-6.46	-0.94	-0.46	-0.42	-0.40
35_Neopentane-Pentane	**-10.9**	-10.38	-10.44	-14.98	-11.38	-11.39	-11.57	-11.21	0.56	0.49	-4.05	-0.45	-0.45	-0.64	-0.28
36_Neopentane-Neopentane	**-7.43**	-7.28	-6.95	-9.96	-7.78	-7.97	-8.32	-7.51	0.15	0.48	-2.52	-0.35	-0.53	-0.88	-0.08
37_Cyclopentane-Neopentane	**-10.0**	-9.79	-9.83	-14.14	-10.75	-10.46	-10.66	-10.34	0.27	0.23	-4.08	-0.69	-0.39	-0.60	-0.28
38_Cyclopentane-Cyclopenta	**-12.5**	-12.22	-12.37	-17.20	-13.56	-12.53	-12.69	-12.60	0.32	0.17	-4.66	-1.02	0.01	-0.15	-0.06
39_Benzene-Cyclopentane	**-14.9**	-15.48	-15.46	-18.33	-15.69	-14.85	-14.75	-15.49	-0.52	-0.51	-3.37	-0.73	0.10	0.21	-0.53
40_Benzene-Neopentane	**-12.1**	-12.30	-12.13	-14.69	-12.38	-12.41	-12.17	-12.66	-0.19	-0.01	-2.57	-0.27	-0.29	-0.06	-0.55
41_Uracil-Pentane	**-20.2**	-19.62	-20.11	-23.56	-20.54	-20.19	-20.09	-20.66	0.66	0.18	-3.27	-0.26	0.09	0.19	-0.38
42_Uracil-Cyclopentane	**-17.3**	-17.03	-17.13	-19.62	-17.53	-17.03	-16.97	-17.49	0.28	0.19	-2.31	-0.22	0.28	0.34	-0.17
43_Uracil-Neopentane	**-15.5**	-15.02	-15.04	-17.66	-15.77	-15.77	-15.32	-15.98	0.51	0.49	-2.13	-0.24	-0.23	0.21	-0.45
44_Ethene-Pentane	**-8.39**	-7.24	-7.55	-10.84	-8.83	-8.18	-8.21	-8.01	1.15	0.83	-2.45	-0.44	0.21	0.18	0.38
45_Ethyne-Pentane	**-7.31**	-6.86	-6.77	-8.58	-7.70	-7.43	-7.20	-7.32	0.45	0.54	-1.26	-0.38	-0.12	0.12	-0.01
46_Peptide-Pentane	**-17.8**	-16.78	-17.51	-21.42	-17.87	-17.88	-17.88	-18.05	1.06	0.33	-3.58	-0.03	-0.04	-0.04	-0.20
47_Benzene-Benzene_TS	**-12.0**	-11.88	-11.94	-13.10	-12.30	-11.34	-10.71	-11.69	0.15	0.10	-1.06	-0.27	0.69	1.32	0.34
48_Pyridine-Pyridine_TS	**-14.7**	-13.93	-14.43	-15.56	-15.10	-13.84	-13.16	-14.15	0.86	0.36	-0.77	-0.31	0.94	1.63	0.64
49_Benzene-Pyridine_TS	**-13.9**	-13.97	-14.20	-15.15	-14.39	-13.33	-12.46	-13.69	-0.04	-0.26	-1.21	-0.46	0.60	1.48	0.24
50_Benzene-Ethyne_CH-pi	**-12.0**	-12.26	-12.81	-12.68	-12.51	-11.94	-11.19	-12.10	-0.26	-0.81	-0.68	-0.51	0.06	0.80	-0.11
51_Ethyne-Ethyne_TS	**-6.38**	-6.61	-6.81	-6.53	-7.11	-6.49	-6.67	-6.40	-0.23	-0.44	-0.15	-0.74	-0.11	-0.29	-0.02
52_Benzene-AcOH_OH-pi	**-19.6**	-21.21	-22.01	-19.41	-19.41	-19.86	-18.53	-20.24	-1.52	-2.32	0.28	0.28	-0.17	1.16	-0.54
53_Benzene-AcNH2_NH-pi	**-18.2**	-18.41	-19.24	-18.87	-18.49	-17.90	-17.23	-18.12	-0.16	-0.99	-0.62	-0.25	0.35	1.02	0.13
54_Benzene-Water_OH-pi	**-13.7**	-14.94	-15.66	-14.64	-14.06	-13.98	-13.10	-14.07	-1.23	-1.94	-0.93	-0.35	-0.27	0.62	-0.36
55_Benzene-MeOH_OH-pi	**-17.5**	-18.33	-19.04	-18.45	-17.82	-17.32	-16.65	-17.73	-0.80	-1.52	-0.93	-0.30	0.20	0.88	-0.21
56_Benzene-MeNH2_NH-pi	**-13.5**	-13.05	-13.58	-14.98	-13.81	-13.16	-12.68	-13.56	0.46	-0.06	-1.46	-0.29	0.36	0.84	-0.04
57_Benzene-Peptide_NH-pi	**-22.1**	-22.64	-23.13	-24.18	-22.59	-21.80	-20.76	-22.37	-0.54	-1.03	-2.08	-0.49	0.30	1.34	-0.27
58_Pyridine-Pyridine_CH-N	**-17.3**	-14.39	-15.73	-16.28	-16.74	-15.91	-15.38	-15.83	2.95	1.62	1.07	0.61	1.42	1.96	1.52
59_Ethyne-Water_CH-O	**-11.9**	-11.84	-12.81	-11.42	-12.55	-12.08	-12.36	-12.00	0.08	-0.88	0.50	-0.63	-0.15	-0.44	-0.08

60_Ethyne-AcOH_OH-pi	**-20.3**	-21.09	-23.52	-20.84	-21.84	-21.30	-21.27	-21.49	-0.72	-3.15	-0.47	-1.47	-0.93	-0.91	-1.13
61_Pentane-AcOH	**-12.1**	-12.22	-12.34	-14.14	-12.43	-12.39	-12.02	-12.19	-0.03	-0.16	-1.96	-0.24	-0.21	0.16	0.00
62_Pentane-AcNH2	**-14.7**	-14.02	-14.59	-17.32	-15.02	-14.80	-14.99	-14.78	0.77	0.20	-2.54	-0.23	-0.01	-0.21	0.00
63_Benzene-AcOH	**-15.9**	-16.19	-16.48	-17.24	-15.98	-15.88	-14.97	-16.43	-0.29	-0.57	-1.33	-0.08	0.02	0.94	-0.52
64_Peptide-Ethene	**-12.5**	-11.72	-12.24	-13.14	-12.84	-12.23	-12.05	-12.28	0.83	0.31	-0.59	-0.30	0.31	0.50	0.27
65_Pyridine-Ethyne	**-16.7**	-16.36	-17.40	-17.36	-18.58	-16.73	-17.20	-16.69	0.34	-0.70	-0.67	-1.88	-0.03	-0.50	0.01
66_MeNH2-Pyridine	**-16.6**	-14.43	-15.49	-17.07	-16.74	-15.65	-15.74	-16.08	2.17	1.11	-0.47	-0.13	0.94	0.86	0.52
MD									**0.29**	**-0.79**	**-1.26**	**-0.92**	**0.13**	**0.39**	**-0.07**
MAD									**0.71**	**1.21**	**1.38**	**0.96**	**0.41**	**0.63**	**0.37**
RMSD									**0.96**	**1.76**	**1.88**	**1.51**	**0.57**	**0.77**	**0.53**
MAX									**2.97**	**7.32**	**6.44**	**5.77**	**2.69**	**1.96**	**2.19**

BS1: 6-311++G(2*d*,*p*) ; BS2: 6311++G(3*df*,*3pd)*; BS3: Def2QZVP; BS4: aug-cc-pVTZ

表 S7 B972-PFD/6-311++G(2*d*,*p*)与 CCSD(T)/CBS 标准基于 S66x8 数据集的比较数据

Table S7 $\Delta E_{\text{B972-PFD}}$ - $\Delta E_{\text{CCSD(T)/CBS}}$ in kJ mol^{-1} for the B972-PFD/6-311++G(2*d*,*p*) methods for the S66x8 data set

S66x8 data set	Ref[29]								ΔE B972-PFD/6-311++G(2d,p)								$\Delta E_{\text{B972-PFd}}$ - $\Delta E_{\text{CCSD(T)/CBS}}$							
	0.90	**0.95**	**1.00**	**1.05**	**1.10**	**1.25**	**1.50**	**2.00**	**0.90**	**0.95**	**1.00**	**1.05**	**1.10**	**1.25**	**1.50**	**2.00**	**0.90**	**0.95**	**1.00**	**1.05**	**1.10**	**1.25**	**1.50**	**2.00**
01_Water-Water	-19.1	-20.4	-20.4	-19.7	-18.6	-14.4	-8.82	-3.64	-18.8	-20.3	-20.6	-20.2	-19.5	-15.9	-10.2	-4.39	0.26	0.10	-0.1	-0.4	-0.8	-1.5	-1.3	-0.7
02_Water-MeOH	-21.7	-23.2	-23.3	-22.5	-21.2	-16.5	-9.98	-3.98	-21.1	-22.7	-23.0	-22.4	-21.5	-17.6	-11.1	-4.56	0.60	0.46	0.25	0.05	-0.3	-1.1	-1.1	-0.5
03_Water-MeNH2	-27.1	-28.7	-28.7	-27.8	-26.2	-20.5	-12.4	-4.77	-28.4	-29.7	-29.6	-28.5	-26.9	-21.6	-13.4	-5.31	-1.2	-1.0	-0.8	-0.7	-0.6	-1.0	-0.9	-0.5
04_Water-Peptide	-31.9	-33.7	-33.7	-32.8	-31.2	-25.0	-16.0	-6.01	-31.5	-33.2	-33.4	-32.5	-31.1	-26.0	-17.3	-6.74	0.39	0.44	0.36	0.22	0.05	-0.9	-1.2	-0.7
05_MeOH-MeOH	-22.0	-23.8	-24.0	-23.3	-22.1	-17.3	-10.5	-4.22	-21.3	-23.1	-23.5	-23.0	-22.1	-18.2	-11.5	-4.73	0.71	0.63	0.48	0.28	-0.0	-0.9	-1.0	-0.5
06_MeOH-MeNH2	-29.1	-31.2	-31.5	-30.6	-29.1	-23.0	-14.0	-5.33	-30.1	-32.0	-32.2	-31.3	-29.7	-24.0	-15.0	-5.90	-0.9	-0.8	-0.7	-0.6	-0.6	-1.0	-1.0	-0.5
07_MeOH-Peptide	-31.9	-34.0	-34.3	-33.5	-32.0	-25.8	-15.2	-4.59	-31.9	-33.8	-34.1	-33.2	-31.8	-26.4	-16.2	-5.02	-0.0	0.17	0.29	0.31	0.25	-0.5	-0.9	-0.4
08_MeOH-Water	-19.1	-20.7	-20.9	-20.2	-19.1	-15.0	-9.20	-3.79	-18.4	-20.1	-20.5	-20.1	-19.5	-16.1	-10.4	-4.44	0.78	0.59	0.36	0.11	-0.3	-1.1	-1.2	-0.6
09_MeNH2-MeOH	-11.7	-12.7	-12.7	-12.1	-11.2	-8.27	-4.60	-1.64	-10.8	-12.2	-12.7	-12.5	-11.8	-9.08	-5.27	-1.88	0.94	0.46	-0.0	-0.3	-0.6	-0.8	-0.6	-0.2
10_MeNH2-MeNH2	-15.4	-17.1	-17.3	-16.7	-15.7	-11.6	-5.47	-1.62	-12.7	-15.0	-15.9	-15.9	-15.3	-11.9	-5.98	-1.76	2.70	2.06	1.43	0.83	0.38	-0.2	-0.5	-0.1
11_MeNH2-Peptide	-20.7	-22.4	-22.6	-21.9	-20.6	-13.4	-5.86	-1.90	-17.6	-20.1	-21.0	-20.9	-20.1	-13.8	-6.53	-2.09	3.05	2.28	1.53	0.95	0.50	-0.4	-0.6	-0.1
12_MeNH2-Water	-28.2	-30.1	-30.3	-29.4	-27.8	-21.8	-13.1	-5.00	-28.6	-30.6	-30.7	-29.9	-28.4	-22.9	-14.2	-5.56	-0.4	-0.4	-0.4	-0.5	-0.5	-1.0	-1.0	-0.5
13_Peptide-MeOH	-23.7	-25.5	-25.8	-25.2	-24.0	-19.2	-12.3	-5.45	-21.8	-23.9	-24.5	-24.3	-23.6	-19.8	-13.3	-6.02	1.85	1.58	1.30	0.91	0.38	-0.6	-0.9	-0.5
14_Peptide-MeNH2	-28.5	-30.7	-31.1	-30.5	-29.1	-23.4	-14.8	-6.23	-28.2	-30.4	-30.9	-30.3	-29.1	-24.0	-15.6	-6.74	0.26	0.26	0.21	0.17	-0.0	-0.5	-0.7	-0.5
15_Peptide-Peptide	-33.5	-35.6	-36.0	-35.3	-33.8	-27.8	-18.4	-7.42	-32.7	-34.8	-35.3	-34.6	-33.5	-28.3	-19.3	-7.95	0.77	0.84	0.77	0.65	0.33	-0.5	-0.9	-0.5
16_Peptide-Water	-19.6	-21.1	-21.4	-20.8	-19.8	-15.8	-10.2	-4.74	-17.9	-19.8	-20.3	-20.3	-19.8	-16.7	-11.4	-5.44	1.65	1.34	1.04	0.47	-0.0	-0.8	-1.2	-0.7
17_Uracil-Uracil_BP	-65.6	-70.7	-71.8	-70.5	-67.6	-55.0	-34.9	-13.9	-66.0	-70.0	-70.6	-68.9	-65.9	-54.4	-35.7	-14.7	-0.3	0.62	1.26	1.61	1.71	0.59	-0.7	-0.7
18_Water-Pyridine	-26.7	-28.4	-28.5	-27.7	-26.2	-20.6	-12.6	-4.96	-27.2	-28.5	-28.4	-27.3	-25.8	-20.7	-13.0	-5.27	-0.5	-0.1	0.18	0.35	0.43	-0.1	-0.4	-0.3
19_MeOH-Pyridine	-28.3	-30.5	-30.9	-30.2	-28.7	-22.9	-14.1	-5.57	-29.0	-30.7	-30.7	-29.8	-28.2	-22.8	-14.5	-5.86	-0.6	-0.1	0.18	0.40	0.51	0.08	-0.3	-0.2
20_AcOH-AcOH	-73.0	-78.6	-79.8	-78.3	-75.0	-60.9	-38.5	-15.0	-77.4	-81.6	-81.7	-79.2	-75.3	-60.7	-39.7	-15.9	-4.4	-3.0	-1.8	-0.9	-0.2	0.16	-1.2	-0.9
21_AcNH2-AcNH2	-62.4	-67.0	-68.0	-66.6	-63.8	-51.9	-33.4	-12.5	-61.6	-65.6	-66.2	-64.7	-62.0	-51.6	-34.1	-13.1	0.82	1.45	1.80	1.95	1.85	0.28	-0.7	-0.6
22_AcOH-Uracil	-74.9	-80.2	-81.5	-80.1	-77.0	-63.3	-41.2	-17.3	-76.9	-81.1	-81.5	-79.5	-76.0	-62.7	-42.1	-18.1	-2.0	-0.9	0.00	0.64	0.99	0.62	-0.8	-0.8
23_AcNH2-Uracil	-74.0	-79.0	-80.2	-79.0	-76.2	-63.6	-42.8	-19.4	-74.3	-78.5	-79.2	-77.7	-74.8	-63.2	-43.6	-20.3	-0.2	0.50	1.05	1.33	1.40	0.41	-0.8	-0.8
24_Benzene-Benzene_pi-pi	-0.94	-8.66	-11.4	-11.7	-10.7	-6.43	-2.04	-0.26	2.80	-7.41	-11.4	-12.3	-11.6	-7.36	-2.68	-0.38	3.74	1.25	-0.0	-0.5	-0.8	-0.9	-0.6	-0.1
25_Pyridine-Pyridine_pi-pi	-5.53	-13.2	-16.0	-16.1	-14.9	-9.86	-4.02	-0.99	-0.63	-11.3	-15.7	-16.6	-15.9	-11.0	-4.90	-1.17	4.90	1.92	0.27	-0.5	-1.0	-1.2	-0.8	-0.1
26_Uracil-Uracil_pi-pi	-32.8	-39.7	-41.0	-39.4	-36.3	-25.4	-12.9	-4.15	-30.6	-40.3	-43.3	-42.5	-39.9	-29.4	-15.9	-5.06	2.24	-0.5	-2.2	-3.1	-3.6	-4.0	-3.0	-0.9

27_Benzene-Pyridine_pi-pi	-3.03	-11.2	-14.1	-14.2	-13.0	-8.24	-3.02	-0.61	1.63	-9.54	-13.8	-14.7	-13.9	-9.33	-3.77	-0.75	4.67	1.72	0.21	-0.5	-0.8	-1.0	-0.7	-0.1
28_Benzene-Uracil_pi-pi	-14.7	-21.8	-23.8	-23.2	-21.2	-13.7	-5.71	-1.05	-9.75	-19.8	-23.5	-23.8	-22.3	-15.4	-7.11	-1.34	5.02	1.99	0.31	-0.5	-1.1	-1.6	-1.4	-0.2
29_Pyridine-Uracil_pi-pi	-15.6	-25.8	-28.5	-27.5	-24.9	-16.1	-7.43	-2.23	-8.62	-22.8	-27.6	-27.8	-25.9	-17.9	-8.74	-2.51	7.03	2.98	0.85	-0.2	-1.0	-1.7	-1.3	-0.2
30_Benzene-Ethene	-1.08	-4.71	-5.91	-5.86	-5.26	-2.88	-0.73	0.04	2.38	-2.76	-4.81	-5.23	-4.85	-2.85	-0.88	0.04	3.47	1.95	1.10	0.63	0.40	0.04	-0.1	0.00
31_Uracil-Ethene	-10.7	-13.5	-14.1	-13.5	-12.3	-8.33	-3.90	-1.06	-6.74	-11.2	-12.8	-12.9	-12.3	-8.91	-4.56	-1.26	4.00	2.33	1.25	0.57	0.08	-0.5	-0.6	-0.1
32_Uracil-Ethyne	-11.6	-14.9	-15.6	-15.0	-13.7	-9.31	-4.36	-1.14	-7.24	-12.3	-14.2	-14.3	-13.6	-9.87	-5.02	-1.30	4.45	2.61	1.41	0.67	0.17	-0.5	-0.6	-0.1
33_Pyridine-Ethene	-3.70	-6.79	-7.79	-7.66	-6.98	-4.30	-1.53	-0.19	0.17	-4.48	-6.40	-6.82	-6.49	-4.31	-1.80	-0.25	3.87	2.31	1.38	0.84	0.49	-0.0	-0.2	-0.0
34_Pentane-Pentane	-11.9	-15.1	-15.7	-15.1	-13.8	-9.35	-4.39	-1.13	-7.57	-13.1	-15.2	-15.5	-14.7	-11.0	-5.73	-1.46	4.38	1.97	0.52	-0.4	-0.9	-1.6	-1.3	-0.3
35_Neopentane-Pentane	-7.75	-10.4	-10.9	-10.3	-9.43	-6.26	-2.92	-0.77	-4.69	-9.00	-10.4	-10.5	-9.92	-7.24	-3.64	-0.92	3.06	1.43	0.46	-0.1	-0.4	-0.9	-0.7	-0.1
36_Neopentane-Neopentane	-6.08	-7.26	-7.41	-7.05	-6.43	-4.38	-2.11	-0.56	-4.94	-6.82	-7.36	-7.24	-6.78	-4.98	-2.51	-0.63	1.15	0.44	0.05	-0.1	-0.3	-0.5	-0.4	-0.0
37_Cyclopentane-Neopentane	-6.72	-9.41	-10.0	-9.73	-8.95	-6.14	-2.95	-0.79	-4.06	-8.20	-9.79	-9.96	-9.50	-7.07	-3.68	-0.96	2.67	1.21	0.27	-0.2	-0.5	-0.9	-0.7	-0.1
38_Cyclopentane-Cyclopentan	-9.36	-11.8	-12.5	-11.9	-10.8	-7.17	-3.31	-0.85	-6.23	-10.4	-12.3	-12.4	-11.7	-8.62	-4.39	-1.09	3.13	1.47	0.24	-0.5	-0.9	-1.4	-1.0	-0.2
39_Benzene-Cyclopentane	-9.02	-13.5	-14.9	-14.5	-13.2	-8.64	-3.74	-0.79	-7.36	-13.2	-15.3	-15.3	-14.2	-9.79	-4.69	-1.00	1.66	0.33	-0.4	-0.7	-0.9	-1.1	-0.9	-0.2
40_Benzene-Neopentane	-7.79	-11.1	-12.1	-11.7	-10.7	-7.13	-3.20	-0.78	-6.78	-10.9	-12.2	-12.0	-11.1	-7.78	-3.85	-0.92	1.02	0.23	-0.1	-0.3	-0.4	-0.6	-0.6	-0.1
41_Uracil-Pentane	-16.0	-19.6	-20.2	-19.2	-17.0	-10.2	-4.08	-0.89	-12.5	-18.0	-19.7	-19.5	-17.9	-12.0	-5.31	-1.13	3.46	1.60	0.46	-0.2	-0.9	-1.7	-1.2	-0.2
42_Uracil-Cyclopentane	-12.7	-16.6	-17.2	-16.4	-14.8	-9.60	-4.26	-1.03	-9.79	-15.4	-17.1	-16.9	-15.8	-11.2	-5.56	-1.34	2.97	1.20	0.13	-0.5	-1.0	-1.6	-1.3	-0.3
43_Uracil-Neopentane	-12.0	-15.0	-15.4	-14.6	-13.1	-8.56	-3.85	-0.96	-9.50	-13.8	-15.1	-14.8	-13.7	-9.75	-4.77	-1.17	2.50	1.17	0.33	-0.2	-0.6	-1.1	-0.9	-0.2
44_Ethene-Pentane	-6.93	-8.25	-8.32	-7.79	-7.00	-4.56	-2.06	-0.50	-3.89	-6.57	-7.53	-7.53	-7.15	-5.23	-2.64	-0.63	3.04	1.68	0.79	0.26	-0.1	-0.6	-0.5	-0.1
45_Ethyne-Pentane	-4.74	-6.82	-7.32	-7.01	-6.36	-4.09	-1.76	-0.41	-2.68	-5.77	-6.90	-6.95	-6.49	-4.56	-2.18	-0.50	2.07	1.05	0.41	0.07	-0.1	-0.4	-0.4	-0.1
46_Peptide-Pentane	-15.6	-17.5	-17.7	-16.9	-15.6	-11.0	-4.97	-1.20	-12.2	-15.8	-17.0	-16.9	-16.1	-12.4	-6.32	-1.51	3.44	1.78	0.73	-0.0	-0.5	-1.4	-1.3	-0.3
47_Benzene-Benzene_TS	-6.87	-10.7	-11.9	-11.7	-10.9	-7.39	-3.46	-0.94	-4.56	-9.75	-11.6	-11.8	-11.2	-8.03	-4.10	-1.09	2.31	1.04	0.32	-0.1	-0.3	-0.6	-0.6	-0.1
48_Pyridine-Pyridine_TS	-10.5	-13.8	-14.7	-14.4	-13.4	-9.59	-4.93	-1.55	-7.36	-12.0	-13.8	-14.1	-13.4	-10.1	-5.69	-1.76	3.20	1.79	0.93	0.35	0.03	-0.5	-0.7	-0.2
49_Benzene-Pyridine_TS	-8.73	-12.7	-13.9	-13.6	-12.6	-8.78	-4.39	-1.39	-6.57	-11.8	-13.8	-13.9	-13.2	-9.62	-5.15	-1.59	2.16	0.84	0.10	-0.3	-0.5	-0.8	-0.7	-0.2
50_Benzene-Ethyne_CH-pi	-7.82	-11.0	-11.9	-11.6	-10.7	-7.47	-3.72	-1.13	-6.32	-10.6	-12.1	-12.2	-11.5	-8.37	-4.44	-1.34	1.50	0.40	-0.1	-0.5	-0.7	-0.9	-0.7	-0.2
51_Ethyne-Ethyne_TS	-5.05	-6.15	-6.37	-6.12	-5.63	-3.90	-1.93	-0.56	-4.94	-6.23	-6.61	-6.44	-6.02	-4.35	-2.26	-0.63	0.11	-0.0	-0.2	-0.3	-0.3	-0.4	-0.3	-0.0
52_Benzene-AcOH_OH-pi	-16.6	-19.1	-19.6	-19.0	-17.7	-13.0	-7.11	-2.32	-17.4	-20.4	-21.2	-20.7	-19.5	-14.7	-8.37	-2.72	-0.8	-1.2	-1.5	-1.6	-1.7	-1.6	-1.2	-0.4
53_Benzene-AcNH2_NH-pi	-15.8	-17.8	-18.2	-17.6	-16.6	-12.4	-6.88	-2.01	-15.1	-17.7	-18.4	-18.1	-17.2	-13.3	-7.66	-2.26	0.74	0.15	-0.2	-0.4	-0.6	-0.8	-0.7	-0.2
54_Benzene-Water_OH-pi	-11.7	-13.4	-13.6	-13.1	-12.1	-8.79	-4.84	-1.74	-12.4	-14.5	-14.9	-14.5	-13.6	-10.2	-5.86	-2.09	-0.6	-1.0	-1.2	-1.4	-1.4	-1.4	-1.0	-0.3
55_Benzene-MeOH_OH-pi	-14.4	-16.9	-17.5	-17.0	-15.9	-11.7	-6.39	-2.16	-14.0	-17.2	-18.3	-18.1	-17.2	-13.2	-7.66	-2.59	0.39	-0.3	-0.8	-1.1	-1.3	-1.5	-1.2	-0.4
56_Benzene-MeNH2_NH-pi	-10.5	-12.9	-13.5	-13.0	-11.9	-8.16	-3.93	-1.09	-8.45	-11.8	-13.0	-13.0	-12.3	-8.91	-4.64	-1.26	2.06	1.12	0.46	0.00	-0.3	-0.7	-0.7	-0.1
57_Benzene-Peptide_NH-pi	-15.6	-20.7	-22.0	-21.5	-20.0	-14.2	-7.54	-2.59	-13.8	-20.3	-22.5	-22.4	-21.1	-15.7	-8.79	-2.97	1.82	0.40	-0.4	-0.9	-1.1	-1.4	-1.2	-0.3
58_Pyridine-Pyridine_CH-N	-11.7	-15.9	-17.3	-16.2	-14.4	-9.13	-4.23	-1.15	-6.07	-11.5	-14.4	-14.3	-13.1	-8.74	-4.27	-1.13	5.67	4.47	2.91	1.95	1.32	0.38	-0.0	0.02

59_Ethyne-Water_CH-O	-10.5	-11.7	-11.9	-11.5	-10.8	-8.29	-4.89	-1.92	-9.83	-11.3	-11.9	-11.8	-11.4	-9.16	-5.69	-2.26	0.69	0.41	-0.0	-0.3	-0.5	-0.8	-0.8	-0.3
60_Ethyne-AcOH_OH-pi	-17.9	-20.0	-20.3	-19.6	-18.3	-13.6	-7.41	-2.33	-18.0	-20.5	-21.0	-20.5	-19.3	-14.6	-8.24	-2.64	-0.1	-0.5	-0.7	-0.9	-1.0	-1.0	-0.8	-0.3
61_Pentane-AcOH	-11.3	-12.1	-12.0	-11.4	-10.5	-7.48	-3.28	-0.70	-10.3	-11.9	-12.4	-12.1	-11.5	-8.91	-4.39	-0.92	0.92	0.17	-0.3	-0.7	-1.0	-1.4	-1.1	-0.2
62_Pentane-AcNH2	-13.1	-14.6	-14.6	-13.9	-12.7	-8.85	-4.36	-1.14	-10.9	-13.4	-14.2	-13.9	-13.1	-9.96	-5.44	-1.42	2.23	1.18	0.44	-0.0	-0.4	-1.1	-1.0	-0.2
63_Benzene-AcOH	-11.4	-15.0	-15.9	-15.2	-13.9	-9.36	-4.27	-1.10	-9.33	-14.4	-16.2	-16.1	-15.1	-10.6	-5.23	-1.30	2.11	0.59	-0.3	-0.8	-1.1	-1.3	-0.9	-0.2
64_Peptide-Ethene	-10.8	-12.3	-12.5	-11.9	-11.0	-7.77	-3.67	-0.79	-8.74	-11.1	-11.8	-11.7	-11.0	-8.41	-4.35	-0.92	2.13	1.21	0.62	0.23	-0.0	-0.6	-0.6	-0.1
65_Pyridine-Ethyne	-14.7	-16.3	-16.6	-16.2	-15.3	-11.9	-6.99	-2.58	-14.7	-16.0	-16.3	-16.0	-15.3	-12.0	-7.24	-2.68	0.02	0.29	0.33	0.20	0.08	-0.1	-0.2	-0.1
66_MeNH2-Pyridine	-14.4	-16.2	-16.5	-16.1	-15.1	-11.3	-6.29	-2.07	-10.6	-13.3	-14.5	-14.7	-14.2	-11.3	-6.78	-2.30	3.79	2.91	2.08	1.38	0.87	0.01	-0.4	-0.2
MD																	**1.72**	**0.84**	**0.29**	**-0.0**	**-0.3**	**-0.8**	**-0.8**	**-0.3**
MAD																	**2.09**	**1.13**	**0.67**	**0.63**	**0.71**	**0.92**	**0.88**	**0.33**
RMSD																	**2.64**	**1.46**	**0.92**	**0.84**	**0.92**	**1.09**	**0.96**	**0.42**
MAX																	**7.03**	**4.48**	**2.93**	**3.14**	**3.64**	**4.06**	**3.01**	**0.92**

Ref[38]: Rezac, J.; Riley, K. E.; Hobza, P. *J. Chem. Theory Comput.* **2011,** *7*, 2427. doi:10.1021/ct2002946

Part 2　SAM 色散校正模型算法简要描述

SAM 色散校正(Spherical Atom Model)，也称 PFD (Petersson-Frisch Dispersion)校正 [15]，已被 Petersson，Frisch 等结合 APF 泛函作为 APF-PFD 标准方法加入到 Gaussian 09 和 Gaussian 16 程序中 [16,17]。它的基本算法如下：

两个非成键原子之间的 London 色散作用能通常表示为(1)多级展开式：

$$V\left(R_{\mathrm{AB}}\right)=\frac{C_{6,\ \mathrm{AB}}}{R_{\mathrm{AB}}^{6}}+\frac{C_{8,\ \mathrm{AB}}}{R_{\mathrm{AB}}^{8}}+\frac{C_{10,\ \mathrm{AB}}}{R_{\mathrm{AB}}^{10}}+\ \cdots \tag{1}$$

SAM 模型定义了一种新的势函数来描述原子对之间的色散作用，并与公式(1)前三项展开式精度相同。SAM 描述了两个可极化介质的球形外壳之间的相互作用，它假定这些球壳的厚度为无穷小，半径分别为 $r_{\mathrm{s,A}}$ 和 $r_{\mathrm{s,B}}$。由此产生的原子间电势可由(2)式表达：

$$\begin{aligned} V\left(R_{\mathrm{AB}}\right)=&\ \frac{C_{6,\ \mathrm{AB}}}{\left[R_{\mathrm{AB}}^{2}-\left(r_{\mathrm{s,A}}+r_{\mathrm{s,B}}\right)^{2}\right]^{3}} \\ &\times\left\{1-\frac{2}{R_{\mathrm{AB}}^{2}}\left[r_{\mathrm{s,A}}r_{\mathrm{s,B}}-\left(r_{\mathrm{s,A}}-r_{\mathrm{s,B}}\right)^{2}\right]+O\left(R_{\mathrm{AB}}^{-4}\right)\right\} \end{aligned} \tag{2}$$

由于(2)式的第二项在数值上远小于第一项，并且不影响主导行为。近似使用式(2)中的前项来定义 SAM 电势，表示为式(3)：

$$V^{\mathrm{SAM}}\left(R_{\mathrm{AB}}\right)=\frac{C_{6,\mathrm{AB}}}{\left[R_{\mathrm{AB}}^{2}-\left(r_{\mathrm{s,A}}+r_{\mathrm{s,B}}\right)^{2}\right]^{3}} \tag{3}$$

考虑阻力校正后 SAM 色散能表示为(4)及(5)式：

$$V^{\mathrm{SAM}}\left(R_{\mathrm{AB}}\right)=\begin{cases} 0 & R_{\mathrm{AB}}\le R_{\mathrm{d,AB}} \\ \dfrac{C_{6,\mathrm{AB}}}{\left[R_{\mathrm{AB}}^{2}-R_{\mathrm{s,AB}}^{2}\right]^{3}}f\left(R_{\mathrm{AB}}\right)\times g\left(R_{\mathrm{AB}}\right) & R_{\mathrm{AB}}>R_{\mathrm{d,AB}} \end{cases} \tag{4}$$

SAM 与每个原子对的 $C_{6,\mathrm{AB}}$ 系数，偏移距离 $R_{\mathrm{s,AB}}$ 和阻尼半径 $R_{\mathrm{d,AB}}$ 三个变量相关，最终使用原子电离电位(IPs)和极化率(α)以及少量可调参数来确定这三个变量。

SAM 使用经验色散模型中是常见的处理方式，假定分子间色散作用是成对

的球形对称原子间相互作用的总和，即式(5)。

$$E_{\mathrm{disp}} = \sum_{\mathrm{A>B}} V^{\mathrm{SAM}}\left(R_{\mathrm{AB}}\right) \tag{5}$$

显然这种近似没有考虑多体色散效应，存在一定的误差，但是避免了给 Post SCF 计算带来计算量的增加。

Part 3 Definition of MD, MAD and RMSD:

$$\mathrm{MD} = \frac{1}{n}\sum_{\mathrm{sys}}^{n}\left(\Delta E - \Delta E_{\mathrm{ref}}\right)$$

$$\mathrm{MAD} = \frac{1}{n}\sum_{\mathrm{sys}}^{n}\left|\Delta E - \Delta E_{\mathrm{ref}}\right|$$

$$\mathrm{RMSD} = \sqrt{\frac{1}{n}\sum_{\mathrm{sys}}^{n}\left(\Delta E - \Delta E_{\mathrm{ref}}\right)^{2}}$$