Subsystem-DFT Potential-Energy Curves for Weakly Interacting Systems

— Supporting Information —

Danny Schlüns[†], Kevin Klahr[†], Christian Mück-Lichtenfeld[†], Lucas Visscher[‡], and Johannes Neugebauer[†1]

[†]Theoretische Organische Chemie,
Organisch-Chemisches Institut and Center for Multiscale Theory and Computation,
Westfälische Wilhelms-Universität Münster
Corrensstraße 40, 48149 Münster, Germany

[‡]Amsterdam Center for Multiscale Modeling, Vrije Universiteit Amsterdam,
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Date: November 24, 2014

[1]Email: j.neugebauer@uni-muenster.de

Contents

1 Computational Details

All sDFT calculations were carried out with the FDE/subsystem DFT implementation [1, 2] in the ADF 2014.01 [3] program package. Usual KS-DFT calculations were also carried out with ADF 2014.01. All calculations were done without explicit use of point-group symmetry. The TZ2P [4] basis set was used in all calculations and we used the mono-molecular expansion in the case of sDFT. KS-DFT interaction energies were corrected for basis set superposition errors (BSSE) using the counterpoise method [5]. The SCF and sDFT-SCF were always converged to 10^{-8} a.u. when possible, but at least 10^{-6} a.u. . The numerical integration was done with the option BECKEGRID in the quality VERYGOOD. The sDFT components were always evaluated on a super-molecular grid. The density fitting was performed with the pair-fitting scheme [6], together with the standard auxiliary fit functions for the basis set (STOFIT option; in order to improve the fit also the option A1FIT 10.0 was added).

The DFT-D3(BJ) correction [7,8] was calculated using the dftd3 program (V3.1 Rev 0) [9].

CCSD(T) calculations were carried out with TURBOMOLE 6.3.1 [10]. For the elements He, Ne, Ar and Kr we used the aug-cc-pVQZ basis sets [11–14]. For Xe we employed the aug-cc-pVQZ-PP basis set [15] where 28 core electrons are described through pseudo-potentials. Interaction energies here were also BSSE-corrected. The SCF convergence for all CCSD(T) calculations was set to 10^{-8} a.u. .

The KS-DFT and sDFT interaction energies for the xenon dimer in the main text do not employ relativistic corrections, because the zeroth order relativistic approximations (ZORA) formalism [16, 17] is not yet implemented for sDFT. The qualitative description for KS-PW91 is, however, quite similar with and without ZORA as shown in Fig. 1.

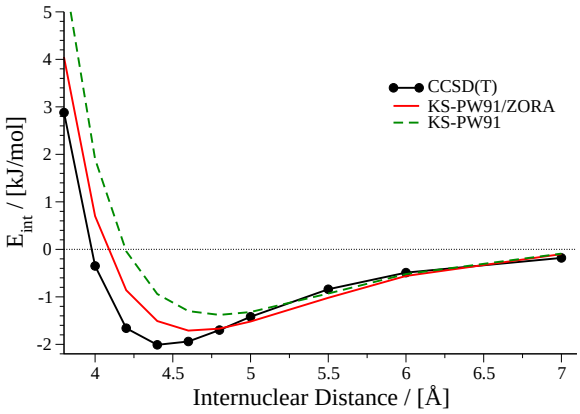

Figure 1: KS-PW91 interaction energies with and without ZORA corrections for the xenon dimer.

The mean deviation (MD) of n interaction energies is calculated as

$$\mathrm{MD} = \frac{1}{n}\sum_{i=1}^{n}\left(E_{\mathrm{int}}^{\mathrm{ref}}(i) - E_{\mathrm{int}}^{\mathrm{DFT}}(i)\right), \tag{1}$$

where $E_{\mathrm{int}}^{\mathrm{ref}}(i)$ is the reference interaction energy and $E_{\mathrm{int}}^{\mathrm{DFT}}(i)$ is the KS-DFT or sDFT interaction energy of a complex at an intermolecular distance i, respectively.

The mean absolute deviation (MAD) of n interaction energies is calculated as

$$\mathrm{MAD} = \frac{1}{n}\sum_{i=1}^{n}|E_{\mathrm{int}}^{\mathrm{ref}}(i) - E_{\mathrm{int}}^{\mathrm{DFT}}(i)|, \tag{2}$$

where $E_{\mathrm{int}}^{\mathrm{ref}}(i)$ is the reference interaction energy and $E_{\mathrm{int}}^{\mathrm{DFT}}(i)$ is the KS-DFT or sDFT interaction energy of complex at an intermolecular distance i, respectively.

2 Single-Point Interaction Energies

Table I: Errors between sDFT- and reference CCSD(T)/CBS (from Ref. [18]) interaction energies for the S22 [19] test set. Errors are defined as $\Delta E = E_{\rm int}^{\rm ref} - E_{\rm int}^{\rm DFT}$, where $E_{\rm int}^{\rm DFT}$ refers to the interaction energy derived from KS-DFT or sDFT. Errors from KS-DFT have been included for comparison. All values are given in kJ/mol. "2-PY" and "2-PO" are 2-pyridoxine and 2-aminopyridine, respectively. (HB), (S) and (TS) stand for hydrogen-bonded, stacked and T-shaped, respectively. The mean deviation and mean absolute deviation are denoted as MD and MAD, repectively.

			Errors with respect to $E_{\rm int}^{\rm ref}$					
			KS-DFT			sDFT		
No.	Complex	$E_{\rm int}^{\rm ref}$ [18]	LDA	PW91	BP86	LDA/TF	PW91/PW91k	BP86/LLP91
1	Ammonia dimer	−13.14	7.79	-0.55	-5.56	0.98	3.60	-3.76
2	Water dimer	−20.79	11.52	0.70	-3.96	-2.57	1.10	-6.84
3	Formic acid dimer	−77.78	35.05	1.48	-5.77	-21.93	-5.75	-22.26
4	Formamide dimer	−66.73	24.99	-2.52	-9.62	-5.45	4.47	-10.34
5	Uracil dimer (HB)	−85.60	24.20	-5.37	-13.23	-13.50	-1.06	-17.25
6	2-PY$\cdots$2-PO	−69.87	26.12	-2.81	-11.10	-5.79	5.15	-10.94
7	Adenine$\cdots$Thymine	−68.49	24.00	-5.85	-14.83	-8.23	2.98	-14.18
8	Methane dimer	−2.22	1.18	-0.77	-5.49	-0.54	1.18	-4.66
9	Ethene dimer	−6.19	3.61	-3.99	-10.51	-1.96	0.55	-8.39
10	Benzene$\cdots$Methane	−6.28	1.85	-5.07	-10.79	-3.62	-0.96	-8.82
11	Benzene dimer (S)	−11.76	-1.40	-18.23	-27.56	-11.24	-4.61	-18.71
12	Pyrazine dimer (S)	−18.87	-0.89	-20.43	-30.11	-12.86	-5.74	-20.77
13	Uracil dimer (S)	−41.30	0.38	-28.48	-41.50	-20.49	-10.59	-31.14
14	Indole$\cdots$Benzene (S)	−21.67	-3.88	-29.17	-40.49	-20.45	-10.15	-28.27
15	Adenine$\cdots$Thymine (S)	−51.13	-2.40	-44.05	-59.26	-36.01	-20.36	-46.31
16	Ethene$\cdots$Ethyne	−6.23	2.81	-0.64	-4.93	0.64	2.00	-3.73
17	Benzene$\cdots$Water	−13.68	3.64	-5.15	-10.95	-3.77	-1.41	-9.82
18	Benzene$\cdots$Ammonia	−9.83	1.94	-5.65	-11.39	-4.35	-2.08	-10.10
19	Benzene$\cdots$HCN	−18.91	3.88	-7.09	-13.45	-6.32	-3.09	-12.56
20	Benzene dimer (TS)	−11.72	0.25	-10.42	-17.62	-8.48	-4.53	-14.79
21	Indole$\cdots$Benzene (TS)	−24.02	1.05	-14.86	-23.64	-11.65	-6.55	-19.80
22	Phenole dimer (HB)	−29.50	7.53	-12.12	-20.29	-12.36	-5.98	-19.55
	MD		7.87	-10.05	-17.82	-9.54	-2.81	-15.59
	MAD		8.65	10.25	17.82	9.69	4.72	15.59

Table II: Errors between sDFT- and reference CCSD(T)/CBS (from Ref. [18]) interaction energies for the S66 [20] test set. Errors are defined as $\Delta E = E_{\rm int}^{\rm ref} - E_{\rm int}^{\rm DFT}$, where $E_{\rm int}^{\rm DFT}$ refers to the interaction energy derived from KS-DFT or sDFT. Errors from KS-DFT have been included for comparison. All values are given in kJ/mol. The "Peptide" is N-methylacetamide. (TS) stands for T-shaped. The mean deviation and mean absolute deviation are denoted as MD and MAD, repectively.

			Errors with respect to $E_{\rm int}^{\rm ref}$					
			KS-DFT			sDFT		
No.	Complex	$E_{\rm int}^{\rm ref}$ [18]	LDA	PW91	BP86	LDA/TF	PW91/PW91k	BP86/LLP91
1	Water-Water	−20.46	10.16	0.63	−3.95	−1.95	0.98	−6.51
2	Water-MeOH	−23.30	10.94	−0.56	−5.91	−4.07	−0.33	−8.99
3	Water-$MeNH_2$	−28.79	14.24	1.88	−2.79	−2.55	1.16	−7.00
4	Water-Peptide	−33.81	13.79	−2.04	−8.37	−5.94	−0.72	−11.39
5	MeOH-MeOH	−24.06	10.58	−1.32	−7.18	−5.49	−1.14	−10.49
6	MeOH-$MeNH_2$	−31.55	14.78	0.13	−6.44	−5.15	0.11	−10.75
7	MeOH-Peptide	−34.39	14.45	−2.55	−9.49	−7.54	−1.27	−12.97
8	MeOH-Water	−20.92	9.98	0.07	−4.96	−3.03	0.42	−7.69
9	$MeNH_2$-MeOH	−12.72	5.49	−2.00	−8.34	−1.94	0.84	−8.05
10	$MeNH_2$-$MeNH_2$	−17.36	9.22	−3.09	−9.86	−2.49	1.30	−8.97
11	$MeNH_2$-Peptide	−22.64	8.56	−6.83	−14.71	−5.02	−0.29	−12.51
12	$MeNH_2$-Water	−30.33	14.97	0.67	−4.94	−4.20	0.44	−9.06
13	Peptide-MeOH	−25.86	8.39	−5.24	−12.34	−5.31	−1.07	−12.02
14	Peptide-$MeNH_2$	−31.17	11.70	−3.70	−10.95	−3.68	1.28	−10.26
15	Peptide-Peptide	−36.07	9.62	−7.56	−15.69	−6.68	−0.86	−13.89
16	Peptide-Water	−21.42	7.30	−2.29	−7.99	−1.81	1.13	−7.49
17	Uracil-Uracil	−71.88	23.76	−4.39	−12.30	−10.57	0.88	−14.97
18	Water-Pyridine	−28.58	13.31	1.19	−3.83	−2.87	1.20	−7.11
19	MeOH-Pyridine	−30.96	13.14	−0.40	−6.30	−5.73	−0.36	−10.06
20	AcOH-AcOH	−79.87	34.16	1.03	−6.21	−21.00	−6.14	−22.39
21	$AcNH_2$-$AcNH_2$	−68.03	24.08	−2.81	−9.97	−6.01	3.23	−11.37
22	AcOH-Uracil	−81.55	29.00	−1.98	−9.45	−15.94	−2.66	−18.71
23	$AcNH_2$-Uracil	−80.29	25.23	−3.57	−11.14	−9.60	1.36	−14.17
24	Benzene-Benzene	−11.46	−1.24	−17.59	−26.87	−10.06	−3.68	−17.63
25	Pyridine-Pyridine	−16.02	−0.38	−18.46	−28.04	−10.51	−3.82	−18.44
26	Uracil-Uracil	−41.09	0.59	−28.27	−41.28	−20.70	−10.80	−31.35
27	Benzene-Pyridine	−14.10	−0.62	−18.00	−27.44	−10.28	−3.70	−18.03
28	Benzene-Uracil	−23.89	−1.25	−24.68	−35.98	−17.73	−8.88	−26.62
29	Pyridine-Uracil	−28.49	−0.69	−24.40	−35.63	−17.30	−8.67	−26.36
30	Benzene-Ethene	−5.90	1.99	−8.40	−15.49	−4.92	−0.75	−10.99
31	Uracil-Ethene	−14.14	1.86	−10.97	−19.20	−7.23	−2.47	−14.51
32	Uracil-Ethyne	−15.65	2.27	−9.94	−17.64	−6.13	−1.31	−12.66
33	Pyridine-Ethene	−7.78	2.40	−8.69	−15.94	−5.31	−0.96	−11.54
34	Pentane-Pentane	−15.77	5.30	−15.24	−27.91	−11.07	−5.30	−23.92
35	Neopentane-Pentane	−10.92	3.79	−9.68	−19.26	−6.80	−3.14	−16.67
36	Neopentane-Neopentane	−7.41	2.35	−6.02	−13.77	−3.36	−1.22	−11.60
37	Cyclopentane-Neopentane	−10.08	4.27	−9.34	−18.41	−6.26	−2.62	−15.63
38	Cyclopentane-Cyclopentane	−12.55	4.42	−11.18	−21.25	−8.95	−4.38	−19.01
39	Benzene-Cyclopentane	−14.94	1.88	−15.00	−24.70	−11.00	−5.04	−19.56
40	Benzene-Neopentane	−12.09	1.65	−10.96	−19.45	−6.79	−2.86	−15.00
41	Uracil-Pentane	−20.25	2.12	−19.84	−32.10	−15.20	−8.33	−26.69
42	Uracil-Cyclopentane	−17.28	1.28	−17.18	−28.16	−13.47	−7.48	−23.72
43	Uracil-Neopentane	−15.48	1.01	−13.41	−23.17	−9.60	−4.72	−18.69
44	Ethene-Pentane	−8.33	3.40	−6.46	−14.68	−4.77	−1.58	−12.83
45	Ethyne-Pentane	−7.32	2.83	−5.59	−13.13	−3.22	−0.15	−10.35
46	Peptide-Pentane	−17.74	4.56	−15.03	−27.00	−11.29	−5.33	−23.05
47	Benzene-Benzene (TS)	−12.01	0.80	−10.88	−18.34	−8.06	−4.06	−14.86
48	Pyridine-Pyridine (TS)	−14.77	1.72	−11.24	−18.74	−7.81	−3.93	−15.03
49	Benzene-Pyridine (TS)	−13.89	1.16	−10.96	−18.48	−8.14	−4.16	−15.09
50	Benzene-Ethyne	−11.97	2.35	−6.63	−12.83	−5.27	−2.37	−11.24
51	Ethyne-Ethyne (TS)	−6.36	2.98	−0.39	−4.68	0.57	2.12	−3.58
52	Benzene-AcOH	−19.66	3.66	−9.51	−16.82	−9.72	−5.71	−16.72
53	Benzene-$AcNH_2$	−18.24	4.29	−7.87	−14.96	−4.67	−1.38	−11.94
54	Benzene-Water	−13.68	3.67	−5.16	−10.97	−4.83	−2.49	−10.91
55	Benzene-MeOH	−17.53	4.07	−8.99	−16.87	−8.87	−4.69	−16.42
56	Benzene-$MeNH_2$	−13.51	2.69	−9.32	−17.07	−7.73	−3.68	−14.96
57	Benzene-Peptide	−22.09	2.39	−14.32	−23.59	−11.15	−5.88	−19.88
58	Pyridine-Pyridine	−17.36	6.71	−4.93	−11.13	−1.63	1.28	−8.26
59	Ethyne-Water	−11.92	5.51	0.01	−4.44	1.02	2.95	−3.44
60	Ethyne-AcOH	−20.33	9.87	−2.12	−8.16	−2.43	1.73	−7.95
61	Pentane-AcOH	−12.05	2.97	−9.66	−19.69	−7.01	−3.00	−16.99
62	Pentane-$AcNH_2$	−14.69	4.37	−10.99	−21.28	−8.05	−3.57	−18.39
63	Benzene-AcOH	−15.90	1.59	−12.57	−21.34	−8.76	−3.89	−16.82
64	Peptide-Ethene	−12.51	3.78	−6.90	−14.87	−4.32	−0.95	−12.19
65	Pyridine-Ethyne	−16.69	7.39	0.03	−4.62	2.53	5.00	−2.07
66	$MeNH_2$-Pyridine	−16.61	5.40	−8.10	−15.74	−6.77	−2.18	−13.64
	MD		6.94	−7.87	−15.67	−7.15	−2.07	−14.12
	MAD		7.07	8.04	15.67	7.27	2.90	14.12

2.1 Promotion energies

As explained in the main text, the promotion energy should always be positive. This can clearly be seen in all cases studied here. Exceptions are the methane dimer (Tab. III) with sDFT-PW91/PW91k and the neopentane dimer (Tab. IV) with sDFT-LDA/TF. The negative sign can be attributed to different numerical grids used in the respective calculations: The energy of the isolated monomer $E^{\mathrm{KS}}[\rho_I^{\mathrm{iso}}]$ was calculated on a mono-molecular grid. The polarized subsystem energies $E^{\mathrm{KS}}[\rho_I]$ in the sDFT calculations were calculated on a super-molecular grid, because we aimed for accurate interaction energies. If we use a mono-molecular grid, we get a promotion energy $\Delta E^{\mathrm{prom}}_{\mathrm{monomers}} = 0.01$ kJ/mol for both examples with the respective approximations. In these examples the error of the employed grid introduces an error of the order of 10^{-2} kJ/mol.

Table III: Promotion energies $\Delta E^{\mathrm{prom}}_{\mathrm{monomers}}$ from sDFT for the S22 [19] test set. All values are given in kJ/mol. "2-PY" and "2-PO" are 2-pyridoxine and 2-aminopyridine, respectively. (HB), (S) and (TS) stand for hydrogen-bonded, stacked and T-shaped, respectively.

		Monomer polarization energy		
No.	Complex	LDA/TF	PW91/PW91k	BP86/LLP91
1	Ammonia dimer	2.10	1.92	1.76
2	Water dimer	5.04	4.72	4.28
3	Formic acid dimer	52.37	50.14	47.73
4	Formamide dimer	33.66	31.79	30.00
5	Uracil dimer (HB)	42.99	41.22	39.37
6	2-PY$\cdots$2-PO	36.59	34.75	32.88
7	Adenine$\cdots$Thymine	32.52	31.20	29.49
8	Methane dimer	0.01	-0.01	0.10
9	Ethene dimer	0.12	0.14	0.35
10	Benzene$\cdots$Methane	0.69	0.58	0.59
11	Benzene dimer (S)	3.77	3.57	3.62
12	Pyrazine dimer (S)	0.67	0.61	1.18
13	Uracil dimer (S)	2.92	2.90	3.87
14	Indole$\cdots$Benzene (S)	5.07	4.71	4.66
15	Adenine$\cdots$Thymine (S)	4.67	4.38	5.06
16	Ethene$\cdots$Ethyne	0.98	0.91	1.05
17	Benzene$\cdots$Water	0.77	0.58	0.79
18	Benzene$\cdots$Ammonia	1.04	0.90	1.02
19	Benzene$\cdots$HCN	4.00	3.71	4.05
20	Benzene dimer (TS)	1.52	1.28	1.31
21	Indole$\cdots$Benzene (TS)	3.39	2.97	3.49
22	Phenole dimer (HB)	8.92	8.37	8.05
	Average $\Delta E^{\mathrm{prom}}_{\mathrm{monomers}}$	11.08	10.52	10.21
	Maximum $\Delta E^{\mathrm{prom}}_{\mathrm{monomers}}$	52.37	50.14	47.73

Table IV: Promotion energies $\Delta E^{\text{prom}}_{\text{monomers}}$ from sDFT for the S66 [19] test set. All values are given in kJ/mol. The "Peptide" is N-methylacetamide. (TS) stands for T-shaped.

		Monomer polarization energy		
No.	Complex	LDA/TF	PW91/PW91k	BP86/LLP91
1	Water-Water	5.71	5.31	4.82
2	Water-MeOH	7.81	7.26	6.62
3	Water-$MeNH_2$	10.14	9.48	8.76
4	Water-Peptide	13.43	12.65	11.64
5	MeOH-MeOH	8.77	8.14	7.43
6	MeOH-$MeNH_2$	12.63	11.81	11.03
7	MeOH-Peptide	15.19	14.31	13.13
8	MeOH-Water	6.45	6.00	5.44
9	$MeNH_2$-MeOH	3.17	2.91	2.63
10	$MeNH_2$-$MeNH_2$	5.11	4.62	4.20
11	$MeNH_2$-Peptide	6.38	5.92	5.38
12	$MeNH_2$-Water	11.38	10.59	9.77
13	Peptide-MeOH	8.37	7.66	7.24
14	Peptide-$MeNH_2$	11.90	11.00	10.63
15	Peptide-Peptide	14.20	13.31	12.64
16	Peptide-Water	5.92	5.47	5.09
17	Uracil-Uracil	47.21	45.14	43.06
18	Water-Pyridine	11.17	10.66	9.83
19	MeOH-Pyridine	13.34	12.74	11.81
20	AcOH-AcOH	62.57	59.87	57.06
21	$AcNH_2$-$AcNH_2$	41.69	39.30	37.15
22	AcOH-Uracil	56.99	54.52	52.05
23	$AcNH_2$-Uracil	50.36	47.85	45.61
24	Benzene-Benzene	3.67	3.35	3.35
25	Pyridine-Pyridine	2.98	2.67	3.01
26	Uracil-Uracil	4.43	4.37	5.22
27	Benzene-Pyridine	3.36	3.04	3.20
28	Benzene-Uracil	3.52	3.42	3.78
29	Pyridine-Uracil	3.28	3.20	3.56
30	Benzene-Ethene	1.39	1.24	1.31
31	Uracil-Ethene	1.29	1.35	1.79
32	Uracil-Ethyne	1.50	1.55	1.88
33	Pyridine-Ethene	1.05	0.94	1.12
34	Pentane-Pentane	0.17	0.16	0.77
35	Neopentane-Pentane	0.12	0.14	0.54
36	Neopentane-Neopentane	−0.02	0.02	0.41
37	Cyclopentane-Neopentane	0.12	0.15	0.48
38	Cyclopentane-Cyclopentane	0.10	0.13	0.47
39	Benzene-Cyclopentane	1.84	1.57	1.72
40	Benzene-Neopentane	1.58	1.38	1.56
41	Uracil-Pentane	1.62	1.62	2.40
42	Uracil-Cyclopentane	0.72	0.78	1.42
43	Uracil-Neopentane	0.74	0.85	1.41
44	Ethene-Pentane	0.35	0.34	0.65
45	Ethyne-Pentane	0.74	0.69	0.89
46	Peptide-Pentane	2.62	2.41	2.66
47	Benzene-Benzene (TS)	1.88	1.57	1.61
48	Pyridine-Pyridine (TS)	2.05	1.82	1.94
49	Benzene-Pyridine (TS)	2.44	2.09	2.20
50	Benzene-Ethyne	2.36	2.04	2.23
51	Ethyne-Ethyne (TS)	1.02	0.94	1.01
52	Benzene-AcOH	4.77	4.32	4.43
53	Benzene-$AcNH_2$	4.60	4.24	4.32
54	Benzene-Water	2.23	2.01	2.15
55	Benzene-MeOH	2.78	2.47	2.70
56	Benzene-$MeNH_2$	1.70	1.43	1.59
57	Benzene-Peptide	4.36	4.02	4.51
58	Pyridine-Pyridine	7.15	6.65	5.68
59	Ethyne-Water	3.15	2.88	2.63
60	Ethyne-AcOH	5.53	5.23	4.97
61	Pentane-AcOH	1.06	1.03	1.41
62	Pentane-$AcNH_2$	2.91	2.71	2.86
63	Benzene-AcOH	2.52	2.23	2.40
64	Peptide-Ethene	2.39	2.24	2.27
65	Pyridine-Ethyne	6.24	5.86	5.44
66	$MeNH_2$-Pyridine	2.90	2.65	2.52
	Average $\Delta E^{\text{prom}}_{\text{monomers}}$	8.05	7.58	7.36
	Maximum $\Delta E^{\text{prom}}_{\text{monomers}}$	62.57	59.87	57.06

3 Potential-energy curves from sDFT

The following figures contain potential-energy surfaces for the S22x5 and S66x8 test sets. Note that some of the potential-energy curves (e.g., the BP86 curves for examples 13 and 21 of S22x5) may leave the impression that the energies converge to values below zero for large distances. We analyzed several of those examples and confirmed in all cases tested that this is actually not the case: the potential-energy curves approach zero for large distances (as they should).

Table V: MADs per molecule of sDFT interaction energies with respect to CCSD(T)/CBS reference taken from [18] for the S22x5 [21] test set. MADs from KS-DFT have been included for comparison. All values are given in kJ/mol. "2-PY" and "2-PO" are 2-pyridoxine and 2-aminopyridine, respectively. (HB), (S) and (TS) stand for hydrogen-bonded, stacked and T-shaped, respectively.

		KS-DFT			sDFT		
No.	Complex	LDA	PW91	BP86	LDA/TF	PW91/PW91k	BP86/LLP91
1	Ammonia dimer	4.74	0.27	3.58	0.86	2.69	2.16
2	Water dimer	6.93	0.58	2.97	1.59	0.88	4.61
3	Formic acid dimer	21.67	1.30	5.20	13.15	3.21	15.09
4	Formamide dimer	15.29	1.43	7.25	3.29	3.58	7.59
5	Uracil dimer (HB)	14.51	3.74	10.19	8.55	3.05	12.30
6	2-PY$\cdots$2-PO	15.81	1.86	8.53	3.64	4.06	8.30
7	Adenine$\cdots$Thymine	14.50	3.77	11.04	4.96	3.65	10.12
8	Methane dimer	0.96	0.72	3.24	0.27	0.94	2.45
9	Ethene dimer	2.60	2.30	6.24	1.04	1.15	4.33
10	Benzene$\cdots$Methane	1.36	2.97	6.87	2.27	0.54	5.48
11	Benzene dimer (S)	1.94	10.54	16.57	5.85	3.05	9.40
12	Pyrazine dimer (S)	2.28	11.82	18.16	7.37	2.98	11.10
13	Uracil dimer (S)	3.58	16.39	24.89	12.07	3.75	16.88
14	Indole$\cdots$Benzene (S)	2.88	16.89	24.65	12.01	4.00	15.85
15	Adenine$\cdots$Thymine (S)	4.68	25.64	36.05	21.55	9.19	26.05
16	Ethene$\cdots$Ethyne	1.82	0.35	3.08	0.81	1.51	2.15
17	Benzene$\cdots$Water	2.36	3.12	7.19	2.90	1.17	6.76
18	Benzene$\cdots$Ammonia	1.53	3.35	7.31	2.76	1.04	6.35
19	Benzene$\cdots$HCN	2.64	4.51	9.07	4.19	1.93	8.32
20	Benzene dimer (TS)	1.54	6.54	11.62	5.60	2.78	9.68
21	Indole$\cdots$Benzene (TS)	2.40	9.69	16.13	8.57	5.02	14.13
22	Phenole dimer (HB)	4.94	7.83	14.34	8.28	3.99	13.79
	Average MAD	5.95	6.16	11.55	5.98	2.92	9.68

Table VI: MADs per molecule of sDFT interaction energies with respect to CCSD(T)/CBS reference taken from [18] for the S66x8 [20] test set. MADs from KS-DFT have been included for comparison. All values are given in kJ/mol. The "Peptide" is N-methylacetamide. (TS) stands for T-shaped.

		KS-DFT			sDFT		
No.	Complex	LDA	PW91	BP86	LDA/TF	PW91/PW91k	BP86/LLP91
1	Water-Water	7.12	0.56	3.24	1.38	0.83	4.99
2	Water-MeOH	7.65	0.35	4.77	2.92	0.33	6.88
3	Water-$MeNH_2$	10.16	1.46	2.52	1.78	0.94	5.51
4	Water-Peptide	9.77	1.40	6.80	4.23	0.61	8.90
5	MeOH-MeOH	7.40	0.89	5.72	3.95	0.71	8.00
6	MeOH-$MeNH_2$	10.50	0.21	5.26	3.69	0.62	8.33
7	MeOH-Peptide	10.16	1.82	7.63	5.45	0.91	10.06
8	MeOH-Water	6.99	0.19	3.98	2.15	0.43	5.85
9	$MeNH_2$-MeOH	3.83	1.31	6.22	1.43	0.79	5.93
10	$MeNH_2$-$MeNH_2$	6.35	2.07	7.42	1.81	1.19	6.66
11	$MeNH_2$-Peptide	5.87	4.62	10.75	3.61	1.04	9.12
12	$MeNH_2$-Water	10.61	0.57	4.17	2.96	0.66	7.07
13	Peptide-MeOH	5.81	3.74	9.65	3.94	0.93	9.34
14	Peptide-$MeNH_2$	8.20	2.66	8.72	2.79	1.56	8.22
15	Peptide-Peptide	6.64	5.61	12.45	5.11	1.44	11.12
16	Peptide-Water	5.09	1.52	6.19	1.32	0.95	5.76
17	Uracil-Uracil	16.63	3.48	10.41	7.82	2.47	12.27
18	Water-Pyridine	9.42	0.93	3.29	1.97	1.00	5.55
19	MeOH-Pyridine	9.24	0.34	5.20	4.10	0.56	7.83
20	AcOH-AcOH	24.35	1.18	6.04	14.98	4.51	17.53
21	$AcNH_2$-$AcNH_2$	16.95	2.20	8.44	4.42	3.04	9.42
22	AcOH-Uracil	20.46	1.84	8.46	11.57	2.47	15.04
23	$AcNH_2$-Uracil	17.79	2.94	9.63	7.16	2.72	11.88
24	Benzene-Benzene	1.88	11.98	18.98	6.73	2.91	11.60
25	Pyridine-Pyridine	1.95	12.58	19.87	7.08	3.03	12.32
26	Uracil-Uracil	3.15	19.48	29.78	14.59	6.55	22.10
27	Benzene-Pyridine	1.93	12.27	19.41	6.88	2.97	11.87
28	Benzene-Uracil	2.62	16.94	25.73	12.42	5.17	18.46
29	Pyridine-Uracil	2.87	16.63	25.24	11.97	4.85	17.67
30	Benzene-Ethene	1.80	5.61	10.91	3.34	1.15	7.37
31	Uracil-Ethene	1.92	7.48	13.81	5.17	1.57	10.23
32	Uracil-Ethyne	2.10	6.73	12.67	4.30	1.41	8.84
33	Pyridine-Ethene	2.07	5.80	11.33	3.71	1.05	7.97
34	Pentane-Pentane	4.47	10.68	20.57	8.26	3.31	17.39
35	Neopentane-Pentane	3.34	6.78	14.14	5.08	1.85	12.02
36	Neopentane-Neopentane	2.10	4.23	10.12	2.57	0.82	8.45
37	Cyclopentane-Neopentane	3.53	6.57	13.60	4.72	1.54	11.37
38	Cyclopentane-Cyclopentane	3.71	7.66	15.46	6.58	2.69	13.66
39	Benzene-Cyclopentane	2.41	10.29	17.73	7.82	2.93	13.71
40	Benzene-Neopentane	1.96	7.62	14.12	4.91	1.85	10.63
41	Uracil-Pentane	2.98	13.48	22.78	10.84	5.22	18.69
42	Uracil-Cyclopentane	2.52	11.91	20.40	9.81	4.74	16.91
43	Uracil-Neopentane	2.14	9.34	16.80	7.04	2.90	13.34
44	Ethene-Pentane	2.77	4.40	10.68	3.57	0.82	9.24
45	Ethyne-Pentane	2.31	3.78	9.43	2.32	0.71	7.23
46	Peptide-Pentane	3.81	10.46	19.86	8.37	3.49	16.90
47	Benzene-Benzene (TS)	1.77	7.68	13.43	5.87	2.53	10.61
48	Pyridine-Pyridine (TS)	2.16	7.99	13.89	5.81	2.60	11.01
49	Benzene-Pyridine (TS)	1.92	7.77	13.56	5.95	2.64	10.82
50	Benzene-Ethyne	2.12	4.60	9.33	3.81	1.51	7.94
51	Ethyne-Ethyne (TS)	2.11	0.31	3.40	0.63	1.70	2.49
52	Benzene-AcOH	2.98	6.78	12.58	7.12	3.96	12.34
53	Benzene-$AcNH_2$	3.17	5.56	11.20	3.52	1.28	8.98
54	Benzene-Water	2.69	3.57	8.10	3.49	1.56	7.90
55	Benzene-MeOH	3.19	6.24	12.47	6.43	3.09	11.98
56	Benzene-$MeNH_2$	2.26	6.36	12.29	5.49	2.26	10.62
57	Benzene-Peptide	2.67	10.08	17.30	8.07	3.70	14.23
58	Pyridine-Pyridine	4.95	3.21	7.97	1.18	2.11	5.40
59	Ethyne-Water	3.85	0.16	3.34	0.75	2.26	2.57
60	Ethyne-AcOH	6.88	1.37	6.27	1.78	1.45	6.02
61	Pentane-AcOH	2.51	6.68	14.47	5.22	1.94	12.49
62	Pentane-$AcNH_2$	3.53	7.58	15.70	5.98	2.22	13.51
63	Benzene-AcOH	2.04	8.64	15.37	6.22	2.30	11.80
64	Peptide-Ethene	2.84	4.70	10.88	3.17	0.80	8.86
65	Pyridine-Ethyne	5.15	0.21	3.61	1.85	3.71	2.06
66	$MeNH_2$-Pyridine	3.90	5.63	11.82	5.00	1.41	10.26
	Average MAD	5.45	5.60	11.63	5.24	2.11	10.32

3.1 S22x5 Potential energy surfaces

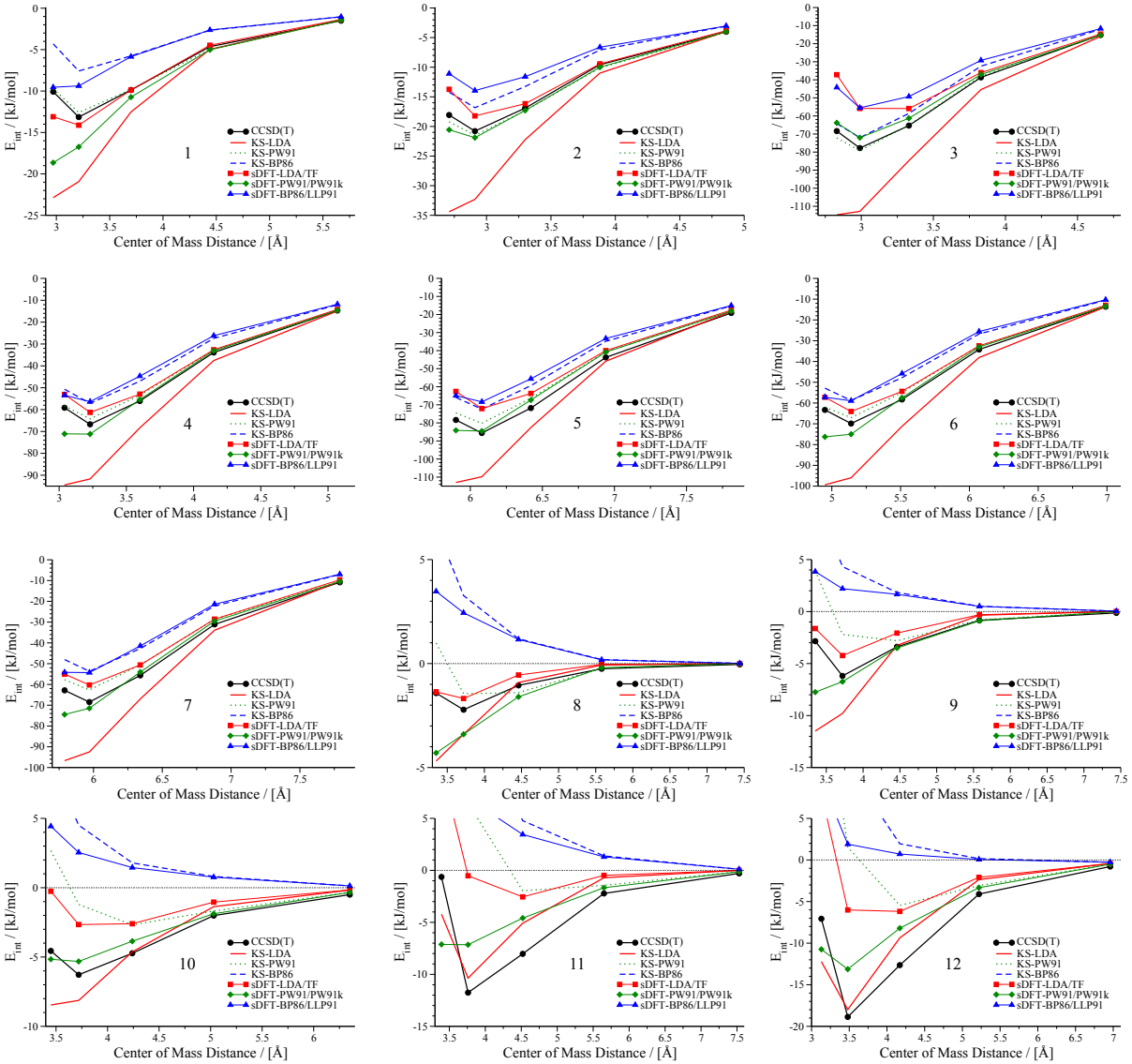

Figure 2: PESs for complexes no. 1–12 of the S22x5 test set.

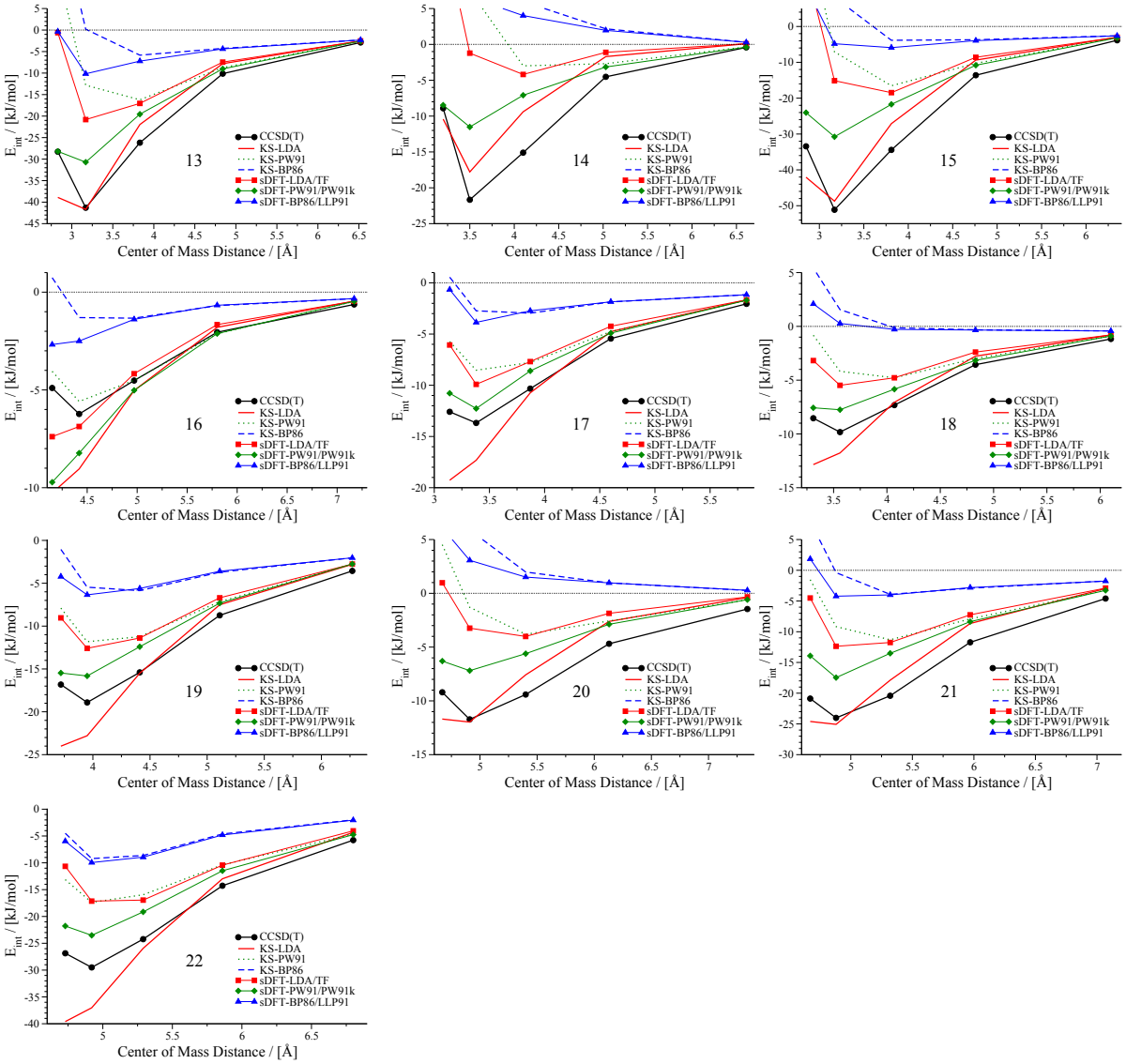

Figure 3: PESs for complexes no. 13–22 of the S22x5 test set.

3.2 S66x8 Potential energy surfaces

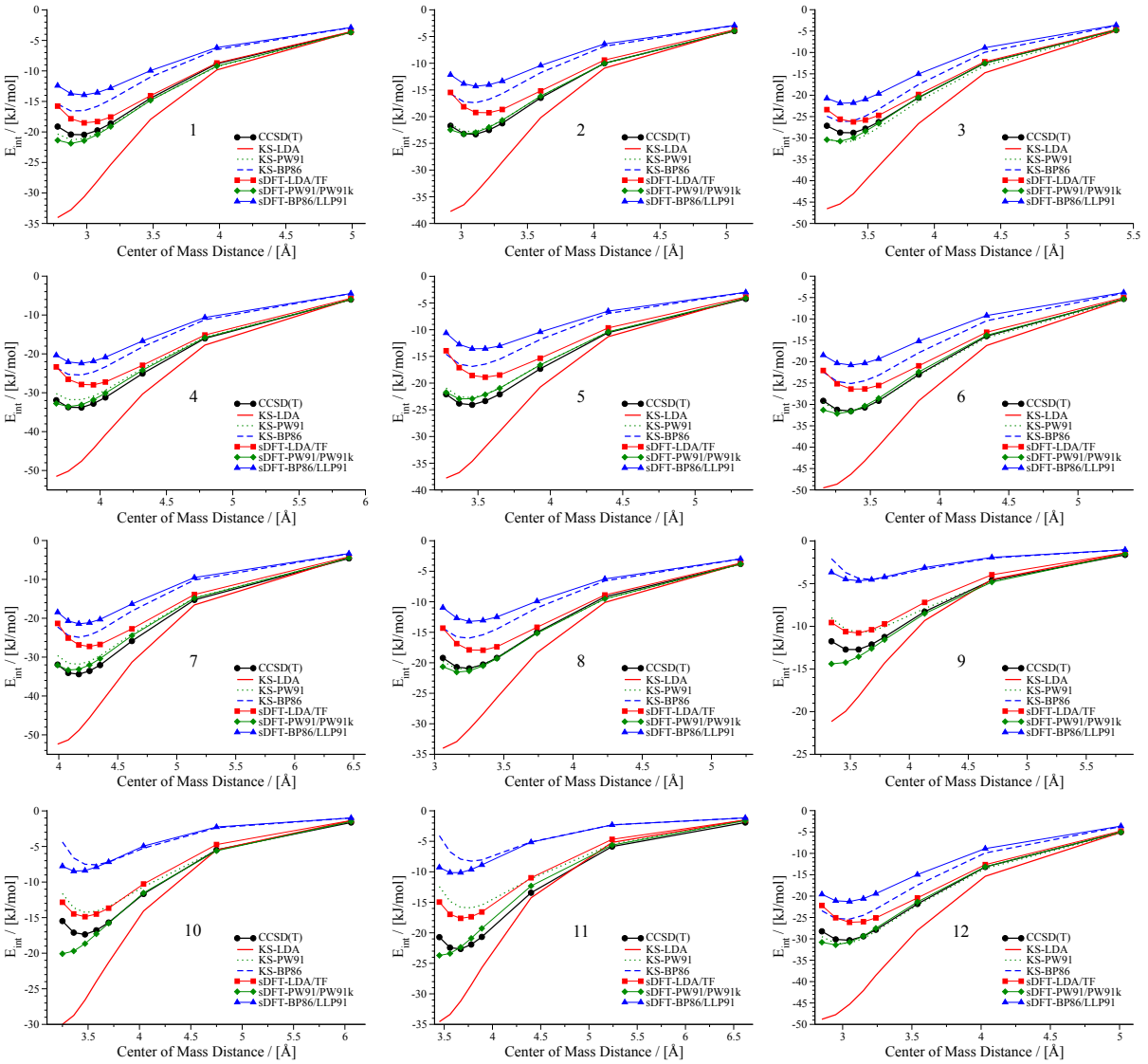

Figure 4: PESs for complexes no. 1–12 of the S66x8 test set.

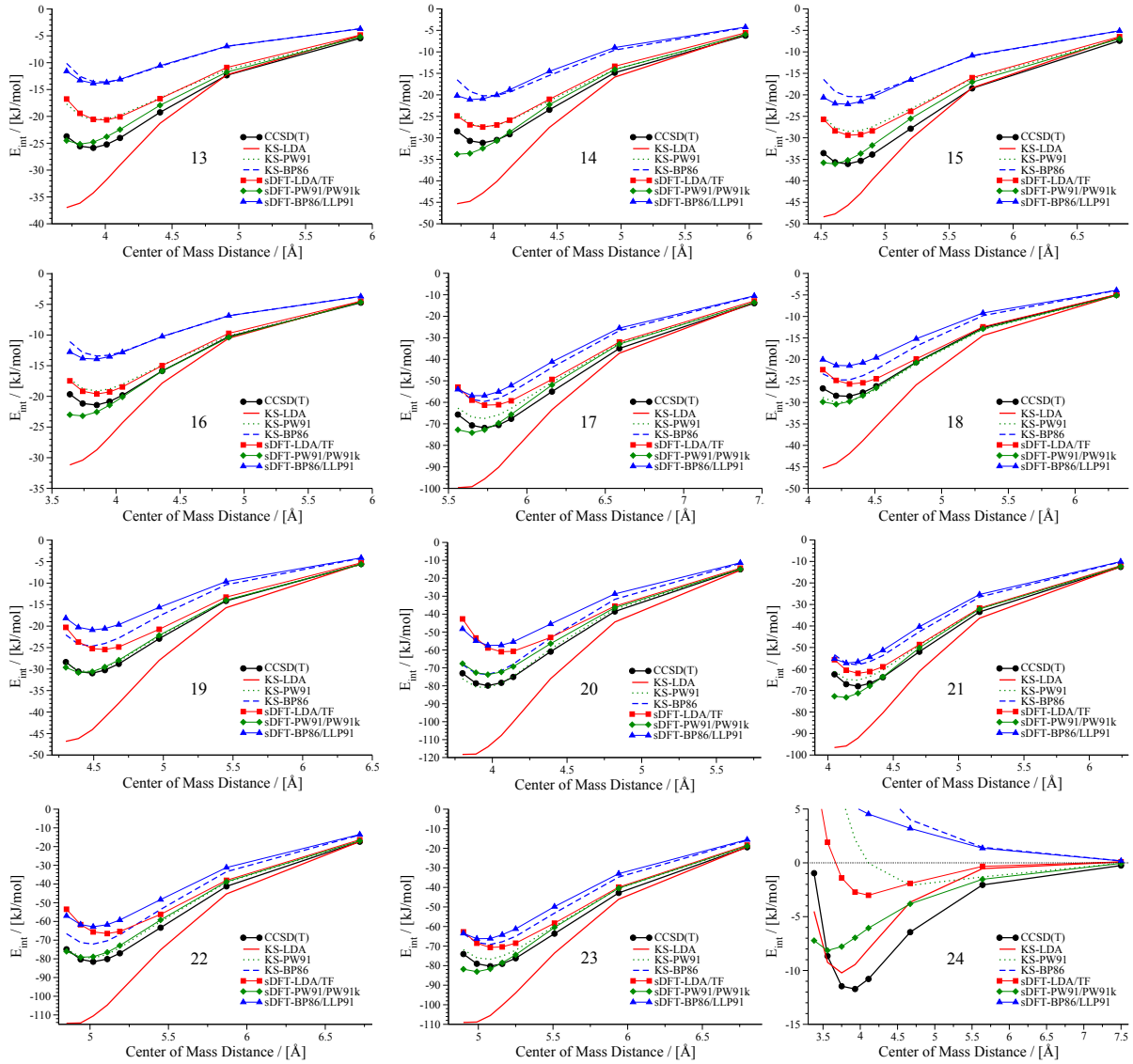

Figure 5: PESs for complexes no. 13–24 of the S66x8 test set.

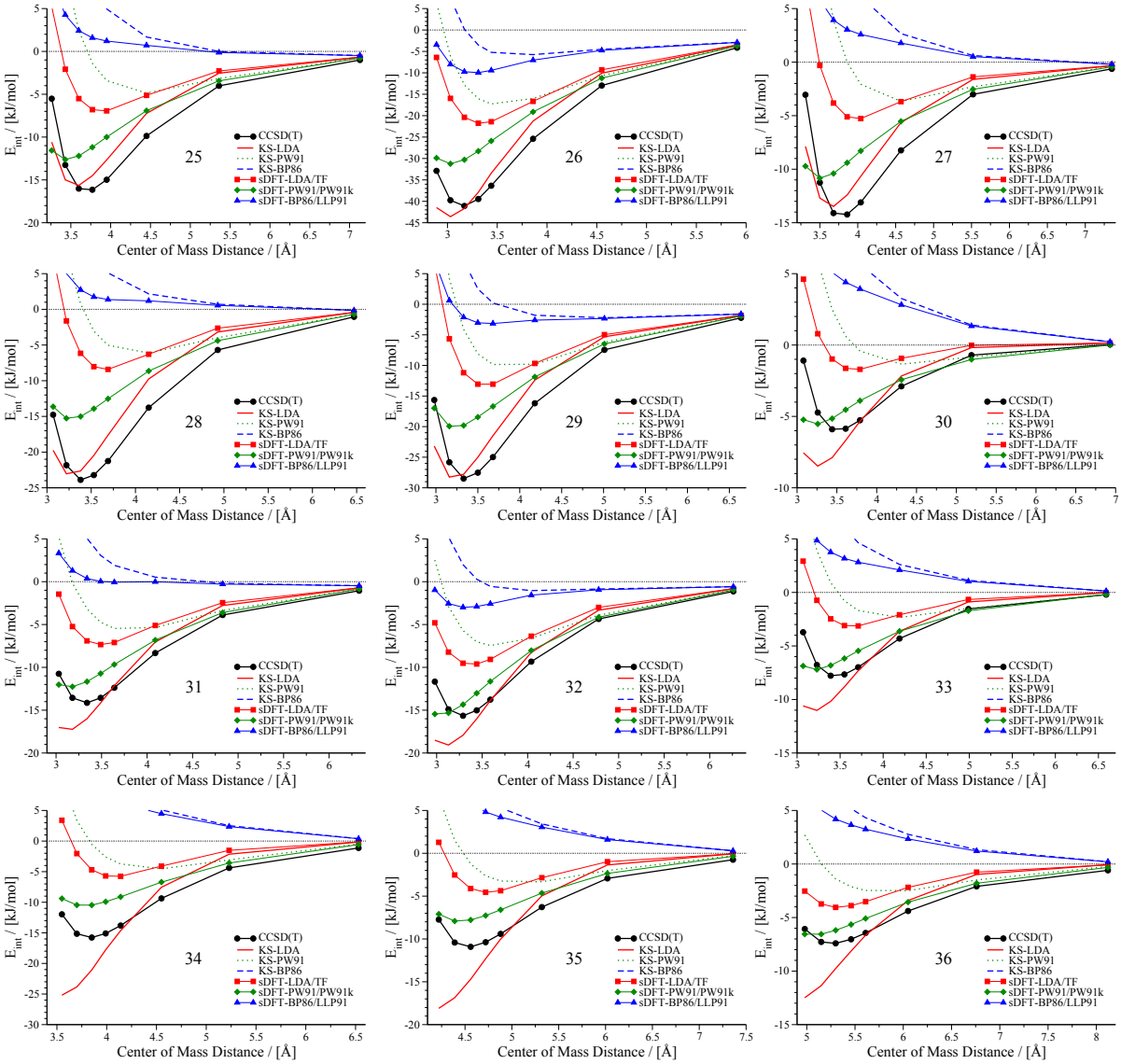

Figure 6: PESs for complexes no. 25–36 of the S66x8 test set.

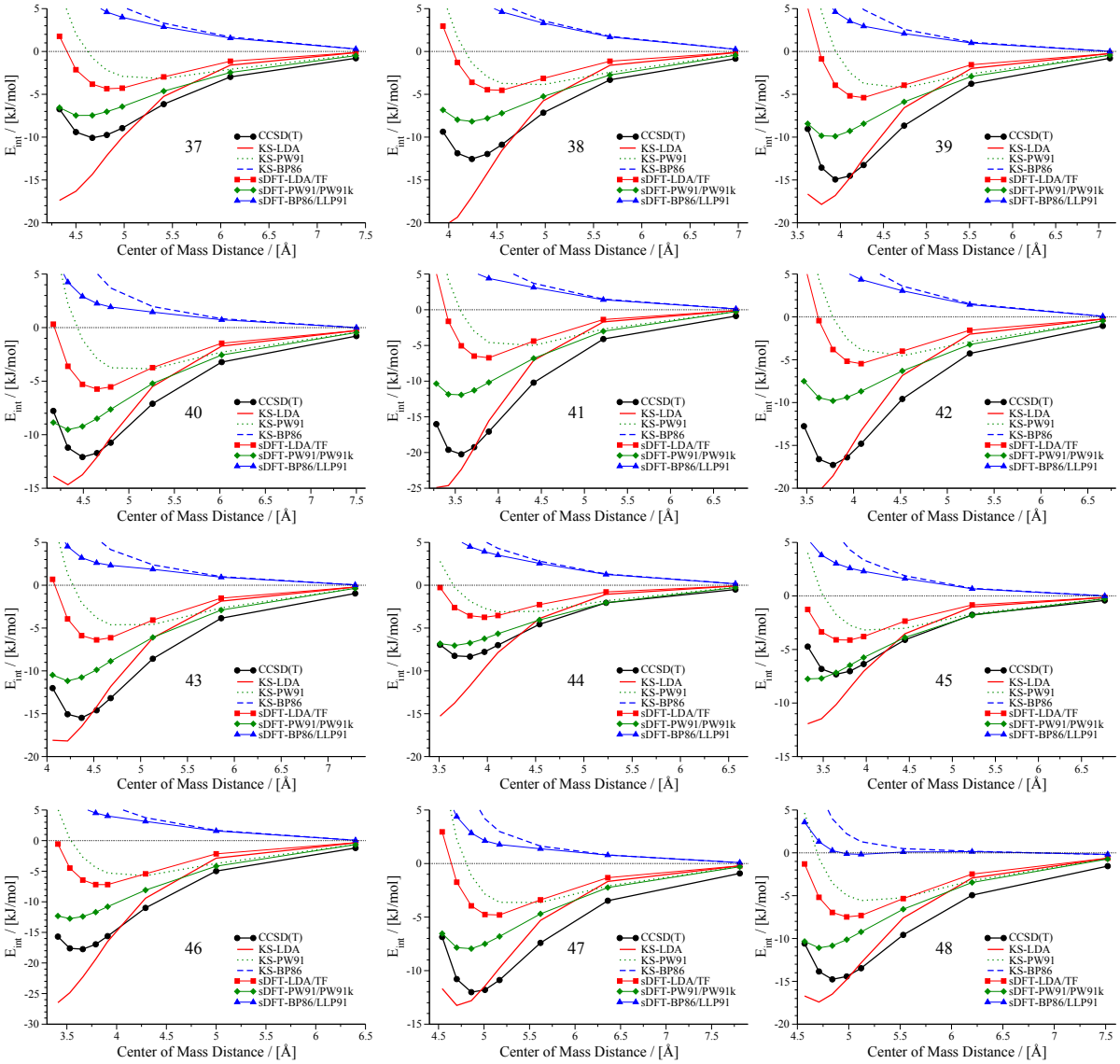

Figure 7: PESs for complexes no. 37–48 of the S66x8 test set.

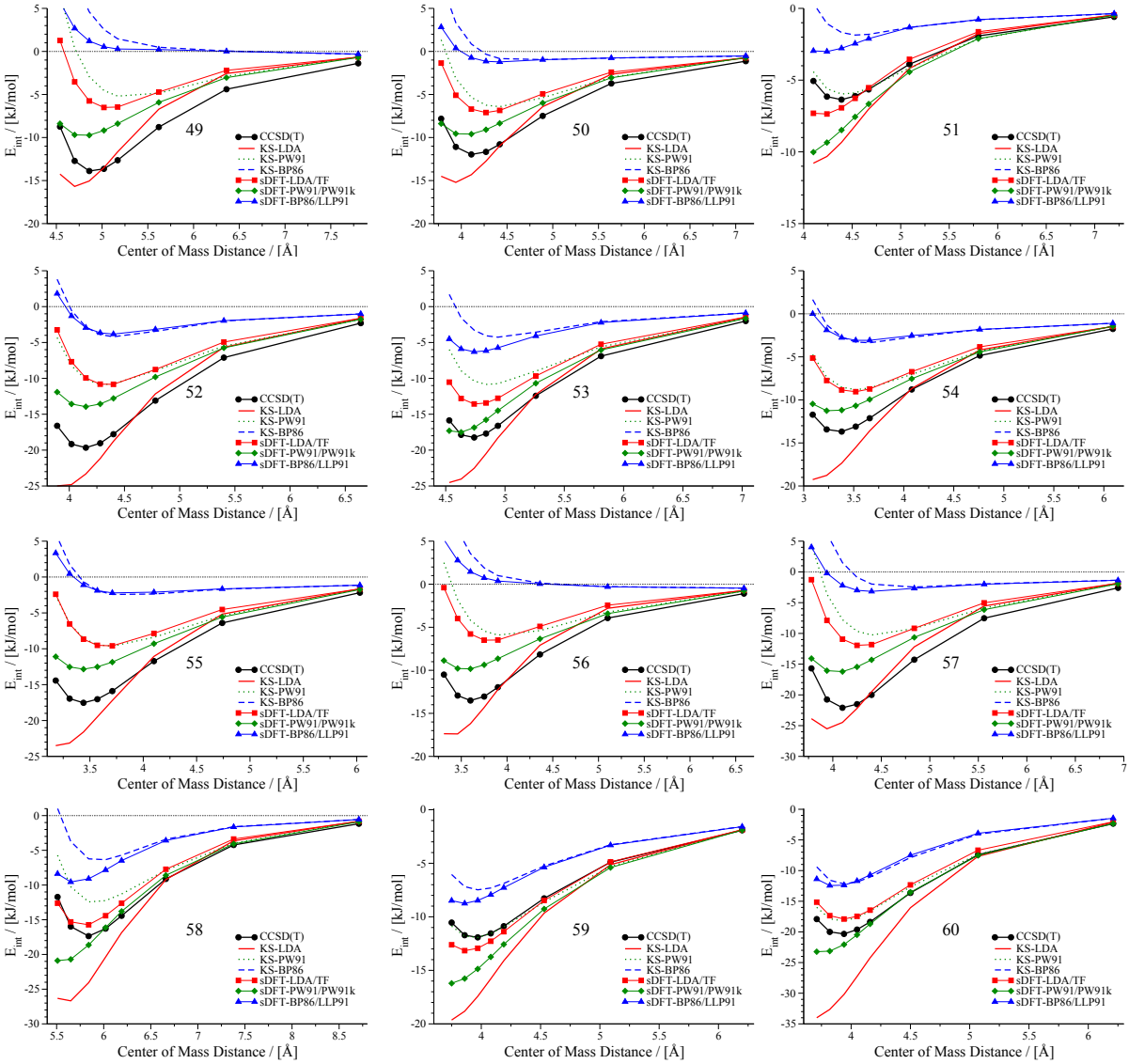

Figure 8: PESs for complexes no. 49–60 of the S66x8 test set.

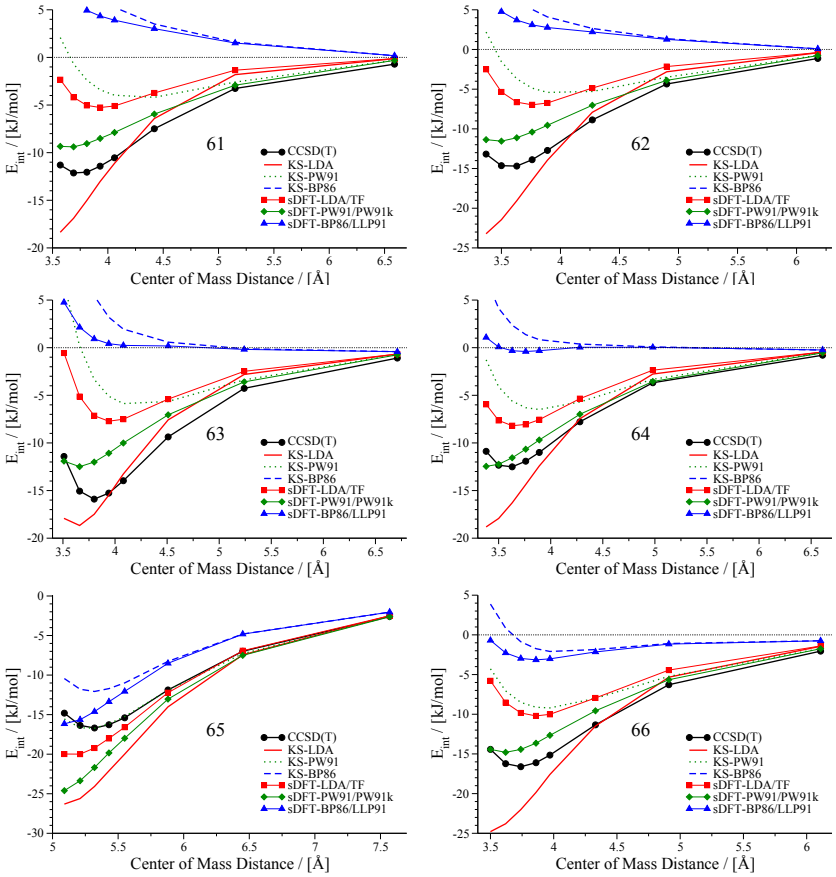

Figure 9: PESs for complexes no. 61–66 of the S66x8 test set.

4 sDFT-D3(BJ) Potential energy surfaces

4.1 Dispersion-corrected sDFT PESs for the S22x5 test set

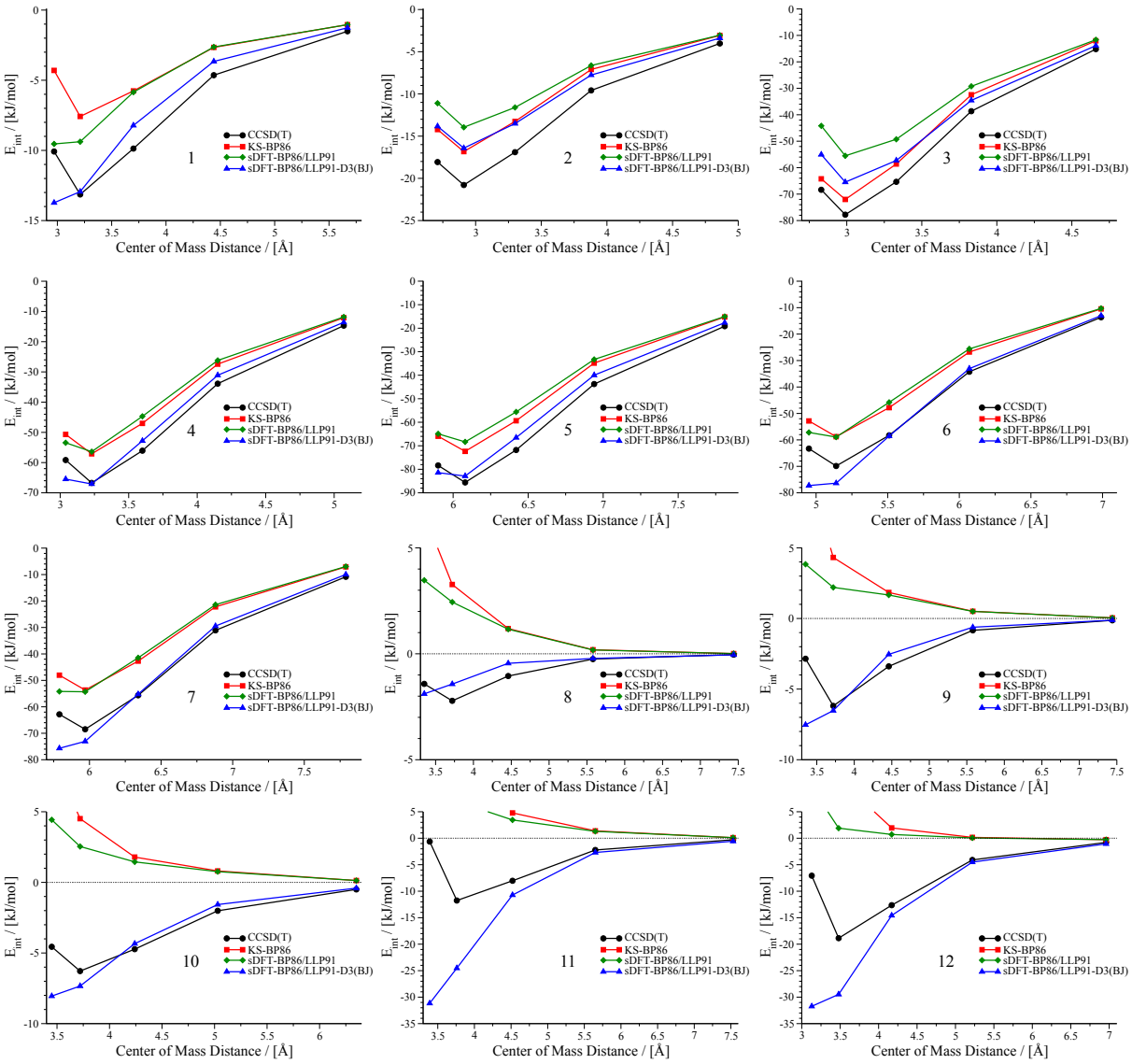

Figure 10: PESs for complexes no. 1–12 of the S22x5 test set.

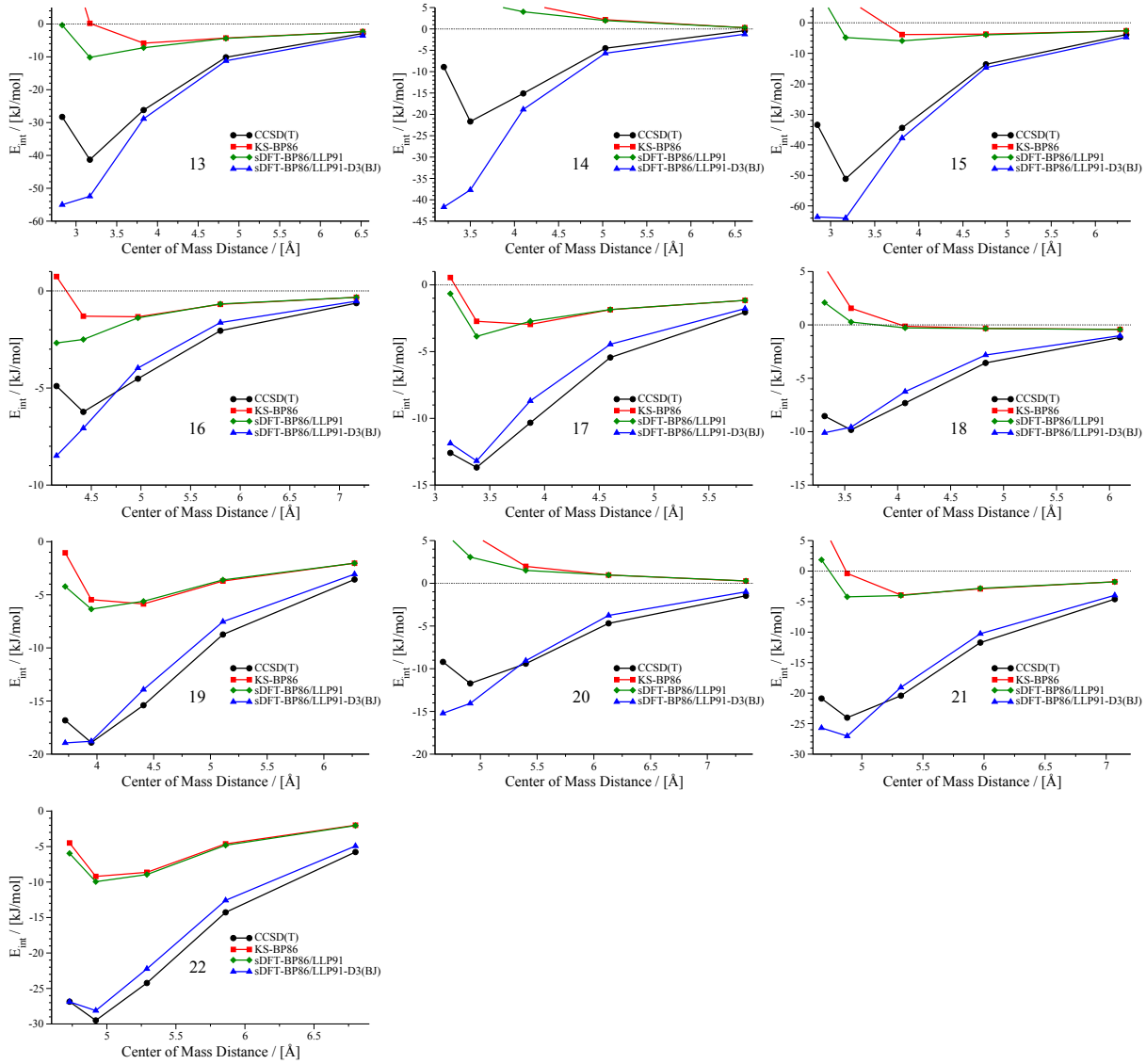

Figure 11: PESs for complexes no. 13–22 of the S22x5 test set.

4.2 Dispersion-corrected sDFT PESs for the S66x8 test set

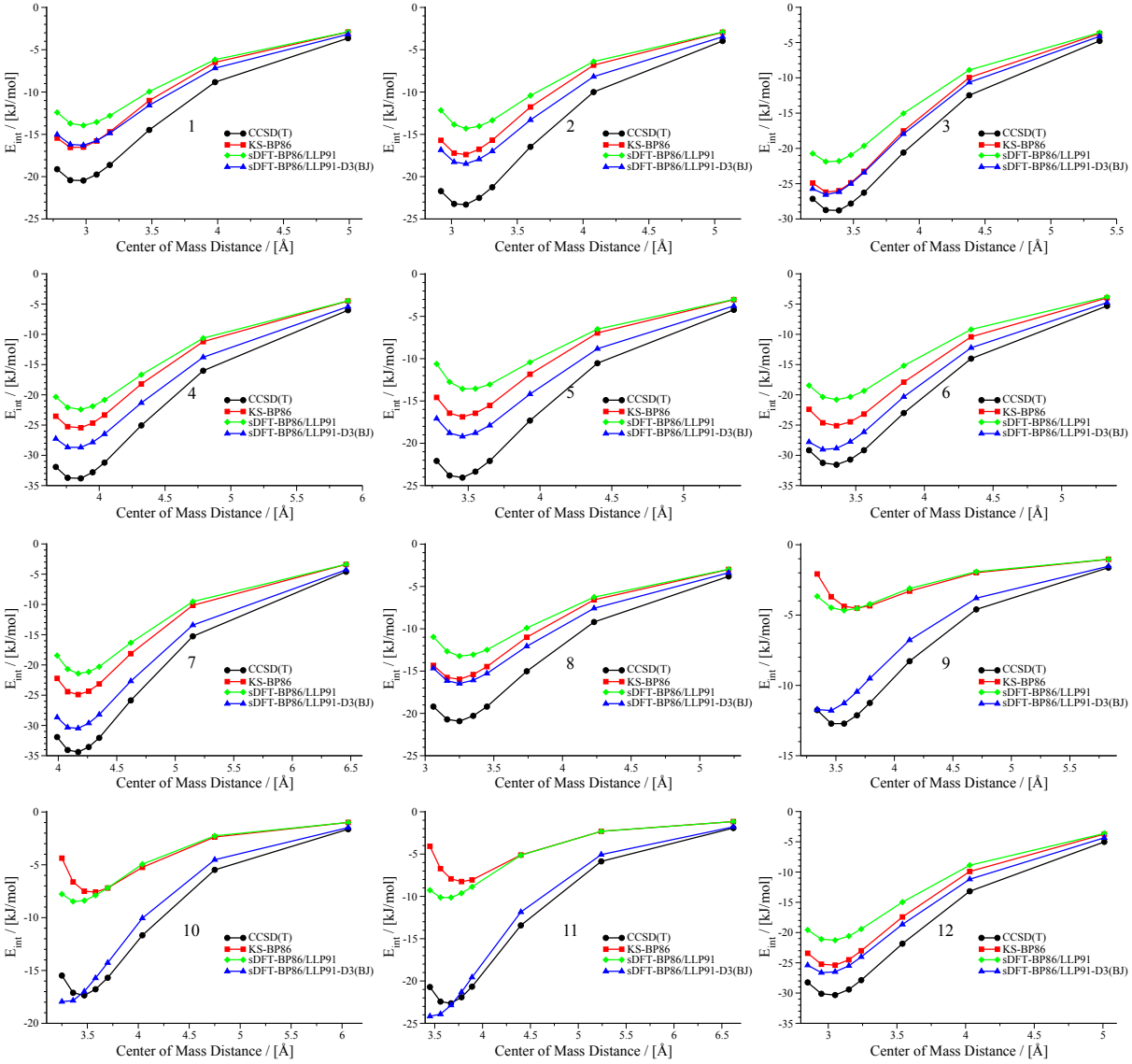

Figure 12: PESs for complexes no. 1–12 of the S66x8 test set.

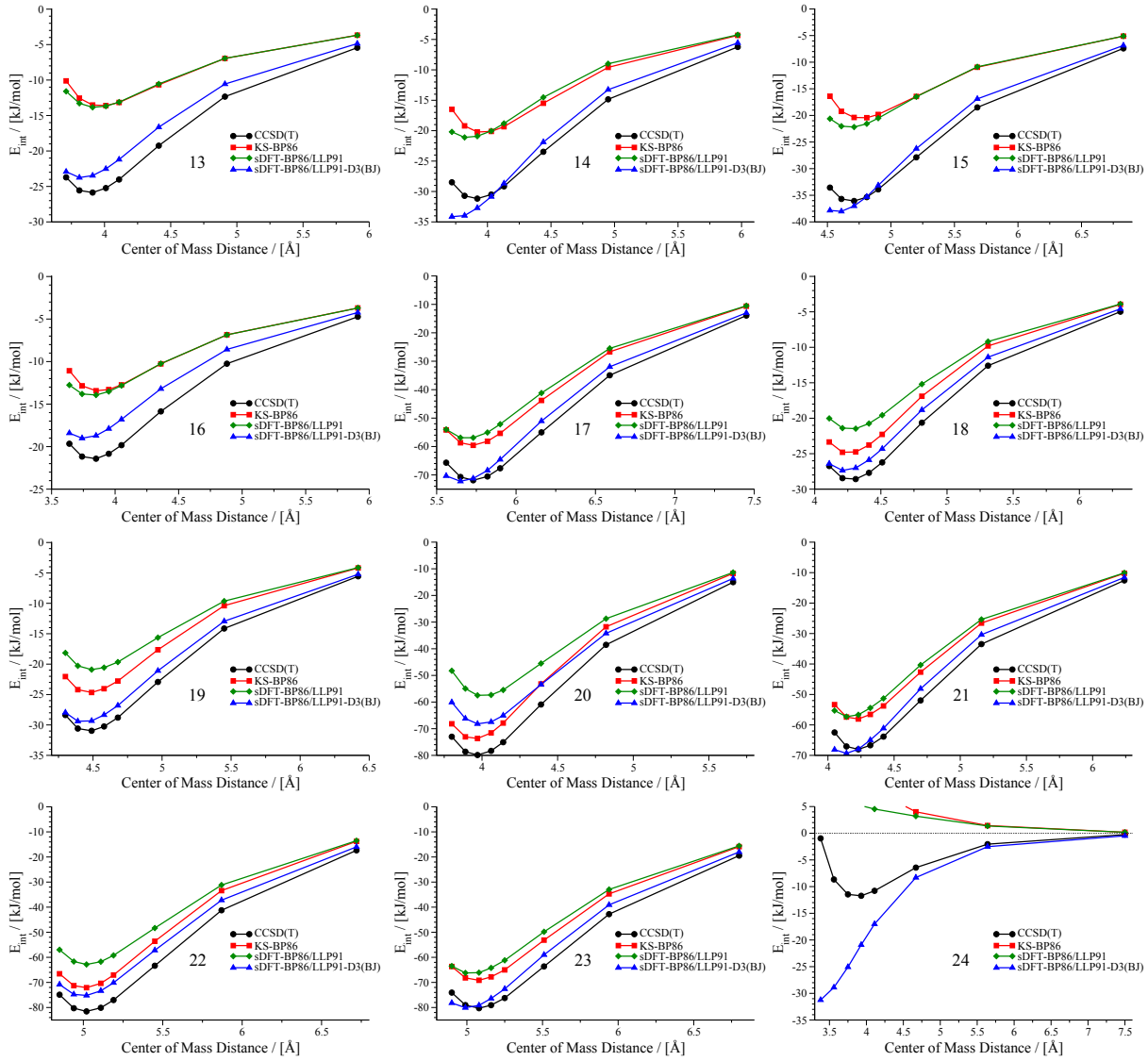

Figure 13: PESs for complexes no. 13–24 of the S66x8 test set.

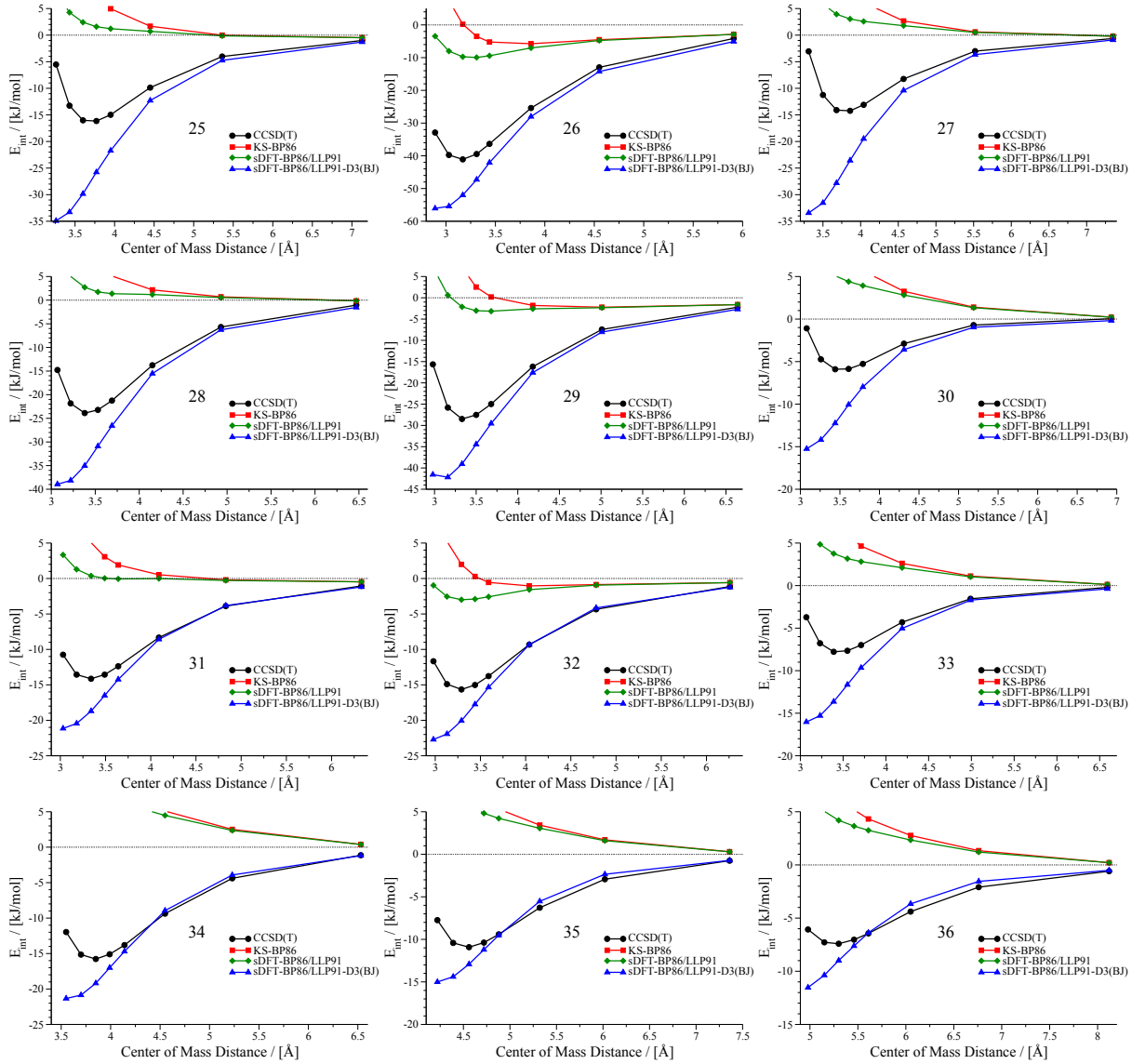

Figure 14: PESs for complexes no. 25–36 of the S66x8 test set.

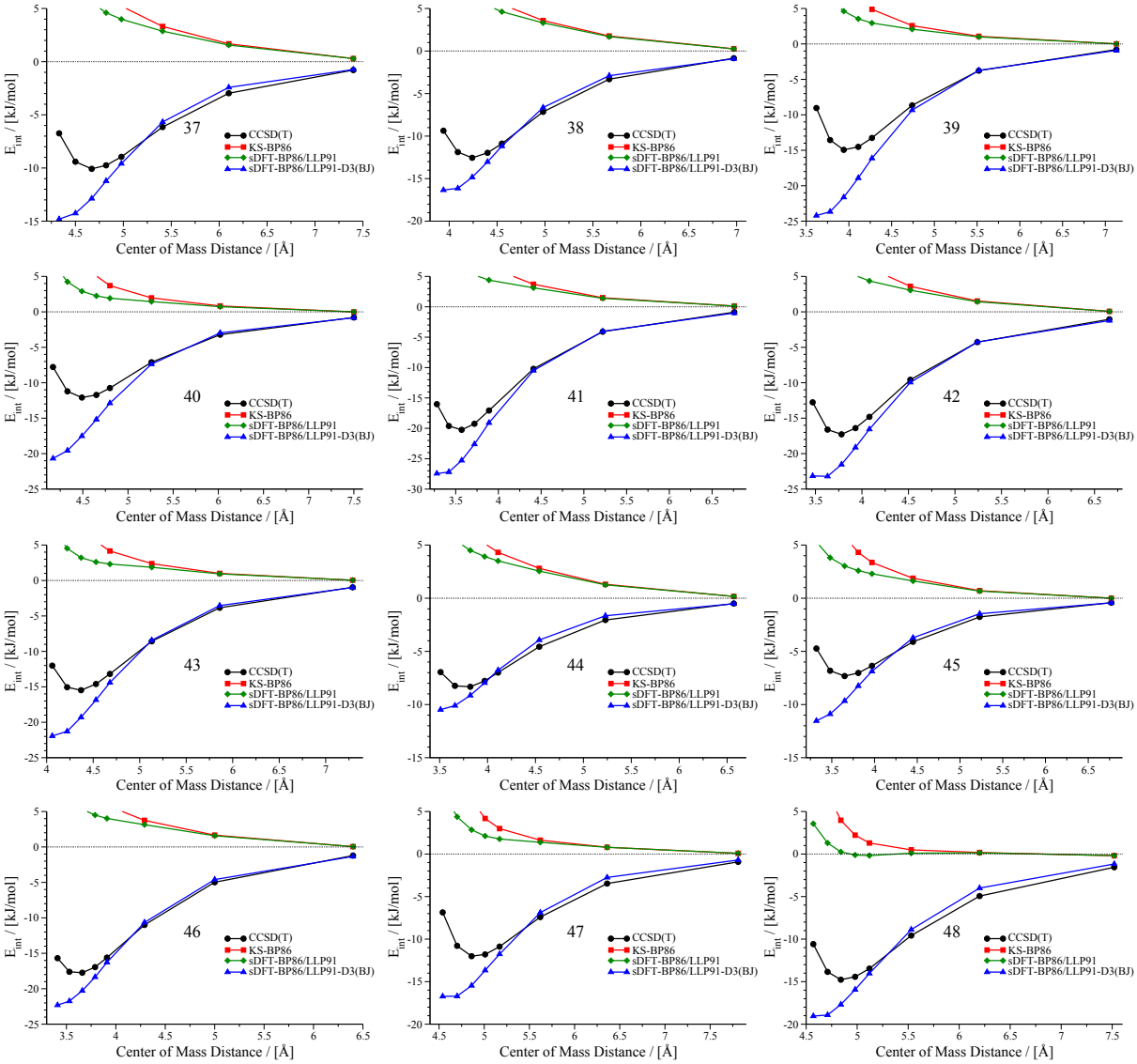

Figure 15: PESs for complexes no. 37–48 of the S66x8 test set.

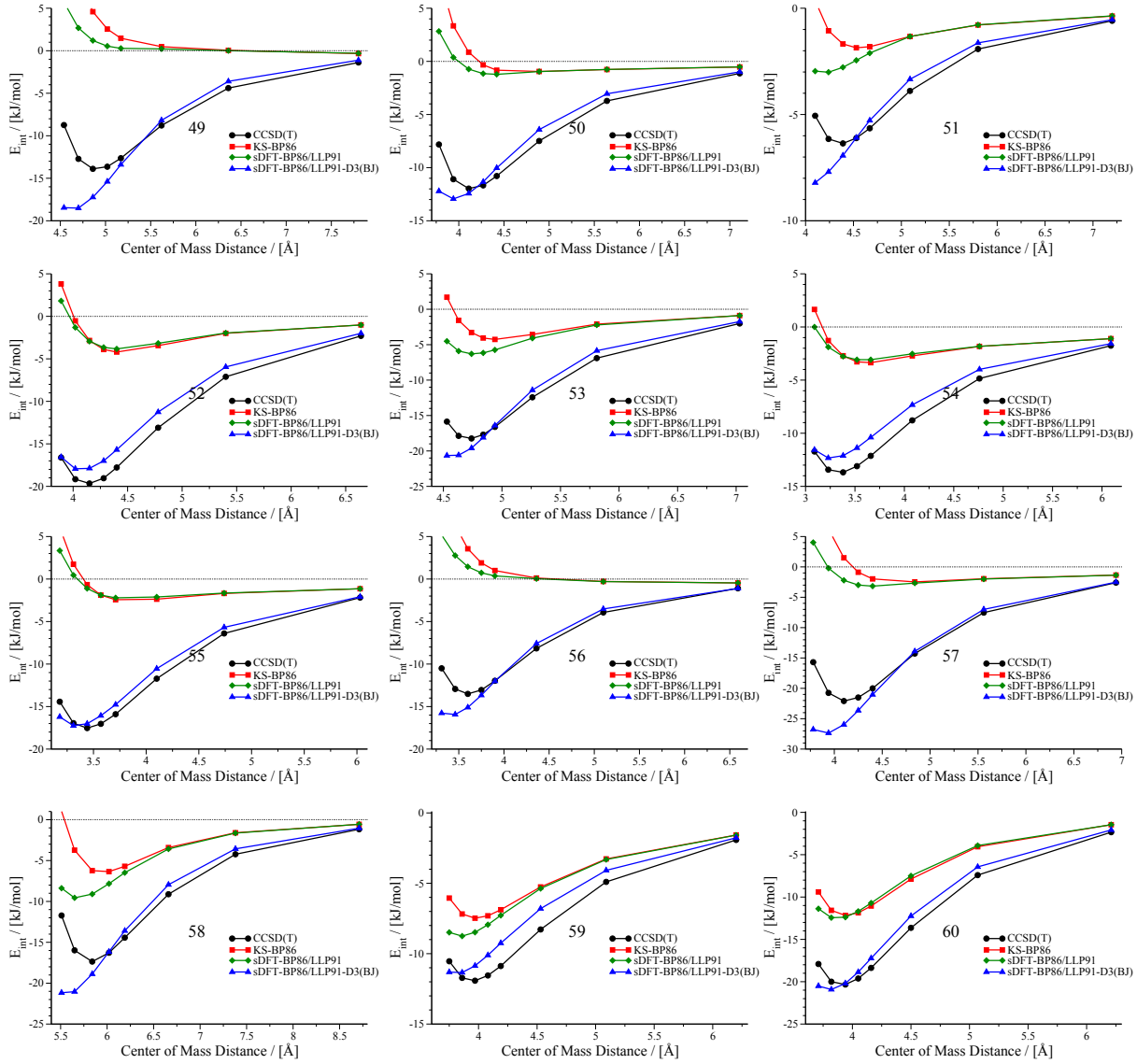

Figure 16: PESs for complexes no. 49–60 of the S66x8 test set.

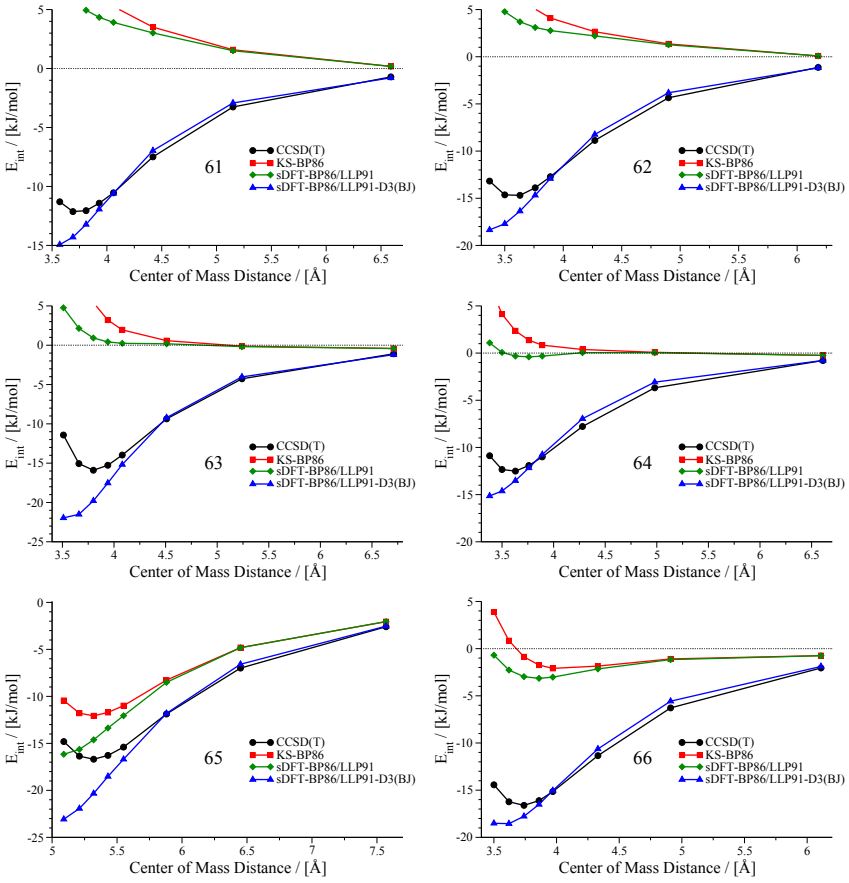

Figure 17: PESs for complexes no. 61–66 of the S66x8 test set.

References

[1] Ch. R. Jacob, J. Neugebauer, and L. Visscher, J. Comput. Chem. **29**, 1011 (2008).

[2] A. W. Götz, S. M. Beyhan, and L. Visscher, J. Chem. Theory Comput. **5**, 3161 (2009).

[3] Amsterdam density functional program, Theoretical Chemistry, Vrije Universiteit, Amsterdam, URL: http://www.scm.com.

[4] E. van Lenthe and E. J. Baerends, J. Comput. Chem. **24**, 1142 (2003).

[5] S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).

[6] G. te Velde et al., J. Comput. Chem. **22**, 931 (2001).

[7] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, J. Chem. Phys. **132**, 154104 (2010).

[8] S. Grimme, S. Ehrlich, and L. Goerigk, J. Comput. Chem. **32**, 1456 (2011).

[9] S. Grimme, http://www.thch.uni-bonn.de/tc/.

[10] R. Ahlrichs et al., http://www.cosmologic.de/turbomole.html.

[11] D. E. Woon and T. H. Dunning, J. Chem. Phys **100** (1994).

[12] T. H. D. Jr., J. Chem. Phys. **90**, 1007 (1989).

[13] D. E. Woon and T. H. Dunning, J. Chem. Phys **98** (1993).

[14] A. K. Wilson, D. E. Woon, K. A. Peterson, and T. H. Dunning, J. Chem. Phys **110** (1999).

[15] K. A. Peterson, D. Figgen, E. Goll, H. Stoll, and M. Dolg, J. Chem. Phys **119** (2003).

[16] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **99**, 4597 (1993).

[17] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **101**, 9783 (1994).

[18] J. Řezáč et al., Collect. Czech. Chem. Commun. **73**, 1261 (2008).

[19] P. Jurecka, J. Sponer, J. Cerny, and P. Hobza, Phys. Chem. Chem. Phys. **8**, 1985 (2006).

[20] J. Řezáč, K. E. Riley, and P. Hobza, J. Chem. Theory Comput. **7**, 2427 (2011).

[21] L. Gráfová, M. Pitoňák, J. Řezáč, and P. Hobza, J. Chem. Theory Comput. **6**, 2365 (2010).