

Supplementary Information of: Regularized and Opposite Spin-scaled Functionals from Møller-Plesset Adiabatic Connection - Higher Accuracy at Lower Cost

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Extra graphs and tables main text

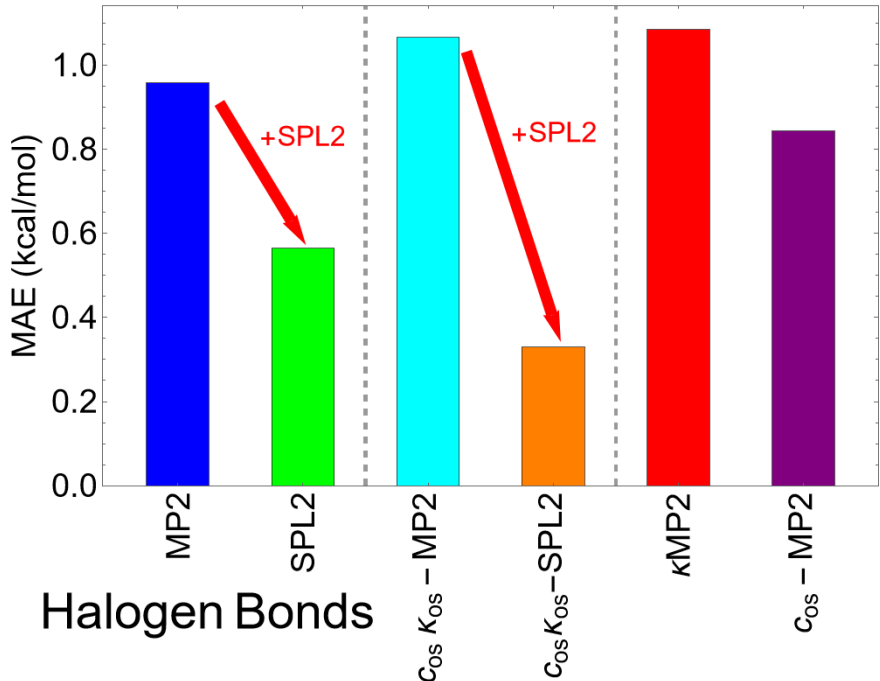


Figure S1: The MAE (Mean Absolute Error) of MP2, SPL2, $c_{os}\kappa_{os}$ -MP2 and $c_{os}\kappa_{os}$ -SPL2, κ MP2 and c_{os} -MP2 for the halogen bonded complexes of B30¹ and X40² (see Fig. 8 for more detail on the complexes and Table S1 for individual methods)

Table S1: The 20 different combinations of functionals that we have studied in this work. The bolded red functionals were also shown in Tab.I of the paper.

	Method	κ -Method	$\kappa_{ss}\kappa_{os}$ -Method	$c_{os}\kappa_{os}$ -Method	c_{os} -Method
MP2	$c_{ss} = c_{os} = 1$	$c_{ss} = c_{os} = 1$	$c_{ss} = c_{os} = 1$	$c_{ss} = 0, c_{os} = 2.1$	$c_{ss} = 0, c_{os} = 1.7$
	$\kappa_{ss} = \kappa_{os} = \infty$	$\kappa_{ss} = \kappa_{os} = 1.1$	$\kappa_{ss} = 0.9, \kappa_{os} = 1.4$	$\kappa_{ss} = 0, \kappa_{os} = 0.9$	$\kappa_{ss} = \kappa_{os} = \infty$
SPL2	$c_{ss} = c_{os} = 1$	$c_{ss} = c_{os} = 1$	$c_{ss} = c_{os} = 1$	$c_{ss} = 0, c_{os} = 2.1$	$c_{ss} = 0, c_{os} = 1.8$
	$\kappa_{ss} = \kappa_{os} = \infty$	$\kappa_{ss} = \kappa_{os} = 1.7$	$\kappa_{ss} = 1.1, \kappa_{os} = 1.7$	$\kappa_{ss} = 0, \kappa_{os} = 1.3$	$\kappa_{ss} = \kappa_{os} = \infty$
MPACF1	$c_{ss} = c_{os} = 1$	$c_{ss} = c_{os} = 1$	$c_{ss} = c_{os} = 1$	$c_{ss} = 0, c_{os} = 2.3$	$c_{ss} = 0, c_{os} = 2.2$
	$\kappa_{ss} = \kappa_{os} = \infty$	$\kappa_{ss} = \kappa_{os} = 1.3$	$\kappa_{ss} = 1, \kappa_{os} = 1.4$	$\kappa_{ss} = 0, \kappa_{os} = 1.1$	$\kappa_{ss} = \kappa_{os} = \infty$
F1	$c_{ss} = c_{os} = 1$	$c_{ss} = c_{os} = 1$	$c_{ss} = c_{os} = 1$	$c_{ss} = 0, c_{os} = 2.4$	$c_{ss} = 0, c_{os} = 2.0$
	$\kappa_{ss} = \kappa_{os} = \infty$	$\kappa_{ss} = \kappa_{os} = 1.5$	$\kappa_{ss} = 1.6, \kappa_{os} = 1.3$	$\kappa_{ss} = 0, \kappa_{os} = 1.0$	$\kappa_{ss} = \kappa_{os} = \infty$

Additional S66x8 Plots

In Fig. S6, we show the SPL2 correction for the S66x8 dissociation curves for small bond distances. We see that all that at $R = 0.9R_e$, MP2 performs the worse but that SPL2 is

Table S2: The 20 different combinations of functionals that we have studied in this work. The bolded red functionals have been studied in the paper.

Method	fitted parameters
SPL2	$b_2 = 0.117, m_2 = 10.68, \alpha = 1.1472, \beta = -0.7397$
κ -SPL2	$b_2 = -0.433, m_2 = 5.775, \alpha = 1.843, \beta = -1.750$
$\kappa_{ss}\kappa_{os}$ -SPL2	$b_2 = -0.690, m_2 = 3.831, \alpha = 3.382, \beta = -4.026$
$c_{os}\kappa_{os}$ - SPL2	$b_2 = 0.287, m_2 = 148.982, \alpha = 1.674, \beta = -1.973$
c_{os} - SPL2	$b_2 = 0.527, m_2 = 58.850, \alpha = 1.278, \beta = -1.059$
MPACF1	$d_1 = 0.294, d_2 = 0.934$
κ -MPACF1	$d_1 = -0.3660, d_2 = 0.4677$
$\kappa_{ss}\kappa_{os}$ -MPACF1	$d_1 = 0.0001615, d_2 = -0.0151$
$c_{os}\kappa_{os}$ -MPACF1	$d_1 = 0.9965, d_2 = 0.6799$
c_{os} -MPACF1	$d_1 = 2.206, d_2 = 0.7068$
F1	$d_1 = 2.151, d_2 = 0.413, \alpha = 3.837, \beta = -6.620$
κ - F1	$d_1 = 1.147, d_2 = -0.6191, \alpha = 2.279, \beta = -4.989$
$\kappa_{ss}\kappa_{os}$ -F1	$d_1 = 0.398, d_2 = 0.663, \alpha = 2.715, \beta = -3.982$
$c_{os}\kappa_{os}$ -F1	$d_1 = 1.380, d_2 = -0.5590, \alpha = 2.902, \beta = -7.836$
c_{os} -F1	$d_1 = 2.769, d_2 = -0.3665, \alpha = 8.3970, \beta = -14.2015$

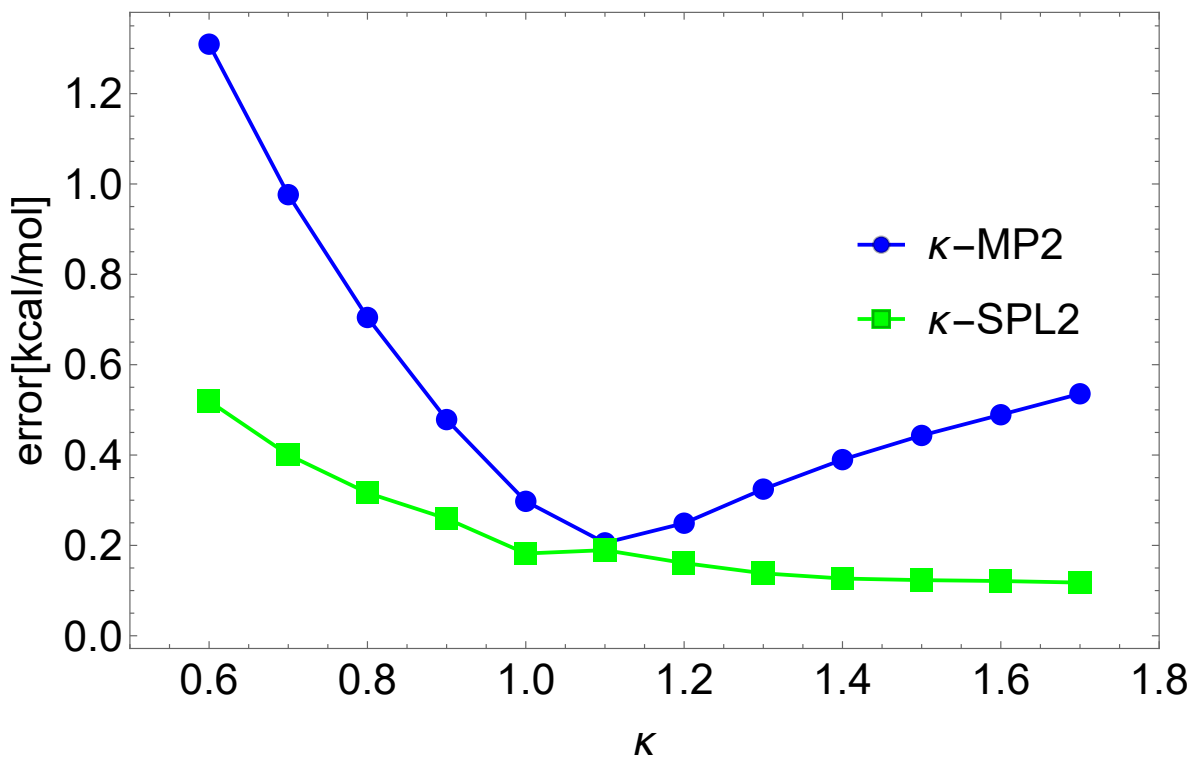


Figure S2: The error between the interaction energy of κ -MP2 and κ -SPL2 and the CCSD(T) reference data for a range of κ 's between 0.6 and 1.7 of the S22 dataset.

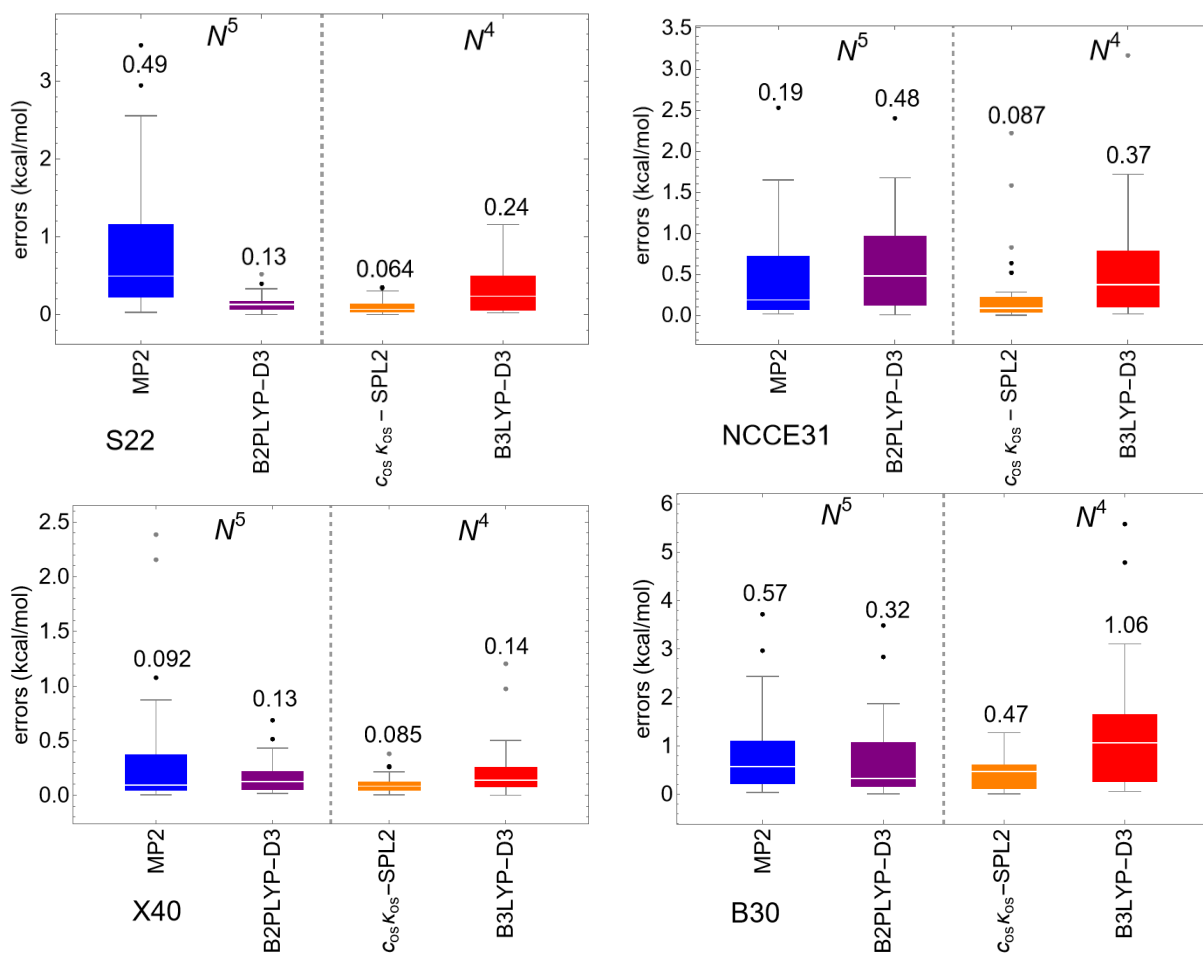


Figure S3: The box-plots containing the errors of the S22 (top left), NCCE (top right), X40 (bottom right) and B30 (bottom left) for MP2, B2PLYP-D3, $c_{0s}k_{0s}$ -SPL2 and B3LYP-D3 with their median values.

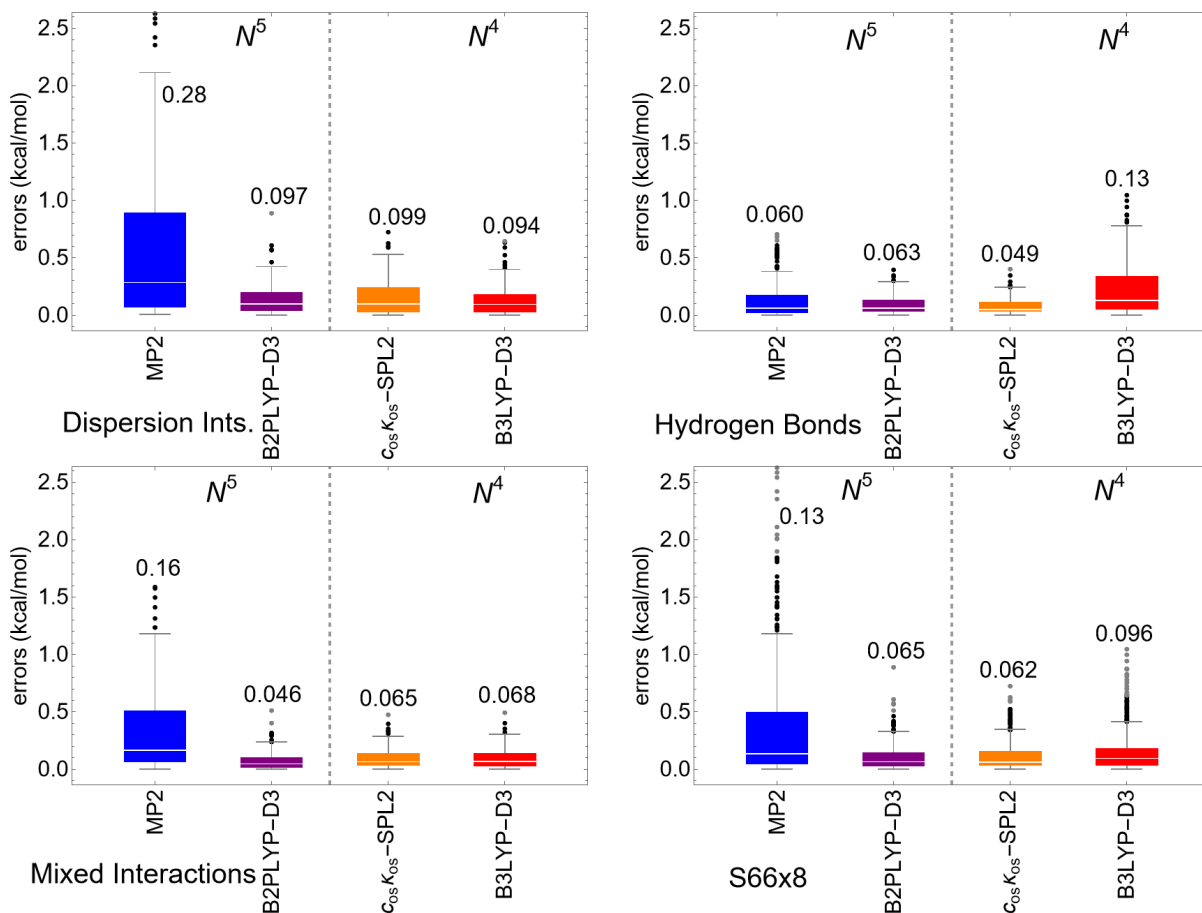


Figure S4: The box-plots containing the errors of the full S66x8 (bottom right), dispersion interactions only (top left), hydrogen bonds only (top right) and mixed interactions (bottom left) for MP2, B2PLYP-D3, $c_{os}\kappa_{os}$ -SPL2 and B3LYP-D3 with their median values. Some of the outliers of MP2 are outside of the plotted range to better visualize the distributions of the other 3 functionals, see Figure S5 for all the outliers.

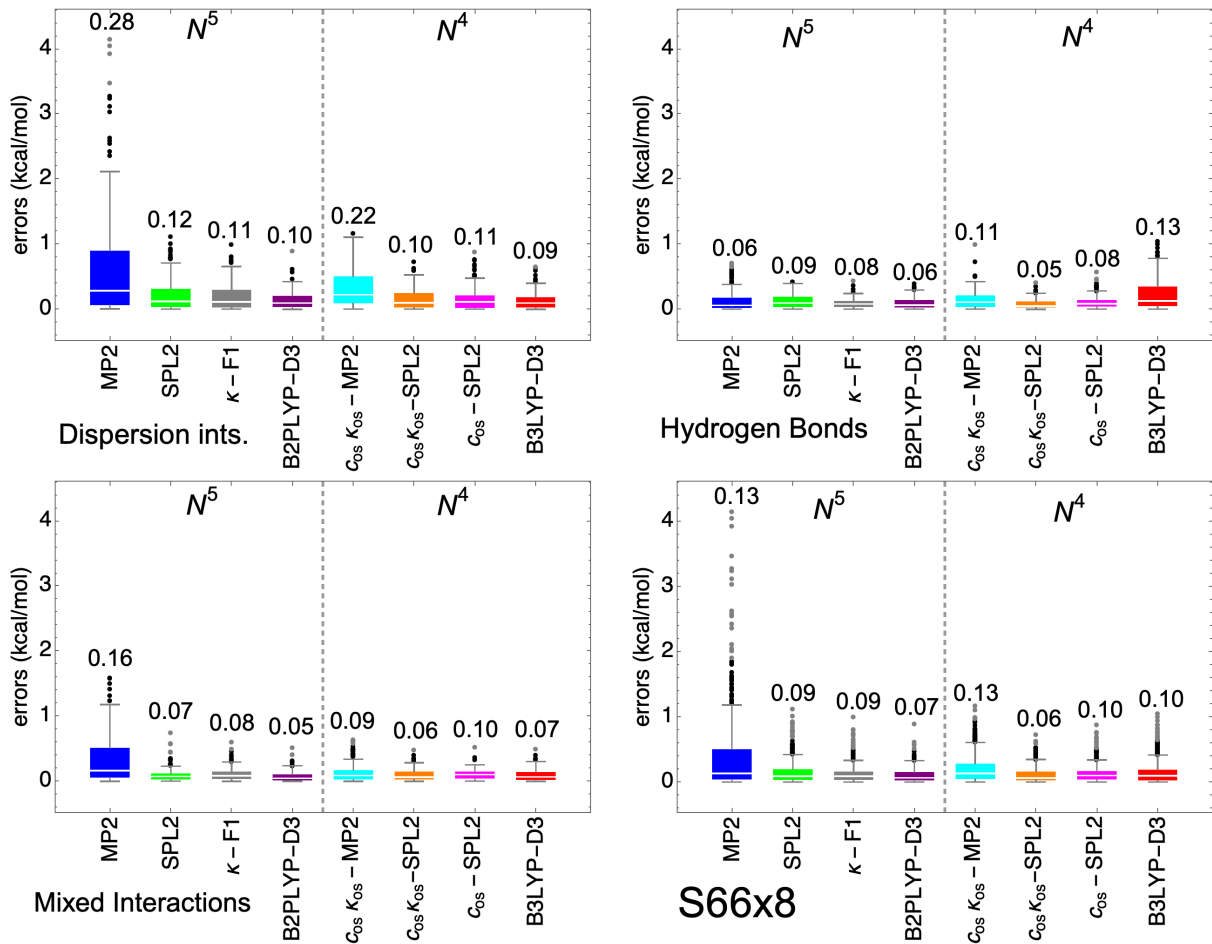


Figure S5: The box-plots containing the errors of all the 8 functionals for the S66x8 dataset split into the 3 different kind of interactions and the full dataset.

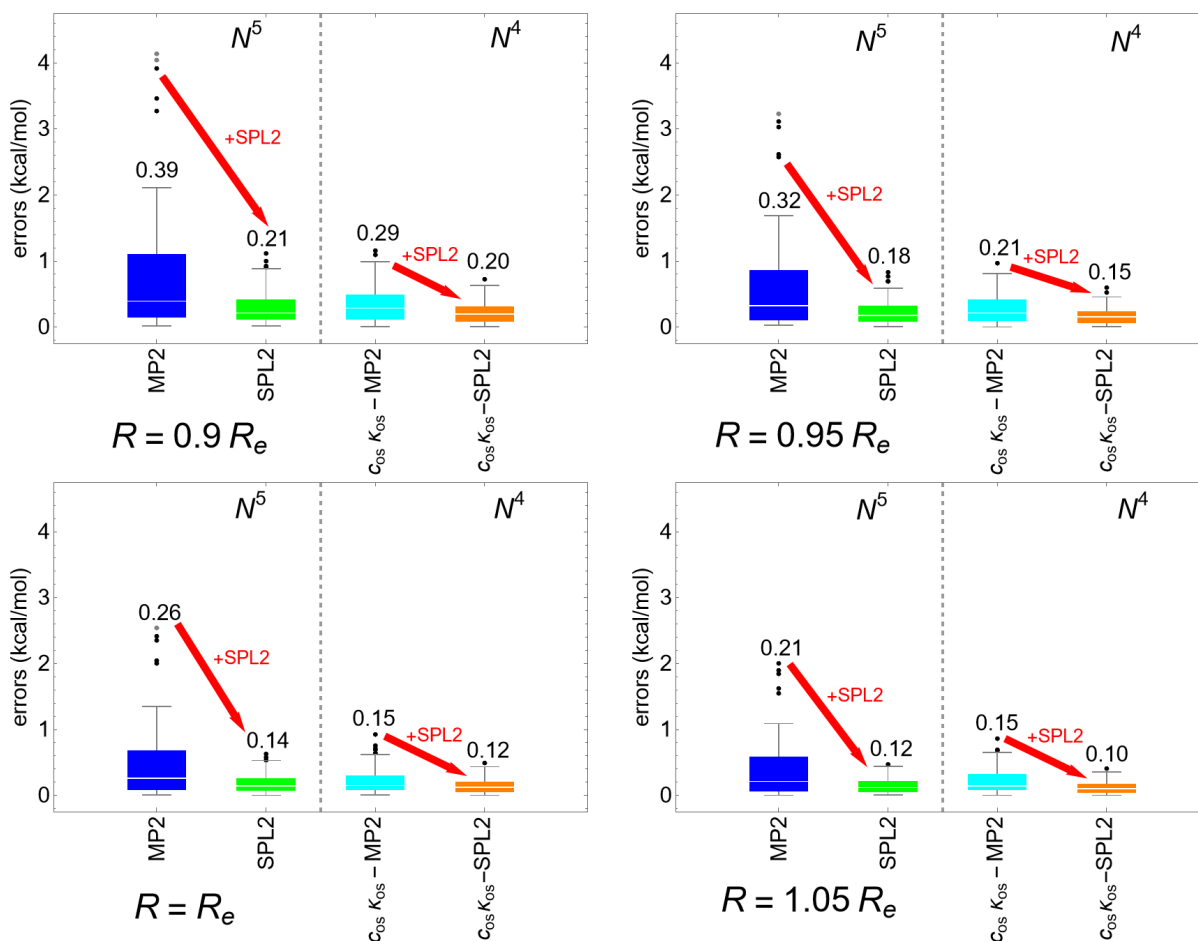


Figure S6: The box-plots containing the errors of MP2, SPL2 and $c_{os} \kappa_{os}$ -MP2 and $c_{os} \kappa_{os}$ -MP2 for the positions along the dissociation curve around the equilibrium distance, where it can be seen that the SPL2 corrections can fix the errors of MP2 forms even at small distances.

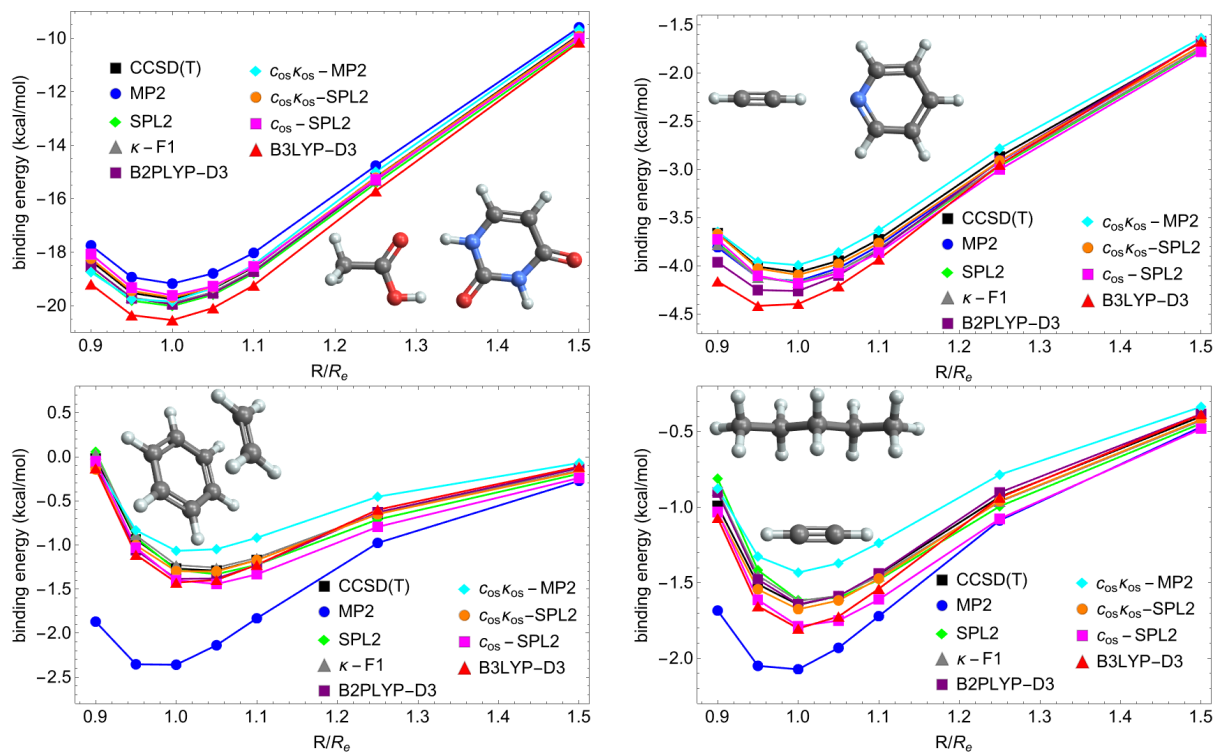


Figure S7: The dissociation curves of a dimer containing hydrogen bonds (top left), containing mixed interactions (top right) and two dimers containing dispersion interactions (bottom) for all 9 functionals and methods studied in the paper.

Table S3: The total MAE’s and maximum errors of the S22 dataset for the 11 studied functionals. Best result for each column is highlighted in boldface.

Method	S22	
	MAE	MAX
MP2	0.86	3.47
SPL2	0.15	0.55
κ -F1	0.14	0.54
B2PLYP-D3	0.15 ³	0.71 ³
RPA-SOSEX@PBE	0.43 ⁴	1.26 ⁴
MP2C	0.17 ⁵	0.73 ⁵
$c_{os}\kappa_{os}$ – MP2	0.19	0.89
$c_{os}\kappa_{os}$ – SPL2	0.11	0.36
c_{os} – SPL2	0.15	0.61
B3LYP-D3	0.31 ³	1.16 ³
dRPA@PBE	0.23 ⁴	1.00 ⁴

Table S4: The total MAE’s and maximum errors of the NCCE31 dataset of 8 functionals split as well as the MAE’s of the separate sets containing hydrogen bonds, charge transfer interaction, dipole interactions, weak interactions, and π - π -stacking interactions. NA means not available, because the authors⁶ only reported the MAEs not maximum absolute error.

Method	Total		HB6		CT7		DI6		WI7		PPS5	
	MAE	MAX	MAE	MAX	MAE	MAX	MAE	MAX	MAE	MAX	MAE	MAX
MP2	0.5	2.53	0.42	1.65	0.86	2.53	0.46	1.37	0.04	0.09	0.79	1.57
SPL2	0.25	2.16	0.54	2.16	0.41	1.55	0.18	0.83	0.04	0.11	0.08	0.12
κ – F1	0.32	2.66	0.73	2.66	0.52	1.82	0.18	0.69	0.03	0.04	0.11	0.22
B2PLYP-D3	0.61	2.41	0.51	1.21	1.05	2.41	0.77	1.68	0.02	0.06	0.73	1.19
$c_{os}\kappa_{os}$ – MP2	0.4	2.92	0.77	2.92	0.67	2.41	0.26	0.36	0.06	0.16	0.24	0.42
$c_{os}\kappa_{os}$ – SPL2	0.27	2.23	0.55	2.23	0.47	1.59	0.18	0.53	0.04	0.09	0.11	0.20
c_{os} – SPL2	0.21	1.84	0.47	1.84	0.25	0.82	0.17	0.46	0.09	0.18	0.07	0.21
B3LYP-D3	0.60	3.18	0.46	1.33	1.43	3.18	0.71	1.72	0.05	0.09	0.28	0.48
dRPA@PBE ⁶	0.69	NA	0.22	NA	2.37	NA	0.22	NA	0.07	NA	0.33	NA

able to reduce the median and reduce the amount of outliers. The same is true of the more accurate $c_{os}\kappa_{os}$ -MP2 form which still has a quite large median but SPL2 is able to correct it as well. This shows that the SPL2 form is also able to correct the poor accuracy of MP2 for smaller bond lengths, although the methods are still more accurate at larger bond length such as the equilibrium distances or $R = 1.05R_e$. However, the errors are not as bad as the original MP2 forms meaning that SPL2 can describe better these types of interactions at small bond distances.

Table S5: The total MAE’s and maximum errors of the S66x8 dataset of 8 functionals as well as the MAE’s for only the hydrogen bonding complexes, the dispersion interactions dominated complexes and the mixed set. Best result for each column is highlighted in boldface. For comparison, the MAEs of RPA-SOSEX(W, v_c)⁷ are 0.22, 0.23, 0.25 and 0.17 respectively with the maximum error being 3.33, 1.43, 3.33 and 1.04.

Method	Total		H-bonds		Dispersion		Mixed	
	MAE	MAX	MAE	MAX	MAE	MAX	MAE	MAX
MP2	0.39	4.15	0.14	0.71	0.67	4.15	0.34	1.59
SPL2	0.15	1.12	0.12	0.42	0.21	1.12	0.1	0.75
κ - F1	0.13	1.00	0.09	0.44	0.19	1.00	0.11	0.60
B2PLYP-D3	0.11	0.90	0.09	0.40	0.14	0.90	0.08	0.52
RPA-SOSEX	0.22	3.33	0.23	1.43	0.25	3.33	0.17	1.04
$c_{os}\kappa_{os}$ - MP2	0.2	1.17	0.14	1.00	0.32	1.17	0.14	0.64
$c_{os}\kappa_{os}$ - SPL2	0.11	0.73	0.08	0.41	0.16	0.73	0.1	0.48
c_{os} - SPL2	0.13	0.88	0.11	0.58	0.16	0.88	0.1	0.53
B3LYP-D3	0.15	1.05	0.22	1.05	0.13	0.65	0.08	0.50

Table S6: The total MAE’s and maximum errors of the B30/Bauza30 dataset of 3 different RPA variants split as well as the MAE’s of the separate halogen bonding (containing mostly anions as donors), chalcogen bonding and pnictogen bonding complexes.

Method	Total		aHGB		CHB		PNB	
	MAE	MAX	MAE	MAX	MAE	MAX	MAE	MAX
RPA-SOSEX ⁴	1.17	3.16	1.35	3.03	1.33	3.16	0.48	1.20
dRPA ⁴	1.47	4.27	3.36	4.27	1.09	2.28	0.74	1.04
C(HF)-dRPA ⁴	0.61	1.55	0.96	1.55	0.58	1.53	0.37	0.71

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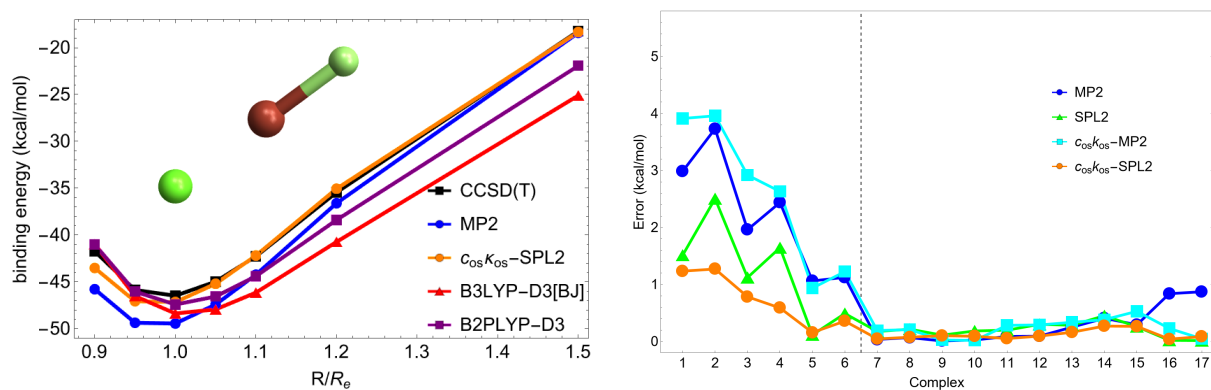


Figure S8: On the left the dissociation curve of NH₃-FBr for CCSD(T), MP2, $c_{os}\kappa_{os}$ -SPL2, B3LYP-D3[BJ] and B2PLYP-D3 and on the right the errors between the CCSD(T) reference data^{2,8} and MP2, SPL2, $c_{os}\kappa_{os}$ -MP2 and $c_{os}\kappa_{os}$ -SPL2 respectively for the halogen bonded complexes of the B30^{1,8} and X40² datasets.

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