

Supporting Information for Third order Møller-Plesset theory made more useful? The role of density functional theory orbitals

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1 Results without non-Brillouin MP2 singles

Table 1: Scaling coefficients for MP2:DFT and MP3:DFT (with no singles) fit to the non MR subset of W4-11 dataset.

Name	c_2 (sMP2/Model 2)	c_3 (sMP3/Model 4)
HF	0.9035	0.7157
HFLYP	0.9030	0.6542
Slater	0.8516	0.6870
SPW92	0.8611	0.6517
PBE	0.8651	0.6501
BLYP	0.8650	0.6447
B97M-V	0.8644	0.6834
SCAN	0.8705	0.6706
revM06-L	0.8798	0.6715
TPSS	0.8709	0.6444
B3LYP	0.8644	0.6832
PBE0	0.8665	0.6931
MN15	0.8485	0.7375
CAM-B3LYP	0.8631	0.6987
ω B97X-V	0.8640	0.7080
ω B97M-V	0.8503	0.7334

Table 2: Root mean square errors (RMSE), mean signed errors (MSE), and maximum absolute errors (MAX) in kcal/mol for MP:DFT (with no singles) on the non MR subset of W4-11 dataset (training set).

Name	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX
	MP2 (NS)			sMP2 (NS)			MP3 (NS)			sMP3 (NS)		
HF	12.0	-5.0	51.1	10.4	-2.7	43.4	9.2	-0.9	38.6	8.5	-2.0	39.5
HFLYP	9.3	-3.9	35.5	7.1	-1.8	30.0	6.5	-0.1	26.1	5.1	-1.4	24.6
Slater	12.1	-3.6	53.4	5.9	-0.2	33.2	5.9	1.2	28.7	2.3	-0.3	10.7
SPW92	11.5	-3.3	51.1	5.8	-0.2	32.1	6.3	1.4	30.5	1.9	-0.2	10.5
PBE	11.2	-3.3	49.7	5.9	-0.3	30.5	6.2	1.3	30.1	1.9	-0.3	9.3
BLYP	11.3	-3.3	50.9	6.0	-0.3	30.2	6.4	1.3	29.9	1.8	-0.3	8.9
B97M-V	10.7	-3.6	47.5	5.2	-0.6	27.7	5.2	0.7	24.1	1.9	-0.7	6.2
SCAN	10.9	-3.7	48.7	6.2	-0.7	29.0	5.8	0.8	26.1	2.5	-0.7	11.9
revM06-L	10.3	-3.2	47.5	6.1	-0.5	33.4	5.3	1.2	23.5	2.0	-0.3	10.6
TPSS	10.8	-3.3	48.0	5.9	-0.3	29.5	6.2	1.3	30.1	1.9	-0.3	8.2
B3LYP	11.0	-3.5	50.4	5.8	-0.5	29.4	5.4	0.8	23.9	1.8	-0.6	6.6
PBE0	10.8	-3.6	48.9	5.8	-0.6	28.5	5.1	0.7	23.1	1.9	-0.6	7.8
MN15	11.6	-4.0	52.2	5.3	-0.7	30.8	4.6	0.2	20.2	2.1	-0.9	8.4
CAM-B3LYP	11.0	-3.6	50.4	5.7	-0.6	28.6	5.0	0.6	21.7	1.8	-0.7	6.3
ω B97X-V	10.8	-3.6	49.6	5.6	-0.6	27.8	4.7	0.4	20.4	1.8	-0.7	6.5
ω B97M-V	11.3	-4.0	51.1	5.0	-0.8	22.3	4.6	0.0	19.8	2.2	-1.0	10.1

Table 3: Root mean square errors (RMSE), mean signed errors (MSE), and maximum absolute errors (MAX) in kcal/mol for MP:DFT (with no singles) on the BH76RC dataset.

Name	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX
CCSD	1.9	-0.6	7.2									
	MP2 (NS)			sMP2 (NS)			MP3 (NS)			sMP3 (NS)		
HF	6.3	-0.1	21.2	5.6	-0.1	21.6	4.5	-1.0	21.6	4.3	-0.7	21.5
SPW92	5.7	0.8	20.7	3.6	0.6	12.1	3.4	-1.0	14.0	1.4	-0.4	3.6
PBE	5.6	0.8	20.7	3.6	0.5	12.4	3.3	-1.1	13.7	1.3	-0.4	3.9
BLYP	5.7	0.9	20.7	3.6	0.6	12.3	3.4	-1.0	14.0	1.4	-0.3	3.8
B97M-V	5.0	0.6	19.0	3.1	0.4	11.1	3.0	-1.0	12.5	1.1	-0.5	2.9
SCAN	5.5	0.8	20.4	3.6	0.6	12.5	3.0	-0.9	12.5	1.2	-0.4	2.9
revM06-L	5.4	0.8	19.7	3.7	0.6	12.6	2.8	-0.9	11.7	1.3	-0.3	2.4
TPSS	5.5	0.8	20.5	3.6	0.6	12.6	3.2	-0.9	13.4	1.3	-0.3	3.5
B3LYP	5.6	0.8	20.0	3.6	0.6	12.1	2.7	-0.8	11.2	1.1	-0.3	2.3
PBE0	5.4	0.8	19.7	3.5	0.6	12.1	2.5	-0.8	10.5	1.1	-0.3	2.1
MN15	5.2	0.5	18.8	3.1	0.3	10.4	2.7	-1.0	10.8	1.1	-0.6	3.0
CAM-B3LYP	5.5	0.8	19.3	3.5	0.6	11.7	2.4	-0.7	10.0	1.1	-0.3	2.2
ω B97X-V	5.4	0.8	19.0	3.5	0.6	11.7	2.3	-0.7	9.2	1.1	-0.3	2.1
ω B97M-V	5.1	0.6	18.2	3.1	0.5	10.2	2.5	-0.8	9.9	1.0	-0.4	2.4

Table 4: Root mean square errors (RMSE), mean signed errors (MSE), and maximum absolute errors (MAX) in kcal/mol for MP:DFT (with no singles) on the RSE43 dataset.

Name	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX
CCSD	0.4	0.3	1.0									
	MP2 (NS)			sMP2 (NS)			MP3 (NS)			sMP3 (NS)		
HF	4.1	2.3	16.4	3.7	2.2	14.5	2.4	1.6	9.3	2.9	1.8	11.4
SPW92	1.0	-0.4	2.6	0.8	0.6	1.9	1.3	1.1	3.5	0.8	0.6	2.2
PBE	0.9	-0.5	2.4	0.6	0.3	1.2	0.8	0.6	2.4	0.5	0.2	1.4
BLYP	0.9	-0.5	2.5	0.6	0.3	1.4	0.9	0.8	2.6	0.5	0.3	1.5
B97M-V	0.9	-0.5	2.4	0.5	0.2	1.1	0.5	0.3	1.4	0.3	0.1	0.8
SCAN	1.1	-0.4	3.8	0.7	0.2	3.3	0.4	0.2	1.2	0.4	-0.0	1.5
revM06-L	1.0	-0.5	2.3	0.6	0.0	1.2	0.4	0.1	1.0	0.4	-0.1	0.7
TPSS	0.9	-0.5	2.3	0.5	0.1	1.0	0.5	0.4	1.6	0.3	0.1	0.8
B3LYP	0.9	-0.5	2.4	0.4	0.1	1.0	0.4	0.3	1.1	0.2	0.0	0.6
PBE0	0.9	-0.5	2.2	0.4	0.1	1.2	0.3	0.1	0.8	0.2	-0.1	0.6
MN15	0.8	-0.4	2.3	0.4	0.2	1.2	0.4	0.2	0.9	0.2	0.0	0.5
CAM-B3LYP	0.9	-0.5	2.3	0.4	0.0	1.4	0.3	0.1	0.7	0.2	-0.1	0.7
ω B97X-V	0.9	-0.5	2.2	0.4	0.0	1.4	0.3	0.1	0.6	0.2	-0.1	0.6
ω B97M-V	0.9	-0.6	2.4	0.4	0.0	1.1	0.3	0.1	0.7	0.3	-0.1	0.7

Table 5: Root mean square errors (RMSE), mean signed errors (MSE), and maximum absolute errors (MAX) in kcal/mol for MP:DFT (with no singles) on the HTBH38 dataset.

Name	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX
CCSD	2.2	1.9	4.1									
	MP2 (NS)			sMP2 (NS)			MP3 (NS)			sMP3 (NS)		
HF	4.0	3.0	12.1	4.6	4.0	10.3	3.9	3.5	7.2	3.7	3.4	6.3
SPW92	3.9	-0.5	10.7	4.0	2.8	11.3	4.9	3.9	14.4	3.1	2.4	7.8
PBE	3.7	-0.5	9.9	3.6	2.5	9.9	4.0	3.3	11.4	2.5	1.9	6.2
BLYP	3.7	-0.5	9.8	3.6	2.5	9.8	4.1	3.4	12.3	2.6	2.0	6.4
B97M-V	3.3	-0.4	8.3	3.2	2.3	7.6	2.5	2.3	4.8	1.7	1.5	3.5
SCAN	3.5	-0.5	9.2	3.2	2.0	8.7	2.6	2.3	5.3	1.8	1.4	4.7
revM06-L	3.5	-0.1	9.1	3.4	2.2	8.3	2.6	2.4	5.0	2.0	1.6	4.1
TPSS	3.5	-0.5	9.3	3.2	2.1	8.9	3.1	2.6	7.7	2.0	1.5	5.1
B3LYP	3.5	-0.7	9.0	3.0	1.9	8.3	2.3	2.1	4.6	1.5	1.2	4.2
PBE0	3.4	-0.8	8.7	2.8	1.7	8.0	2.0	1.8	4.2	1.4	1.0	3.7
MN15	3.4	-0.5	8.9	3.2	2.4	7.9	2.3	2.1	4.2	1.6	1.4	3.3
CAM-B3LYP	3.5	-0.9	8.7	2.7	1.5	7.8	1.7	1.6	3.9	1.2	0.8	3.5
ω B97X-V	3.4	-0.9	8.6	2.7	1.5	7.7	1.6	1.5	3.7	1.1	0.8	3.3
ω B97M-V	3.4	-1.0	8.1	2.7	1.7	7.1	1.6	1.4	3.7	1.0	0.8	2.5

Table 6: Root mean square errors (RMSE), mean signed errors (MSE), and maximum absolute errors (MAX) in kcal/mol for MP:DFT (with no singles) on the NHTBH38 dataset.

Name	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX
CCSD	2.5	2.1	7.6									
	MP2 (NS)			sMP2 (NS)			MP3 (NS)			sMP3 (NS)		
HF	7.0	4.4	25.6	7.1	4.8	25.0	6.7	5.2	23.3	6.6	4.9	24.0
SPW92	3.7	-0.7	15.3	3.2	1.9	7.1	5.5	4.6	13.6	3.1	2.8	6.6
PBE	3.6	-0.9	15.8	2.9	1.5	6.4	5.1	4.2	13.1	2.7	2.4	5.2
BLYP	3.7	-0.9	15.3	3.0	1.5	6.8	5.0	4.1	13.6	2.6	2.3	5.0
B97M-V	3.3	-0.8	14.4	2.7	1.4	6.1	4.1	3.3	11.8	2.2	2.0	5.6
SCAN	3.5	-0.5	15.2	2.9	1.6	6.4	4.5	3.8	11.9	2.6	2.4	5.6
revM06-L	3.3	-0.4	14.3	2.9	1.5	6.7	4.4	3.7	12.1	2.5	2.3	5.1
TPSS	3.6	-0.8	15.5	2.9	1.4	6.4	4.6	3.8	13.1	2.4	2.1	4.8
B3LYP	3.6	-1.0	14.8	2.7	1.1	6.6	3.8	3.1	10.8	2.0	1.8	4.7
PBE0	3.5	-1.0	14.8	2.6	1.0	6.2	3.6	3.0	10.0	2.0	1.8	4.7
MN15	3.4	-1.3	14.3	2.5	0.9	6.0	3.4	2.7	10.1	1.9	1.6	5.3
CAM-B3LYP	3.5	-1.1	14.3	2.6	0.8	6.3	3.3	2.7	9.5	1.7	1.5	4.6
ω B97X-V	3.4	-1.0	14.4	2.5	0.8	5.9	3.1	2.5	8.9	1.7	1.5	4.2
ω B97M-V	3.4	-1.3	14.5	2.3	0.8	5.3	3.1	2.4	9.0	1.7	1.4	4.8

Table 7: Root mean square errors (RMSE), mean signed errors (MSE), and maximum absolute errors (MAX) in kcal/mol for MP:DFT (with no singles) on the TA13 dataset.

Name	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX
CCSD	0.72	0.54	1.47									
	MP2 (NS)			sMP2 (NS)			MP3 (NS)			sMP3 (NS)		
HF	1.79	0.16	5.16	1.64	0.45	3.93	1.44	0.39	4.00	1.49	0.33	3.84
SPW92	2.72	2.28	4.50	3.98	3.54	6.95	4.81	3.89	9.20	3.91	3.33	6.82
PBE	1.89	1.44	3.72	3.03	2.51	5.91	3.75	2.68	8.10	2.91	2.24	5.77
BLYP	1.86	1.38	3.61	2.94	2.44	5.81	3.66	2.55	8.01	2.80	2.13	5.67
B97M-V	1.16	0.68	2.16	1.93	1.56	3.14	2.28	1.53	5.15	1.72	1.26	3.20
SCAN	1.09	0.71	1.88	1.95	1.60	3.12	2.53	1.74	5.86	1.88	1.40	3.65
revM06-L	0.93	0.62	1.73	1.66	1.36	2.72	2.23	1.51	5.33	1.64	1.22	3.34
TPSS	1.56	1.10	2.65	2.56	2.06	4.37	3.26	2.21	7.31	2.47	1.82	4.53
B3LYP	1.01	0.42	2.00	1.58	1.28	2.94	1.95	1.24	4.86	1.35	0.98	2.79
PBE0	0.85	0.24	1.77	1.27	1.04	2.54	1.58	1.02	4.00	1.06	0.78	2.24
MN15	1.06	0.09	2.88	1.27	1.01	2.78	1.34	0.96	3.48	0.95	0.73	1.98
CAM-B3LYP	0.95	0.03	2.22	1.05	0.79	2.50	1.21	0.66	3.56	0.70	0.47	1.82
ω B97X-V	0.93	-0.01	2.15	0.97	0.71	2.53	1.09	0.56	3.22	0.61	0.39	1.65
ω B97M-V	1.01	-0.01	2.22	1.09	0.80	2.60	1.02	0.55	3.01	0.62	0.40	1.62

Table 8: Root mean square errors (RMSE), mean signed errors (MSE), and maximum absolute errors (MAX) in kcal/mol for MP:DFT (with no singles) on the A24 dataset.

Name	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX
CCSD	0.25	0.23	0.43									
	MP2 (NS)			sMP2 (NS)			MP3 (NS)			sMP3 (NS)		
HF	0.52	0.08	2.41	0.53	0.20	2.43	0.49	0.19	2.20	0.49	0.16	2.26
SPW92	0.39	0.24	1.00	0.64	0.52	1.62	0.79	0.61	2.61	0.63	0.48	2.02
PBE	0.22	0.06	0.50	0.40	0.31	1.05	0.51	0.36	1.86	0.38	0.25	1.37
BLYP	0.18	0.00	0.40	0.33	0.25	0.85	0.41	0.26	1.58	0.29	0.17	1.11
B97M-V	0.14	-0.03	0.33	0.24	0.20	0.61	0.30	0.24	0.99	0.19	0.15	0.65
SCAN	0.16	-0.03	0.38	0.26	0.19	0.66	0.36	0.26	1.26	0.24	0.16	0.86
revM06-L	0.14	-0.08	0.34	0.16	0.12	0.41	0.26	0.18	0.91	0.15	0.10	0.57
TPSS	0.16	0.01	0.35	0.30	0.23	0.72	0.39	0.27	1.42	0.27	0.18	0.97
B3LYP	0.16	-0.08	0.40	0.19	0.16	0.50	0.20	0.15	0.63	0.11	0.08	0.34
PBE0	0.16	-0.08	0.37	0.18	0.14	0.52	0.20	0.16	0.60	0.12	0.09	0.31
MN15	0.16	-0.00	0.33	0.31	0.26	0.82	0.31	0.28	0.60	0.23	0.20	0.49
CAM-B3LYP	0.19	-0.11	0.44	0.15	0.11	0.36	0.12	0.09	0.32	0.05	0.03	0.11
ω B97X-V	0.18	-0.11	0.44	0.15	0.11	0.37	0.13	0.11	0.34	0.06	0.04	0.13
ω B97M-V	0.18	-0.11	0.45	0.18	0.14	0.48	0.14	0.11	0.37	0.07	0.05	0.17

2 Behavior of Model 5 ($E = E_{\text{HF}} + c_2 E_{\text{MP2}} + c_3 E_{\text{MP3}}$)

Table 9: Scaling coefficients for model 5 fit from the non MR subset of W4-11 dataset.

Name	c_2	c_3
κ -OOMP2	0.9997	0.8135
HF	1.0641	1.0044
HFLYP	1.0351	0.8028
Slater	0.9782	0.7876
SPW92	0.9757	0.7829
PBE	0.9828	0.8069
BLYP	0.9771	0.7891
B97M-V	0.9874	0.7685
SCAN	0.9905	0.8239
revM06-L	0.9860	0.7873
TPSS	0.9879	0.8247
B3LYP	0.9859	0.7844
PBE0	0.9935	0.8014
MN15	0.9814	0.7553
CAM-B3LYP	0.9865	0.7722
ω B97X-V	0.9924	0.7720
ω B97M-V	0.9843	0.7390

Table 10: Root mean square errors (RMSE), mean signed errors (MSE), and maximum absolute errors (MAX) in kcal/mol for MP:DFT Model 5 and CCSD on the thermochemistry datasets.

	W4-11			BH76RC			RSE43		
Name	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX
CCSD	4.9	1.5	20.3	1.9	-0.6	7.2	0.4	0.3	1.0
κ -OOMP2	1.6	-0.4	5.8	0.8	-0.2	1.5	0.6	-0.5	1.7
HF	8.3	-2.4	37.6	4.3	-1.0	21.3	2.7	1.6	10.6
SPW92	2.0	-0.8	7.5	0.9	-0.1	1.7	1.1	-1.0	2.5
PBE	2.1	-0.8	7.3	0.9	-0.1	1.7	1.1	-1.0	2.6
BLYP	1.9	-0.7	7.1	0.8	-0.1	1.5	1.1	-1.0	2.6
B97M-V	1.8	-0.6	6.5	0.7	-0.1	1.6	1.0	-0.9	2.5
SCAN	2.4	-0.9	10.6	0.9	-0.1	2.1	0.9	-0.8	2.0
revM06-L	1.9	-0.6	5.9	1.0	0.0	1.9	1.2	-1.0	2.7
TPSS	2.1	-0.8	7.7	0.9	-0.1	1.9	1.1	-0.9	2.6
B3LYP	1.9	-0.7	6.6	0.8	-0.2	1.5	0.9	-0.8	2.3
PBE0	2.0	-0.8	7.8	0.9	-0.2	1.9	0.9	-0.8	2.2
MN15	1.8	-0.6	6.4	0.8	-0.2	1.6	0.8	-0.7	2.0
CAM-B3LYP	1.8	-0.6	6.4	0.9	-0.2	1.6	0.7	-0.6	1.8
ω B97X-V	1.8	-0.6	6.4	0.8	-0.2	1.4	0.7	-0.6	1.7
ω B97M-V	1.8	-0.6	6.4	0.8	-0.2	1.3	0.7	-0.6	1.8

Table 11: Root mean square errors (RMSE), mean signed errors (MSE), and maximum absolute errors (MAX) in kcal/mol for MP:DFT Model 5 and CCSD on the kinetics datasets.

	HTBH38			NHTBH38		
Name	RMSE	MSE	MAX	RMSE	MSE	MAX
CCSD	2.2	1.9	4.1	2.5	2.1	7.6
κ -OOMP2	0.7	-0.1	1.4	0.8	0.3	1.8
HF	3.2	2.8	5.8	6.4	4.9	23.7
SPW92	1.8	-0.8	7.1	2.0	-0.7	3.9
PBE	1.8	-1.0	6.8	1.7	-0.8	3.7
BLYP	1.9	-1.0	7.4	1.6	-0.7	3.4
B97M-V	1.3	-0.8	4.0	1.2	-0.5	2.6
SCAN	1.2	-0.7	4.2	1.4	-0.4	3.0
revM06-L	1.2	-0.7	3.5	1.1	-0.3	2.4
TPSS	1.5	-0.8	5.5	1.4	-0.6	3.2
B3LYP	1.2	-0.7	3.7	1.1	-0.4	2.4
PBE0	1.0	-0.5	2.8	1.1	-0.3	2.4
MN15	1.0	-0.7	2.3	0.7	-0.1	1.6
CAM-B3LYP	0.8	-0.4	2.1	0.8	-0.0	1.6
ω B97X-V	0.7	-0.3	1.8	0.7	0.1	1.3
ω B97M-V	0.8	-0.5	1.9	0.7	-0.1	1.4

Table 12: Root mean square errors (RMSE), mean signed errors (MSE), and maximum absolute errors (MAX) in kcal/mol for MP:DFT Model 5 and CCSD on the non-covalent interaction datasets.

	TA13			A24		
Name	RMSE	MSE	MAX	RMSE	MSE	MAX
CCSD	0.72	0.54	1.47	0.25	0.23	0.43
κ -OOMP2	0.82	-0.46	2.08	0.08	0.01	0.24
HF	1.47	0.21	3.67	0.47	0.10	2.18
SPW92	0.70	-0.51	1.74	0.16	0.01	0.37
PBE	0.81	-0.61	1.75	0.12	-0.03	0.35
BLYP	0.76	-0.56	1.71	0.11	-0.06	0.37
B97M-V	1.09	-0.70	3.14	0.11	-0.03	0.29
SCAN	1.04	-0.75	2.79	0.13	-0.01	0.32
revM06-L	1.08	-0.68	3.06	0.11	0.00	0.29
TPSS	0.91	-0.67	2.16	0.12	-0.01	0.30
B3LYP	0.99	-0.70	2.65	0.10	-0.04	0.32
PBE0	1.04	-0.74	2.77	0.11	-0.02	0.30
MN15	1.07	-0.72	2.98	0.12	-0.01	0.29
CAM-B3LYP	0.98	-0.67	2.73	0.10	-0.03	0.27
ω B97X-V	0.97	-0.65	2.80	0.10	-0.01	0.24
ω B97M-V	0.94	-0.62	2.75	0.11	-0.02	0.28

Table 13: Root mean square regularized errors (RMSRE) and mean signed regularized errors (MSRE) in % for MP:DFT Model 5 and CCSD on the dipoles datasets.

	NSP		SP	
Name	RMSRE	MSRE	RMSRE	MSRE
CCSD	2.8	1.6	4.6	2.0
κ -OOMP2	1.7	1.0	8.5	0.8
HF	3.2	2.0	31.9	10.5
SPW92	2.4	0.4	5.0	0.5
PBE	2.3	0.4	5.4	0.7
BLYP	2.2	0.4	5.6	0.6
B97M-V	1.8	0.6	5.3	-0.1
SCAN	2.0	0.6	4.6	0.3
revM06-L	1.9	0.9	5.6	0.2
TPSS	2.1	0.5	4.8	0.8
B3LYP	2.0	0.7	5.5	0.6
PBE0	1.9	0.7	4.8	0.7
MN15	1.9	1.1	5.3	0.3
CAM-B3LYP	1.9	1.0	5.1	0.9
ω B97X-V	1.9	1.0	3.9	0.8
ω B97M-V	1.9	0.9	4.0	0.7

3 sMP3 Correlation Coefficients

Table 14: Correlation coefficients (r) computed between sMP3:DFT and CCSD, sMP3:HF, sMP3:HFLYP errors for the nonMR subset of the W4-11 dataset.

Name	CCSD	HF	HFLYP
κ -OOMP2	0.1	0.3	0.3
HF	0.5	1.0	0.9
HFLYP	0.4	0.9	1.0
Slater	0.2	0.4	0.5
SPW92	0.1	0.3	0.3
PBE	0.1	0.3	0.4
BLYP	0.0	0.3	0.3
B97M-V	0.1	0.2	0.3
SCAN	0.1	0.4	0.4
revM06-L	0.0	0.3	0.3
TPSS	0.1	0.4	0.4
B3LYP	0.1	0.3	0.4
PBE0	0.2	0.4	0.5
MN15	0.1	0.3	0.3
CAM-B3LYP	0.1	0.3	0.4
ω B97X-V	0.1	0.3	0.4
ω B97M-V	0.1	0.3	0.4

Table 15: Correlation coefficients (r) computed between sMP3:DFT and CCSD,sMP3:HF errors for the BH76RC and RSE43 datasets.

	BH76RC		RSE43	
Name	CCSD HF		CCSD HF	
κ -OOMP2	−0.2	0.1	−0.2	−0.8
HF	0.4	1.0	0.1	1.0
SPW92	0.1	0.0	0.1	−0.8
PBE	0.0	0.0	0.0	−0.8
BLYP	0.0	−0.0	0.0	−0.8
B97M-V	−0.1	0.0	−0.1	−0.8
SCAN	0.0	0.0	−0.4	−0.6
revM06-L	−0.0	0.0	−0.1	−0.7
TPSS	0.0	0.0	−0.0	−0.8
B3LYP	−0.0	0.1	−0.1	−0.8
PBE0	−0.0	0.2	−0.1	−0.8
MN15	0.1	0.1	−0.2	−0.7
CAM-B3LYP	−0.0	0.1	−0.2	−0.8
ω B97X-V	−0.0	0.2	−0.2	−0.8
ω B97M-V	0.1	0.2	−0.1	−0.8

Table 16: Correlation coefficients (r) computed between sMP3:DFT and CCSD,sMP3:HF errors for the HTBH38 and NHTBH38 datasets.

	HTBH38		NHTBH38	
Name	CCSD HF		CCSD HF	
κ -OOMP2	−0.6	−0.2	−0.0	0.1
HF	0.3	1.0	0.6	1.0
SPW92	−0.4	−0.2	−0.1	0.4
PBE	−0.3	−0.3	−0.1	0.3
BLYP	−0.3	−0.3	−0.1	0.3
B97M-V	−0.3	−0.3	−0.2	0.2
SCAN	−0.4	−0.3	−0.1	0.2
revM06-L	−0.3	−0.2	−0.2	0.1
TPSS	−0.4	−0.3	−0.1	0.2
B3LYP	−0.4	−0.2	−0.0	0.2
PBE0	−0.4	−0.2	−0.1	0.3
MN15	−0.3	−0.2	0.1	0.1
CAM-B3LYP	−0.4	−0.2	0.0	0.2
ω B97X-V	−0.4	−0.2	0.0	0.2
ω B97M-V	−0.4	−0.2	0.1	0.3

Table 17: Correlation coefficients (r) computed between sMP3:DFT and CCSD,sMP3:HF errors for the TA13 and A24 datasets.

	TA13		A24	
Name	CCSD	HF	CCSD	HF
κ -OOMP2	-0.6	-0.5	0.1	0.2
HF	0.1	1.0	0.5	1.0
SPW92	-0.7	0.4	0.0	0.2
PBE	-0.8	-0.0	-0.1	0.2
BLYP	-0.8	-0.1	-0.3	0.0
B97M-V	-0.8	-0.5	-0.1	0.2
SCAN	-0.8	-0.4	0.0	0.3
revM06-L	-0.8	-0.5	0.1	0.3
TPSS	-0.8	-0.2	-0.1	0.2
B3LYP	-0.8	-0.5	-0.2	0.1
PBE0	-0.8	-0.5	-0.1	0.2
MN15	-0.8	-0.4	-0.0	0.2
CAM-B3LYP	-0.8	-0.5	-0.1	0.1
ω B97X-V	-0.8	-0.5	-0.0	0.2
ω B97M-V	-0.8	-0.6	-0.1	0.2

Table 18: Correlation coefficients (r) computed between sMP3:DFT and CCSD,sMP3:HF errors for the not spin-polarized (NSP) and spin-polarized (SP) subsets of the dipoles datasets.

	NSP		SP	
Name	CCSD	HF	CCSD	HF
κ -OOMP2	0.2	0.5	0.0	0.0
HF	0.7	1.0	0.4	1.0
SPW92	-0.1	0.1	0.2	0.1
PBE	-0.1	0.1	0.2	0.1
BLYP	-0.1	0.1	0.2	0.1
B97M-V	0.0	0.3	0.2	0.1
SCAN	0.1	0.3	0.4	0.1
revM06-L	0.1	0.3	0.3	0.1
TPSS	-0.0	0.2	0.2	0.0
B3LYP	0.0	0.3	0.3	0.0
PBE0	0.1	0.3	0.3	0.0
MN15	0.2	0.4	0.1	0.0
CAM-B3LYP	0.2	0.4	0.2	0.0
ω B97X-V	0.2	0.5	0.3	0.0
ω B97M-V	0.2	0.4	0.3	-0.0

4 RSE43 Spin Contamination

Table 19: Root mean square errors (RMSE), mean signed errors (MSE), and maximum absolute errors (MAX) in kcal/mol for MP:DFT on the RSE43 dataset with spin-contaminated reactions removed.

Name	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX	RMSE	MSE	MAX
CCSD	0.4	0.3	1.0									
	MP2			sMP2			MP3			sMP3		
κ -OOMP2	1.2	-0.9	2.7	0.5	-0.3	1.1	0.3	-0.3	0.7	0.5	-0.4	0.9
HF	1.0	0.8	2.3	1.0	0.9	2.2	0.9	0.8	1.6	0.9	0.8	1.5
SPW92	2.4	-2.1	4.8	0.8	-0.6	2.2	0.7	-0.7	1.3	0.9	-0.8	1.6
PBE	2.1	-1.9	4.0	0.8	-0.6	2.0	0.8	-0.7	1.3	0.9	-0.9	1.5
BLYP	2.2	-2.0	4.1	0.8	-0.6	2.0	0.7	-0.7	1.3	0.9	-0.8	1.4
B97M-V	1.8	-1.5	3.5	0.7	-0.6	1.5	0.7	-0.6	1.1	0.8	-0.8	1.4
SCAN	1.6	-1.4	3.5	0.7	-0.5	1.4	0.7	-0.6	1.3	0.8	-0.7	1.3
revM06-L	1.8	-1.5	4.1	0.8	-0.7	1.9	0.8	-0.8	1.4	1.0	-0.9	1.8
TPSS	1.9	-1.6	3.7	0.7	-0.6	1.7	0.7	-0.6	1.2	0.8	-0.8	1.3
B3LYP	1.7	-1.4	3.3	0.7	-0.5	1.3	0.6	-0.5	1.0	0.7	-0.7	1.2
PBE0	1.5	-1.2	3.1	0.6	-0.5	1.3	0.5	-0.5	0.9	0.7	-0.6	1.2
MN15	1.5	-1.3	3.3	0.6	-0.5	1.3	0.5	-0.5	0.9	0.7	-0.6	1.2
CAM-B3LYP	1.4	-1.2	2.9	0.5	-0.4	1.2	0.4	-0.4	0.7	0.6	-0.5	1.0
ω B97X-V	1.3	-1.1	2.8	0.5	-0.4	1.1	0.4	-0.4	0.8	0.6	-0.5	1.0
ω B97M-V	1.4	-1.2	2.8	0.5	-0.4	1.1	0.4	-0.4	0.8	0.6	-0.5	0.9

4.1 Spin-contaminated cases in RSE43

1. Singlet species with UHF $\langle S^2 \rangle > 0$: toluene, acrylonitrile and nitromethane.
2. Doublet radicals with UHF $\langle S^2 \rangle > 0.9$: allyl, acetaldehyde radical (vinoxy), acetonitrile radical, nitromethyl radical, benzyl, acrylonitrile radical, aminoacetonitrile radical, propargyl and 1-fluorovinyl.