Supporting Information for:

Robust and Affordable Multi-Coefficient Methods For Thermochemistry and Thermochemical Kinetics: The MCCM/3 Suite

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Contents

[a]SAC is a single-coefficient correlation method, but SAC/3 is part of the MCCM/3 suite.

[b]MCSAC is the special class of MCCM in which there are two or more coefficients but only one basis set.

Table S1. Atomization Energies (kcal/mol)

Molecule	D_e	Molecule	D_e	Molecule	D_e
CH ($^2\Pi$)	84.00	S_2	101.67	H_2CCH	445.79
CH_2 ($^3B_1$)	190.97	Cl_2	57.97	$HCOOCH_3$	785.26
CH_2 ($^1A_1$)	181.50	SiO	192.08	HCOOH	500.98
CH_3 ($^2A''_2$)	307.46	SC	171.31	NF_3	204.53
CH_4	420.11	SO	125.00	PF_3	363.87
NH	83.67	ClO	64.49	SH	86.98
NH_2	181.90	ClF	61.36	$SiCl_4$	384.94
NH_3	297.90	Si_2H_6	530.81	SiF_4	574.35
OH	107.06	CH_3Cl	394.64	C_2H_5	603.75
OH_2	232.60	CH_3SH	473.84	C_4H_6 [d]	987.2
FH	141.05	HOCl	164.36	C_4H_6 [e]	1001.61
SiH_2 ($^1A_1$)	151.79	SO_2	257.86	HCOCOH	633.35
SiH_2 ($^3B_1$)	131.05	$AlCl_3$	306.26	CH_3CHO	677.03
SiH_3	227.37	AlF_3	426.50	C_2H_4O	650.70
SiH_4	322.40	BCl_3	322.90	C_2H_5O	698.64
PH_2	153.20	BF_3	470.04	H_3COCH_3	798.05
PH_3	242.55	C_2Cl_4	466.28	H_3CCH_2OH	810.36
SH_2	182.74	C_2F_4	583.96	C_3H_4 [f]	703.20
ClH	106.50	C_3H_4 [a]	704.79	C_3H_4 [g]	682.74
HCCH	405.39	C_4H_4O	993.74	H_3CCOOH	803.04
H_2CCH_2	563.47	C_4H_4S	962.73	H_3CCOCH_3	977.96
H_3CCH_3	712.80	C_4H_5N	1071.57	C_3H_6	853.41
CN	180.58	C_4H_6 [b]	1012.37	H_3CCHCH_2	860.61
HCN	313.20	C_4H_6 [c]	1004.13	C_3H_8	1006.87
CO	259.31	C_5H_5N	1237.69	$C_2H_5OCH_3$	1095.12
HCO	278.39	CCH	267.83	C_4H_{10} [h]	1303.04

H_2CO	373.73	CCl_4	312.74	C_4H_{10} [i]	1301.32
H_3COH	512.78	CF_3CN	639.85	C_4H_8 [j]	1149.01
N_2	228.46	CF_4	476.32	C_4H_8 [k]	1158.61
H_2NNH_2	438.60	CH_2OH	409.76	C_5H_8 [l]	1284.28
NO	155.22	CH_3CN	615.84	C_6H_6	1367.56
O_2	119.99	CH_3NH_2	582.56	CH_3CO	581.58
HOOH	268.57	CH_3NO_2	601.27	$(CH_3)_2CH$	900.75
F_2	38.20	$CHCl_3$	343.18	$(CH_3)_3C$	1199.34
CO_2	389.14	CHF_3	457.50	H_2CCO	532.73
Si_2	74.97	ClF_3	125.33		
P_2	117.09	H_2	109.48		

[a] propyne
[b] *trans*-1,3-butadiene
[c] 2-butyne
[d] bicylobutane
[e] cyclobutene
[f] allene
[g] cyclopropene
[h] cyclobutane
[i] isobutane
[j] transbutane
[k] isobutene
[l] spiropentane

Table S2. Ionization potentials (kcal/mol)

	IP	EA
C	259.7	29.1
S	238.9	47.9
SH	238.9	53.3
Cl	299.1	83.4
Cl_2	265.3	55.6
OH	299.1	42.1
O	313.9	33.7
O_2	278.9	10.8
P	241.9	17.2
PH	234.1	23.2
PH_2	226.3	29.4
S_2	216.0	38.5
Si	187.9	31.9

Table S3. Barrier Heights (kcal/mol)

Reaction	$V_f^{\ddagger}$	$V_r^{\ddagger}$
1. $Cl + H_2 \rightarrow HCl + H$	8.7	5.6
2. $OH + H_2 \rightarrow H + H_2O$	5.7	22.0
3. $CH_3 + H_2 \rightarrow H + CH_4$	11.4	14.6
4. $OH + CH_4 \rightarrow CH_3 + H_2O$	6.7	20.2
5. $H + CH_3OH \rightarrow CH_2OH + H_2$	7.3	13.8
6. $H + H_2 \rightarrow H_2 + H$	9.6	9.6
7. $OH + NH_3 \rightarrow H_2O + NH_2$	3.2	13.2
8. $HCl + CH_3 \rightarrow Cl + CH_4$	1.8	7.8
9. $OH + C_2H_6 \rightarrow H_2O + C_2H_5$	3.4	20.7
10. $F + H_2 \rightarrow H + HF$	1.8	33.2
11. $OH + CH_3 \rightarrow O + CH_4$	7.8	13.7
12. $H + PH_3 \rightarrow PH_2 + H_2$	3.2	25.5
13. $H + ClH' \rightarrow HCl + H'$	18.0	18.0
14. $OH + H \rightarrow H_2 + O$	10.1	13.1
15. $H + trans\text{-}N_2H_2 \rightarrow H_2 + N_2H$	5.9	41.0
16. $H + H_2S \rightarrow H_2 + HS$	3.6	17.4
17. $O + HCl \rightarrow OH + Cl$	9.8	9.9
18. $CH_4 + NH \rightarrow NH_2 + CH_3$	8.4	22.7
19. $C_2H_6 + NH \rightarrow NH_2 + C_2H_5$	8.0	18.4
20. $C_2H_6 + NH_2 \rightarrow C_2H_5 + NH_3$	10.4	17.8
21. $NH_2 + CH_4 \rightarrow CH_3 + NH_3$	14.5	17.9
22. *s-trans cis*-$C_5H_8 \rightarrow$ *s-trans cis*-C_5H_8	38.4	38.4

Table S4. Coefficients for other new SAC methods

Method	VERSION	
	v3m[a]	v3s[b]
SAC-MP2/pDZ	1.2638	1.2672
SAC-MP2/6-31+G(2df,p)	1.0530	1.0563
SAC-MP2/MG3S	1.0268	1.0300
SAC/3m	1.1478[d]	
SAC-MP4SDQ/pDZ	1.4281	1.4320
SAC-MP4SDQ/pTZ	1.1569	1.1808
SAC-MP4/pDZ	1.3394	1.3430
SAC-MP4/pTZ	1.0766	1.0803
SAC-CCSD/pDZ	1.4573	1.4613
SAC-CCSD/pTZ	1.1997	1.2036
SAC-CCSD(T)/pDZ	1.3753	1.3790
SAC-CCSD(T)/pTZ	1.1156	1.1193
SAC-MP2/pTZ	1.0219	1.0255
SAC-MP2/6-31G(d)	1.2979	1.3019
SAC-MP2/6-31G†	1.3218	1.3258
SAC-MP2/6-31G(d,p)	1.1671	1.1707
SAC-MP2/6-31+G(d,p)	1.1761	1.1796

[a]Spin-orbit energy is implicitly accounted for in the parameters
[b]Spin-orbit energy corrections (E_{so}) should be added.
[c]In tables we often use the following shorthand notation: pDZ ≡ cc-pVDZ and pTZ ≡ cc-pVTZ.
[d]Same as SAC-MP2/6-31+G(d,2p)/3m

Table S5. Coefficients for new MCSAC methods

Method	VERSION	c_1	c_2	c_3
MCSAC-MP4SDQ/pDZ[a]	v3m	1.3747	0.9511	
	v3s	1.3734	0.9093	
MCSAC-MP4SDQ/pTZ	v3m	1.1366	0.8621	
	v3s	1.1260	0.7771	
MCSAC-MP4/pTZ	v3m	1.1023	1.1119	0.8192
	v3s	1.0917	1.0746	0.9130
MCSAC-CCSD/pDZ	v3m	1.3900	0.9366	
	v3s	1.3886	0.8993	
MCSAC-CCSD/pTZ	v3m	1.1472	0.8347	
	v3s	1.1382	0.7683	
MCSAC-CCSD(T)/pTZ	v3m	1.1119	0.9676	0.8427
	v3s	1.0929	0.9308	1.1310

[a]In tables we often use the following shorthand notation: pDZ ≡ cc-pVDZ and pTZ ≡ cc-pVTZ.

Table S6. Coefficients for other new MCCM methods

Method	VERSION	c_0[a]	c_1	c_2	c_3	c_4	c_5	c_6	c_7
MCCM-CO-MP2	v3m		1.1361	0.7609	2.6099				
	v3s		1.1722	0.7648	2.5938				
MCCM-CO-MP4SDQ	v3m		1.4282	0.9551	1.9690	0.6646	1.1617		
	v3s		1.4285	0.9382	2.0131	0.6384	0.7710		
MCCM-CO-MP4	v3m		1.5666	0.8071	2.1216	1.3189	1.9612	2.3753	2.1027
	v3s		1.5452	0.7907	2.0069	1.4437	2.3951	2.2611	4.3640
MCCM-CO-CCSD	v3m		1.4306	0.9709	1.9298	0.7020	0.8383		
	v3s		1.4321	0.9555	1.9709	0.6752	0.5276		
MCCM-CO-CCSD(T)	v3m		1.5652	0.8370	2.0959	0.9349	1.3857	2.2431	1.1679
	v3s		1.5516	0.8201	2.0907	0.9442	1.1641	2.2793	1.8859
MCCM-UT-MP4SDQ	v3m		1.3772	0.9318	2.0071	0.7505			
	v3s		1.3949	0.9231	2.0361	0.6956			
MCCM-UT-MP4	v3m		1.5394	0.7735	2.3270	1.2431	2.5328		
	v3s		1.5544	0.7645	2.3611	1.1834	2.5178		

Table S6. (continued)

Methods	VERSION	c_0	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8
MCCM-UT-CCSD(T)	v3m		1.5118	0.8062	2.2306	0.9670	2.2989			
	v3s		1.5360	0.7937	2.2635	0.9254	2.3616			
MCCM-UT-CCSD	v3m		1.3800	0.9505	1.9749	0.7531				
	v3s		1.4008	0.9425	1.9995	0.7073				
MC-CO/3m	v3m		0.9383	0.8595	1.9054					
MC-UT/3m	v3m		1.0902	1.1556	1.1524	1.3963				
MC-QCISD/3m	v3m		1.0325	1.1357	1.2226	1.2208				
MCG2	v3m	1.0144	1.1576	1.0266	1.1630	1.3435	1.4462	1.6410	1.2324	1.1482
	v3s	1.0146	1.1567	1.0258	1.1589	1.3331	1.2197	1.5563	1.6337	1.1578
MCG3/3m	v3m	1.0073	1.1172	1.0588	1.1951	1.1212	0.8412	1.3058		

[a]The c_0 coefficient is equal to 1.0000 if not present in the table.

Table S7. Mean unsigned error over Database/3 and cost of SAC methods

Method	VERSION		Cost		
	v3m[a]	v3s[b]	Energy	Gradient	Hessian
SAC-MP2/6-31G(d)	15.4	15.3	1.3	4.4	27
SAC-MP2/6-31G†	14.9	14.9	1.3	4.4	27
SAC-MP2/6-31G(d,p)	9.7	9.7	2.0	7.5	57
SAC-MP2/pDZ[c]	9.7	9.7	2.8	8.3	60
SAC-MP2/6-31+G(d,p)	7.6	7.6	2.2	8.5	91
SAC-MP2/6-31+G(d,2p)	6.0	6.0	4.1	13	160
SAC-MP2/6-31+G(2df,p)	7.8	7.7	8.9	40	520
SAC-MP4SDQ/pDZ	7.1	7.3	4.6	19	840
SAC-MP2/MG3S	7.1	7.0	50	190	2300
SAC-MP2/pTZ	6.5	6.3	67	200	2500
SAC-MP4/pDZ	7.1	7.3	12	570	27000
SAC-CCSD/pDZ	7.2	7.3	15	700	34000
SAC-MP4SDQ/pTZ	4.1	4.5	130	730	34000
SAC-CCSD(T)/pDZ	6.9	7.1	26	1300	61000
SAC-MP4/pTZ	3.2	3.4	400	20000	9.5×10^5
SAC-CCSD/pTZ	4.1	4.4	530	25000	1.2×10^6
SAC-CCSD(T)/pTZ	2.9	3.1	860	41000	2.0×10^6

[a]Spin-orbit energy is implicitly accounted for in the parameters

[b]Spin-orbit energy corrections (E_{SO}) are added for these calculations.

[c]In tables we often use the following shorthand notation: pDZ ≡ cc-pVDZ and pTZ ≡ cc-pVTZ.

Table S8. Mean unsigned error over Database/3 and cost of MCSAC methods[a]

Method	VERSION		Cost		
	v3m[b]	v3s[c]	Energy	Gradient	Hessian
MCSAC-MP4SDQ/pDZ[d]	7.0	7.2	4.6	26	840
MCSAC-CCSD/pDZ	6.7	6.9	15	700	34000
MCSAC-MP4SDQ/pTZ	3.6	3.7	130	920	34000
MCSAC-MP4/pTZ	3.2	3.3	400	20000	9.5×10^5
MCSAC-CCSD/pTZ	3.2	3.3	530	25000	1.2×10^6
MCSAC-CCSD(T)/pTZ	2.9	2.8	860	41000	2.0×10^6

[a]Note that there are no MCSAC methods in the MCCM/3 suite because we have found, both in previous work and in the present re-examination, that the best performance-to-cost ratios are achieved by methods that include at least two different treatments of electron correlation and at least two different basis sets whereas MCSAC methods are based on a single basis set.

[b]Spin-orbit energy is implicitly accounted for in the parameters.

[c]Spin-orbit energy corrections (E_{SO}) are added for these calculations.

[d]In tables we often use the following shorthand notation: pDZ ≡ cc-pVDZ and pTZ ≡ cc-pVTZ.

Table S9. Mean unsigned error (kcal/mol) and cost for MCCM methods

Method	VERSION		Cost		
	v3m[a]	v3s[b]	Energy	gradient	Hessian
MC-CO	3.1	3.1	51	160	1800
MC-UT	2.3	2.2	52	170	2100
MCCM-CO-MP2	4.5	4.3	70	210	2500
MC-QCISD	1.7	1.6	56	180	2800
MCCM-UT-MP4SDQ	3.2	3.1	79	230	3300
MCCM-UT-MP4	2.2	2.1	79	770	30000
MCG3	1.1	1.0	88	810	32000
MCCM-CO-MP4SDQ	3.1	3.1	140	940	35000
MCCM-UT-CCSD	2.9	2.9	82	900	36000
MCCM-UT-CCSD(T)	1.8	1.6	94	1500	63000
MCG2	1.5	1.5	270	10000	4.9×10^5
MCCM-CO-MP4	1.8	1.6	430	20000	9.8×10^5
MCCM-CO-CCSD	2.8	2.8	540	26000	1.2×10^6
MCCM-CO-CCSD(T)	1.5	1.4	880	42000	2.0×10^6

Table S10. Mean unsigned error (kcal/mol) for other *ab initio* methods

	AE	BH	IP	EA	All
HF/6-31G(,p)	183.3	13.6	20.7	23.9	118.2
HF/6-31G†	152.7	13.4	18.0	38.0	100.3
HF/6-31G(d,p)	147.5	13.0	18.2	38.1	97.1
HF/6-31G(2d,d,p)	154.1	12.8	19.2	38.4	101.1
HF/6-31G(2d,p)	146.8	13.0	18.2	39.3	96.8
HF/6-31G(2df)	147.2	13.0	18.0	39.6	97.0
HF/6-31G(2df,2d,)	149.4	12.8	18.1	39.6	98.3
HF/6-31G(2df,d,p)	145.1	12.9	18.5	34.0	95.3
HF/6-31G(2df,2d,p)	146.2	13.2	17.9	26.8	95.5
HF/6-31+G(2df)	147.9	13.3	17.8	26.9	96.6
HF/6-31+G(2df,p)	144.9	13.3	17.8	26.9	94.7
HF/6-31+G(2df,2p)	144.6	13.2	17.8	26.9	94.5
HF/aug-cc-pVDZ	154.2	12.5	17.3	25.7	100.1
HF/6-311G(d,p)	151.9	12.8	17.8	31.9	99.3
HF/6-311G(2df,p)	146.2	12.9	17.9	32.7	95.9
HF/6-311+G(3df,2p)	144.4	13.1	17.9	26.9	94.4
HF/cc-pVTZ	146.6	13.0	17.9	34.7	96.3
MP2/6-31G(,p)	68.9	7.7	11.6	11.5	45.5
MP2/6-31G†	40.6	7.0	11.5	28.1	29.3
MP2/cc-pVDZ	34.9	4.1	9.7	29.4	25.1
MP2/6-31G(d,p)	24.2	5.6	10.8	27.3	18.9
MP2/6-31G(2d,d,p)	33.7	4.9	7.6	22.5	23.9
MP2/6-31G(2d,p)	20.5	5.3	7.9	22.9	16.0
MP2/6-31G(2df)	22.8	5.6	5.6	21.4	17.2
MP2/6-31G(2df,2d,)	31.8	5.6	6.4	21.9	22.8
MP2/6-31G(2df,d,p)	20.3	5.0	6.4	16.4	15.3

Table S10. continued

	AE	BH	IP	EA	All
MP2/6-31G(2df,2d,p)	19.1	5.3	5.1	5.4	13.7
MP2/6-31+G(2df)	21.9	5.8	4.7	5.2	15.5
MP2/6-31+G(2df,p)	11.8	5.1	4.5	5.1	9.1
MP2/6-31+G(2df,2p)	9.9	4.4	4.4	5.0	7.8
MP2/6-311G(d,p)	25.6	4.8	10.4	19.3	18.9
MP2/6-311G(2df,p)	12.7	4.1	4.4	13.3	10.0
MP2/6-311+G(3df,2p)	9.7	4.3	3.8	3.4	7.5
MP2/cc-pVTZ	7.9	3.9	4.1	14.2	7.1
MP3/6-31G(d,p)	35.7	6.2	10.1	28.0	26.1
MP3/6-311G(d,p)	39.4	5.0	9.8	20.3	27.4
MP3/6-311G(2df,p)	23.7	4.4	3.0	14.0	16.7
MP3/cc-pVTZ	20.9	4.1	2.7	14.9	15.0
CCD/6-31G(d)	54.2	7.6	11.3	28.7	37.8
CCD/6-31+G(d)	55.8	7.6	10.5	12.2	37.5
MP4SDQ/6-31G(d,p)	36.2	5.7	11.0	28.4	26.3
MP4SDQ/6-311G(d,p)	39.5	4.3	10.6	20.5	27.4
MP4SDQ/6-311G(2df,p)	24.9	3.9	3.8	14.6	17.5
MP4SDQ/cc-pVTZ	22.3	3.5	3.5	15.5	15.8
CCSD/cc-pVTZ	24.5	2.8	3.8	15.8	17.0
QCISD/6-31+G(d)	53.3	5.5	10.5	11.6	35.4
QCISD/6-31G(d,p)	37.5	4.7	11.2	28.6	26.9
QCISD/6-311G(d,p)	40.9	3.4	10.8	20.7	28.0
MP4/6-311G(d,p)	30.8	3.3	10.9	20.1	21.8
MP4/6-311G(2df,p)	14.3	2.7	3.8	13.9	10.7
QCISD(T)/6-31G(d,p)	31.6	3.8	11.5	28.7	23.1
QCISD(T)/6-311G(d,p)	33.6	2.5	11.0	20.3	23.4