

SUPPORTING INFORMATION

A Comprehensive Benchmark Investigation of Quantum Chemical Methods for Carbocations

Marcelo T. de Oliveira*^{1,2}, Júlia M. A. Alves², Natália Lussari Vrech³,
Ataualpa A. C. Braga³, Cristina A. Barboza^{4,5}

1 – Department of Chemistry and Physics, La Trobe Institute of Molecular Sciences,
La Trobe University, Melbourne, Victoria 3086, Australia

2 – Chemistry Institute of São Carlos, University of São Paulo, Av. Trabalhador São Carlense 400,
13566–590, São Carlos, SP, Brazil

3 – Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes 748,
05508–000, São Paulo, SP, Brazil

4 – Faculty of Chemistry, Wrocław University of Science and Technology, Wrocław, Poland

5 – Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, Warsaw, Poland

mtavareso@usp.br

Table 1. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol⁻¹) for CCSD(T) methods using various basis sets.

Method	MAD	SD	max
CCSD(T)/def2-TZVPP	0.25	0.19	0.96
CCSD(T)/def2-ma-TZVPP	0.21	0.18	0.90
CCSD(T)/def2-QZVPP	0.16	0.11	0.55
CCSD(T)/def2-QZVPP(RIJCOSX)	0.15	0.11	0.58
CCSD(T)/CBS(def2-Q/TZVPP) (RIJCOSX)	0.12	0.10	0.42
CCSD(T)/aug-cc-pVDZ	0.54	0.55	2.81
CCSD(T)/cc-pVTZ	0.20	0.18	0.77
CCSD(T)/aug-cc-pVTZ	0.22	0.17	0.82
CCSD(T)/aug-cc-pwCVTZ	0.19	0.14	0.68
CCSD(T)/cc-pVQZ	0.11	0.10	0.44
CCSD(T)/cc-pVQZ(RIJCOSX)	0.11	0.09	0.45

Table 2. Percentage mean absolute relative error (%MARE), standard deviation (SD) and maximum deviation (max) parameters (%) for CCSD(T) methods using various basis sets.

Method	%MARE	SD	max
CCSD(T)/def2-TZVPP	1.75	1.35	4.57
CCSD(T)/def2-ma-TZVPP	1.51	1.24	4.26
CCSD(T)/def2-QZVPP	1.07	0.76	2.69
CCSD(T)/def2-QZVPP(RIJCOSX)	1.06	0.78	2.51
CCSD(T)/CBS(def2-Q/TZVPP) (RIJCOSX)	0.75	1.12	4.14
CCSD(T)/aug-cc-pVDZ	4.09	4.26	15.30
CCSD(T)/cc-pVTZ	1.28	1.24	3.98
CCSD(T)/aug-cc-pVTZ	1.57	1.27	4.42
CCSD(T)/aug-cc-pwCVTZ	1.38	1.10	3.88
CCSD(T)/cc-pVQZ	0.78	0.76	2.72
CCSD(T)/cc-pVQZ(RIJCOSX)	0.80	0.78	2.88

Table 3. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol⁻¹) for CCSD(T) methods using various basis sets. Values are compared to W1-F12.

Method	MAD	SD	max
CCSD(T)/def2-TZVPP	0.34	0.23	0.96
CCSD(T)/ma-def2-TZVPP	0.32	0.22	0.90
CCSD(T)/def2-QZVPP	0.18	0.14	0.55
CCSD(T)/def2-QZVPP(RIJCOSX)	0.19	0.15	0.58
CCSD(T)/CBS(def2-Q/TZVPP) (RIJCOSX)	0.12	0.12	0.42
CCSD(T)/aug-cc-pVDZ	0.57	0.38	1.47
CCSD(T)/cc-pVTZ	0.26	0.20	0.77
CCSD(T)/aug-cc-pVTZ	0.30	0.21	0.82
CCSD(T)/aug-cc-pwCVTZ	0.27	0.17	0.68
CCSD(T)/cc-pVQZ	0.14	0.11	0.44
CCSD(T)/cc-pVQZ(RIJCOSX)	0.13	0.12	0.45

Table 4. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol⁻¹) comparing CCSD(T)/CBS and W1-F12.

Method	MAD	SD	max
CCSD(T)/CBS x W _n -F12	0.10	0.08	0.30

Table 5. Percentage mean absolute relative error (%MARE), standard deviation (SD) and maximum deviation (max) parameters (%) comparing CCSD(T)/CBS and W1-F12.

Method	%MARE	SD	max
CCSD(T)/CBS x W _n -F12	0.8	0.6	2.2

Table 6. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol⁻¹) for CBS-QB3 composite method.

Method	MAD	SD	max
CBS-QB3	1.58	1.02	3.50

Table 7. Percentage mean absolute relative error (%MARE), standard deviation (SD) and maximum deviation (max) parameters (%) for CBS-QB3 composite method.

Method	%MARE	SD	max
CBS-QB3	10.83	8.79	27.60

Table 8. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol⁻¹) for all 75 dispersion-uncorrected DFAs.

#	DFA	MAD	SD	max	#	DFA	MAD	SD	max
1	SVWN5	2.31	1.73	7.43	39	PBE0	0.86	0.67	2.72
2	Xalpha	1.72	1.32	5.09	40	SOGGA11X	0.95	0.70	2.54
3	BLYP	5.94	3.84	11.35	41	ω B97X	1.31	0.89	3.46
4	HCTH/407	2.38	1.67	5.96	42	X3LYP	4.66	2.73	8.54
5	N12	1.21	0.74	3.14	43	BMK	1.33	1.32	4.68
6	PBE	1.39	0.90	3.22	44	M05	2.33	1.82	6.49
7	RPBE	2.27	1.30	4.77	45	M06	2.12	1.47	5.36
8	revPBE	2.05	1.17	4.31	46	M06-2X	1.04	0.86	3.15
9	rPW86PBE	4.42	2.81	8.95	47	M08-HX	1.07	0.71	3.00
10	XLYP	6.47	4.22	12.43	48	MN15	0.77	0.57	2.77
11	M06-L	3.00	2.36	10.66	49	PW6B95	1.06	0.63	2.50
12	M11-L	4.85	2.49	8.84	50	revPBE0	0.96	0.66	2.59
13	MN12-L	3.27	1.37	5.19	51	revTPSS0	1.30	0.86	3.35
14	MN15-L	1.51	0.84	3.30	52	revTPSSh	1.02	0.81	2.67
15	PKZB	0.92	0.72	2.65	53	SCAN0	1.09	0.63	2.62
16	revTPSS	1.23	0.86	2.98	54	TPSS0	0.65	0.52	2.22
17	RSCAN	2.46	1.03	4.45	55	TPSSh	0.99	0.65	2.36
18	R2SCAN	2.35	0.98	4.14	56	τ HCTHhyb	2.59	1.30	4.89
19	SCAN	1.85	0.67	3.06	57	B2CN-PLYP	2.03	1.37	4.65
20	TPSS	1.38	0.93	3.15	58	B2GP-PLYP	2.01	1.21	3.73
21	τ HCTH	2.95	1.76	6.36	59	B2PLYP	2.76	1.72	5.27
22	APFD	0.81	0.61	2.63	60	DOD-SCAN	3.36	2.32	7.15
23	B1B95	0.81	0.76	2.93	61	DSD-PBEB95	0.89	0.67	2.37
24	B3LYP	4.74	2.81	8.73	62	DSD-PBEP86	0.36	0.30	1.08
25	B97	2.64	1.36	5.19	63	LS1DH-PBE	1.59	1.36	4.26
26	B98	3.10	1.70	6.45	64	mPW2PLYP	2.83	1.67	5.28
27	BB1K	1.35	0.95	3.39	65	PBE0-2	1.72	1.36	4.29
28	BHandHLYP	4.44	2.33	7.81	66	PBE0DH	1.20	0.64	2.29
29	CAMB3LYP	3.33	1.60	5.57	67	PBEQIDH	1.95	1.27	4.41
30	HSE06	1.01	0.67	2.74	68	PWPB95	0.40	0.38	1.39
31	LC- ω HPBE	3.30	2.55	10.27	69	revDOD-PBEP86	0.78	0.46	1.73
32	LC-PBE	3.77	3.73	12.14	70	revDSD-PBEP86	0.73	0.45	1.74
33	MN12SX	1.84	0.87	3.30	71	RSX-0DH	3.24	2.84	8.98
34	mPW1B95	0.85	0.68	2.61	72	RSX-QIDH	2.65	2.31	7.09
35	mPW1PW91	1.01	0.67	2.67	73	ω B97M-2	0.63	0.45	1.66
36	mPWB1K	1.36	1.29	5.70	74	ω B97X-2(TQZ)	0.38	0.31	1.20
37	N12SX	1.01	0.68	2.73	75	SOS0-PBE2-0	1.70	1.10	4.02
38	O3LYP	1.05	0.79	3.31					

Table 9. Mean deviation (MD) for all 75 dispersion-uncorrected DFAs (kcal mol⁻¹).

#	DFA	MD	#	DFA	MD
1	SVWN5	1.02	39	PBE0	-0.27
2	Xalpha	0.07	40	SOGGA11X	-0.71
3	BLYP	-5.54	41	ω B97X	-0.86
4	HCTH/407	-2.10	42	X3LYP	-4.43
5	N12	-0.93	43	BMK	0.50
6	PBE	-1.14	44	M05	0.62
7	RPBE	-1.96	45	M06	-1.83
8	revPBE	-1.74	46	M06-2X	0.29
9	rPW86PBE	-4.14	47	M08-HX	-0.35
10	XLYP	-6.03	48	MN15	-0.21
11	M06-L	-1.22	49	PW6B95	-0.95
12	M11-L	-4.48	50	revPBE0	-0.71
13	MN12-L	-3.03	51	revTPSS0	0.72
14	MN15-L	-1.22	52	revTPSSh	0.43
15	PKZB	-0.55	53	SCAN0	0.90
16	revTPSS	0.71	54	TPSS0	-0.26
17	RSCAN	-2.20	55	TPSSh	-0.72
18	R2SCAN	-1.72	56	τ HCTHhyb	-2.37
19	SCAN	-1.06	57	B2CN-PLYP	1.87
20	TPSS	-2.66	58	B2GP-PLYP	-1.91
21	τ HCTH	-0.33	59	B2PLYP	-2.62
22	APFD	0.11	60	DOD-SCAN	-3.09
23	B1B95	-4.49	61	DSD-PBEB95	0.68
24	B3LYP	-1.35	62	DSD-PBEP86	0.04
25	B97	-2.86	63	revDSD-PBEP86	-0.64
26	B98	-1.02	64	RSX-0DH	2.46
27	BB1K	-4.23	65	RSX-QIDH	2.13
28	BHandHLYP	-3.17	66	ω B97M-2	-0.56
29	CAMB3LYP	-0.81	67	ω B97X-2(TQZ)	-0.12
30	HSE06	2.46	68	SOS0-PBE2-0	-1.35
31	LC- ω HPBE	2.77	69	revDOD-PBEP86	-0.67
32	LC-PBE	-1.60	70	revDSD-PBEP86	-0.64
33	MN12SX	0.16	71	RSX-0DH	2.46
34	mPW1B95	-4.78	72	RSX-QIDH	2.13
35	mPW1PW91	-0.82	73	ω B97M-2	-0.56
36	mPWB1K	0.68	74	ω B97X-2(TQZ)	-0.12
37	N12SX	-0.20	75	SOS0-PBE2-0	-1.35
38	O3LYP	-0.45			

Table 10. Percentage mean absolute relative error (%MARE), standard deviation (SD) and maximum deviation (max) parameters (%) for all 75 dispersion-uncorrected DFAs (%).

#	DFA	%MARE	SD	max	#	DFA	%MARE	SD	max
1	SVWN5	14.6	9.9	41.3	39	PBE0	6.6	7.0	27.1
2	Xalpha	11.1	10.0	41.0	40	SOGGA11X	6.8	6.3	28.3
3	BLYP	40.3	33.8	146.2	41	ω B97X	9.7	8.2	35.6
4	HCTH/407	16.4	14.0	55.3	42	X3LYP	31.6	25.4	104.3
5	N12	10.2	10.0	39.4	43	BMK	9.8	9.4	30.9
6	PBE	11.2	9.7	34.9	44	M05	15.8	17.4	85.2
7	RPBE	16.8	13.4	47.3	45	M06	14.2	10.7	45.6
8	revPBE	15.4	12.4	41.9	46	M06-2X	7.8	8.3	35.7
9	rPW86PBE	29.8	24.9	99.1	47	M08-HX	8.5	7.3	26.5
10	XLYP	43.7	36.6	159.5	48	MN15	5.3	4.6	20.4
11	M06-L	19.4	14.1	56.5	49	PW6B95	7.6	5.6	24.8
12	M11-L	37.1	30.8	143.7	50	revPBE0	7.5	7.5	30.7
13	MN12-L	24.4	16.9	78.1	51	revTPSS0	9.0	6.9	31.9
14	MN15-L	11.2	9.3	47.1	52	revTPSSh	7.2	6.7	21.1
15	PKZB	6.6	6.8	26.4	53	SCAN0	8.3	6.9	26.0
16	revTPSS	9.0	7.6	27.1	54	TPSSh	7.1	6.4	25.7
17	RSCAN	17.7	10.2	34.2	55	TPSS0	4.6	5.1	22.1
18	R2SCAN	16.9	9.9	30.3	56	τ HCTHhyb	18.6	14.4	57.9
19	SCAN	14.1	8.8	45.0	57	B2CN-PLYP	15.3	14.5	56.8
20	TPSS	10.0	8.6	30.3	58	B2GP-PLYP	12.9	8.9	39.0
21	τ HCTH	20.8	16.2	55.1	59	B2PLYP	18.1	13.9	60.4
22	APFD	6.3	7.0	107.0	60	DOD-SCAN	22.1	19.2	71.2
23	B1B95	5.7	6.1	37.0	61	DSD-PBEB95	6.2	5.8	28.5
24	B3LYP	32.1	25.1	62.0	62	DSD-PBEP86	2.3	2.4	10.6
25	B97	19.1	15.3	32.3	63	LS1DH-PBE	10.9	11.0	51.8
25	B98	22.2	18.5	86.6	64	mPW2PLYP	18.6	13.6	59.5
27	BB1K	10.2	8.9	61.7	65	PBE0-2	12.0	11.4	54.6
28	BHandHLYP	30.0	21.0	31.7	66	PBE0-DH	9.0	7.4	34.3
29	CAMB3LYP	23.3	16.1	80.8	67	PBE-QIDH	14.1	11.7	53.9
30	HSE06	7.9	7.6	129.6	68	PWPB95	2.6	2.8	13.8
31	LC- ω HPBE	20.8	16.7	53.8	69	revDOD-PBEP86	5.3	3.8	15.9
32	LC-PBE	25.7	27.8	25.9	70	revDSD-PBEP86	4.8	3.4	13.7
33	MN12SX	14.5	11.3	112.8	71	RSX-0DH	21.4	21.2	98.1
34	mPW1B95	6.3	6.4	34.2	72	RSX-QIDH	17.5	17.8	81.9
35	mPW1PW91	8.1	7.7	31.3	73	ω B97M-2	4.6	3.6	14.8
36	mPWB1K	9.3	8.8	42.2	74	ω B97X-2(TQZ)	2.4	2.3	9.1
37	N12SX	7.9	7.5	28.9	75	SOS0-PBE2-0	11.8	9.0	33.6
38	O3LYP	8.1	8.5	35.5					

Table 11. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol⁻¹) for dispersion-corrected DFAs.

Method	MAD	SD	max
N12-D3	1.04	0.80	2.89
PBE-D3(BJ)	1.36	0.85	2.99
PBE-D4	1.37	0.87	3.01
PBE-NL	0.96	0.68	3.00
B97M-D3(BJ)	4.51	1.88	6.94
B97M-D4	4.53	2.02	7.23
B97M-V	3.88	1.64	6.45
PKZB-D3	0.90	0.51	2.24
revTPSS-D3(BJ)	1.25	0.95	3.46
revTPSS-D4	1.22	0.93	3.29
revTPSS-NL	2.02	1.36	5.22
MN15-D3(BJ)	0.77	0.58	2.77
ωB97X-D3(BJ)	1.12	0.77	2.39
ωB97X-D4	1.31	0.89	3.47
ωB97X-V	1.15	0.58	2.05
ωB97M-D3(BJ)	1.62	0.75	2.98
ωB97M-D4	1.67	0.79	3.26
ωB97M-V	1.07	0.75	2.59
TPSS0-D3(BJ)	0.67	0.56	2.13
TPSS0-D4	0.73	0.54	1.97
TPSS0-NL	1.02	0.93	3.80
DSD-PBEP86-D3(BJ)	0.34	0.30	1.23
DSD-PBEP86-D4	0.38	0.35	1.39
DSD-PBEP86-NL	0.24	0.30	1.20
PWPB95-D3(BJ)	0.41	0.36	1.30
PWPB95-D4	0.36	0.34	1.27
PWPB95-NL	0.35	0.38	1.43
ωB97X-2-D3(BJ)	0.37	0.35	1.30

Table 12. Mean deviation (MD) for dispersion-corrected DFAs (kcal mol⁻¹).

Method	MD
N12-D3	0.76
PBE-D3(BJ)	-1.13
PBE-D4	-1.15
PBE-NL	-0.52
B97M-D3(BJ)	4.28
B97M-D4	4.30
B97M-V	3.68
PKZB-D3	0.21
revTPSS-D3(BJ)	0.72
revTPSS-D4	0.71
revTPSS-NL	1.56
MN15-D3(BJ)	0.18
ωB97X-D3(BJ)	-0.90
ωB97X-D4	-0.88
ωB97X-V	-0.25
ωB97M-D3(BJ)	-1.51
ωB97M-D4	-1.55
ωB97M-V	-0.93
TPSS0-D3(BJ)	-0.18
TPSS0-D4	-0.19
TPSS0-NL	0.40
DSD-PBEP86-D3(BJ)	-0.26
DSD-PBEP86-D4	-0.28
DSD-PBEP86-NL	-0.16
PWPB95-D3(BJ)	-0.30
PWPB95-D4	-0.20
PWPB95-NL	-0.05
ωB97X-2-D3(BJ)	-0.27

Table 13. Percentage mean absolute relative error (%MARE), standard deviation (SD) and maximum deviation (max) parameters for dispersion-corrected DFAs (%).

Method	%MARE	SD	max
N12-D3	10.1	8.0	41.5
PBE-D3(BJ)	10.8	9.5	33.5
PBE-D4	11.1	9.5	34.4
PBE-NL	7.7	7.7	29.8
B97M-D3(BJ)	30.6	17.3	77.7
B97M-D4	30.6	17.8	80.1
B97M-V	26.4	15.0	73.4
PKZB-D3	6.8	4.7	24.4
revTPSS-D3(BJ)	9.1	7.7	29.4
revTPSS-D4	8.9	7.5	28.4
revTPSS-NL	14.0	10.9	40.3
MN15-D3(BJ)	5.3	3.9	20.4
ω B97X-D3(BJ)	9.2	8.4	34.0
ω B97X-D4	10.0	8.2	35.7
ω B97X-V	8.4	7.0	28.5
ω B97M-D3(BJ)	11.5	8.1	30.1
ω B97M-D4	11.9	8.2	32.0
ω B97M-V	8.4	7.1	25.4
TPSS0-D3(BJ)	5.0	5.5	22.3
TPSS0-D4	5.3	5.4	21.3
TPSS0-NL	7.0	6.7	26.7
DSD-PBEP86-D3(BJ)	2.2	2.6	12.2
DSD-PBEP86-D4	2.4	2.9	13.8
DSD-PBEP86-NL	1.7	2.7	11.9
PWPB95-D3(BJ)	2.8	2.7	12.9
PWPB95-D4	2.4	2.6	12.6
PWPB95-NL	2.3	2.7	12.8
ω B97X-2-D3(BJ)	2.2	2.0	8.0

Table 14. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol⁻¹) for RI-MP2-D3(BJ) and RI-SCS-MP2-D3(BJ) using aug-cc-pVQZ basis set.

Method	MAD	SD	max
RI-MP2-D3(BJ)	2.92	1.79	5.44
SCS-MP2-D3(BJ)	1.72	1.08	3.88

Table 15. Percentage mean absolute relative error (%MARE), standard deviation (SD) and maximum deviation (max) parameters (%) for RI-MP2-D3(BJ) and RI-SCS-MP2-D3(BJ) using aug-cc-pVQZ basis set.

Method	%MARE	SD	max
RI-MP2-D3(BJ)	20.6	17.8	65.2
SCS-MP2-D3(BJ)	11.7	9.7	42.1

Table 16. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol⁻¹) for 3-fold corrected (3c) composite methods.

Method	MAD	SD	max
HF-3c	16.06	9.85	33.06
B97-3c	4.12	1.99	6.49
PBEh-3c	2.06	1.48	4.85
r ² SCAN-3c	2.76	1.00	4.73

Table 17. Percentage mean absolute relative error (%MARE), standard deviation (SD) and maximum deviation (max) parameters (%) for 3-fold corrected (3c) composite methods.

Method	%MARE	SD	max
HF-3c	110.6	105.1	386.6
B97-3c	26.9	19.9	73.5
PBEh-3c	13.7	10.9	49.2
r ² SCAN-3c	19.9	14.9	67.9

Table 18. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol⁻¹) for TPSS0 density functional using various basis sets.

Basis Set	MAD	SD	max
6-31G(d)	1.50	1.43	5.33
6-31+G(d,p)	1.05	1.00	4.04
6-311++G(2d,p)	0.81	0.60	2.44
6-311++G(3df,3pd)	0.70	0.62	2.32
cc-pVDZ	0.95	0.77	3.20
cc-pVTZ	0.68	0.56	2.26
cc-pVQZ	0.65	0.56	2.21
aug-cc-pVDZ	0.97	0.88	3.41
aug-cc-pVTZ	0.66	0.55	2.21
aug-cc-pVQZ	0.65	0.56	2.20
def2-mSVP	1.58	1.44	5.49
def2-SVP	1.10	0.78	2.69
def2-TZVP	0.74	0.58	2.25
def2-TZVPPD	0.73	0.56	2.21
def2-QZVPP	0.70	0.54	2.22
ma-def2-TZVP	0.74	0.58	2.24
ma-def2-QZVPP	0.66	0.55	2.22
pcSeg-0	11.12	7.05	23.35
pcSeg-1	2.16	1.24	4.22
aug-pcSeg-1	1.00	0.71	2.41
pcSeg-2	0.73	0.58	2.28
aug-pcSeg-2	0.72	0.56	2.23
pcSeg-3	0.71	0.57	2.22

Table 19. Percentage mean absolute relative error (%MARE), standard deviation (SD) and maximum deviation (max) parameters (%) for TPSS0 density functional using various basis sets.

Basis Set	%MARE	SD	max
6-31G(d)	9.8	9.6	40.0
6-31+G(d,p)	7.0	7.3	29.4
6-311++G(2d,p)	6.1	6.2	25.2
6-311++G(3df,3pd)	4.9	5.2	21.3
cc-pVDZ	7.2	8q.2	33.8
cc-pVTZ	4.9	5.3	22.4
cc-pVQZ	4.6	5.1	21.9
aug-cc-pVDZ	6.6	6.4	21.3
aug-cc-pVTZ	4.7	5.1	21.9
aug-cc-pVQZ	4.6	5.1	21.9
def2-mSVP	10.7	10.3	37.5
def2-SVP	8.2	9.2	43.8
def2-TZVP	5.5	5.7	22.4
def2-TZVPPD	5.4	5.6	21.9
def2-QZVPP	4.6	5.2	22.0
ma-def2-TZVP	5.5	5.7	22.3
ma-def2-QZVPP	4.7	5.1	22.0
pcSeg-0	79.0	73.9	277.2
pcSeg-1	15.4	12.9	59.5
aug-pcSeg-1	7.9	8.6	35.9
pcSeg-2	5.4	5.7	22.6
aug-pcSeg-2	5.3	5.5	22.1
pcSeg-3	5.2	5.6	22.1

Table 20. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (max) parameters (kcal mol⁻¹) for PWPB95-NL density functional method using various basis sets.

Basis Set	MAD	SD	max
cc-pVTZ	0.34	0.38	1.42
cc-pVQZ	0.35	0.38	1.47
aug-cc-pVTZ	0.35	0.38	1.51
aug-cc-pVQZ	0.35	0.38	1.51
def2-TZVPP	0.36	0.39	1.46
def2-QZVPP	0.35	0.38	1.43
ma-def2-QZVPP	0.35	0.38	1.43
aug-pcSeg-2	0.36	0.39	1.31

Table 21. Percentage mean absolute relative error (%MARE), standard deviation (SD) and maximum deviation (max) parameters (%) for PWPB95-NL density functional method using various basis sets.

Basis Set	%MARE	SD	max
cc-pVTZ	2.2	2.7	12.8
cc-pVQZ	2.3	2.7	12.8
aug-cc-pVTZ	2.3	2.7	12.3
aug-cc-pVQZ	2.3	2.7	12.7
def2-TZVPP	2.4	2.8	12.7
def2-QZVPP	2.3	2.7	12.8
ma-def2-QZVPP	2.3	2.7	12.8
aug-pcSeg-2	2.4	2.8	13.1

Table 22. Energies for Example 1 (sesquiterpene cations, A–D) in kcal mol⁻¹. Except for B3LYP, all other density functionals apply def2-QZVPP basis set.

METHOD	ENERGIES			
	E _a (C-to-D2)*	ΔH(D2-C)	E _a (B-to-D1)*	ΔH(D1-B)*
CCSD(T)/cc-pVQZ	65.0	21.0	-1.6	-3.7
N12-D3	58.8	16.1	0.3	-1.5
PBE-NL	55.9	15.2	-0.8	-2.3
PKZB-D3	58.8	16.8	0.4	-0.3
revTPSS-D4	54.7	16.0	0.4	1.3
MN15-D3(BJ)	63.2	18.5	-0.5	-3.4
TPSS0-D3(BJ)	61.7	17.4	-0.5	-2.7
DSD-PBEP86-NL	63.8	20.0	-1.5	-3.0
PWPB95-NL	61.7	19.5	-1.1	-2.8
ωB97X-2-D3(BJ)	64.1	19.9	-1.6	-2.8
B3LYP/6-31+G(d,p)**	59.4	11.1	1.1	-1.1

*D1 and D2 are conformers

**Differently from energies reported here, ZPE contribution was included in the original reference.

Table 23. Energies for Example 2 (aryl cations, E–I) in kcal mol⁻¹. Except for B3LYP, all other density functionals apply def2-QZVPP basis set.

METHOD	ENERGIES			
	ΔE(F-E)	E _a (F-to-G)	ΔH(H-F)	ΔE(I-H)
CCSD(T)/cc-pVQZ	-9.0	6.9	3.2	-14.2
PBE-NL	-11.5	5.1	2.8	-17.1
N12-D3	-11.3	5.1	2.9	-17.4
PKZB-D3	-9.8	5.1	3.3	-15.9
revTPSS-D4	-11.0	3.9	2.9	-16.6
TPSS0-D3(BJ)	-11.0	6.0	3.4	-16.9
MN15-D3(BJ)	-10.9	6.2	3.1	-16.3
DSD-PBEP86-NL	-10.1	5.8	3.3	-15.4
PWPB95-NL	-10.8	5.6	3.0	-16.0
ωB97X-2-D3(BJ)	-9.8	5.9	3.6	-15.3
B3LYP/6-31+G(d,p)*	-10.9	10.0	2.8	-17.4

*In the original reference, solvation contribution was included. Values here are in the gas phase.

Table 24. Mean absolute deviation (MAD), standard deviation (SD) and maximum deviation (kcal mol⁻¹) values for selected density functional methods applied to examples 1 and 2 (cations A–I). Except for B3LYP, all methods apply def2-QZVPP basis set.

Method	MAD	SD	max
B3LYP/6-31+G(d,p)	3.83	3.32	11.0
N12-D3	2.81	1.93	6.30
PBE-NL	3.07	2.98	9.17
PKZB-D3	2.50	2.01	6.24
revTPSS-D4	3.71	3.12	10.35
MN15-D3(BJ)	1.28	0.89	2.50
TPSS0-D3(BJ)	1.83	1.24	3.62
PWPB95-NL	1.38	0.98	3.33
DSD-PBEP86-NL	0.79	0.45	1.24
ω B97X-2-D3(BJ)	0.76	0.34	1.09