Excited-State Methods Based on State-Averaged Long-Range CASSCF Short-Range DFT

Supporting Information

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1 States included in the state-averaged CASSCF-DFT calculations for Thiel's benchmark set

Table 1: States included in the state-averaged CASSCF-DFT calculations. Point-group symmetry was not exploited.

Molecule	CAS	SA roots
ethene (D_{2h})	(2, 2)	2
E-butadiene (C_{2h})	(4, 4)	3
all-E-hexatriene (C_{2h})	(6, 6)	3
all-E-octatetraene (C_{2h})	(8, 8)	3
cyclopropene (C_{2v})	(4, 3)	3
cyclopentadiene (C_{2v})	(4, 4)	3
norbornadiene (C_{2v})	(4, 4)	5
benzene (D_{2h})	(6, 6)	11
naphthalene (D_{2h})	(10,10)	15
furan (C_{2v})	(6, 5)	4
pyrrole (C_{2v})	(6, 5)	4
imidazole (C_s)	(8, 7)	6
pyridine (C_{2v})	(8, 7)	11
pyrazine (D_{2h})	(10, 8)	16
pyrimidine (C_{2v})	(12, 9)	13
pyridazine (C_{2v})	(12, 9)	13
s-triazine (C_{2v})	(12, 9)	19
s-tetrazine (D_{2h})	(14,10)	21
formaldehyde (C_{2v})	(6, 4)	4
acetone (C_{2v})	(6, 5)	4
p-benzoquinone (D_{2h})	(12,10)	18
formamide (C_s)	(6, 4)	4
acetamide (C_s)	(6, 4)	4
propanamide (C_s)	(6, 4)	4
cytosine (C_s)	(14,11)	11
thymine (C_s)	(16,12)	11
uracil (C_s)	(14,10)	11
adenine (C_s)	(18,13)	8

2 Vertical singlet excitation energies using CASSCF-DFT methods.

2.1 CI-DFT method

Table 2: Vertical singlet excitation energies in eV using CI-based CASSCF-DFT methods with complex-translated (ct) functionals. CC3 and icMRCC2 results taken from Refs. 1, 2 and 3. The latter is denoted by an asterisk.

Molecule	State	Type	LDA	PBE	PBE0	srLDA	srPBE	srPBE0	Ref.
ethene	$1\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	6.80	6.94	7.85	7.91	7.96	7.91	8.37
E-butadiene	$1\ ^1B_u$	$\pi \rightarrow \pi^*$	4.50	4.64	5.22	6.41	6.45	6.40	6.22*
	$2\ ^1A_g$	$\pi \rightarrow \pi^*$	6.34	6.29	7.73	6.60	6.58	7.07	6.57*
all-E-hexatriene	$1\ ^1B_u$	$\pi \rightarrow \pi^*$	3.49	3.61	4.13	5.50	5.53	5.46	5.59*
	$2\ ^1A_g$	$\pi \rightarrow \pi^*$	5.04	5.02	6.25	5.45	5.44	5.88	5.56*
all-E-octatetraene	$2\ ^1A_g$	$\pi \rightarrow \pi^*$	4.17	4.16	3.93	4.66	4.65	5.04	4.79*
	$1\ ^1B_u$	$\pi \rightarrow \pi^*$	2.85	2.95	2.59	4.88	4.91	4.83	4.97*
cyclopropene	$1\ ^1B_1$	$\sigma \rightarrow \pi^*$	6.71	6.72	8.05	6.71	6.73	7.07	6.90
	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	5.61	5.83	6.95	6.78	6.84	6.93	7.10
cyclopentadiene	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	4.44	4.53	4.99	5.65	5.66	5.59	5.73
	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	6.11	6.07	7.33	6.51	6.50	6.95	6.61
	$3\ ^1A_1$	$\pi \rightarrow \pi^*$	7.00	7.19	8.36	8.63	8.67	8.76	8.69
norbornadiene	$1\ ^1A_2$	$\pi \rightarrow \pi^*$	4.47	4.58	5.74	5.63	5.64	5.69	5.64
	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	5.16	5.25	6.54	6.75	6.77	6.98	6.49
	$2\ ^1B_2$	$\pi \rightarrow \pi^*$	6.03	6.18	7.36	7.89	7.90	7.98	7.64
	$2\ ^1A_2$	$\pi \rightarrow \pi^*$	6.59	6.68	8.04	7.90	7.93	8.18	7.71
benzene	$1\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	5.15	5.12	6.26	5.01	5.01	5.39	5.07
	$1\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	5.70	5.84	6.75	6.19	6.23	6.19	6.68
	$1\ ^1E_{1u}$	$\pi \rightarrow \pi^*$	5.51	5.62	6.57	7.56	7.58	7.71	7.45
	$2\ ^1E_{2g}$	$\pi \rightarrow \pi^*$	7.99	7.90	9.62	8.19	8.17	8.81	8.43
naphthalene[a] TODO	$1\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	4.10	4.10	4.10	4.23	4.23	4.56	4.27
	$1\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	6.40	6.40	6.40	4.91	4.93	4.93	5.03
	$2\ ^1A_g$	$\pi \rightarrow \pi^*$	5.70	5.70	5.70	5.87	5.87	6.33	5.98
	$1\ ^1B_{2g}$	$\pi \rightarrow \pi^*$	8.51	8.51	8.51	6.04	6.03	6.37	6.07
	$3\ ^1A_g$	$\pi \rightarrow \pi^*$	6.70	6.70	6.70	6.67	6.66	7.17	6.90
	$2\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	8.04	8.04	8.04	6.59	6.60	6.75	6.33
	$2\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	8.05	8.05	8.05	6.49	6.51	6.64	6.57

Molecule	State	Type	LDA	PBE	PBE0	srLDA	srPBE	srPBE0	Ref.
	$2\ ^1B_{2g}$	$\pi \rightarrow \pi^*$	6.34	6.34	6.34	6.47	6.50	6.56	6.79
	$3\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	7.73	7.73	7.73	7.79	7.78	8.41	8.12
	$4\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	8.97	8.97	8.97	8.54	8.56	8.80	8.44
furan	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	6.15	6.14	7.52	6.48	6.48	6.93	6.62
	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	5.44	5.53	6.20	6.43	6.46	6.48	6.60
	$3\ ^1A_1$	$\pi \rightarrow \pi^*$	6.84	6.96	8.28	8.53	8.55	8.78	8.53
pyrrole	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	5.99	5.99	7.34	6.26	6.26	6.64	6.40
	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	5.60	5.70	6.53	6.54	6.56	6.67	6.71
	$3\ ^1A_1$	$\pi \rightarrow \pi^*$	6.64	6.73	8.04	8.22	8.23	8.47	8.17
imidazole	$2\ ^1A'$	$\pi \rightarrow \pi^*$	5.58	5.66	6.76	6.45	6.46	6.72	6.58
	$1\ ^1A''$	$n \rightarrow \pi^*$	6.24	6.29	8.04	6.69	6.74	7.34	6.82
	$3\ ^1A'$	$\pi \rightarrow \pi^*$	6.52	6.59	7.93	6.87	6.89	7.17	7.10
	$4\ ^1A'$	$\pi \rightarrow \pi^*$	6.88	6.94	8.46	8.50	8.52	8.84	8.45
	$2\ ^1A''$	$n \rightarrow \pi^*$	7.34	7.46	9.37	7.79	7.84	8.48	7.93
pyridine	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	4.98	4.98	6.07	5.11	5.01	5.59	5.15
	$1\ ^1B_1$	$n \rightarrow \pi^*$	4.56	4.69	6.44	4.96	4.89	5.49	5.05
	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	5.63	5.75	6.82	6.35	6.52	6.39	6.85
	$1\ ^1A_2$	$n \rightarrow \pi^*$	4.72	4.84	6.78	5.45	5.28	6.17	5.50
	$2\ ^1B_2$	$\pi \rightarrow \pi^*$	5.98	6.05	7.34	7.69	7.71	7.94	7.59
	$3\ ^1A_1$	$\pi \rightarrow \pi^*$	5.89	6.01	7.09	7.80	7.86	7.99	7.70
	$4\ ^1A_1$	$\pi \rightarrow \pi^*$	8.22	8.15	9.97	8.43	8.26	9.05	8.68
	$3\ ^1B_2$	$\pi \rightarrow \pi^*$	8.41	8.30	10.34	8.57	8.36	9.26	8.77
pyrazine	$1\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	4.63	4.64	5.54	4.99	4.99	5.70	4.99*
	$1\ ^1B_{3u}$	$n \rightarrow \pi^*$	3.57	3.70	5.11	4.10	4.16	4.59	4.24
	$1\ ^1B_{2g}$	$n \rightarrow \pi^*$	4.96	5.07	7.82	5.63	5.69	6.24	5.76*
	$1\ ^1A_u$	$n \rightarrow \pi^*$	4.13	4.25	6.18	5.03	5.09	5.70	5.08*
	$1\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	5.70	5.84	7.05	6.54	6.57	6.58	7.07
	$2\ ^1A_g$	$\pi \rightarrow \pi^*$	7.25	7.48	10.41	7.73	7.84	8.77	8.37*
	$2\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	6.69	6.75	8.44	8.17	8.19	8.52	8.05
	$2\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	6.25	6.34	7.49	8.08	8.10	8.30	8.06
	$1\ ^1B_{1g}$	$n \rightarrow \pi^*$	5.50	5.62	7.05	6.61	6.68	7.42	6.78*
pyrimidine	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	5.17	5.17	6.37	5.33	5.33	5.76	5.36
	$1\ ^1B_1$	$n \rightarrow \pi^*$	3.87	3.97	5.71	4.57	4.60	5.13	4.50
	$1\ ^1A_2$	$n \rightarrow \pi^*$	4.11	4.22	6.13	5.00	5.03	5.63	4.93
	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	5.76	5.88	7.07	6.55	6.59	6.65	7.06
	$3\ ^1A_1$	$\pi \rightarrow \pi^*$	6.24	6.34	7.58	7.82	7.83	8.10	7.74
	$3\ ^1B_2$	$\pi \rightarrow \pi^*$	6.27	6.33	7.80	8.11	8.13	8.39	8.01
pyridazine	$1\ ^1B_1$	$n \rightarrow \pi^*$	3.19	3.34	4.85	3.74	3.80	4.24	3.92
	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	5.07	5.06	6.18	5.15	5.15	5.57	5.22
	$1\ ^1A_2$	$n \rightarrow \pi^*$	3.65	3.79	5.74	4.38	4.44	5.03	4.49

Molecule	State	Type	LDA	PBE	PBE0	srLDA	srPBE	srPBE0	Ref.
	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	5.60	5.68	6.63	6.41	6.44	6.46	6.93
	$2\ ^1A_2$	$n \rightarrow \pi^*$	5.46	5.55	7.34	5.68	5.72	6.26	5.74
	$2\ ^1B_2$	$\pi \rightarrow \pi^*$	5.99	6.12	7.43	7.68	7.71	7.91	7.55
	$3\ ^1A_1$	$\pi \rightarrow \pi^*$	6.00	6.07	7.47	7.91	7.94	8.19	7.82
	$2\ ^1B_1$	$n \rightarrow \pi^*$	5.89	5.97	8.21	6.40	6.43	7.07	6.41
s-triazine	$1\ ^1A_2$'	$\pi \rightarrow \pi^*$	5.78	5.74	7.27	5.70	5.70	7.01	5.71
	$1\ ^1A_1$"	$n \rightarrow \pi^*$	3.99	4.04	5.81	4.87	4.92	5.52	4.78
	$1\ ^1$E"	$n \rightarrow \pi^*$	4.08	4.14	5.74	4.85	4.91	5.50	4.81
	$1\ ^1A_2$"	$n \rightarrow \pi^*$	4.17	4.26	5.74	4.87	4.93	5.52	4.76
	$2\ ^1A_1$'	$\pi \rightarrow \pi^*$	6.41	6.53	7.81	6.84	6.86	6.24	7.41
	$1\ ^1$E'	$\pi \rightarrow \pi^*$	6.18	6.27	7.60	8.15	8.16	8.48	8.04
	$2\ ^1$E'	$\pi \rightarrow \pi^*$	8.54	8.72	10.80	9.31	9.31	10.10	9.44
	$2\ ^1$E"	$n \rightarrow \pi^*$	6.75	6.88	9.02	7.47	7.62	8.43	7.80
s-tetrazine	$1\ ^1A_u$	$n \rightarrow \pi^*$	2.81	2.93	4.63	3.74	3.80	4.40	3.79
	$1\ ^1B_{1g}$	$n \rightarrow \pi^*$	3.88	4.02	5.54	4.64	4.75	5.31	4.97
	$1\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	6.28	6.43	7.78	7.92	7.94	8.19	7.45
	$1\ ^1B_{2g}$	$n \rightarrow \pi^*$	4.73	4.77	6.39	5.37	5.39	5.97	5.34
	$1\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	4.73	4.72	5.70	5.08	5.08	5.49	5.12
	$1\ ^1B_{3u}$	$n \rightarrow \pi^*$	1.76	1.86	2.95	2.40	2.46	2.84	2.53
	$2\ ^1A_u$	$n \rightarrow \pi^*$	5.21	5.30	6.94	5.30	5.37	5.86	5.46
	$2\ ^1B_{1g}$	$n \rightarrow \pi^*$	5.78	5.81	8.05	6.85	6.87	7.65	6.87
	$2\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	6.69	6.94	9.83	6.75	6.78	6.84	7.79
	$2\ ^1B_{2g}$	$n \rightarrow \pi^*$	5.03	5.21	7.27	5.88	5.98	6.78	6.23
	$2\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	6.85	6.91	8.65	7.86	8.01	8.90	8.51
	$2\ ^1B_{3u}$	$n \rightarrow \pi^*$	6.22	6.33	8.59	6.59	6.66	7.35	6.67
	$3\ ^1B_{1g}$	$n \rightarrow \pi^*$	6.11	6.16	8.36	6.59	6.65	7.43	7.08
formaldehyde	$1\ ^1A_2$	$n \rightarrow \pi^*$	3.74	3.82	5.43	4.28	4.27	4.54	3.95
	$1\ ^1B_1$	$\sigma \rightarrow \pi^*$	8.65	8.74	10.44	9.08	9.08	9.37	9.18
	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	8.07	8.25	9.39	9.10	9.11	9.67	10.45
acetone	$1\ ^1A_2$	$n \rightarrow \pi^*$	4.21	4.22	5.91	4.77	4.74	5.15	4.40
	$1\ ^1B_1$	$\sigma \rightarrow \pi^*$	8.74	8.79	10.53	9.11	9.11	9.72	9.17
	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	7.79	7.93	9.20	8.92	8.93	9.24	9.65
p-benzoquinone	$1\ ^1B_{1g}$	$n \rightarrow \pi^*$	2.23	2.31	3.67	2.85	2.89	3.32	2.75
	$1\ ^1A_u$	$n \rightarrow \pi^*$	2.27	2.34	3.72	3.08	3.10	3.54	2.85
	$1\ ^1B_{3g}$	$\pi \rightarrow \pi^*$	3.15	3.19	3.75	4.45	4.47	4.51	4.59
	$1\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	3.49	3.55	4.24	5.57	5.58	5.70	5.62
	$2\ ^1B_{3g}$	$\pi \rightarrow \pi^*$	6.11	6.24	7.20	7.21	7.21	7.58	7.27
	$1\ ^1B_{3u}$	$n \rightarrow \pi^*$	4.78	4.88	7.20	5.85	5.87	6.55	5.82
formamide	$1\ ^1$A"	$n \rightarrow \pi^*$	5.30	5.33	6.99	5.63	5.67	6.30	5.65

Molecule	State	Type	LDA	PBE	PBE0	srLDA	srPBE	srPBE0	Ref.
	2 ^{1}A'	$\pi \rightarrow \pi^*$	6.48	6.50	7.75	7.65	7.65	8.13	7.24
	3 ^{1}A'	$\pi \rightarrow \pi^*$	9.90	9.99	11.39	10.51	10.53	11.00	10.93
acetamide	1 ^{1}A"	$n \rightarrow \pi^*$	5.30	5.31	7.02	5.74	5.76	6.42	5.69
	2 ^{1}A'	$\pi \rightarrow \pi^*$	6.43	6.45	7.80	7.68	7.69	8.19	7.67
	3 ^{1}A'	$\pi \rightarrow \pi^*$	9.27	9.37	10.80	10.08	10.11	10.59	10.50
propanamide	1 ^{1}A"	$n \rightarrow \pi^*$	5.31	5.32	7.04	5.77	5.78	6.44	5.72
	2 ^{1}A'	$\pi \rightarrow \pi^*$	6.38	6.40	7.78	7.68	7.68	8.19	7.62
	3 ^{1}A'	$\pi \rightarrow \pi^*$	9.13	9.24	10.68	9.86	9.92	10.40	10.06
cytosine	1 ^{1}A"	$n \rightarrow \pi^*$	4.51	4.56	6.92	5.12	5.17	5.76	5.16
	2 ^{1}A'	$\pi \rightarrow \pi^*$	4.12	4.18	5.45	4.75	4.75	5.18	4.72
	2 ^{1}A"	$n \rightarrow \pi^*$	4.82	4.91	6.92	5.60	5.64	6.39	5.52
	3 ^{1}A'	$\pi \rightarrow \pi^*$	4.33	4.39	5.96	5.59	5.60	6.06	5.61
	4 ^{1}A'	$\pi \rightarrow \pi^*$	5.33	5.39	6.69	6.67	6.70	7.13	6.61
	3 ^{1}A"	$n \rightarrow \pi^*$	5.56	5.65	7.77	5.96	6.00	6.73	5.97
	4 ^{1}A"	$n \rightarrow \pi^*$	5.78	5.89	8.15	6.68	6.75	7.47	6.83
thymine	1 ^{1}A"	$n \rightarrow \pi^*$	4.42	4.46	6.36	5.00	5.03	5.69	4.98
	2 ^{1}A'	$\pi \rightarrow \pi^*$	4.06	4.12	5.30	5.36	5.38	5.70	5.34
	2 ^{1}A"	$n \rightarrow \pi^*$	5.01	5.06	7.08	6.41	6.45	7.20	6.49
	3 ^{1}A'	$\pi \rightarrow \pi^*$	5.19	5.26	6.65	6.36	6.36	6.91	6.34
	4 ^{1}A'	$\pi \rightarrow \pi^*$	5.10	5.15	6.83	6.66	6.70	7.16	6.71
uracil	1 ^{1}A"	$n \rightarrow \pi^*$	4.36	4.41	6.31	4.98	5.00	5.65	4.90
	2 ^{1}A'	$\pi \rightarrow \pi^*$	4.18	4.24	5.46	5.48	5.49	5.83	5.44
	2 ^{1}A"	$n \rightarrow \pi^*$	5.43	5.50	7.66	6.34	6.37	7.98	6.32
	3 ^{1}A'	$\pi \rightarrow \pi^*$	5.08	5.13	6.83	6.32	6.32	6.87	6.29
	4 ^{1}A'	$\pi \rightarrow \pi^*$	5.26	5.33	6.74	6.80	6.83	7.30	6.84
	3 ^{1}A"	$n \rightarrow \pi^*$	4.98	5.04	7.07	7.09	7.11	7.85	6.87
	4 ^{1}A"	$n \rightarrow \pi^*$	6.14	6.22	8.50	7.18	7.21	7.11	7.12
adenine	2 ^{1}A'	$\pi \rightarrow \pi^*$	3.97	4.04	5.28	5.12	5.13	5.56	5.18
	3 ^{1}A'	$\pi \rightarrow \pi^*$	4.34	4.44	6.31	5.34	5.36	5.61	5.39
	1 ^{1}A"	$n \rightarrow \pi^*$	4.52	4.59	6.13	5.30	5.35	5.99	5.34
	2 ^{1}A"	$n \rightarrow \pi^*$	5.18	5.21	6.66	5.87	5.92	6.55	5.96
	3 ^{1}A"	$n \rightarrow \pi^*$	5.45	5.50	7.24	6.22	6.29	6.97	6.34
	4 ^{1}A'	$\pi \rightarrow \pi^*$	4.98	5.10	7.25	6.73	6.74	7.15	6.53

[d]Subscript labels of B species are inline with IUPAC convention[4] but deviate from Ref. 1.

2.2 State-averaged CAS-DFT method

Table 3: Vertical singlet excitation energies in eV using state-averaged (SA) CASSCF-DFT methods with complex-translated (ct) functionals. CC3 and icMRCC2 results taken from Refs. 1, 2 and 3. The latter is denoted by an asterisk.

Molecule	State	Type	LDA	PBE	PBE0	srLDA	srPBE	srPBE0	Ref.
ethene	$1\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	6.66	6.68	7.51	7.87	7.91	7.89	8.37
E-butadiene	$1\ ^1B_u$	$\pi \rightarrow \pi^*$	4.29	4.33	4.97	6.35	6.38	6.38	6.58
	$2\ ^1A_g$	$\pi \rightarrow \pi^*$	6.83	6.81	8.63	6.64	6.63	7.09	6.77
all-E-hexatriene	$1\ ^1B_u$	$\pi \rightarrow \pi^*$	6.77	6.77	8.90	5.44	5.46	5.45	5.58
	$2\ ^1A_g$	$\pi \rightarrow \pi^*$	5.56	5.56	7.28	5.50	5.49	5.91	5.72
all-E-octatetraene	$2\ ^1A_g$	$\pi \rightarrow \pi^*$	4.70	4.70	3.93	4.69	4.69	5.06	4.97
	$1\ ^1B_u$	$\pi \rightarrow \pi^*$	5.95	5.96	2.59	4.82	4.84	4.81	4.94
cyclopropene	$1\ ^1B_1$	$\sigma \rightarrow \pi^*$	6.84	6.88	8.05	6.89	6.90	7.24	6.90
	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	5.43	5.56	6.56	6.72	6.78	6.89	7.10
cyclopentadiene	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	4.09	4.10	4.64	5.61	5.63	5.59	5.73
	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	7.14	6.56	8.38	6.53	6.53	6.97	6.61
	$3\ ^1A_1$	$\pi \rightarrow \pi^*$	7.14	7.17	8.45	8.58	8.62	8.74	8.69
norbornadiene	$1\ ^1A_2$	$\pi \rightarrow \pi^*$	4.36	4.42	5.28	5.64	5.64	5.70	5.64
	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	4.99	5.05	6.29	6.73	6.75	6.97	6.49
	$2\ ^1B_2$	$\pi \rightarrow \pi^*$	5.99	6.05	7.27	7.82	7.83	7.95	7.64
	$2\ ^1A_2$	$\pi \rightarrow \pi^*$	6.32	6.36	7.49	7.88	7.90	8.17	7.71
benzene	$1\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	5.26	5.27	6.97	5.05	5.06	5.43	5.07
	$1\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	5.18	5.21	6.17	6.18	6.22	6.20	6.68
	$1\ ^1E_{1u}$	$\pi \rightarrow \pi^*$	5.47	5.50	6.71	7.50	7.52	7.70	7.45
	$2\ ^1E_{2g}$	$\pi \rightarrow \pi^*$	8.81	8.84	10.48	8.51	8.51	9.01	8.43
naphthalene[a]	$1\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	4.10	4.10		4.27	4.28		4.27
	$1\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	6.40	6.40		4.93	4.95		5.03
	$2\ ^1A_g$	$\pi \rightarrow \pi^*$	5.70	5.70		5.96	5.96		5.98
	$1\ ^1B_{2g}$	$\pi \rightarrow \pi^*$	8.51	8.51		6.45	6.47		6.07
	$3\ ^1A_g$	$\pi \rightarrow \pi^*$	6.70	6.70		6.80	6.79		6.90
	$2\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	8.04	8.04		6.55	6.56		6.33
	$2\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	8.05	8.05		6.45	6.47		6.57
	$2\ ^1B_{2g}$	$\pi \rightarrow \pi^*$	6.34	6.34		6.08	6.08		6.79
	$3\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	7.73	7.73		7.95	7.95		8.12
	$4\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	8.97	8.97		8.51	8.52		8.44
furan	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	6.68	6.67	8.60	6.60	6.61	7.01	6.62

Molecule	State	Type	LDA	PBE	PBE0	srLDA	srPBE	srPBE0	Ref.
	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	5.25	5.28	6.20	6.50	6.52	6.54	6.60
	$3\ ^1A_1$	$\pi \rightarrow \pi^*$	7.81	7.83	9.73	8.56	8.58	8.79	8.53
pyrrole	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	6.45	6.45	8.31	6.38	6.39	6.74	6.40
	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	5.83	5.86	7.03	6.60	6.62	6.69	6.71
	$3\ ^1A_1$	$\pi \rightarrow \pi^*$	7.57	7.58	9.46	8.26	8.28	8.49	8.17
imidazole	$2\ ^1A'$	$\pi \rightarrow \pi^*$	6.05	6.08	7.27	6.78	6.80	6.91	6.58
	$1\ ^1A''$	$n \rightarrow \pi^*$	6.91	6.95	8.36	7.05	7.07	7.59	6.82
	$3\ ^1A'$	$\pi \rightarrow \pi^*$	7.88	7.89	9.52	6.92	6.93	7.29	7.10
	$4\ ^1A'$	$\pi \rightarrow \pi^*$	6.84	6.83	8.77	8.51	8.53	8.82	8.45
	$2\ ^1A''$	$n \rightarrow \pi^*$	7.83	7.88	9.52	8.37	8.39	8.97	7.93
pyridine	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	5.38	5.38	7.12	5.27	5.28	5.65	5.15
	$1\ ^1B_1$	$n \rightarrow \pi^*$	5.09	5.14	6.40	5.20	5.24	5.69	5.05
	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	6.74	6.75	8.24	6.36	6.39	6.40	6.85
	$1\ ^1A_2$	$n \rightarrow \pi^*$	5.71	5.78	7.36	6.20	6.23	6.79	5.50
	$2\ ^1B_2$	$\pi \rightarrow \pi^*$	8.56	5.89	7.18	7.74	7.75	7.99	7.59
	$3\ ^1A_1$	$\pi \rightarrow \pi^*$	7.43	7.43	9.32	7.77	7.79	7.99	7.70
	$4\ ^1A_1$	$\pi \rightarrow \pi^*$	5.87	5.89	7.18	8.84	8.84	9.31	8.68
	$3\ ^1B_2$	$\pi \rightarrow \pi^*$	8.56	8.53	10.87	8.65	8.64	9.29	8.77
pyrazine	$1\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	5.35	5.34	7.02	5.36	5.37	5.72	5.02
	$1\ ^1B_{3u}$	$n \rightarrow \pi^*$	4.01	4.11	5.73	4.07	4.13	4.60	4.24
	$1\ ^1B_{2g}$	$n \rightarrow \pi^*$	5.52	5.61	7.52	5.66	5.73	6.30	5.74
	$1\ ^1A_u$	$n \rightarrow \pi^*$	4.81	4.94	6.98	5.43	5.48	6.09	5.05
	$1\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	5.37	5.40	6.28	6.58	6.62	6.61	7.07
	$2\ ^1A_g$	$\pi \rightarrow \pi^*$	7.76	7.86	10.16	7.96	8.01	8.70	8.69
	$2\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	6.04	6.06	7.38	8.36	8.36	8.67	8.05
	$2\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	5.97	5.98	7.20	8.09	8.10	8.33	8.06
	$1\ ^1B_{1g}$	$n \rightarrow \pi^*$	6.52	6.64	9.10	7.31	7.38	8.14	6.75
pyrimidine	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	5.62	5.61	7.43	5.40	5.41	5.85	5.36
	$1\ ^1B_1$	$n \rightarrow \pi^*$	4.42	4.50	6.14	4.37	4.43	5.04	4.50
	$1\ ^1A_2$	$n \rightarrow \pi^*$	4.83	4.93	6.79	5.03	5.08	5.74	4.93
	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	7.91	7.89	9.61	6.49	6.53	6.59	7.06
	$3\ ^1A_1$	$\pi \rightarrow \pi^*$	6.27	6.28	7.63	7.79	7.80	8.06	7.74
	$3\ ^1B_2$	$\pi \rightarrow \pi^*$	6.17	6.20	7.71	8.05	8.07	8.35	8.01
pyridazine	$1\ ^1B_1$	$n \rightarrow \pi^*$	3.59	3.71	5.23	3.64	3.75	4.26	3.92
	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	5.46	5.45	7.22	5.32	5.32	5.70	5.22
	$1\ ^1A_2$	$n \rightarrow \pi^*$	4.38	4.52	6.38	4.48	4.60	5.29	4.49
	$1\ ^1B_2$	$\pi \rightarrow \pi^*$	5.77	5.80	10.21	6.52	6.55	6.54	6.93
	$2\ ^1A_2$	$n \rightarrow \pi^*$	5.65	5.74	7.77	5.57	5.63	6.21	5.74
	$2\ ^1B_2$	$\pi \rightarrow \pi^*$	5.85	5.87	7.00	7.73	7.74	7.96	7.55
	$3\ ^1A_1$	$\pi \rightarrow \pi^*$	6.16	6.18	7.05	8.02	8.04	8.29	7.82

Molecule	State	Type	LDA	PBE	PBE0	srLDA	srPBE	srPBE0	Ref.
	$2\ ^1B_1$	$n \rightarrow \pi^*$	6.57	6.66	8.85	6.55	6.64	7.35	6.41
s-triazine	$1\ ^1A_2$'	$\pi \rightarrow \pi^*$	5.95	5.94	7.44	5.56	5.53	6.05	5.71
	$1\ ^1A_1$"	$n \rightarrow \pi^*$	4.61	4.72	6.89	4.53	4.55	5.25	4.78
	$1\ ^1E$"	$n \rightarrow \pi^*$	4.51	4.62	6.75	4.49	4.52	5.21	4.81
	$1\ ^1A_2$"	$n \rightarrow \pi^*$	4.29	4.40	6.53	4.50	4.52	5.22	4.76
	$2\ ^1A_1$'	$\pi \rightarrow \pi^*$	6.37	6.36	7.86	6.68	6.67	6.80	7.41
	$1\ ^1E$'	$\pi \rightarrow \pi^*$	6.67	6.71	8.46	8.04	8.03	8.34	8.04
	$2\ ^1E$'	$\pi \rightarrow \pi^*$	9.22	9.19	11.65	9.64	9.63	10.21	9.44
	$2\ ^1E$"	$n \rightarrow \pi^*$	7.57	7.72	10.44	7.26	7.36	8.23	7.80
s-tetrazine	$1\ ^1A_u$	$n \rightarrow \pi^*$	3.44	4.53	5.58	3.84	3.96	4.69	3.79
	$1\ ^1B_{1g}$	$n \rightarrow \pi^*$	4.59	5.35	6.92	4.60	4.74	5.39	4.97
	$1\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	5.54	9.54	6.58	7.76	8.13	8.87	7.45
	$1\ ^1B_{2g}$	$n \rightarrow \pi^*$	5.24	5.18	7.62	5.30	5.36	6.01	5.34
	$1\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	5.46	4.83	7.21	5.27	5.35	5.92	5.12
	$1\ ^1B_{3u}$	$n \rightarrow \pi^*$	2.07	3.09	3.73	2.31	2.39	2.89	2.53
	$2\ ^1A_u$	$n \rightarrow \pi^*$	5.82	6.44	8.18	5.41	5.38	6.01	5.46
	$2\ ^1B_{1g}$	$n \rightarrow \pi^*$	6.53	7.47	9.37	6.52	6.60	7.49	6.87
	$2\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	7.33	9.14	10.74	6.89	6.92	6.93	7.79
	$2\ ^1B_{2g}$	$n \rightarrow \pi^*$	5.77	6.75	8.66	5.86	6.03	6.98	6.23
	$2\ ^1B_{2u}$	$\pi \rightarrow \pi^*$	7.59	8.56	10.69	8.78	8.80	9.14	8.51
	$2\ ^1B_{3u}$	$n \rightarrow \pi^*$	7.27	7.98	10.11	6.75	6.89	7.60	6.67
	$3\ ^1B_{1g}$	$n \rightarrow \pi^*$	6.44	7.04	9.51	8.04	8.15	9.09	7.08
formaldehyde	$1\ ^1A_2$	$n \rightarrow \pi^*$	4.19	4.23	5.54	3.68	3.71	4.19	3.95
	$1\ ^1B_1$	$\sigma \rightarrow \pi^*$	9.11	9.13	10.48	8.71	8.70	9.24	9.18
	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	9.17	9.10	9.57	9.01	9.02	9.09	10.45
acetone	$1\ ^1A_2$	$n \rightarrow \pi^*$	4.64	4.65	6.04	4.15	4.16	4.67	4.40
	$1\ ^1B_1$	$\sigma \rightarrow \pi^*$	9.04	9.06	10.47	8.61	8.62	9.17	9.17
	$2\ ^1A_1$	$\pi \rightarrow \pi^*$	8.58	8.56	9.20	8.56	8.59	8.81	9.65
p-benzoquinone	$1\ ^1B_{1g}$	$n \rightarrow \pi^*$	2.74	2.81	4.66	2.66	2.72	3.27	2.75
	$1\ ^1A_u$	$n \rightarrow \pi^*$	2.75	2.82	4.67	2.88	2.92	3.50	2.85
	$1\ ^1B_{3g}$	$\pi \rightarrow \pi^*$	4.43	4.45	5.82	4.99	5.02	5.03	4.59
	$1\ ^1B_{1u}$	$\pi \rightarrow \pi^*$	6.21	6.20	7.93	5.49	5.50	5.66	5.62
	$2\ ^1B_{3g}$	$\pi \rightarrow \pi^*$	5.69	5.72	7.18	7.30	7.28	7.66	7.27
	$1\ ^1B_{3u}$	$n \rightarrow \pi^*$	5.59	5.66	8.48	5.83	5.86	6.68	5.82
formamide	$1\ ^1A$"	$n \rightarrow \pi^*$	6.08	6.10	7.49	5.91	5.92	6.44	5.65
	$2\ ^1A$'	$\pi \rightarrow \pi^*$	7.17	7.19	8.69	7.62	7.63	8.09	8.27
	$3\ ^1A$'	$\pi \rightarrow \pi^*$	10.08	10.09	11.85	10.34	10.37	10.84	10.93
acetamide	$1\ ^1A$"	$n \rightarrow \pi^*$	6.10	6.11	7.56	5.97	5.97	6.52	5.69
	$2\ ^1A$'	$\pi \rightarrow \pi^*$	7.11	7.15	8.70	7.65	7.65	8.14	7.67

Molecule	State	Type	LDA	PBE	PBE0	srLDA	srPBE	srPBE0	Ref.
	3 ^{1}A'	$\pi \rightarrow \pi^*$	9.41	9.44	11.15	9.83	9.88	10.38	10.50
propanamide	1 ^{1}A"	$n \rightarrow \pi^*$	6.10	6.11	7.57	5.96	5.96	6.51	5.72
	2 ^{1}A'	$\pi \rightarrow \pi^*$	7.06	7.10	8.66	7.66	7.66	8.16	7.62
	3 ^{1}A'	$\pi \rightarrow \pi^*$	9.26	9.30	11.01	9.65	9.70	10.22	10.06
cytosine	1 ^{1}A"	$n \rightarrow \pi^*$	5.36	5.41	7.32	5.44	5.43	5.96	5.16
	2 ^{1}A'	$\pi \rightarrow \pi^*$	4.35	4.38	5.78	4.74	4.74	5.11	4.72
	2 ^{1}A"	$n \rightarrow \pi^*$	5.63	5.71	7.76	6.21	5.66	6.89	5.52
	3 ^{1}A'	$\pi \rightarrow \pi^*$	5.34	5.38	7.19	5.65	5.66	6.08	5.61
	4 ^{1}A'	$\pi \rightarrow \pi^*$	5.55	5.59	7.42	6.68	6.71	7.11	6.61
	3 ^{1}A"	$n \rightarrow \pi^*$	6.13	6.15	7.77	6.56	6.20	7.06	5.97
	4 ^{1}A"	$n \rightarrow \pi^*$	7.16	7.22	9.08	7.68	6.71	8.25	6.83
thymine	1 ^{1}A"	$n \rightarrow \pi^*$	5.34	5.33	6.56	5.48	5.47	6.00	4.98
	2 ^{1}A'	$\pi \rightarrow \pi^*$	4.62	4.68	6.14	5.37	5.40	5.70	5.34
	2 ^{1}A"	$n \rightarrow \pi^*$	6.70	6.71	8.27	6.91	6.90	7.50	6.49
	3 ^{1}A'	$\pi \rightarrow \pi^*$	5.91	5.94	7.83	6.49	6.51	6.98	6.34
	4 ^{1}A'	$\pi \rightarrow \pi^*$	6.23	6.29	8.00	6.54	6.63	7.03	6.71
uracil	1 ^{1}A"	$n \rightarrow \pi^*$	5.19	5.19	6.51	5.31	5.30	5.94	4.90
	2 ^{1}A'	$\pi \rightarrow \pi^*$	4.65	4.71	6.20	5.46	5.48	5.81	5.44
	2 ^{1}A"	$n \rightarrow \pi^*$	6.62	6.64	9.48	6.51	6.51	7.03	6.32
	3 ^{1}A'	$\pi \rightarrow \pi^*$	5.86	5.91	7.81	6.81	6.80	7.83	6.29
	4 ^{1}A'	$\pi \rightarrow \pi^*$	6.29	6.35	8.16	6.95	7.00	7.44	6.84
	3 ^{1}A"	$n \rightarrow \pi^*$	7.66	7.68	9.33	6.94	7.07	7.78	6.87
	4 ^{1}A"	$n \rightarrow \pi^*$	7.36	7.39	8.17	7.03	7.03	7.36	7.12
adenine	2 ^{1}A'	$\pi \rightarrow \pi^*$	5.27	5.29	5.79	5.32	5.34	5.58	5.18
	3 ^{1}A'	$\pi \rightarrow \pi^*$	4.49	4.52	7.02	5.20	5.21	5.59	5.39
	1 ^{1}A"	$n \rightarrow \pi^*$	5.15	5.23	7.15	5.46	5.50	6.10	5.34
	2 ^{1}A"	$n \rightarrow \pi^*$	5.95	6.00	8.73	6.08	6.12	6.67	5.96
	3 ^{1}A"	$n \rightarrow \pi^*$	6.40	6.46	8.90	6.56	6.62	7.23	6.34
	4 ^{1}A'	$\pi \rightarrow \pi^*$	6.52	6.55	7.66	6.80	6.81	7.17	6.53

[d]Subscript labels of B species are inline with IUPAC convention[4] but deviate from Ref. 1.

2.3 CAS-LDA type singlet excitation energies

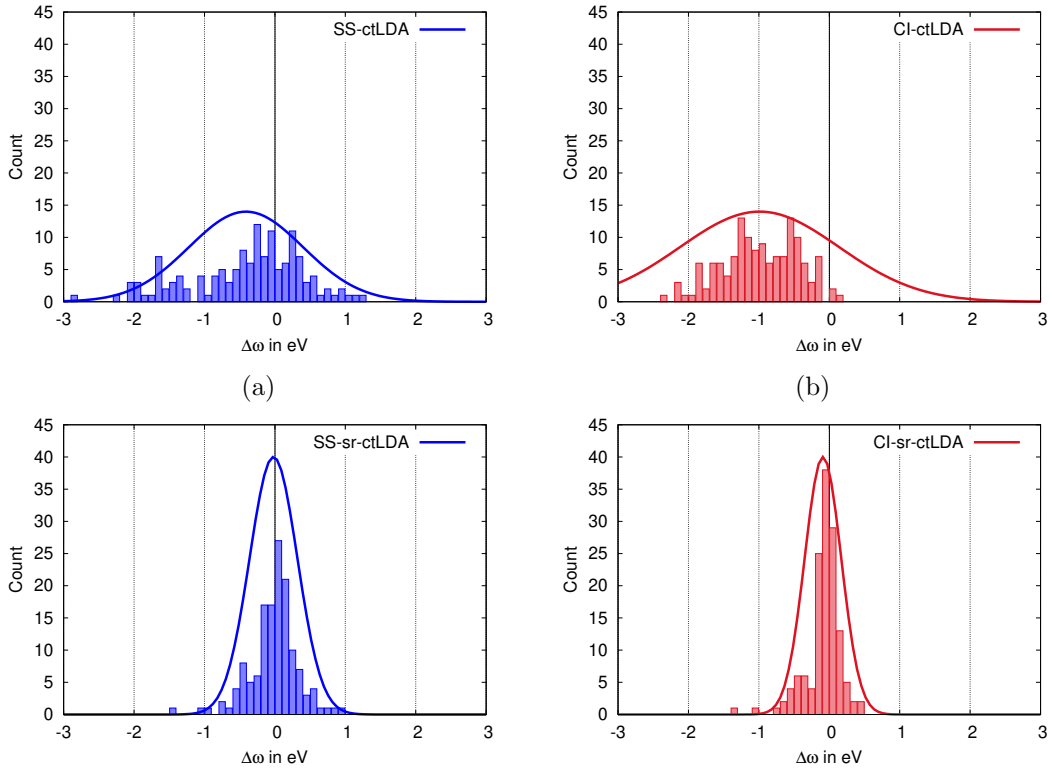

Figure 1: Histogram of CAS-LDA deviations from the CC3 and icMRCC2 reference for 139 singlet excitation energies from Thiel's benchmark set.[1, 5, 2, 3].

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