Supporting Information of

A Correlation-Relaxation-Balanced Direct Method at the Second Order Perturbation Theory for Accurate Ionization Potential Predictions

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Supplemental test results

Here list the detailed test results of the first IPs (Table S1), valence IPs (Table S2) and core IPs (Table S3) calculated by MP2-based direct methods. The data set of the first IP was taken from Ref 1. The cc-pVQZ[2, 3] basis set was used as it was in Ref 1. The data sets of valence and core IPs were taken from Ref. 4. The aug-cc-pVTZ[2, 3] basis set was used as it was in Ref. 4. The small positive number (SPN[5]) approximation was used for all EKT-MP2 calculations to cure the negative occupation number problems. All calculations were performed with a locally modified version of the GAUSSIAN09[6] software package.

Table S1 The first IPs predicted by some MP2-based direct methods with the cc-pVQZ basis set.[a] KT-HF is also included for comparison.

	KT-HF	NKS-MP2	EKT-MP2	CRB-MP2	Exp.[b]
Li	5.34	5.36	5.36	5.36	5.39
Be	8.42	8.67	8.73	8.85	9.32
B	8.67	8.18	8.23	8.58	8.3
C	11.94	11.11	11.22	11.62	11.26
N	15.52	14.27	14.46	14.90	14.54
O	14.19	12.93	13.08	13.56	13.61
F	18.47	16.36	16.71	17.24	17.42
F_2	18.12	13.50	14.88	15.41	15.7
OH	13.94	12.00	12.35	12.90	13.01
NH_2	12.58	11.16	11.33	11.97	12.0
CH_3	10.47	9.21	9.44	10.02	9.84
CN	14.14	11.55	12.64	13.82	13.6
O_2	15.17	10.13	11.93	12.63	12.3
MAD[c]	**0.97**	**0.91**	**0.46**	**0.22**	--

[a] All energies are in eV.

[b] Experimental values are taken from Ref. 7.

[c] Mean absolute deviation.

Table S2 Valence IPs predicted by some MP2-based direct methods with the aug-cc-pVTZ basis set.[a] KT-HF is also included for comparison.

Molecule	Orb.	KT-HF	NKS-MP2	EKT-MP2	CRB-MP2	Exp.[b]
N_2	σ_g	17.27	14.02	15.05	15.79	15.60
	π_u	16.72	16.64	16.70	17.30	16.68
	σ_u	21.22	16.96	18.52	18.96	18.78
HF	π	17.70	14.48	15.42	15.64	16.19
	σ	20.92	18.92	19.33	19.64	19.90
CO	σ	15.10	13.19	13.64	14.48	14.01
	π	17.43	16.24	16.36	16.96	16.85
	σ	21.90	17.88	19.30	19.35	19.78
C_2H_2	π_u	11.19	10.85	10.83	11.49	11.49
	σ_g	18.56	15.90	16.73	17.33	16.70
	σ_u	20.91	17.75	18.84	19.28	18.70
HCN	π	13.50	13.19	13.17	13.85	13.61
	σ	15.85	11.91	13.38	13.79	14.01
	σ^*	22.16	19.34	20.24	20.83	19.86
HCCF	π	11.38	10.77	10.75	11.54	11.50
	π	20.69	15.97	17.84	17.75	18.00
	σ	19.78	17.04	17.88	18.51	18.00
	σ	23.44	19.40	20.84	21.04	21.20
	σ	28.63	23.36	26.71	25.63	24.30
NNO	π	13.38	11.70	11.92	12.93	12.89
	σ	19.02	14.31	16.08	16.79	16.38
	π	20.77	16.76	18.42	18.71	18.23
	σ	22.70	17.44	19.58	19.47	20.11
NCCN	π_g	13.58	12.90	12.83	13.82	13.51
	σ_g	16.99	12.15	14.16	14.47	14.49
	σ_u	17.42	12.45	14.52	14.76	14.86
	π_u	16.35	15.04	15.12	16.12	15.60
	σ_g	26.63	21.16	24.33	23.82	22.80
CO_2	π_g	14.83	12.50	13.01	13.78	13.79
	π_u	19.46	16.41	17.31	17.92	17.60
	σ_u	20.24	16.14	17.53	17.93	18.08
	σ_g	21.81	17.26	18.91	19.13	19.40
OCS	π	11.48	10.60	10.66	11.41	11.24
	π^*	17.93	14.27	15.56	16.03	15.53
	σ	17.34	15.07	15.65	16.43	16.04
	σ^*	21.19	15.55	18.04	17.80	17.96
FCN	π	13.65	12.97	12.92	13.81	13.65
	σ	16.35	12.55	13.88	14.42	14.56
	π	22.20	17.63	19.38	19.48	19.30
	σ	25.30	21.27	22.70	22.98	22.60

HCl	π	12.99	12.14	12.26	12.72	12.77
	σ	17.02	16.17	16.28	16.77	16.60
	σ	30.41	25.64	28.74	27.46	25.80
F_2	π_g	18.16	13.47	15.08	15.29	15.87
	π_u	22.10	16.17	18.37	18.35	18.80
	σ_g	20.49	20.36	20.34	20.78	21.10
CS	σ	12.82	9.95	10.91	11.74	11.34
	π	12.61	12.67	12.95	13.08	12.90
	σ	18.85	16.11	17.19	17.44	18.03
P_2	π_u	10.12	10.15	10.11	10.61	10.65
	σ_g	11.12	9.79	10.15	10.77	10.84
H_2O	b_1	13.89	11.16	11.99	12.32	12.78
	a_1	15.92	13.56	14.18	14.54	14.83
	b_2	19.54	18.09	18.35	18.72	18.72
CH_4	t_2	14.85	13.77	13.95	14.46	14.40
	a_1	25.70	22.77	23.89	24.05	23.00
NH_3	a_1	11.69	9.80	10.30	10.78	10.80
	e	17.11	15.75	16.00	16.46	16.80
CH_2O	b_2	12.23	9.27	10.21	10.55	10.90
	b_1	14.25	13.58	13.58	14.13	14.50
	a_1	17.38	14.23	15.21	15.55	16.10
	b_2	19.41	16.45	17.66	17.80	17.00
	a_1	23.97	20.69	21.94	22.18	21.40
CH_3CN	e	12.55	11.90	11.87	12.64	12.46
	a_1	15.13	11.18	12.65	13.04	13.17
	e	17.10	15.46	15.85	16.46	15.70
	a_1	18.93	16.00	16.97	17.56	17.40
	a_1	28.27	23.66	26.04	25.71	24.90
CHF_3	a_1	16.02	13.75	14.26	14.82	14.80
	a_2	17.94	13.97	15.21	15.47	15.50
	e	18.41	14.77	15.84	16.15	16.20
	e	19.49	15.62	16.89	17.07	17.20
	e	22.63	19.27	20.36	20.57	20.70
	a_1	23.08	19.70	20.83	21.04	20.70
	a_1	27.00	23.43	24.61	24.84	24.40
C_2H_6	e_g	13.27	12.08	12.29	12.81	12.00
	a_{1g}	13.76	12.01	12.44	13.06	12.70
	e_u	16.22	14.71	15.05	15.53	15.00
	a_{2u}	22.89	20.19	21.18	21.39	20.40
	a_{1g}	27.63	23.42	25.77	25.16	23.90
C_2H_4	b_{3u}	10.23	9.94	9.88	10.49	10.68
	b_{3g}	13.84	12.31	12.66	13.20	12.80
	a_g	15.93	13.75	14.39	14.98	14.80
	b_{2u}	17.50	15.29	15.97	16.38	16.00

	b_{1u}	21.55	18.39	19.66	19.81	19.10
	a_g	28.09	22.72	26.26	24.92	23.60
	b_2	9.59	8.68	8.81	9.26	9.38
	b_1	11.39	11.32	11.49	11.79	11.76
H_2CS	a_1	14.74	13.14	13.53	14.14	13.85
	b_2	17.56	14.54	15.70	16.09	15.20
	a_1	22.14	18.13	20.04	19.91	19.90
	a′	12.70	10.09	10.76	11.80	11.82
	a′	14.02	13.62	12.89	13.65	13.50
	a″	15.05	11.96	13.45	14.22	13.87
NSF	a′	18.22	13.69	15.34	15.57	15.62
	a″	19.12	14.15	16.51	15.99	16.47
	a′	19.29	14.69	16.78	16.35	17.20
	b_1	10.78	9.95	9.98	10.75	10.70
	b_2	16.37	14.46	14.71	15.50	14.90
	a_1	17.39	14.57	15.35	15.57	15.80
	b_2	18.17	14.04	15.65	15.94	16.10
$CH_2=CF_2$	a_2	18.78	14.40	15.97	16.02	16.10
	a_1	20.46	16.62	18.10	18.12	18.20
	b_1	20.76	16.55	18.14	18.15	18.20
	b_2	21.85	18.26	19.53	19.66	19.70
	a_1	24.13	20.12	21.60	21.68	21.50
MAD[c]		**1.68**	**1.19**	**0.53**	**0.37**	**-**

[a] All energies are in eV.

[b] Experimental values are taken from Ref. 4.

[c] Mean absolute deviation.

Table S3 Core IPs predicted by some MP2-based direct methods with the aug-cc-pVTZ basis set.[a] KT-HF is also included for comparison.

Molecule	Orb.	KT-HF	NKS-MP2	EKT-MP2	CRB-MP2	Exp.[b]
N_2	N_{1s}	426.83	401.02	424.63	410.58	409.90
	N_{1s}	426.74	400.97	424.38	410.51	409.90
HF	F_{1s}	715.65	680.10	711.39	691.94	694.22
CO	O_{1s}	562.42	528.38	560.97	539.86	542.57
	C_{1s}	309.17	293.53	305.80	299.67	296.20
C_2H_2	C_{1s}	305.96	284.86	304.50	292.69	291.20
	C_{1s}	305.86	284.79	304.29	292.61	291.20
HCN	N_{1s}	424.53	395.29	422.63	405.90	406.15
	C_{1s}	307.31	288.58	305.38	295.66	293.50
NNO	O_{1s}	562.15	525.55	561.11	537.77	541.42
	N_{1s}	431.20	403.38	427.98	414.27	412.50
	N_{1s}	427.21	397.47	423.98	408.75	408.60
NCCN	N_{1s}	426.01	395.24	424.24	406.51	407.40
	N_{1s}	426.01	395.24	423.79	406.51	407.40
	C_{1s}	309.00	289.53	309.43	296.87	294.50
	C_{1s}	308.97	289.49	307.04	296.84	294.50
CO_2	O_{1s}	562.01	526.85	560.63	538.95	541.28
	C_{1s}	311.91	294.85	308.90	301.92	297.65
OCS	O_{1s}	562.16	523.94	560.47	537.05	540.30
	C_{1s}	311.26	290.07	308.10	298.64	295.20
F_2	F_{1s}	719.30	681.43	717.22	694.30	696.71
	F_{1s}	719.29	681.43	711.46	694.30	696.71
H_2O	O_{1s}	559.67	527.24	558.21	538.35	539.88
CH_4	C_{1s}	304.90	286.11	303.58	293.03	290.83
NH_3	N_{1s}	422.92	396.48	421.34	405.84	405.60
CH_2O	O_{1s}	559.87	524.04	558.42	536.16	539.44
	C_{1s}	308.44	290.86	306.90	297.53	294.47
CH_3CN	N_{1s}	423.73	394.22	422.02	404.82	405.60
	C_{1s}	307.25	288.14	305.98	295.25	293.20
	C_{1s}	306.93	287.58	305.07	294.82	293.10
CHF_3	F_{1s}	717.01	680.83	715.30	692.86	694.62
	F_{1s}	717.01	680.83	715.30	692.86	694.62
	F_{1s}	717.01	680.83	715.27	692.86	694.62
	C_{1s}	313.20	296.70	312.46	303.04	299.24
C_2H_6	C_{1s}	305.10	285.82	303.83	292.85	290.71
	C_{1s}	305.08	285.80	303.49	292.83	290.71
C_2H_4	C_{1s}	305.69	285.22	304.46	292.73	290.88
	C_{1s}	305.65	285.18	304.28	292.68	290.88
$CH_2{=}CF_2$	F_{1s}	716.98	679.98	715.45	692.25	694.44
	F_{1s}	716.98	679.97	715.24	692.25	694.44
	C_{1s}	311.01	291.73	309.19	299.02	296.10

	C_{1s}	306.01	286.19	304.66	293.51	291.33
MAD_n[c]		**17.56**	**9.24**	**15.60**	**2.06**	**--**
MAD_r[d]		**17.88**	**8.92**	**15.92**	**1.92**	**--**

[a] All energies are in eV.

[b] Experimental values are taken from Ref. 8.

[c] Mean absolute deviations calculated without relativistic effect corrections.

[d] Mean absolute deviations calculated with relativistic effect corrections.[9]

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