Supplementary Material for "Slater transition methods for core-level electron binding energies"

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January 1, 2023

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References

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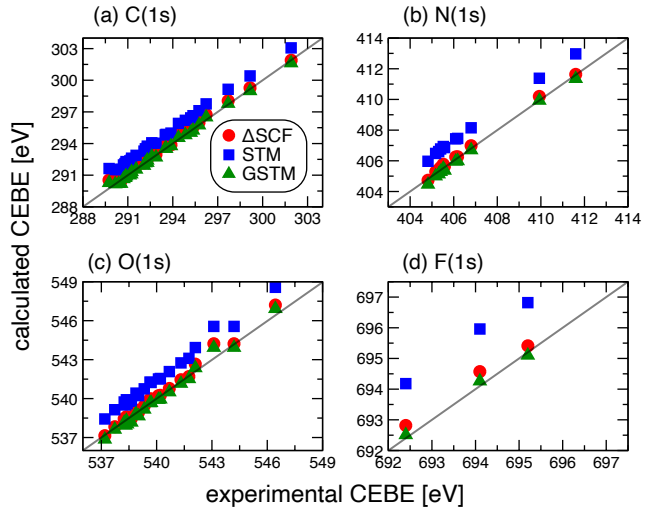

Fig. S1: Absolute CEBEs versus experiment, computed using the B3LYP functional in conjunction with the ΔSCF, STM, and GSTM methods for (a) C(1s), (b) N(1s), (c) O(1s), and (d) F(1s) ionization energies in the CORE65 data set.

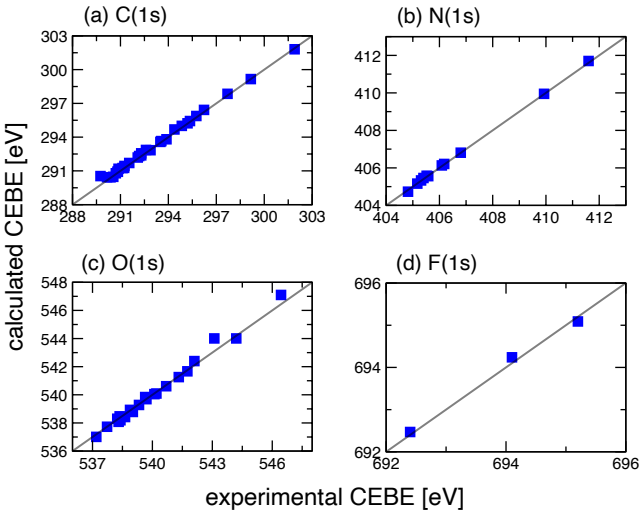

Fig. S2: CEBEs in the CORE65 data set for (a) carbon, (b) nitrogen, (c) oxygen, and (d) fluorine, computed using an empirically-shifted version of STM-B3LYP, Eq. (25) with $\beta = 2.1$.

Table S1: K-shell CEBEs for the CORE65 data set (including relativistic corrections), computed using the SCAN functional in conjunction with the conventional def2-QZVP basis set versus an uncontracted version of the same basis.[a]

Molecule	Core Orbital	Expt.[b]	ΔSCF		STM		GSTM		Shifted	
			normal	uncontr.	normal	uncontr.	normal	uncontr.	normal	uncontr.
methane	C1s	290.84	290.92	290.84	293.16	293.10	290.47	290.41	290.75	290.70
ethane	C1s	290.71	290.78	290.70	293.04	292.97	289.87	289.83	290.67	290.60
ethene	C1s	290.82	290.85	290.70	293.10	292.97	290.42	290.31	290.77	290.60
ethyne	C1s	291.25	291.35	291.26	293.58	293.52	290.93	289.02	291.22	291.16
carbon monoxide	O1s	542.1	542.74	542.57	545.59	545.44	542.30	542.14	542.47	542.34
carbon monoxide	C1s	296.23	296.45	296.37	298.59	298.54	296.13	296.06	295.99	295.94
carbon dioxide	O1s	541.32	541.52	541.36	544.41	544.27	541.07	540.92	541.36	541.24
carbon dioxide	C1s	297.7	297.70	297.63	299.96	299.91	297.27	297.21	297.43	297.38
tetrafluoromethane	F1s	695.2	695.55	695.33	698.73	698.53	695.06	694.85	695.22	695.04
tetrafluoromethane	C1s	301.9	301.65	301.59	304.00	303.96	301.25	301.19	301.48	301.45
fluoromethane	F1s	692.4	693.04	692.81	696.19	696.00	692.55	692.34	692.70	692.53
fluoromethane	C1s	293.56	293.64	293.56	295.92	295.87	293.21	293.14	293.48	293.43
trifluoromethane	F1s	694.1	694.74	694.52	697.91	697.72	694.25	694.05	694.42	694.24
trifluoromethane	C1s	299.16	299.06	298.99	301.41	301.36	298.65	298.58	298.91	298.87
methanol	O1s	538.88	539.22	539.06	542.11	541.96	538.77	538.61	539.06	538.92
methanol	C1s	292.3	292.55	292.48	294.83	294.77	292.12	292.05	292.42	292.37
formaldehyde	O1s	539.33	539.55	539.38	542.43	542.28	539.11	538.94	539.41	539.27
formaldehyde	C1s	294.38	294.57	294.49	296.86	296.80	294.14	294.07	294.42	294.36
dimethyl ether	O1s	538.36	538.74	538.56	541.64	541.48	538.29	538.12	538.66	538.51
dimethyl ether	C1s	292.17	292.30	292.23	294.59	294.53	291.86	291.80	292.21	292.15
formic acid	O1s (OH)	540.69	540.89	540.72	543.78	543.63	540.45	540.29	540.75	540.62
formic acid	O1s (C=O)	539.02	539.00	538.83	541.87	541.72	538.55	538.39	538.88	538.74
formic acid	C1s	295.75	295.77	295.69	298.06	298.01	295.34	295.28	295.61	295.56
acetone	O1s	537.73	537.90	537.73	540.81	540.66	537.52	537.36	537.87	537.73
acetone	C1s (C=O)	293.88	293.66	293.58	296.00	295.94	293.40	293.33	293.63	293.57
acetone	C1s (CH_3)	291.23	291.21	291.14	293.48	293.42	290.77	290.74	291.13	291.07
methyl formate	O1s (OCH_3)	539.64	540.10	539.92	543.01	542.85	539.66	539.49	540.05	539.91
methyl formate	O1s (C=O)	538.24	538.52	538.35	541.41	541.25	538.08	537.91	538.44	538.30
acetic acid	O1s (OH)	540.1	540.30	540.14	543.20	543.05	539.87	539.71	540.20	540.06
acetic acid	O1s (C=O)	538.31	538.27	538.10	541.15	541.00	537.83	537.66	538.19	538.05
acetic acid	C1s (COOH)	295.35	295.29	295.21	297.59	297.54	294.87	294.80	295.18	295.13
acetic acid	C1s (CH_3)	291.55	291.67	291.59	293.94	293.88	291.22	291.15	291.56	291.50
water	O1s	539.7	540.01	539.86	542.87	542.73	539.57	539.42	539.74	539.62
ozone	O1s middle	546.44	547.09	546.92	550.01	549.88	546.63	546.36	546.99	546.86
ozone	O1s terminal	541.75	541.65	541.52	544.70	544.54	541.35	541.14	541.73	541.59
oxygen	O1s weaker	544.2	544.14	543.96	547.03	546.98	543.70	543.57	543.90	543.85
oxygen	O1s stronger	543.1	544.14	543.96	547.03	546.95	543.70	543.56	543.91	543.82
nitrogen	N1s	409.93	410.07	409.96	412.62	412.52	408.54	408.43	409.77	409.69
ammonia	N1s	405.52	405.71	405.61	408.28	408.19	405.29	405.19	405.55	405.47
hydrogen cyanide	N1s	406.8	406.86	406.75	409.41	409.32	406.43	406.32	406.70	406.61
hydrogen cyanide	C1s	293.5	293.56	293.47	295.78	295.72	293.14	293.06	293.31	293.25
acetonitrile	N1s	405.58	405.50	405.39	408.10	408.00	405.07	404.96	405.45	405.37
acetonitrile	C1s (CH_3)	292.88	292.86	292.78	295.13	295.07	292.42	292.35	292.74	292.68
acetonitrile	C1s (CN)	292.6	292.78	292.69	295.03	294.97	292.36	292.28	292.61	292.55
glycine	O1s (OH)	540.2	540.32	540.16	543.22	543.08	539.88	539.72	540.23	540.09
glycine	O1s (C=O)	538.4	538.38	538.21	541.26	541.11	537.94	537.77	538.31	538.17
glycine	N1s	405.4	405.56	405.45	408.16	408.06	405.13	405.02	405.49	405.40
glycine	C1s (COOH)	295.2	295.05	294.98	297.36	297.31	294.64	294.58	294.97	294.92
glycine	C1s (CH_2)	292.3	292.34	292.26	294.64	294.58	291.89	291.83	292.28	292.22
pyridine	N1s	404.82	404.72	404.60	407.34	407.23	404.29	404.17	404.79	404.69
pyrrole	N1s	406.18	406.28	406.16	408.90	408.80	405.86	405.75	406.31	406.22
aniline	N1s	405.31	405.45	405.34	408.03	407.94	405.01	404.90	405.44	405.35
urea	O1s	537.19	537.23	537.05	540.10	539.94	536.78	536.62	537.15	537.01
urea	N1s	406.09	406.22	406.11	408.84	408.73	405.80	405.69	406.18	406.08
urea	C1s	294.84	294.86	294.79	297.16	297.10	294.43	294.36	294.75	294.70
methylamine	N1s	405.17	405.26	405.15	407.87	407.78	404.82	404.72	405.19	405.10
nitrobenzene	O1s	538.63	538.50	538.32	541.44	541.29	538.07	537.90	538.59	538.45
nitrobenzene	N1s	411.6	411.43	411.33	414.19	414.10	410.98	410.89	411.60	411.51
nitrobenzene	C1s (C1)	292.08	292.01	291.92	294.32	294.25	291.58	291.50	292.08	292.02
nitrobenzene	C1s (C2-4)	291.13	291.11	291.03	293.40	293.34	290.68	290.60	291.16	291.10
benzene	C1s	290.38	290.31	290.22	292.57	292.57	289.91	289.88	290.32	290.31
phenylacetylene	C1s (C3)	290.88	291.10	291.01	293.40	293.34	290.67	290.59	291.15	291.09
phenylacetylene	C1s (C2)	290.55	290.31	290.23	292.60	292.53	289.88	289.80	290.37	290.32
phenylacetylene	C1s (C4-6)	290.16	290.27	290.19	292.56	292.50	289.84	289.77	290.34	290.28
phenylacetylene	C1s (C1)	289.75	290.40	290.32	292.71	292.63	289.97	289.90	290.47	290.40
MAE (eV)			0.19	0.16	2.71	2.61	0.37	0.48	0.15	0.17

[a]Conventional values are the same as those reported in Tables S3, S4, S5, and S6. [b]Taken from Ref. 1.

Table S2: K-shell CEBEs for the CORE65 data set (including relativistic corrections), computed using the SCAN functional in conjunction with the conventional def2-TZVP basis set versus an uncontracted version of the same basis.[a]

Molecule	Core Orbital	Expt.[a]	ΔSCF		STM		GSTM		Shifted	
			normal	uncontr.	normal	uncontr.	normal	uncontr.	normal	uncontr.
methane	C1s	290.84	291.31	290.88	293.51	293.12	290.84	290.42	291.06	290.71
ethane	C1s	290.71	291.13	290.73	293.35	293.00	290.20	289.83	290.94	290.63
ethene	C1s	290.82	291.21	290.80	293.43	293.05	290.76	290.35	291.05	290.72
ethyne	C1s	291.25	291.74	291.29	293.99	293.59	291.32	290.89	291.57	291.22
carbon monoxide	O1s	542.1	543.25	542.61	546.08	545.47	542.79	542.17	542.91	542.37
carbon monoxide	C1s	296.23	296.85	296.41	298.98	298.58	296.51	296.09	296.33	295.98
carbon dioxide	O1s	541.32	542.04	541.38	544.92	544.29	541.57	540.93	541.81	541.25
carbon dioxide	C1s	297.7	298.01	297.67	300.24	299.94	297.57	297.23	297.67	297.41
tetrafluoromethane	F1s	695.2	696.14	695.36	699.30	698.56	695.63	694.88	695.72	695.07
tetrafluoromethane	C1s	301.9	301.92	301.62	304.25	303.97	301.50	301.21	301.69	301.45
fluoromethane	F1s	692.4	693.62	692.83	696.78	696.01	693.11	692.34	693.21	692.52
fluoromethane	C1s	293.56	293.98	293.57	296.25	295.87	293.54	293.14	293.76	293.43
trifluoromethane	F1s	694.1	695.33	694.55	698.49	697.74	694.82	694.06	694.92	694.25
trifluoromethane	C1s	299.16	299.35	299.01	301.68	301.36	298.93	298.59	299.14	298.87
methanol	O1s	538.88	539.73	539.06	542.62	541.97	539.26	538.61	539.50	538.92
methanol	C1s	292.3	292.90	292.49	295.15	294.78	292.45	292.05	292.70	292.37
formaldehyde	O1s	539.33	540.07	539.40	542.93	542.30	539.60	538.95	539.85	539.29
formaldehyde	C1s	294.38	294.93	294.52	297.19	296.82	294.49	294.08	294.70	294.38
dimethyl ether	O1s	538.36	539.24	538.57	542.13	541.50	538.77	538.12	539.09	538.52
dimethyl ether	C1s	292.17	292.65	292.25	294.92	294.55	292.20	291.81	292.49	292.17
formic acid	O1s (OH)	540.69	541.40	540.74	544.29	543.65	540.94	540.30	541.20	540.63
formic acid	O1s (C=O)	539.02	539.51	538.85	542.37	541.74	539.04	538.40	539.32	538.76
formic acid	C1s	295.75	296.09	295.72	298.36	298.02	295.66	295.29	295.86	295.57
acetone	O1s	537.73	538.41	537.76	541.30	540.68	538.01	537.37	538.30	537.75
acetone	C1s (C=O)	293.88	293.95	293.60	296.24	295.94	293.68	293.34	293.83	293.57
acetone	C1s (CH_3)	291.23	291.55	291.17	293.79	293.44	291.09	290.74	291.40	291.08
methyl formate	O1s (OCH_3)	539.64	540.59	539.94	543.49	542.86	540.13	539.50	540.47	539.91
methyl formate	O1s (C=O)	538.24	539.03	538.37	541.90	541.27	538.56	537.92	538.87	538.32
acetic acid	O1s (OH)	540.1	540.81	540.16	543.70	543.07	540.35	539.72	540.64	540.08
acetic acid	O1s (C=O)	538.31	538.78	538.12	541.65	541.02	538.31	537.67	538.63	538.07
acetic acid	C1s (COOH)	295.35	295.58	295.23	297.86	297.56	295.14	294.81	295.40	295.14
acetic acid	C1s (CH_3)	291.55	291.99	291.61	294.24	293.88	291.53	291.16	291.82	291.51
water	O1s	539.7	540.54	539.84	543.40	542.72	540.07	539.39	540.19	539.59
ozone	O1s middle	546.44	547.55	546.95	550.46	549.89	547.07	546.50	547.37	546.88
ozone	O1s terminal	541.75	542.20	541.51	545.44	544.72	541.91	541.15	542.39	541.75
oxygen	O1s weaker	544.2	544.67	544.00	547.56	546.91	545.67	543.54	544.36	543.79
oxygen	O1s stronger	543.1	544.67	544.00	547.56	546.91	544.22	543.55	544.36	543.79
nitrogen	N1s	409.93	410.53	410.00	413.07	412.56	408.97	408.47	410.17	409.73
ammonia	N1s	405.52	406.18	405.61	408.74	408.19	405.73	405.18	405.94	405.46
hydrogen cyanide	N1s	406.8	407.33	406.78	409.87	409.35	406.88	406.35	407.10	406.64
hydrogen cyanide	C1s	293.5	293.91	293.50	296.11	295.75	293.47	293.07	293.59	293.28
acetonitrile	N1s	405.58	405.97	405.42	408.54	408.02	405.51	404.99	405.84	405.38
acetonitrile	C1s (CH_3)	292.88	293.21	292.81	295.45	295.09	292.74	292.37	293.01	292.70
acetonitrile	C1s (CN)	292.6	293.09	292.72	295.31	294.99	292.66	292.29	292.85	292.57
glycine	O1s (OH)	540.2	540.83	540.18	543.73	543.09	540.37	539.73	540.67	540.11
glycine	O1s (C=O)	538.4	538.89	538.23	541.76	541.13	538.42	537.78	538.74	538.19
glycine	N1s	405.4	405.99	405.46	408.58	408.08	405.54	405.03	405.86	405.41
glycine	C1s (COOH)	295.2	295.34	295.00	297.63	297.33	294.91	294.58	295.19	294.93
glycine	C1s (CH_2)	292.3	292.63	292.27	294.90	294.58	292.17	291.82	292.51	292.22
pyridine	N1s	404.82	405.13	404.62	407.73	407.25	404.68	404.19	405.13	404.70
pyrrole	N1s	406.18	406.66	406.18	409.26	408.80	406.22	405.75	406.63	406.22
aniline	N1s	405.31	405.87	405.35	408.45	407.96	405.42	404.91	405.80	405.36
urea	O1s	537.19	537.72	537.05	540.58	539.94	537.25	536.61	537.57	537.00
urea	N1s	406.09	406.65	406.12	409.24	408.74	406.20	405.69	406.53	406.09
urea	C1s	294.84	295.13	294.79	297.41	297.11	294.69	294.36	294.95	294.70
methylamine	N1s	405.17	405.70	405.16	408.31	407.79	405.24	404.72	405.57	405.11
nitrobenzene	O1s	538.63	539.01	538.34	541.93	541.31	538.55	537.91	539.02	538.46
nitrobenzene	N1s	411.6	411.77	411.34	414.50	414.11	411.30	410.88	411.87	411.53
nitrobenzene	C1s (C1)	292.08	292.30	291.94	294.59	294.26	291.85	291.50	292.31	292.03
nitrobenzene	C1s (C2-4)	291.13	291.42	291.05	293.69	293.35	290.97	290.61	291.41	291.11
benzene	C1s	290.38	290.62	290.24	292.91	292.56	290.21	289.84	290.61	290.31
phenylacetylene	C1s (C3)	290.88	291.38	291.03	293.64	293.35	290.93	290.59	291.36	291.10
phenylacetylene	C1s (C2)	290.55	290.62	290.24	292.88	292.55	290.17	289.80	290.62	290.33
phenylacetylene	C1s (C4-6)	290.16	290.59	290.21	292.85	292.52	290.13	289.78	290.59	290.30
phenylacetylene	C1s (C1)	289.75	290.72	290.34	292.95	292.65	290.27	289.90	290.67	290.41
MAE (eV)			0.55	0.16	3.11	2.63	0.26	0.45	0.38	0.16

[a]Experimental values taken from Ref. 1.

Table S3: K-shell CEBEs for the CORE65 data set (including relativistic corrections), computed using the ΔSCF/def2-QZVP approach with various functionals.

Molecule	Core Orbital	CEBE (eV)									
		Expt.[a]	SCAN	SCAN0	B3LYP	BH&HLYP	ωB97X-V	LC-ωPBE	LC-ωPBEh	SRC1-r1	HF
methane	C1s	290.84	290.92	291.03	291.08	291.47	291.27	290.07	290.36	292.45	290.80
ethane	C1s	290.71	290.78	290.89	290.91	291.29	291.12	289.94	290.24	292.26	290.59
ethene	C1s	290.82	290.85	290.98	291.02	291.36	291.19	290.03	290.33	292.32	290.46
ethyne	C1s	291.25	291.35	291.48	291.57	291.96	291.75	290.57	290.89	292.88	290.86
carbon monoxide	C1s	296.23	296.45	296.76	296.75	297.42	296.97	295.58	295.98	298.22	296.52
carbon dioxide	C1s	297.7	297.70	298.30	298.05	299.14	298.38	296.87	297.33	299.82	299.31
tetrafluoromethane	C1s	301.9	301.65	302.15	301.91	302.89	302.18	300.70	301.16	303.61	302.67
fluoromethane	C1s	293.56	293.64	293.80	293.80	294.29	294.01	292.75	293.06	295.20	293.70
trifluoromethane	C1s	299.16	299.06	299.43	299.27	300.07	299.53	298.12	298.52	300.86	299.71
methanol	C1s	292.3	292.55	292.68	292.69	293.13	292.90	291.67	291.97	294.06	292.48
formaldehyde	C1s	294.38	294.57	294.70	294.82	295.28	295.01	293.74	294.06	296.18	294.98
dimethyl ether	C1s	292.17	292.30	292.43	292.42	292.86	292.65	291.41	291.71	293.79	292.22
formic acid	C1s	295.75	295.77	296.09	296.01	296.73	296.30	294.91	295.29	297.53	296.63
acetone	C1s (C=O)	293.88	293.66	293.88	293.87	294.42	294.19	292.93	293.25	295.23	294.11
acetone	C1s (CH_3)	291.23	291.21	291.37	291.37	291.82	291.59	290.37	290.68	292.75	291.20
acetic acid	C1s (COOH)	295.35	295.29	295.65	295.52	296.26	295.86	294.50	294.87	297.02	296.15
acetic acid	C1s (CH_3)	291.55	291.67	291.83	291.81	292.29	292.04	290.80	291.12	293.22	291.69
hydrogen cyanide	C1s	293.5	293.56	293.71	293.79	294.24	293.94	292.72	293.05	295.12	293.02
acetonitrile	C1s (CH_3)	292.88	292.86	293.01	292.97	293.44	293.16	291.98	292.29	294.37	292.83
acetonitrile	C1s (CN)	292.6	292.78	293.00	293.02	293.53	293.25	292.04	292.36	294.36	292.41
glycine	C1s (COOH)	295.2	295.05	295.44	295.30	296.07	295.66	294.29	294.65	296.81	295.98
glycine	C1s (CH_2)	292.3	292.34	292.52	292.46	292.96	292.71	291.47	291.79	293.86	292.36
urea	C1s	294.84	294.86	295.29	295.08	295.93	295.48	294.09	294.45	296.66	295.89
nitrobenzene	C1s (C1)	292.08	292.01	292.28	292.17	292.74	292.46	291.24	291.58	293.57	292.07
nitrobenzene	C1s (C2-4)	291.13	291.11	291.36	291.26	291.76	291.53	290.33	290.66	292.63	290.93
benzene	C1s	290.38	290.31	290.47	290.45	290.87	290.70	289.53	289.84	291.77	289.95
phenylacetylene	C1s (C3)	290.88	291.10	291.27	291.19	291.63	291.44	290.28	290.61	292.52	290.61
phenylacetylene	C1s (C2)	290.55	290.31	290.49	290.46	290.91	290.75	289.57	289.88	291.79	290.29
phenylacetylene	C1s (C4-6)	290.16	290.27	290.47	290.42	290.99	290.71	289.54	289.85	291.75	289.93
phenylacetylene	C1s (C1)	289.75	290.40	290.57	290.54	290.87	290.71	289.54	289.95	291.88	289.93
nitrogen	N1s	409.93	410.07	410.25	410.20	410.73	410.42	409.13	409.50	411.52	409.69
ammonia	N1s	405.52	405.71	405.79	405.78	406.17	406.03	404.80	405.11	407.08	405.44
hydrogen cyanide	N1s	406.8	406.86	406.98	406.98	407.39	407.22	405.99	406.33	408.24	406.34
acetonitrile	N1s	405.58	405.50	405.67	405.64	406.10	405.90	404.68	405.01	406.92	405.20
glycine	N1s	405.4	405.56	405.67	405.58	406.00	405.89	404.66	404.98	406.88	405.27
pyridine	N1s	404.82	404.72	404.86	404.74	405.15	405.07	403.88	404.21	405.99	404.28
pyrrole	N1s	406.18	406.28	406.39	406.27	406.65	406.58	405.42	405.75	407.52	405.80
aniline	N1s	405.31	405.45	405.53	405.43	405.82	405.72	404.51	404.83	406.70	405.06
urea	N1s	406.09	406.22	406.36	406.25	406.73	406.55	405.30	405.64	407.58	406.07
methylamine	N1s	405.17	405.26	405.35	405.29	405.66	405.57	404.37	404.69	406.57	404.88
nitrobenzene	N1s	411.6	411.43	412.00	411.63	412.65	412.38	410.98	411.33	413.14	412.70
carbon monoxide	O1s	542.1	542.74	542.72	542.65	542.93	542.84	541.76	542.01	543.62	541.81
carbon dioxide	O1s	541.32	541.52	541.62	541.45	541.90	541.68	540.47	540.80	542.58	541.05
methanol	O1s	538.88	539.22	539.23	539.12	539.46	539.39	538.22	538.50	540.20	538.52
formaldehyde	O1s	539.33	539.55	539.51	539.46	539.69	539.67	538.56	538.82	540.43	538.53
dimethyl ether	O1s	538.36	538.74	538.74	538.60	538.89	538.87	537.74	538.03	539.63	537.86
formic acid	O1s (OH)	540.69	540.89	540.94	540.79	541.22	541.05	539.84	540.15	541.93	540.40
formic acid	O1s (C=O)	539.02	539.00	539.04	538.94	539.30	539.18	538.01	538.29	539.99	538.29
acetone	O1s	537.73	537.90	537.93	537.84	538.16	538.13	536.97	537.22	538.86	537.11
methyl formate	O1s (OCH_3)	539.64	540.10	540.14	539.96	540.31	540.22	539.07	539.37	541.02	539.37
methyl formate	O1s (C=O)	538.24	538.52	538.57	538.45	538.81	538.71	537.52	537.81	539.50	537.84
acetic acid	O1s (OH)	540.1	540.30	540.38	540.22	540.67	540.51	539.28	539.59	541.36	539.87
acetic acid	O1s (C=O)	538.31	538.27	538.32	538.22	538.59	538.50	537.31	537.58	539.26	537.61
water	O1s	539.7	540.01	540.03	539.98	540.36	540.23	539.02	539.29	541.10	539.50
ozone	O1s middle	546.44	547.09	547.44	547.21	547.96	547.69	546.38	546.72	548.43	547.49
ozone	O1s terminal	541.75	541.65	541.88	541.70	542.12	541.85	540.65	540.94	542.86	540.81
oxygen	O1s weaker	544.2	544.14	544.18	544.23	544.59	544.49	543.25	543.54	545.23	542.98
oxygen	O1s stronger	543.1	544.14	544.18	544.23	544.59	544.49	543.25	543.54	545.22	542.98
glycine	O1s (OH)	540.2	540.32	540.41	540.25	540.72	540.57	539.33	539.63	541.38	539.94
glycine	O1s (C=O)	538.4	538.38	538.44	538.33	538.71	538.61	537.42	537.69	539.36	537.73
urea	O1s	537.19	537.23	537.27	537.15	537.53	537.44	536.24	536.52	538.20	536.60
nitrobenzene	O1s	538.63	538.50	538.63	538.47	538.94	538.91	537.70	537.96	539.52	538.13
tetrafluoromethane	F1s	695.20	695.55	695.64	695.41	695.95	695.63	694.40	694.70	696.39	695.10
fluoromethane	F1s	692.40	693.04	692.96	692.82	693.10	693.01	691.91	692.13	693.62	691.98
trifluoromethane	F1s	694.10	694.74	694.78	694.57	695.03	694.78	693.59	693.86	695.50	694.10
MAE (eV)[b]			0.19	0.29	0.23	0.69	0.47	0.76	0.47	1.47	0.41

[a]Taken from Ref. 1. [b]MAE with respect to experiment, as reported also in Table II.

Table S4: K-shell CEBEs for the CORE65 data set (including relativistic corrections), computed using the conventional STM/def2-QZVP approach with various functionals.

Molecule	Core Orbital	CEBE (eV)									
		Expt.[a]	SCAN	SCAN0	B3LYP	BH&HLYP	ωB97X-V	LC-ωPBE	LC-ωPBEh	SRC1-r1	HF
methane	C1s	290.84	293.16	292.71	292.12	292.03	292.49	291.63	291.65	292.94	290.96
ethane	C1s	290.71	293.04	292.60	291.97	291.88	292.36	291.53	291.54	292.76	290.77
ethene	C1s	290.82	293.10	292.66	292.08	291.59	292.43	291.62	291.65	292.83	290.57
ethyne	C1s	291.25	293.58	293.17	292.61	292.52	292.96	292.14	292.18	293.39	290.93
carbon monoxide	C1s	296.23	298.59	298.42	297.76	297.98	298.09	297.11	297.25	298.71	297.01
carbon dioxide	C1s	297.7	299.96	300.03	299.14	299.77	299.63	298.48	298.67	300.37	299.58
tetrafluoromethane	C1s	301.9	304.00	303.98	303.07	303.59	303.53	302.40	302.58	304.23	303.05
fluoromethane	C1s	293.56	295.92	295.54	294.87	294.89	295.26	294.35	294.39	295.73	293.93
trifluoromethane	C1s	299.16	301.41	301.25	300.41	300.74	300.84	299.79	299.92	301.45	300.05
methanol	C1s	292.3	294.83	294.42	293.75	293.72	294.15	293.27	293.29	294.58	292.70
formaldehyde	C1s	294.38	296.86	296.44	295.91	295.93	296.26	295.35	295.41	296.74	295.16
dimethyl ether	C1s	292.17	294.59	294.18	293.50	293.48	293.91	293.02	293.05	294.33	292.44
formic acid	C1s	295.75	298.06	297.89	297.11	297.42	297.57	296.54	296.65	298.12	296.88
acetone	C1s (C=O)	293.88	296.00	295.72	294.99	295.13	295.47	294.58	294.64	295.85	294.33
acetone	C1s (CH_3)	291.23	293.48	293.10	292.43	292.42	292.84	291.96	292.00	293.27	291.39
acetic acid	C1s (COOH)	295.35	297.59	297.47	296.64	296.96	297.15	296.15	296.25	297.63	295.64
acetic acid	C1s (CH_3)	291.55	293.94	293.56	292.88	292.88	293.28	292.40	292.44	293.73	291.88
hydrogen cyanide	C1s	293.5	295.78	295.41	294.82	294.81	295.13	294.28	294.34	295.62	293.83
acetonitrile	C1s (CH_3)	292.88	295.13	294.74	294.03	294.03	294.44	293.57	293.61	294.88	293.03
acetonitrile	C1s (CN)	292.6	295.03	294.73	294.07	294.12	294.48	293.62	293.67	294.88	292.49
glycine	C1s (COOH)	295.2	297.36	297.26	296.43	296.77	296.96	295.96	296.05	297.42	295.55
glycine	C1s (CH_2)	292.3	294.64	294.27	293.55	293.59	293.98	293.10	293.14	294.40	292.58
urea	C1s	294.84	297.16	297.06	296.20	296.59	296.79	295.75	295.84	297.23	296.00
nitrobenzene	C1s (C1)	292.08	294.32	294.05	293.28	293.37	293.76	292.89	292.97	294.14	292.36
nitrobenzene	C1s (C2-4)	291.13	293.40	293.10	292.35	292.46	292.83	291.97	292.03	293.35	291.44
benzene	C1s	290.38	292.57	292.23	291.54	291.62	291.97	291.16	291.19	292.37	290.46
phenylacetylene	C1s (C3)	290.88	293.40	293.04	292.29	292.44	292.74	291.93	291.98	293.24	291.17
phenylacetylene	C1s (C2)	290.55	292.60	292.27	291.55	291.57	292.04	291.21	291.25	292.63	290.50
phenylacetylene	C1s (C4-6)	290.16	292.56	292.23	291.53	292.55	292.01	291.18	291.22	292.29	290.45
phenylacetylene	C1s (C1)	289.75	292.71	292.35	291.63	291.08	292.01	291.18	291.31	292.48	290.47
nitrogen	N1s	409.93	412.62	412.19	411.38	411.39	411.74	410.86	410.92	412.13	409.71
ammonia	N1s	405.52	408.28	407.71	406.93	406.79	407.36	406.52	406.51	407.64	405.52
hydrogen cyanide	N1s	406.8	409.41	408.90	408.15	408.03	408.55	407.73	407.75	408.82	406.35
acetonitrile	N1s	405.58	408.10	407.62	406.86	406.77	407.31	406.46	406.47	407.54	405.29
glycine	N1s	405.4	408.16	407.63	406.77	406.66	407.25	406.42	406.42	407.47	405.38
pyridine	N1s	404.82	407.34	406.84	405.97	405.85	406.47	405.68	405.68	406.62	405.38
pyrrole	N1s	406.18	408.90	408.36	407.46	407.30	407.94	407.19	407.18	408.10	405.88
aniline	N1s	405.31	408.03	407.48	406.60	406.46	407.08	406.25	406.25	407.27	405.15
urea	N1s	406.09	408.84	408.32	407.43	407.41	407.90	407.05	407.06	408.28	406.17
methylamine	N1s	405.17	407.87	407.32	406.48	406.31	406.92	406.11	406.11	407.15	404.99
nitrobenzene	N1s	411.6	414.19	414.13	412.97	413.47	413.87	412.87	412.91	413.91	412.97
carbon monoxide	O1s	542.1	545.59	544.84	543.93	543.61	544.28	543.63	543.51	544.25	541.80
carbon dioxide	O1s	541.32	544.41	543.78	542.75	542.60	543.13	542.37	542.33	543.23	541.06
methanol	O1s	538.88	542.11	541.39	540.42	540.16	540.85	540.11	540.03	540.84	538.55
formaldehyde	O1s	539.33	542.43	541.65	540.75	540.37	541.11	540.45	540.33	541.06	538.51
dimethyl ether	O1s	538.36	541.64	540.93	539.91	539.61	540.35	539.66	539.58	540.30	537.92
formic acid	O1s (OH)	540.69	543.78	543.11	542.08	541.91	542.51	541.73	541.67	542.57	540.43
formic acid	O1s (C=O)	539.02	541.87	541.18	540.23	539.97	540.62	539.89	539.80	540.62	538.28
acetone	O1s	537.73	540.81	540.09	539.14	538.85	539.60	538.87	538.75	539.50	537.09
methyl formate	O1s (OCH_3)	539.64	543.01	542.32	541.27	541.03	541.70	540.98	540.92	541.68	539.42
methyl formate	O1s (C=O)	538.24	541.41	540.72	539.74	539.50	540.17	539.42	539.33	540.14	537.83
acetic acid	O1s (OH)	540.1	543.20	542.54	541.51	541.37	541.97	541.18	541.12	542.01	539.91
acetic acid	O1s (C=O)	538.31	541.15	540.47	539.51	539.27	539.94	539.20	539.10	539.89	537.60
water	O1s	539.7	542.87	542.15	541.24	541.01	541.65	540.87	540.78	541.71	539.49
ozone	O1s middle	546.44	550.01	549.65	548.57	548.73	549.21	548.34	548.32	549.15	547.59
ozone	O1s terminal	541.75	544.70	544.07	543.10	542.86	543.42	542.65	542.68	543.52	540.64
oxygen	O1s weaker	544.2	547.03	546.71	545.56	545.86	545.96	545.18	545.09	546.10	544.01
oxygen	O1s stronger	543.1	547.03	546.71	545.56	545.86	545.96	545.18	545.09	546.10	544.01
glycine	O1s (OH)	540.2	543.22	542.59	541.55	541.42	542.03	541.23	541.16	542.04	539.98
glycine	O1s (C=O)	538.4	541.26	540.59	539.62	539.39	540.07	539.31	539.21	540.00	537.72
urea	O1s	537.19	540.10	539.40	538.43	538.19	538.88	538.11	538.02	538.82	536.57
nitrobenzene	O1s	538.63	541.44	540.82	539.79	539.63	540.40	539.64	539.51	540.17	538.07
tetrafluoromethane	F1s	695.2	698.73	698.00	696.82	696.70	697.20	696.42	696.31	697.10	695.04
fluoromethane	F1s	692.4	696.19	695.29	694.18	693.81	694.54	693.90	693.71	694.28	691.89
trifluoromethane	F1s	694.1	697.91	697.12	695.96	695.77	696.34	695.60	695.46	696.19	694.04
MAE (eV)[b]			2.71	2.25	1.39	1.38	1.83	0.99	1.00	2.08	0.45

[a]Taken from Ref. 1. [b]MAE with respect to experiment, as reported also in Table II.

Table S5: K-shell CEBEs for the CORE65 data set (including relativistic corrections), computed using the GSTM/def2-QZVP approach with various functionals.[a]

Molecule	Core Orbital	CEBE (eV)									
		Expt.[b]	SCAN	SCAN0	B3LYP	BH&HLYP	ωB97X-V	LC-ωPBE	LC-ωPBEh	SRC1-r1	HF
methane	C1s	290.84	290.47	290.71	290.82	291.32	291.05	289.70	290.06	292.32	290.81
ethane	C1s	290.71	289.87	290.58	290.65	290.82	290.91	289.57	289.94	292.25	290.59
ethene	C1s	290.82	290.42	290.67	290.76	291.21	290.98	289.66	290.04	292.19	290.47
ethyne	C1s	291.25	290.93	291.20	291.32	291.68	291.54	290.21	290.60	292.81	290.86
carbon monoxide	C1s	296.23	296.13	296.55	296.50	297.27	296.77	295.23	295.68	298.07	296.54
carbon dioxide	C1s	297.7	297.27	298.02	297.79	298.99	298.16	296.51	297.04	299.69	299.31
tetrafluoromethane	C1s	301.9	301.25	301.88	301.63	302.73	301.95	300.31	300.84	303.47	302.66
fluoromethane	C1s	293.56	293.21	293.50	293.52	294.13	293.78	292.38	292.76	295.07	293.70
trifluoromethane	C1s	299.16	298.65	299.15	298.99	299.91	299.30	297.74	298.21	300.71	299.71
methanol	C1s	292.3	292.12	292.38	292.41	292.97	292.67	291.29	291.66	293.92	292.48
formaldehyde	C1s	294.38	294.14	294.42	294.55	295.13	294.79	293.37	293.76	296.04	294.98
dimethyl ether	C1s	292.17	291.86	292.13	292.15	292.71	292.43	291.05	291.42	293.66	292.22
formic acid	C1s	295.75	295.34	295.81	295.74	296.58	296.08	294.55	294.99	297.39	296.54
acetone	C1s (C=O)	293.88	293.40	293.77	293.77	294.47	294.15	292.73	293.12	295.30	294.33
acetone	C1s (CH_3)	291.23	290.77	291.07	291.10	291.68	291.37	290.01	290.39	292.62	291.21
acetic acid	C1s (COOH)	295.35	294.87	295.37	295.25	296.12	295.64	294.14	294.57	296.91	296.10
acetic acid	C1s (CH_3)	291.55	291.22	291.53	291.55	292.14	291.82	290.43	290.83	293.09	291.69
hydrogen cyanide	C1s	293.5	293.14	293.43	293.53	294.09	293.73	292.37	292.76	294.99	293.03
acetonitrile	C1s (CH_3)	292.88	292.42	292.70	292.70	293.29	293.03	291.61	292.00	294.24	292.84
acetonitrile	C1s (CN)	292.6	292.36	292.72	292.76	293.38	293.08	291.68	292.07	294.23	292.36
glycine	C1s (COOH)	295.2	294.64	295.17	295.04	295.94	295.45	293.93	294.36	296.70	295.98
glycine	C1s (CH_2)	292.3	291.89	292.22	292.19	292.81	292.49	291.10	291.50	293.73	292.36
urea	C1s	294.84	294.43	295.00	294.81	295.79	295.26	293.72	294.15	296.53	295.54
nitrobenzene	C1s (C1)	292.08	291.58	291.99	291.91	292.59	292.26	290.89	291.30	293.48	292.27
nitrobenzene	C1s (C2-4)	291.13	290.68	291.16	291.00	291.78	291.33	289.98	290.38	292.49	291.24
benzene	C1s	290.38	289.91	290.20	290.19	290.70	290.49	289.18	289.56	292.06	290.32
phenylacetylene	C1s (C3)	290.88	290.67	290.98	290.92	291.99	291.24	289.94	290.34	292.55	291.01
phenylacetylene	C1s (C2)	290.55	289.88	290.24	290.20	290.78	290.55	289.21	289.59	291.54	290.34
phenylacetylene	C1s (C4-6)	290.16	289.84	290.16	290.16	290.93	290.51	289.18	289.55	292.00	290.30
phenylacetylene	C1s (C1)	289.75	289.97	290.28	290.28	290.53	290.51	289.17	289.66	292.39	290.28
nitrogen	N1s	409.93	408.54	409.90	409.93	409.45	410.21	407.66	409.20	410.29	409.69
ammonia	N1s	405.52	405.29	405.49	405.49	406.01	405.80	404.41	404.80	406.94	405.44
hydrogen cyanide	N1s	406.8	406.43	406.67	406.70	407.23	407.00	405.62	406.03	408.09	406.33
acetonitrile	N1s	405.58	405.07	405.36	405.37	405.94	405.74	404.31	404.71	406.79	405.20
glycine	N1s	405.4	405.13	405.37	405.29	405.84	405.65	404.27	404.67	406.74	405.27
pyridine	N1s	404.82	404.29	404.56	404.46	405.00	404.85	403.50	403.91	405.85	404.36
pyrrole	N1s	406.18	405.86	406.10	405.99	406.49	406.35	405.04	405.44	407.37	405.81
aniline	N1s	405.31	405.01	405.22	405.13	405.65	405.49	404.12	404.53	406.56	405.05
urea	N1s	406.09	405.80	406.07	405.96	406.60	406.31	404.91	405.33	407.45	406.07
methylamine	N1s	405.17	404.82	405.04	405.00	405.50	405.33	404.78	404.37	406.42	404.88
nitrobenzene	N1s	411.6	410.98	411.69	411.35	412.49	412.16	410.60	411.03	413.01	412.68
carbon monoxide	O1s	542.1	542.30	542.40	542.36	542.77	542.61	541.37	541.70	543.47	541.81
carbon dioxide	O1s	541.32	541.07	541.30	541.16	541.73	541.44	540.08	540.49	542.43	541.06
methanol	O1s	538.88	538.77	538.91	538.83	539.28	539.15	537.82	538.18	540.04	538.52
formaldehyde	O1s	539.33	539.11	539.19	539.17	539.52	539.43	538.16	538.50	540.27	538.53
dimethyl ether	O1s	538.36	538.29	538.43	538.30	538.72	538.63	537.34	537.71	539.48	537.86
formic acid	O1s (OH)	540.69	540.45	540.63	540.50	541.05	540.81	539.44	539.84	542.55	540.40
formic acid	O1s (C=O)	539.02	538.55	538.72	538.65	539.13	538.94	537.61	537.98	539.84	538.29
acetone	O1s	537.73	537.52	537.69	537.62	538.07	537.97	536.64	536.98	538.79	537.21
methyl formate	O1s (OCH_3)	539.64	539.66	539.82	539.66	540.14	539.98	538.67	539.06	540.87	538.86
methyl formate	O1s (C=O)	538.24	538.08	538.25	538.15	538.65	538.47	537.13	537.50	539.35	537.83
acetic acid	O1s (OH)	540.1	539.87	540.07	539.92	540.50	540.27	538.89	539.28	541.21	539.87
acetic acid	O1s (C=O)	538.31	537.83	538.01	537.93	538.42	538.26	536.91	537.27	539.11	537.61
water	O1s	539.7	539.57	539.71	539.68	540.18	539.99	538.61	538.97	540.95	539.50
ozone	O1s middle	546.44	546.63	547.11	546.92	547.79	547.45	545.99	546.40	548.28	547.49
ozone	O1s terminal	541.75	541.35	541.57	541.52	541.95	539.02	540.36	540.76	542.70	540.80
oxygen	O1s weaker	544.2	543.70	544.04	543.93	544.55	544.24	542.85	543.21	545.22	544.09
oxygen	O1s stronger	543.1	543.70	544.04	543.93	544.55	544.24	542.85	543.21	545.22	544.08
glycine	O1s (OH)	540.2	539.88	540.10	539.95	540.55	540.32	538.93	539.31	541.23	539.94
glycine	O1s (C=O)	538.4	537.94	538.12	538.03	538.54	538.38	537.02	537.37	539.21	537.73
urea	O1s	537.19	536.78	536.95	536.86	537.36	537.20	535.84	536.20	538.05	536.59
nitrobenzene	O1s	538.63	538.07	538.32	538.17	538.71	538.68	537.32	537.65	539.36	538.13
tetrafluoromethane	F1s	695.2	695.06	695.29	695.10	695.79	695.02	693.98	694.37	696.17	695.09
fluoromethane	F1s	692.4	692.55	692.62	692.51	692.93	692.76	691.49	691.80	693.46	691.98
trifluoromethane	F1s	694.1	694.25	694.43	694.26	694.86	694.53	693.17	693.54	695.33	694.09
MAE (eV)[c]			0.37	0.15	0.17	0.54	0.30	1.14	0.74	1.36	0.41

[a]The GSTM approach used here is the $\mathcal{F}[0;3]+\mathcal{F}[1;3]$ ($n=3$) method from Table I. [b]Taken from Ref. 1. [c]MAE with respect to experiment, as reported also in Table II.

Table S6: K-shell CEBEs for the CORE65 data set (including relativistic corrections), computed using the shifted-STM/def2-QZVP approach with various functionals.

Molecule	Core Orbital	CEBE (eV)									
		Expt.[a]	SCAN	SCAN0	B3LYP	BH&HLYP	ωB97X-V	LC-ωPBE	LC-ωPBEh	SRC1-r1	HF
methane	C1s	290.84	290.75	290.66	290.92	290.60	290.91	290.82	290.77	290.59	291.07
ethane	C1s	290.71	290.67	290.60	290.79	290.55	290.82	290.73	290.69	290.60	290.88
ethene	C1s	290.82	290.77	290.72	290.93	290.51	290.93	290.84	290.81	290.87	290.68
ethyne	C1s	291.25	291.22	291.19	291.44	291.23	291.43	291.34	291.33	291.27	291.04
carbon monoxide	C1s	296.23	295.99	296.06	296.42	295.94	296.30	296.22	296.26	295.33	297.10
carbon dioxide	C1s	297.7	297.43	297.76	297.85	297.91	297.91	297.62	297.72	297.31	299.67
tetrafluoromethane	C1s	301.9	301.48	301.75	301.81	301.87	301.85	301.55	301.65	301.43	303.15
fluoromethane	C1s	293.56	293.48	293.44	293.65	293.40	293.66	293.53	293.50	293.28	294.03
trifluoromethane	C1s	299.16	298.91	299.06	299.16	299.09	299.18	298.95	299.00	298.75	300.14
methanol	C1s	292.3	292.42	292.36	292.56	292.31	292.57	292.45	292.42	292.26	292.80
formaldehyde	C1s	294.38	294.42	294.34	294.68	294.39	294.64	294.52	294.51	294.21	295.26
dimethyl ether	C1s	292.17	292.21	292.15	292.32	292.12	292.36	292.22	292.19	292.13	292.54
formic acid	C1s	295.75	295.61	295.75	295.88	295.83	295.94	295.71	295.75	295.53	296.98
acetone	C1s (C=O)	293.88	293.63	293.71	293.81	293.76	293.92	293.78	293.78	293.66	294.44
acetone	C1s (CH_3)	291.23	291.13	291.11	291.27	291.12	291.31	291.17	291.15	291.17	291.50
acetic acid	C1s (COOH)	295.35	295.18	295.39	295.43	295.47	295.55	295.33	295.36	295.21	295.74
acetic acid	C1s (CH_3)	291.55	291.56	291.54	291.70	291.53	291.74	291.60	291.59	291.54	291.98
hydrogen cyanide	C1s	293.5	293.31	293.27	293.58	293.21	293.49	293.44	293.43	292.98	293.93
acetonitrile	C1s (CH_3)	292.88	292.74	292.70	292.84	292.64	292.84	292.76	292.74	292.61	293.13
acetonitrile	C1s (CN)	292.6	292.61	292.64	292.86	292.62	292.84	292.80	292.78	292.44	292.59
glycine	C1s (COOH)	295.2	294.97	295.20	295.23	295.33	295.39	295.15	295.18	295.09	295.66
glycine	C1s (CH_2)	292.3	292.28	292.28	292.38	292.30	292.46	292.30	292.30	292.32	292.68
urea	C1s	294.84	294.75	294.98	295.00	295.11	295.19	294.93	294.96	294.84	296.11
nitrobenzene	C1s (C1)	292.08	292.08	292.24	292.19	292.40	292.35	292.14	292.18	292.61	292.48
nitrobenzene	C1s (C2-4)	291.13	291.16	291.28	291.25	291.46	291.41	291.22	291.24	291.70	291.55
benzene	C1s	290.38	290.32	290.39	290.43	290.57	290.54	290.40	290.40	290.73	290.57
phenylacetylene	C1s (C3)	290.88	291.15	291.22	291.19	291.39	291.32	291.17	291.19	291.58	291.28
phenylacetylene	C1s (C2)	290.55	290.37	290.48	290.47	290.63	290.64	290.46	290.47	291.01	290.61
phenylacetylene	C1s (C4-6)	290.16	290.34	290.44	290.44	291.28	290.61	290.44	290.44	290.83	290.57
phenylacetylene	C1s (C1)	289.75	290.47	290.53	290.54	290.27	290.60	290.43	290.53	290.90	290.58
nitrogen	N1s	409.93	409.77	409.77	409.95	409.68	409.79	409.86	409.85	409.51	409.84
ammonia	N1s	405.52	405.55	405.45	405.58	405.39	405.53	405.56	405.51	405.56	405.65
hydrogen cyanide	N1s	406.8	406.70	406.68	406.81	406.70	406.74	406.77	406.76	406.85	406.49
acetonitrile	N1s	405.58	405.45	405.49	405.56	405.60	405.51	405.53	405.51	405.86	405.43
glycine	N1s	405.4	405.49	405.46	405.46	405.43	405.48	405.48	405.45	405.69	405.52
pyridine	N1s	404.82	404.79	404.85	404.73	404.95	404.82	404.78	404.78	405.42	405.52
pyrrole	N1s	406.18	406.31	406.31	406.21	406.31	406.26	406.28	406.26	406.73	406.03
aniline	N1s	405.31	405.44	405.40	405.33	405.39	405.38	405.34	405.32	405.79	405.28
urea	N1s	406.09	406.18	406.17	406.13	406.19	406.15	406.12	406.10	406.47	406.30
methylamine	N1s	405.17	405.19	405.13	405.16	405.06	405.15	405.18	405.14	405.33	405.13
nitrobenzene	N1s	411.6	411.60	412.06	411.70	412.41	412.16	411.95	411.97	412.47	413.11
carbon monoxide	O1s	542.1	542.47	542.30	542.40	542.14	542.16	542.51	542.36	542.21	541.96
carbon dioxide	O1s	541.32	541.36	541.33	541.26	541.29	541.08	541.27	541.21	541.48	541.22
methanol	O1s	538.88	539.06	538.94	538.93	538.83	538.79	539.02	538.91	539.07	538.71
formaldehyde	O1s	539.33	539.41	539.25	539.28	539.17	539.09	539.36	539.23	539.50	538.67
dimethyl ether	O1s	538.36	538.66	538.57	538.47	538.47	538.36	538.59	538.50	538.84	538.08
formic acid	O1s (OH)	540.69	540.75	540.68	540.61	540.63	540.47	540.64	540.57	540.87	540.59
formic acid	O1s (C=O)	539.02	538.88	538.81	538.78	538.82	538.62	538.82	538.72	539.13	538.44
acetone	O1s	537.73	537.87	537.80	537.73	537.84	537.64	537.82	537.70	538.30	537.25
methyl formate	O1s (OCH_3)	539.64	540.05	539.99	539.84	539.94	539.73	539.92	539.85	540.32	539.58
methyl formate	O1s (C=O)	538.24	538.44	538.39	538.30	538.41	538.19	538.35	538.26	538.77	537.99
acetic acid	O1s (OH)	540.1	540.20	540.15	540.05	540.14	539.95	540.10	540.03	540.41	540.07
acetic acid	O1s (C=O)	538.31	538.19	538.14	538.08	538.19	537.97	538.13	538.03	538.54	537.76
water	O1s	539.7	539.74	539.58	539.69	539.46	539.51	539.74	539.61	539.53	539.65
ozone	O1s middle	546.44	546.99	547.25	547.10	547.52	547.17	547.25	547.21	547.56	547.76
ozone	O1s terminal	541.75	541.73	541.77	541.67	541.89	541.46	541.59	541.62	542.31	540.81
oxygen	O1s weaker	544.2	543.90	544.10	544.01	544.20	543.81	544.05	543.93	543.92	544.16
oxygen	O1s stronger	543.1	543.91	544.10	544.01	544.19	543.81	544.05	543.93	543.91	544.16
glycine	O1s (OH)	540.2	540.23	540.20	540.09	540.21	540.02	540.15	540.07	540.46	540.14
glycine	O1s (C=O)	538.4	538.31	538.27	538.19	538.33	538.10	538.25	538.15	538.69	537.88
urea	O1s	537.19	537.15	537.10	537.01	537.15	536.92	537.06	536.96	537.54	536.73
nitrobenzene	O1s	538.63	538.59	538.65	538.42	538.85	538.52	538.61	538.50	539.35	538.24
tetrafluoromethane	F1s	695.2	695.22	695.13	695.09	695.03	694.76	695.14	695.00	694.82	695.21
fluoromethane	F1s	692.4	692.70	692.46	692.47	692.23	692.12	692.62	692.41	692.17	692.07
trifluoromethane	F1s	694.1	694.42	694.28	694.24	694.14	693.91	694.32	694.16	693.99	694.22
MAE (eV)[b]			0.15	0.14	0.14	0.19	0.20	0.14	0.14	0.34	0.44

[a]Taken from Ref. 1. [b]MAE with respect to experiment, as reported also in Table III using β parameters optimized for each functional.

Table S7: K-shell CEBEs (in eV) for adenine computed using ΔSCF/def2-QZVP methods and compared to ADC(4) results. All values include relativistic corrections

Atom	ΔSCF							ADC(4)[a]	Expt.[a]
	SCAN	SCAN0	B3LYP	BH&HLYP	ωB97X-V	LC-ωPBE	LC-ωPBEh		
N1	406.95	407.06	406.74	407.21	407.28	405.89	406.22	406.63	406.70
N3	405.96	406.01	405.72	406.14	406.22	404.83	405.14	405.62	405.70
N2	404.93	405.04	404.74	405.20	405.28	403.87	404.21	404.99	
N4	404.56	404.66	404.36	404.80	404.88	403.48	403.81	404.40	
N5	404.40	404.50	404.20	404.64	404.74	403.34	403.67	404.27	404.40
C6	292.87	293.12	292.80	293.46	293.41	291.95	292.26	292.96	
C7	292.33	292.54	292.28	292.88	292.80	291.35	291.68	292.47	292.50
C8	292.36	292.58	292.28	292.88	292.80	291.38	291.70	292.66	
C9	291.94	292.18	291.88	292.54	292.47	290.99	291.31	291.94	
C10	291.09	291.21	291.00	291.43	291.39	290.06	290.38	291.19	291.00

[a]From Ref. 2

Table S8: K-shell CEBEs (in eV) for adenine computed using the conventional STM/def2-QZVP method and compared to ADC(4) results. All values include relativistic corrections.

Atom	STM							ADC(4)[a]	Expt.[a]
	SCAN	SCAN0	B3LYP	BH&HLYP	ωB97X-V	LC-ωPBE	LC-ωPBEh		
N1	409.36	408.88	407.94	407.88	408.47	407.67	407.68	406.63	406.70
N3	408.34	407.78	406.88	406.77	407.37	406.56	406.55	405.62	405.70
N2	407.34	406.88	405.96	405.90	406.49	405.67	405.68	404.99	
N4	406.98	406.50	405.58	405.58	406.09	405.28	405.29	404.40	
N5	406.82	406.33	405.42	405.33	405.94	405.13	405.14	404.27	404.40
C6	294.98	294.77	293.94	294.17	294.56	293.64	293.67	292.96	
C7	294.44	294.19	293.42	293.59	293.96	293.05	293.10	292.47	292.50
C8	294.47	294.20	293.40	293.76	293.93	293.04	293.09	292.66	
C9	294.04	293.83	293.02	292.49	293.62	292.68	292.72	291.94	
C10	293.18	292.81	292.10	292.07	292.50	291.70	291.75	291.19	291.00

[a]From Ref. 2

Table S9: K-shell CEBEs (in eV) for adenine computed using GSTM/def2-QZVP methods and compared to ADC(4) results. All values include relativistic corrections.

Atom	GSTM							ADC(4)[a]	Expt.[a]
	SCAN	SCAN0	B3LYP	BH&HLYP	ωB97X-V	LC-ωPBE	LC-ωPBEh		
N1	409.36	408.88	407.94	407.88	408.47	407.67	407.68	406.63	406.70
N3	408.34	407.78	406.88	406.77	407.37	406.56	406.55	405.62	405.70
N2	407.34	406.88	405.96	405.90	406.49	405.67	405.68	404.99	
N4	406.98	406.50	405.58	405.58	406.09	405.28	405.29	404.40	
N5	406.82	406.33	405.42	405.33	405.94	405.13	405.14	404.27	404.40
C6	294.98	294.77	293.94	294.17	294.56	293.64	293.67	292.96	
C7	294.44	294.19	293.42	293.59	293.96	293.05	293.10	292.47	292.50
C8	294.47	294.20	293.40	293.76	293.93	293.04	293.09	292.66	
C9	294.04	293.83	293.02	292.49	293.62	292.68	292.72	291.94	
C10	293.18	292.81	292.10	292.07	292.50	291.70	291.75	291.19	291.00

[a]From Ref. 2

Table S10: K-shell CEBEs (in eV) for adenine computed using shifted-STM/def2-QZVP methods and compared to ADC(4) results. All values include relativistic corrections.

Atom	Shifted-STM							ADC(4)[a]	Expt.[a]
	SCAN	SCAN0	B3LYP	BH&HLYP	ωB97X-V	LC-ωPBE	LC-ωPBEh		
N1	406.30	406.60	406.46	407.05	406.87	405.52	405.93	406.63	406.70
N3	405.31	405.55	405.44	405.98	405.81	404.45	404.85	405.62	405.70
N2	404.26	404.57	404.46	405.05	404.88	403.51	403.91	404.99	
N4	403.90	404.18	404.08	404.64	404.48	403.10	403.52	404.40	
N5	403.74	404.03	403.92	404.49	404.34	402.97	403.37	404.27	404.40
C6	292.22	292.68	304.76	293.34	293.03	291.61	291.98	292.96	
C7	291.67	292.09	292.02	292.74	292.43	291.01	291.39	292.47	292.50
C8	291.71	292.13	292.02	292.70	292.41	291.03	291.43	292.66	
C9	291.28	291.73	291.62	292.57	292.09	290.65	291.04	291.94	
C10	290.43	290.78	290.75	291.29	291.01	289.72	290.11	291.19	291.00

[a]From Ref. 2

Table S11: K-shell CEBEs (in eV) for thymine computed using ΔSCF/def2-QZVP methods and compared to ADC(4) results. All values include relativistic corrections.

Atom	ΔSCF							ADC(4)[a]	Expt.[a]
	SCAN	SCAN0	B3LYP	BH&HLYP	ωB97X-V	LC-ωPBE	LC-ωPBEh		
O1	537.51	537.51	537.15	537.58	537.70	536.29	536.56	537.46	537.30
O2	537.18	537.17	536.83	537.24	537.38	535.97	536.24	537.24	
N3	407.19	407.30	406.94	407.43	407.44	406.03	406.39	406.80	406.70
N4	406.85	406.99	406.62	407.16	407.17	405.73	406.08	406.52	
C5	295.39	295.84	295.39	296.36	296.11	294.49	294.84	295.36	295.20
C6	294.18	294.60	294.17	295.07	294.89	293.30	293.64	294.19	294.20
C7	292.62	292.84	292.56	293.17	293.09	291.62	291.96	292.29	292.30
C9	291.21	291.35	291.10	291.56	291.52	290.16	290.49	290.67	291.00
C8	291.39	291.48	291.27	291.71	291.70	290.28	290.60	290.95	

[a]From Ref. 2

Table S12: K-shell CEBEs (in eV) for thymine computed using the conventional STM/def2-QZVP method and compared to ADC(4) results. All values include relativistic corrections.

Atom	STM							ADC(4)[a]	Expt.[a]
	SCAN	SCAN0	B3LYP	BH&HLYP	ωB97X-V	LC-ωPBE	LC-ωPBEh		
O1	540.15	539.47	538.43	538.25	538.95	538.18	538.08	537.46	537.30
O2	539.81	539.13	538.11	537.87	538.64	537.87	537.76	537.24	
N3	409.56	409.08	408.14	408.08	408.62	407.81	407.84	406.80	406.70
N4	409.23	408.79	407.82	407.81	408.34	407.50	407.53	406.52	
C5	297.51	297.49	296.56	297.07	297.26	296.19	296.27	295.36	295.20
C6	296.28	296.23	295.33	295.79	296.04	295.01	295.07	294.19	294.20
C7	294.68	294.44	293.66	293.82	294.20	293.29	293.35	292.29	292.30
C9	293.26	292.93	292.20	292.20	292.62	291.81	291.87	290.67	291.00
C8	293.41	293.03	292.33	291.21	292.77	291.90	291.94	290.95	

[a]From Ref. 2

Table S13: K-shell CEBEs (in eV) for thymine computed using GSTM/def2-QZVP methods and compared to ADC(4) results. All values include relativistic corrections.

Atom	GSTM							ADC(4)[a]	Expt.[a]
	SCAN	SCAN0	B3LYP	BH&HLYP	ωB97X-V	LC-ωPBE	LC-ωPBEh		
O1	536.81	537.00	536.85	537.40	537.27	535.89	536.25	537.46	537.30
O2	536.49	536.67	536.53	537.07	536.96	535.58	535.92	537.24	
N3	406.51	406.81	406.66	407.33	407.03	405.65	406.09	406.80	406.70
N4	406.17	406.51	406.34	407.00	406.75	405.36	405.78	406.52	
C5	294.72	295.38	295.12	296.21	295.69	294.12	294.54	295.36	295.20
C6	293.51	294.13	293.91	294.94	294.48	292.93	293.34	294.19	294.20
C7	291.95	292.39	292.30	292.99	292.69	291.27	291.68	292.29	292.30
C9	290.53	291.08	290.84	291.50	291.13	289.80	290.21	290.67	291.00
C8	290.70	291.00	291.00	291.59	291.30	289.92	290.31	290.95	

[a]From Ref. 2

Table S14: K-shell CEBEs (in eV) for thymine computed using shifted-STM/def2-QZVP methods and compared to ADC(4) results. All values include relativistic corrections.

Atom	Shifted-STM							ADC(4)[a]	Expt.[a]
	SCAN	SCAN0	B3LYP	BH&HLYP	ωB97X-V	LC-ωPBE	LC-ωPBEh		
O1	537.26	537.24	537.04	537.34	537.05	537.14	537.05	537.46	537.30
O2	536.94	536.94	536.74	537.06	536.76	536.84	536.74	537.24	
N3	406.99	407.05	406.89	407.13	406.96	406.91	406.93	406.80	406.70
N4	406.65	406.74	406.57	406.83	406.67	406.60	406.62	406.52	
C5	295.17	295.51	295.40	295.75	295.73	295.40	295.43	295.36	295.20
C6	293.96	294.28	294.19	294.53	294.52	294.22	294.24	294.19	294.20
C7	292.43	292.61	292.56	292.80	292.77	292.53	292.55	292.29	292.30
C9	291.02	291.10	291.11	291.21	291.20	291.06	291.08	290.67	291.00
C8	291.07	291.07	291.18	290.32	291.25	291.11	291.10	290.95	

[a]From Ref. 2