Surpporing Information for LibSC: Library for Scaling Correction Methods in Density Functional Theory

Yuncai Mei[1],† Jincheng Yu[1],† Zehua Chen,† Neil Qiang Su,† and Weitao Yang*,†,‡

†*Department of Chemistry, Duke University, Durham, North Carolina 27708, USA*

‡*Department of Physics, Duke University, Durham, North Carolina 27708, USA*

E-mail: weitao.yang@duke.edu

[1]Y.M. and J.Y. contributed equally to this work and share the first authorship.

Contents

1 Localization Algorithm

Following the same notation as used in the supporting information for the paper of LOSC2,[1] the cost function of LOSC2 localization is define as

$$F = (1-\lambda)\sum_p R_{pppp} + \lambda C \sum_p H_{pppp}, \tag{1}$$

where

$$R_{pqrs} = \iint \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\phi_p(\mathbf{r})\phi_q(\mathbf{r})|\mathbf{r}-\mathbf{r}'|^2\phi_r(\mathbf{r}')\phi_s(\mathbf{r}') \tag{2}$$

$$= \iint \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\phi_p(\mathbf{r})\phi_q(\mathbf{r})(r^2+r'^2-2\mathbf{r}\cdot\mathbf{r}')\phi_r(\mathbf{r}')\phi_s(\mathbf{r}') \tag{3}$$

$$= \langle p|r^2|q\rangle\delta_{rs} + \langle r|r^2|s\rangle\delta_{pq} - 2\langle p|\mathbf{r}|q\rangle\cdot\langle r|\mathbf{r}|s\rangle, \tag{4}$$

and

$$H_{pqrs} = \iint \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\phi_p(\mathbf{r})\phi_q(\mathbf{r})\Big[H_\mathrm{s}(\mathbf{r}) - H_\mathrm{s}(\mathbf{r}')\Big]^2\phi_r(\mathbf{r}')\phi_s(\mathbf{r}') \tag{5}$$

$$= \iint \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\phi_p(\mathbf{r})\phi_q(\mathbf{r})\Big([H_\mathrm{s}(\mathbf{r})]^2 + [H_\mathrm{s}(\mathbf{r}')]^2 - 2H_\mathrm{s}(\mathbf{r})H_\mathrm{s}(\mathbf{r}')\Big)\phi_r(\mathbf{r}')\phi_s(\mathbf{r}') \tag{6}$$

$$= \langle p|H_\mathrm{s}^2|q\rangle\delta_{rs} + \langle r|H_\mathrm{s}^2|s\rangle\delta_{pq} - 2\langle p|H_\mathrm{s}|q\rangle\langle r|H_\mathrm{s}|s\rangle. \tag{7}$$

ϕ_p and ϕ_q refer to the localized orbitals. H_s is the one-electron Hamiltonian of the parent density functional approximation (DFA). The Jacobi-Sweep algorithm to optimize the orbitalets is to iterate all the unique pairs of localized orbitals with a 2×2 rotation matrix at each time. For each rotation, the algorithm is to find the best rotation angle θ that minimizes the change

$$\Delta F_{pq}(\theta) = (1-\lambda)(R_{p'p'p'p'} + R_{q'q'q'q'} - R_{pppp} - R_{qqqq}) + \lambda C(H_{p'p'p'p'} + H_{q'q'q'q'} - H_{pppp} - H_{qqqq}) \tag{8}$$

where the rotation is associated with the p-th and q-th localized orbitals, p and q refer to the orbitals before the rotation, p' and q' refer to the orbitals after the rotation, and the orbitals are related with the rotation matrix as

$$\begin{pmatrix} \phi'_p \\ \phi'_q \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \phi_p \\ \phi_q \end{pmatrix}. \tag{9}$$

Based on Eqs. 2, 5 and 9, one can derive the change of cost function as

$$\Delta F_{pq}(\theta) = x_1 \cos 4\theta + x_2 \sin 4\theta - x_1, \tag{10}$$

where

$$x_1 = (1-\lambda)\Big(-\frac{1}{2}|\langle p|\mathbf{r}|p\rangle - \langle q|\mathbf{r}|q\rangle|^2 + 2|\langle p|\mathbf{r}|q\rangle|^2\Big) + \lambda C\Big(-\frac{1}{2}|\langle p|H_{\rm s}|p\rangle - \langle q|H_{\rm s}|q\rangle|^2 + 2|\langle p|H_{\rm s}|q\rangle|^2\Big), \tag{11}$$

and

$$x_2 = (1-\lambda)\Big(2\langle p|\mathbf{r}|q\rangle \cdot \Big[\langle q|\mathbf{r}|q\rangle - \langle p|\mathbf{r}|p\rangle\Big]\Big) + \lambda C\Big(2\langle p|H_{\rm s}|q\rangle\Big[\langle q|H_{\rm s}|q\rangle - \langle p|H_{\rm s}|p\rangle\Big]\Big). \tag{12}$$

Next we need to find the optimal θ_0 that makes

$$\frac{\mathrm{d}}{\mathrm{d}\theta}\Delta F_{pq}(\theta)\Big|_{\theta=\theta_0} = 0, \tag{13}$$

and

$$\frac{\mathrm{d}^2}{\mathrm{d}\theta^2}\Delta F_{pq}(\theta)\Big|_{\theta=\theta_0} > 0. \tag{14}$$

Based on Eq. 13, one can derive the following relations

$$2x_1 \sin 2\theta_0 \cos 2\theta_0 - x_2(\cos^2 2\theta_0 - \sin^2 2\theta_0) = 0, \tag{15}$$

$$2x_1 \tan 2\theta_0 - x_2 + x_2 \tan^2 2\theta_0 = 0 \tag{16}$$

and

$$\tan 2\theta_0 = \frac{-x_1 \pm \sqrt{x_1^2 + x_2^2}}{x_2}. \tag{17}$$

It can be verified that the minimum takes only one of the two solutions as shown in Eq. 17, while the other solution corresponds to the maximum.

2 Additional Numerical Results

A series of calculations that have been done with `QM4D`[2] were repeated to test the performance of `LibSC`. Refer to our previous works[3 4 1] for information about molecular structures and reference values. aug-cc-pVTZ-RIFIT is used as the fitting basis for all the calculations.

2.1 Atomization Energies

For atomization energy (AE) test sets, both B3LYP and BLYP calculations were done using 6-311++G(3df, 3pd) basis set with `Psi4`. The results are shown in Table 1 - 5.

Table 1: Detailed data for the atomization energies (in kcal/mol) of the G2-1 test set. Some data is not available because of the SCF convergence issue from DFT.

		B3LYP			BLYP		
mol	ref	DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
BeH	49.8	57.9	57.9	57.9	56.9	56.9	56.9
C2H2	405.3	402.5	402.5	402.5	404.6	404.6	404.6
C2H4	562.6	563.0	563.0	563.0	560.4	560.4	560.4
C2H6	710.7	711.3	711.3	711.3	703.9	703.9	703.9
CH2_1A1	180.6	180.8	180.8	180.8	179.0	179.0	179.0
CH3	306.6	309.8	309.8	309.8	306.8	306.7	306.7
CH4	419.2	420.7	420.7	420.7	416.6	416.6	416.6
CH	83.9	85.4	85.4	85.4	-	-	-
Cl2	57.9	54.9	54.9	54.9	-	-	-
ClF	61.4	60.1	60.1	60.1	-	-	-
ClO	64.4	65.8	65.8	65.8	-	-	-
CN	180.9	178.5	178.5	178.5	189.2	189.2	189.2
CO2	389.2	388.0	388.0	388.0	400.8	400.8	400.8
CO	259.3	255.0	255.0	255.0	262.1	262.1	262.1
CS	171.3	166.3	166.2	166.2	-	-	-
F2	38.5	35.9	35.9	35.9	48.2	48.2	48.2
H2CO	373.7	373.7	373.6	373.6	378.1	378.1	378.1
H2NNH2	437.8	444.0	444.0	444.0	447.3	447.3	447.3
H2O	232.2	231.2	231.2	231.2	233.1	233.0	233.0
H2S	182.3	182.1	182.1	182.1	-	-	-
H3COH	511.9	511.9	511.9	511.9	511.2	511.1	511.1
HCl	106.4	105.2	105.2	105.2	-	-	-
HCN	312.5	312.3	312.3	312.3	319.8	319.8	319.8
HF	140.8	139.6	139.6	139.6	141.5	141.5	141.5
HCO	278.7	280.6	280.6	280.6	287.5	287.5	287.5

Table 1 continued

mol	ref	DFA	post-LOSC	SCF-LOSC	DFA	post-LOSC	SCF-LOSC
HOCl	164.4	162.8	162.8	162.8	-	-	-
HOOH	268.7	267.1	267.1	267.1	276.4	276.4	276.4
N2	228.6	226.8	226.8	226.8	238.7	238.7	238.7
NH2	181.5	187.9	187.9	187.9	189.4	189.4	189.4
NH3	297.5	300.9	300.9	300.9	301.6	301.6	301.6
NH	83.5	88.0	88.0	88.0	89.4	89.4	89.4
NO	152.8	155.4	155.4	155.4	166.3	166.3	166.3
O2	120.5	122.3	122.3	122.3	135.7	135.7	135.7
OH	106.3	108.4	108.4	108.4	109.9	109.9	109.9
P2	117.3	114.8	114.8	114.8	121.1	121.1	121.1
PH2	152.8	158.5	158.5	158.5	157.2	157.2	157.2
PH3	241.8	244.5	244.5	244.5	242.1	242.1	242.1
S2	101.7	102.7	102.7	102.7	-	-	-
Si2H6	529.7	529.9	529.9	529.9	519.1	519.1	519.1
Si2	74.7	69.1	69.1	69.1	75.9	75.9	75.9
SiH2_1A1	151.4	153.4	153.4	153.4	151.5	151.5	151.5
SiH2_3B1	130.6	132.9	132.9	132.9	130.2	130.2	130.2
SiH3	225.1	228.2	228.2	228.2	224.0	223.9	223.9
SiH4	321.4	323.3	323.3	323.3	317.2	317.2	317.2
SiO	125.1	186.6	186.6	186.6	194.6	194.6	194.6
SO2	258.5	248.3	248.3	248.3	-	-	-
SO	125.1	125.6	125.6	125.6	-	-	-
	MAE	3.8	3.8	3.8	6.9	6.9	6.9

Table 2: Detailed data for the atomization energies (in kcal/mol) of the Hydrocarbon test set. Some data is not available because of the SCF convergence issue from DFT.

		B3LYP			BLYP		
mol	ref	DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
allene	702.4	704.07	704.06	704.06	704.01	704.00	704.00
benzene	1366.2	1360.83	1360.82	1360.82	1356.09	1356.06	1356.07
bicyclobutane	985.9	978.64	978.63	978.63	971.32	971.30	971.30
cyclobutane	1147	1141.63	1141.62	1141.62	1130.28	1130.26	1130.27
cyclobutene	1000.4	994.17	994.16	994.16	988.07	988.05	988.05
cyclopropane	851.8	849.59	849.58	849.58	841.88	841.87	841.87
cyclopropene	681.9	678.50	678.50	678.50	676.58	676.57	676.57
isobutane	1300.4	1295.45	1295.43	1295.43	1281.32	1281.29	1281.29
isobutene	1156.6	1153.31	1153.30	1153.30	1144.28	1144.25	1144.25
methylenecyclopropane	989.4	989.16	989.15	989.15	983.90	983.87	983.87
propane	1004.6	1003.14	1003.14	1003.14	992.50	992.48	992.48
propene	859.2	858.31	858.30	858.30	852.62	852.61	852.61
propyne	704.1	701.87	701.87	701.87	700.94	700.93	700.93
spiropentane	1282.3	1276.64	1276.62	1276.62	1265.89	1265.85	1265.85
t13butadiene	1011.3	1009.21	1009.21	1009.21	1005.59	1005.57	1005.57
trans-butane	1298.6	1294.82	1294.80	1294.80	1280.84	1280.81	1280.81
MAE		3.51	3.52	3.51	10.58	10.59	10.59

Table 3: Detailed data for the atomization energies (in kcal/mol) of the NonHydrocarbon test set. Some data is not available because of the SCF convergence issue from DFT.

mol	ref	B3LYP			BLYP		
		DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
AlCl3	306.2	294.00	294.00	294.00	-	-	-
AlF3	426.6	414.10	414.10	414.10	418.73	418.74	418.74
BCl3	322.6	313.82	313.81	313.81	-	-	-
BF3	469.8	464.95	464.95	464.95	468.92	468.92	468.92
C2Cl4	466.8	452.76	452.75	452.75	-	-	-
C2F4	583.8	585.40	585.40	585.40	598.66	598.66	598.66
CCl4	312.8	296.99	296.98	296.98	-	-	-
CF2O	423.2	416.60	416.60	416.60	428.14	428.14	428.14
CF3CN	639.7	634.48	634.48	634.48	650.14	650.13	650.13
CF4	476.2	470.30	470.30	470.30	478.48	478.48	478.48
ClNO	191.3	192.72	192.72	192.72	-	-	-
COS	333.3	332.99	332.99	332.99	-	-	-
CS2	277.6	276.60	276.60	276.60	-	-	-
F2O	93.2	92.75	92.75	92.75	114.08	114.08	114.08
N2O	270.5	272.68	272.68	272.68	295.61	295.61	295.61
NF3	205.3	208.66	208.66	208.66	229.84	229.84	229.84
O3	147.1	138.25	138.25	138.25	170.47	170.47	170.47
SiCl4	383.3	362.56	362.55	362.55	-	-	-
	MAE	6.99	6.99	6.99	13.52	13.51	13.51

Table 4: Detailed data for the atomization energies (in kcal/mol) of the SubHydrocarbon test set. Some data is not available because of the SCF convergence issue from DFT.

		B3LYP			BLYP		
mol	ref	DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
acetaldehyde	676.3	675.56	675.54	675.55	676.98	676.93	676.93
acetamide	867.2	868.13	868.10	868.11	870.82	870.76	870.77
aceticacid	802.2	799.07	799.06	799.06	803.33	803.31	803.31
acetone	977.1	974.74	974.72	974.72	972.70	972.63	972.63
acetylfluoride	705.5	703.14	703.14	703.14	708.26	708.24	708.24
acrylonitrile	763.4	760.69	760.69	760.69	767.38	767.37	767.37
aziridine	719	719.81	719.81	719.81	717.97	717.95	717.95
CH2Cl2	369.6	364.30	364.29	364.29	-	-	-
CH2F2	436.3	435.78	435.77	435.77	438.82	438.82	438.82
CHCl3	343.3	332.95	332.93	332.93	-	-	-
CHF3	457.8	454.71	454.70	454.70	460.64	460.63	460.63
dimethylamine	868.8	870.46	870.44	870.44	865.15	865.09	865.10
dimethylether	796.8	796.34	796.33	796.33	792.82	792.77	792.77
ethanethiol	767.6	763.99	763.97	763.98	-	-	-
ethanol	808.8	806.97	806.96	806.96	802.92	802.89	802.89
ethylchloride	690.2	686.90	686.89	686.89	-	-	-
furan	993.1	988.07	988.07	988.07	989.87	989.86	989.86
glyoxal	633.4	631.05	631.04	631.04	641.57	641.52	641.53
HCOOH	500.7	499.39	499.38	499.38	507.33	507.31	507.31
isopropanol	1106.3	1101.78	1101.76	1101.76	1094.31	1094.26	1094.26
ketene	532.1	533.76	533.75	533.75	540.55	540.55	540.55
methylamine	581.2	584.15	584.14	584.14	581.87	581.85	581.85
methylcyanide	615.1	615.21	615.21	615.21	619.58	619.57	619.57
methylethylether	1093.1	1091.32	1091.30	1091.30	1084.48	1084.42	1084.43
methylformate	784.2	783.13	783.12	783.12	788.28	788.25	788.26
methylnitrite	598.3	598.94	598.94	598.94	615.74	615.73	615.73
methylsilane	626.1	625.10	625.10	625.10	615.84	615.84	615.84
nitromethane	600.6	602.23	602.22	602.22	618.45	618.42	618.42

Table 4 continued:

mol	ref	DFA	post-LOSC	SCF-LOSC	DFA	post-LOSC	SCF-LOSC
oxirane	650	648.32	648.31	648.31	648.75	648.72	648.73
propylchloride	983.8	978.64	978.63	978.63	-	-	-
pyridine	1236.3	1235.34	1235.32	1235.32	1236.23	1236.19	1236.19
pyrrole	1070.5	1068.99	1068.99	1068.99	1068.35	1068.34	1068.34
trans-ethylamine	875.8	877.84	877.83	877.83	872.36	872.32	872.33
trimethylamine	1158.6	1158.33	1158.29	1158.30	1149.83	1149.72	1149.73
vinylchloride	538.6	539.44	539.43	539.43	-	-	-
vinylfluoride	571.5	572.38	572.37	572.37	573.95	573.94	573.94
	MAE	2.24	2.24	2.24	5.22	5.22	5.22

Table 5: Detailed data for the atomization energies (in kcal/mol) of the radical test set. Some data is not available because of the SCF convergence issue from DFT.

		B3LYP			BLYP		
mol	ref	DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
C2H3	443.9	446.94	446.94	446.94	446.05	446.04	446.04
C2H5	602.3	604.94	604.93	604.93	599.20	599.18	599.18
CCH	265.8	262.04	262.04	262.04	264.89	264.89	264.89
CH3_2CH	898.8	900.44	900.42	900.42	891.76	891.72	891.72
CH3_3C	1197	1195.75	1195.71	1195.72	1183.95	1183.85	1183.86
CH3CH2O	697.1	698.22	698.21	698.21	695.94	695.92	695.92
CH3CO	580.9	582.55	582.54	582.54	586.55	586.52	586.52
CH3O	400.5	403.89	403.88	403.88	404.70	404.68	404.68
H2COH	408.9	411.14	411.14	411.14	412.42	412.41	412.41
H2	109.2	110.13	110.13	110.13	109.26	109.26	109.26
NO2	227.5	232.00	232.00	232.00	255.09	255.09	255.09
SH	86.7	88.20	88.19	88.20	-	-	-
	MAE	2.31	2.30	2.30	6.22	6.23	6.23

2.2 Quasiparticle Energies

Quasiparticle energies (QE) of some organic systems were calculated using B3LYP/cc-pVTZ with `Psi4`. The detailed data is shown in Table 6 and Table 7.

Table 6: IP values (in eV) of some systems from the QE test set calculated from B3LYP and compared with experimental values. Some data is not available because of the SCF convergence issue from DFT.

mol	ref	B3LYP	post-LOSC2	SCF-LOSC2	GSC (v0)[a]	GSC (v1)[b]	GSC (v2)[c]
Acridine	7.99	5.99	7.90	7.89	7.23	6.99	6.99
Anthracene	7.4	5.51	7.52	7.52	6.78	6.55	6.55
Azulene	7.43	5.52	7.38	7.38	7.22	6.95	6.95
Benzonitrile	9.75	7.58	9.71	9.64	9.41	9.13	9.13
Benzoquinone	10.03	7.67	11.34	11.02	9.54	9.16	9.16
Benzothiadiazole	9	6.85	8.68	8.67	8.61	8.32	8.32
Benzothiazole	8.8	6.69	8.73	8.59	8.34	8.07	8.07
C60	7.6	6.32	7.97	7.96	7.20	7.03	7.03
C70	7.32	6.30	8.01	7.93	7.03	6.86	6.86
Dichlone	9.59	7.64	9.50	9.49	9.17	8.91	8.91
Dinitrobenzonitrile		8.90	11.23	11.07	10.62	10.34	10.34
Fluorene	7.9	6.05	7.93	7.93	7.52	7.28	7.28
Fumaronitrile	11.23	8.68	11.11	11.09	10.58	10.26	10.26
H2PC	6.4	5.48	7.69	7.11	6.51	6.28	6.28
Maleicanhydride	11.09	8.45	12.27	11.94	10.71	10.27	10.27
mDCBN	10.4	8.14	10.27	10.17	9.73	9.45	9.45
Naphthalenedione	9.54	7.49	11.09	9.57	9.33	8.95	8.95
NDCA	8.98	7.10	9.23	9.22	8.52	8.27	8.27
Nitrobenzene	9.93	7.87	9.81	9.80	10.04	9.74	9.74
Nitrobenzonitrile	10.4	8.37	10.56	10.45	10.12	9.83	9.83
Pentacene	6.6	4.87	6.49	6.44	5.84	5.63	5.63
Phenazine	8.38	6.39	8.25	8.25	7.61	7.37	7.37
Phthalicanhydride	10.18	8.23	12.03	10.16	10.47	10.04	10.04
Phthalimide	9.84	7.66	11.40	9.66	9.84	9.42	9.42

Table 6 continued:

mol	ref	B3LYP	post-LOSC2	SCF-LOSC2	GSC (v0)[a]	GSC (v1)[b]	GSC (v2)[c]
PTCDA	8.2	6.68	8.80	8.80	7.60	7.39	7.39
TCNE	11.78	9.42	12.58	12.58	10.93	10.65	10.65
TCNQ	9.61	7.63	10.06	10.03	8.73	8.48	8.48
Tetrachlorobenzoquinone	9.82	7.86	9.73	9.73	9.24	8.99	8.99
Tetrachloro-isobenzofuranedione	10.8	7.94	9.97	9.87	9.42	9.16	9.16
Tetrafluorobenzenedicarbonitrile	10.65	8.39	10.03	10.03	10.29	9.97	9.97
Tetrafluorobenzoquinone	10.83	8.39	10.52	10.52	10.25	9.93	9.93
Thiadiazole	10.1	7.73	9.76	9.76	10.07	9.75	9.75
Thiophene	8.85	6.58	8.64	8.64	8.95	8.64	8.64
	MAE	2.03	0.50	0.32	0.48	0.72	0.72

[a] The original GSC.[5]

[b] LOSC1 expression for the curvature matrix is used.[6]

[c] LOSC2 expression for the curvature matrix is used.[1]

Table 7: EA values (in eV) of the QE test set calculated from B3LYP and compared with experimental values. Some data is not available because of the SCF convergence issue from DFT.

mol	ref	B3LYP	post-LOSC2	SCF-LOSC2	GSC(v0)[a]	GSC(v1)[b]	GSC(v2)[c]
Acridine	0.9	2.33	0.69	0.69	1.04	1.27	1.27
Anthracene	0.6	2.09	0.44	0.44	0.85	1.08	1.08
Azulene	0.75	2.21	0.79	0.79	0.61	0.87	0.87
Benzonitrile	0.26	1.77	0.27	0.27	0.08	0.35	0.35
Benzoquinone	1.88	3.81	2.34	2.34	2.05	2.35	2.35
Benzothiadiazole		2.70	1.02	1.02	1.11	1.39	1.39
Benzothiazole		1.41	-0.51	-0.46	-0.22	0.05	0.05
C60	2.7	3.73	2.02	2.03	2.93	3.09	3.09
C70	2.76	3.70	2.25	2.29	2.98	3.13	3.13

Table 7 continued:

mol	ref	B3LYP	post-LOSC2	SCF-LOSC2	GSC(v0)[a]	GSC(v1)[b]	GSC(v2)[c]
Dichlone	2.21	3.73	2.24	2.24	2.19	2.46	2.46
Dinitrobenzonitrile	2.16	3.88	1.56	1.71	2.56	2.84	2.84
Fluorene		1.19	-0.44	-0.44	-0.13	0.11	0.11
Fumaronitrile	1.25	3.37	1.57	1.57	1.40	1.71	1.71
H2PC		2.60	1.10	1.10	1.68	1.89	1.89
Maleicanhydride	1.42	3.42	1.66	1.66	1.42	1.73	1.73
mDCBN	0.91	2.58	1.07	1.07	0.96	1.24	1.24
Naphthalenedione	1.81	3.45	1.89	1.89	1.84	2.12	2.12
NDCA		3.01	1.48	1.48	1.75	1.99	1.99
Nitrobenzene	1.01	2.71	0.32	0.38	0.73	1.07	1.07
Nitrobenzonitrile	1.71	3.44	1.27	1.41	1.82	2.13	2.13
Pentacene		2.80	1.18	1.17	1.83	2.03	2.03
Phenazine	1.31	2.75	1.16	1.16	1.41	1.65	1.65
Phthalicanhydride	1.26	2.87	1.30	1.30	1.27	1.55	1.55
Phthalimide	1.02	2.56	0.99	0.99	0.97	1.25	1.25
PTCDA		4.18	2.65	2.65	3.31	3.50	3.50
TCNE	3.17	5.22	3.65	3.65	3.53	3.82	3.82
TCNQ	2.8	5.08	3.55	3.55	3.88	4.13	4.13
Tetrachlorobenzoquinone	2.77	4.39	3.01	3.01	2.74	3.03	3.03
Tetrachloro-isobenzofuranedione	1.96	3.43	1.81	1.81	1.91	2.19	2.19
Tetrafluorobenzenedicarbonitrile	1.89	3.57	2.11	2.11	2.06	2.33	2.33
Tetrafluorobenzoquinone	2.69	4.49	3.04	3.04	2.74	3.05	3.05
Thiadiazole		1.99	0.17	0.17	-0.15	0.18	0.18
Thiophene		0.68	-0.99	-0.99	-1.28	-0.99	-0.99
	MAE	1.64	0.30	0.28	0.18	0.39	0.39

[a] The original GSC.[5]

[b] LOSC1 expression for the curvature matrix is used.[6]

[c] LOSC2 expression for the curvature matrix is used.[1]

2.3 Reaction Barriers

Reaction barriers (RB) were calculated using both B3LYP/6-311++G(3df, 3pd) and BLYP/6-311++G(3df, 3pd) with `Psi4`. The results are shown in Table 8 and Table 9.

Table 8: Detailed data for the reaction barriers (in kcal/mol) of the HTBH38 test set. Some data is not available because of the SCF convergence issue from DFT.

		B3LYP			BLYP		
case	ref	DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
Forward: $E_{TS} - \sum T_{reactants}$							
TS1	5.7	−0.81	−0.81	−0.81	-	-	-
TS2	4.9	0.52	0.52	0.52	−3.49	−3.49	−3.49
TS3	12.1	8.69	8.70	8.70	7.09	7.10	7.10
TS4	6.5	1.99	1.99	1.99	−2.70	−2.70	−2.70
TS5	9.6	4.22	4.22	4.22	2.86	2.86	2.86
TS6	3	−2.59	−2.59	−2.59	−9.18	−9.12	−9.12
TS7	1.7	−1.50	−1.50	−1.50	-	-	-
TS8	3.2	−0.96	−0.96	−0.96	−6.04	−6.03	−6.03
TS9	1.42	−5.86	−5.86	−5.86	-	-	-
TS10	13.47	7.03	7.03	7.03	1.65	1.66	1.65
TS11	3.1	−1.03	−1.02	−1.02	−2.56	−2.54	−2.54
TS12	10.5	4.05	4.05	4.05	1.49	1.49	1.49
TS13	3.5	−0.55	−0.55	−0.55	-	-	-
TS14	9.57	1.10	1.11	1.11	-	-	-
TS15	8	6.07	6.08	6.08	3.48	3.50	3.50
TS16	7.5	8.18	8.18	8.18	5.89	5.91	5.91
TS17	10.4	8.74	8.75	8.75	5.25	5.29	5.29
TS18	14.5	11.25	11.26	11.26	7.95	7.99	7.98
TS19	38.4	38.68	38.68	38.68	-	-	-
	MAE	4.30	4.30	4.30	7.31	7.30	7.30
Backward: $E_{TS} - \sum T_{products}$							
case	ref	DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
TS1	7.86	4.14	4.14	4.14	-	-	-
TS2	21.2	13.26	13.26	13.26	10.27	10.27	10.27
TS3	15.3	9.49	9.49	9.49	7.60	7.61	7.61
TS4	19.6	13.93	13.93	13.93	10.55	10.55	10.55
TS5	9.6	4.22	4.22	4.22	2.86	2.86	2.86
TS6	12.7	7.29	7.29	7.29	1.76	1.83	1.82
TS7	7.06	4.24	4.24	4.24	-	-	-
TS8	19.9	15.61	15.61	15.61	12.33	12.33	12.33
TS9	33.4	23.66	23.66	23.66	-	-	-
TS10	7.9	4.44	4.44	4.44	1.63	1.64	1.63

Table 8 continued:

case	ref	DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
TS11	23.2	23.01	23.01	23.01	21.86	21.87	21.87
TS12	12.87	5.84	5.84	5.84	1.00	1.00	1.00
TS13	16.76	15.68	15.69	15.69	-	-	-
TS14	9.36	4.26	4.28	4.27	-	-	-
TS15	22.4	17.11	17.12	17.12	13.33	13.35	13.35
TS16	18.3	14.58	14.59	14.59	10.62	10.65	10.65
TS17	17.4	15.44	15.45	15.44	12.67	12.70	12.70
TS18	17.8	13.32	13.32	13.32	10.26	10.29	10.29
TS19	38.4	38.68	38.68	38.68	-	-	-
	MAE	4.39	4.39	4.39	7.80	7.79	7.79

Table 9: Detailed data for the reaction barriers (in kcal/mol) of the NHTBH38 test set. Some data is not available because of the SCF convergence issue from DFT.

		B3LYP			BLYP		
case	ref	DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
Forward: $E_{TS} - \sum T_{reactants}$							
TS1	17.13	11.33	11.33	11.33	8.50	8.50	8.50
TS2	42.18	30.96	30.96	30.96	25.97	25.97	25.97
TS3	18	12.48	12.48	12.48	9.87	9.87	9.87
TS4	30.38	21.76	21.76	21.76	16.09	16.09	16.09
TS5	2.27	−7.31	−7.31	−7.31	-	-	-
TS6	6.75	−1.17	−1.14	−1.14	-	-	-
TS7	−0.34	−3.88	−3.85	−3.86	−7.87	−7.77	−7.79
TS8	13.38	10.18	10.07	10.10	6.44	5.84	6.09
TS9	3.1	-	-	-	-	-	-
TS10	13.41	-	-	-	-	-	-
TS11	−12.54	-	-	-	-	-	-
TS12	3.44	-	-	-	-	-	-
TS13	−2.44	−5.79	−5.72	−5.73	−9.75	−9.49	−9.55
TS14	10.96	45.40	45.41	45.42	40.17	40.16	40.20
TS15	14.36	7.43	7.43	7.43	5.20	5.20	5.20
TS16	3.17	−0.60	−0.60	−0.60	−1.96	−1.96	−1.96
TS17	1.72	−0.19	−0.19	−0.19	−0.71	−0.70	−0.70
TS18	6.85	5.94	5.95	5.95	4.66	4.67	4.67
TS19	48.07	47.29	47.29	47.29	46.66	46.66	46.66
	MAE	7.17	7.17	7.16	9.12	9.14	9.13
Forward: $E_{TS} - \sum T_{products}$							
case	ref	dfa	postlosc	scflosc	dfa	postlosc	scflosc
TS1	82.27	72.89	72.89	72.89	61.74	61.74	61.74

Table 9 continued:

case	ref	DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
TS2	42.18	30.96	30.96	30.96	25.97	25.97	25.97
TS3	18	12.48	12.48	12.48	9.87	9.87	9.87
TS4	57.02	48.60	48.60	48.60	42.21	42.21	42.21
TS5	105.8	96.12	96.12	96.12	-	-	-
TS6	59.16	51.47	51.49	51.49	-	-	-
TS7	−0.34	−3.88	−3.85	−3.86	−7.87	−7.77	−7.79
TS8	13.38	10.18	10.07	10.10	6.44	5.84	6.09
TS9	3.1	-	-	-	-	-	-
TS10	13.41	-	-	-	-	-	-
TS11	20.11	-	-	-	-	-	-
TS12	29.42	-	-	-	-	-	-
TS13	17.66	14.21	14.28	14.27	9.14	9.40	9.34
TS14	47.2	7.64	7.47	7.53	3.67	2.91	3.21
TS15	10.61	10.79	10.79	10.79	8.40	8.39	8.39
TS16	22.68	24.44	24.44	24.44	23.15	23.14	23.14
TS17	41.75	41.77	41.77	41.77	38.15	38.15	38.15
TS18	32.97	29.54	29.53	29.53	25.01	24.98	24.99
TS19	32.82	33.32	33.32	33.32	31.68	31.67	31.67
	MAE	7.17	7.18	7.18	10.89	10.97	10.94

2.4 Ionization Potentials and Electron Affinities

Ionization potentials (IPs) and electron affinities (EAs) of a series of systems were calculated using both B3LYP/6-311++G(3df, 3pd) and BLYP/6-311++G(3df, 3pd) with `Psi4`. The results are shown in Table 10 and Table 11.

Table 10: Detailed data for the ionization potentials (in eV) of the IP test set. Some data is not available because of the SCF convergence issue from DFT.

		BLYP			B3LYP		
mol	ref	DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
H4C	14.4	9.36	13.75	13.75	10.75	14.26	14.25
H3N	11.03	6.16	11.40	11.39	7.56	11.75	11.75
HO	13.07	7.35	13.54	13.54	8.99	13.96	13.96
H2O	12.74	7.18	13.24	13.23	8.81	13.67	13.67
HF	16.2	9.59	16.80	16.80	11.51	17.30	17.30
H4Si	12.84	8.43	12.00	11.97	9.65	12.51	12.51
HP	10.18	5.89	9.31	9.31	7.02	9.78	9.78
H2P	9.82	5.78	9.22	9.20	6.89	9.63	9.63
H3P	10.61	6.59	10.06	10.05	7.67	10.46	10.46
HS	10.41	-	-	-	7.25	10.27	10.27
H2S(2B1)	10.48	6.15	9.92	9.91	7.31	10.33	10.32
HCl	12.82	7.90	12.17	12.17	9.22	12.64	12.64
H2C2	11.51	7.04	10.98	10.98	8.19	11.34	11.34
H4C2	10.74	6.61	10.31	10.31	7.66	10.62	10.62
CO	14.08	9.03	13.95	13.95	10.56	14.52	14.52
N2(2Sg)	15.61	10.26	14.51	14.51	11.97	15.38	15.38
O2	12.49	6.88	11.51	11.50	8.80	12.52	12.52
P2	10.82	6.88	9.67	9.67	7.82	10.05	10.05
S2	9.56	5.72	8.37	8.37	6.91	9.04	9.04
Cl2	11.77	7.29	10.13	10.13	8.59	10.87	10.87
FCl	12.95	7.87	11.53	11.53	9.34	12.35	12.35
CS	11.51	7.34	11.69	11.69	8.71	12.17	12.16
BF3	16.18	10.03	16.53	16.52	11.97	17.09	17.09
BCl3	11.91	7.57	11.64	11.64	8.88	12.11	12.10
CO2	13.9	8.99	12.56	12.56	10.46	13.32	13.32
CF2	12.4	7.35	11.59	11.59	8.82	12.26	12.26
COS	11.36	7.32	10.42	10.42	8.45	10.93	10.93
CS2	10.18	6.62	8.93	8.93	7.62	9.47	9.47
H2C	10.4	5.49	10.04	10.03	6.81	10.45	10.45
H3C	9.78	5.21	9.65	9.65	6.47	10.02	10.02
H5C2	8.6	4.43	8.41	8.41	5.66	8.82	8.81
CN	14.22	9.25	13.74	13.74	10.53	14.14	14.13
HCO	9.37	4.94	8.54	8.54	6.32	9.21	9.21
CH2OH	8.18	3.85	7.63	7.63	5.18	8.22	8.22
CH3O	10.94	6.03	10.94	10.93	7.59	11.37	11.37

Table 10 continued:

mol	ref	DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
H4CO	11.17	6.26	11.02	11.01	7.76	11.44	11.44
H3CF	13.47	8.04	12.35	12.34	9.66	12.78	12.77
H2CS	9.47	5.41	8.86	8.85	-	-	-
CH2SH	7.79	-	-	-	-	-	-
H3CCl	11.49	-	-	-	-	-	-
H6C2O	10.89	6.17	10.86	10.85	7.65	11.25	11.25
H4C2O	10.38	5.92	10.30	10.29	7.35	10.74	10.73
H3COF	11.68	6.62	10.92	10.91	8.32	11.64	11.63
H4C2S	9.15	5.23	8.75	8.75	-	-	-
C2N2	13.59	-	-	-	-	-	-
H4B2	10.17	6.22	9.86	9.85	7.29	10.18	10.18
HN	13.48	7.73	13.37	13.36	9.36	13.89	13.89
H2N	12.12	7.22	12.53	12.53	8.61	12.86	12.85
H2N2	10.28	5.64	9.25	9.24	7.03	9.92	9.92
H3N2	8.34	4.07	7.90	7.90	5.51	8.56	8.55
HOF	13.03	7.31	12.04	12.04	9.14	12.96	12.96
H2Si	9.55	5.76	8.77	8.77	6.73	9.16	9.15
H3Si	8.86	5.13	8.34	8.34	6.14	8.71	8.71
H2Si2	8.22	4.92	7.38	7.38	5.80	7.76	7.75
H4Si2	8.36	5.24	8.30	8.30	6.01	7.97	7.97
H5Si2	8.37	5.01	8.07	8.07	5.99	8.41	8.40
H6Si2	10.73	7.16	9.99	9.99	8.21	10.49	10.49
B2F4	13.3	8.39	11.55	11.52	9.93	12.47	12.46
H4C3(cyclo)	10.04	5.98	9.01	9.01	7.04	9.48	9.48
H4C3(allene)	10.31	6.42	9.89	9.89	7.51	10.28	10.27
H7C3	7.8	3.94	7.66	7.65	5.14	8.07	8.07
H4CS	9.55	-	-	-	-	-	-
H4C4O	9.09	5.53	8.25	8.25	6.51	8.66	8.66
H5C4N	8.42	5.01	7.88	7.88	5.96	8.19	8.18
	MAE	4.52	0.63	0.64	3.22	0.37	0.37

Table 11: Detailed data for the electron affinities (in eV) of the EA test set. Some data is not available because of the SCF convergence issue from DFT.

		BLYP			B3LYP		
mol	ref	DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
HC	1.19	5.16	0.66	0.66	4.15	0.73	0.73
H2C	0.83	3.60	−0.59	−0.59	2.69	−0.47	−0.46
H3C	−0.06	3.06	−0.84	−0.84	2.20	−0.73	−0.73
HN	0.33	4.50	−0.41	−0.41	3.30	−0.34	−0.34
H2N	0.75	4.62	−0.23	−0.24	3.45	−0.18	−0.18
HO	1.83	6.53	0.59	0.58	5.03	0.55	0.55
HSi	1.26	-	-	-	3.44	1.16	1.16

Table 11 continued:

mol	ref	DFA	post-LOSC2	SCF-LOSC2	DFA	post-LOSC2	SCF-LOSC2
H2Si	1.07	3.91	0.96	0.96	3.34	1.03	1.03
H3Si	0.93	3.59	0.57	0.56	3.01	0.62	0.62
HP	1.02	4.08	0.84	0.84	3.39	0.90	0.89
H2P	1.26	4.23	0.97	0.98	3.55	1.01	1.00
HS	2.36	-	-	-	4.97	2.07	2.07
O2	−0.02	4.59	0.16	0.16	3.53	0.09	0.09
NO	−0.35	4.24	−0.06	−0.06	3.27	−0.07	−0.07
CN	3.93	7.76	3.52	3.52	7.00	3.71	3.71
OP	1.09	-	-	-	-	-	-
S2	1.64	4.52	1.92	1.92	3.97	1.91	1.91
Cl2	1.16	4.57	1.66	1.66	3.89	1.59	1.59
C2	3.24	-	-	-	7.31	4.41	4.41
C2O	2.18	5.66	2.47	2.47	4.87	2.36	2.36
CF2	−0.28	3.68	−0.37	−0.37	2.85	−0.33	−0.33
CNO	3.55	7.20	3.75	3.75	6.32	3.63	3.63
NO2	1.53	5.18	1.70	1.70	4.46	1.70	1.70
O3	1.82	6.08	2.58	2.58	5.51	2.73	2.73
OF	1.94	6.60	1.40	1.40	5.41	1.27	1.26
O2S	1.06	4.57	1.72	1.72	4.03	1.75	1.75
OS2	1.88	4.83	2.32	2.32	4.43	2.50	2.50
HC2	2.95	6.50	1.79	1.78	5.61	2.18	2.18
H3C2	0.19	3.26	−0.58	−0.58	2.43	−0.53	−0.52
H2C3	1.7	4.89	2.11	2.10	4.24	2.05	2.05
H3C3	0.68	3.57	0.79	0.79	2.86	0.69	0.69
H5C3	0.38	3.20	0.55	0.54	2.46	0.39	0.39
HCO	−0.07	3.35	−0.17	−0.16	2.57	−0.15	−0.15
HCF	0.24	4.12	0.00	0.00	3.23	0.05	0.05
CH3O	1.43	5.33	0.48	0.47	4.12	0.34	0.34
H3CS	1.88	-	-	-	-	-	-
H2CS	0.31	3.50	0.61	0.60	-	-	-
CH2CN	1.54	4.68	1.63	1.62	3.92	1.56	1.56
CH2NC	0.99	4.11	1.03	1.03	3.31	0.92	0.92
HC2O	2.28	5.58	2.42	2.42	4.81	2.33	2.32
CH2CHO	1.71	4.92	1.86	1.85	4.08	1.70	1.70
CH3CO	0.16	2.95	−0.47	−0.45	2.20	−0.44	−0.39
H5C2O	1.57	5.20	0.40	0.40	4.05	0.30	0.31
H5C2S	1.95	4.96	1.43	1.42	4.19	1.43	1.43
HLi	0.31	1.72	−0.87	−0.62	1.41	−0.56	−0.43
HNO	−0.07	4.35	0.20	0.19	3.37	0.14	0.14
HO2	0.62	4.82	0.24	0.24	3.71	0.10	0.10
	MAE	3.47	0.48	0.47	2.67	0.45	0.44

2.5 Maleic Anhydride Photoemission Spectrum

Detailed data for the photoemission spectrum of maleic anhydride is shown in Table 12. The calculations were done using the cc-pVTZ basis set. LOSC2 expression for the curvature matrix is used for all the GSC data.

Table 12: Detailed data for the calculated maleic anhydride photoemission spectrums.

	PySCF			Psi4			QM4D		
orbital idex	B3LYP	post-LOSC2	GSC	B3LYP	post-LOSC2	GSC	B3LYP	post-LOSC2	GSC
9	−29.9596	−35.3469	−32.5339	−29.9595	−35.0442	−32.5338	−29.9596	−35.0443	−32.5339
10	−28.8943	−34.2425	−31.1914	−28.8944	−33.9189	−31.1915	−28.8944	−33.9189	−31.1915
11	−23.5409	−26.408	−26.7315	−23.5402	−26.7499	−26.7307	−23.5404	−26.7501	−26.7308
12	−19.4774	−21.8111	−21.6859	−19.4772	−21.7815	−21.6855	−19.4773	−21.7816	−21.6856
13	−17.7091	−20.1481	−19.8787	−17.709	−20.3885	−19.878	−17.7091	−20.3887	−19.8782
14	−16.7073	−18.7443	−18.9117	−16.7072	−19.0144	−18.9116	−16.7073	−19.0146	−18.9117
15	−14.505	−17.8058	−16.1869	−14.5046	−17.9429	−16.1861	−14.5048	−17.943	−16.1863
16	−14.1245	−17.1707	−16.3842	−14.1244	−16.7312	−16.3832	−14.1245	−16.7313	−16.3833
17	−13.5302	−16.7281	−14.9552	−13.53	−17.0378	−14.955	−13.5301	−17.0378	−14.955
18	−13.1498	−17.1344	−14.7096	−13.1496	−17.3195	−14.7091	−13.1497	−17.3196	−14.7092
19	−12.5666	−15.7323	−14.069	−12.5664	−16.0465	−14.0688	−12.5665	−16.0467	−14.0689
20	−11.9415	−15.3805	−13.872	−11.9414	−15.1345	−13.8705	−11.9415	−15.1349	−13.8705
21	−11.7123	−15.273	−14.6494	−11.7125	−15.2525	−14.649	−11.7124	−15.2525	−14.6491
22	−9.75473	−12.9103	−12.0462	−9.75495	−12.774	−12.0445	−9.75496	−12.7739	−12.0445
23	−9.33239	−11.9534	−11.2233	−9.33171	−12.0372	−11.2225	−9.33188	−12.0373	−11.2226
24	−9.2066	−13.6835	−10.9182	−9.20645	−13.0259	−10.9179	−9.20651	−13.026	−10.9179
25	−8.45411	−12.9352	−10.2718	−8.45413	−12.2697	−10.2719	−8.45417	−12.2698	−10.2719
26	−3.42258	−1.64852	−1.72846	−3.42258	−1.65754	−1.72974	−3.42255	−1.65722	−1.72969

2.6 Multi-minimum Problem Tests

To investigate the multi-minimum problem with the localization procedure, a series of tests, for which the localization procedure started from random U matrices, were performed with B3LYP/cc-pVTZ. The results are shown in Table 13. To investigate the influence of the multi-minimum problem on real calculations, for which the procedure starts with a unit U matrix, ten tests were done by each of three different computers. The results are shown in Table 14, Table 15, and Table 16. The convergence threshold of the Jacobi-Sweep algorithm is 10^{-10}.

Table 13: HOMO energies (in eV), LUMO energies (in eV), cost function ($F^{\alpha} - \langle r^2 \rangle$) values (in a.u.^{2}), relative cost function values (in a.u.^{2}) and total energies (in a.u.) from post-LOSC2 calculations with $\gamma = 0.707$ for the 4-unit polyacene molecule starting from random initial guesses. The calculations were done with `QM4D`.

test	$\varepsilon_{\mathrm{HOMO}}$	$\varepsilon_{\mathrm{LUMO}}$	$F^{\alpha} - \langle r^2 \rangle$	ΔF	E_{tot}
1	−7.1857557	−0.7739358	1104.8373100	0.0000000	−693.4080854
2	−7.1854673	−0.7686762	1105.2675100	0.4302000	−693.4080885
3	−7.1854509	−0.7684723	1105.9856900	1.1483800	−693.4080890
4	−7.1857672	−0.7736912	1106.3789700	1.5416600	−693.4080876
5	−7.1854497	−0.7684748	1105.9873500	1.1500400	−693.4080890
6	−7.1854469	−0.7684743	1104.9755100	0.1382000	−693.4080885
7	−7.1854507	−0.7684742	1106.3345100	1.4972000	−693.4080892
8	−7.1854471	−0.7684721	1105.9856900	1.1483800	−693.4080875
9	−7.1854735	−0.7685931	1106.5693400	1.7320300	−693.4080892
10	−7.1857680	−0.7738340	1106.3392000	1.5018900	−693.4080859
11	−7.1857680	−0.7738318	1106.2645000	1.4271900	−693.4080875
12	−7.1854516	−0.7684729	1105.1405300	0.3032200	−693.4080885
13	−7.1857671	−0.7736910	1104.5431000	−0.2942100	−693.4080868
14	−7.1857699	−0.7736920	1106.0300900	1.1927800	−693.4081046
15	−7.1857641	−0.7736912	1104.5432500	−0.2940600	−693.4080869
16	−7.1854480	−0.7684722	1104.5165000	−0.3208100	−693.4080868
17	−7.1854724	−0.7685941	1106.2203800	1.3830700	−693.4080875
18	−7.1854518	−0.7684729	1105.4378400	0.6005300	−693.4080869
19	−7.1854504	−0.7684720	1104.5165000	−0.3208100	−693.4080884
20	−7.1857681	−0.7736888	1106.0284300	1.1911200	−693.4080874
21	−7.1854743	−0.7685936	1106.2203797	1.3830697	−693.4080876
22	−7.1857668	−0.7736914	1106.3789684	1.5416584	−693.4080876
23	−7.1854737	−0.7685968	1106.5693353	1.7320253	−693.4080892
24	−7.1854509	−0.7684702	1106.0620404	1.2247304	−693.4080891
25	−7.1857678	−0.7736909	1106.1047769	1.2674669	−693.4080875
26	−7.1857690	−0.7736886	1106.1047218	1.2674118	−693.4080875
27	−7.1854747	−0.7685960	1104.7346826	−0.1026274	−693.4080885

Table 13 continued:

test	$\varepsilon_{\mathrm{HOMO}}$	$\varepsilon_{\mathrm{LUMO}}$	$F^{\alpha} - \langle r^2 \rangle$	ΔF	E_{tot}
28	−7.1854491	−0.7684723	1105.4378364	0.6005264	−693.4080869
29	−7.1857691	−0.7736885	1106.0300851	1.1927751	−693.4080874
30	−7.1854499	−0.7684754	1104.5005150	−0.3367950	−693.4080884
31	−7.1857679	−0.7736927	1106.3789703	1.5416603	−693.4080876
32	−7.1854516	−0.7684730	1105.5649831	0.7276731	−693.4080884
33	−7.1854483	−0.7684713	1104.5165009	−0.3208091	−693.4080884
34	−7.1857665	−0.7736904	1106.0300851	1.1927751	−693.4080874
35	−7.1854503	−0.7684755	1104.5003646	−0.3369454	−693.4080884
36	−7.1857687	−0.7738311	1105.7150504	0.8777404	−693.4080870
37	−7.1854494	−0.7684737	1104.5004976	−0.3368124	−693.4080869
38	−7.1857650	−0.7736903	1105.8936436	1.0563336	−693.4080869
39	−7.1857525	−0.7739354	1104.8380636	0.0007536	−693.4080870
40	−7.1857658	−0.7736900	1106.1047779	1.2674679	−693.4080876
41	−7.1857573	−0.7739347	1105.3127782	0.4754682	−693.4080854
42	−6.6749685	−0.7725987	1104.9162453	0.0789353	−693.4081098
43	−7.1854521	−0.7684729	1104.5005132	−0.3367968	−693.4080869
44	−7.1854490	−0.7684723	1105.0059094	0.1685994	−693.4080886
45	−7.1854490	−0.7684730	1106.3362332	1.4989232	−693.4080892
46	−7.1857687	−0.7736897	1106.0284275	1.1911175	−693.4080858
47	−7.1854491	−0.7684741	1104.5003820	−0.3369280	−693.4080884
48	−7.1854493	−0.7684747	1106.0620386	1.2247286	−693.4081061
49	−7.1854501	−0.7684730	1106.0620386	1.2247286	−693.4080875
50	−7.1863954	−0.7731759	1106.0896303	1.2523203	−693.4080848
51	−7.1854519	−0.7684724	1105.1404911	0.3031811	−693.4080868
52	−6.6717332	−0.7699059	1106.2469732	1.4096632	−693.4081007
53	−7.1854504	−0.7684723	1104.5180367	−0.3192733	−693.4080887
54	−7.1854510	−0.7684739	1104.5003820	−0.3369280	−693.4080884
55	−7.1857672	−0.7736892	1105.0182520	0.1809420	−693.4080853
56	−6.6749781	−0.7728017	1104.6946488	−0.1426612	−693.4081214
57	−7.1857643	−0.7736921	1104.5607771	−0.2765329	−693.4080869
58	−7.1857690	−0.7736891	1106.1030476	1.2657376	−693.4080875
59	−7.1854689	−0.7686781	1106.3535288	1.5162188	−693.4080876
60	−7.1854489	−0.7684721	1105.1405733	0.3032633	−693.4080869
61	−7.1857642	−0.7736881	1105.0471192	0.2098092	−693.4080869
62	−7.1854480	−0.7684694	1104.5003820	−0.3369280	−693.4080869
63	−7.1854498	−0.7684719	1104.9753165	0.1380065	−693.4080869
64	−7.1857667	−0.7736913	1106.3772489	1.5399389	−693.4080876
65	−7.1857677	−0.7736895	1106.0284292	1.1911192	−693.4080875
66	−7.1854520	−0.7684747	1106.0603084	1.2229984	−693.4080875
67	−7.1854500	−0.7684742	1105.0059075	0.1685975	−693.4080886
68	−7.1854490	−0.7684718	1104.9755106	0.1382006	−693.4080872
69	−7.1857658	−0.7736901	1105.1832327	0.3459227	−693.4080868
70	−7.1854489	−0.7684758	1104.5004995	−0.3368105	−693.4080868
71	−7.1857519	−0.7739360	1106.6726644	1.8353544	−693.4080877
72	−7.1854495	−0.7684738	1104.5165028	−0.3208072	−693.4080869
73	−7.1857688	−0.7736899	1104.5432548	−0.2940552	−693.4080868
74	−7.1854752	−0.7685963	1106.2949497	1.4576397	−693.4080892

Table 13 continued:

test	$\varepsilon_{\mathrm{HOMO}}$	$\varepsilon_{\mathrm{LUMO}}$	$F^{\alpha} - \langle r^2 \rangle$	ΔF	E_{tot}
75	−7.1854511	−0.7684736	1106.0619827	1.2246727	−693.4080891
76	−7.1857686	−0.7736900	1106.3772470	1.5399370	−693.4080991
77	−7.1854502	−0.7684735	1104.9753217	0.1380117	−693.4080869
78	−7.1863977	−0.7731752	1105.9548426	1.1175326	−693.4080843
79	−7.1854510	−0.7684711	1106.3362314	1.4989214	−693.4080876
80	−7.1857669	−0.7736907	1106.0300832	1.1927732	−693.4080874
81	−7.1854486	−0.7684732	1104.9755087	0.1381987	−693.4081055
82	−7.1854511	−0.7684699	1104.5003646	−0.3369454	−693.4080884
83	−7.1854725	−0.7685929	1104.7344772	−0.1028328	−693.4080885
84	−7.1854714	−0.7685944	1106.2203797	1.3830697	−693.4080891
85	−7.1854491	−0.7684737	1106.0602525	1.2229425	−693.4080875
86	−7.1857637	−0.7736893	1105.0486461	0.2113361	−693.4080869
87	−7.1854664	−0.7686787	1104.8096190	−0.0276910	−693.4080885
88	−7.1857650	−0.7736900	1104.5432529	−0.2940571	−693.4080869
89	−7.1863957	−0.7731750	1104.6044386	−0.2328714	−693.4080845
90	−6.6749684	−0.7725980	1105.9264261	1.0891161	−693.4081220
91	−7.1854476	−0.7684734	1104.9753217	0.1380117	−693.4080885
92	−7.1857693	−0.7738323	1105.8432899	1.0059799	−693.4080872
93	−7.1857707	−0.7736902	1104.5607752	−0.2765348	−693.4081039
94	−7.1857644	−0.7736918	1106.0300853	1.1927753	−693.4080874
95	−7.1854529	−0.7684737	1106.1210955	1.2837855	−693.4080890
96	−7.1854502	−0.7684721	1106.0602544	1.2229444	−693.4080890
97	−7.1854762	−0.7685911	1105.6710043	0.8336943	−693.4080870
98	−7.1854745	−0.7685953	1105.2093998	0.3720898	−693.4080870
99	−7.1857673	−0.7736903	1106.3772472	1.5399372	−693.4080876
100	−7.1854484	−0.7684744	1106.0603103	1.2230003	−693.4080875
101	−7.1854508	−0.7684728	1106.0603084	1.2229984	−693.4080875
102	−7.1854517	−0.7684752	1106.0602525	1.2229425	−693.4080875
103	−7.1857673	−0.7736893	1106.0300834	1.1927734	−693.4080874
104	−7.1854504	−0.7684748	1105.9873459	1.1500359	−693.4080874
105	−7.1854474	−0.7684734	1104.9753217	0.1380117	−693.4080885
106	−7.1857676	−0.7736900	1106.3789701	1.5416601	−693.4080876
107	−7.1854463	−0.7684720	1105.9856896	1.1483796	−693.4080874
108	−7.1857658	−0.7736883	1106.0284294	1.1911194	−693.4080874
109	−7.1857683	−0.7736917	1106.0300853	1.1927753	−693.4080874
110	−7.1854488	−0.7684763	1106.0603084	1.2229984	−693.4080875
111	−7.1857693	−0.7736887	1106.1047218	1.2674118	−693.4080875
112	−7.1854520	−0.7684725	1106.0603084	1.2229984	−693.4080890
113	−7.1854657	−0.7686776	1106.2788812	1.4415712	−693.4080890
114	−7.1857660	−0.7736903	1106.1030488	1.2657388	−693.4080875
115	−7.1854527	−0.7684706	1106.3345080	1.4971980	−693.4080875
116	−7.1857654	−0.7738353	1106.2645769	1.4272669	−693.4080875
117	−7.1854494	−0.7684734	1104.5180386	−0.3192714	−693.4080869
118	−7.1854516	−0.7684720	1106.0603103	1.2230003	−693.4080891
119	−7.1857636	−0.7736887	1105.0182502	0.1809402	−693.4080869
120	−7.1854702	−0.7686794	1106.3535288	1.5162188	−693.4080876
121	−7.1854721	−0.7686793	1106.3533769	1.5160669	−693.4080875

Table 13 continued:

test	$\varepsilon_{\mathrm{HOMO}}$	$\varepsilon_{\mathrm{LUMO}}$	$F^{\alpha} - \langle r^2 \rangle$	ΔF	E_{tot}
122	−7.1854503	−0.7684720	1105.9856896	1.1483796	−693.4080874
123	−7.1857654	−0.7738328	1106.2645769	1.4272669	−693.4080875
124	−6.6717309	−0.7699056	1105.9727755	1.1354655	−693.4081176
125	−6.6749701	−0.7725981	1104.9162508	0.0789408	−693.4081098
126	−7.1854500	−0.7684713	1105.0043245	0.1670145	−693.4080869
127	−7.1857682	−0.7736896	1104.5432510	−0.2940590	−693.4080868
128	−7.1857680	−0.7738319	1105.2831659	0.4458559	−693.4080869
129	−7.1857650	−0.7736924	1105.6077211	0.7704111	−693.4080869
130	−7.1864005	−0.7731745	1106.2250357	1.3877257	−693.4080847
131	−7.1857672	−0.7736884	1105.0471211	0.2098111	−693.4080869
132	−7.1857636	−0.7736889	1105.0180600	0.1807500	−693.4080869
133	−6.6717295	−0.7699048	1105.8998119	1.0625019	−693.4080991
134	−7.1857671	−0.7736889	1106.3789682	1.5416582	−693.4080876
135	−7.1857668	−0.7736894	1106.1047769	1.2674669	−693.4080875
136	−7.1857645	−0.7736903	1104.5607752	−0.2765348	−693.4080869
137	−7.1857649	−0.7736881	1106.3772491	1.5399391	−693.4080875
138	−7.1854464	−0.7684736	1105.9873460	1.1500360	−693.4080890
139	−7.1854487	−0.7684712	1106.0603084	1.2229984	−693.4080875
140	−6.6717658	−0.7700263	1104.6472231	−0.1900869	−693.4081001
141	−7.1854747	−0.7685950	1104.7340719	−0.1032381	−693.4080872
142	−7.1854509	−0.7684726	1106.0602544	1.2229444	−693.4080875
143	−7.1857713	−0.7736881	1105.0485916	0.2112816	−693.4080869
144	−7.1857658	−0.7736903	1106.1047779	1.2674679	−693.4080876
145	−7.1857685	−0.7736918	1104.5432529	−0.2940571	−693.4081039
146	−6.6749673	−0.7725988	1104.4411037	−0.3962063	−693.4081102
147	−7.1857666	−0.7736873	1105.1831924	0.3458824	−693.4081039
148	−7.1857661	−0.7736894	1106.1029927	1.2656827	−693.4080875
149	−7.1857643	−0.7736870	1104.5431182	−0.2941918	−693.4080868
150	−7.1857667	−0.7736892	1106.0300834	1.1927734	−693.4080875
151	−6.6733265	−0.7740915	1104.4178522	−0.4194578	−693.4081225
152	−7.1857677	−0.7736888	1106.1029938	1.2656838	−693.4080875
153	−7.1854746	−0.7685957	1106.2949497	1.4576397	−693.4080875
154	−7.1857674	−0.7736897	1104.5432547	−0.2940553	−693.4080856
155	−7.1857686	−0.7738344	1106.2645030	1.4271930	−693.4080859
156	−7.1857532	−0.7739339	1106.3237868	1.4864768	−693.4080859
157	−7.1854490	−0.7684718	1106.0602525	1.2229425	−693.4080875
158	−7.1854482	−0.7684750	1105.1405714	0.3032614	−693.4080885
159	−7.1857673	−0.7736901	1106.1047769	1.2674669	−693.4080875
160	−7.1854504	−0.7684762	1104.5005150	−0.3367950	−693.4080885
161	−6.6733290	−0.7740917	1104.8929848	0.0556748	−693.4081039
162	−7.1854499	−0.7684720	1104.5005131	−0.3367969	−693.4080869
163	−7.1854720	−0.7685944	1105.2093998	0.3720898	−693.4080869
164	−7.1857517	−0.7739354	1106.3237103	1.4864003	−693.4080875
165	−7.1854516	−0.7684731	1104.5165028	−0.3208072	−693.4080885
166	−7.1857677	−0.7736872	1106.3772491	1.5399391	−693.4080860
167	−7.1863970	−0.7731760	1106.0896303	1.2523203	−693.4080848
168	−7.1854522	−0.7684745	1105.9856896	1.1483796	−693.4080891

Table 13 continued:

test	$\varepsilon_{\mathrm{HOMO}}$	$\varepsilon_{\mathrm{LUMO}}$	$F^{\alpha} - \langle r^2 \rangle$	ΔF	E_{tot}
169	−7.1854722	−0.7685953	1106.2949497	1.4576397	−693.4080875
170	−7.1857542	−0.7739368	1106.3984548	1.5611448	−693.4080875
171	−7.1857525	−0.7739345	1104.8545222	0.0172122	−693.4080869
172	−7.1857652	−0.7736884	1106.1047218	1.2674118	−693.4080875
173	−7.1854741	−0.7685947	1106.2204521	1.3831421	−693.4080891
174	−7.1854710	−0.7686779	1105.2681421	0.4308321	−693.4080889
175	−7.1857655	−0.7736887	1104.5592416	−0.2780684	−693.4080869
176	−7.1863983	−0.7731773	1106.0896303	1.2523203	−693.4080848
177	−7.1854499	−0.7684720	1104.5165009	−0.3208091	−693.4080871
178	−7.1854516	−0.7684733	1106.0619846	1.2246746	−693.4080891
179	−7.1854516	−0.7684735	1105.0058533	0.1685433	−693.4080885
180	−7.1857664	−0.7736883	1105.0471210	0.2098110	−693.4080873
181	−7.1857670	−0.7736888	1106.0284294	1.1911194	−693.4080859
182	−7.1854738	−0.7685964	1106.2949497	1.4576397	−693.4080875
183	−7.1857667	−0.7736896	1104.5592418	−0.2780682	−693.4080869
184	−6.6733268	−0.7740926	1104.9217954	0.0844854	−693.4081171
185	−7.1857680	−0.7736890	1106.3772489	1.5399389	−693.4080860
186	−7.1854508	−0.7684726	1104.5003801	−0.3369299	−693.4080885
187	−7.1854488	−0.7684745	1105.9873478	1.1500378	−693.4081007
188	−7.1854485	−0.7684753	1106.0620404	1.2247304	−693.4080891
189	−7.1854489	−0.7684740	1105.9856877	1.1483777	−693.4080874
190	−7.1857670	−0.7736913	1106.0284275	1.1911175	−693.4080874
191	−7.1857514	−0.7739370	1106.3984138	1.5611038	−693.4080876
192	−7.1854515	−0.7684712	1106.3362332	1.4989232	−693.4080876
193	−7.1857552	−0.7739378	1104.8373081	−0.0000019	−693.4080869
194	−7.1854501	−0.7684725	1106.0602544	1.2229444	−693.4080875
195	−7.1854496	−0.7684715	1104.5003646	−0.3369454	−693.4080868
196	−7.1854509	−0.7684753	1104.5003820	−0.3369280	−693.4080884
197	−7.1854485	−0.7684701	1104.5003646	−0.3369454	−693.4080885
198	−7.1854508	−0.7684747	1105.0059094	0.1685994	−693.4080869
199	−7.1857655	−0.7736917	1106.3789701	1.5416601	−693.4080876
200	−7.1854730	−0.7685948	1104.7511153	−0.0861947	−693.4080885

Table 14: HOMO energies (in eV), LUMO energies (in eV), cost function ($F^{\alpha} - \langle r^2 \rangle$) values (in a.u.^{2}), and total energies (in a.u.) from post-LOSC2 calculations with $\gamma = 0.707$ for the 4-unit polyacene molecule starting from a unit U matrix. The calculations were done with `QM4D` by computer #1 (Model: Intel(R) Xeon(R) CPU E5-2630 v3 @ 2.40GHz).

test	$\varepsilon_{\mathrm{HOMO}}$	$\varepsilon_{\mathrm{LUMO}}$	$F^{\alpha} - \langle r^2 \rangle$	E_{tot}
1	−6.67175387	−0.76991913	1104.428322	−693.4081215
2	−6.67175387	−0.76991913	1104.428322	−693.4081215
3	−6.67175387	−0.76991913	1104.428322	−693.4081215
4	−6.67175387	−0.76991913	1104.428322	−693.4081215

Table 14 continued:

test	$\varepsilon_{\mathrm{HOMO}}$	$\varepsilon_{\mathrm{LUMO}}$	$F^{\alpha} - \langle r^2 \rangle$	E_{tot}
5	−6.67175387	−0.76991913	1104.428322	−693.4081215
6	−6.67175387	−0.76991913	1104.428322	−693.4081215
7	−6.67175387	−0.76991913	1104.428322	−693.4081215
8	−6.67175387	−0.76991913	1104.428322	−693.4081215
9	−6.67175387	−0.76991913	1104.428322	−693.4081215
10	−6.67175387	−0.76991913	1104.428322	−693.4081215

Table 15: HOMO energies (in eV), LUMO energies (in eV), cost function ($F^{\alpha} - \langle r^2 \rangle$) values (in a.u.^{2}), and total energies (in a.u.) from post-LOSC2 calculations with $\gamma = 0.707$ for the 4-unit polyacene molecule starting from a unit U matrix. The calculations were done with `QM4D` by computer #2 (Model: Intel(R) Xeon(R) CPU E5-2630 v4 @ 2.20GHz).

test	$\varepsilon_{\mathrm{HOMO}}$	$\varepsilon_{\mathrm{LUMO}}$	$F^{\alpha} - \langle r^2 \rangle$	E_{tot}
1	−6.67175387	−0.76991913	1104.428322	−693.4081215
2	−6.67175387	−0.76991913	1104.428322	−693.4081215
3	−6.67175387	−0.76991913	1104.428322	−693.4081215
4	−6.67175387	−0.76991913	1104.428322	−693.4081215
5	−6.67175387	−0.76991913	1104.428322	−693.4081215
6	−6.67175387	−0.76991913	1104.428322	−693.4081215
7	−6.67175387	−0.76991913	1104.428322	−693.4081215
8	−6.67175387	−0.76991913	1104.428322	−693.4081215
9	−6.67175387	−0.76991913	1104.428322	−693.4081215
10	−6.67175387	−0.76991913	1104.428322	−693.4081215

Table 16: HOMO energies (in eV), LUMO energies (in eV), cost function ($F^{\alpha} - \langle r^2 \rangle$) values (in a.u.^{2}), and total energies (in a.u.) from post-LOSC2 calculations with $\gamma = 0.707$ for the 4-unit polyacene molecule starting from a unit U matrix. The calculations were done with `QM4D` by computer #3 (Model: Intel(R) Xeon(R) Gold 6226R CPU @ 2.90GHz).

test	$\varepsilon_{\mathrm{HOMO}}$	$\varepsilon_{\mathrm{LUMO}}$	$F^{\alpha} - \langle r^2 \rangle$	E_{tot}
1	-6.67173081	-0.76990552	1104.428966	-693.4080984
2	-6.67173081	-0.76990552	1104.428966	-693.4080984
3	-6.67173081	-0.76990552	1104.428966	-693.4080984
4	-6.67173081	-0.76990552	1104.428966	-693.4080984
5	-6.67173081	-0.76990552	1104.428966	-693.4080984
6	-6.67173081	-0.76990552	1104.428966	-693.4080984
7	-6.67173081	-0.76990552	1104.428966	-693.4080984
8	-6.67173081	-0.76990552	1104.428966	-693.4080984

Table 16 continued:

test	$\varepsilon_{\mathrm{HOMO}}$	$\varepsilon_{\mathrm{LUMO}}$	$F^{\alpha} - \langle r^2 \rangle$	E_{tot}
9	-6.67173081	-0.76990552	1104.428966	-693.4080984
10	-6.67173081	-0.76990552	1104.428966	-693.4080984

References

(1) Su, N. Q.; Mahler, A.; Yang, W. Preserving Symmetry and Degeneracy in the Localized Orbital Scaling Correction Approach. *J. Phys. Chem. Lett.* **2020**, *11*, 1528–1535.

(2) An in-house program for QM/MM simulations; available from `https://qm4d.org/`.

(3) Mei, Y.; Chen, Z.; Yang, W. Self-Consistent Calculation of the Localized Orbital Scaling Correction for Correct Electron Densities and Energy-Level Alignments in Density Functional Theory. *J. Phys. Chem. Lett.* **2020**, *11*, 10269–10277.

(4) Mei, Y.; Li, C.; Su, N. Q.; Yang, W. Approximating Quasiparticle and Excitation Energies from Ground State Generalized Kohn-Sham Calculations. **2019**,

(5) Zheng, X.; Cohen, A. J.; Mori-Sánchez, P.; Hu, X.; Yang, W. Improving Band Gap Prediction in Density Functional Theory from Molecules to Solids. *Phys. Rev. Lett.* **2011**, *107*, 026403.

(6) Li, C.; Zheng, X.; Su, N. Q.; Yang, W. Localized Orbital Scaling Correction for Systematic Elimination of Delocalization Error in Density Functional Approximations. *Natl. Sci. Rev.* **2018**, *5*, 203–215.