Supporting information to "Boosting the OEP2-sc method with spin-component scaling."

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Contents

1 The OS and SS proportionalities

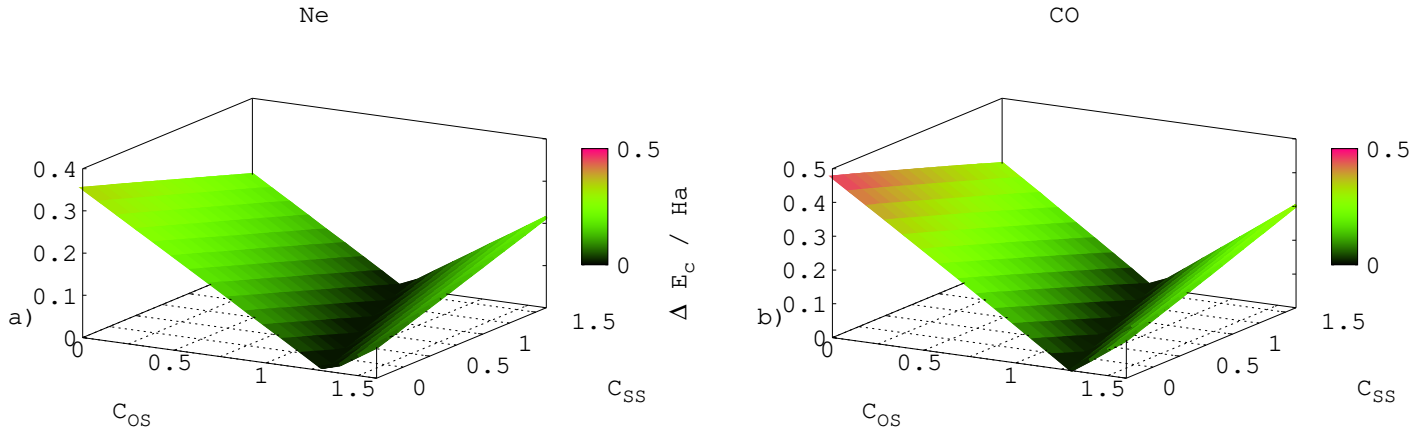

Figure S1: The value of error on the correlation energy as a function of the c_{OS} and c_{SS} parameters ($\Delta E_{\mathrm{c}}(c_{OS}, c_{SS}) = \left| E_{\mathrm{c}}^{\text{OEP2-SCS-sc}}(c_{OS}, c_{SS}) - E_{\mathrm{c}}^{\mathrm{CCSD(T)}} \right|$), for two representative systems. The calculations have been performed using fully uncontracted ROOS-ATZ and cc-pVTZ basis sets for Ne and CO, respectively. The CCSD(T) results have been obtained using the same computational setup.

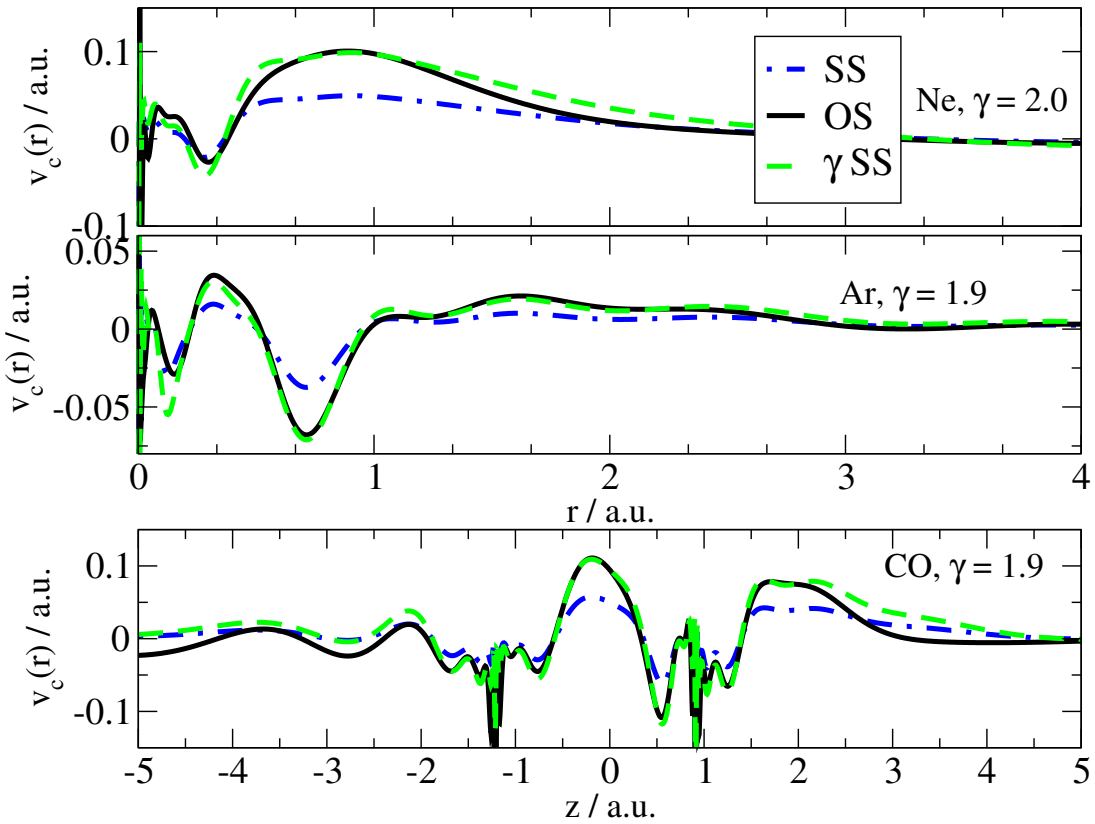

Figure S2: The OS and SS parts of correlation potentials for Ne (top, uncontracted ROOS-ATZ), Ar (middle, ROOS-ATZPU-MOD-CC-PWCVQZ), and CO (bottom, plot along the molecular axis, uncontracted cc-pVTZ) obtained from self-consisted OEP2-sc calculations. On each plot, the rescaled SS part of the potential is reported together with rescaling γ coefficient.

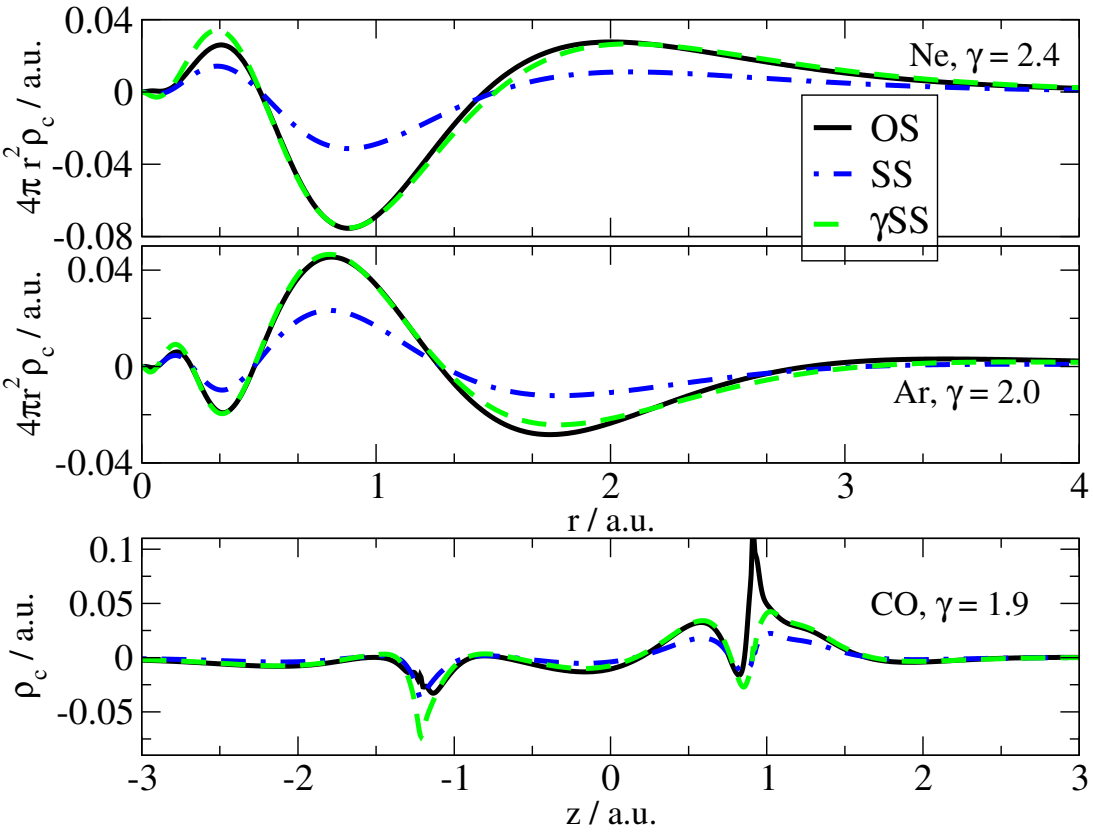

Figure S3: The OS and SS parts of correlated density ($\rho_c = \rho^{method} - \rho^{\mathrm{X}}$, X = OEPx) for Ne (top, uncontracted ROOS-ATZ), Ar (middle, ROOS-ATZPU-MOD-CC-PWCVQZ), and CO (bottom, plot along the molecular axis, uncontracted cc-pVTZ) obtained from self-consisted OEP2-SCS-sc calculations. On each plot, the rescaled SS part of the correlated density is reported together with rescaling γ coefficient.

2 The c_{OS} coefficient

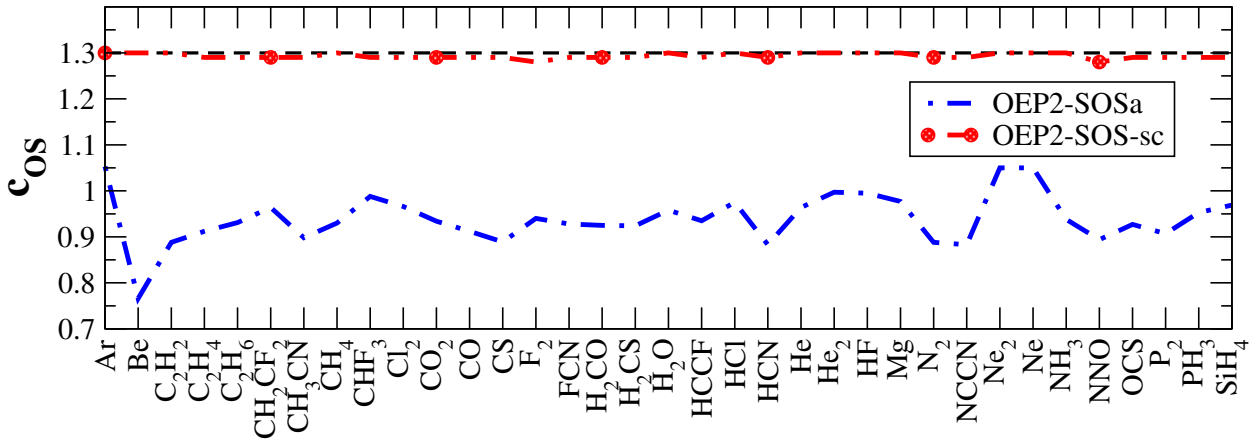

Figure S4: The c_{OS} coefficient values calculated via Eq.(8) for OEP2-SOS and OEP2-SOS-sc methods for several systems. The black dashed horizontal line denotes $c_{\mathrm{OS}} = 1.3$.

3 The correlation potentials and densities of N_2

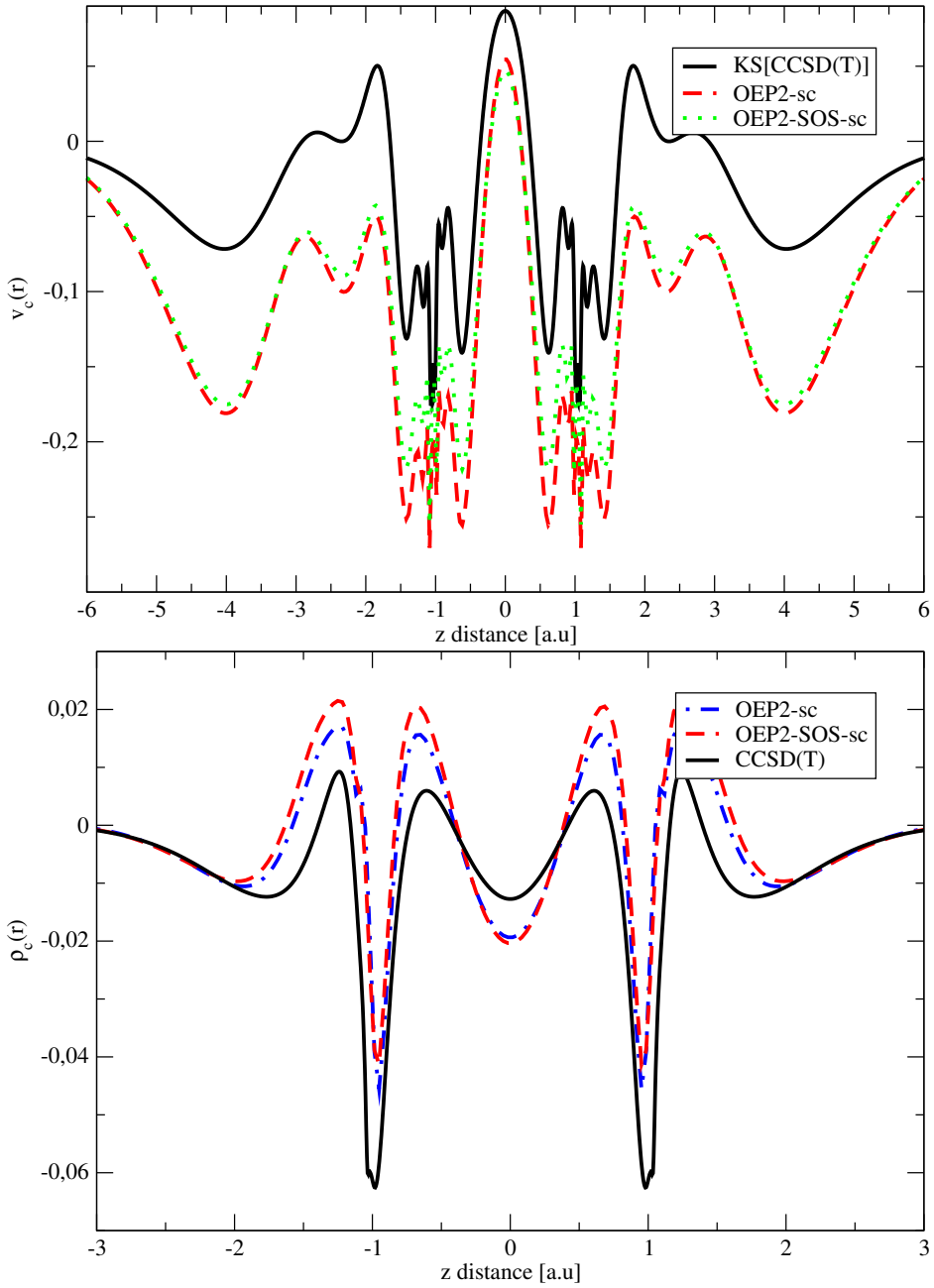

Figure S5. Correlated potentials (top) and densities (bottom) of N_2 molecule obtained from various methods.

4 Correlation energies

Table S1: Correlation energy (in Ha) used to generate the data reported on Fig. 3. All calculation have been performed in uncontracted cc-pVTZ (cc-pVTZU) basis set. Errors calculated with respect to CCSD(T)/cc-pVTZU data.

	CCSD(T)	CCSD	MP2	SOS-MP2	OEP2-sc	OEP2-SOS-sc
He	-0.039660	-0.039660	-0.033722	-0.043839	-0.033759	-0.043902
Li	-0.037664	-0.037640	-0.032766	-0.041935	-0.033113	-0.042044
Be	-0.086245	-0.085811	-0.066051	-0.084157	-0.067314	-0.085160
B	-0.109096	-0.107408	-0.084970	-0.103328	-0.087452	-0.105066
C	-0.135090	-0.132711	-0.111021	-0.123306	-0.113715	-0.124818
N	-0.162907	-0.160316	-0.143243	-0.141675	-0.145089	-0.142452
O	-0.214710	-0.211429	-0.194242	-0.198121	-0.197836	-0.200055
F	-0.271139	-0.267139	-0.254910	-0.257903	-0.259624	-0.260404
Ne	-0.330714	-0.326025	-0.323416	-0.318018	-0.328523	-0.320849
BeH	-0.084363	-0.083700	-0.070275	-0.087580	-0.071935	-0.088573
OH	-0.271866	-0.266249	-0.251585	-0.257657	-0.258501	-0.262007
NH_2	-0.258278	-0.252097	-0.233404	-0.244464	-0.240494	-0.249049
NH	-0.209239	-0.205023	-0.184706	-0.191331	-0.190263	-0.195473
NO	-0.523898	-0.504193	-0.495963	-0.494126	-0.535165	-0.522021
PH_2	-0.341964	-0.335084	-0.308711	-0.315825	-0.321864	-0.322342
O_2	-0.560216	-0.541146	-0.538007	-0.518530	-0.577888	-0.543257
S_2	-0.701416	-0.679118	-0.655289	-0.633016	-0.689624	-0.650820
SiH_2	-0.288381	-0.283985	-0.261218	-0.265914	-0.272959	-0.272261
C_2H_5	-0.470713	-0.457726	-0.422178	-0.448401	-0.438171	-0.456770
CH_2	-0.187226	-0.229277	-0.162452	-0.171284	-0.167273	-0.175187
CH_3	-0.231320	-0.226181	-0.203690	-0.220378	-0.209144	-0.223763
CN	-0.428080	-0.408354	-0.368123	-0.366998	-0.467363	-0.459466
COH	-0.492578	-0.474406	-0.464970	-0.468730	-0.496161	-0.490255
CH_4	-0.273230	-0.266482	-0.244444	-0.264838	-0.251094	-0.267735
LiF	-0.379001	-0.370466	-0.368097	-0.370573	-0.383314	-0.380364
Li_2	-0.107293	-0.106789	-0.087716	-0.112372	-0.089084	-0.113155
F_2	-0.654028	-0.635331	-0.630457	-0.628267	-0.664311	-0.652652
CO	-0.476203	-0.458068	-0.452759	-0.457203	-0.480533	-0.475813
CH_2	-0.216482	-0.211151	-0.184017	-0.207590	-0.189700	-0.210798
H_2	-0.039681	-0.039681	-0.031980	-0.041574	-0.032188	-0.041928
CS	-0.558780	-0.535316	-0.519899	-0.518272	-0.556076	-0.540868
LiH	-0.073802	-0.073685	-0.060677	-0.077983	-0.061393	-0.078567
N_2	-0.491774	-0.471984	-0.471751	-0.474469	-0.496969	-0.491525
P_2	-0.660820	-0.635773	-0.621909	-0.610861	-0.653345	-0.628142
NaCl	-0.579755	-0.568599	-0.553435	-0.543280	-0.569281	-0.549924
H_2O	-0.329409	-0.321085	-0.314495	-0.317191	-0.323122	-0.322531
MAE [mHa]		9.78	24.18	19.49	14.44	11.22
MARE		2.71%	10.42%	6.30%	7.90%	4.46%

5 Total energies

Table S2: Total energies (in Ha). All calculation have been performed in cc-pVTZU basis set. Errors calculated with respect to CCSD(T)/cc-pVTZU data.

	CCSD(T)	CCSD	MP2	SOS-MP2	OEP2-sc	OEP2-SOS-sc
He	-2.900813	-2.900813	-2.894876	-2.904992	-2.896974	-2.905009
Li	-7.470373	-7.470349	-7.465474	-7.474644	-7.465506	-7.474428
Be	-14.659124	-14.658690	-14.638931	-14.657036	-14.642692	-14.656827
B	-24.641216	-24.639528	-24.617090	-24.635449	-24.617688	-24.635089
C	-37.826786	-37.824408	-37.802717	-37.815003	-37.803308	-37.814274
N	-54.563846	-54.561255	-54.544182	-54.542615	-54.544543	-54.541914
O	-75.026667	-75.023386	-75.006199	-75.010079	-75.007006	-75.009280
F	-99.676827	-99.672827	-99.660599	-99.663591	-99.661575	-99.662597
Ne	-128.862745	-128.858055	-128.855447	-128.850049	-128.894009	-128.849238
BeH	-15.237263	-15.236600	-15.223176	-15.240481	-15.223453	-15.239944
OH	-75.691313	-75.685696	-75.671032	-75.677103	-75.672907	-75.676561
NH_2	-55.844388	-55.838207	-55.819514	-55.830574	-55.821560	-55.830097
NH	-55.190655	-55.186439	-55.166121	-55.172747	-55.167780	-55.172698
NO	-129.821453	-129.801748	-129.793518	-129.791681	-129.810395	-129.799719
PH_2	-342.229195	-342.222315	-342.195943	-342.203056	-342.199724	-342.200059
O_2	-150.236779	-150.217709	-150.214570	-150.195093	-150.229971	-150.200380
S_2	-795.798003	-795.775705	-795.751875	-795.729603	-795.764473	-795.727447
SiH_2	-290.312473	-290.308077	-290.285310	-290.290007	-290.288379	-290.287323
C_2H_5	-79.099141	-79.086154	-79.050606	-79.076829	-79.055447	-79.074535
CH_2	-39.125140	-39.121398	-39.100367	-39.109199	-39.101766	-39.109227
CH_3	-39.809085	-39.803946	-39.781455	-39.798143	-39.782938	-39.797441
CN	-92.664132	-92.644407	-92.604175	-92.603051	-92.657614	-92.652596
COH	-113.785974	-113.767802	-113.758367	-113.762126	-113.769085	-113.765378
CH_4	-40.486839	-40.480090	-40.458052	-40.478447	-40.459893	-40.476872
LiF	-107.360825	-107.352290	-107.349921	-107.352397	-107.353496	-107.352937
Li_2	-14.978999	-14.978495	-14.959422	-14.984078	-14.959644	-14.983603
F_2	-199.410039	-199.391342	-199.386468	-199.384278	-199.398597	-199.387386
CO	-113.257426	-113.239291	-113.233982	-113.238426	-113.137299	-113.240488
CH_2	-39.108603	-39.103272	-39.076138	-39.099711	-39.077491	-39.098381
H_2	-1.172743	-1.172743	-1.165041	-1.174636	-1.165110	-1.174752
CS	-435.912069	-435.888604	-435.873188	-435.871560	-435.886328	-435.872679
LiH	-8.060790	-8.060673	-8.047665	-8.064971	-8.047790	-8.064826
N_2	-109.476293	-109.456504	-109.456270	-109.458989	-109.464758	-109.460792
P_2	-682.150961	-682.125913	-682.112049	-682.101002	-682.122054	-682.097814
NaCl	-622.033824	-622.022667	-622.007504	-621.997348	-622.010959	-621.992567
H_2O	-76.386895	-76.378571	-76.371981	-76.374678	-76.374266	-76.374241
MAE [mHa]		8.71	24.18	19.49	22.10	18.15
MARE		0.008%	0.067%	0.03%	0.062%	0.029%

6 Atomization energies

Table S3: Atomization energies (in kcal/mol) for various methods. Errors calculated with respect to CCSD(T)/cc-pVTZU data.

	CCSD(T)	CCSD	MP2	SOS-MP2	OEP2-sc	OEP2-SOS-sc
BeH	-49.15	-49.01	-52.98	-52.48	-53.01	-52.28
OH	-103.44	-101.97	-103.55	-104.93	-104.22	-105.09
NH_2	-176.28	-174.03	-173.01	-180.94	-174.07	-181.08
NH	-79.69	-78.67	-76.64	-81.78	-77.45	-82.19
NO	-144.92	-136.24	-152.57	-149.97	-162.43	-155.95
PH_2	-149.07	-147.88	-142.01	-151.2	-143.65	-151.43
O_2	-115.11	-107.26	-126.86	-109.77	-135.52	-114.09
S_2	-94.41	-87.66	-100.09	-91.01	-105.18	-93.02
SiH_2	-129.98	-129.62	-126.63	-128.45	-127.48	-128.61
C_2H_5	-593.95	-588.78	-593.7	-594.74	-596	-594.21
CH_2	-187.46	-186.6	-187.02	-184.85	-187.52	-185.32
CH_3	-303	-301.27	-300.77	-303.53	-301.33	-303.55
CN	-171.62	-162.36	-161.44	-154.01	-194.38	-186
COH	-271.53	-263.68	-282.15	-274.37	-288	-277.37
CH_4	-414.67	-411.92	-411.71	-416.79	-412.49	-416.26
LiF	-134.05	-131.22	-140.47	-134.39	-142.08	-135.49
Li_2	-24	-23.72	-17.87	-21.83	-17.97	-21.8
F_2	-35.38	-28.67	-40.96	-35.83	-47.34	-39.03
CO	-253.5	-245.67	-266.73	-259.38	-271.54	-261.63
CH_2	-177.08	-175.23	-171.81	-178.9	-170.61	-178.52
H_2	-108.64	-108.64	-103.8	-109.82	-103.85	-109.9
CS	-164.1	-154.49	-172.12	-165.84	-178.58	-168.67
LiH	-56.86	-56.8	-51.69	-56.8	-51.75	-56.85
N_2	-218.75	-209.58	-230.86	-234.54	-235.74	-236.55
P_2	-104.75	-95.28	-107.94	-110.46	-112.76	-112.68
NaCl	-93.3	-91.5	-96.27	-93.07	-96.1	-92.78
H_2O	-226.28	-223.12	-229.77	-229.03	-230.7	-229.25
MAE		4.08	5.51	3.47	8.07	3.92
MARE		3.15%	5.19%	2.65%	7.35%	3.14%

7 Reactions

Table S4: Close-shell reaction energies (in kcal/mol) for various methods.
Errors calculated with respect to CCSD(T)/cc-pVTZU data.

	CCSD(T)	CCSD	MP2	SOS-MP2	OEP2-sc	OEP2-SOS-sc
$F_2O+H_2 \rightarrow F_2+H_2O$	-66.83	-69.5	-70.1	-67.81	-62.78	-66.51
$H2O2+H2 \rightarrow 2H_2O$	-84.27	-86.23	-88.41	-84.18	-85.31	-83.02
$CO+H_2 \rightarrow CH_2O$	-3.55	-3.82	-4	-1.69	-3.51	-0.64
$CO+3H_2 \rightarrow CH_4+H_2O$	-61.55	-63.47	-63.33	-56.97	-60.11	-54.2
$N_2+3H_2 \rightarrow 2NH_3$	-34.7	-36.73	-34.22	-27.54	-31.3	-25.06
$N_2O+H_2 \rightarrow N_2+H_2O$	-79.86	-85.65	-75.13	-80	-65.2	-74.7
$HNO_2+3H_2 \rightarrow 2H_2O+NH_3$	-117.82	-123.88	-121.89	-116.99	-108.26	-110.95
$C_2H_2+H_2 \rightarrow C_2H_4$	-49.62	-50.46	-47.55	-47.05	-47.29	-45.91
CH_2-$CO+2H_2 \rightarrow CH_2O+CH_4$	-42.64	-44.86	-40.51	-42.41	-37.57	-40.52
$BH_3+3HF \rightarrow BF_3+3H_2$	-98.1	-96.3	-99.17	-97.07	-102.65	-98.23
$HCOOH \rightarrow CO_2+H_2$	1.17	2.57	-1.4	-2.09	-3.19	-4.22
$CO+H_2O \rightarrow CO_2+H_2$	-7.67	-5.24	-11.7	-8.28	-16.35	-10.47
$C_2H_2+HF \rightarrow CH_2CHF$	-28.48	-28.48	-25.51	-25.96	-27.47	-25.17
$HCN+H_2O \rightarrow CO+NH_3$	-13.37	-13.92	-10.46	-12.58	-11.27	-12.75
$HCN+H_2O \rightarrow HCONH_2$	-21.73	-21.48	-21.12	-18.21	-23.89	-18.18
$HCONH_2+H_2O \rightarrow HCOOH+NH_3$	-0.49	-0.25	0.35	-0.55	-0.54	-0.83
$HCN+NH_3 \rightarrow N_2+CH_4$	-40.22	-40.66	-39.57	-42.01	-40.07	-41.89
$CO+CH_4 \rightarrow CH_3CHO$	4.56	5.1	3.3	7.14	2.62	8.25
$N_2+F_2 \rightarrow$trans-N_2F_2	17.32	19.95	18.62	24.42	11.03	24.41
$N_2+F_2 \rightarrow$cis-N_2F_2	18.83	20.86	20.3	25.35	16.19	24.41
$2BH_3 \rightarrow B_2H_6$	-43.09	-40.37	-44.58	-36.81	-46.07	-36.32
$CH_3ONO \rightarrow CH_3NO_2$	-0.89	-0.27	-5.61	-2.89	-1.7	-2.72
$CH_2{=}C \rightarrow C_2H_2$	-44.28	-43.01	-51.94	-47.01	-49.9	-47.46
Allene→Propyne	-1.1	-1.42	-4.43	-3.57	-3.43	-3.37
Cyclopropene→Propyne	-23.38	-23.77	-23.68	-24.79	-23.99	-24.75
Oxirane→CH_3CHO	-26.73	-26.86	-25.75	-27.04	-26.63	-27.35
Vinlyalcohol→CH_3CHO	-9.79	-9.99	-10	-11.35	-10.8	-11.38
Cyclobutene→1,3-butadiene	-15.48	-11.5	-11.24	-9.41	-11.3	-9.81
$2NH_3 \rightarrow (NH_3)_2$	-3.84	-3.55	-4	-3.27	-4.25	-3.08
$2H_2O \rightarrow (H_2O)_2$	-5.67	-5.32	-5.84	-5.02	-6.26	-4.87
$2HF \rightarrow (HF)_2$	-4.19	-3.78	-4.22	-3.42	-4.81	-3.13
MAE		1.39	2.06	2.17	2.98	3.03
MARE		13.70%	46.93%	35.24%	34.53%	45.77%

Table S6: Open-shell reaction energies (in kcal/mol) for various methods.
Errors calculated with respect to the CCSD(T)/cc-pVTZU data.

	CCSD(T)	CCSD	MP2	SOS-MP2	OEP2-sc	OEP2-SOS-sc
$HCl+H \rightarrow Cl+H_2$	4.13	5.57	-1.17	5.28	-1.17	5.67
$CH_4+OH \rightarrow CH_3+H_2O$	11.19	10.5	15.28	10.84	15.31	11.45
$OH+H_2 \rightarrow H_2O+H$	14.21	12.51	22.41	14.28	22.63	14.27
$CO+OH \rightarrow CO_2+H$	21.89	17.76	34.12	22.55	38.98	24.74
$CH_3+Cl_2 \rightarrow CH_3Cl+Cl$	31.32	32.33	31.85	32.8	30.75	32.49
$S+2HCl \rightarrow H_2S+Cl_2$	22.54	18.87	23.43	23.4	26.05	22.75
$2NO+O_2 \rightarrow 2NO_2$	24.51	13.47	41.49	34.5	51.82	39.2
$N+O_2 \rightarrow NO+O$	29.8	28.97	25.71	40.19	26.91	41.86
$4HCl+O_2 \rightarrow 2H_2O+2Cl_2$	25.73	24.32	28.07	35.67	25.25	31.86
$NO+H_2O_2 \rightarrow NO_2+H_2O$	36.43	32.11	46.62	37.12	52.13	40.31
$2NO \rightarrow N_2+O_2$	44.03	44.38	52.59	44.38	46.4	38.74
$2H_2O_2 \rightarrow 2H_2O+O_2$	48.36	50.75	51.74	39.73	52.44	41.42
$Cl_2+H \rightarrow HCl+Cl$	51.36	54.26	47.33	51.76	45.3	52.06
$2SO_2+O_2 \rightarrow 2SO_3$	35.68	34.87	44.58	45.91	42.25	42.54
$Cl+OH \rightarrow HOCl$	54.45	49.48	60.84	55.21	64.3	55.88
$H_2S+F_2 \rightarrow S+2HF$	61.25	66.47	66.52	60.71	60.81	58.99
$4NO_2+O_2+2H_2O \rightarrow 4HNO_3$	53.51	51	60.07	68.08	50.02	51.38
$2NH_2 \rightarrow N_2H_4$	70.78	67.43	78.08	72.65	79	71.95
$NO+N \rightarrow O+N_2$	73.83	73.35	78.29	84.57	73.31	80.6
$O+2HCl \rightarrow H_2O+Cl_2$	70.42	65.79	77.47	72.72	80.39	72.97
$2SiH_3 \rightarrow Si_2H_6$	76.97	75.37	77.02	78.1	77.61	76.88
$CH_3+SH \rightarrow CH_3SH$	76.72	73.57	81.14	78.1	82.15	77.03
$SO_2+O \rightarrow SO_3$	75.4	71.07	85.72	77.84	88.88	78.32
$CS+O \rightarrow CO+S$	89.4	91.18	94.62	93.54	92.98	92.96
$CH_3+Cl \rightarrow CH_3Cl$	84.47	81.14	89.49	85.59	90.46	84.65
$CH_3OH+O \rightarrow HCHO+H_2O$	37.66	33.94	41.41	39.2	44.45	40.99
$CH_3+OH \rightarrow CH_3OH$	96.18	92.91	102.95	98.43	104.37	97.9
$NH+H \rightarrow NH_2$	96.59	95.36	96.37	99.16	96.62	98.89
$Si+2H_2 \rightarrow SiH_4$	101.49	100.64	102.58	103.24	103.41	101.69
$2C_2H_4+O_2 \rightarrow 2CH_3CHO$	104.35	104.07	110.31	115.43	109.71	112.5

Table S4: Continued

	CCSD(T)	CCSD	MP2	SOS-MP2	OEP2-sc	OEP2-SOS-sc
$CS+S \rightarrow CS_2$	102.56	96.82	114.1	104.39	115.14	104.2
$NH_2+H \rightarrow NH_3$	113.4	112.08	115.24	114.84	115.22	114.57
$2H_2+O_2 \rightarrow 2H_2O$	120.18	121.7	125.07	128.63	118.19	124.62
$CO_2+C \rightarrow 2CO$	128.17	125.94	129.06	131.9	128.34	131.8
$CO+O \rightarrow CO_2$	125.32	119.73	137.67	127.48	143.2	129.83
$C+H_2O \rightarrow CO+H_2$	135.85	131.18	140.77	140.17	144.69	142.27
$N_2H_4+O_2 \rightarrow N_2+2H_2O$	132.86	133.07	139.43	148.29	134.48	146.86
$2NH \rightarrow N_2+H_2$	168	160.87	181.39	180.8	184.68	182.07
$C+S_2 \rightarrow CS_2$	172.24	163.65	186.12	179.21	188.57	179.86
$2CO+2NO \rightarrow N_2+2CO_2$	179.56	176.56	201.06	189.57	197.29	184.3
$CH_4+2O_2 \rightarrow CO_2+2H_2O$	186.5	185.18	198.51	208.57	192.62	205.52
$4NH_3+5O_2 \rightarrow 4NO+6H_2O$	203.1	202.91	201.58	242.06	199.16	246.27
$2NH_3+2NO+O \rightarrow 2N_2+3H_2O$	247.16	243.84	269.4	264.67	260.13	257.66
$C+O_2 \rightarrow CO_2$	263.71	258.13	277.54	277.09	279.23	277.36
$CS_2+3O_2 \rightarrow CO_2+2SO_2$	237.56	231.97	257.21	274.68	264.61	276.71
$CH_4+4NO \rightarrow 2N_2+CO_2+2H_2O$	274.55	273.93	303.68	297.33	285.41	282.99
$CH_4+NH_3+3O \rightarrow HCN+3H_2O$	278.03	266.07	304.1	288.06	309.18	291.13
$2C+H_2 \rightarrow C_2H_2$	286.98	279.1	301.39	289.72	303.82	290.64
$4NH_3+3O_2 \rightarrow 2N_2+6H_2O$	291.16	291.66	306.76	330.82	291.96	323.75
MAE		3.23	8.48	7.89	8.35	7.09
MARE		5.73%	14.32%	8.63%	15.68%	8.47%