Supplementary materials – Extent of Fock-exchange mixing for a hybrid van der Waals density functional?

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TABLE S.I. Atomization energies (39 molecules from the G2-1 data set[1]). All energies in kcal/mol. This calculation uses vdW-DF-cx orbitals for $\Delta E^{\rm tlh}$, which is only meaningful for this subset of the G2-1 benchmark set. Atomization energies at listed reference geometries (at relaxed geometries) are listed outside (inside) brackets. The first subgroup corresponds to cases with a downward concave coupling-constant variation, where $\Delta E^{\rm tlh}$ is calculated using Eq. (19). The second subgroup corresponds to cases with a upward concave coupling-constant variation, where $\Delta E^{\rm tlh}$ is calculated using Eq. (20). The two-legged constructions and the $\Delta E^{\rm tlh}$ results are not necessarily accurate for the second subgroup where the Fock-exchange mixing coefficient $a_{\rm sys}$ is large. Accordingly we provide estimates for the average $a_{\rm sys}$ values, for the mean absolute deviation (MAD) and for the mean absolute relative deviation (MARD) separately. We do, however, also include an overall, such characterization at the bottom of the table.

	$\Delta E_{\rm x}^{\rm Fo}$	$\Delta E_{\rm x}^{\rm cx}$	$\Delta E_{\rm xc}^{\rm cx}$	$\Delta E_{\rm xc,\lambda=1}^{\rm cx}$	$\Delta E^{\rm cx}$	$\Delta E^{\rm tlh}$	$\Delta E^{\rm cx0}$	$\Delta E^{\rm ref}$	$a_{\rm sys}$
LiH	27	28	51	64	58[58]	57	57[57]	58	0.23
NH	17	27	54	72	87[87]	85	84[84]	84	0.22
NH_2	49	69	121	155	187[187]	183	182[182]	182	0.22
NH_3	99	127	202	252	303[303]	297	296[296]	298	0.22
OH	-81	28	55	73	105[105]	92	106[105]	106	0.12
H_2O	80	110	160	193	237[237]	230	229[229]	233	0.21
HF	52	74	98	115	145[150]	141	139[140]	141	0.20
PH_2	37	43	90	119	160[160]	158	158[158]	153	0.23
PH_3	65	73	141	184	247[247]	245	245[245]	242	0.23
Li_2	-5	-3	11	18	19[19]	19	19[19]	24	0.21
LiF	98	124	148	165	140[145]	135	134[134]	138	0.19
N_2	-65	6	59	97	228[230]	215	211[214]	228	0.18
N_2H_4	143	203	331	417	449[450]	436	435[435]	438	0.22
NO	-118	30	73	105	161[161]	141	144[145]	153	0.13
O_2	-54	32	61	83	138[138]	125	116[119]	120	0.14
H_2O_2	43	123	195	244	281[281]	266	261[262]	269	0.19
F_2	-65	10	27	41	52[61]	43	34[34]	38	0.12
CO_2	206	213	277	325	408[408]	406	378[380]	389	0.24
Na_2	-12	-7	5	11	15[15]	14	14[14]	17	0.20
P_2	-60	-13	30	60	120[121]	112	109[110]	117	0.19
ClO	-6	36	60	78	78[79]	71	62[64]	65	0.17
SO_2	104	153	212	256	277[279]	267	243[247]	258	0.20
Average $a_{\rm sys}$									0.19
MAD(kcal/mol)					7.35[8.40]	5.37	5.14[4.36]		
MARD(%)					6.92[8.42]	5.33	4.74[4.22]		
BeH	69	67	78	85	61[61]	62	62[62]	50	0.18
CH_3	272	180	242	282	317[317]	348	311[311]	307	0.34
CH_4	310	222	307	362	429[429]	451	423[423]	420	0.25
$SiH_2\_s_1A_1d$	122	63	104	130	155[155]	174	129[154]	151	0.32
SiH_3	176	110	165	199	232[232]	250	232[232]	225	0.27
SiH_4	211	141	218	265	326[326]	342	327[327]	322	0.23
SH_2	140	75	117	145	190[190]	213	183[183]	182	0.36
C_2H_4	490	326	436	510	579[579]	636	563[564]	563	0.34
C_2H_6	583	410	556	653	730[730]	778	717[717]	712	0.28
CN	126	94	136	167	188[189]	195	168[168]	181	0.24
HCN	163	125	188	232	320[321]	328	301[303]	313	0.21
CO	144	101	137	164	265[266]	278	248[249]	259	0.30
HCO	188	150	202	239	294[294]	302	275[276]	279	0.23
H_2CO	245	203	277	327	387[387]	395	369[370]	374	0.21
CH_3OH	346	292	402	476	526[526]	537	512[512]	513	0.20
SiO	88	82	115	139	195[195]	196	179[181]	192	0.19
SO	87	73	99	119	141[142]	144	122[124]	125	0.22
Si_2H_6	382	249	378	459	539[539]	571	538[539]	530	0.24
CH_3SH	412	263	367	436	490[490]	540	476[476]	474	0.33
HOCl	131	96	139	170	177[177]	185	161[162]	164	0.23
Average $a_{\rm sys}$									0.26
MAD(kcal/mol)					10.13[10.36]	29.38	6.73[5.31]		
MARD(%)					4.51[4.62]	10.26	3.90[3.02]		
Average $a_{\rm sys}$									0.22
MAD(kcal/mol)					8.67[9.34]	16.81	5.90[4.81]		
MARD(%)					5.77[6.61]	7.68	4.34[3.65]		

TABLE S.II. Atomization energies ΔE for molecules in the G2-1 data set,[1] at listed reference geometries, using Hartree-Fock orbitals in $\Delta E^{\rm tlh}$. Results at relaxed geometries are listed in brackets. The subgroups are organized as in Table S.I.

	$\Delta E_{\rm x}^{\rm HF}$	$\Delta E_{\rm x}^{\rm cx}$	$\Delta E_{\rm xc}^{cx}$	$\Delta E_{\rm xc,\lambda=1}^{\rm cx}$	$\Delta E^{\rm cx}$	$\Delta E^{\rm tlh}$	$\Delta E^{\rm cx0}$	$\Delta E^{\rm ref}$	$a_{\rm sys}$
BeH	7	67	78	85	61[61]	55	62[62]	50	0.10
CH	88	114	119	124	77[77]	74	71[72]	84	0.11
CH_2_s_3B_1d	111	146	182	205	201[201]	194	196[196]	190	0.19
CH_2_s_1A_1d	101	138	172	195	191[201]	184	185[196]	181	0.19
CH_3	135	180	242	282	317[317]	308	311[311]	307	0.20
CH_4	168	222	307	362	429[429]	418	423[423]	420	0.21
NH	15	27	54	72	87[87]	84	84[84]	84	0.22
NH_2	40	69	121	155	187[187]	181	182[182]	182	0.21
NH_3	82	127	202	252	303[303]	293	296[296]	298	0.21
H_2O	67	110	160	193	237[237]	228	229[229]	233	0.20
HF	39	74	98	115	145[150]	139	139[140]	141	0.18
SiH_2_s_1A_1d	62	63	104	130	155[155]	155	129[154]	151	0.23
SiH_2_s_3B_1d	71	84	115	135	138[138]	136	137[138]	131	0.22
SiH_3	99	110	165	199	232[232]	230	232[232]	225	0.23
SiH_4	131	141	218	265	326[326]	324	327[327]	322	0.23
PH_2	38	43	90	119	160[160]	159	158[158]	153	0.23
PH_3	63	73	141	184	247[247]	245	245[245]	242	0.23
SH_2	28	75	117	145	190[190]	181	183[183]	182	0.19
HCl	13	52	73	86	110[111]	104	106[106]	106	0.16
LiF	111	124	148	165	140[145]	137	134[134]	138	0.21
C_2H_2	112	237	310	361	417[417]	395	398[399]	406	0.17
C_2H_4	212	326	436	510	579[579]	557	563[564]	563	0.19
C_2H_6	307	410	556	653	730[730]	709	717[717]	712	0.21
CN	51	94	136	167	188[189]	179	168[168]	181	0.19
HCN	11	125	188	232	320[321]	301	301[303]	313	0.17
CO	5	101	137	164	265[266]	251	248[249]	259	0.15
HCO	57	150	202	239	294[294]	278	275[276]	279	0.17
H_2CO	104	203	277	327	387[387]	369	369[370]	374	0.18
CH_3OH	201	292	402	476	526[526]	508	512[512]	513	0.20
N_2	-96	6	59	97	228[230]	211	211[214]	228	0.17
N_2H_4	117	203	331	417	449[450]	432	435[435]	438	0.21
NO	-41	30	73	105	161[161]	148	144[145]	153	0.17
O_2	-24	32	61	83	138[138]	128	116[119]	120	0.17
H_2O_2	21	123	195	244	281[281]	263	261[262]	269	0.18
F_2	-95	10	27	41	52[61]	42	34[34]	38	0.10
CO_2	65	213	277	325	408[408]	385	378[380]	389	0.16
Si_2	-14	47	67	81	82[82]	74	74[75]	75	0.14
P_2	-68	-13	30	60	120[121]	110	109[110]	117	0.18
S_2	-26	68	91	108	121[121]	109	104[104]	102	0.12
Cl_2	-18	60	77	89	70[70]	61	57[58]	58	0.11
NaCl	74	84	103	115	96[96]	93	92[93]	98	0.21
SiO	13	82	115	139	195[195]	183	179[181]	192	0.16
CS	-37	75	105	127	181[181]	166	162[162]	171	0.13
SO	-17	73	99	119	141[142]	129	122[124]	125	0.13
ClO	-6	36	60	78	78[79]	71	62[64]	65	0.17
ClF	-22	57	74	88	74[79]	65	59[61]	61	0.12
Si_2H_6	227	249	378	459	539[539]	534	538[539]	530	0.23
CH_3Cl	151	237	319	374	408[408]	392	396[397]	394	0.19
CH_3SH	168	263	367	436	490[490]	471	476[476]	474	0.20
HOCl	7	96	139	170	177[177]	162	161[162]	164	0.16
SO_2	-4	153	212	256	277[279]	254	243[247]	258	0.15
Average $a_{\rm sys}$									0.18
MAD(kcal/mol)					9.48[10.33]	4.56	5.83[5.08]		
MARD(%)					6.36[7.32]	2.96	3.70[3.16]		
LiH	31	28	51	64	58[58]	58	57[57]	58	0.13
OH	31	28	55	73	105[105]	106	106[105]	106	0.17
Li_2	16	-3	11	18	19[19]	24	19[19]	24	0.27
Na_2	8	-7	5	11	15[15]	19	14[14]	17	0.24
Average $a_{\rm sys}$									0.20
MAD(kcal/mol)					2.06[2.02]	0.74	2.38[2.55]		
MARD(%)					7.94[7.84]	3.27	10.15[10.28]		
Average $a_{\rm sys}$									0.18
MAD(kcal/mol)					8.94[9.73]	4.29	5.58[4.90]		
MARD(%)					6.47[7.36]	2.98	4.17[3.68]		

TABLE S.III. Reaction energies (17 reactions from the G2RC data set[2]) at listed reference geometries. All energies in kcal/mol. This calculation uses vdW-DF-cx orbitals for $\Delta E^{\rm tlh}$, which is only meaningful for this subset of the G2RC benchmark set. Reaction energies at relaxed geometries are listed in brackets, where available. Organization of data split into two subgroups depending on the nature of the vdW-DF-tlh construction, as in Table S.I.

	$\Delta E_{\rm x}^{\rm Fo}$	$\Delta E_{\rm x}^{\rm cx}$	$\Delta E_{\rm xc}^{\rm cx}$	$\Delta E_{{\rm xc},\lambda=1}^{\rm cx}$	$\Delta E^{\rm cx}$	$\Delta E^{\rm tlh}$	$\Delta E^{\rm cx0}$	$\Delta E^{\rm ref}$	$a_{\rm sys}$
$C_2H_6OS \rightarrow C_2H_4S+H_2O$	13	23	32	39	1.97[2.04]	0.06	0.07[0.71]	-2.23	0.19
$C_2H_4O \rightarrow CO+CH_4$	55	63	77	87	4.98[5.03]	3.24	3.22[3.23]	-2.18	0.21
$H_6Si_2+H_2 \rightarrow 2H_4Si$	-13	-6	-3	-1	-1.54[-1.50]	-2.63	-3.32[-3.27]	-4.10	0.15
$CO+H_2O \rightarrow CO_2+H_2$	-13	-33	-38	-42	-18.11[-18.13]	-15.67	-13.46[-13.51]	-7.10	0.12
$C_2H_3N+H_2O \rightarrow C_2H_5NO$	-61	-62	-78	-90	-27.18[-27.16]	-26.87	-27.22[-27.24]	-19.47	0.24
$BCl_3+AlF_3 \rightarrow BF_3+AlCl_3$	-17	-2	-1	-2	-25.51[-25.53]	-26.61	-29.30[-29.61]	-27.15	0.07
$N_2O+H_2 \rightarrow N_2+H_2O$	-54	-9	-5	-3	-62.25[-62.16]	-64.88	-73.11[-73.04]	-81.21	0.06
$C_2H_4+CH_2 \rightarrow C_3H_6$	-73	-78	-112	-136	-111.08[-100.41]	-109.86	-109.80[-98.65]	-109.11	0.23
Average $a_{\rm sys}$									0.16
MAD(kcal/mol)					6.90[7.77]	5.35	4.19[5.56]		
MARD(%)					100.67[102.22]	71.10	64.71[69.90]		
$CO_2+H_2 \rightarrow CH_2O_2$	-43	-35	-44	-51	-0.12[-0.13]	-2.50	-2.32[-2.29]	-2.26	0.27
$C_2H_2+HF \rightarrow C_2H_3F$	-39	-39	-51	-60	-32.98[-33.00]	-32.98	-33.36[-33.37]	-26.97	0.18
$CH_2O+H_2 \rightarrow CH_4O$	-65	-54	-64	-71	-27.25[-27.25]	-30.53	-29.89[-29.92]	-29.46	0.30
$C_2H_2+C_2H_4 \rightarrow C_4H_6$	-75	-72	-94	-111	-39.67[-39.71]	-40.31	-40.68[-40.79]	-32.71	0.19
$N_2+3H_2 \rightarrow 2H_3N$	-149	-137	-155	-169	-38.79[-38.79]	-41.67	-41.60[-41.55]	-39.43	0.25
$C_2H_2+H_2 \rightarrow C_2H_4$	-63	-54	-64	-71	-50.15[-50.16]	-52.58	-52.44[-52.41]	-49.20	0.27
$CO+3H_2 \rightarrow H_2O+CH_4$	-147	-136	-153	-167	-63.61[-63.63]	-66.57	-66.43[-66.36]	-65.15	0.25
$3C_2H_2 \rightarrow C_6H_6$	-185	-171	-215	-247	-169.48[-169.45]	-172.33	-173.10[-173.20]	-154.04	0.20
$Li_2+F_2 \rightarrow 2FLi$	-256	-234	-251	-264	-208.90[-209.04]	-215.79	-214.92[-214.95]	-216.11	0.31
Average $a_{\rm sys}$									0.25
MAD(kcal/mol)					4.79[4.78]	4.51	4.65[4.65]		
MARD(%)					18.35[18.30]	9.62	8.78[8.68]		
Average $a_{\rm sys}$									0.21
MAD(kcal/mol)					5.78[6.18]	4.90	4.43[5.08]		
MARD(%)					57.08[57.79]	38.55	35.10[37.49]		

TABLE S.IV. Ionization potential (26 elements from the G21IP data set[3]) at listed reference geometries. All energies in kcal/mol. This calculation uses vdW-DF-cx orbitals for $\Delta E^{\rm tlh}$, which is only meaningful for this subset of the G21IP benchmark set. Organization of data split into two subgroups depending on the nature of the vdW-DF-tlh construction, as in Table S.I.

	$\Delta E_{\rm x}^{\rm Fo}$	$\Delta E_{\rm x}^{\rm cx}$	$\Delta E_{\rm xc}^{\rm cx}$	$\Delta E_{{\rm xc},\lambda=1}^{\rm cx}$	$\Delta E^{\rm cx}$	$\Delta E^{\rm tlh}$	$\Delta E^{\rm cx0}$	$\Delta E^{\rm ref}$	$a_{\rm sys}$
B	83	155	174	184	195[195]	186	200[200]	190	0.12
O	183	189	227	249	317[317]	316	316[316]	314	0.23
F	226	234	270	292	403[403]	401	401[401]	402	0.22
Mg	78	80	102	113	173[173]	172	172[172]	176	0.21
Al	59	102	118	125	136[136]	130	140[140]	138	0.13
S	47	120	154	173	235[235]	224	240[240]	239	0.15
H_3N	160	166	196	213	234[234]	233	233[233]	236	0.22
HO	65	167	201	222	298[296]	284	300[299]	301	0.14
H_2O	198	204	236	255	291[291]	289	289[289]	293	0.22
HF	234	242	275	295	371[371]	369	369[369]	371	0.22
HS	78	133	164	182	236[236]	227	239[239]	239	0.16
C_2H_2	178	180	210	227	258[258]	258	258[258]	265	0.23
C_2H_4	175	175	205	222	237[237]	237	237[237]	244	0.23
Average $a_{\rm sys}$									0.19
MAD(kcal/mol)					3.26[3.42]	6.62	3.27[3.35]		
MARD(%)					1.38[1.44]	2.83	1.43[1.45]		
H	191	179	189	193	311[311]	313	314[314]	315	0.24
Be	93	87	114	126	206[206]	207	208[208]	215	0.11
C	226	212	231	241	269[269]	271	266[266]	260	0.17
Si	151	140	155	163	189[189]	190	189[189]	188	0.16
Cl	176	168	198	216	299[299]	300	299[299]	299	0.15
CH_4	217	197	227	244	286[286]	290	291[291]	296	0.18
H_4Si	182	164	194	210	247[247]	250	252[252]	255	0.17
H_2P	165	156	176	187	228[228]	229	255[243]	226	0.15
H_3P	135	134	162	178	225[225]	225	225[225]	228	0.13
CO	187	169	201	220	318[318]	321	323[323]	323	0.17
N_2	269	227	258	276	354[354]	367	365[365]	359	0.30
ClF	202	182	210	226	283[283]	287	288[288]	292	0.19
CS	144	133	163	180	257[257]	259	260[260]	261	0.15
Average $a_{\rm sys}$									0.17
MAD(kcal/mol)					5.25[5.25]	4.52	5.11[4.18]		
MARD(%)					1.95[1.95]	1.72	2.07[1.66]		
Average $a_{\rm sys}$									0.18
MAD(kcal/mol)					4.25[4.34]	5.57	4.19[3.77]		
MARD(%)					1.66[1.69]	2.28	1.75[1.56]		

TABLE S.V. Binding energies ΔE for molecular complexes in the S22 benchmark set,[4,5] at their listed reference geometries, here computed using vdW-DF-cx wavefunctions. This Table provides details behind Table III in the main text. In all of these molecular complexes, the coupling-constant scaling remains downward concave with the evaluation of $\Delta E^{\rm tlh}$ thus being based on Eq. (19). The results are sorted into three groups, namely, with a hydrogen bonded, dispersion bonded, or a mixed bonding character, respectively. We provide estimates of the average value for the $\Delta E_{\rm b}^{\rm tlh}$ Fock-exchange mixing parameter $a_{\rm sys}$ for each group separately and for the entire S22 benchmark set.

	$\Delta E_{\rm x}^{\rm Fo}$	$\Delta E_{x}^{\rm cx}$	$\Delta E_{xc}^{\rm cx}$	$\Delta E_{xc,\lambda=1}^{\rm cx}$	$\Delta E^{\rm cx}$	$\Delta E^{\rm tlh}$	$\Delta E^{\rm cx0}$	$\Delta E^{\rm ref}$	$a_{\rm sys}$
Ammonia dimer	3.27	2.45	5.00	6.84	2.63	2.79	2.87	3.133	0.20
Water dimer	7.18	6.21	8.91	10.92	4.57	4.77	4.86	4.989	0.21
Formic acid dimer	36.28	32.77	42.12	49.02	18.65	19.38	19.64	18.753	0.21
Formamide dimer	26.79	23.02	31.16	37.07	14.93	15.72	15.91	16.062	0.21
Uracil dimer h-bonded	26.43	22.62	31.98	38.67	19.01	19.78	20.04	20.641	0.20
2-pyridoxine 2-aminopyridine complex	22.07	20.69	30.44	37.33	16.88	17.13	17.32	16.934	0.18
Adenine-thymine Watson-Crick complex	22.80	20.78	31.33	38.73	15.45	15.82	16.06	16.660	0.18
Average $a_{\rm sys}$									0.20
MAD(kcal/mol)					0.72	0.49	0.43		
MARD(%)					6.78	4.44	3.63		
Methane dimer	1.07	0.44	2.12	3.26	0.63	0.75	0.79	0.527	0.19
Ethene dimer	2.99	1.23	4.92	7.46	0.98	1.33	1.42	1.472	0.20
Benzene-methane complex	1.81	0.42	4.41	7.11	1.29	1.55	1.65	1.448	0.19
Benzene dimer parallel displaced	1.83	-0.65	9.89	16.88	2.60	3.04	3.25	2.654	0.17
Pyrazine dimer	3.87	0.86	12.08	19.63	3.90	4.44	4.69	4.255	0.18
Uracil dimer stack	8.29	2.37	18.47	29.32	9.30	10.40	10.79	9.805	0.19
Indole-benzene complex stack	1.71	-1.81	13.20	23.17	4.27	4.88	5.18	4.524	0.17
Adenine-thymine complex stack	7.86	0.67	23.21	38.35	10.84	12.15	12.69	11.730	0.18
Average $a_{\rm sys}$									0.18
MAD(kcal/mol)					0.35	0.30	0.52		
MARD(%)					11.60	11.98	16.53		
Ethene-ethyne complex	2.13	1.31	3.28	4.62	1.54	1.69	1.75	1.496	0.19
Benzene-water complex	4.41	2.57	6.72	9.60	2.94	3.30	3.41	3.275	0.20
Benzene-ammonia complex	2.86	1.27	5.31	8.07	2.06	2.36	2.46	2.312	0.19
Benzene-HCN complex	6.35	3.57	8.68	12.21	4.11	4.69	4.83	4.541	0.21
Benzene dimer T-shaped	3.10	1.00	7.29	11.49	2.55	2.93	3.09	2.717	0.18
Indole-benzene T-shape complex	6.27	3.26	11.94	17.78	5.24	5.80	6.01	5.627	0.18
Phenol dimer	10.13	6.84	15.13	20.83	6.29	6.92	7.14	7.097	0.19
Average $a_{\rm sys}$									0.19
MAD(kcal/mol)					0.35	0.14	0.23		
MARD(%)					8.28	4.71	7.88		
Average $a_{\rm sys}$									0.19
MAD(kcal/mol)					0.47	0.31	0.40		
MARD(%)					9.01	7.27	9.68		

TABLE S.VI. Intra-molecular dissipative binding (or noncovalent intra-molecular binding) energies of the IDISP data set, at listed reference geometries.[2] All energies in kcal/mol, binding energies of relaxed structures are shown in brackets, where available. Reference energies from Ref. 2. The detailed reactions are[2,3] 1) the anthracene dimerization, 2) the 2,2-paracyclophane + $2H_2$ to 2 p-xylene reaction, 3) the n-octane to iso-octane transformation, 4) the n-undecane to 2,2,3,3,4,4-hexamethyl-pentane transformation 5) the unfolding of $C_{14}H_{30}$ and 6) the unfolding of $C_{22}H_{46}$.

	$\Delta E_{\rm x}^{\rm Fo}$	$\Delta E_{\rm x}^{\rm cx}$	$\Delta E_{\rm xc}^{\rm cx}$	$\Delta E_{\rm xc,\lambda=1}^{\rm cx}$	$\Delta E^{\rm cx}$	$\Delta E^{\rm tlh}$	$\Delta E^{\rm cx0}$	$\Delta E^{\rm cx0p}$	$\Delta E^{\rm ref}$	$a_{\rm sys}$
1	-79	-56	-109	-145	-6.63[-6.93]	-11.11	-12.50[-12.45]	-11.31[-11.45]	-9.15	0.19
2	-43	-29	-3	14	-52.50[-52.55]	-55.32	-55.67[-55.85]	-55.05[-55.22]	-60.28	0.21
3	7	9	-6	-16	-0.42[-0.42]	-0.75	-0.96[-0.97]	-0.85[-0.85]	-1.21	0.17
4	15	17	-11	-31	10.52[10.60]	10.25	9.95[9.99]	10.09[10.14]	9.10	0.17
5	1	1	8	13	-3.01[-2.51]	-2.85	-2.74[-2.15]	-2.80[-2.25]	-3.64	0.17
6	20	11	44	67	-2.96[1.06]	-1.32	-0.51[2.08]	-1.03[1.84]	-1.96	0.18
Average									0.18	
MAD(kcal/Mol)					2.36[2.73]	1.66	1.90[2.40]	1.75[2.32]		
MARD(%)					31.52[50.64]	22.44	28.79[53.38]	24.00[51.11]		

TABLE S.VII. Dimerization of aluminum complexes (AL2X6) at listed reference geometries. All energies in kcal/mol. Dimerization energies at relaxed geometries are listed in brackets, where available.

	$\Delta E_{\rm x}^{\rm Fo}$	$\Delta E_{\rm x}^{\rm cx}$	$\Delta E_{\rm xc}^{\rm cx}$	$\Delta E_{\rm xc,\lambda=1}^{\rm cx}$	$\Delta E^{\rm cx}$	$\Delta E^{\rm tlh}$	$\Delta E^{\rm cx0}$	$\Delta E^{\rm cx0p}$	$\Delta E^{\rm ref}$	$a_{\rm sys}$
H_6Al_2→2H_3Al	26	27	36	43	36.6[36.6]	36.3	36.4[36.5]	36.5[36.5]	38.5	0.24
Al_2F_6→2AlF_3	57	42	55	65	44.5[44.6]	48.7	48.0[47.9]	47.3[47.3]	51.6	0.29
Al_2Cl_6→2$AlCl_3$	33	28	46	59	30.3[30.3]	31.2	31.5[31.5]	31.3[31.3]	32.5	0.19
$C_4H_{14}Al_2$→2C_2H_7Al	32	30	43	52	36.2[36.2]	36.5	36.7[36.7]	36.6[36.6]	38.4	0.18
$C_5H_{16}Al_2$→C_2H_7Al+C_3H_9Al	31	29	47	59	29.5[29.5]	29.8	30.0[30.0]	29.9[29.9]	31.2	0.18
$C_6H_{18}Al_2$→2C_3H_9Al	30	28	50	66	22.1[22.0]	22.5	22.7[22.7]	22.6[22.5]	23.1	0.18
Average $a_{\rm sys}$										0.21
MAD(kcal/mol)					2.67[2.67]	1.70	1.65[1.67]	1.86[1.88]		
MARD(%)					6.81[6.81]	4.51	4.21[4.26]	4.75[4.81]		

TABLE S.VIII. Diels-Alder reaction (DARC) energies at listed reference geometries. All energies in kcal/mol. Reaction energies at relaxed geometries are listed in brackets, where available. However, the vdW-DF-cx, vdW-DF-cx0 and vdW-DF-cx0p all get the structure essentially exact and there are no discernible differences in the two sets of results.

	$\Delta E_{\rm x}^{\rm Fo}$	$\Delta E_{\rm x}^{\rm cx}$	$\Delta E_{\rm xc}^{\rm cx}$	$\Delta E_{\rm xc,\lambda=1}^{\rm cx}$	$\Delta E^{\rm cx}$	$\Delta E^{\rm tlh}$	$\Delta E^{\rm cx0}$	$\Delta E^{\rm cx0p}$	$\Delta E^{\rm ref}$	$a_{\rm sys}$
C_2H_4+C_4H_6→C_6H_{10}	-102	-87	-116	-138	-47.2[-47.2]	-50.5	-51.1[-51.1]	-50.3[-50.3]	-45.4	0.22
C_2H_2+C_4H_6→C_6H_8	-110	-97	-125	-146	-65.3[-65.3]	-68.1	-68.6[-68.6]	-68.0[-67.9]	-60.8	0.21
C_2H_4+C_5H_6→C_7H_{10}	-83	-70	-100	-122	-31.1[-31.1]	-33.8	-34.5[-34.5]	-33.8[-33.8]	-29.9	0.21
C_2H_2+C_5H_6→C_7H_8	-80	-72	-101	-122	-37.2[-37.2]	-38.8	-39.4[-39.3]	-38.9[-38.9]	-33.6	0.20
C_2H_4+C_6H_8→C_8H_{12}	-89	-75	-107	-131	-39.3[-39.3]	-42.2	-42.9[-42.8]	-42.1[-42.1]	-37.6	0.20
C_2H_2+C_6H_8→C_8H_{10}	-91	-82	-113	-136	-53.7[-53.6]	-55.4	-56.0[-56.0]	-55.5[-55.5]	-49.0	0.20
C_4H_4O+$C_4H_2O_3$→$C_8H_6O_4$(endo)	-66	-49	-82	-104	-12.6[-12.7]	-16.1	-17.0[-17.0]	-16.1[-16.1]	-14.0	0.21
C_4H_4O+$C_4H_2O_3$→$C_8H_6O_4$(exo)	-68	-50	-81	-104	-14.2[-14.3]	-18.0	-18.8[-18.8]	-17.9[-17.9]	-15.9	0.21
C_4H_4O+$C_4H_3NO_2$→$C_8H_7NO_3$(endo)	-68	-50	-83	-106	-15.4[-15.5]	-19.1	-20.0[-20.0]	-19.0[-19.1]	-16.8	0.21
C_4H_4O+$C_4H_3NO_2$→$C_8H_7NO_3$(exo)	-68	-51	-82	-105	-17.3[-17.3]	-21.1	-22.0[-22.0]	-21.0[-21.0]	-18.9	0.21
C_5H_6+$C_4H_2O_3$→$C_9H_8O_3$(endo)	-84	-66	-102	-127	-31.8[-31.9]	-35.4	-36.2[-36.2]	-35.3[-35.4]	-31.7	0.21
C_5H_6+$C_4H_2O_3$→$C_9H_8O_3$(exo)	-84	-67	-102	-127	-32.3[-32.3]	-35.8	-36.6[-36.5]	-35.7[-35.7]	-32.2	0.21
C_5H_6+$C_4H_3NO_2$→$C_9H_9NO_2$(endo)	-85	-67	-103	-128	-34.3[-34.3]	-38.1	-38.8[-38.8]	-37.9[-37.9]	-34.2	0.21
C_5H_6+$C_4H_3NO_2$→$C_9H_9NO_2$(exo)	-85	-67	-102	-127	-34.6[-34.6]	-38.3	-39.0[-39.0]	-38.1[-38.1]	-34.6	0.21
Average $a_{\rm sys}$										0.21
MD(kcal/mol)					-0.84[-0.86]	-4.00	-4.74[-4.72]	-3.94[-3.94]		
MAD(kcal/mol)					1.70[1.70]	4.00	4.74[4.72]	3.94[3.94]		
MARD(%)					5.60[5.52]	12.49	15.39[15.35]	12.30[12.33]		

TABLE S.IX. Atomization energies of the G2-1 dataset,[1] in kcal/mol. Atomization energies at listed reference geometries (optimized geometries) are reported outside (inside) square brackets.

	ΔE^{PBE0}	ΔE^{cx}	ΔE^{cx0}	ΔE^{cx0p}	ΔE^{ref}
LiH	52[52]	58[58]	57[57]	57[57]	58
BeH	59[59]	61[61]	62[62]	62[62]	50
CH	74[74]	77[77]	71[72]	72[72]	84
$CH_2(^3B_1)$	196[196]	201[201]	196[196]	196[196]	190
$CH_2(^1A_1)$	185[196]	191[201]	185[196]	185[196]	181
CH_3	310[310]	317[317]	311[311]	312[312]	307
CH_4	418[418]	429[429]	423[423]	423[423]	420
NH	85[85]	87[87]	84[84]	85[85]	84
NH_2	182[182]	187[187]	182[182]	183[183]	182
NH_3	293[293]	303[303]	296[296]	297[297]	298
OH	104[105]	105[105]	106[105]	107[107]	106
H_2O	225[225]	237[237]	229[229]	230[231]	233
HF	136[137]	145[150]	139[140]	141[141]	141
$SiH_2(^1A_1)$	125[134]	155[155]	129[154]	154[154]	151
$SiH_2(^3B_1)$	133[134]	138[138]	137[138]	138[138]	131
SiH_3	224[225]	232[232]	232[232]	232[232]	225
SiH_4	315[316]	326[326]	327[327]	327[327]	322
PH_2	154[154]	160[160]	158[158]	159[159]	153
PH_3	238[238]	247[247]	245[245]	245[245]	242
SH_2	180[180]	190[190]	183[183]	184[184]	182
HCl	104[104]	110[111]	106[106]	107[107]	106
Li_2	17[17]	19[19]	19[19]	19[19]	24
LiF	131[132]	140[145]	134[134]	135[135]	138
C_2H_2	402[402]	417[417]	398[399]	400[401]	406
C_2H_4	562[563]	579[579]	563[564]	565[565]	563
C_2H_6	712[712]	730[730]	717[717]	718[718]	712
CN	175[175]	188[189]	168[168]	171[172]	181
HCN	305[307]	320[321]	301[303]	304[306]	313
CO	250[251]	265[266]	248[249]	250[252]	259
HCO	276[277]	294[294]	275[276]	278[278]	279
H_2CO	368[368]	387[387]	369[370]	372[372]	374
CH_3OH	506[507]	526[526]	512[512]	514[514]	513
N_2	215[219]	228[230]	211[214]	214[217]	228
N_2H_4	432[432]	449[450]	435[435]	437[438]	438
NO	147[147]	161[161]	144[145]	148[148]	153
O_2	116[119]	138[138]	116[119]	121[123]	120
H_2O_2	256[257]	281[281]	261[262]	265[266]	269
F_2	31[32]	52[61]	34[34]	37[38]	38
CO_2	382[384]	408[408]	378[380]	383[385]	389
Na_2	14[14]	15[15]	14[14]	14[14]	17
Si_2	76[77]	82[82]	74[75]	76[76]	75
P_2	110[111]	120[121]	109[110]	111[112]	117
S_2	105[106]	121[121]	104[104]	106[106]	102
Cl_2	58[58]	70[70]	57[58]	60[60]	58
NaCl	92[92]	96[96]	92[93]	93[93]	98
SiO	178[180]	195[195]	179[181]	183[184]	192
CS	165[165]	181[181]	162[162]	164[164]	171
SO	122[124]	141[142]	122[124]	125[126]	125
ClO	63[64]	78[79]	62[64]	66[67]	65
ClF	58[59]	74[79]	59[61]	62[63]	61
Si_2H_6	522[523]	539[539]	538[539]	539[539]	530
CH_3Cl	394[394]	408[408]	396[397]	398[398]	394
CH_3SH	472[472]	490[490]	476[476]	478[478]	474
HOCl	158[159]	177[177]	161[162]	164[164]	164
SO_2	243[247]	277[279]	243[247]	249[253]	258
MD(kcal/mol)	-4.37[-3.36]	8.28[9.09]	-2.85[-1.48]	-0.61[0.04]	
MAD(kcal/mol)	5.51[4.99]	8.94[9.73]	5.58[4.90]	4.18[4.13]	
MARD(%)	4.42[4.12]	6.47[7.36]	4.17[3.68]	3.24[3.27]	

TABLE S.X. Reaction energies of the G2RC dataset[2] (25 reactions), in kcal/mol. Results at listed reference geometries (optimized geometries) are outside (inside) the brackets.

	ΔE^{PBE0}	ΔE^{cx}	ΔE^{cx0}	ΔE^{cx0p}	ΔE^{ref}
$C_2H_6OS \rightarrow C_2H_4S+H_2O$	-2.05[-1.55]	1.97[2.04]	0.07[0.71]	0.36[0.86]	-2.23
$CO_2+H_2 \rightarrow CH_2O_2$	-3.78[-3.87]	-0.12[-0.13]	-2.32[-2.29]	-1.87[-1.88]	-2.26
$C_2H_4O \rightarrow CO+CH_4$	4.03[4.04]	4.98[5.03]	3.22[3.23]	3.53[3.64]	-2.18
$H_6Si_2+H_2 \rightarrow 2H_4Si$	-3.30[-3.25]	-1.54[-1.50]	-3.32[-3.27]	-2.97[-2.92]	-4.10
$CO+H_2O \rightarrow CO_2+H_2$	-13.02[-12.95]	-18.11[-18.13]	-13.46[-13.51]	-14.32[-14.43]	-7.10
$C_2H_3ClO+H_2O \rightarrow C_2H_4O_2+HCl$	-10.60[-10.32]	-8.22[-8.18]	-10.48[-10.24]	-10.04[-9.84]	-10.70
$C_2H_3N+H_2O \rightarrow C_2H_5NO$	-26.53[-26.55]	-27.18[-27.16]	-27.22[-27.24]	-27.15[-27.17]	-19.47
$C_2H_2+HF \rightarrow C_2H_3F$	-33.19[-33.23]	-32.98[-33.00]	-33.36[-33.37]	-33.24[-33.35]	-26.97
$F_2+Cl_2 \rightarrow 2ClF$	-28.48[-28.29]	-27.02[-26.71]	-28.51[-28.40]	-28.18[-28.03]	-27.30
$BCl_3+AlF_3 \rightarrow BF_3+AlCl_3$	-30.15[-30.13]	-25.51[-25.53]	-29.30[-29.61]	-28.56[-28.58]	-27.15
$Cl_4Si+CF_4 \rightarrow F_4Si+CCl_4$	-14.08[-14.76]	-19.11[-19.07]	-17.59[-18.15]	-17.89[-18.35]	-24.89
$CH_2O+H_2 \rightarrow CH_4O$	-32.72[-32.78]	-27.25[-27.25]	-29.89[-29.92]	-29.38[-29.40]	-29.46
$C_2H_2+C_2H_4 \rightarrow C_4H_6$	-40.66[-40.83]	-39.67[-39.71]	-40.68[-40.79]	-40.45[-40.62]	-32.71
$OSi+3H_2 \rightarrow H_4Si+H_2O$	-45.10[-44.89]	-31.70[-31.72]	-39.60[-39.32]	-38.04[-37.88]	-36.32
$N_2+3H_2 \rightarrow 2H_3N$	-50.55[-50.44]	-38.79[-38.79]	-41.60[-41.55]	-41.04[-40.87]	-39.43
$CH_4+2Cl_2 \rightarrow CH_2Cl_2+2HCl$	-46.11[-44.73]	-41.83[-41.36]	-45.74[-44.62]	-44.98[-43.99]	-48.52
$C_2H_2+H_2 \rightarrow C_2H_4$	-54.83[-54.85]	-50.15[-50.16]	-52.44[-52.41]	-51.98[-52.03]	-49.20
$O_2S+3H_2 \rightarrow H_2S+2H_2O$	-67.55[-66.43]	-48.19[-48.16]	-59.69[-58.33]	-57.49[-56.50]	-61.67
$CO+3H_2 \rightarrow H_2O+CH_4$	-75.52[-75.51]	-63.61[-63.63]	-66.43[-66.36]	-65.88[-65.93]	-65.15
$F_2O+H_2 \rightarrow F_2+H_2O$	-66.25[-66.00]	-56.04[-56.01]	-62.97[-62.75]	-61.70[-61.57]	-68.90
$N_2O+H_2 \rightarrow N_2+H_2O$	-73.69[-73.62]	-62.25[-62.16]	-73.11[-73.04]	-71.02[-70.99]	-81.21
$C_2H_4+CH_2 \rightarrow C_3H_6$	-109.84[-98.69]	-111.08[-100.41]	-109.80[-98.65]	-110.05[-99.00]	-109.11
$H_2+F_2 \rightarrow 2HF$	-136.55[-136.46]	-125.82[-125.78]	-133.28[-133.20]	-131.81[-131.72]	-135.40
$3C_2H_2 \rightarrow C_6H_6$	-171.83[-171.90]	-169.48[-169.45]	-173.10[-173.20]	-172.36[-172.65]	-154.04
$Li_2+F_2 \rightarrow 2FLi$	-214.79[-214.85]	-208.90[-209.04]	-214.92[-214.95]	-213.66[-213.78]	-216.11
MD(kcal/mol)	-2.62[-2.05]	2.16[2.62]	-0.96[-0.39]	-0.34[0.19]	
MAD(kcal/mol)	5.18[5.59]	6.16[6.47]	4.01[4.53]	4.24[4.72]	
MARD(%)	29.54[31.00]	43.68[44.26]	26.43[28.20]	28.93[30.62]	

TABLE S.XI. Ionization potentials of the G21IP dataset[3] (36 elements), in kcal/mol. Results at listed reference geometries (optimized geometries) are outside (inside) the brackets.

	ΔE^{PBE0}	ΔE^{cx}	ΔE^{cx0}	ΔE^{cx0p}	ΔE^{ref}
H	314[314]	311[311]	314[314]	313[313]	315
Li	128[128]	127[127]	128[128]	128[128]	123
Be	205[205]	206[206]	208[208]	208[208]	215
B	199[199]	195[195]	200[200]	200[200]	190
C	266[266]	269[269]	266[266]	265[265]	260
N	340[340]	343[343]	339[339]	339[339]	335
O	317[317]	317[317]	316[316]	316[316]	314
F	399[399]	403[403]	401[401]	402[402]	402
Na	122[122]	122[122]	122[122]	122[122]	118
Mg	173[173]	173[173]	172[172]	173[173]	176
Al	140[140]	136[136]	140[140]	139[139]	138
Si	190[190]	189[189]	189[189]	188[188]	188
P	241[241]	241[241]	241[241]	241[241]	242
S	240[240]	235[235]	240[240]	240[240]	239
Cl	297[297]	299[299]	299[299]	298[298]	299
CH_4	289[289]	286[286]	291[291]	290[290]	296
H_3N	230[230]	234[234]	233[233]	233[233]	236
HO	299[298]	298[296]	300[299]	301[299]	301
H_2O	287[287]	291[291]	289[289]	289[289]	293
HF	366[366]	371[371]	369[369]	369[369]	371
H_4Si	249[249]	247[247]	252[252]	251[251]	255
HP	237[237]	236[236]	236[236]	236[236]	234
H_2P	253[241]	228[228]	255[243]	254[242]	226
H_3P	223[223]	225[225]	225[225]	225[225]	228
HS	238[238]	236[236]	239[239]	238[238]	239
HCl	291[291]	293[293]	292[292]	292[292]	294
C_2H_2	257[257]	258[258]	258[258]	258[258]	265
C_2H_4	236[236]	237[237]	237[237]	237[237]	244
CO	320[320]	318[318]	323[323]	322[322]	323
N_2	362[362]	354[354]	365[365]	363[363]	359
O_2	285[285]	283[283]	287[287]	286[286]	278
P_2	239[238]	242[238]	240[238]	240[238]	243
S_2	220[220]	216[216]	221[221]	220[220]	216
Cl_2	259[259]	255[255]	261[261]	260[260]	265
ClF	286[286]	283[283]	288[288]	287[287]	292
CS	257[257]	257[257]	260[260]	259[259]	261
MD(kcal/mol)	-0.51[-0.92]	-1.66[-1.81]	0.48[0.07]	0.16[-0.25]	
MAD(kcal/mol)	4.94[4.68]	4.08[4.23]	4.13[3.87]	4.10[3.86]	
MARD(%)	2.09[1.97]	1.66[1.72]	1.79[1.67]	1.77[1.66]	

TABLE S.XII. Binding distance deviations and binding energies at energy minimum of the S22 data set. The reference binding distances are at either the CCSD(T) or MP2 level as taken from Ref. 4. The reference interaction energies are all calculated using both CCSD(T)/CBS counterpoise corrected (CP) and MP2/CBS CP as taken from Ref. 5. (Length unit: Å; energy unit: kcal/mol)

	$d^{\mathrm{cx}} - d^{\mathrm{ref}}$	$d^{\mathrm{cx0}} - d^{\mathrm{ref}}$	$d^{\mathrm{cx0p}} - d^{\mathrm{ref}}$	d^{ref}	ΔE^{cx}	ΔE^{cx0}	ΔE^{cx0p}	ΔE^{ref}
Ammonia dimer	0.100	0.075	0.075	2.504	2.66	2.89	2.84	3.133
Water dimer	0.025	0.025	0.025	1.952	4.57	4.86	4.79	4.989
Formic acid dimer	-0.025	-0.025	-0.025	1.670	18.68	19.68	19.46	18.753
Formamide dimer	0.000	-0.025	0.000	1.841	14.91	15.90	15.69	16.062
Uracil dimer h-bonded	-0.025	-0.025	-0.025	1.775	18.87	19.90	19.68	20.641
2-pyridoxine 2-aminopyridine complex	-0.025	-0.025	-0.025	1.859	16.91	17.35	17.25	16.934
Adenine-thymine Watson-Crick complex	-0.025	-0.025	-0.025	1.819	15.51	16.13	15.99	16.660
MD	0.004	-0.004	0.000		-0.72	-0.07	-0.21	
MAD	0.032	0.032	0.029		0.72	0.45	0.50	
MARD (%)	1.557	1.608	1.414		6.65	3.66	4.27	
Methane dimer	0.275	0.125	0.125	3.718	0.73	0.82	0.79	0.527
Ethene dimer	0.400	0.275	0.300	3.718	1.34	1.57	1.52	1.472
Benzene-methane complex	0.300	0.150	0.200	2.630	1.45	1.71	1.65	1.448
Benzene dimer parallel displaced	0.300	0.200	0.225	3.765	2.98	3.45	3.35	2.654
Pyrazine dimer	0.250	0.150	0.175	3.479	4.20	4.85	4.72	4.255
Uracil dimer stack	0.075	0.025	0.025	3.365	9.34	10.78	10.49	9.805
Indole-benzene complex stack	0.250	0.150	0.175	3.252	4.63	5.40	5.24	4.524
Adenine-thymine complex stack	0.100	0.075	0.075	3.186	11.06	12.75	12.41	11.730
MD	0.244	0.144	0.162		-0.09	0.61	0.47	
MAD	0.244	0.144	0.162		0.24	0.61	0.47	
MARD (%)	7.221	4.224	4.815		9.19	20.21	16.72	
Ethene-ethyne complex	0.125	0.025	0.025	2.752	1.56	1.76	1.72	1.496
Benzene-water complex	0.075	0.000	0.000	2.468	2.95	3.41	3.32	3.275
Benzene-ammonia complex	0.175	0.075	0.075	2.583	2.13	2.49	2.42	2.312
Benzene-HCN complex	0.100	0.025	0.025	2.326	4.14	4.84	4.70	4.541
Benzene dimer T-shaped	0.175	0.100	0.150	2.433	2.69	3.14	3.05	2.717
Indole-benzene T-shape complex	0.150	0.075	0.075	2.231	5.36	6.05	5.91	5.627
Phenol dimer	0.025	0.000	0.025	1.937	6.28	7.12	6.94	7.097
MD	0.118	0.043	0.054		-0.28	0.25	0.14	
MAD	0.118	0.043	0.054		0.30	0.25	0.18	
MARD (%)	4.838	1.766	2.244		6.85	8.55	6.20	
MD	0.127	0.065	0.076		-0.35	0.28	0.15	
MAD	0.136	0.076	0.085		0.41	0.45	0.39	
MARD (%)	4.660	2.610	2.915		7.64	11.24	9.41	