Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPLEMENTARY INFORMATION

CBS extrapolation in electronic structure pushed to end: A revival of minimal and sub-minimal basis sets

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Table 1: TS-106 and TS-106' of molecular systems

# in TS-106	Formula	Name	# in TS-106'
1	CFN	Cyanogen fluoride	1
2	CFN	Isocyanogen fluoride	2
3	CF_2	Singlet difluoromethylene	3
4	CF_2O	Carbonyl fluoride	4
5	CF_4	Tetrafluoromethane	5

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# in TS-106	Formula	Name	# in TS-106'
6	CHF	Singlet fluoromethylene	6
7	CHFO	Formyl fluoride	7
8	CHF_3	Trifluoromethane	8
9	CHN	Hydrogen cyanide	9
10	CHN	Hydrogen isocyanide	10
11	CHNO	Cyanic acid	11
12	CHNO	Isocyanic acid	12
13	CHNO	Formonitrile oxide	13
14	CHNO	Isofulminic acid	14
15	CH_2	Singlet methylene	15
16	CH_2F_2	Difluoromethane	16
17	CH_2N_2	Cyanamide	17
18	CH_2N_2	3H-Diazirine	18
19	CH_2N_2	Diazomethane	19
20	CH_2O	Formaldehyde	20
21	CH_2O	Hydroxymethylene	21
22	CH_2O_2	Dioxirane	22
23	CH_2O_2	Formic acid	23
24	CH_2O_3	Performic acid*	**74**
25	CH_3F	Fluoromethane	24
26	CH_3N	Methanimine	25
27	CH_3NO	Formamide	26
28	CH_3NO_2	Methyl nitrite*	**75**
29	CH_3NO_2	Nitromethane*	**76**

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# in TS-106	Formula	Name	# in TS-106'
30	CH_4	Methane	27
31	CH_4N_2O	Urea*	**77**
32	CH_4O	Methanol	28
33	CH_5N	Methylamine*	**78**
34	CO	Carbon monoxide	29
35	CO_2	Carbon dioxide	30
36	C_2F_2	Difluoroacetylene	31
37	C_2F_4	Tetrafluoroethylene*	**79**
38	C_2HF	Fluoroacetylene	32
39	C_2HF_3	Trifluoroethylene	33
40	C_2H_2	Acetylene	34
41	$C_2H_2F_2$	1,1-Difluoroethylene	35
42	C_2H_2O	Ketene	36
43	C_2H_2O	Oxirene	37
44	$C_2H_2O_2$	Glyoxal	38
45	C_2H_3F	Fluoroethylene	39
46	C_2H_3FO	Acetyl fluoride*	**80**
47	C_2H_3N	Acetonitrile*	**81**
48	C_2H_3N	Methyl isocyanide*	**82**
49	C_2H_4	Ethylene	40
50	C_2H_4O	Acetaldehyde*	**83**
51	C_2H_4O	Oxirane*	**84**
52	$C_2H_4O_2$	Acetic acid*	**85**
53	$C_2H_4O_2$	Methyl formate*	**86**

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# in TS-106	Formula	Name	# in TS-106'
54	C_2H_5F	Fluoroethane*	**87**
55	C_2H_5N	Aziridine*	**88**
56	C_2H_6	Ethane*	**89**
57	C_2H_6O	Dimethyl ether*	**90**
58	C_2H_6O	Ethanol*	**91**
59	C_2N_2	Cyanogen	41
60	C_3H_3N	Acrylonitrile*	**92**
61	C_3H_4	Allene*	**93**
62	C_3H_4	Cyclopropene*	**94**
63	C_3H_4	Propyne*	**95**
64	C_3H_6	Cyclopropane*	**96**
65	C_3H_6	Propene*	**97**
66	C_3H_8	Propane*	*not included*
67	C_3O_2	Carbon suboxide	42
68	C_4H_4	Butatriene*	**98**
69	C_4H_4	Cyclobutadiene*	**99**
70	C_4H_4	Tetrahedran*	**100**
71	C_4H_4	Vinylacetylene*	**101**
72	C_4N_2	Dicyanoacetylene*	**102**
73	FH	Hydrogen fluoride	43
74	FHO	Hypofluorous acid	44
75	FHO_2	Fluoroperoxide	45
76	FH_2N	Monofluoroamine	46
77	FH_3N_2	Fluorohydrazine*	**103**

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# in TS-106	Formula	Name	# in TS-106'
78	FNO	Nitrosyl fluoride	47
79	F_2	Difluorine	48
80	F_2N_2	Difluorodiazene (cis)	49
81	F_2N_2	Difluorodiazene (trans)	50
82	F_2O	Difluorine monoxide	51
83	F_2O_2	Perfluoroperoxide	52
84	F_3N	Trifluoroamine	53
85	HNO	Nitrosylhydride	54
86	HNO_2	Nitrous acid (cis)	55
87	HNO_2	Nitrous acid (trans)	56
88	HNO_2	Nitrous acid	57
89	HNO_3	Nitric acid	58
90	HN_3	Hydrogen azide	59
91	H_2N_2	Diazene (cis)	60
92	H_2N_2	Diazene (trans)	61
93	H_2N_2	Diazene (iso)	62
94	H_2N_2O	Nitrosamide	63
95	H_2O	Water	64
96	H_2O_2	Hydrogen peroxide	65
97	H_3N	Ammonia	66
98	H_3NO	Ammonia oxide	67
99	H_3NO	Hydroxylamine	68
100	H_4N_2	Hydrazine	69
101	N_2	Dinitrogen	70

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# in TS-106	Formula	Name	# in TS-106'
102	N_2O	Nitrous oxide	71
103	N_2O_3	Dinitrogen trioxide*	**104**
104	N_2O_4	Dinitrogen tetraoxide*	**105**
105	O_3	Ozone	72
106	H_2	Dihydrogen	73

[a]Reference energy obtained at CBS$(Q, 5)$ level of theory; see the text.

Table 2: MP2 energies of TS-106' molecular systems

# in TS-106'	Formula	VQZ	V5Z	V6Z
1	CFN	-192.4168110	-192.4389694	-192.4477896
2	CFN	-192.2952459	-192.3171560	-192.3259231
3	CF_2	-237.4637416	-237.4924614	-237.5037001
4	CF_2O	-312.7137241	-312.7513145	-312.7660616
5	CF_4	-437.1056107	-437.1590880	-437.1798800
6	CHF	-138.2418549	-138.2585043	-138.2650096
7	CHFO	-213.5393509	-213.5651719	-213.5753165
8	CHF_3	-337.9282717	-337.9699629	-337.9861015
9	CHN	-93.2536552	-93.2638314	-93.2680493
10	CHN	-93.2536552	-93.2638314	-93.2680493
11	CHNO	-168.4208418	-168.4403596	-168.4481783
12	CHNO	-168.4612249	-168.4809629	-168.4888935
13	CHNO	-168.3531717	-168.3729350	-168.3808744
14	CHNO	-168.3194518	-168.3387535	-168.3465406

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# in TS-106'	Formula	VQZ	V5Z	V6Z
15	CH_2	-39.0432568	-39.0476355	-39.0494140
16	CH_2F_2	-238.7466314	-238.7764479	-238.7879401
17	CH_2N_2	-148.5653415	-148.5824284	-148.5893443
18	CH_2N_2	-148.4942549	-148.5111754	-148.5180363
19	CH_2N_2	-148.5106944	-148.5274470	-148.5342996
20	CH_2O	-114.3446951	-114.3584348	-114.3638983
21	H_2CO	-114.3446952	-114.3584349	-114.3638984
22	CH_2O_2	-189.3836465	-189.4068096	-189.4159413
23	CH_2O_2	-189.5337125	-189.5568538	-189.5659707
24	CH_3F	-139.5759008	-139.5936256	-139.6004715
25	CH_3N	-94.4702319	-94.4815053	-94.4860284
26	CH_3NO	-169.6626832	-169.6836413	-169.6919382
27	CH_4	-40.4262767	-40.4312904	-40.4333455
28	CH_4O	-115.5582790	-115.5732467	-115.5790450
29	CO	-113.1698907	-113.1823469	-113.1874205
30	CO_2	-188.3680041	-188.3899078	-188.3986979
31	C_2F_2	-275.4444659	-275.4770692	-275.4899000
32	C_2HF	-176.3188402	-176.3392862	-176.3474702
33	C_2HF_3	-375.8968998	-375.9427491	-375.9606354
34	C_2H_2	-77.1834610	-77.1920470	-77.1956437
35	$C_2H_2F_2$	-276.7544823	-276.7879092	-276.8010425
36	C_2H_2O	-152.3722921	-152.3897679	-152.3968762
37	C_2H_2O	-152.2456751	-152.2645982	-152.2721411
38	$C_2H_2O_2$	-227.5161130	-227.5429040	-227.5536251

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# in TS-106'	Formula	VQZ	V5Z	V6Z
39	C_2H_3F	-177.5870136	-177.6085008	-177.6170131
40	C_2H_4	-78.4252408	-78.4343603	-78.4381259
41	C_2H_4	-185.3771456	-185.3965943	-185.4046841
42	C_3O_2	-264.3575000	-264.3868760	-264.3988863
43	HF	-100.3652008	-100.3787343	-100.3837152
44	HOF	-175.3682431	-175.3904320	-175.3989433
45	FHO_2	-250.4286797	-250.4601941	-250.4723537
46	FH_2N	-155.5504730	-155.5704679	-155.5781227
47	FNO	-229.4783878	-229.5066395	-229.5176605
48	F_2	-199.3378006	-199.3622782	-199.3717715
49	F_2N_2	-308.7007823	-308.7384220	-308.7531031
50	F_2N_2	-308.6982892	-308.7360274	-308.7508004
51	F_2O	-274.4046920	-274.4387627	-274.4519852
52	F_2O_2	-349.4735628	-349.5171787	-349.5340958
53	F_3N	-353.7574478	-353.8015637	-353.8185529
54	HNO	-130.3148267	-130.3306024	-130.3368508
55	HNO_2	-205.4697719	-205.4947369	-205.5045969
56	HNO_2	-205.4697695	-205.4947341	-205.5045940
57	HNO_2	-205.4650401	-205.4904181	-205.5003470
58	HNO_3	-280.5821214	-280.6163814	-280.6298149
59	HN_3	-164.5675878	-164.5864998	-164.5941563
60	H_2N_2	-110.4745293	-110.4878384	-110.4931250
61	N_2H_2	-110.4833099	-110.4968243	-110.5021991
62	H_2N_2	-110.4388911	-110.4526089	-110.4580220

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# in TS-106'	Formula	VQZ	V5Z	V6Z
63	H_2N_2O	-185.6127757	-185.6357762	-185.6448320
64	H_2O	-76.3476362	-76.3585910	-76.3626020
65	H_2O_2	-151.3844279	-151.4040418	-151.4115383
66	NH_3	-56.4746225	-56.4826100	-56.4855479
67	H_3NO	-131.5124022	-131.5314753	-131.5386176
68	H_3NO	-131.5542924	-131.5715782	-131.5781831
69	H_4N_2	-111.7043054	-111.7190870	-111.7247005
70	N_2	-109.3899927	-109.4020295	-109.4070558
71	N_2O	-184.4498497	-184.4709232	-184.4794520
72	O_3	-225.1910263	-225.2187169	-225.2296273
73	H_2	-1.1665587	-1.1672484	-1.1675104
74	CH_2O_3	-264.5690721	-264.6012447	n.c.[a)]
75	CH_3NO_2	-244.6915009	-244.7210187	n.c.
76	CH_2NO_2	-169.5530958	-169.5735104	n.c.
77	CH_4N_2O	-224.9660436	-224.9938307	n.c.
78	CH_5N	-95.6918898	-95.7041763	n.c.
79	C_2F_4	-475.0505601	-475.1084864	n.c.
80	C_2H_3FO	-252.7868338	-252.8172834	n.c.
81	C_2H_3N	-132.5303992	-132.5451544	n.c.
82	C_2H_3N	-132.5303983	-132.5451535	n.c.
83	C_2H_4O	-153.5928026	-153.6111327	n.c.
84	C_2H_4O	-153.5521777	-153.5710377	n.c.
85	$C_2H_4O_2$	-228.7796183	-228.8073626	n.c.
86	$C_2H_4O_2$	-228.7516521	-228.7793003	n.c.

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# in TS-106'	Formula	VQZ	V5Z	V6Z
87	C_2H_5F	-178.8164487	-178.8385742	n.c.
88	C_2H_5N	-133.6865411	-133.7026970	n.c.
89	C_2H_6	-79.6574116	-79.6669947	n.c.
90	C_2H_6O	-154.7774169	-154.7966116	n.c.
91	C_2H_6O	-154.7979722	-154.8173662	n.c.
92	C_3H_3N	-170.5350543	-170.5537213	n.c.
93	C_3H_4	-116.4199121	-116.4328908	n.c.
94	C_3H_4	-116.3894188	-116.4026202	n.c.
95	C_3H_4	-116.4274525	-116.4404930	n.c.
96	C_3H_6	-117.6567539	-117.6705144	n.c.
97	C_3H_6	-117.6648719	-117.6785271	n.c.
98	C_4H_4	-154.4176777	-154.4344774	n.c.
99	C_4H_4	-154.3774029	-154.3949109	n.c.
100	C_4H_4	-154.3451429	-154.3629012	n.c.
101	C_4H_4	-154.4359725	-154.4529605	n.c.
102	C_4N_2	-261.3961109	-261.4231930	n.c.
103	FH_3N_2	-210.8015230	-210.8287246	n.c.
104	N_2O_3	-334.6043172	-334.6445046	n.c.
105	N_2O_4	-409.7293143	-409.7784280	n.c.

[a)] n.c. = not calculated; see text.

Table 3: CCSD(T) energies of TS-106' molecular systems

# in TS-106'	Formula	VQZ	V5Z	V6Z
1	CFN	-192.4383628	-192.4572487	-192.4638089
2	CFN	-192.3253916	-192.3440245	-192.3505449
3	CF_2	-237.4926678	-237.5180404	-237.5268150
4	CF_2O	-312.7401565	-312.7733186	-312.7847943
5	CF_4	-437.1397222	-437.1877153	-437.2042352
6	CHF	-138.2710222	-138.2853134	-138.2902101
7	CHFO	-213.5640877	-213.5864486	-213.5941661
8	CHF_3	-337.9600092	-337.9971762	-338.0098885
9	CHN	-93.2776684	-93.2856446	-93.2884868
10	CHN	-93.2776684	-93.2856446	-93.2884868
11	CHNO	-168.4454175	-168.4615034	-168.4670836
12	CHNO	-168.4841038	-168.5004276	-168.5061272
13	CHNO	-168.3721860	-168.3884713	-168.3941665
14	CHNO	-168.3508298	-168.3666985	-168.3722541
15	CH_2	-39.0719118	-39.0750367	-39.0761029
16	CH_2F_2	-238.7763206	-238.8025990	-238.8115246
17	CH_2N_2	-148.5950151	-148.6086882	-148.6134514
18	CH_2N_2	-148.5274770	-148.5410369	-148.5457801
19	CH_2N_2	-148.5418717	-148.5552661	-148.5599990
20	CH_2O	-114.3690059	-114.3803010	-114.3842021
21	H_2CO	-114.3690059	-114.3803010	-114.3842021
22	CH_2O_2	-189.4154746	-189.4350424	-189.4417823
23	CH_2O_2	-189.5616530	-189.5811479	-189.5878502
24	CH_3F	-139.6034027	-139.6186302	-139.6237840

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# in TS-106'	Formula	VQZ	V5Z	V6Z
25	CH_3N	-94.5013422	-94.5101724	-94.5132139
26	CH_3NO	-169.6955604	-169.7128672	-169.7188261
27	CH_4	-40.4508883	-40.4545472	-40.4558120
28	CH_4O	-115.5889213	-115.6012073	-115.6053325
29	CO	-113.1879027	-113.1981807	-113.2018222
30	CO_2	-188.3845594	-188.4030805	-188.4095733
31	C_2F_2	-275.4758852	-275.5041758	-275.5139405
32	C_2HF	-176.3470971	-176.3643310	-176.3703306
33	C_2HF_3	-375.9411342	-375.9814449	-375.9953157
34	C_2H_2	-77.2093168	-77.2157750	-77.2180625
35	$C_2H_2F_2$	-276.7950094	-276.8240245	-276.8340401
36	C_2H_2O	-152.4036705	-152.4178434	-152.4228283
37	C_2H_2O	-152.2790084	-152.2945037	-152.2998574
38	$C_2H_2O_2$	-227.5562607	-227.5785081	-227.5862595
39	C_2H_3F	-177.6257707	-177.6438614	-177.6501135
40	C_2H_4	-78.4617376	-78.4685601	-78.4709540
41	C_2H_4	-185.4044583	-185.4198570	-185.4253614
42	C_3O_2	-264.3857595	-264.4099578	-264.4185462
43	HF	-100.3731799	-100.3851749	-100.3891032
44	HOF	-175.3907358	-175.4103008	-175.4169411
45	FHO_2	-250.4622393	-250.4899988	-250.4994648
46	FH_2N	-155.5758273	-155.5931794	-155.5990373
47	FNO	-229.5008744	-229.5255472	-229.5340722
48	F_2	-199.3589065	-199.3809830	-199.3886080

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# in TS-106'	Formula	VQZ	V5Z	V6Z
49	F_2N_2	-308.7379819	-308.7710791	-308.7824955
50	F_2N_2	-308.7356466	-308.7687794	-308.7802580
51	F_2O	-274.4358003	-274.4663258	-274.4768497
52	F_2O_2	-349.5178709	-349.5567483	-349.5701404
53	F_3N	-353.7931992	-353.8327767	-353.8463127
54	HNO	-130.3381313	-130.3513328	-130.3559138
55	HNO2	-205.4974537	-205.5186940	-205.5260604
56	HNO_2	-205.4974526	-205.5186925	-205.5260587
57	HNO_2	-205.4850656	-205.5067206	-205.5141683
58	HNO_3	-280.6085778	-280.6380369	-280.6481821
59	HN_3	-164.5872941	-164.6027238	-164.6081660
60	H_2N_2	-110.5032675	-110.5140074	-110.5177116
61	N_2H_2	-110.5115770	-110.5224908	-110.5262672
62	H_2N_2	-110.4715586	-110.4827583	-110.4865982
63	H_2N_2O	-185.6444163	-185.6636819	-185.6703206
64	H_2O	-76.3597932	-76.3690303	-76.3720062
65	H_2O_2	-151.4082120	-151.4249947	-151.4306262
66	NH_3	-56.4930450	-56.4994246	-56.5014399
67	H_3NO	-131.5399324	-131.5561314	-131.5614705
68	H_3NO	-131.5817363	-131.5961707	-131.6009860
69	H_4N_2	-111.7359393	-111.7478990	-111.7518170
70	N_2	-109.4043906	-109.4141911	-109.4177722
71	N_2O	-184.4616236	-184.4792421	-184.4854875
72	O_3	-225.2022539	-225.2260918	-225.2343949

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# in TS-106'	Formula	VQZ	V5Z	V6Z
73	H_2	-1.1737960	-1.1742221	-1.1743447
74	CH_2O_3	-264.6082328	-264.6355688	n.c.[a)]
75	CH_3NO_2	-244.7365022	-244.7612566	n.c.
76	CH_2NO_2	-169.5930967	-169.6098675	n.c.
77	CH_4N_2O	-225.0092316	-225.0321914	n.c.
78	CH_5N	-95.7277987	-95.7374370	n.c.
79	C_2F_4	-475.0975449	-475.1488911	n.c.
80	C_2H_3FO	-252.8282834	-252.8541942	n.c.
81	C_2H_3N	-132.5657800	-132.5772705	n.c.
82	C_2H_3N	-132.5657800	-132.5772705	n.c.
83	C_2H_4O	-153.6333290	-153.6481492	n.c.
84	C_2H_4O	-153.5910479	-153.6064036	n.c.
85	$C_2H_4O_2$	-228.8241500	-228.8471710	n.c.
86	$C_2H_4O_2$	-228.7973815	-228.8203339	n.c.
87	C_2H_5F	-178.8606306	-178.8791732	n.c.
88	C_2H_5N	-133.7301786	-133.7428448	n.c.
89	C_2H_6	-79.6987179	-79.7058462	n.c.
90	C_2H_6O	-154.8257043	-154.8412046	n.c.
91	C_2H_6O	-154.8449689	-154.8606029	n.c.
92	C_3H_3N	-170.5811641	-170.5956489	n.c.
93	C_3H_4	-116.4667897	-116.4765586	n.c.
94	C_3H_4	-116.4314489	-116.4414751	n.c.
95	C_3H_4	-116.4688696	-116.4787132	n.c.
96	C_3H_6	-117.7049287	-117.7153601	n.c.

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# in TS-106'	Formula	VQZ	V5Z	V6Z
97	C_3H_6	-117.7171012	-117.7273750	n.c.
98	C_4H_4	-154.4745516	-154.4872340	n.c.
99	C_4H_4	-154.4342290	-154.4475405	n.c.
100	C_4H_4	-154.3903407	-154.4040407	n.c.
101	C_4H_4	-154.4877366	-154.5006097	n.c.
102	C_4N_2	-261.4360530	-261.4573112	n.c.
103	FH_3N_2	-210.8387662	-210.8621327	n.c.
104	N_2O_3	-334.6340301	-334.6682153	n.c.
105	N_2O_4	-409.7513224	-409.7934223	n.c.

[a)] n.c. = not calculated; see text.

Table 4: Calculated MP2/VXZ-F12 and CCSD(T)/VXZ-F12 energies for the 68-TS

			MP2			CCSD(T)		
#	#'	System	VDZ-F12	VTZ-F12	VQZ-F12	VDZ-F12	VTZ-F12	VQZ-F12
1	15	CH_2	-39.0480023	-39.0510605	-39.0517424	-39.0695056	-39.0750860	-39.0765457
2	34	CO	-113.1833122	-113.1918599	-113.1942114	-113.1840450	-113.1997511	-113.2043977
3	73	HF	-100.3765504	-100.3870614	-100.3899505	-100.3694829	-100.3869653	-100.3920176
4	79	F_2	-199.3582516	-199.3783806	-199.3838868	-199.3509823	-199.3850780	-199.3944466
5	95	H_2O	-76.3581096	-76.3654875	-76.3675223	-76.3567438	-76.3698264	-76.3739322
6	101	N_2	-109.4044803	-109.4116778	-109.4136423	-109.4025197	-109.4162642	-109.4201683
7	9	HCN	-93.2654290	-93.2719532	-93.2736588	-93.2742091	-93.2867041	-93.2902396
8	21	H_2CO	-114.3590646	-114.3685190	-114.3710522	-114.3642083	-114.3816206	-114.3868180
9	30	CH_4	-40.4316842	-40.4351178	-40.4359523	-40.4480083	-40.4543608	-40.4563325
10	35	CO_2	-188.3907525	-188.4061884	-188.4103736	-188.3772617	-188.4058601	-188.4143354
11	40	C_2H_2	-77.1933165	-77.1988966	-77.2003671	-77.2056626	-77.2162589	-77.2192838
12	49	C_2H_4	-78.4355013	-78.4415535	-78.4429696	-78.4576538	-78.4688929	-78.4721332
13	74	HOF	-175.3880166	-175.4051308	-175.4098314	-175.3834818	-175.4132439	-175.4218130
14	85	HNO	-130.3314495	-130.3420952	-130.3449180	-130.3337776	-130.3533375	-130.3590158
15	92	N_2H_2	-110.4986567	-110.5070059	-110.5090716	-110.5086067	-110.5241976	-110.5285944
16	96	H_2O2	-151.4033131	-151.4172946	-151.4211402	-151.4016174	-151.4268454	-151.4345257
17	97	NH_3	-56.4829522	-56.4878997	-56.4891745	-56.4906270	-56.4997706	-56.5025248
18	105	O_3	-225.2189393	-225.2382918	-225.2435691	-225.1944802	-225.2300002	-225.2403170
19	1	CFN	-192.4384346	-192.4550657	-192.4466011	-192.4312487	-192.4604791	-192.4406561
20	2	CFN	-192.3161840	-192.3330473	-192.3244059	-192.3178238	-192.3471078	-192.3273984
21	3	CF_2	-237.4894975	-237.5121098	-237.5008174	-237.4839501	-237.5225719	-237.4956805
22	4	CF_2O	-312.7481330	-312.7773847	-312.7630667	-312.7281392	-312.7789105	-312.7444222
23	6	CHF	-138.2572001	-138.2699989	-138.2634971	-138.2654897	-138.2875385	-138.2726268
24	7	CHFO	-213.5640079	-213.5833057	-213.5736276	-213.5557759	-213.5899227	-213.5673173
25	8	CHF_3	-337.9644141	-337.9979063	-337.9820630	-337.9466842	-338.0034005	-337.9647678
26	10	HCN	-93.2654290	-93.2719532	-93.2736588	-93.2742091	-93.2867041	-93.2902396
27	11	CHNO	-168.4416657	-168.4550622	-168.4480799	-168.4389479	-168.4637260	-168.4481960
28	12	CHNO	-168.4825039	-168.4959165	-168.4993830	-168.4778586	-168.5028761	-168.5100982

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#[a)]	#'[a)]	System	VDZ-F12	VTZ-F12	VQZ-F12	VDZ-F12	VTZ-F12	VQZ-F12
29	13	CHNO	-168.3742896	-168.3877415	-168.3912647	-168.3657752	-168.3907505	-168.3979923
30	14	CHNO	-168.3397853	-168.3533012	-168.3568136	-168.3441240	-168.3688073	-168.3759848
31	16	CH_2F_2	-238.7729196	-238.7963993	-238.8027531	-238.7666996	-238.8066792	-238.8181943
32	17	CH_2N_2	-148.5847524	-148.5957539	-148.5985236	-148.5896945	-148.6106165	-148.6165146
33	18	CH_2N_2	-148.5137266	-148.5246159	-148.5271699	-148.5230221	-148.5432055	-148.5488031
34	19	CH_2N_2	-148.5297387	-148.5405454	-148.5432995	-148.5367010	-148.5571489	-148.5629701
35	20	CH_2O	-114.3590645	-114.3685189	-114.3710521	-114.3642083	-114.3816205	-114.3868180
36	22	CH_2O_2	-189.4071032	-189.4234822	-189.4278259	-189.4075667	-189.4375475	-189.4464043
37	23	CH_2O_2	-189.5574278	-189.5735602	-189.5779406	-189.5538120	-189.5835760	-189.5925840
38	25	CH_3F	-139.5921186	-139.6055993	-139.6092097	-139.5974466	-139.6206286	-139.6273880
39	26	CH_3N	-94.4829597	-94.4901648	-94.4919051	-94.4976555	-94.5111511	-94.5149921
40	27	CH_3NO	-169.6851979	-169.6990698	-169.7027156	-169.6889954	-169.7150645	-169.7227871
41	32	CH_4O	-115.5734688	-115.5837339	-115.5864248	-115.5835005	-115.6021702	-115.6079138
42	36	C_2F_2	-275.4737407	-275.4997936	-275.5066541	-275.4644794	-275.5087368	-275.5212027
43	38	C_2HF	-176.3382112	-176.3540330	-176.3581952	-176.3393593	-176.3668216	-176.3745637
44	41	$C_2H_2F_2$	-276.7850970	-276.8111834	-276.8180819	-276.7838831	-276.8286372	-276.8413950
45	42	C_2H_2O	-152.3910338	-152.4031525	-152.4062560	-152.3970943	-152.4196026	-152.4261299
46	43	C_2H_2O	-152.2661291	-152.2786315	-152.2818197	-152.2737906	-152.2966003	-152.3032708
47	44	$C_2H_2O_2$	-227.5445210	-227.5629506	-227.5678221	-227.5472995	-227.5815805	-227.5916414
48	45	C_2H_3F	-177.6077728	-177.6238342	-177.6279992	-177.6183642	-177.6463928	-177.6543994
49	59	C_2N_2	-185.4000066	-185.4125129	-185.4156860	-185.3983333	-185.4224705	-185.4290224
50	67	C_3O_2	-264.3887037	-264.4094802	-264.4149260	-264.3745067	-264.4134026	-264.4246034
51	75	FHO_2	-250.4578174	-250.4814745	-250.4879644	-250.4525347	-250.4942717	-250.5063964
52	76	FH_2N	-155.5690466	-155.5838916	-155.5878669	-155.5699908	-155.5958117	-155.6031785
53	78	FNO	-229.5064573	-229.5263258	-229.5318214	-229.4944002	-229.5300283	-229.5403105
54	80	F_2N_2	-308.7367385	-308.7646857	-308.7720945	-308.7288190	-308.7773988	-308.7909646
55	81	F_2N_2	-308.7342165	-308.7623238	-308.7697843	-308.7264935	-308.7751321	-308.7887173
56	82	F_2O	-274.4347734	-274.4615691	-274.4688817	-274.4256783	-274.4718263	-274.4847838
57	83	F_2O_2	-349.5136752	-349.5466491	-349.5556738	-349.5060732	-349.5637388	-349.5801118
58	86	HNO_2	-205.4956357	-205.5127721	-205.5174163	-205.4902905	-205.5218550	-205.5312508

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#[a)]	#'[a)]	System	VDZ-F12	VTZ-F12	VQZ-F12	VDZ-F12	VTZ-F12	VQZ-F12
59	87	HNO_2	-205.4956335	-205.5127691	-205.5174132	-205.4902895	-205.5218533	-205.5312488
60	88	HNO_2	-205.4912999	-205.5085464	-205.5131864	-205.4782268	-205.5099930	-205.5193680
61	91	H_2N_2	-110.4895168	-110.4979326	-110.4999843	-110.4999549	-110.5156290	-110.5200185
62	93	H_2N_2	-110.4541494	-110.4627475	-110.4649581	-110.4682513	-110.4843466	-110.4889556
63	94	H_2N_2O	-185.6375567	-185.6526023	-185.6565306	-185.6385857	-185.6666196	-185.6747763
64	98	H_3NO	-131.5321499	-131.5441535	-131.5473691	-131.5366212	-131.5582604	-131.5648380
65	99	H_3NO	-131.5718709	-131.5834849	-131.5865721	-131.5764810	-131.5976926	-131.6041071
66	100	H_4N_2	-111.7201719	-111.7294832	-111.7318163	-111.7317084	-111.7490011	-111.7541169
67	102	N_2O	-184.4726820	-184.4868830	-184.4906690	-184.4555952	-184.4821419	-184.4898357
68	103	N_2O_3	-334.6472498	-334.6738866	-334.6811159	-334.6245133	-334.6740662	-334.6886055

[a)] Actual number (#') and number of appearance (#) in Figure 11 of the text and Figure 5 of the ESI, respectively. The systems are listed such as to show the reference ones as the first 6, and TS-18 as the first 18.

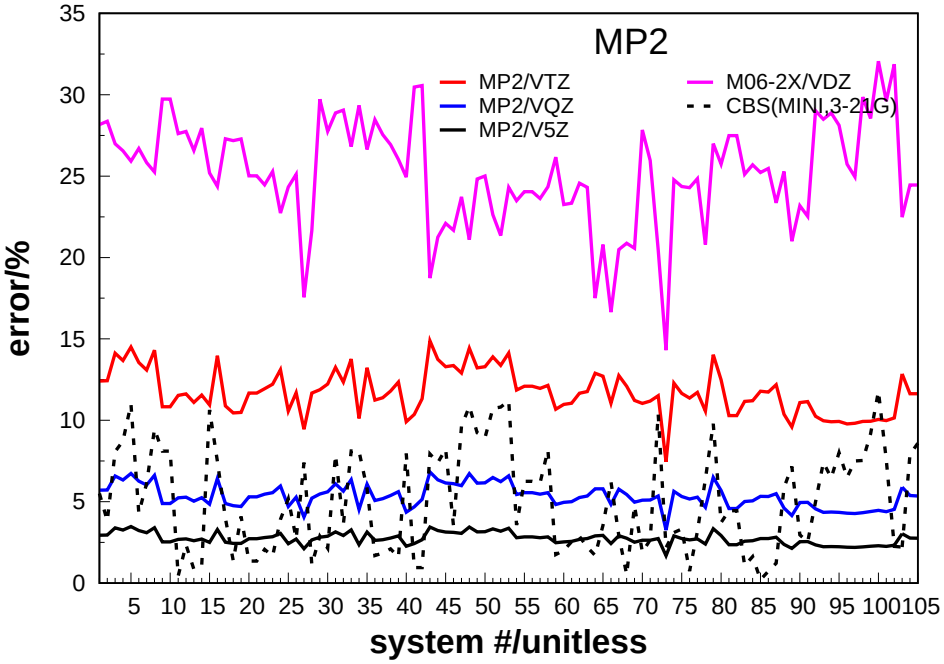

Figure 1: Errors in MP2/CBS(bs_1, bs_2) for the systems of the 106-TS', with bs_i standing for basis set #i; the references are MP2/CBS(5, 6) [CBS(4, 5) where appropriate] energies. Illustrated basis-set pairs are (MINI,bs_2); bs_2=3-21G, 4-31G, VDZ, VTZ.

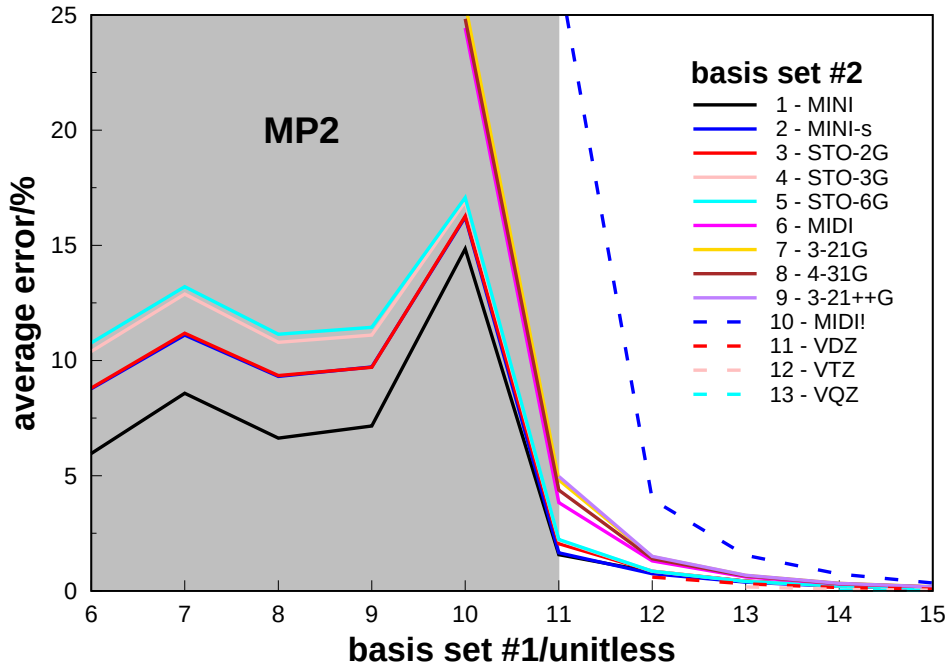

Figure 2: MUE for CCCSD(T)/CBS($\mathrm{bs}_1, \mathrm{bs}_2$). Shaded in grayish is the region where CBS extrapolation uses only subminimal basis sets, while the magenta and blue horizontal lines indicate the average error of VTZ and VQZ energies relative to CBS(4, 5) or CBS(5, 6) values. Shown in yellow is the horizontal line for M06-2X.

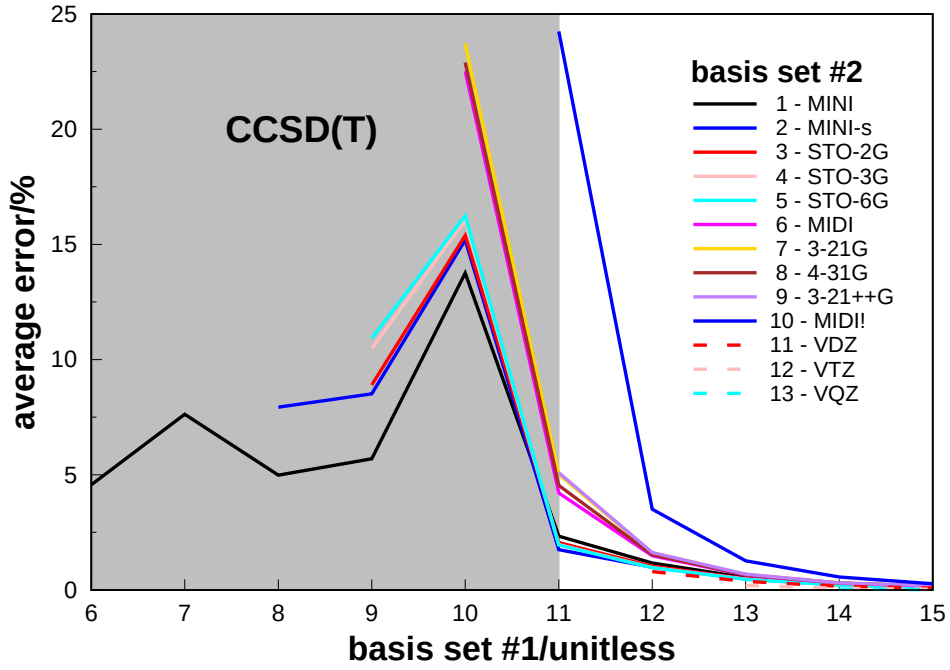

Figure 3: As Figure 2 but for CCSD(T)/CBS.

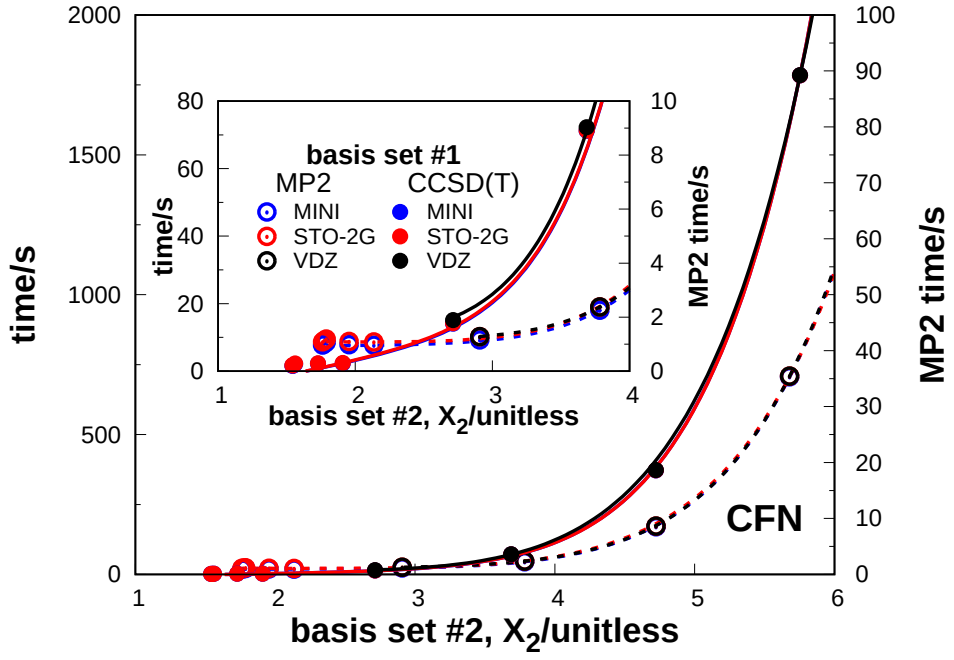

Figure 4: MP2/CBS($\mathrm{bs}_1, \mathrm{bs}_2$) and CCSD(T)/ CBS($\mathrm{bs}_1, \mathrm{bs}_2$) computer times for CFN. Curves are drawn starting at bs_2 (x_2 hierarCHical number): solid lines for CCSD(T), dashed for MP2.

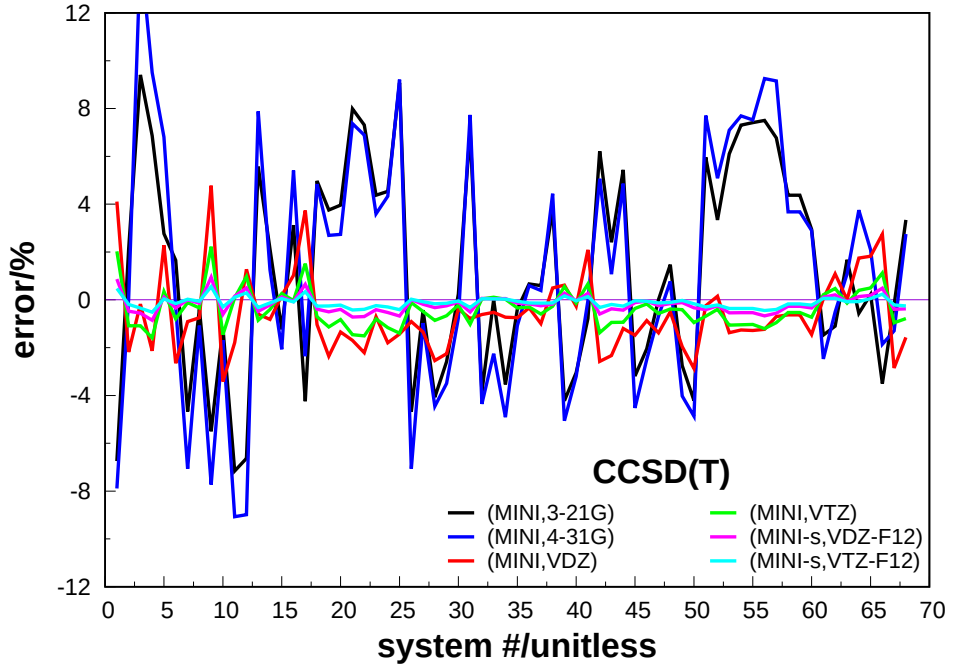

Figure 5: As Figure 11 of the text but for CCSD(T) and the basis-set pairs (MINI,bs_2); bs_2=3-21G, 4-31G, VDZ, VTZ, VDZ-F12, and VTZ-F12; see the text.

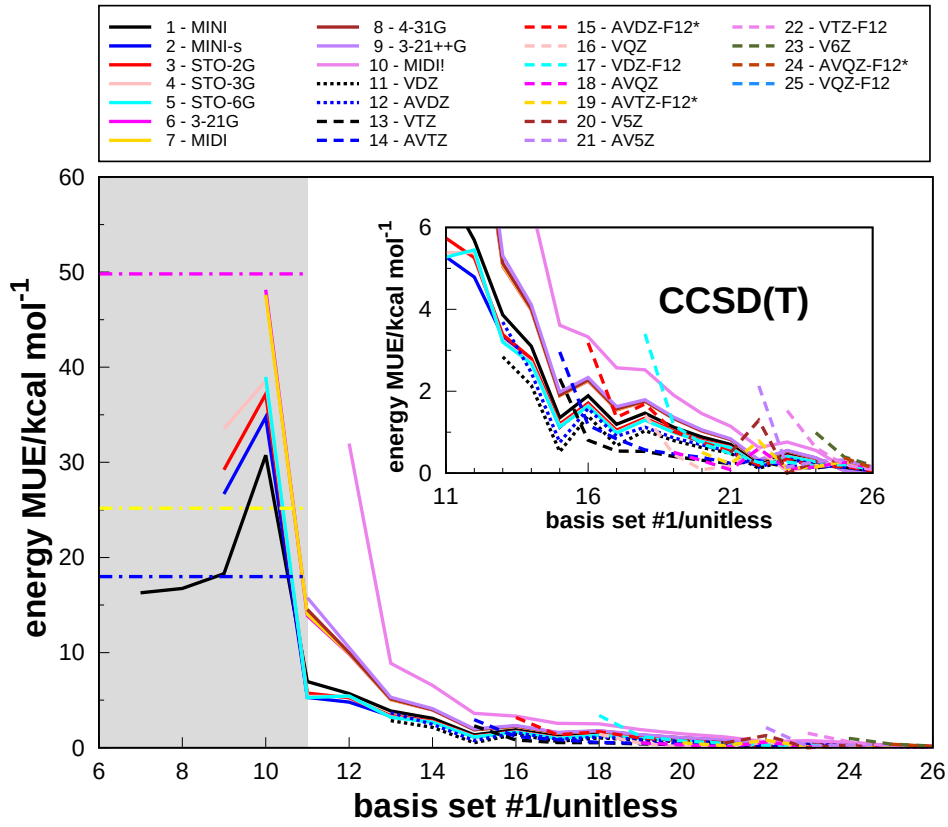

Figure 6: Figure 12 of the text but with legend.

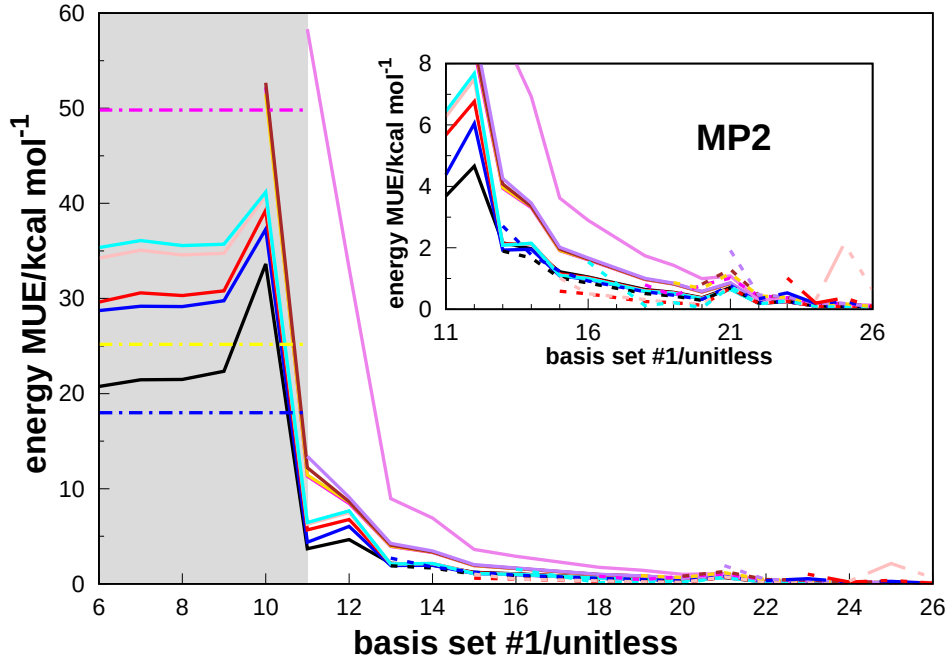

Figure 7: As in Figure 12 of text but for MP2; the references are now CBS(18,20) energies [thence CBS(V5Z,V6Z)].

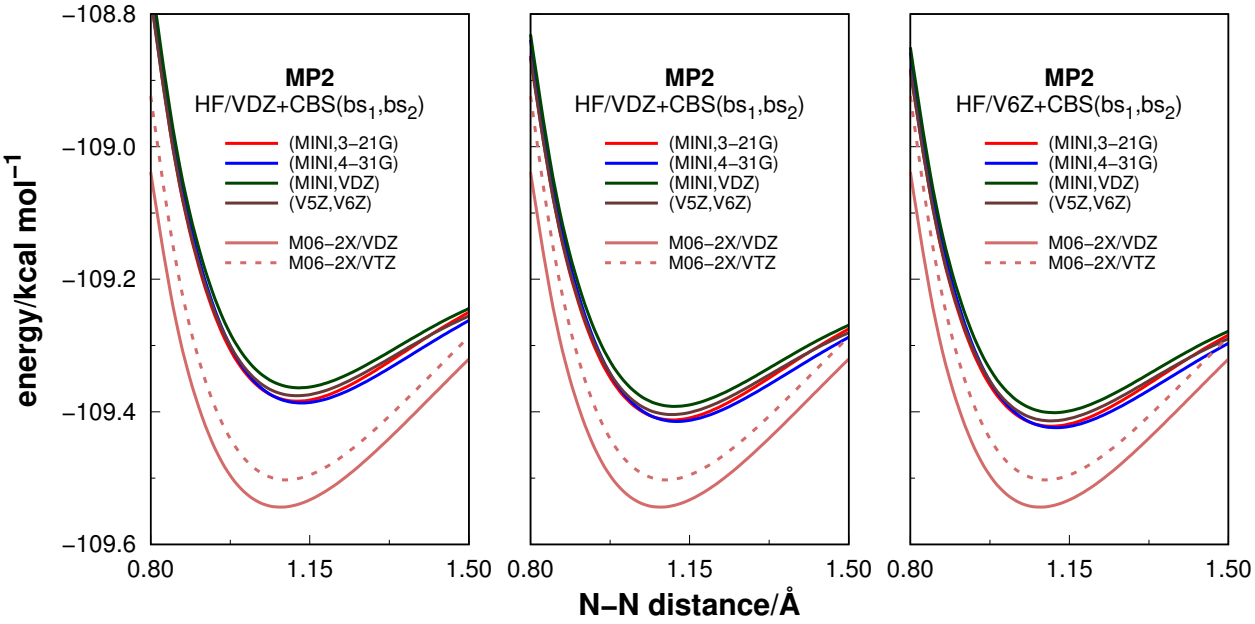

Figure 8: Potential curves for ground-state N_2 obtained by adding correlation energies at various MP2/CBS(bs_1, bs_2) levels of theory to raw HF curves calculated with VDZ, VTZ, and V6Z basis sets. See the text.