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

SUPLEMENTARY INFORMATION

Post-complete-basis-set extrapolation of conventional and explicitly correlated coupled-cluster energies: can the convergence to CBS limit be diagnosed?

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Table 1: Systems in A24

# in A24	Formula	Name	# in A24 + TS-106
1	$NH_3 \cdots H_2O$	Ammonia-water	1
2	$(H_2O)_2$	Water dimer	2
3	$(HCN)_2$	Hydrgen-cyanide dimer	3
4	$(HF)_2$	Hydrogen fluoride dimer	4

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# in A24	Formula	Name	# in A24 + TS-106
5	$(NH_3)_2$	Ammonia dimer	5
6	$CH_4 \cdots HF$	Methane-HF	6
7	$CH_4 \cdots NH_3$	Methane-ammonia	7
8	$CH_4 \cdots H_2O$	Methane-water	8
9	$(CH_2O)_2$	Formaldehyde dimer	9
10	$H_2O \cdots C_2H_4$	Water-ethene	10
11	$CH_2O \cdots C_2H_4$	Formaldehyde-ethene	11
12	$(C_2H_2)_2$	Ethyne dimer	12
13	$NH_3 \cdots C_2H_4$	Ammonia-ethene	13
14	$(C_2H_4)_2$	Ethene dimer	14
15	$CH_4 \cdots C_2H_4$	Methane-ethene	15
16	$BH_3 \cdots CH_4$	Borane-methane	16
17	$CH_4 \cdots C_2H_6$	Methane-ethane	17
18	$CH_4 \cdots C_2H_6$	Methane-ethane	18
19	$(CH_4)_2$	Methane dimer	19
20	$CH_4 \cdots Ar$	Methane-Ar	20
21	$C_4H_4 \cdots Ar$	Ethene-Ar	21
22	$C_2H_4 \cdots C_2H_2$	Ethene-ethyne	22
23	$(C_2H_4)_2$	Ethene dimer	23
24	$(C_2H_2)_2$	Ethyne dimer	24

Table 2: Systems in TS-106

# in TS-106	Formula	Name	# in A24 + TS-106
1	CFN	Cyanogen fluoride	25
2	CFN	Isocyanogen fluoride	26
3	CF_2	Singlet difluoromethylene	27
4	CF_2O	Carbonyl fluoride	28
5	CF_4	Tetrafluoromethane	29
6	CHF	Singlet fluoromethylene	30
7	CHFO	Formyl fluoride	31
8	CHF_3	Trifluoromethane	32
9	CHN	Hydrogen cyanide	33
10	CHN	Hydrogen isocyanide	34
11	CHNO	Cyanic acid	35
12	CHNO	Isocyanic acid	36
13	CHNO	Formonitrile oxide	37
14	CHNO	Isofulminic acid	38
15	CH_2	Singlet methylene	39
16	CH_2F_2	Difluoromethane	40
17	CH_2N_2	Cyanamide	41
18	CH_2N_2	3H-Diazirine	42
19	CH_2N_2	Diazomethane	43
20	CH_2O	Formaldehyde	44
21	CH_2O	Hydroxymethylene	45
22	CH_2O_2	Dioxirane	46
23	CH_2O_2	Formic acid	47
24	CH_2O_3	Performic acid*	48

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# in TS-106	Formula	Name	# in A24 + TS-106
25	CH_3F	Fluoromethane	49
26	CH_3N	Methanimine	50
27	CH_3NO	Formamide	51
28	CH_3NO_2	Methyl nitrite*	52
29	CH_3NO_2	Nitromethane*	53
30	CH_4	Methane	54
31	CH_4N_2O	Urea*	55
32	CH_4O	Methanol	56
33	CH_5N	Methylamine*	57
34	CO	Carbon monoxide	58
35	CO_2	Carbon dioxide	59
36	C_2F_2	Difluoroacetylene	60
37	C_2F_4	Tetrafluoroethylene*	61
38	C_2HF	Fluoroacetylene	62
39	C_2HF_3	Trifluoroethylene	63
40	C_2H_2	Acetylene	64
41	$C_2H_2F_2$	1,1-Difluoroethylene	65
42	C_2H_2O	Ketene	66
43	C_2H_2O	Oxirene	67
44	$C_2H_2O_2$	Glyoxal	68
45	C_2H_3F	Fluoroethylene	69
46	C_2H_3FO	Acetyl fluoride*	70
47	C_2H_3N	Acetonitrile*	71
48	C_2H_3N	Methyl isocyanide*	72

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# in TS-106	Formula	Name	# in A24 + TS-106
49	C_2H_4	Ethylene	73
50	C_2H_4O	Acetaldehyde*	74
51	C_2H_4O	Oxirane*	75
52	$C_2H_4O_2$	Acetic acid*	76
53	$C_2H_4O_2$	Methyl formate*	77
54	C_2H_5F	Fluoroethane*	78
55	C_2H_5N	Aziridine*	79
56	C_2H_6	Ethane*	80
57	C_2H_6O	Dimethyl ether*	81
58	C_2H_6O	Ethanol*	82
59	C_2N_2	Cyanogen	83
60	C_3H_3N	Acrylonitrile*	84
61	C_3H_4	Allene*	85
62	C_3H_4	Cyclopropene*	86
63	C_3H_4	Propyne*	87
64	C_3H_6	Cyclopropane*	88
65	C_3H_6	Propene*	89
66	C_3H_8	Propane*	90
67	C_3O_2	Carbon suboxide	91
68	C_4H_4	Butatriene*	92
69	C_4H_4	Cyclobutadiene*	93
70	C_4H_4	Tetrahedran*	94
71	C_4H_4	Vinylacetylene*	95
72	C_4N_2	Dicyanoacetylene*	96

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# in TS-106	Formula	Name	# in A24 + TS-106
73	FH	Hydrogen fluoride	97
74	FHO	Hypofluorous acid	98
75	FHO_2	Fluoroperoxide	99
76	FH_2N	Monofluoroamine	100
77	FH_3N_2	Fluorohydrazine*	101
78	FNO	Nitrosyl fluoride	102
79	F_2	Difluorine	103
80	F_2N_2	Difluorodiazene (cis)	104
81	F_2N_2	Difluorodiazene (trans)	105
82	F_2O	Difluorine monoxide	106
83	F_2O_2	Perfluoroperoxide	107
84	F_3N	Trifluoroamine	108
85	HNO	Nitrosylhydride	109
86	HNO_2	Nitrous acid (cis)	110
87	HNO_2	Nitrous acid (trans)	111
88	HNO_2	Nitrous acid	112
89	HNO_3	Nitric acid	113
90	HN_3	Hydrogen azide	114
91	H_2N_2	Diazene (cis)	115
92	H_2N_2	Diazene (trans)	116
93	H_2N_2	Diazene (iso)	117
94	H_2N_2O	Nitrosamide	118
95	H_2O	Water	119
96	H_2O_2	Hydrogen peroxide	120

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# in TS-106	Formula	Name	# in A24 + TS-106
97	H_3N	Ammonia	121
98	H_3NO	Ammonia oxide	122
99	H_3NO	Hydroxylamine	123
100	H_4N_2	Hydrazine	124
101	N_2	Dinitrogen	125
102	N_2O	Nitrous oxide	126
103	N_2O_3	Dinitrogen trioxide*	127
104	N_2O_4	Dinitrogen tetraoxide*	128
105	O_3	Ozone	129
106	H_2	Dihydrogen	130

Table 3: CBS extrapolated CCSD(T) correlation energies[a)] for linear HCN$\cdots$HCN, HF dimer, ethyne dimer (T-shaped), and Ar-methane (systems #3, #4, #12 and #20 in A24, respectively) at their optimized CCSD(T) equilibrium geometries[b)] and separated-monomers[c)].

	HCN dimer			HF dimer		
CBS ext. pair	$E_e^{cord)}$	$E_\infty^{core)}$	$D_e^{corf)}$	$E_e^{cord)}$	$E_\infty^{core)}$	$D_e^{corf)}$
CCSD(T)						
(d,t)	−0.8013002	−0.8001526	−0.720	−0.6370521	−0.6353949	−1.040
(d,q)	−0.8008283	−0.7997567	−0.672	−0.6415298	−0.6400659	−0.919
(t,q)	−0.8006320	−0.7995920	−0.653	−0.6433931	−0.6420095	−0.868
$(d,5)$	−0.8004848	−0.7994604	−0.643	−0.6438361	−0.6424731	−0.855
$(t,5)$	−0.8003688	−0.7993620	−0.632	−0.6448007	−0.6434795	−0.829
$(q,5)$	−0.8002322	−0.7992425	−0.621	−0.6455313	−0.6442425	−0.809
$(d,6)$	−0.8004195	−0.7993834	−0.650	−0.6445631	−0.6432336	−0.834
$(t,6)$	−0.8003588	−0.7993305	−0.645	−0.6450801	−0.6437732	−0.820
$(q,6)$	−0.8003047	−0.7992786	−0.644	−0.6454145	−0.6441227	−0.810
$(5,6)$	−0.8003495	−0.7993009	−0.658	−0.6453423	−0.6440488	−0.812
$\langle CBS(x,6)\rangle^{g)}$	−0.8003581	−0.7993234	−0.649	−0.6451000	−0.6437946	−0.819
pCBS	−0.8003676	−0.7993702	−0.626	−0.6459013	−0.6446260	−0.800
CCSD(T)-F12a						
(d,t)	−0.7973798	−0.7963312	−0.658	−0.6465005	−0.6451507	−0.847
(d,q)	−0.7993468	−0.7983000	−0.657	−0.6456660	−0.6443392	−0.833
(t,q)	−0.7998818	−0.7988355	−0.657	−0.6454390	−0.6441185	−0.829
$(d,5)$	−0.7996664	−0.7986118	−0.662	−0.6459074	−0.6445936	−0.824
$(t,5)$	−0.7998355	−0.7987805	−0.662	−0.6458635	−0.6445524	−0.823
$(q,5)$	−0.7998182	−0.7987599	−0.664	−0.6460220	−0.6447145	−0.820
pCBS	−0.8005017	−0.7994560	−0.656	−0.6451760	−0.6438627	−0.824
CCSD(T)-F12b						
(d,t)	−0.8002632	−0.7992189	−0.655	−0.6465997	−0.6452436	−0.851
(d,q)	−0.8001146	−0.7990744	−0.653	−0.6461354	−0.6448106	−0.831
(t,q)	−0.8000742	−0.7990351	−0.652	−0.6460091	−0.6446928	−0.826
$(d,5)$	−0.7998983	−0.7988437	−0.662	−0.6460217	−0.6447025	−0.828
$(t,5)$	−0.7998713	−0.7988160	−0.662	−0.6459789	−0.6446624	−0.810
$(q,5)$	−0.7997956	−0.7987341	−0.666	−0.6459676	−0.6446511	−0.810
pCBS	−0.8000274	−0.7989896	−0.651	−0.6458628	−0.6445563	−0.810
	C_2H_2 dimer (C_{2v})			Ar-methane		
CBS ext. pair	$E_e^{cord)}$	$E_\infty^{core)}$	$D_e^{corf)}$	$E_e^{cord)}$	$E_\infty^{core)}$	$D_e^{corf)}$
CCSD(T)						
(d,t)	−0.7359935	−0.7344587	−0.963	−0.5143765	−0.5135106	−0.543
(d,q)	−0.7338925	−0.7322838	−1.010	−0.5139311	−0.5130278	−0.567
(t,q)	−0.7330182	−0.7313787	−1.029	−0.5130428	−0.5120820	−0.603
$(d,5)$	−0.7325314	−0.7309106	−1.017	−0.5141176	−0.5131458	−0.643
$(t,5)$	−0.7320392	−0.7304061	−1.025	−0.5137458	−0.5128270	−0.610
$(q,5)$	−0.7315310	−0.7299013	−1.023	−0.5128532	−0.5118789	−0.611
$(d,6)$	−0.7321145	−0.7304842	−1.023	−0.5140997	−0.5131207	−0.614
$(t,6)$	−0.7318475	−0.7302106	−1.027	−0.5123899	−0.5113868	−0.629
$(q,6)$	−0.7316155	−0.7299791	−1.027	−0.5141699	−0.5131789	−0.621
$(5,6)$	−0.7316676	−0.7300272	−1.029	−0.5152695	−0.5142860	−0.617
$\langle CBS(x,6)\rangle^{g)}$	−0.7318113	−0.7301753	−1.027	−0.5144142	−0.5134329	−0.616
pCBS	−0.7318413	−0.7301604	−1.055	−0.5134963	−0.5125565	−0.590
CCSD(T)-F12a						
(d,t)	−0.7286123	−0.7268782	−1.088	−0.5132348	−0.5122754	−0.602
(d,q)	−0.7305188	−0.7288844	−1.026	−0.5141489	−0.5131788	−0.609
(t,q)	−0.7307085	−0.7290787	−1.023	−0.5142002	−0.5132201	−0.615
$(d,5)$	−0.7310374	−0.7294302	−1.009	−0.5143976	−0.5134246	−0.610
$(t,5)$	−0.7308636	−0.7292415	−1.018	−0.5142716	−0.5132900	−0.616
$(q,5)$	−0.7307986	−0.7291710	−1.021	−0.5142246	−0.5132397	−0.618
pCBS	−0.7316382	−0.7300623	−0.989	−0.5146856	−0.5137092	−0.613
CCSD(T)-F12b						
(d,t)	−0.7313294	−0.7296198	−1.073	−0.5132713	−0.5123008	−0.609
(d,q)	−0.7311866	−0.7295546	−1.024	−0.5142654	−0.5132955	−0.609
(t,q)	−0.7309066	−0.7292769	−1.023	−0.5142256	−0.5132446	−0.616
$(d,5)$	−0.7311478	−0.7295369	−1.011	−0.5145358	−0.5135661	−0.608
$(t,5)$	−0.7308753	−0.7292515	−1.019	−0.5142962	−0.5133144	−0.616
$(q,5)$	−0.7307736	−0.7291449	−1.022	−0.5142068	−0.5132204	−0.619
pCBS	−0.7311028	−0.7295164	−0.996	−0.5148490	−0.5138796	−0.608

[a)] Energies in E_h, except for D_e^{cor} that are in kcal mol^{-1}. [b)] All optimizations employed a VTZ basis set, except for the HF dimer where a VQZ basis set was employed (see Figures 1 and 2 of this SI). Optimized distances (in) for the HCN dimer are $R_{HC}=1.0679$, $R_{CN}=1.1584$, $R_{NH}=2.2138$, $R_{HC}=1.0728$, and $R_{CN}=1.1606$; the valence angles were constrained at 0 deg, and the dihedrals at 180 deg. For $(HF)_2$, the geometry has been fully optimized, with the dimer broken apart keeping all but one (the nearest distance from H of one monomer to the F of the other) coordinates frozen at the equilibrium values. For the C_2H_2 dimer, the T-shaped equilibrium geometry was fully optimized at CCSD(T)/VTZ level. For Ar-methane, the only optimized coordinates were $R_{CH_i}=1.0890$ ($i=1-4$) and $R_{CO}=3.5882$, with the angles inactive at their values in A24. [c)] The monomers were considered as separated when distant apart by 10^3. [d)] Correlation energy at equilibrium. [e)] Correlation energy for separated monomers. [f)] Dissociation energy. [g)] Average value, see text.

```
xyz coordinates and vibrational frequencies for the HF dimer at its optimized geometry
and CCSD(T)/VQZ level of theory:

    4
 RCCSD(T)/VQZ  ENERGY=-200.75416677
 H           0.0000000000        0.0000000000        0.0000000000
 F           0.0000000000        0.0000000000        0.9194848541
 H           0.0000000000        1.6749342253        1.6260755440
 F           0.0063728969        2.5783749829        1.8091273760


   Low Vibration      Wavenumber
        Nr             [1/cm]
        1               0.00
        2               0.00
        3               0.00
        4               0.00
        5               0.00
        6               0.00

     Vibration        Wavenumber
        Nr             [1/cm]
        1              161.53
        2              217.53
        3              471.02
        4              579.61
        5             4048.26
        6             4120.28
```

Figure 1: The HF dimer at its optimized geometry and CCSD(T)/VQZ level of theory

xyz coordinates and vibrational frequencies for the ethyne dimer at its optimized geometry at CCSD(T)/VTZ level of theory:

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   8
RCCSD(T)/VTZ  ENERGY=-154.37763758
C          0.0000000000        0.0000000000        0.0000000000
H          0.0000000000        0.0000000000        1.0642250961
C          0.0000000000        0.0007225296       -1.2104815698
H          0.0001288060        0.0017780842       -2.2746985231
C         -1.9685941093       -3.2216710162       -0.6405744488
H         -1.4134749593       -2.3121314488       -0.6165865682
C         -2.5991624530       -4.2547554471       -0.6677846183
H         -3.1529935381       -5.1624474241       -0.6918492403

  Low Vibration      Wavenumber
       Nr             [1/cm]
        1               0.00
        2               0.00
        3               0.00
        4               0.00
        5               0.00
        6               0.00
        7              42.11

    Vibration        Wavenumber
       Nr             [1/cm]
        1              60.27
        2              70.46
        3             104.80
        4             573.15
        5             578.64
        6             585.06
        7             595.88
        8             745.10
        9             752.38
       10             761.25
       11             774.60
       12            1993.75
       13            1996.36
       14            3393.35
       15            3404.80
       16            3499.23
       17            3504.63
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Figure 2: The ethyne dimer at its optimized geometry and CCSD(T)/VQZ level of theory