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


# SUPLEMENTARY INFORMATION

# Canonical and explicitly-correlated coupled cluster correlation energies of sub-kJ/mol accuracy via cost-effective hybrid-post-CBS extrapolation

A.J.C. Varandas*,†,‡,¶

†*Department of Physics, Qufu Normal University, China*

‡*Department of Physics, Universidade Federal do Espírito Santo, 29075-910 Vitória, Brazil*

¶*Department of Chemistry, and Chemistry Centre, University of Coimbra, 3004-535 Coimbra, Portugal*

E-mail: varandas@uc.pt

Table 1: 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 |

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| # in TS-106 | Formula | Name | # in A24 + TS-106 |
|---|---|---|---|
| 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 |
| 25 | $CH_3F$ | Fluoromethane | 49 |
| 26 | $CH_3N$ | Methanimine | 50 |
| 27 | $CH_3NO$ | Formamide | 51 |
| 28 | $CH_3NO_2$ | Methyl nitrite* | 52 |

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| # in TS-106 | Formula | Name | # in A24 + TS-106 |
|---|---|---|---|
| 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 |
| 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 |

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| # in TS-106 | Formula | Name | # in A24 + TS-106 |
|---|---|---|---|
| 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 |
| 73 | FH | Hydrogen fluoride | 97 |
| 74 | FHO | Hypofluorous acid | 98 |
| 75 | $FHO_2$ | Fluoroperoxide | 99 |
| 76 | $FH_2N$ | Monofluoroamine | 100 |

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| # in TS-106 | Formula | Name | # in A24 + TS-106 |
|---|---|---|---|
| 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 |
| 97 | $H_3N$ | Ammonia | 121 |
| 98 | $H_3NO$ | Ammonia oxide | 122 |
| 99 | $H_3NO$ | Hydroxylamine | 123 |
| 100 | $H_4N_2$ | Hydrazine | 124 |

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| # in TS-106 | Formula | Name | # in A24 + TS-106 |
|---|---|---|---|
| 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 |

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

Table 2: CBS extrapolated PNO-LCCSD(T)/V$X$Z 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] limit.

| | HCN dimer | | | HF dimer | | |
|---|---|---|---|---|---|---|
| CBS ext. pair | $E_e^{\mathrm{cor}}$[d] | $E_\infty^{\mathrm{core}}$[e] | $D_e^{\mathrm{cor}}$[f] | $E_e^{\mathrm{cor}}$[d] | $E_\infty^{\mathrm{core}}$[e] | $D_e^{\mathrm{cor}}$[f] |
| CCSD(T) | | | | | | |
| $(d,t)$ | −0.80230164 | −0.80117666 | −0.706 | −0.63737814 | −0.63613851 | −0.778 |
| $(d,q)$ | −0.80143966 | −0.80039410 | −0.656 | −0.64186294 | −0.64057387 | −0.809 |
| $(t,q)$ | −0.80108098 | −0.80006846 | −0.635 | −0.64407563 | −0.64241951 | −0.822 |
| $(d,5)$ | −0.80088421 | −0.79987557 | −0.633 | −0.64372915 | −0.64281505 | −0.791 |
| $(t,5)$ | −0.80068268 | −0.79969057 | −0.623 | −0.64502791 | −0.64376435 | −0.793 |
| $(q,5)$ | −0.80047594 | −0.79949443 | −0.616 | −0.64570203 | −0.64446238 | −0.778 |
| pCBS[g] | −0.80059817 | −0.79963014 | −0.607 | −0.64624114 | −0.64490381 | −0.839 |
| pCBS[h] | −0.8003676 | −0.7993702 | −0.626 | −0.6459013 | −0.6446260 | −0.800 |
| CCSD(T)-F12b | | | | | | |
| $(d,t)$ | −0.79964694 | −0.79866528 | −0.616 | −0.64351886 | −0.64211475 | −0.881 |
| $(d,q)$ | −0.79855259 | −0.79751559 | −0.651 | −0.64377769 | −0.64236484 | −0.887 |
| $(t,q)$ | −0.79825489 | −0.79720283 | −0.660 | −0.64384810 | −0.64243287 | −0.888 |
| pCBS[i] | −0.79791029 | −0.79684080 | −0.671 | −0.64392960 | −0.64251162 | −0.890 |
| pCBS[j] | −0.8000274 | −0.7989896 | −0.651 | −0.6458628 | −0.6445563 | −0.810 |
| h-pCBS$(dt,dt)$ | −0.79928143 | −0.79831951 | −0.604 | −0.64436433 | −0.64293757 | −0.895 |
| h-pCBS$(dt,tq)$ | −0.79841908 | −0.79738522 | −0.649 | −0.64400559 | −0.64258657 | −0.890 |
| | $C_2H_2$ dimer ($C_{2v}$) | | | Ar-methane | | |
| CBS ext. pair | $E_e^{\mathrm{cor}}$[d] | $E_\infty^{\mathrm{core}}$[e] | $D_e^{\mathrm{cor}}$[f] | $E_e^{\mathrm{cor}}$[d] | $E_\infty^{\mathrm{core}}$[e] | $D_e^{\mathrm{cor}}$[f] |
| CCSD(T) | | | | | | |
| $(d,t)$ | −0.73667232 | −0.73523741 | −0.900 | −0.51476205 | −0.51420012 | −0.353 |
| $(d,q)$ | −0.73437935 | −0.73283454 | −0.969 | −0.51451643 | −0.51387710 | −0.401 |
| $(t,q)$ | −0.73287815 | −0.73127895 | −1.004 | −0.51441422 | −0.51374269 | −0.421 |
| $(d,5)$ | −0.73342520 | −0.73183466 | −0.998 | −0.51342741 | −0.51259286 | −0.524 |
| $(t,5)$ | −0.73233868 | −0.73071612 | −1.018 | −0.51323764 | −0.51236433 | −0.548 |
| $(q,5)$ | −0.73177472 | −0.73013555 | −1.023 | −0.51262695 | −0.51164890 | −0.614 |
| pCBS[g] | −0.73214088 | −0.73048878 | −1.037 | −0.51427665 | −0.51356176 | −0.449 |
| pCBS[h] | −0.7318413 | −0.7301604 | −1.055 | −0.5134963 | −0.5125565 | −0.590 |
| CCSD(T)-F12b | | | | | | |
| $(d,t)$ | −0.73061866 | −0.72897963 | −1.028 | −0.51351496 | −0.51313920 | −0.236 |
| $(d,q)$ | −0.72932376 | −0.72771873 | −1.007 | −0.51271739 | −0.51183231 | −0.555 |
| $(t,q)$ | −0.72897150 | −0.72737572 | −1.001 | −0.51250042 | −0.51147679 | −0.642 |
| pCBS[i] | −0.72856375 | −0.72697867 | −0.995 | −0.51224927 | −0.51106526 | −0.743 |
| pCBS[j] | −0.7311028 | −0.7295164 | −0.996 | −0.5148490 | −0.5138796 | −0.608 |
| h-pCBS$(dt,dt)$ | −0.72978518 | −0.72811804 | −1.046 | −0.51334326 | −0.51299313 | −0.220 |
| h-pCBS$(dt,tq)$ | −0.72906207 | −0.72745098 | −1.011 | −0.51264458 | −0.51174799 | −0.563 |

[a] Energies in hartree ($E_h$), except for $D_e^{\mathrm{cor}}$ that are in kcal mol$^{-1}$. [b] Ref. 1 [c] Separated monomers.[1] [d] Correlation energy at equilibrium. [e] Correlation energy for separated monomers. [f] Dissociation energy. [g] Using only PNO-LCCSD(T) energies. [h] See this work, Table 2. [i] Using only PNO-LCCSD(T)-F12b energies.

# References

(1) A. J. C. Varandas, Phys. Chem. Chem. Phys. (submitted for publication), 0 (2020).