Supplementary Material for:

Comparing counterpoise-corrected, uncorrected, and averaged binding energies in benchmarking noncovalent interactions

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Electronic Energies

- Interaction energies are derived from electronic energy terms stored in file `electronic_energies.tar` . Each file therein contains bimolecular complex and monomer energies for certain bimolecular complexes and computation types, which can be decoded through the `README` file, reproduced below.

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FILE LABEL GUIDES
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A24             A24 database, used in Figs. 2--6
MISC            extra systems discussed in text, plotted in SI
   NCCN2_PD is the parallel displaced orientation of cyanogen dimer
   NBC1-BzBz_S-3.9 is the sandwich orientation of benzene dimer at equilibrium (3.9 A) separation
   S22-3 is formic acid dimer
S22 is the S22 database, used in Figs. 5 & 6

CCSDTcorl       CCSD(T) correlation energies
MP2corl         MP2 correlation energies
SCFtot          HF total energies
DFMP2corl       DF-MP2 correlation energies
DFSCFtot        DF-HF total energies

CP              counterpoise-corrected monomers
unCP            non-counterpoise-corrected monomers

aXz             aug-cc-pVXZ basis set, X = d, t, q, 5, 6
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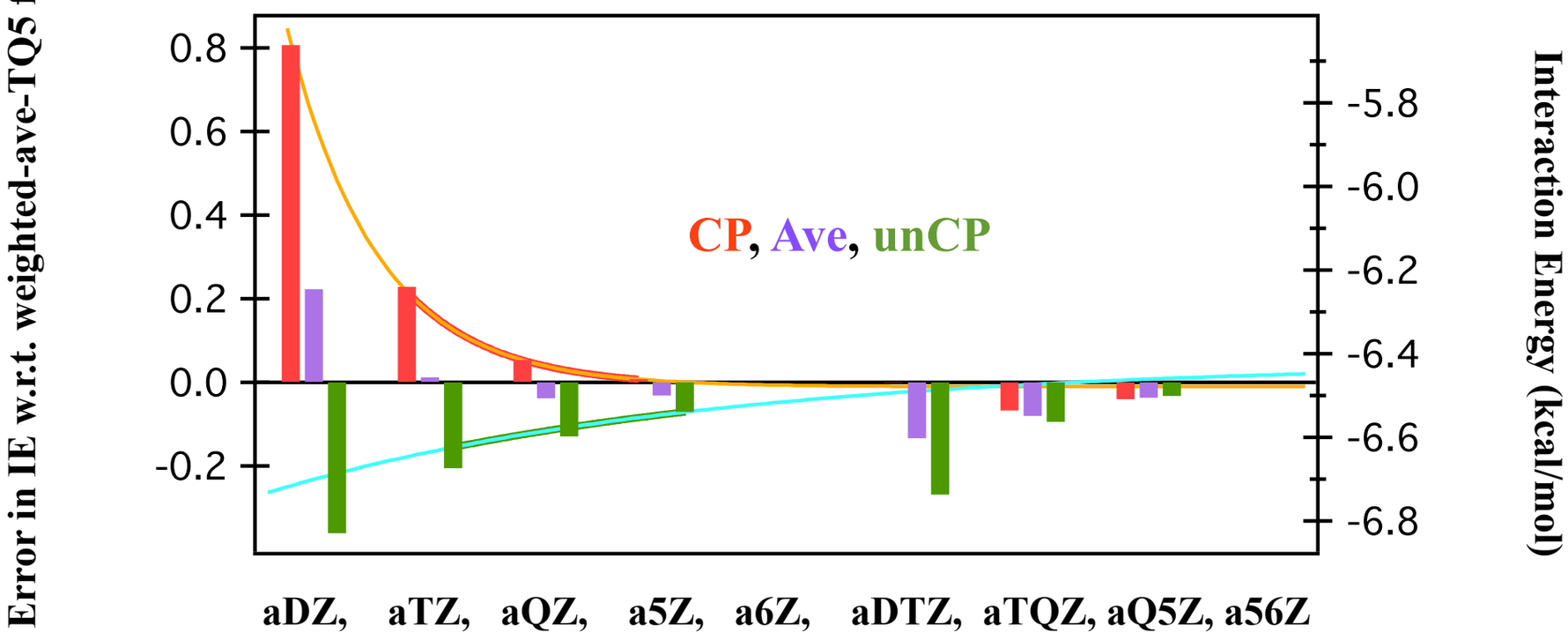
Example Figure for Basis Set Convergence of IE



- Figures such as these are presented on the next pages for CCSD(T) interaction energies (IE), MP2 IE, and delta CCSD(T) terms for misc. systems (formic acid dimer, cyanogen dimer, and benzene dimer) and for the A24 database.
- In a plot such as this, CP (red), Ave (purple), and unCP (green) IE for a given basis set are plotted adjacent to one another. Read off the right axis for the IE value. Read off the left axis for the error in IE w.r.t. the reference. Usually, the reference is a (CP/unCP) weighted average of the CBS limit as obtained by fitting (orange and turquoise traces) the three highest aXZ basis sets to an exponential function (see text for details of procedure and following slide for actual values for A24).
- Basis sets run along the bottom axis: aDZ–a6Z, then aDTZ–a56Z. The latter use the SCF of the larger basis.
- Some figures may look outright wrong, such as the above plot where the unCP IE value for MP2/aDTZ looks wrong as an extrapolation of aDZ and aTZ values. Here, the aDZ is atop a HF/aDZ SCF and so displays a weaker IE than atop the HF/aTZ reference employed in the aDTZ extrapolation procedure.
- Magnitude of BSSE is span between the extremes of the red and green bars.

A24 Reference IE

$$E_{X,\mathrm{CP}}^{\mathrm{corl}} = E_{\mathrm{CBS,CP}}^{\mathrm{corl}} + Ae^{-\alpha_{\mathrm{CP}}X};\ X = TQ5 \text{ or } Q56$$

$$E_{X,\mathrm{unCP}}^{\mathrm{corl}} = E_{\mathrm{CBS,unCP}}^{\mathrm{corl}} + Ae^{-\alpha_{\mathrm{unCP}}X};\ X = TQ5 \text{ or } Q56$$

$$E_{\mathrm{Ref}} = \left(\left(E_{\mathrm{CBS,CP}}^{\mathrm{corl}} + E_{\mathrm{SCF/aXZ,CP}}\right)\cdot\alpha_{\mathrm{CP}} + \left(E_{\mathrm{CBS,unCP}}^{\mathrm{corl}} + E_{\mathrm{SCF/aXZ,unCP}}\right)\cdot\alpha_{\mathrm{unCP}}\right)\Big/\left(\alpha_{\mathrm{CP}} + \alpha_{\mathrm{unCP}}\right);\ X = 5 \text{ or } 6$$

A24-1	-6.502
A24-2	-5.007
A24-3	-4.758
A24-4	-4.569
A24-5	-3.141
A24-6	-1.633
A24-7	-0.761
A24-8	-0.669
A24-9	-4.520
A24-10	-2.560
A24-11	-1.618
A24-12	-1.520
A24-13	-1.376
A24-14	-1.088
A24-15	-0.505
A24-16	-1.484
A24-17	-0.831
A24-18	-0.610
A24-19	-0.534
A24-20	-0.397
A24-21	-0.347
A24-22	0.835
A24-23	0.945
A24-24	1.131

To obtain an unbiased reference, CP and unCP IE basis set series are independently fitted to an exponential form with the highest three zeta basis sets available (TQ5 or Q56), noting both the extrpolated IE limit and the decay rate toward that limit (E_CBS and alpha). The final reference IE is the weighted average of the former with weights supplied by the latter.

Basis Convergence of CCSD(T)/aXZ for A24

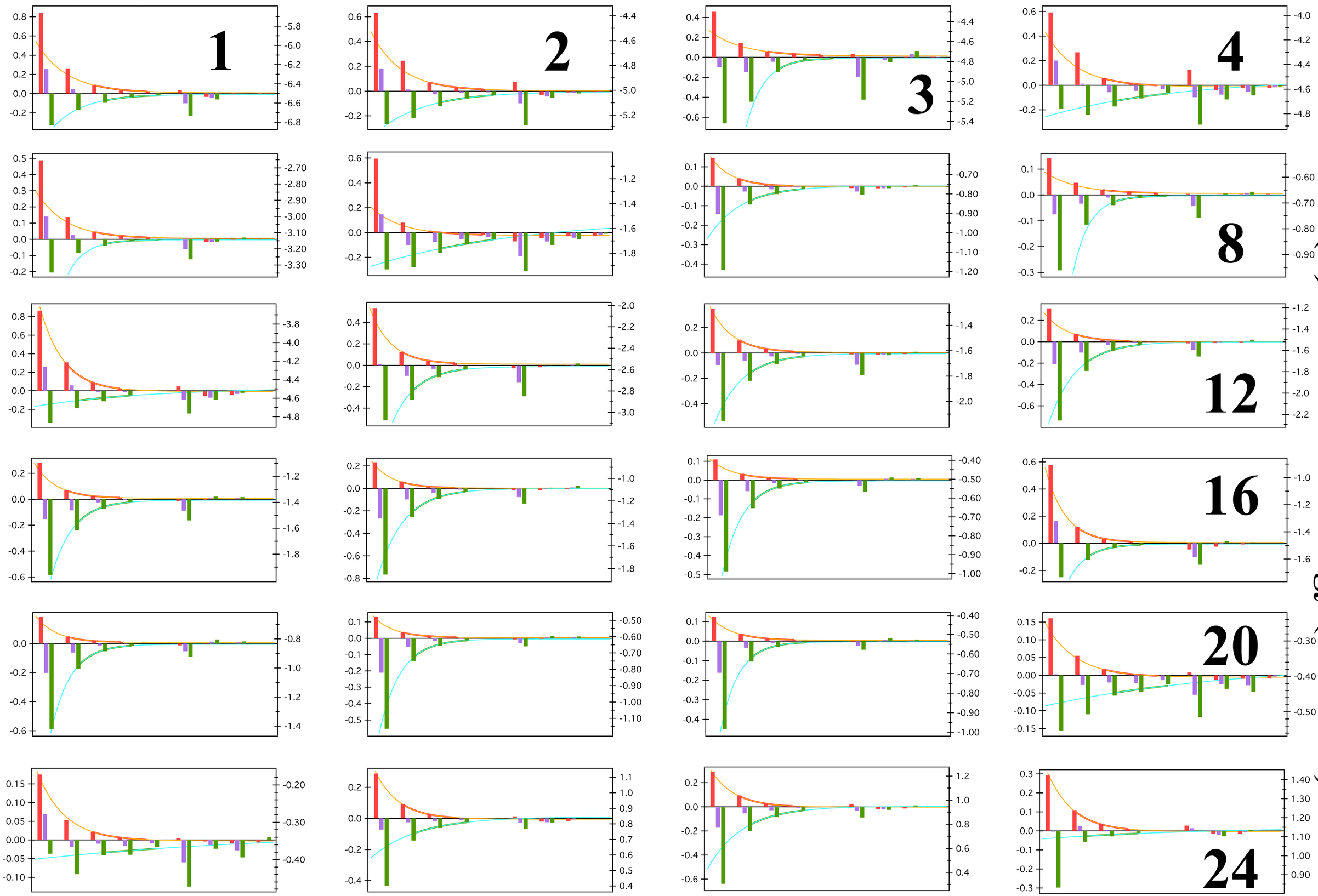
CP, **Ave**, **unCP**

CP-weighted-ave of 3-basis fit)

Error in IE w.r.t. Ref (CP/un

CCSD(T) Interacti

on Energy (kcal/mol)



(each graph) Basis Set: aDZ, aTZ, aQZ, a5Z, a6Z, aDTZ, aTQZ, aQ5Z, a56Z

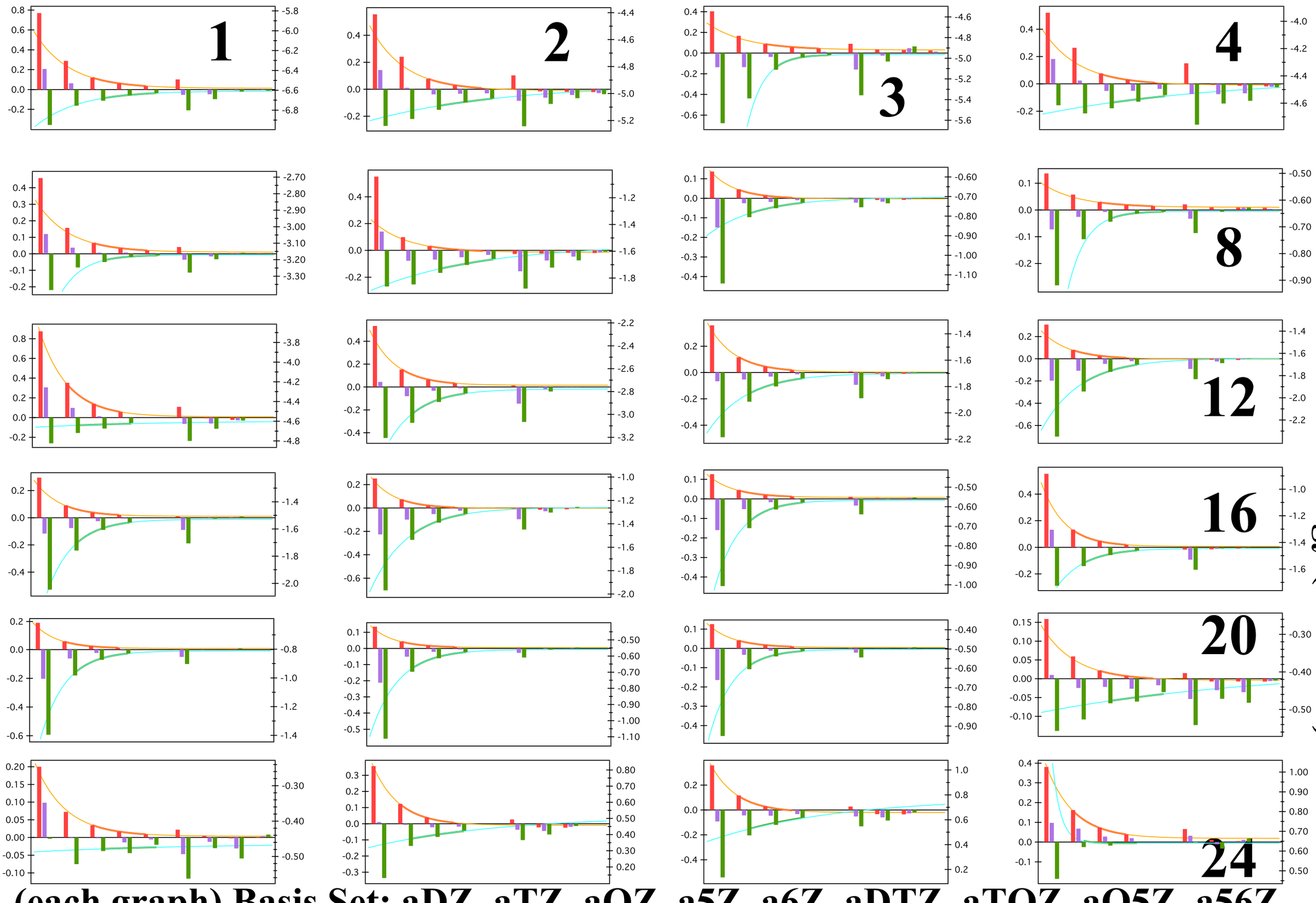
Basis Convergence of MP2/aXZ for A24

CP, **Ave**, **unCP**

unCP-weighted-ave of 3-basis fit)

Error in IE w.r.t. Ref (CP/unC

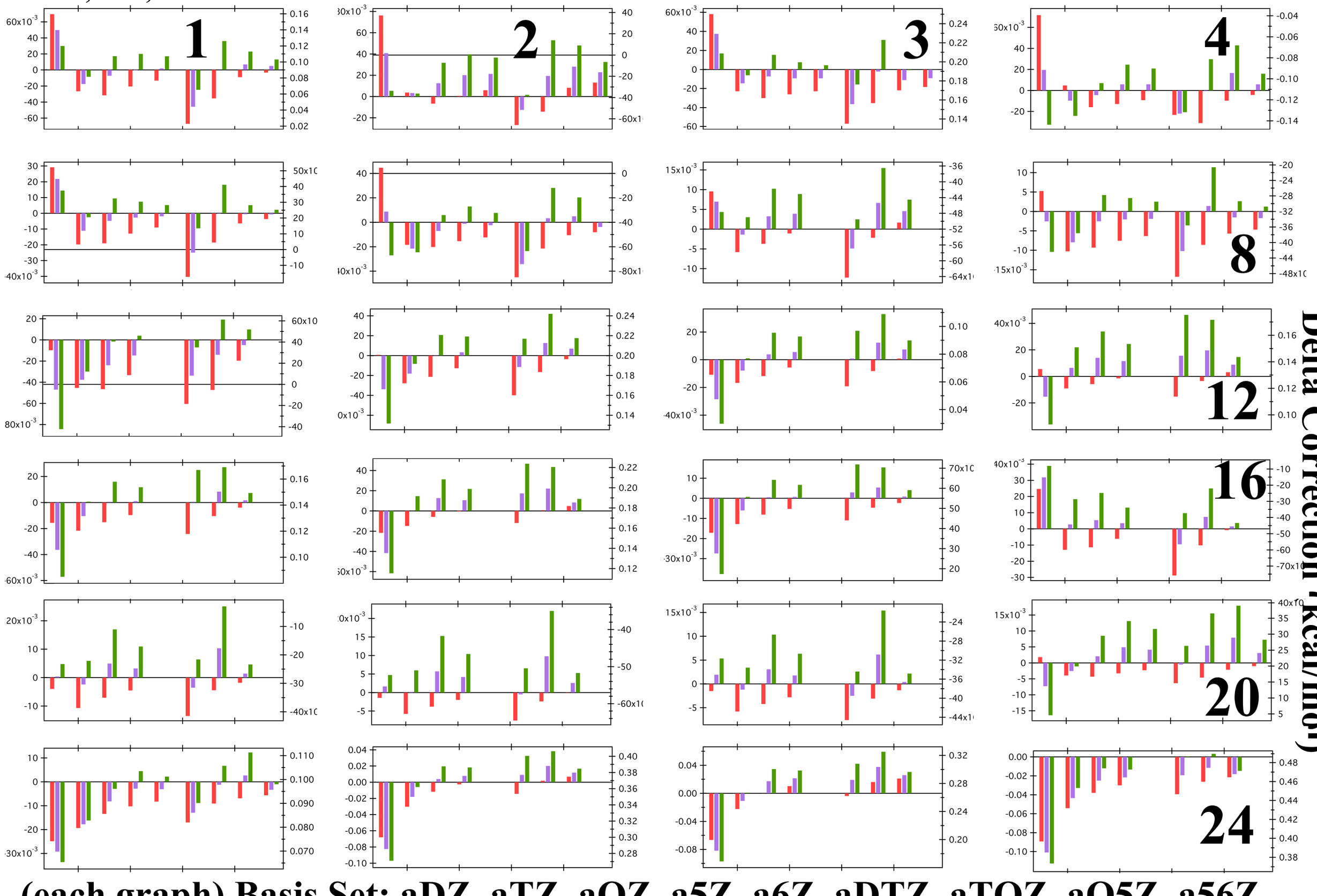
MP2 Interaction Energy (kcal/mol)



(each graph) Basis Set: aDZ, aTZ, aQZ, a5Z, a6Z, aDTZ, aTQZ, aQ5Z, a56Z

Basis Conv. of Delta Correction (CCSD(T)–MP2)/aXZ for A24

CP, Ave, unCP



Error in Delta Correction w.r.t. Ref

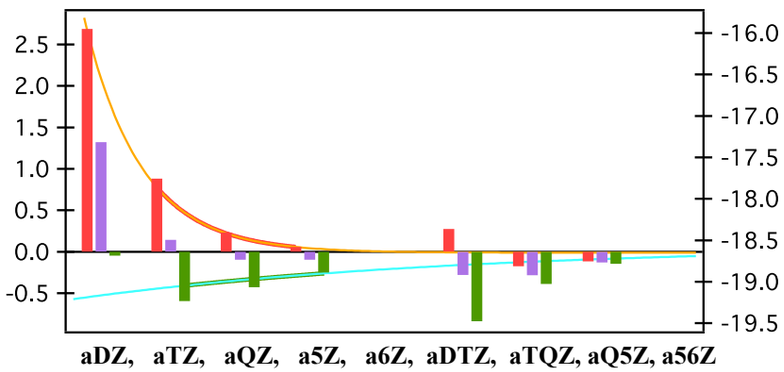
Delta Correction (kcal/mol)

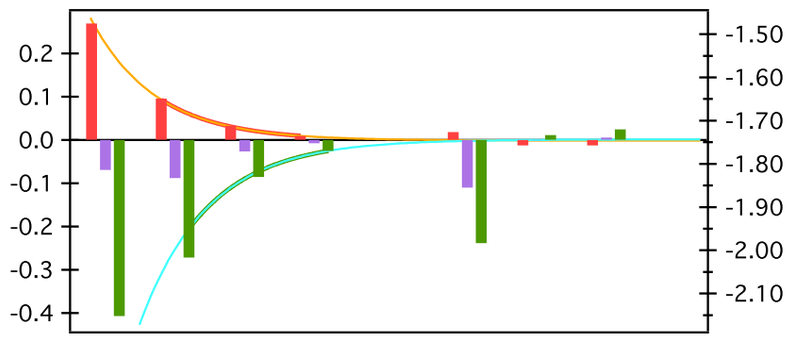
(each graph) Basis Set: aDZ, aTZ, aQZ, a5Z, a6Z, aDTZ, aTQZ, aQ5Z, a56Z

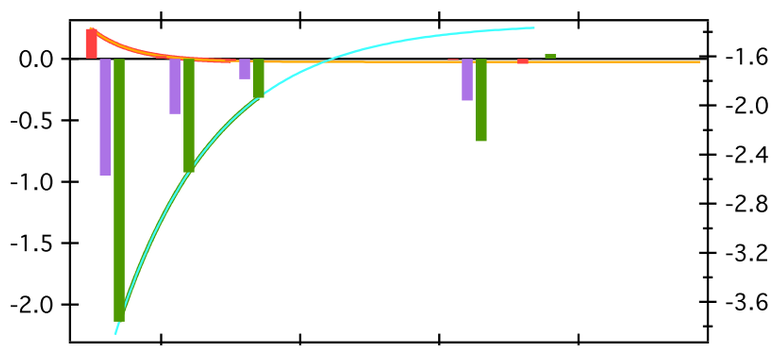
Formic Acid Dimer **Parallel-Disp. Cyanogen Dimer** **Sandwich Benzene Dimer**

CCSD(T)/aXZ for Misc.

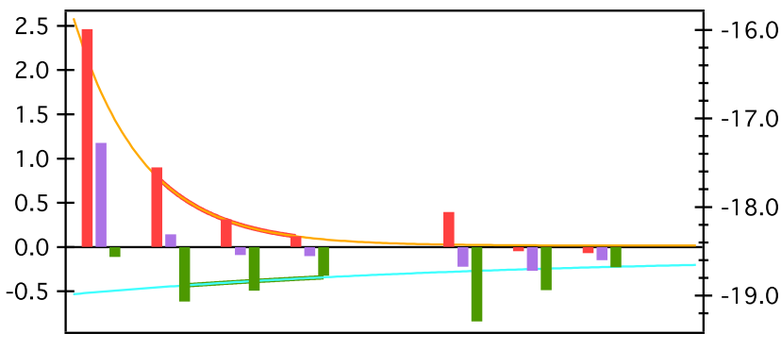
CP, **Ave**, **unCP**

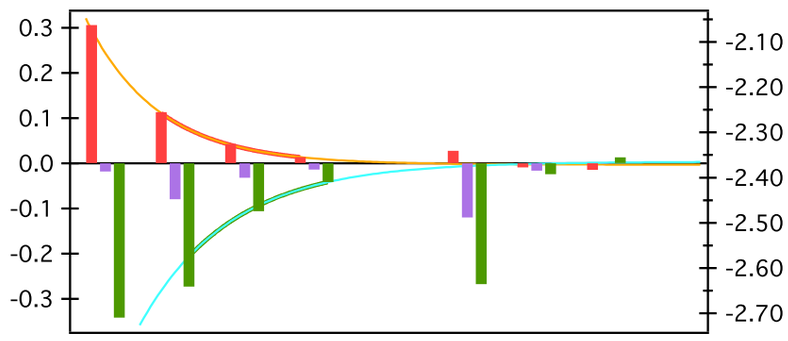


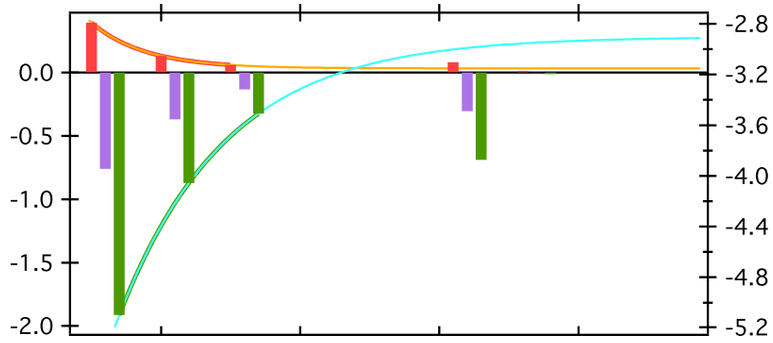




MP2/aXZ for Misc.







Delta/aXZ for Misc.