Focal Point Analysis

Marcus Bartlett

June 28, 2016

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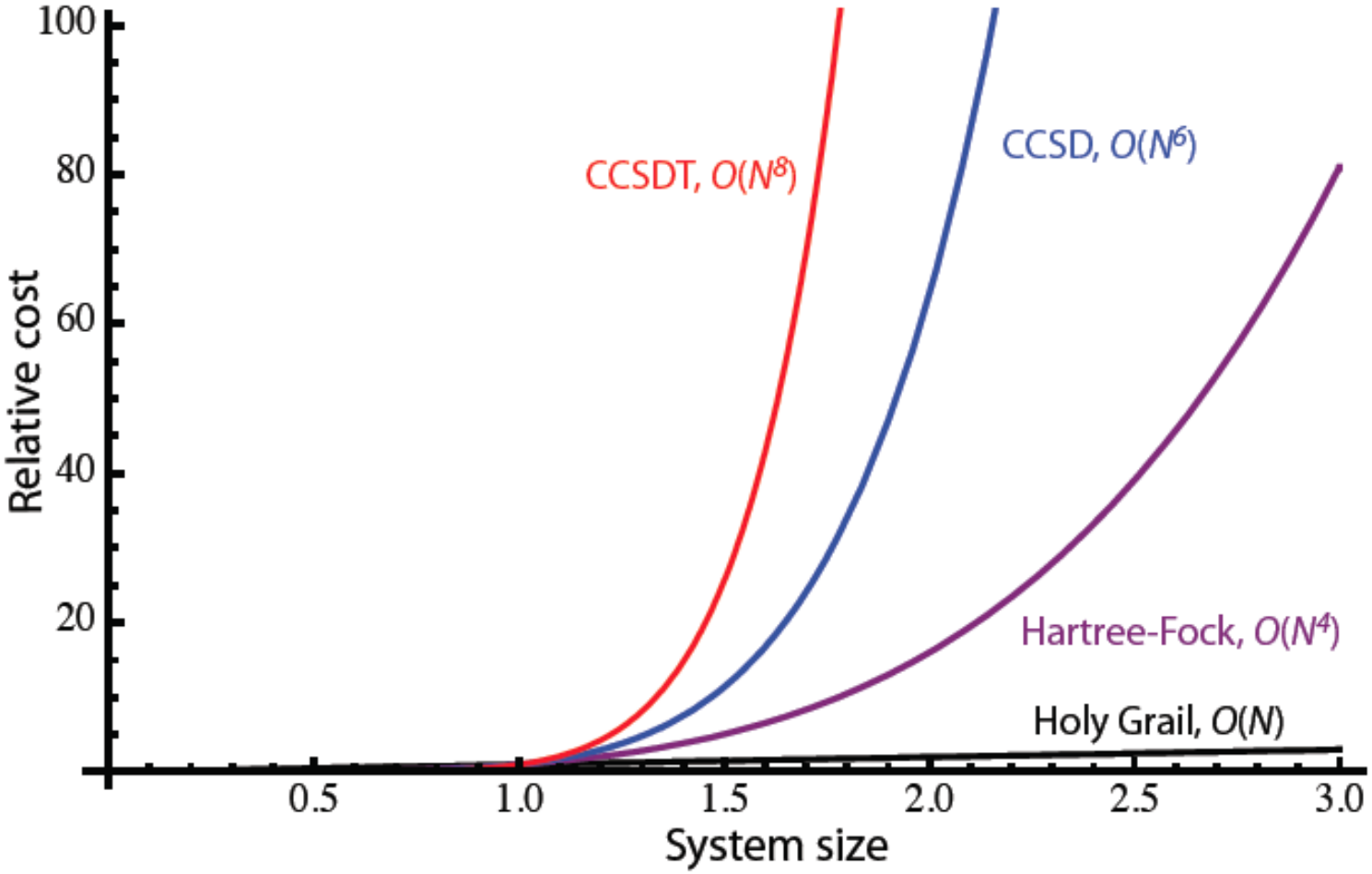
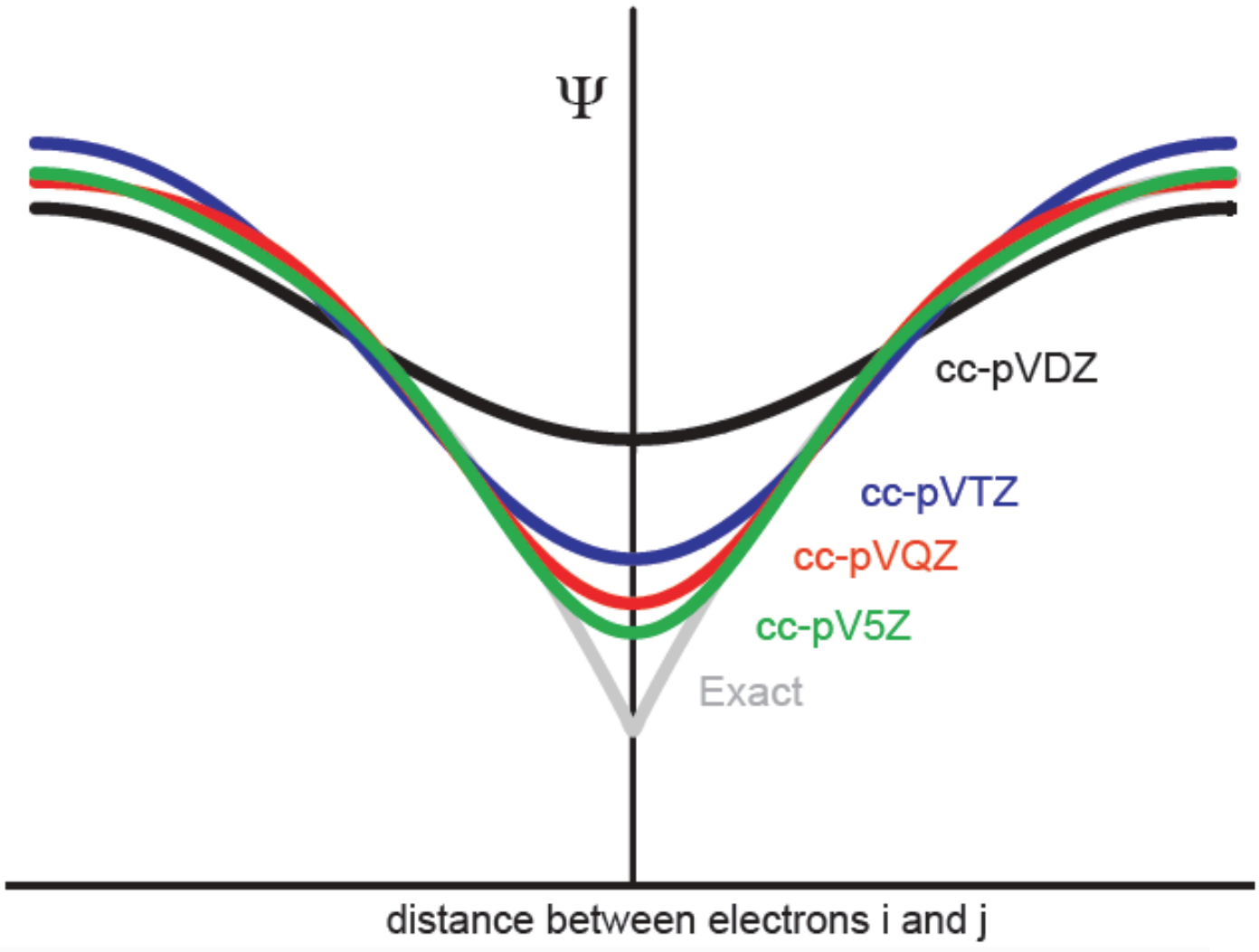
- Large, flexible basis sets are needed to describe correlation properly.
- So, why not use a lot of correlation and a large basis set?

Computational Scaling



The electron-electron cusp problem



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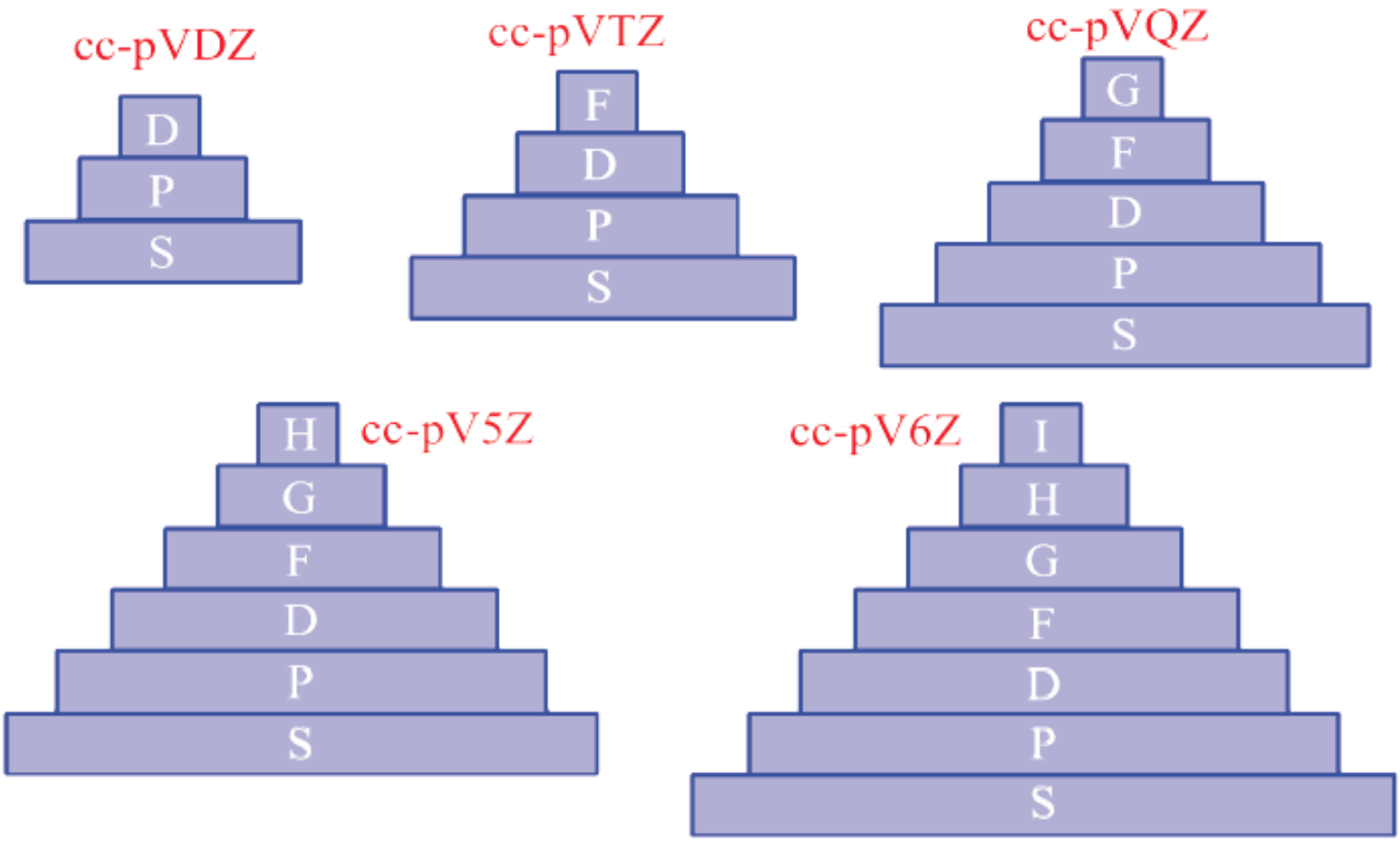
- R12 Methods

The Dunning cc-pVXZ Basis Sets



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- Why are these different?

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$$\frac{E_3 - E_2}{E_2 - E_1} = \frac{B(e^{-CX_3} - e^{-CX_2})}{B(e^{-CX_2} - e^{-CX_1})} = \frac{e^{-CX_3} - e^{-CX_2}}{e^{-CX_2} - e^{-CX_1}}$$

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Now insert $X_3 = X_2 + 1$ up top and $X_2 = X_1 + 1$ down below.

$$\frac{E_3 - E_2}{E_2 - E_1} = \frac{e^{-C(X_2+1)} - e^{-CX_2}}{e^{-C(X_1+1)} - e^{-CX_1}} = \frac{e^{-CX_2}(e^{-C} - 1)}{e^{-CX_1}(e^{-C} - 1)} = \frac{e^{-C(x_1+1)}}{e^{-C(x_1)}} = e^{-C}$$

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$$\frac{E_3 - E_2}{E_2 - E_1} = \frac{e^{-C(X_2+1)} - e^{-CX_2}}{e^{-C(X_1+1)} - e^{-CX_1}} = \frac{e^{-CX_2}(e^{-C} - 1)}{e^{-CX_1}(e^{-C} - 1)} = \frac{e^{-C(x_1+1)}}{e^{-C(x_1)}} = e^{-C}$$

$$C = -\ln \frac{E_3 - E_2}{E_2 - E_1}$$

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N.B Having solved for the correlated CBS limit, the SCF contribution must be added back in.

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- Assume that high-level differences, *e.g.* CCSDT(Q)-CCSDT are independent of basis set.

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T	-0.86
Q	-0.85
5	-0.66
6	-0.64
CBS	[-0.64]

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X	HF	$+\delta$ MP2
D	-1.01	+1.92
T	-0.86	+5.28
Q	-0.85	+6.05
5	-0.66	+6.23
6	-0.64	+6.29
CBS	[-0.64]	[+6.38]

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X	HF	$+\delta$ MP2	$+\delta$ CCSD
D	-1.01	+1.92	-0.11
T	-0.86	+5.28	-0.40
Q	-0.85	+6.05	-0.47
5	-0.66	+6.23	-0.51
6	-0.64	+6.29	-0.52
CBS	[-0.64]	[+6.38]	[-0.53]

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X	HF	$+\delta$ MP2	$+\delta$ CCSD	$+\delta$ CCSD(T)
D	-1.01	+1.92	-0.11	-0.51
T	-0.86	+5.28	-0.40	-0.26
Q	-0.85	+6.05	-0.47	-0.14
5	-0.66	+6.23	-0.51	-0.10
6	-0.64	+6.29	-0.52	-0.09
CBS	[-0.64]	[+6.38]	[-0.53]	[-0.08]

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D	-1.01	+1.92	-0.11	-0.51	+0.39
T	-0.86	+5.28	-0.40	-0.26	[+0.39]
Q	-0.85	+6.05	-0.47	-0.14	[+0.39]
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D	-1.01	+1.92	-0.11	-0.51	+0.39	-0.04
T	-0.86	+5.28	-0.40	-0.26	[+0.39]	[-0.04]
Q	-0.85	+6.05	-0.47	-0.14	[+0.39]	[-0.04]
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X	HF	$+\delta$ MP2	$+\delta$ CCSD	$+\delta$ CCSD(T)	$+\delta$ CCSDT	$+\delta$ CCSDT(Q)	NET ΔE
D	-1.01	+1.92	-0.11	-0.51	+0.39	-0.04	[+0.63]
T	-0.86	+5.28	-0.40	-0.26	[+0.39]	[-0.04]	[+4.12]
Q	-0.85	+6.05	-0.47	-0.14	[+0.39]	[-0.04]	[+4.94]
5	-0.66	+6.23	-0.51	-0.10	[+0.39]	[-0.04]	[+5.31]
6	-0.64	+6.29	-0.52	-0.09	[+0.39]	[-0.04]	[+5.39]
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X	HF	MP2	CCSD	CCSD(T)	CCSDT	CCSDT(Q)
D	-113.8763304	-114.1926331	-114.2084486	-114.2183049	-114.2230689	-114.2241103
T	-113.9118562	-114.3071360	-114.3172953	-114.3338164	[· · ·]	[· · ·]
Q	-113.9208607	-114.3446832	-114.3506913	-114.3689983	[· · ·]	[· · ·]
5	-113.9230808	-114.3584278	-114.3613341	-114.3802999	[· · ·]	[· · ·]
6	-113.9233532	-114.3638931	-114.3650070	-114.3842030	[· · ·]	[· · ·]
CBS	[· · ·]	[· · ·]	[· · ·]	[· · ·]	[· · ·]	[· · ·]

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- Product Energies (E_h):

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D	-113.8779450	-114.1911938	-114.2071892	-114.2178577	-114.2220016	-114.2231031
T	-113.9132204	-114.3000897	-114.3108849	-114.3278140	[···]	[···]
Q	-113.9222118	-114.3363952	-114.3431590	-114.3616887	[···]	[···]
5	-113.9241250	-114.3495499	-114.3532714	-114.3724039	[···]	[···]
6	-113.9243751	-114.3548881	-114.3568268	-114.3761717	[···]	[···]
CBS	[···]	[···]	[···]	[···]	[···]	[···]

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS Hartree-Fock energy for formaldehyde.

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS Hartree-Fock energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

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$$C = -\ln \frac{E_3 - E_2}{E_2 - E_1}$$

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6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$C = -\ln \frac{E_3 - E_2}{E_2 - E_1}$$

$$C = -\ln \frac{-113.9243751 - (-113.9241250)}{-113.9241250 - (-113.9222118)}$$

Step 2: Extrapolate Reactant and Product Absolute Energies

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Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
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$$C = -\ln \frac{E_3 - E_2}{E_2 - E_1}$$

$$C = -\ln \frac{-113.9243751 - (-113.9241250)}{-113.9241250 - (-113.9222118)}$$

$$C = 2.034671674$$

Step 2: Extrapolate Reactant and Product Absolute Energies

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D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
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5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$B = \frac{E_3 - E_2}{e^{-CX_2}(e^{-C} - 1)}$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS Hartree-Fock energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$B = \frac{E_3 - E_2}{e^{-CX_2}(e^{-C} - 1)}$$

$$B = \frac{-113.9243751 - (-113.9241250)}{e^{-(2.034671674)(5)}(e^{-2.034671674} - 1)}$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS Hartree-Fock energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$B = \frac{E_3 - E_2}{e^{-CX_2}(e^{-C} - 1)}$$

$$B = \frac{-113.9243751 - (-113.9241250)}{e^{-(2.034671674)(5)}(e^{-2.034671674} - 1)}$$

$$B = 7.536836654$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS Hartree-Fock energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
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6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$A = E_3 - Be^{-CX_3}$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS Hartree-Fock energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$A = E_3 - Be^{-CX_3}$$

$$A = -113.9243751 - (7.536836654)e^{-(2.034671674)(6)}$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS Hartree-Fock energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$A = E_3 - Be^{-CX_3}$$

$$A = -113.9243751 - (7.536836654)e^{-(2.034671674)(6)}$$

$$A = -113.9244127$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Step 2: Extrapolate Reactant and Product Absolute Energies

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Formaldehyde Energies

X	HF	MP2
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Q	-113.9222118	-114.3363952
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Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
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5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$E_1 = -114.3495499 - (-113.9241250)$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$E_1 = -114.3495499 - (-113.9241250)$$

$$E_1 = -0.4254248$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
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Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$E_2 = -114.3548881 - (-113.9243751)$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$E_2 = -114.3548881 - (-113.9243751)$$

$$E_2 = -0.4305130$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
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Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
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5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$B = \frac{E_2 - E_1}{X_2^{-3} - X_1^{-3}}$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$B = \frac{E_2 - E_1}{X_2^{-3} - X_1^{-3}}$$

$$B = \frac{-0.4305130 - (-0.4254248)}{6^{-3} - 5^{-3}}$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$B = \frac{E_2 - E_1}{X_2^{-3} - X_1^{-3}}$$

$$B = \frac{-0.4305130 - (-0.4254248)}{6^{-3} - 5^{-3}}$$

$$B = 1.5096857$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
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Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

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X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$A = E_2 - BX_2^{-3}$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$A = E_2 - BX_2^{-3}$$

$$A = -0.4305130 - (1.5096857)(6)^{-3}$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$A = E_2 - BX_2^{-3}$$

$$A = -0.4305130 - (1.5096857)(6)^{-3}$$

$$A = -0.4375023$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

Formaldehyde Energies

X	HF	MP2
D	-113.8779450	-114.1911938
T	-113.9132204	-114.3000897
Q	-113.9222118	-114.3363952
5	-113.9241250	-114.3495499
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CBS	[-113.9244127]	[-114.3619149]

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the CBS MP2 energy for formaldehyde.

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D	-113.8779450	-114.1911938
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5	-113.9241250	-114.3495499
6	-113.9243751	-114.3548881
CBS	[-113.9244127]	[-114.3619149]

$$E = -113.9244127 + (-0.4375023) = -114.3619149$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the cc-pV5Z CCSDT energy for formaldehyde.

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the cc-pV5Z CCSDT energy for formaldehyde.

Formaldehyde Energies

X	CCSD(T)	CCSDT
D	-114.2178577	-114.2220016
T	-114.3278140	[-114.3319580]
Q	-114.3616887	[-114.3658326]
5	-114.3724039	[-114.3765479]
6	-114.3761717	[-114.3803157]
CBS	[-114.3810414]	[-114.3851854]

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the cc-pV5Z CCSDT energy for formaldehyde.

Formaldehyde Energies

X	CCSD(T)	CCSDT
D	-114.2178577	-114.2220016
T	-114.3278140	[-114.3319580]
Q	-114.3616887	[-114.3658326]
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6	-114.3761717	[-114.3803157]
CBS	[-114.3810414]	[-114.3851854]

Here we assume additivity:

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the cc-pV5Z CCSDT energy for formaldehyde.

Formaldehyde Energies

X	CCSD(T)	CCSDT
D	-114.2178577	-114.2220016
T	-114.3278140	[-114.3319580]
Q	-114.3616887	[-114.3658326]
5	-114.3724039	[-114.3765479]
6	-114.3761717	[-114.3803157]
CBS	[-114.3810414]	[-114.3851854]

Here we assume additivity:

$$E_{CCSDT/cc-pV5Z} = E_{CCSDT/cc-pVDZ} - E_{CCSD(T)/cc-pVDZ} + E_{CCSD(T)/cc-pV5Z}$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the cc-pV5Z CCSDT energy for formaldehyde.

Formaldehyde Energies

X	CCSD(T)	CCSDT
D	-114.2178577	-114.2220016
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5	-114.3724039	[-114.3765479]
6	-114.3761717	[-114.3803157]
CBS	[-114.3810414]	[-114.3851854]

Here we assume additivity:

$$E_{CCSDT/cc-pV5Z} = E_{CCSDT/cc-pVDZ} - E_{CCSD(T)/cc-pVDZ} + E_{CCSD(T)/cc-pV5Z}$$

$$E_{CCSDT/cc-pV5Z} = -114.2220016 - (-114.2178577) + (-114.3724039)$$

Step 2: Extrapolate Reactant and Product Absolute Energies

Getting the cc-pV5Z CCSDT energy for formaldehyde.

Formaldehyde Energies

X	CCSD(T)	CCSDT
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CBS	[-114.3810414]	[-114.3851854]

Here we assume additivity:

$$E_{CCSDT/cc-pV5Z} = E_{CCSDT/cc-pVDZ} - E_{CCSD(T)/cc-pVDZ} + E_{CCSD(T)/cc-pV5Z}$$

$$E_{CCSDT/cc-pV5Z} = -114.2220016 - (-114.2178577) + (-114.3724039)$$

$$E_{CCSDT/cc-pV5Z} = -114.3765479$$

Step 3: Compute the Focal Point Table Using The Absolute Energies

X	HF	MP2	CCSD	CCSD(T)	CCSDT	CCSDT(Q)	NET ΔE
D	-1.01	+0.90	+0.79	+0.28	+0.67	+0.63	[+0.63]
T	-0.86	+4.42	+4.02	+3.77	[+4.16]	[+4.12]	[+4.12]
Q	-0.85	+5.20	+4.73	+4.59	[+4.98]	[+4.94]	[+4.94]
5	-0.66	+5.57	+5.06	+4.95	[+5.34]	[+5.31]	[+5.31]
6	-0.64	+5.65	+5.13	+5.04	[+5.43]	[+5.39]	[+5.39]
CBS	[-0.64]	[+5.74]	[+5.22]	[+5.14]	[+5.53]	[+5.49]	[+5.49]

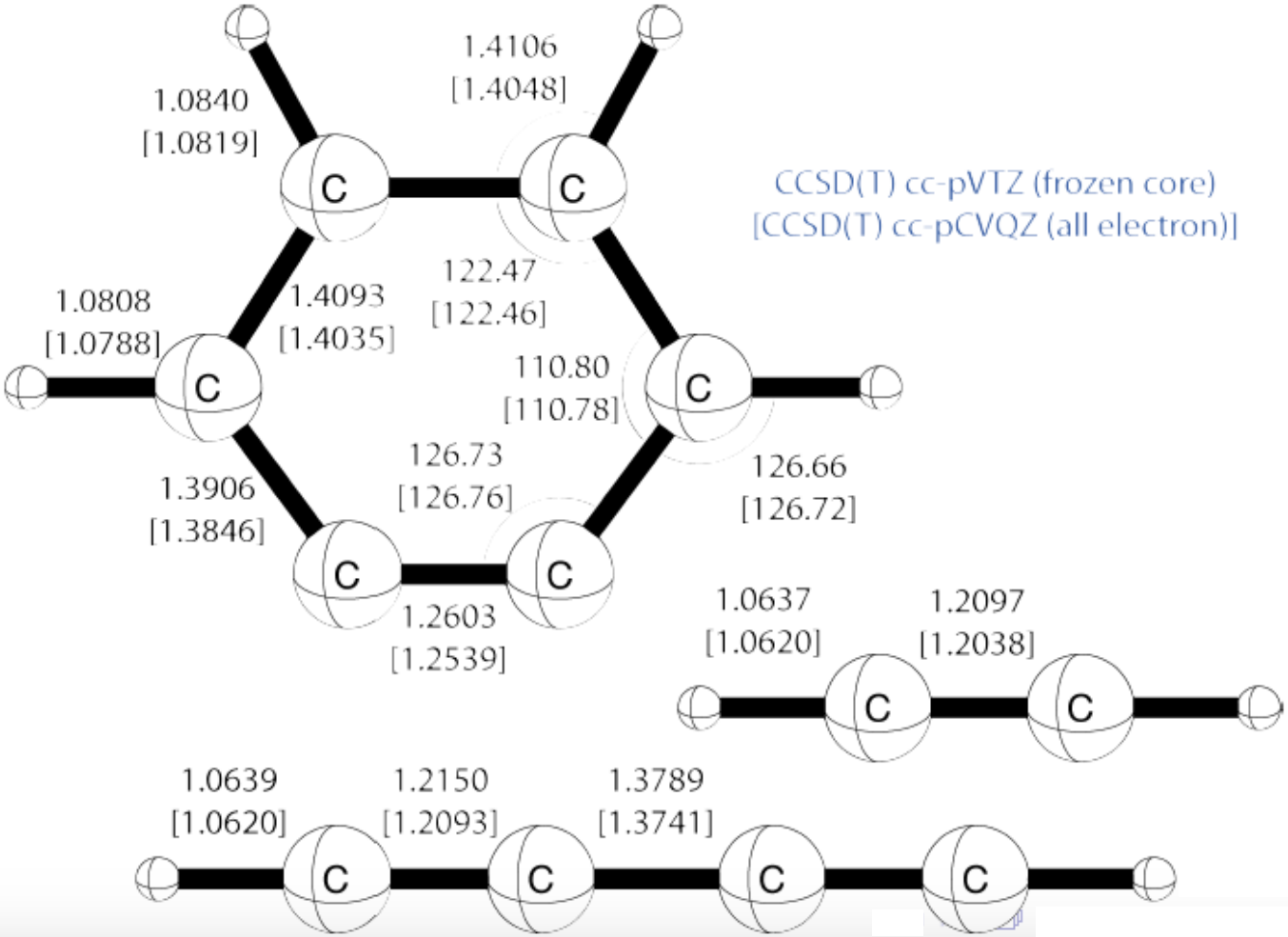
Step 4: Compute Differences to Form the Incremented Focal Point Table

X	HF	$+\delta$ MP2	$+\delta$ CCSD	$+\delta$ CCSD(T)	$+\delta$ CCSDT	$+\delta$ CCSDT(Q)	NET ΔE
D	-1.01	+1.92	-0.11	-0.51	+0.39	-0.04	[+0.63]
T	-0.86	+5.28	-0.40	-0.26	[+0.39]	[-0.04]	[+4.12]
Q	-0.85	+6.05	-0.47	-0.14	[+0.39]	[-0.04]	[+4.94]
5	-0.66	+6.23	-0.51	-0.10	[+0.39]	[-0.04]	[+5.31]
6	-0.64	+6.29	-0.52	-0.09	[+0.39]	[-0.04]	[+5.39]
CBS	[-0.64]	[+6.38]	[-0.53]	[-0.08]	[+0.39]	[-0.04]	[+5.49]

Geometry Dependence

Benzyne Decomposition

- Optimized Geometries



Geometry Dependence

Benzyne Decomposition

- Focal Point Analysis

cc-pVTZ (frozen core) geometries

X	HF	+δMP2	+δCCSD	+δCCSD(T)	+δCCSDT	net ΔE
D	+44.38	+22.55	-7.84	+4.44	-0.64	[+62.90]
T	+38.74	+24.34	-8.97	+4.69	[-0.64]	[+58.17]
Q	+38.77	+24.88	-8.99	+4.81	[-0.64]	[+58.83]
5	+38.89	+25.09	[-8.99]	[+4.81]	[-0.64]	[+59.16]
6	+38.92	+25.13	[-8.99]	[+4.81]	[-0.64]	[+59.23]
CBS	[+38.92]	[+25.19]	[-8.99]	[+4.81]	[-0.64]	[+59.29]

Geometry Dependence

Benzyne Decomposition

- Focal Point Analysis

cc-pVTZ (frozen core) geometries

X	HF	+δMP2	+δCCSD	+δCCSD(T)	+δCCSDT	net ΔE
D	+44.38	+22.55	-7.84	+4.44	-0.64	[+62.90]
T	+38.74	+24.34	-8.97	+4.69	[-0.64]	[+58.17]
Q	+38.77	+24.88	-8.99	+4.81	[-0.64]	[+58.83]
5	+38.89	+25.09	[-8.99]	[+4.81]	[-0.64]	[+59.16]
6	+38.92	+25.13	[-8.99]	[+4.81]	[-0.64]	[+59.23]
CBS	[+38.92]	[+25.19]	[-8.99]	[+4.81]	[-0.64]	[+59.29]

cc-pCVQZ (all electron) geometries

X	HF	+δMP2	+δCCSD	+δCCSD(T)	+δCCSDT	net ΔE
D	+44.27	+23.00	-7.98	+4.41	-0.64	[+63.06]
T	+38.45	+24.80	-9.11	+4.66	[-0.64]	[+58.16]
Q	+38.47	+25.34	-9.13	+4.78	[-0.64]	[+58.82]
5	+38.59	+25.55	[-9.13]	[+4.78]	[-0.64]	[+59.15]
6	+38.62	+25.59	[-9.13]	[+4.78]	[-0.64]	[+59.22]
CBS	[+38.63]	[+25.64]	[-9.13]	[+4.78]	[-0.64]	[+59.28]

Method is Cheap

Only the calculations in blue need to be ran, the rest come for free.

X	SCF	+δMP2	+δCCSD	+δCCSD(T)	+δCCSDT	+δCCSDT(Q)	+δCCSDTQ	+δCCSDTQ(P)	net ΔE
D	+214.79	-4.60	+1.83	-0.70	-0.02	-0.07	+0.01	-0.00	[+211.23]
T	+215.89	-5.26	+2.15	-0.95	+0.01	-0.08	[+0.01]	[-0.00]	[+211.76]
Q	+216.03	-5.39	+2.26	-1.00	+0.02	[-0.08]	[+0.01]	[-0.00]	[+211.85]
5	+216.07	-5.44	+2.31	-1.01	[+0.02]	[-0.08]	[+0.01]	[-0.00]	[+211.88]
6	+216.07	-5.48	+2.35	-1.02	[+0.02]	[-0.08]	[+0.01]	[-0.00]	[+211.87]
CBS	[+216.08]	[-5.54]	[+2.39]	[-1.03]	[+0.02]	[-0.08]	[+0.01]	[-0.00]	[+211.85]

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- With large enough basis sets (6Z) we can achieve chemical accuracy of within 0.1 mHartree of the CBS limit.