FOCAL POINT ANALYSIS: computing energies

· What is comp chem?

-Using computers to compute parameters and physical observables of molecular systems

· Problem :

- balance of speed and accuracy

-computer power is plateauing; we need to do more with what we have - CCSD(T) scales N7

· Assumptions to Increase Speed

-relax convergence criteria (cheating)

- use a smaller basis set

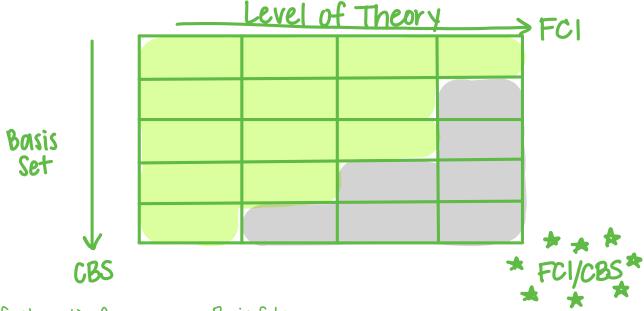
-truncate coupled cluster expansion

- freeze the core

- use a non-relativistic Hamiltonian
- assume molecule has no vibrational energy (not worrying about ZPVE)

- use a pseudopotential

· Focal Point Table: use different methods to converge to FCI/CBS



· Systematic Convergence: Basis Sets

- We need basis sets that systematically converge to the CBS limit.

- Generally, we use the Dunning family of BS.

(the "cc" means they sys. conv. when you add higher angular momentum)

- We change the cardinality (X) usually from DZ > whatever we can

- Various extrapolation schemes exist to extrapolate the computed energies to the CBS lim.

- If you desire a small uncertainty, many extrapolation schemes can be used and the standard deviation used as a metric for uncertainty.

· Systematic Convergence : Level of Theory

- CC is an expansion of FCI wavefunction that systematically conv.

- Higher order terms are less important and can be truncated.

$$|\gamma_{cc}\rangle = e^{\hat{T}}|\phi_{o}\rangle$$

$$= \left(|+\hat{T} + \frac{\hat{T}^{2}}{2!} + \frac{\hat{T}^{3}}{3!} + ...\right)|\phi_{o}\rangle$$

· Ex : HOBr +	H ₂ 0 →	Complex +8MP2	+8 CCSD	+8 (T)	+8T	+8(Q) NET
aug-cc-pV(D+d)Z	-1.17	-2.10	+0.52	-0.35	+0.02	-0.02 -3.10
ang-cc-pV(T+d)Z	-0.76	-2.35	+0.56	-0.38	+0.02	[-0.02] [-2.92]
aug-cc-pv(Q+d)Z	-0.69	-2.36	+ 0.58	-0.39	[+0.02]	[-0.02] [-2.86]
aug-cc-pv(5+d)Z	-0.68	-2.35	+ 0.59	-0.40	[+0.02]	[-0.02] $[-2.92]$
CBS Limit	[-0.67]	[-2.34]	[+0.59]	[-0.40]	[+0.02]	[-0.02] $[-2.82]$
· As a Diagnos - basis set dep - bolution - multireference	pendence : do biga	ger basis se	ets			
· Corrections : h Eint = -2.82 - higher order			= -1.71 \ 5	e compute the pecies and our FP er	we add (p	ion for each product -reactants)
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· We exclude co						valence: 1 energy
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