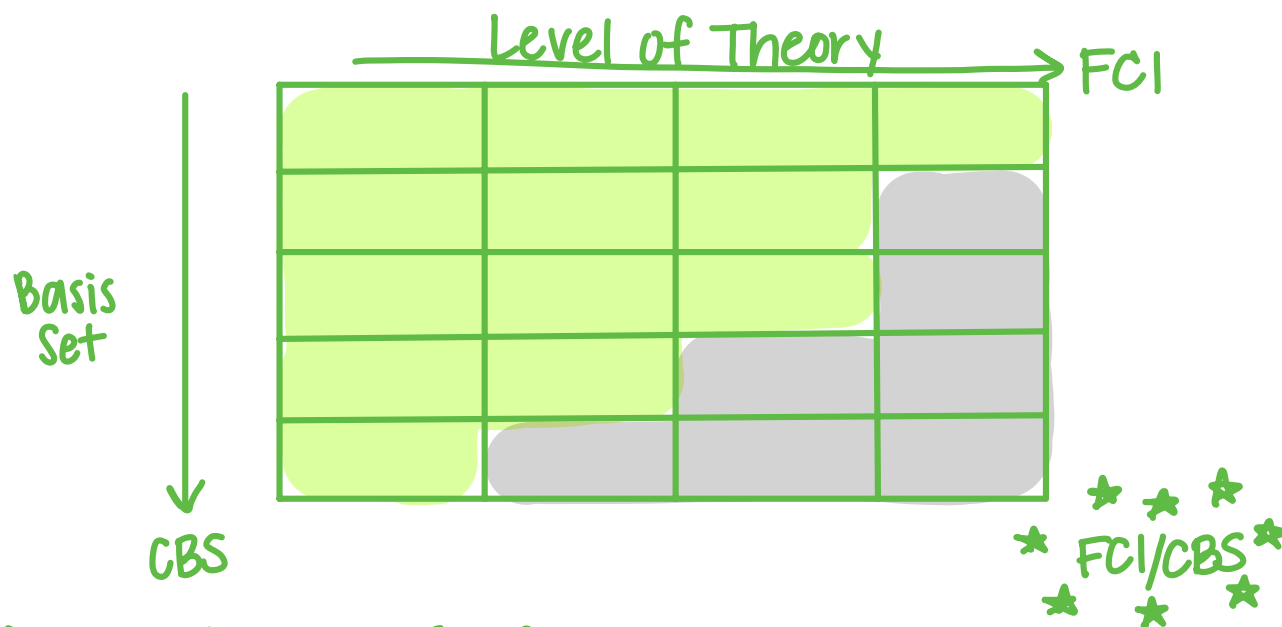


# FOCAL POINT ANALYSIS: computing energies

- 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  $N^7$
- 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  $\rightarrow$  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.

$$\begin{aligned}
 |\Psi_{CC}\rangle &= e^{\hat{T}} |\Phi_0\rangle \\
 &= \left(1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \dots\right) |\Phi_0\rangle
 \end{aligned}$$

Ex:  $\text{HOBr} + \text{H}_2\text{O} \rightarrow \text{Complex}$

	HF	+8 MP2	+8 CCSD	+8 (T)	+8 T	+8 (Q)	NET
aug-cc-pV(D+d)Z	-1.17	-2.10	+0.52	-0.35	+0.02	-0.02	-3.10
aug-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]	[-2.82]
CBS Limit	[-0.67]	[-2.34]	[+0.59]	[-0.40]	[+0.02]	[-0.02]	[-2.82]

## As a Diagnostic Tool

- basis set dependence: significant changes down a column  
     ↳ solution: do bigger basis sets
- multireference issues: bad convergence in coupled cluster

Corrections: hope they are small ☺

$$E_{\text{int}} = -2.82 + 1.07 + 0.04 + 0.00 = -1.71$$

We compute the correction for each species and we add (product - reactants) to our FP energy.

- higher order correlation (CCSDT(Q))

If we see evidence that correlation corrections are not very BS dependent, we sometimes use a smaller basis set to compute a higher order coupled cluster computation we otherwise could not afford.

$$\text{CCSDTQ correction} = \text{CCSDTQ} / (\text{small basis}) - \text{CCSDT}(Q) / (\text{small basis})$$

- frozen core

Core orbitals are generally separated in energy from valence orbitals.

We exclude correlating core orbitals in our computations.

$$\text{FC correction} = \frac{\text{CCSD(T)} / (\text{CW basis})}{\text{all-e}^- \text{ correlated}} - \frac{\text{CCSD(T)} / (\text{CW basis})}{\text{frozen core}}$$

valence: ↑ energy  
core e<sup>-</sup> won't contribute much to correlation energy so leave out to see effect, do CW

- Relativistic Effects

Our computations generally use a non-relativistic Hamiltonian

Heavy atoms have increasingly large relativistic effects that need to be accounted for, due to high velocity of core e<sup>-</sup>

We compute effect by turning on relativistic H (dkh, X2C, ...)

$$\text{Rel Correction} = \frac{\text{CCSD(T)} / (\text{CW BS})}{\text{X2C on}} - \frac{\text{CCSD(T)} / (\text{CW BS})}{\text{X2C off}}$$

All e<sup>-</sup> correlated

All e<sup>-</sup> correlated

\* usually, ECP captures most of the relativistic effects

- Zero Point Vibrational Energy

includes the fact that the molecule is vibrating at 0 K.

converts energy to H at 0 K.

$$\text{ZPVE} = (\text{sum of harm freq}) / 2$$

- Diagonal Born-Oppenheimer Correction

represents clamped nuclei approx.

can be directly computed via keywords

magnitude is usually insignificant but serves as diagnostic to ensure nonadiabatic effects are present like conical intersection

- Anharmonic Correction

computed when harmonic oscillator approx. fails

usually needed for "floppy" systems

can be very expensive to compute, so only included if necessary