

Truncated CI

$$\Psi_{el}(x_1, x_2, x_3, \dots, x_N) = \sum_{\{ijkl\dots\}} C_{ijkl\dots} |\psi_i(x_1) \psi_j(x_2) \psi_k(x_3) \dots \psi_l(x_N)|$$

$\{ \} \rightarrow$ restrict sum (Truncate)

$$\underline{\underline{H}} \cdot \underline{\underline{C}} = E \underline{\underline{C}}$$

How do we choose these configurations?

Singles

$$\hat{T}_1 |\Phi_{HF}\rangle = \sum_{ia} t_i^a |\Phi_i^a\rangle$$

Doubles

$$\hat{T}_2 |\Phi_{HF}\rangle = \sum_{ijab} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle$$

Triples ...

$$\hat{T}_3 |\Phi_{HF}\rangle = \sum_{ijkabc} t_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle$$

$t_i^a \rightarrow$ amplitudes

Hierarchy: CIS (T_1), CID (T_2), CISD (T_1+T_2), CISDT ($T_1+T_2+T_3$), ...

Size Consistency

$$|\Psi_A^{\text{CID}}\rangle = (1 + \hat{T}_2^A) |\Psi_{HF}^A\rangle$$



$$|\Psi_B^{\text{CID}}\rangle = (1 + \hat{T}_2^B) |\Psi_{HF}^B\rangle$$

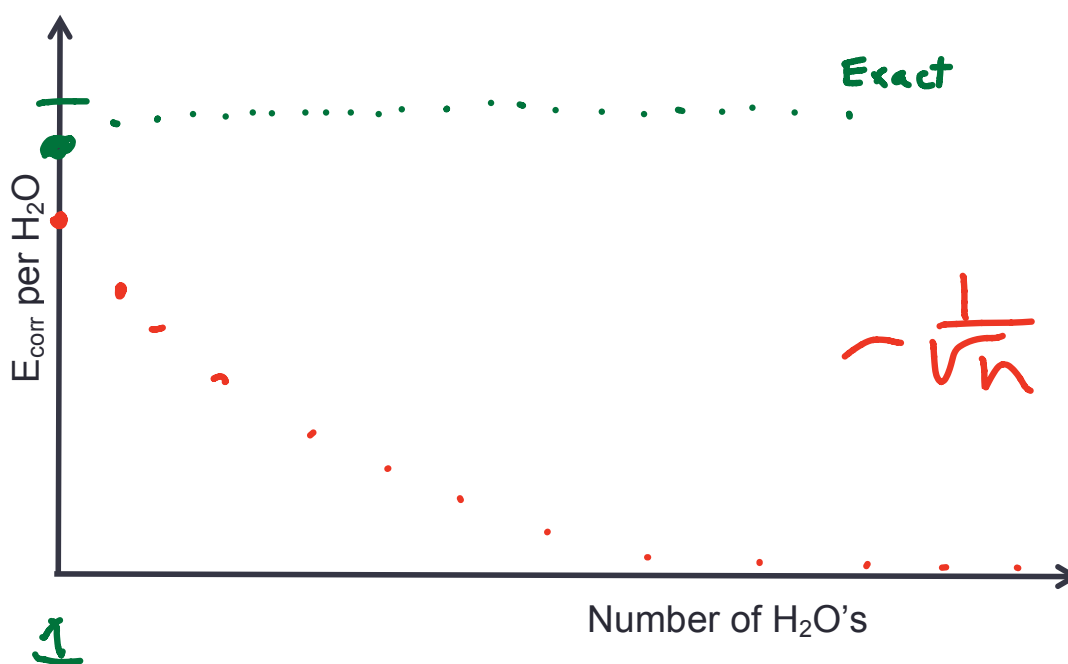
Product of
CID Ψ 's

$$\begin{aligned} |\Psi_{A\dots B}\rangle &= |\Psi_A\rangle |\Psi_B\rangle = (1 + \hat{T}_2^A) |\Phi_{HF}^A\rangle (1 + \hat{T}_2^B) |\Phi_{HF}^B\rangle \\ &= (1 + \hat{T}_2^A) (1 + \hat{T}_2^B) |\Phi_{HF}^B\rangle |\Phi_{HF}^A\rangle \\ &= (1 + \hat{T}_2^A + \hat{T}_2^B + \hat{T}_2^A \hat{T}_2^B) |\Phi_{HF}^B\rangle |\Phi_{HF}^A\rangle \end{aligned}$$

~~$\hat{T}_2^A \hat{T}_2^B = ?$~~

CID on A...B
Supersystem

$$|\Psi_{A\dots B}^{\text{CID}}\rangle = (1 + \hat{T}_2^{A\dots B}) |\Phi_{HF}^{A\dots B}\rangle = (1 + \hat{T}_2^{A\dots B}) |\Phi_{HF}^A\rangle |\Phi_{HF}^B\rangle$$



Worthless!
Coupled Cluster

$$e^x e^y = e^{x+y}$$

$$|\Psi_{\text{cc}}\rangle = e^{\hat{T}} |\Phi_{\text{HF}}\rangle$$

$$\begin{aligned} |\Psi_{A...B}\rangle &= |\Psi_A^{\text{CCD}}\rangle |\Psi_B^{\text{CCD}}\rangle = e^{\hat{T}_2^A} |\Phi_{\text{HF}}^A\rangle e^{\hat{T}_2^B} |\Phi_{\text{HF}}^B\rangle \\ &= e^{\hat{T}_2^A} e^{\hat{T}_2^B} |\Phi_{\text{HF}}^A\rangle |\Phi_{\text{HF}}^B\rangle = e^{\hat{T}_2^A + \hat{T}_2^B} |\Phi_{\text{HF}}^A\rangle |\Phi_{\text{HF}}^B\rangle \end{aligned}$$

✓ ☺

Problem:

$$\langle \Phi_{\text{HF}} | e^{\hat{T}} | \Phi_{\text{HF}} \rangle = \left(1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \frac{1}{6} \hat{T}^3 + \frac{1}{24} \hat{T}^4 + \frac{1}{120} \hat{T}^5 + \dots \right) | \Phi_{\text{HF}} \rangle \quad \ddots$$

$$= \langle \Phi_{\text{HF}} | 1 + \hat{T} + \frac{1}{2} \hat{T}^2 + \frac{1}{6} \hat{T}^3 + \dots | \Phi_{\text{HF}} \rangle$$

$$= \langle \Phi_{\text{HF}} | \Phi_{\text{HF}} \rangle + \langle \Phi_{\text{HF}} | \hat{T} | \Phi_{\text{HF}} \rangle + \frac{1}{2} \langle \Phi_{\text{HF}} | \hat{T}^2 | \Phi_{\text{HF}} \rangle$$

$$= 1 + \langle \Phi_{\text{HF}} | \hat{T} | \Phi_{\text{HF}} \rangle + \frac{1}{2} \langle \Phi_{\text{HF}} | \hat{T}^2 | \Phi_{\text{HF}} \rangle$$

Want:

$$\underbrace{e^{-\hat{T}} \hat{H} e^{\hat{T}}}_{\bar{H}} |\Phi_{HF}\rangle = \underbrace{e^{-\hat{T}}}_{\hat{H}} E e^{\hat{T}} |\Phi_{HF}\rangle = E \cancel{e^{-\hat{T}}} e^{\hat{T}} |\Phi_{HF}\rangle = E |\Phi_{HF}\rangle$$

$$\bar{H} |\Phi_{HF}\rangle = E |\Phi_{HF}\rangle$$

Similarity \hat{H} Transformed \rightarrow eigenvalues unchanged!

$$e^{-\hat{T}} H e^{\hat{T}} = H + [H, T] + \frac{1}{2} [[H, T], T] + \dots + \frac{1}{24} [[[[H, T], T], T], T]$$

\bar{H} has the same eigenvalues as H , but Φ_{HF} is the exact ground state of the full \bar{H} (and nearly the ground state for truncated T).

Amplitude Equations

Now, how do we actually solve for the amplitudes?

$$\hat{T}_2 \rightarrow t_{ij}^{ab}$$

$$\langle \Phi_{ij}^{ab} | \hat{\bar{H}} - E | \Phi_{HF} \rangle = 0$$

Summation Convention: Repeated indices are summed over $t_{ij}^{ab} \langle ab | cd \rangle$

$$0 = \langle ij || ab \rangle + (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) t_{ij}^{ab} + \left[\frac{1}{2} \langle ij || kl \rangle + \frac{1}{8} \langle kl || cd \rangle t_{ij}^{cd} \right] t_{kl}^{ab} \sum_{ab} t_{ij}^{ab} \langle ab | cd \rangle$$

$$+ \left[\frac{1}{2} \langle ab || cd \rangle + \frac{1}{8} \langle cd || kl \rangle t_{kl}^{ab} \right] t_{ij}^{cd} + P(ij) P(ab) \left[\langle kb || cj \rangle + \frac{1}{2} \langle kl || cd \rangle t_{lj}^{db} \right] t_{ik}^{ac}$$

$$- \frac{1}{2} P(ij) \left[\langle kl || cd \rangle t_{jl}^{cd} \right] t_{ik}^{ab} - \frac{1}{2} P(ab) \left[\langle kl || cd \rangle t_{kl}^{bd} \right] t_{ij}^{ac}$$

Notation: $P(xy) [?] \rightarrow \frac{1}{2} (? + ?^{x \leftrightarrow y})$

CCD

Hierarchy of CC approximations:

CCD

CCSD

CCSD(T)

CCSDT

"Gold Standard"

Typical Accuracy For Various Properties

| Property | HF | MP2 | CCSD(T) |
|-------------------------|--------------|-------------------|--------------------------|
| IPs and EAs | ± 0.5 eV | ± 0.2 eV | ± 0.05 eV |
| Bond Lengths | -1% | ± 1 pm | ± 0.5 pm |
| Vibrational Frequencies | +10% | +3% | ± 5 cm ⁻¹ |
| Barrier Heights | +30-50% | +10% | ± 2 kcal/mol |
| Bond Energies | -50% | ± 10 kcal/mol | ± 1 kcal/mol |

Suggested Further Reading: Crawford and Schaefer, "An Introduction to Coupled Cluster Theory for Computational Chemists" *Rev. Comp. Chem.* **14**, pp.33-136 (2000).

Computational Time

Most Time Consuming (Rate Limiting) Steps in Each Method:

| HF | MP2 | CCSD |
|---|---|--|
| $\sum_{\lambda\sigma} P_{\lambda\sigma} \langle \mu\lambda v\sigma \rangle$ | $\langle ij ab \rangle = \sum_{\mu} c_{\mu i} \langle \mu j ab \rangle$ | $\sum_{ab} t_{ij}^{ab} \langle ab cd \rangle$ |

Scaling: How computational time grows with system size (N)

To get scaling, count the # of indices in rate limiting step:

$$\begin{aligned} \text{HF: } \sum_{\lambda\sigma} P_{\lambda\sigma} \langle \mu\lambda | v\sigma \rangle &\rightarrow O(N^4) \\ \text{MP2: } \langle ij | ab \rangle = \sum_{\mu} c_{\mu i} \langle \mu j | ab \rangle &\rightarrow O(N^5) \\ \text{CCSD: } \sum_{ab} t_{ij}^{ab} \langle ab || cd \rangle &\rightarrow O(N^6) \end{aligned}$$

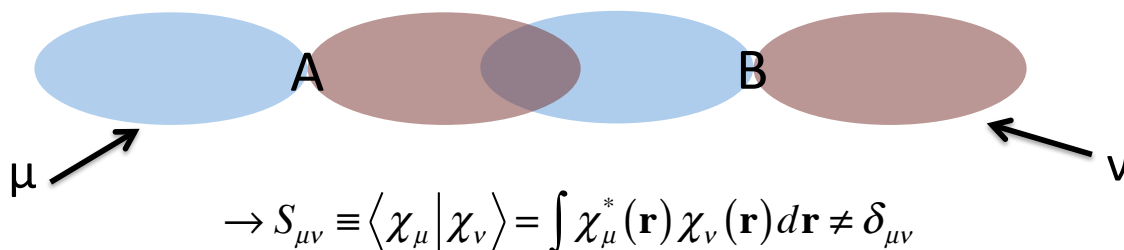
Implication 1: Going from one water molecule to water dimer, the HF time will go up by $\sim 2^4=16$, the MP2 time will go up by $\sim 2^5=32$ and the CCSD time will go up by $\sim 2^6=64$.

Implication 2: For a molecule with $N \sim 100$, an MP2 calculation will take $\sim 100x$ as long as a HF calculation and a CCSD calculation will take $\sim 10,000x$ as long as HF.

An ongoing area of research is using **locality** to reduce the cost of these calculations. Basically, one can neglect terms in the sums when the basis functions are very far apart, reducing the cost. This has been very effective for HF, so that the effective scaling of HF is now more like $O(N^2)$. It has also been effective for MP2 – the scaling is typically more like $O(N^4)$. Locality has yet to really improve the scaling of CCSD, but it will eventually happen.

Basis Sets

In chemistry, we typically use atomic orbital (AO) basis sets (e.g. 6-31g*, cc-pVTZ, LANL2DZ...). In this situation, the basis functions on different atoms are **not orthogonal** to each other.



This changes the equations in a few places:

Non-Orthogonality Cheat Sheet

| Object | Orthogonal Basis | Non-Orthogonal Basis |
|--|---|--|
| h_{ij} | $\mathbf{c}_i^\dagger \mathbf{h} \mathbf{c}_j$ | $\mathbf{c}_i^\dagger \mathbf{h} \mathbf{c}_j$ |
| $\langle ij kl \rangle$ | $c_{\mu i}^* c_{\nu j}^* \langle \mu\nu \lambda\sigma \rangle c_{\lambda k} c_{\sigma l}$ | $c_{\mu i}^* c_{\nu j}^* \langle \mu\nu \lambda\sigma \rangle c_{\lambda k} c_{\sigma l}$ |
| $\langle \psi_i \psi_j \rangle$ | $\mathbf{c}_i^\dagger \mathbf{c}_j$ | $\mathbf{c}_i^\dagger \mathbf{S} \mathbf{c}_j$ |
| $\hat{F} \psi_i\rangle = \epsilon_i \psi_i\rangle$ | $\mathbf{F} \mathbf{c}_i = \epsilon_i \mathbf{c}_i$ | $\mathbf{F} \mathbf{c}_i = \epsilon_i \mathbf{S} \mathbf{c}_i$ |
| $[\hat{F}, \hat{\gamma}]$ | $\mathbf{FP} - \mathbf{PF}$ | $\mathbf{FPS} - \mathbf{SPF}$ |
| $\hat{\gamma}\hat{\gamma} = \hat{\gamma}$ | $\mathbf{PP} = \mathbf{P}$ | $\mathbf{PSP} = \mathbf{P}$ |
| q_A | $Z_A - \sum_{\mu \in A} \sum_{i=1}^N c_{\mu i} c_{\mu i}$ | $Z_A - \sum_{\substack{\mu \in A \\ \text{All } \nu}} \sum_{i=1}^N c_{\mu i} S_{\mu\nu} c_{\nu i}$ |

Note: Atomic charge definition is ambiguous, so there are many choices. Here, we show the Mulliken definition.