Stochastic Coupled Cluster Theory

Alex Thom

Quantum Monte Carlo in the Apuan Alps VII, 2012

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Electronic Structure Theory: Scaling

$\text{Calculation Time / s}$

- age of universe
- aeon
- $^{239}$Pu half life
- millennium
century
decade
year
week
day
minute
hour
decade
century
millennium
aeon
age of universe
$^{239}$Pu half life

# Water molecules

- $10^{-6}$
- $10^{-4}$
- $10^{-2}$
- $10^0$
- $10^2$
- $10^4$
- $10^6$
- $10^8$
- $10^{10}$
- $10^{12}$
- $10^{14}$

- force-field
- good SCF
- poor SCF

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Electronic Structure Theory: Accuracy

- HF
- DFT: GGA
- DFT: Hybrid
- MP2
- CCSD
- CCSD(T)
- CCSDT
- CCSDT(Q)

Deviation from experiment / kJ/mol

Helgaker T. et al., Molecular Electronic Structure Theory
For an $N$-electron system, $N$ spin-orbitals are chosen out of $2M$ spin-orbitals $\{\phi_1, \phi_2, ..., \phi_{2M}\}$ to form a Slater Determinant, $|D_i\rangle$. 
For an \( N \)-electron system, \( N \) spin-orbitals are chosen out of \( 2M \) spin-orbitals \( \{ \phi_1, \phi_2, \ldots, \phi_{2M} \} \) to form a Slater Determinant, \( |D_1\rangle \).

Complete space of determinants is finite, but exponentially growing in \( N \) and \( M \) as \( \left( \frac{2M}{N} \right) \).
We can project the many-electron Hamiltonian into the space of Slater Determinants and solve in this space. 

\[ H_{ij} = \langle D_i | \hat{H} | D_j \rangle. \]

Iterative diagonalization of the sparse Hamiltonian in this space gives the “Full Configuration Iteration” (FCI) solution.
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\[ H_{ij} = \langle D_i | \hat{H} | D_j \rangle. \]

Iterative diagonalization of the sparse Hamiltonian in this space gives the “Full Configuration Interaction” (FCI) solution.

As \( \hat{H} \) contains at most 2-electron operators, matrix elements between determinants are a simple combination of one- and two-electron Hamiltonian integrals.

Energy is variationally minimized — all of the basis set correlation energy captured.
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Energy is variationally minimized — all of the basis set correlation energy captured.

Solve as \( |\Psi_{CI}\rangle = \sum_i c_i |D_i\rangle \)

Exponentially scaling with system size (\( N \) or \( M \))
F CI Quantum Monte Carlo

- Solutions to $\hat{H} |\Psi\rangle = E |\Psi\rangle$ also solve $e^{-\tau \hat{H}} |\Psi\rangle = e^{-\tau E} |\Psi\rangle$. 
Solutions to $\hat{H}|\Psi\rangle = E|\Psi\rangle$ also solve $e^{-\tau\hat{H}}|\Psi\rangle = e^{-\tau E}|\Psi\rangle$.

Propagate $\frac{\partial|\Psi\rangle}{\partial\tau} = -\hat{H}|\Psi\rangle$.

Lowest energy eigenfunction $|\Psi_{CI}\rangle$ becomes dominant.
Solutions to $\hat{H}\ket{\Psi} = E\ket{\Psi}$ also solve $e^{-\tau\hat{H}}\ket{\Psi} = e^{-\tau E}\ket{\Psi}$.

Propagate $\frac{\partial \ket{\Psi}}{\partial \tau} = -\hat{H}\ket{\Psi}$.

Lowest energy eigenfunction $\ket{\Psi_{CI}}$ becomes dominant.

Let $\ket{\Psi_{CI}} = \sum_i c_i \ket{D_i}$

$$\frac{\partial c_i}{\partial \tau} = -\sum_j H_{ij} c_j.$$ 

Represent $c_i$ as populations of signed psips (walkers) propagating through space.

\[
\frac{\partial c_i}{\partial \tau} = -H_{ii}c_i - \sum_{j \rightarrow i} H_{ij}c_j.
\]

- Given a psip at \( j \), at time \( \tau + \delta \tau \) spawn a new one at randomly chosen \( i \) based on \( -\delta \tau H_{ij} \). This sample \( \sum_j \).
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Dynamics

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- Given a psip at \( j \), at time \( \tau + \delta \tau \) **spawn** a new one at randomly chosen \( i \) based on \( -\delta \tau H_{ij} \). This sample \( \sum_j \).

- Opposite-signed psips at the same determinant **annihilate**.
Dynamics

\[ \frac{\partial c_i}{\partial \tau} = -[H_{ii} - S]c_i - \sum_{j\rightarrow i} H_{ij}c_j. \]

- Given a psip at \( j \), at time \( \tau + \delta \tau \) spawn a new one at randomly chosen \( i \) based on \( -\delta \tau H_{ij} \). This sample \( \sum_j \).
- Psips at \( i \) die based on \( \delta \tau (H_{ii} - S) \). Usually \( S < E_{HF} \).
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FCIQMC  Coupled Cluster  Coupled Cluster Monte Carlo

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Dynamics

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- Start \( S = E_{HF} \). Once enough psips created change \( S \) in response to population. e.g. for growth, make \( S \) more negative, so more death.

\( ^\wedge \) FCIQMC  
Coupled Cluster  
Coupled Cluster Monte Carlo  
$
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- Start \( S = E_{HF} \). Once enough psips created change \( S \) in response to population. e.g. for growth, make \( S \) more negative, so more death.
- Opposite-signed psips at the same determinant annihilate.
\[
\frac{\partial c_i}{\partial \tau} = -[H_{ii} - S]c_i - \sum_{j \to i} H_{ij}c_j.
\]

- Given a psip at \( j \), at time \( \tau + \delta \tau \) *spawn* a new one at randomly chosen \( i \) based on \(-\delta \tau H_{ij}\). This sample \( \sum_j \).
- Psips at \( i \) *die* based on \( \delta \tau (H_{ii} - S) \). Usually \( S < E_{HF} \).
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- Opposite-signed psips at the same determinant *annihilate*. 
Example

- Initial configuration
Example

- Initial configuration
- Spawning
Example

- Initial configuration
- Spawning
- Death
Example

- Initial configuration
- Spawning
- Death
- Annihilation
- Initial configuration
- Spawning
- Death
- Annihilation
- Spawning

FCIQMC  Coupled Cluster  Coupled Cluster Monte Carlo

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Example

- Initial configuration
- Spawning
- Death
- Annihilation
- Spawning
- Death

FCIQMC

Coulled Cluster

Coulled Cluster Monte Carlo

$
Example

- Initial configuration
- Spawning
- Death
- Annihilation
- Spawning
- Death
- Annihilation
Example

- Initial configuration
- Spawning
- Death
- Annihilation
- Spawning
- Death
- Annihilation
- Many steps later
With a system-dependent critical number of psips, FCIQMC reproduces CI energy essentially exactly.

Critical psip number, $N_c$, needed to allow the correct sign structure of the wavefunction to develop.

Below this, energy is wrong. Plateau shows what $N_c$ is.
The Initiator Approximation

- Only allow psips on determinants with a significant population \((3+)\) to spawn to unoccupied determinants.
- Vastly reduces \(N_c\). Introduces systematic, but controllable error.


The Initiator Approximation

- Only allow psi's on determinants with a significant population (3+) to spawn to unoccupied determinants.
- Vastly reduces $N_C$. Introduces systematic, but controllable error.
- Scaling exponential with increasing system size — even with initiators.
- Able to calculate energies for previously insoluble systems (larger by many orders of magnitude).


Excitors

\[
|D_0\rangle \rightarrow \hat{a}_i^a |D_0\rangle
\]
Excitors

\[
|D_0\rangle \quad \hat{a}_i^a |D_0\rangle \quad |D_0\rangle \quad \hat{a}_{jk}^{bc} |D_0\rangle
\]

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Excitators

\[ |D_0\rangle \rightarrow \hat{a}_i^a |D_0\rangle \]

\[ |D_0\rangle \rightarrow \hat{a}_j^b |D_0\rangle \]

\[ |D_0\rangle \rightarrow \hat{a}_{ij}^{abc} |D_0\rangle = \hat{a}_{ijk}^{abc} |D_0\rangle \]
Coupled Cluster Theory uses a cluster operator $\hat{T} = \sum_i t_i \hat{a}_i$ which can be split into excitation levels (and truncated): $\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots$

- $\hat{T}_1 = \sum_i a_i t_i a_i \hat{a}_i$
- $\hat{T}_2 = \sum_{i<j} a_i < b_j a_i \hat{a}_{ij}$

Use an exponential to generate the wavefunction $|\Psi_{CC}\rangle = e^{\hat{T}} |D_0\rangle$

Exponential generates products of excitors $e^{\hat{T}} = 1 + \hat{T}_1 + \hat{T}_2 + \cdots + \frac{1}{2!} \hat{T}_1 \hat{T}_2 + \cdots$. $\hat{T}$ is often denoted with a caret (hat) symbol.
The exponential Ansatz

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- which can be split into excitation levels (and truncated)
  \( \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots \)

\[
\hat{T}_1 = \sum_i t^a_i \hat{a}^a_i \\
\hat{T}_2 = \sum_{i<j} t^{ab}_{ij} \hat{a}^{ab}_{ij} \\
\ldots
\]
The exponential Ansatz

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- which can be split into excitation levels (and truncated)
  \[ \hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \ldots \]

\[
\hat{T}_1 = \sum_{i,a} t^a_i \hat{a}^a_i \\
\hat{T}_2 = \sum_{i<j, a<b} t^{ab}_{ij} \hat{a}^{ab}_{ij} \\
\]

- Use an exponential to generate the wavefunction
  \[ |\Psi_{CC}\rangle = e^{\hat{T}} |D_0\rangle \]
- Exponential generates products of excitors
  \[ e^{\hat{T}} = \hat{1} + \hat{T}_1 + \hat{T}_2 + \cdots + \frac{1}{2} \hat{T}_1^2 + \frac{1}{2} \hat{T}_1 \hat{T}_2 + \cdots \]
Consider a single atom.

- Excitation $\hat{a}_{ij}^{ab}$ is present in both CISD and CCSD.
Size Consistency

- Consider a single atom.
- Excitation $\hat{a}_{ij}^{ab}$ is present in both CISD and CCSD.
- Consider two separated non-interacting atoms: $X$ and $Y$.
- Simultaneous excitation $\hat{a}_{i X j X}^{a X b X} \hat{a}_{i Y j Y}^{a Y b Y}$ needed for same level of description of each atom.
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- Consider two separated non-interacting atoms: $X$ and $Y$.
- Simultaneous excitation $\hat{a}_{iXjX}^{aXbX} \hat{a}_{iYjY}^{aYbY}$ needed for same level of description of each atom.
- Present in CCSD in $\frac{1}{2} \hat{T}_2^2$ product $\hat{a}_{iXjX}^{aXbX} \hat{a}_{iYjY}^{aYbY}$.
- Only present in CISDTQ level and beyond.
Consider a single atom.

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Only present in CISDTQ level and beyond.

As number of electrons increases, truncated CI rapidly worsens.
Size Consistency

Error in Energy per atom / kJ/mol

CC

1 kcal/mol

$1 \text{kcal/mol} = 10 \text{ meV}$

FCIQMC

Coupled Cluster

Coupled Cluster Monte Carlo

$\approx$
Size Consistency

![Graph showing the relationship between truncation level and error in energy per atom (kJ/mol)]

- Blue line represents CC (Coupled Cluster)
- Green line represents Ne$_1$ Cl
- Dotted blue line represents 1 kcal/mol

Error in Energy per atom: 1 kcal/mol = 10 meV

Legend:
- FCIQMC
- Coupled Cluster
- Coupled Cluster Monte Carlo

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Size Consistency

- **CC**: 1 kcal/mol
- **Ne**: 1 CI
- **Ne**: 2 CI

Error in Energy per atom / kJ/mol

1 kcal/mol = 10 meV

FCIQMC Coupled Cluster

Stochastic Coupled Cluster Theory
Size Consistency

Truncation Level

Error in Energy per atom / kJ/mol

CC

1 kcal/mol

Ne

1 Cl

Ne

2 Cl

Ne

3 Cl

1 kcal/mol = 10 meV

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Coupled Cluster

Coupled Cluster Monte Carlo

$
Solve $\hat{H}\ket{\Psi_{CC}} = E\ket{\Psi_{CC}}$. Could solve projected equations like

$$\langle D_0 | \hat{H} - E | e^{\hat{T}} D_0 \rangle = 0$$

$$\langle D_a | \hat{H} - E | e^{\hat{T}} D_0 \rangle = 0$$

$$\langle D_{ab} | \hat{H} - E | e^{\hat{T}} D_0 \rangle = 0$$

Complicated and non-linear, so solve iteratively.

Not variational.

Full CI and Full CC are equivalent.

Normally easier to solve

$$\langle D_i | e^{-\hat{T}} (\hat{H} - E) e^{\hat{T}} | D_0 \rangle = 0$$.
Naïve Coupled Cluster Theory

- Solve $\hat{H}\chi_{CC} = E\chi_{CC}$.
- Could solve projected equations like
  \[
  \langle D_0 | \hat{H} - E | e^{\hat{T}} D_0 \rangle = 0 \\
  \langle D^a_i | \hat{H} - E | e^{\hat{T}} D_0 \rangle = 0 \\
  \langle D^{ab}_{ij} | \hat{H} - E | e^{\hat{T}} D_0 \rangle = 0, \text{ etc.}
  \]
Naïve Coupled Cluster Theory

- Solve $\hat{H}\lvert \Psi_{CC}\rangle = E\lvert \Psi_{CC}\rangle$.
- Could solve projected equations like
  $$\langle D_0 \lvert \hat{H} - E \lvert e^{\hat{T}} D_0 \rangle = 0$$
  $$\langle D_i^a \lvert \hat{H} - E \lvert e^{\hat{T}} D_0 \rangle = 0$$
  $$\langle D_{ij}^{ab} \lvert \hat{H} - E \lvert e^{\hat{T}} D_0 \rangle = 0$$, etc.
- Complicated and non-linear, so solve iteratively.
- Not variational.
- Full CI and Full CC are equivalent. $\hat{C} = e^{\hat{T}}$.
- Normally easier to solve $\langle D_i \lvert e^{-\hat{T}}(\hat{H} - E)e^{\hat{T}} \lvert D_0 \rangle = 0$. 

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Stochastic Coupled Cluster Theory
\[ \langle D_i | (\hat{H} - E) | \Psi_{\text{CI}} \rangle = 0 \]
CI vs. CC Theory

\[
\begin{align*}
\langle D_i | (\hat{H} - E) | \Psi_{CI} \rangle &= 0 \\
\langle D_i | 1 - \delta \tau (\hat{H} - E) | \Psi_{CI} \rangle &= \langle D_i | \Psi_{CI} \rangle
\end{align*}
\]
\[ \langle D_i | (\hat{H} - E) | \Psi_{\text{CI}} \rangle = 0 \]
\[ \langle D_i | 1 - \delta \tau (\hat{H} - E) | \Psi_{\text{CI}} \rangle = \langle D_i | \Psi_{\text{CI}} \rangle \]
\[ \sum_j \langle D_i | 1 - \delta \tau (\hat{H} - E) | c_j D_j \rangle = c_i \]
\[ \langle D_i | (\hat{H} - E) | \Psi_{\text{CI}} \rangle = 0 \]

\[ \langle D_i | 1 - \delta \tau (\hat{H} - E) | \Psi_{\text{CI}} \rangle = \langle D_i | \Psi_{\text{CI}} \rangle \]

\[ \sum_j \langle D_i | 1 - \delta \tau (\hat{H} - E) | c_j D_j \rangle = c_i \]

\[ c_i - \delta \tau \sum_j (H_{ij} - E\delta_{ij}) c_j = c_i \]
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\sum_j \langle D_i | 1 - \delta \tau (\hat{H} - E) | c_j D_j \rangle &= c_i \\
\langle D_i | \Psi_{CI} \rangle &= \sum_j \langle D_i | 1 - \delta \tau (\hat{H} - E) | c_j \rangle c_j \\
c_i - \delta \tau \sum_j (H_{ij} - E\delta_{ij}) c_j &= c_i \\
c_i(\tau) - \delta \tau \sum_j (H_{ij} - E\delta_{ij}) c_j(\tau) &= c_i(\tau + \delta \tau)
\end{align*}
\]
\[
\langle D_i | (\hat{H} - E) | \Psi_{\text{CC}} \rangle = 0
\]
\[
\langle D_i | 1 - \delta \tau (\hat{H} - E) | \Psi_{\text{CI}} \rangle = \langle D_i | \Psi_{\text{CI}} \rangle
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\langle D_i | 1 - \delta \tau (\hat{H} - E) | \Psi_{\text{CC}} \rangle &= \langle D_i | \Psi_{\text{CC}} \rangle \\
\sum_j \langle D_i | 1 - \delta \tau (\hat{H} - E) | c_j D_j \rangle &= c_i \\
\sum_j (H_{ij} - E \delta_{ij}) c_j &= c_i \\
\sum_j (H_{ij} - E \delta_{ij}) c_j(\tau) &= c_i(\tau + \delta \tau)
\end{align*}
\[ \langle D_i | (H - E) | \Psi_{\text{CC}} \rangle = 0 \]
\[ \langle D_i | 1 - \delta \tau (\hat{H} - E) | \Psi_{\text{CC}} \rangle = \langle D_i | \Psi_{\text{CC}} \rangle \]
\[ \sum_j \langle D_i | 1 - \delta \tau (\hat{H} - E) | D_j \rangle \langle D_j | \Psi_{\text{CC}} \rangle = \langle D_i | \Psi_{\text{CC}} \rangle \]
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\]
\[
c_i(\tau) - \delta \tau \sum_j (H_{ij} - E \delta_{ij}) c_j(\tau) = c_i(\tau + \delta \tau)
\]
e.g. \( D_i = D_{ij}^{ab}. \langle D_i | \Psi_{CC} \rangle = t_{ij}^{ab} + t_i^{a}t_j^{b} - t_i^{b}t_j^{a} = t_i + \mathcal{O}[T^2]. \)
\[
\langle D_i | (\hat{H} - E) | \Psi_{CC} \rangle = 0
\]
\[
\langle D_i | 1 - \delta \tau (\hat{H} - E) | \Psi_{CC} \rangle = \langle D_i | \Psi_{CC} \rangle
\]
\[
\sum_j \langle D_i | 1 - \delta \tau (\hat{H} - E) | D_j \rangle \langle D_j | \Psi_{CC} \rangle = \langle D_i | \Psi_{CC} \rangle
\]
\[
\langle D_i | \Psi_{CC} \rangle - \delta \tau \sum_j (H_{ij} - E \delta_{ij}) \langle D_j | \Psi_{CC} \rangle = \langle D_i | \Psi_{CC} \rangle
\]
\[
t_i(\tau) - \delta \tau \sum_j (H_{ij} - E \delta_{ij}) \langle D_j | \Psi_{CC}(\tau) \rangle = t_i(\tau + \delta \tau)
\]

e.g. \( D_i = D_{ij}^{ab} \). \( \langle D_i | \Psi_{CC} \rangle = t_{i,j}^{ab} + t_i^a t_j^b - t_j^b t_i^a = t_i + O[T^2] \).
Sampling the CC equations

\[ t_i(\tau) - \delta \tau \sum_j (H_{ij} - E\delta_{ij}) \langle D_j | \Psi_{CC}(\tau) \rangle = t_i(\tau + \delta \tau) \]

- \( \forall i, \forall j \), calculate \( \langle D_j | \Psi_{CC}(\tau) \rangle \) and update \( t_i \).
Sampling the CC equations

\[ t_i(\tau) - \delta \tau \sum_j (H_{ij} - E\delta_{ij}) \langle D_j | \Psi_{CC}(\tau) \rangle = t_i(\tau + \delta \tau) \]

- \forall i, \forall j, calculate \langle D_j | \Psi_{CC}(\tau) \rangle and update \( t_i \).
- \forall j, calculate \langle D_j | \Psi_{CC}(\tau) \rangle. Now randomly pick \( i \), and update \( t_i \).
Sampling the CC equations

\[ t_i(\tau) - \delta \tau \sum_j (H_{ij} - E_{ij}) \langle D_j | \Psi_{CC}(\tau) \rangle = t_i(\tau + \delta \tau) \]

\[ e^\hat{T} = 1 + \sum_i t_i \hat{a}_i + \frac{1}{2!} \sum_{i,j} t_i t_j \hat{a}_i \hat{a}_j + \frac{1}{3!} \sum_{i,j,k} t_i t_j t_k \hat{a}_i \hat{a}_j \hat{a}_k + \ldots \]

▶ \forall i, \forall j, calculate \langle D_j | \Psi_{CC}(\tau) \rangle and update \( t_i \).
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- ∀i, ∀j, calculate \( \langle D_j | \Psi_{CC}(\tau) \rangle \) and update \( t_i \).
- ∀j, calculate \( \langle D_j | \Psi_{CC}(\tau) \rangle \). Now randomly pick i, and update \( t_i \).
- Pick a random term in \( e^\hat{T} \) and work out j and \( \langle D_j | \Psi_{CC}(\tau) \rangle \) from just this term. Now randomly pick i, and update \( t_i \).
Discretization

- Represent $\hat{T} = \sum_i t_i \hat{a}_i$ as a population of excips for each excitation.

- Need to sample

$$e^{\hat{T}} = 1 + \sum_i t_i \hat{a}_i + \frac{1}{2!} \sum_{i,j} t_i t_j \hat{a}_i \hat{a}_j + \frac{1}{3!} \sum_{i,j,k} t_i t_j t_k \hat{a}_i \hat{a}_j \hat{a}_k + \ldots$$
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- From list of excips randomly select a number of them (remembering signs). Need normalized probabilities.

$$+ a_i + b_i + b_i - a_j - b_j + c_j + c_j + c_j - a_{ij} + a_{ik} - a_{ijk}$$

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$$+ \frac{a}{i} + \frac{b}{i} + \frac{b}{i} - \frac{a}{j} - \frac{b}{j} + \frac{c}{j} + \frac{c}{j} + \frac{c}{j} - \frac{ab}{ij} + \frac{ac}{ik} - \frac{abc}{ijk}$$

Discretization

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- From list of excips randomly select a number of them (remembering signs). Need normalized probabilities.

$$+ a_i + b_i + b_i \quad - a_j - \frac{b}{j} \quad + c_j \quad + c_j \quad + c_j \quad - a b_{ij} + \frac{ac}{ik} - \frac{abc}{ijk}$$

Discretization

\[ + \frac{ac}{ik} - \frac{b}{j} \]
Discretization

\[ + \frac{ac}{ik} - \frac{b}{j} \rightarrow -\hat{a}_{ijk} \]

- **Collapse** this into a single excitor and apply to the reference, resulting in a determinant.

\[ -\hat{a}_{ijk} |D_0\rangle = -|D_{ijk}\rangle \]
Discretization

\[ +_{\frac{ac}{ik}} -_{\frac{b}{j}} \rightarrow -\hat{a}_{ijk} \]

- **Collapse**: this into a single excitor and apply to the reference, resulting in a determinant.

\[ -\hat{a}_{ijk} |D_0\rangle = -|D_{ijk}\rangle \]

- **Spawning**: Pick random excitation from \(|D_{ijk}\rangle\) (e.g. \(c_i\)) and spawn according to 

\[ -\delta \tau \langle D_i^c | \hat{H} | D_{ijk}^{abc} \rangle. \]
Discretization

\[ \left. + \frac{a_c}{i_k} - \frac{b}{j} \right. \rightarrow - \hat{a}_{ijk}^{abc} \]

**Collapse** this into a single excitor and apply to the reference, resulting in a determinant.

\[ -\hat{a}_{ijk}^{abc}|D_0\rangle = -|D_{ijk}^{abc}\rangle \]

**Spawning**: Pick random excitation from \(|D_{ijk}^{abc}\rangle\) (e.g. \(c_i\)) and spawn according to \(-\delta \tau \langle D_{i}^{c} | \hat{H} | D_{ijk}^{abc} \rangle\). . . Create new \(+_{i}^{c}\) excip.
Discretization

\[ \hat{a}^a_{ik} \hat{a}^b_j \rightarrow -\hat{a}^{abc}_{ijk} \]

- **Collapse**: This into a single excitor and apply to the reference, resulting in a determinant.

\[ -\hat{a}^{abc}_{ijk} |D_0\rangle = -|D^{abc}_{ijk}\rangle \]

- **Spawning**: Pick random excitation from \(|D^{abc}_{ijk}\rangle\) (e.g. \(c_i\)) and spawn according to \(-\delta \tau \langle D^c_i | \hat{H} | D^{abc}_{ijk}\rangle\). . . Create new \(+c_i\) excip.

- **Death**: Die according to \(\delta \tau \left( \langle D^{abc}_{ijk} | \hat{H} | D^{abc}_{ijk}\rangle - S' \right)\).
Discretization

\[ +a_{ik}^c -b_j^b \rightarrow -\hat{a}^{abc}_{ijk} \]

- **Collapse**: Collapse this into a single excitor and apply to the reference, resulting in a determinant.

\[ -\hat{a}^{abc}_{ijk} |D_0\rangle = -|D^{abc}_{ijk}\rangle \]

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- **Death**: Die according to \( \delta \tau (\langle D^{abc}_{ijk} | \hat{H} | D^{abc}_{ijk}\rangle - S)\). ... Create new \( +abc_{ijk} \) excip.

\^ FCIQMC Coupled Cluster Coupled Cluster Monte Carlo $
Discretization

\[ +^{ac}_{ik} -^{b}_{j} \rightarrow -\hat{a}_{ijk} \]

- **Collapse** this into a single excitor and apply to the reference, resulting in a determinant.

\[ -\hat{a}_{ijk} |D_0\rangle = - |D_{ijk}\rangle \]

- **Spawning**: Pick random excitation from \( |D_{ijk}^{abc}\rangle \) (e.g. \( ^{c}_{i} \)) and spawn according to \(-\delta\tau \langle D_{i}^{c} | \hat{H} | D_{ijk}^{abc}\rangle \). ... Create new \(+^{c}_{i}\) excip.

- **Death**: Die according to \(\delta\tau (\langle D_{ijk}^{abc} | \hat{H} | D_{ijk}^{abc}\rangle - S)\). ... Create new \(+^{abc}_{ijk}\) excip.

- **Annihilate** as in FCIQMC.
Coupled Cluster

![Graph showing energy/ Hartree vs iterations]

Alex Thom
Stochastic Coupled Cluster Theory

UNIVERSITY OF CAMBRIDGE
Performance

- Initial excip growth much faster than FCIQMC.
- Critical number of excips required otherwise growth unstable.
Performance

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- Critical number of excips seems to scale with size of space. e.g. CCSD $N_c \sim N^4$.
- Able to reproduce large coupled cluster calculations in less time.
Performance

- Initial excip growth much faster than FCIQMC.
- Critical number of excips required otherwise growth unstable.
- Critical number of excips seems to scale with size of space. e.g. CCSD $N_c \sim N^4$.
- Able to reproduce large coupled cluster calculations in less time.
- Initiator approximation also applicable.
- Cluster is initiator iff all component excips have sufficient amplitude.
- Much fewer excips, so much faster.
Ne cc-pVQZ initiator

![Graph showing correlation energy versus number of excitations.](image)

- Correlation Energy/Hartree as a function of # excitations.
- Various methods represented by different symbols:
  - FCIQMC
  - Coupled Cluster
  - Coupled Cluster Monte Carlo

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Stochastic Coupled Cluster Theory
Scaling

- **CPU Time / s**: minute, day, week, year, decade, millennium
- **Storage / bytes**
  - Full CCSDTQ mem
  - MC CCSDTQ mem

Graph showing the scaling of Full CCSDTQ time and MC CCSDTQ time with basis set size.

- **Basis**: TZ, QZ, 5Z, 6Z
- **Additional Elements**:
  - Pu half life
  - 239 Pu half life
  - FCIQMC
  - Coupled Cluster
  - Coupled Cluster Monte Carlo
  - Dollar sign

**Authors**:
- Alex Thom
- Stochastic Coupled Cluster Theory
Parallel Scaling

Ideal Scaling
CCMC
FCIQMC
Coupled Cluster
Coupled Cluster Monte Carlo

**Stochastic Coupled Cluster Theory**

Alex Thom
The Uniform Electron Gas

\[ r_s = 1 \]

\begin{figure}
\centering
\includegraphics[width=\textwidth]{plot.png}
\caption{Correlation Energy/electron /eV vs. \# basis functions}
\end{figure}

J. J. Shepherd, G. H. Booth and A. Alavi
J. J. Shepherd, A. Grünéis, G. H. Booth, G. Kresse, and A. Alavi
$r_s = 1$

The Uniform Electron Gas

Correlation Energy/electron (eV)

# basis functions

-1.10
-1.05
-1.00
-0.95
-0.90

n14 iFCIQMC
n14 CCSD

J. J. Shepherd, G. H. Booth and A. Alavi

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The Uniform Electron Gas

\[ r_s = 1 \]

\[ n = 14 \text{ Cutoff 64Ry, } M = 4218, \text{ triples: } 3 \times 10^8, \text{ full } 10^{34} \]
The Uniform Electron Gas

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\[ n = 14 \text{ Cutoff 64 Ry, } M = 4218, \text{ triples: } 3 \times 10^8, \text{ full } 10^{34} \]

\[ n = 54 \text{ Cutoff 64 Ry, } M = 4218, \text{ triples: } 2 \times 10^{10}, \text{ full } 10^{117} \]

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The Uniform Electron Gas

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The Uniform Electron Gas

The Uniform Electron Gas

The Uniform Electron Gas

Correlation Energy / electron / eV

\( n_{14} \) FCI
\( n_{14} \) MP2
\( n_{14} \) CCSD
\( n_{14} \) CCSDT

The Uniform Electron Gas

The Uniform Electron Gas

\[ n_{54} \text{iCCSD} \]

\[ \text{Correlation Energy/electron} / \text{eV} \]

\[ rs / a_0 \]

\[ 10^{-1} \quad 10^{0} \quad 10^{1} \]

Correlation Energy/electron / eV

-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4

\[ 10^{-1} \quad 10^{0} \quad 10^{1} \]

\[ rs / a_0 \]

\[ 10^{-1} \quad 10^{0} \quad 10^{1} \]

\[ n_{54} \text{iCCSD} \]

\[ \text{Correlation Energy/electron} / \text{eV} \]

-0.2
-0.4
-0.6
-0.8
-1.0
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-1.4

\[ 10^{-1} \quad 10^{0} \quad 10^{1} \]

\[ rs / a_0 \]

\[ 10^{-1} \quad 10^{0} \quad 10^{1} \]

\[ n_{54} \text{iCCSD} \]

\[ \text{Correlation Energy/electron} / \text{eV} \]

-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4

\[ 10^{-1} \quad 10^{0} \quad 10^{1} \]

\[ rs / a_0 \]
The Uniform Electron Gas

The Uniform Electron Gas

Conclusions

- Stochastic Coupled Cluster (CCMC) behaves very similar to FCIQMC.
- Truncated CC allows polynomial scaling spaces to be used.
- Much simpler to implement than deterministic CC.
- Required number of excips appears to scale with size of space.
- Initiator approximation very successful at reducing critical number of excips.
- Feasible on workstations, and very parallelizable.
Directions

- Benchmarking.
- Solids. Complex excips.
- Large-scale parallelization.
- f12-CCMC.
- CASCC.
- Soon to be available in MOLPRO
- Applications...
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- James Spencer, Andreas Grüneis — VASP integration
Ne cc-pVQZ growth
Ne cc-pVQZ growth

Number of excitations vs iteration for CCSDMC and CCSDTMC.
Ne cc-pVQZ growth

![Graph showing the growth of Ne cc-pVQZ with iteration and number of excitations for CCSDMC, CCSDTMC, and iCCSDTMC methods.](image)
Ne cc-pVQZ growth

![Graph showing Ne cc-pVQZ growth with iterations and excips for CCSDMC, CCSDTMC, and iCCSDTMC methods.](image)