Semistochastic importance sampling of second-quantized operators in determinant space

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Overview

1. Motivation
2. Algorithm
3. Applications

Motivation

Types of quantum chemistry algorithms

1. Orbital-space algorithms:
   1. Coupled cluster
   2. Moller-Plesset perturbation theory
2. Determinant-space algorithms:
   1. Full CI
   2. Selected CI
   3. Epstein-Nesbet perturbation theory
   4. Full CI Quantum Monte Carlo (FCIQMC)

Determinant-space algorithms

Slater determinants, second-quantized operators in this basis

In determinant-space algorithms, one of the key steps is applying a second-quantized operator (usually H) to a Slater determinant!

1. Full CI: Iterative diagonalization of the Hamiltonian (e.g. using Davidson) diagonalizes in the basis of Krylov vectors

$$\{v_i = f(Hv_{i-1})\} \tag{1}$$

2. Selected CI: New determinants are 'selected' using a criterion that is a function of $H\psi_0$
3. Epstein-Nesbet perturbation theory:

$$\Delta E = \left\langle \psi_0 \left| V \frac{1}{E_0 - H_0} V \right| \psi_0 \right\rangle \tag{2}$$

4. FCIQMC: Stochastically simulate the power method,

$$\psi_0 \propto \lim_{n\to\infty} (1 - \tau H)^n \psi_T \tag{3}$$

Approaches for computing $H|D_i\rangle$

Broadly, there are three main approaches:

1. **Deterministic:** Simply evaluating all single and double excitations from the initial Slater determinant. Complexity: $\mathcal{O}(N^2(M-N)^2)$
2. **Stochastic:** Sampling excitations according to some distribution. Reduces the complexity, but introduces a stochastic uncertainty (and in projector methods, the fermion sign problem!)
3. **Semistochastic:** Evaluating the largest-magnitude components, and sampling the remaining, smaller components. Reduces complexity relative to the deterministic approach, but with a greatly reduced stochastic uncertainty relative to fully stochastic methods. In projector methods, it also mitigates the bias incurred in taming the fermion sign problem, such as the initiator bias in FCIQMC.

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$$H\,|D_i\rangle = \sum_j H_{ji} \tag{4}$$

$$= \underbrace{\sum_j H_{ji}\Big|_{|H_{ji}|\geq\epsilon}}_{\substack{\text{few large terms:}\\ \text{sum deterministically}}} + \underbrace{\sum_j H_{ji}\Big|_{|H_{ji}|<\epsilon}}_{\substack{\text{many small terms:}\\ \text{importance sample}}} \tag{5}$$

Algorithm

Deterministic component

- **Setup:**
  - For each pair of orbitals $\{p, q\}$, store a list of $\{r, s, |H(rs \leftarrow pq)|\}$, sorted by $|H(rs \leftarrow pq)|$ in decreasing order

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Deterministic component

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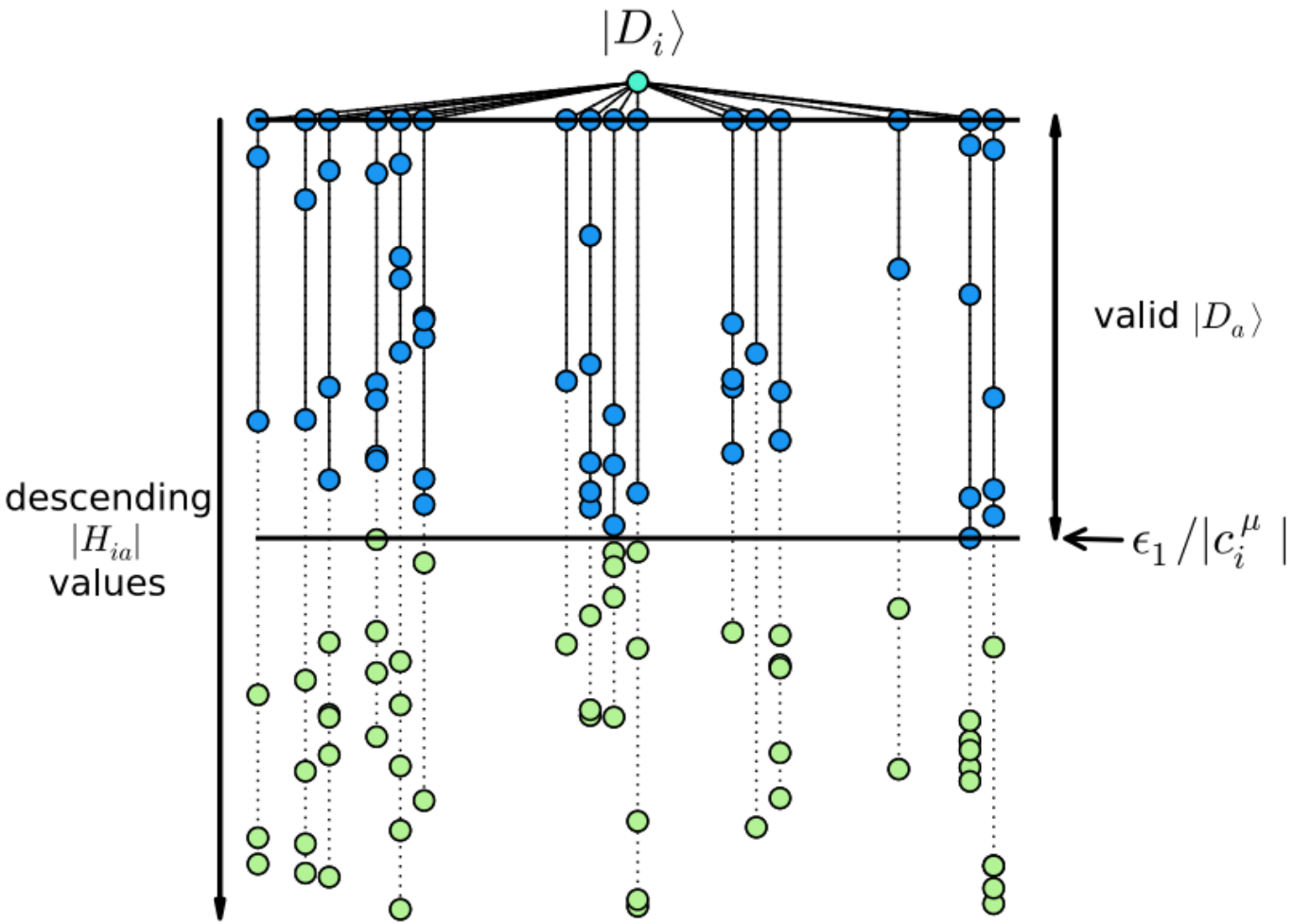
- **Finding important connected determinants** D_j (for which $|H_{ji}| > \epsilon$):

  - **Generate only those double excitations that exceed** ϵ**.**
    For each pair of occupied orbitals $\{p, q\}$, look up the stored list of triplets $\{r, s, |H(rs \leftarrow pq)|\}$ and iterate through the list until a triplet is reached for which $|H(rs \leftarrow pq)| < \epsilon$

Deterministic component



Discrete sampling algorithms

- **Alias sampling:**
  1. Sample an element with uniform probability
  2. If a low-probability element was selected, it has some probability of 'aliasing' to another, high-probability element

  Setup time: $\mathcal{O}(N)$, Time per sample: $\mathcal{O}(1)$
- **Cumulative distribution function (CDF) searching:**
  1. Sample a real number r uniformly between 0 and 1
  2. Binary-search the CDF for r (i.e., find the smallest index i for which $r < \mathrm{CDF}_i$)

  Setup time: $\mathcal{O}(N)$, Time per sample: $\mathcal{O}(\log N)$

Usually, Alias sampling is preferred because it has lower sampling complexity, but CDF searching has a unique use case that we will need...

CDF searching's unique use case

Suppose we have a stored CDF, and we want to be able to efficiently sample one of the first n elements, where n is not known ahead of time. CDF searching can do this efficiently with a small modification:

1. Sample a real number r uniformly between 0 and CDF_n (Note that $\mathrm{CDF}_N = 1$ reduces to the original algorithm)
2. Binary-search the CDF for r (i.e., find the smallest index i for which $r < \mathrm{CDF}_i$)

Importance-sampling excitations

- Recall that we have already described how to treat the large-magnitude ($|H_{ji}| \geq \epsilon$) excitations deterministically
- Now, we want to "importance-sample" the remaining small-magnitude ($|H_{ji}| < \epsilon$) excitations, i.e.:

$$P(H_{ji}) \begin{cases} \propto f(|H_{ji}|), & \text{if } |H_{ji}| < \epsilon; \\ = 0, & \text{if } |H_{ji}| \geq \epsilon. \end{cases} \tag{6}$$

Examples of importance-sampling distributions include:

$$f(|H_{ji}|) = |H_{ji}|, \qquad f(|H_{ji}|) = |H_{ji}|^2 \tag{7}$$

Importance-sampling excitations

We divide the sampling of an excitation into two stages:

1. Sample an exciting electron pair
   - with probability proportional to the sum of remaining (small-magnitude) targets it could excite to
2. Sample a target orbital pair
   - with probability proportional to its excitation magnitude

Sampling an exciting electron pair

- During the deterministic step, for each exciting electron pair, we iterate over the sorted excitation magnitudes
- As soon as the threshold is reached, we record the sum of remaining excitation magnitudes as that electron pair's relative probability
- After doing this for all electron pairs, we set up the Alias sampling data structure in $\mathcal{O}(N^2)$ time
- This enables **importance-sampling an exciting electron pair in $\mathcal{O}(1)$ time**

Sampling a target orbital pair

- Once an exciting electron pair is selected, we now have to sample a target orbital pair to excite to
- Since the deterministic stage has already been completed, we know which target orbital pair (r, s) is the first one that hasn't been treated deterministically
- We have a CDF (in reverse order) corresponding to all target orbital pairs, and we need to sample one of the orbital pairs whose index is at least as high as this one
- So, we just use CDF searching to **sample a target orbital pair in $\mathcal{O}(\log M)$ time**

What about single excitations?

- Unlike double excitations, single excitation matrix element magnitudes depend on the orbital occupancies of the exciting determinant
- But we can compute upper bounds to the single excitation magnitudes:

$$|H(p \to r)| \leq |H(p \to r)|_{\max}\,, \tag{8}$$

  where $|H(p \to r)|_{\max}$ is the largest magnitude the $p \to r$ excitation can have from any initial determinant
- The simplest way to incorporate singles is to sample them with probability $P(|H(p \to r)|) \propto f(|H(p \to r)|_{\max})$ and skip them in the deterministic step

Sampling 'invalid' excitations

- Sometimes this algorithm will sample 'invalid' excitations to already-occupied orbitals
- While unbiased, this increases the variance in the samples
- We can fix this as follows:
  1. If an 'invalid' excitation is sampled, discard it and resample until a valid excitation is sampled
  2. Scale the sample probabilities by a constant factor so they remain normalized (can be performed in $\mathcal{O}(N^3)$ time during deterministic step)

Applications

Epstein-Nesbet perturbation theory

Given a variational wavefunction $\psi_0 = \sum_i c_i |D_i\rangle$ with energy E_0, the Epstein-Nesbet perturbative correction to the energy is give by

$$\Delta E\left[V|\psi_0\rangle\right] = \left\langle \psi_0 \middle| V \frac{1}{E_0 - H_0} V \middle| \psi_0 \right\rangle \tag{9}$$

$$= \sum_{\substack{a \in \mathcal{C}(\mathcal{V}) \\ \notin \mathcal{V}}} \frac{1}{E_0 - E_a} \left(\sum_{ij \in \mathcal{V}} c_j H_{ja} H_{ai} c_i \right), \tag{10}$$

so we can now evaluate the H_{ai} components semistochastically using importance sampling.

Semistochastic Epstein-Nesbet Perturbation Theory

1. Divide $V|\psi_0\rangle$ into two pieces:

$$H|\psi_0\rangle = (V|\psi_0\rangle)_{\geq\epsilon} + (V|\psi_0\rangle)_{<\epsilon}\,. \tag{11}$$

2. Estimate ΔE deterministically:

$$\Delta E\left[V|\psi_0\rangle\right] \approx \Delta E\left[(V|\psi_0\rangle)_{\geq\epsilon}\right] \tag{12}$$

3. Stochastically evaluate the difference between the exact and approximate ΔE

Sampling algorithm in Epstein-Nesbet PT

How to evaluate the stochastic component?

- Old approach (SHCI):
  - Sample a batch of determinants $\{D_i\}$ from ψ_0, compute $\sum_a H_{ai} c_i$ deterministically for each sampled D_i
  - Drawbacks:
    - No importance sampling of H matrix elements
    - Memory-limited because requires computing all determinants $\{D_a\}$ for which $H_{ai} \neq 0$
    - Wastes time on small-magnitude H_{ai} elements

Sampling algorithm in Epstein-Nesbet PT

- New approach (Importance sampling):
  - Sample pairs of determinants $\{D_i, D_a\}$ using importance sampling:

$$P(D_i, D_a) \propto (H_{ai} c_i)^2 \tag{13}$$

  - Use those samples to evaluate the stochastic component of ΔE,whose largest-magnitude component is

$$\sum_{ai} \frac{(H_{ai} c_i)^2}{E_0 - E_a} \tag{14}$$

  - Advantages:
    - Uses importance sampling to greatly reduce the variance!
    - No time or memory is wasted on deterministically evaluating contributions from small-magnitude H_{ai} elements!

FCIQMC Overview

- Power method to project out the Full CI ground state:

$$\psi_0 \propto \lim_{n\to\infty} (1-\tau H)^n \psi_T \tag{15}$$

- When the Hilbert space is too large, we can simulate each iteration of the power method

$$\psi^{(t)} = (1-\tau H)\psi^{(t-1)} \tag{16}$$

by applying H stochastically (or semistochastically)

- The energy can be estimated using a mixed estimator:

$$E_0 = \frac{\langle \psi_T | H | \psi_0 \rangle}{\langle \psi_T | \psi_0 \rangle}, \tag{17}$$

using a precomputed ψ_T (e.g. from Selected CI)

Semistochastic algorithm in FCIQMC

How to perform the semistochastic projection $\psi^{(t)} = (1 - \tau H)\psi^{(t-1)}$?

- Old approach (Semistochastic FCIQMC):
  1. Choose a fixed set of 'important' determinants $\mathcal{D}$ (e.g., using Selected CI) before the run
  2. Deterministically apply the diagonal Hamiltonian matrix elements, and the off-diagonal elements between pairs of important determinants
  3. Importance-sample off-diagonal elements, discard the ones that were already treated deterministically

Semistochastic algorithm in FCIQMC

- New approach (Dynamic, importance-sampled semistochastic FCIQMC):
  1. Apply the Hamiltonian using semistochastic importance sampling to each determinant in $\psi^{(t)}$
- Advantages:
  - Deterministic/stochastic division is dynamic: it depends on the current $\psi^{(t)}$, which should greatly reduce the stochastic fluctuations and mitigate the fermion sign problem
  - Directly samples the off-diagonal H elements that were not treated deterministically, which should greatly reduce the computational time