Semistochastic importance sampling of second-quantized operators in determinant space

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Overview

Motivation

Types of quantum chemistry algorithms

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   3. Epstein-Nesbet perturbation theory
   4. Full CI Quantum Monte Carlo (FCIQMC)

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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:

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

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

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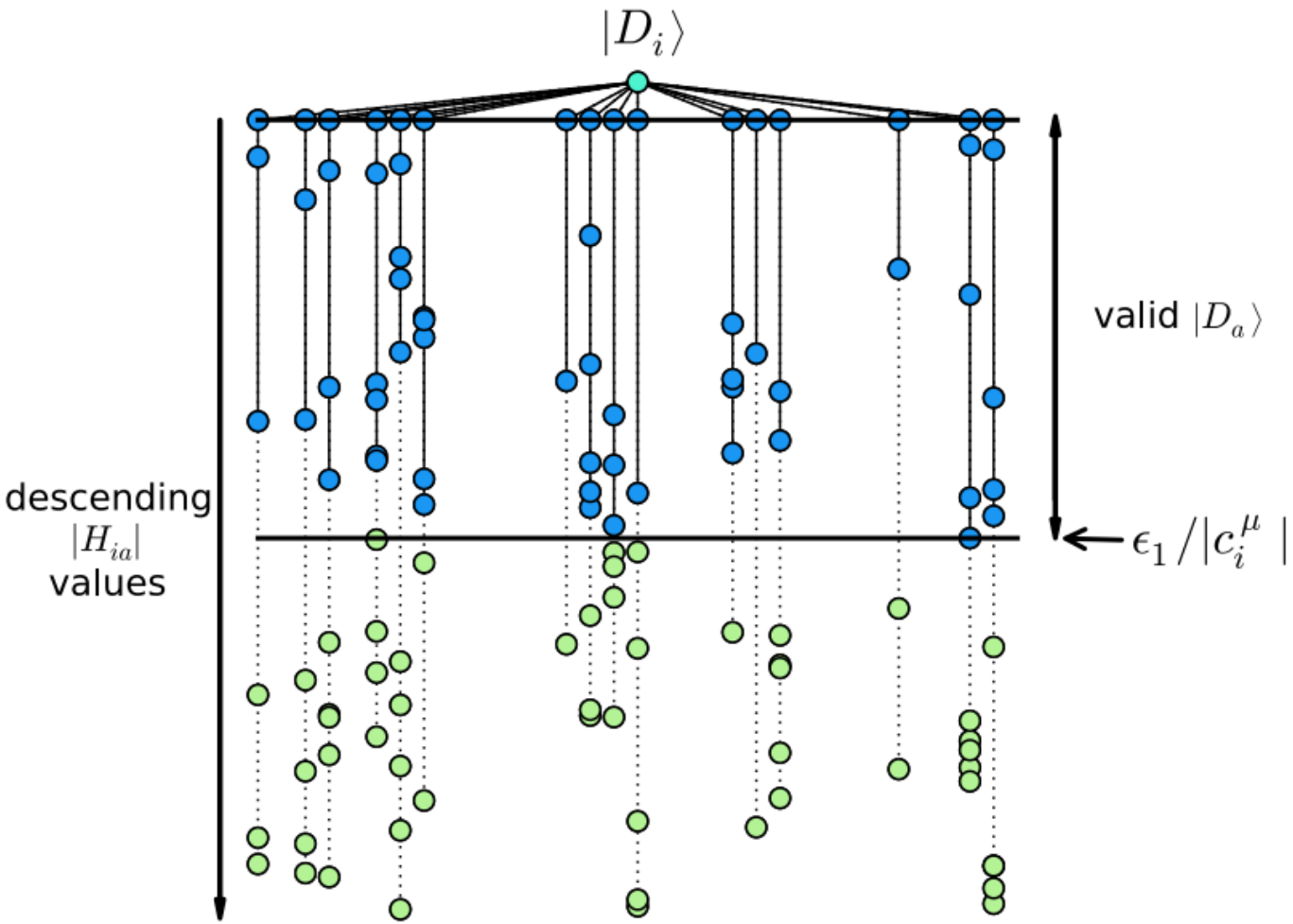
- **Finding important connected determinants** D_j (for which $|H_{ji}| > \epsilon$):
  - For each pair of occupied orbitals $\{p, q\}$, look up the stored list of triplets $\{r, s, |H\,(rs \leftarrow pq)|\}$ and iterate through the list until a triplet is reached for which $|H\,(rs \leftarrow pq)| < \epsilon$

Deterministic component



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     - 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:

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Importance-sampling excitations

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$$P(H_{ji}) \begin{cases} \propto f(|H_{ji}|), & \text{if } |H_{ji}| < \epsilon; \\ = 0, & \text{if } |H_{ji}| \geq \epsilon. \end{cases} \tag{7}$$

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- Examples of importance-sampling distributions include:

$$f(|H_{ji}|) = |H_{ji}|, \qquad f(|H_{ji}|) = |H_{ji}|^2 \tag{8}$$

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- This enables **importance-sampling an exciting electron pair in $\mathcal{O}(1)$ time**

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- So, we just use CDF searching to **sample a target orbital pair in $\mathcal{O}(\log M)$ time**

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  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

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  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

$$\Delta E\left[V|\psi_0\rangle\right] = \left\langle \psi_0 \middle| V \frac{1}{E_0 - H_0} V \middle| \psi_0 \right\rangle \tag{10}$$

$$= \sum_{\substack{a \in \mathcal{C}(\mathcal{V}) \\ \notin \mathcal{V}}} \frac{1}{E_0 - E_a} \left(\sum_{ij \in \mathcal{V}} c_j H_{ja} H_{ai} c_i \right), \tag{11}$$

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

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

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    - Memory-limited because requires computing all determinants $\{D_a\}$ for which $H_{ai} \neq 0$
    - Wastes time on small-magnitude H_{ai} elements

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    - No time or memory is wasted on deterministically evaluating contributions from small-magnitude H_{ai} elements!

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- The energy can be estimated using a mixed estimator:

$$E_0 = \frac{\langle \psi_T | H | \psi_0 \rangle}{\langle \psi_T | \psi_0 \rangle}, \tag{18}$$

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

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  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

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  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

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  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