Selected Configuration Interactions + Perturbation: Theory and Parallel Implementations

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Goal of the Talk

- Introduction on SCI+PT methods for ground state calculations
- Discussion on SCI+PT parallel implementations
- Not included in this talk:
  - SCI+PT methods for excited states
  - Comparison with other CI methods (e.g. FCIQMC)
  - Where to eat dinner tonight

Outline

1. Background
2. SCI+PT Methods
   - Selected CI: How to select?
   - Perturbation: How to perturb?
3. Parallel Implementations
   - Load Balancing
   - Reduce MPI Communications

The Many-Body Time-Independent Schrödinger Equation

- Ground-state wavefunction $|\mathbf{\Phi_0}\rangle$ and energy E_0 of a chemical system given by

$$\hat{H}|\mathbf{\Phi_0}\rangle = E_0|\mathbf{\Phi_0}\rangle,$$

  where $\hat{H} = -\frac{1}{2}\sum_{i=1}^{n_{\text{elec}}} \nabla_i^2 + V(x_1, x_2, \ldots, x_{n_{\text{elec}}})$.
- Application: Molecular property calculations
- Computational Methods:
  - Density Functional Theory (DFT)
  - Many-Body Perturbation Theory (MBPT)
  - Coupled Cluster (CC)
  - **Full Configuration Interaction (FCI)**: for strongly-correlated system

Configuration Interaction Method

- Based on one-electron spin–orbitals $\{\chi_p\}_{p=1}^{n_{\text{orb}}}$ from Hartree–Fock procedure
- Wavefunction approximated as linear combination of anti-symmetrized tensor products (Slater determinants)

$$|\mathbf{\Phi_0}\rangle = \sum_{i=1}^{N_{\text{FCI}}} c_i |D_i\rangle = \sum_{i=1}^{N_{\text{FCI}}} c_i |\chi_{p_i}\chi_{p_j}\cdots\chi_{p_k}\rangle$$

- FCI variational space dimension: $N_{\text{FCI}} = \binom{n_{\text{orb}}}{n_{\text{elec}}}$
- Schrödinger equation transformed to eigenvalue problem

$$H\mathbf{c} = E_0\mathbf{c}, \quad H \in \mathbb{R}^{N_{\text{FCI}}\times N_{\text{FCI}}}, \quad \mathbf{c} \in \mathbb{R}^{N_{\text{FCI}}}$$

FCI Matrix Properties

Entry: $H_{ij} = \langle D_i | \hat{H} | D_j \rangle$, not guaranteed to be non-negative.

- Symmetric: $H_{ij} = H_{ji}$.
- Sparse: $H_{ij} = 0$ if $|D_i\rangle$ and $|D_j\rangle$ differ by more than two orbitals. H has $O(n_{\text{elec}}^2 n_{\text{orb}}^2)$ entries per row.
- Ground-state eigenvalue $E_0 < 0$, ground-state eigenvector $\mathbf{v_0}$ sparse in the sense of truncation.

Memory usage

Table: Different Molecule Systems and Storage cost

Molecule	Basis	Electrons	Spin–Orbitals	Dimension	Memory
H_2O	cc-pVDZ	10	48	$\sim 10^8$	~ 1 GB
N_2	cc-pVDZ	14	56	$\sim 10^{11}$	~ 1 TB
N_2	cc-pVTZ	14	120	$\sim 10^{16}$	~ 100 PB
Cr_2	Ahlrichs	48	84	$\sim 10^{22}$	-

Solution: Select a part of configurations (on-the-fly)!

Basic Algorithmic Steps of Selected CI Program

1. Determine an initial variational space.
2. Find the ground state of the Hamiltonian in the current variational space.
3. Which determinants outside the space are most important? Perform some search algorithm based on perturbative or energy minimization estimates.
4. Construct a new variational space based on the search results.
5. Go to step 3, continue until the space stop changing.

Notations

notation	description
$\hat{H}$	Hamiltonian operator
H	Hamiltonian matrix
H_{ij}	the i,j-th entry of the Hamiltonian matrix
E_0	ground-state energy
$\|\mathbf{\Phi_0}\rangle$	ground-state wavefunction
$\|D_i\rangle$	the i-th Slater determinant
$\mathbf{c}$	wavefunction coefficient vector
$\mathbf{b}$	$\mathbf{b} = H\mathbf{c}$

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Perturbation Theory

If we have ground-state wavefunction $|\mathbf{\Phi_0}\rangle = \sum_{i=1} c_i |D_i\rangle$, then

$$c_i = \frac{\sum_{j \neq i} H_{ij} c_j}{H_{ii} - E_0}.$$

Selecting Important Determinants

Different methods define different importance measure $f(D_k)$.

- Configuration Interaction by Perturbatively Selecting Iteration (CIPSI) or Adaptive Sampling Configuration Interaction (ASCI):

$$f_{\text{CIPSI}}(D_k) = \left| \frac{\sum_i H_{ki} c_i}{H_{kk} - E_0} \right|.$$

- Heat-Bath Configuration Interaction (HCI):

$$f_{\text{HCI}}(D_k) = \max_i(|H_{ki} c_i|),$$

where D_i in selected space.

Coordinate Descent FCI (CDFCI)

FCI eigenvalue problem to unconstrained minimization problem

$$\min_{\mathbf{c}\in\mathbb{R}^{N_{\mathrm{FCI}}}} f(\mathbf{c}) = \min_{\mathbf{c}} \|H + \mathbf{c}\mathbf{c}^{\mathsf{T}}\|_F^2$$

- The only two local minimizers are $\pm\sqrt{E_0}\mathbf{v_0}$.
- Ensures convergence to the ground state wavefunction, given a good starting point (Hartree–Fock ground state).

Coordinate gradient descent method

- Minimizes computational costs by avoiding operations with the entire Hamiltonian matrix.
- In each iteration, only *one coordinate* of the optimizing vector is updated.
- Computation for updating involves only *one column* of the Hamiltonian matrix.

CDFCI Framework

Store $\mathbf{c}$ and $\mathbf{b} = H\mathbf{c}$ in memory. Initialize $\mathbf{c}^{(0)}$, $\mathbf{b}^{(0)} = H\mathbf{c}^{(0)}$.

For iteration $\ell = 1, 2, \ldots$

1. Select coordinate $i^{(\ell)} = \arg\max_i |\nabla_i f(\mathbf{c}^{(\ell-1)})|$.
2. Find stepsize by exact line search $\alpha^{(\ell)} = \arg\min_\alpha f(\mathbf{c}^{(\ell-1)} + \alpha \mathbf{e}_{i^{(\ell)}})$.
3. Update $\mathbf{c}^{(\ell)} = \mathbf{c}^{(\ell-1)} + \alpha^{(\ell)} \mathbf{e}_{i^{(\ell)}}$, $\mathbf{b}^{(\ell)} = \mathbf{b}^{(\ell-1)} + \alpha^{(\ell)} H_{:,i^{(\ell)}}$.

Remark: Gradient $\nabla f(\mathbf{c}) = 4H\mathbf{c} + 4\mathbf{c}^\mathsf{T}\mathbf{c}\mathbf{c} = 4\mathbf{b} + 4\mathbf{c}^\mathsf{T}\mathbf{c}\mathbf{c}$.

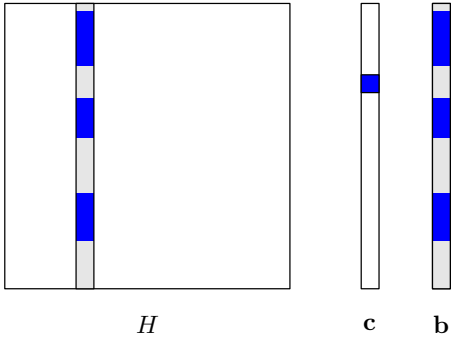


Figure: Update for one coordinate.

CDFCI Framework - for Two Coordinates?

Initialize $\mathbf{c}^{(0)}$, $\mathbf{b}^{(0)} = H\mathbf{c}^{(0)}$.
For iteration $\ell = 1, 2, \ldots$

1. Select coordinate
   $i^{(\ell)} = \arg\max_i |\nabla_i f(\mathbf{c}^{(\ell-1)})|$,
   $j^{(\ell)} = \arg\max_{j \neq i^{(\ell)}} |\nabla_j f(\mathbf{c}^{(\ell-1)})|$.
2. Find stepsize
   $\alpha^{(\ell)} = \arg\min_\alpha f(\mathbf{c}^{(\ell-1)} + \alpha \mathbf{e}_{i^{(\ell)}})$,
   $\beta^{(\ell)} = \arg\min_\beta f(\mathbf{c}^{(\ell-1)} + \beta \mathbf{e}_{j^{(\ell)}})$.
3. Update $\mathbf{c}^{(\ell)} = \mathbf{c}^{(\ell-1)} + \alpha^{(\ell)} \mathbf{e}_{i^{(\ell)}} + \beta^{(\ell)} \mathbf{e}_{j^{(\ell)}}$,
   $\mathbf{b}^{(\ell)} = \mathbf{b}^{(\ell-1)} + \alpha^{(\ell)} H_{:,i^{(\ell)}} + \beta^{(\ell)} H_{:,j^{(\ell)}}$.

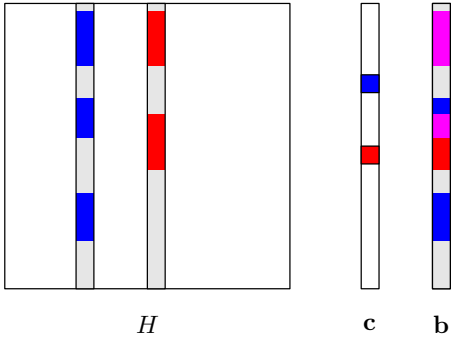


Figure: Update for two coordinates.

CDFCI Framework - Exact Line Search?

Initialize $\mathbf{c}^{(0)}$, $\mathbf{b}^{(0)} = H\mathbf{c}^{(0)}$.
For iteration $\ell = 1, 2, \ldots$

1. Select coordinate
   $i^{(\ell)} = \arg\max_i |\nabla_i f(\mathbf{c}^{(\ell-1)})|$,
   $j^{(\ell)} = \arg\max_{j \neq i^{(\ell)}} |\nabla_j f(\mathbf{c}^{(\ell-1)})|$.
2. Find stepsize $\alpha^{(\ell)}, \beta^{(\ell)} =$
   $\arg\min_{\alpha,\beta} f(\mathbf{c}^{(\ell-1)} + \alpha \mathbf{e}_{i^{(\ell)}} + \beta \mathbf{e}_{j^{(\ell)}})$.
3. Update $\mathbf{c}^{(\ell)} = \mathbf{c}^{(\ell-1)} + \alpha^{(\ell)} \mathbf{e}_{i^{(\ell)}} + \beta^{(\ell)} \mathbf{e}_{j^{(\ell)}}$,
   $\mathbf{b}^{(\ell)} = \mathbf{b}^{(\ell-1)} + \alpha^{(\ell)} H_{:,i^{(\ell)}} + \beta^{(\ell)} H_{:,j^{(\ell)}}$.

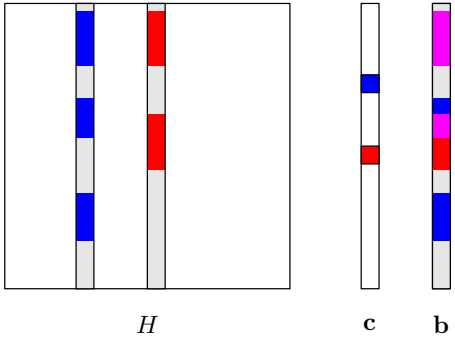


Figure: Update for two coordinates.

Add a Scalar γ for Exact Line Search

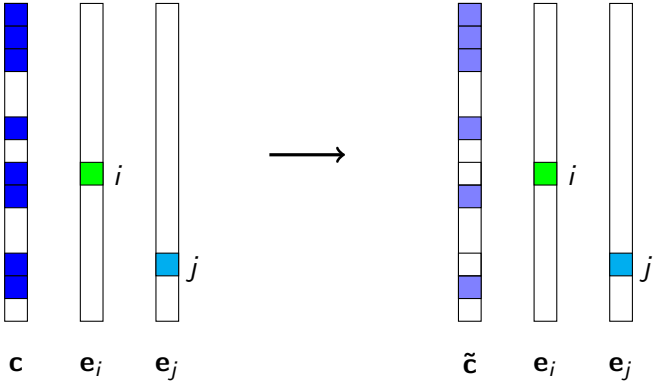
Modify the minimization problem from $\min_{\alpha,\beta} f(\mathbf{c}+\alpha\mathbf{e}_i+\beta\mathbf{e}_j)$ to

$$\min_{\gamma,\alpha,\beta} f(\gamma\mathbf{c}+\alpha\mathbf{e}_i+\beta\mathbf{e}_j) = f(\begin{bmatrix}\mathbf{c} & \mathbf{e}_i & \mathbf{e}_j\end{bmatrix}\begin{bmatrix}\gamma\\ \alpha\\ \beta\end{bmatrix})$$

$$= \left\| H + \begin{bmatrix}\mathbf{c} & \mathbf{e}_i & \mathbf{e}_j\end{bmatrix}\begin{bmatrix}\gamma\\ \alpha\\ \beta\end{bmatrix}\begin{bmatrix}\gamma & \alpha & \beta\end{bmatrix}\begin{bmatrix}\mathbf{c}^{\mathsf{T}}\\ \mathbf{e}_i^{\mathsf{T}}\\ \mathbf{e}_j^{\mathsf{T}}\end{bmatrix} \right\|_F^2 .$$

Matrix Orthogonalization

Construct $\begin{bmatrix}\tilde{\mathbf{c}} & \mathbf{e}_i & \mathbf{e}_j\end{bmatrix}$, where $\|\tilde{\mathbf{c}}\|_2 = 1$, $(\tilde{\mathbf{c}}, \mathbf{e}_i) = 0$, $(\tilde{\mathbf{c}}, \mathbf{e}_j) = 0$.



Add γ and $\tilde{\mathbf{c}}$ for Exact Line Search

Modify the minimization problem from $\min_{\alpha,\beta} f(\mathbf{c} + \alpha\mathbf{e}_i + \beta\mathbf{e}_j)$ to

$$\begin{aligned}
\min_{\gamma,\alpha,\beta} f(\gamma\tilde{\mathbf{c}} + \alpha\mathbf{e}_i + \beta\mathbf{e}_j) &= f\left(\begin{bmatrix}\tilde{\mathbf{c}} & \mathbf{e}_i & \mathbf{e}_j\end{bmatrix}\begin{bmatrix}\gamma\\ \alpha\\ \beta\end{bmatrix}\right) \\
&= \left\| H + \begin{bmatrix}\tilde{\mathbf{c}} & \mathbf{e}_i & \mathbf{e}_j\end{bmatrix}\begin{bmatrix}\gamma\\ \alpha\\ \beta\end{bmatrix}\begin{bmatrix}\gamma & \alpha & \beta\end{bmatrix}\begin{bmatrix}\tilde{\mathbf{c}}^{\mathsf{T}}\\ \mathbf{e}_i^{\mathsf{T}}\\ \mathbf{e}_j^{\mathsf{T}}\end{bmatrix} \right\|_F^2 \\
&= \left\| \underbrace{\begin{bmatrix}\tilde{\mathbf{c}}^{\mathsf{T}}\\ \mathbf{e}_i^{\mathsf{T}}\\ \mathbf{e}_j^{\mathsf{T}}\end{bmatrix} H \begin{bmatrix}\tilde{\mathbf{c}} & \mathbf{e}_i & \mathbf{e}_j\end{bmatrix}}_{\in \mathbb{R}^{3\times 3}} + \begin{bmatrix}\gamma\\ \alpha\\ \beta\end{bmatrix}\begin{bmatrix}\gamma & \alpha & \beta\end{bmatrix} \right\|_F^2 .
\end{aligned}$$

Extension to Multi Coordinate Descent FCI

- Select a set of coordinates $I = \{i_1, \ldots, i_k\}, 1 \leq i_j \leq N_{\text{FCI}}$ based on gradient $\nabla f(\mathbf{c}) = 4H\mathbf{c} + 4\mathbf{c}^{\mathsf{T}}\mathbf{c}\mathbf{c}$.
- Denote $\mathcal{E}_I = [e_{i_1}, \ldots, e_{i_k}] \in \mathbb{R}^{N_{\text{FCI}} \times k}$.
- The update is given by

$$\mathbf{c} \leftarrow \gamma \mathbf{c} + \mathcal{E}_I \mathbf{a}.$$

- The values of γ and $\mathbf{a}$ are given by the eigenvector of

$$\begin{bmatrix} \tilde{\mathbf{c}}^{\mathsf{T}} \\ \mathcal{E}_I^{\mathsf{T}} \end{bmatrix} H \begin{bmatrix} \tilde{\mathbf{c}} & \mathcal{E}_I \end{bmatrix} \in \mathbb{R}^{(k+1)\times(k+1)}$$

corresponding to the minimal eigenvalue $\lambda_{\min}$, which is the current energy estimate.

Epstein–Nesbet(EN) Energy

Adding E_{EN} to E_{var} to recover the energy outside variational space.

$$E_{\text{EN}} = \sum_k \frac{(\sum_i H_{ki} c_i)^2}{E_{\text{var}} - H_{kk}},$$

where k iterates over determinants excluded.
To accelerate,

$$E_{\text{EN}} \approx \sum_k \frac{(\sum_i^{|H_{ki} c_i| > \epsilon} H_{ki} c_i)^2}{E_{\text{var}} - H_{kk}}.$$

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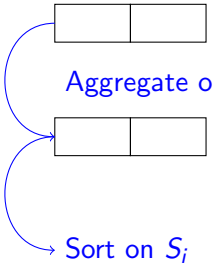
Parallel ASCI

- Classify determinants by their three highest-occupied orbitals
- Pre-compute the amount of work for each set
- Assign work to individual processing units

$D_j \in |\mathbf{\Phi_0}\rangle$: $D_j \to \tilde{D}_i \in \{D_j^{\mathrm{sd}}\}$

Compute $S_i^{(j)} = \frac{H_{ij} c_j}{H_{ii} - E_{\mathrm{var}}}$



Parallel HCI

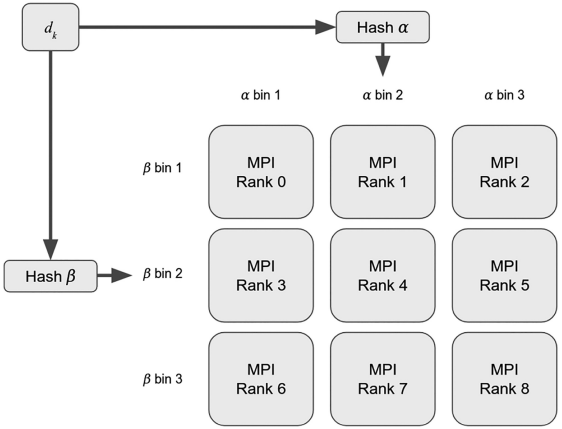
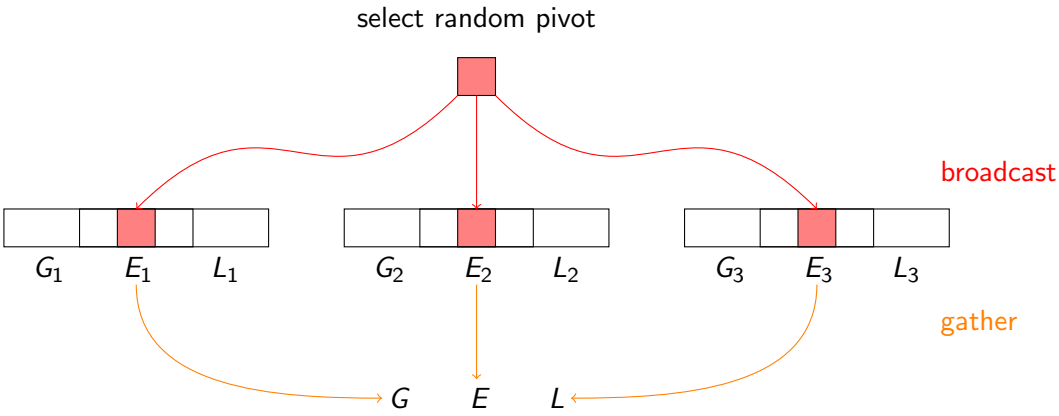


Figure: 2D hash over α and β strings to assign MPI Ranks

QuickSelect instead of QuickSort



Summary

- Configuration Interaction Method transforms the many-body time-independent Schrödinger equation to FCI eigenvalue problem under a basis consisting of Slater determinants of configuration combinations.
- Full CI is exact (under predefined one-electron basis) but too expensive; selected CI + perturbation provides approximations.
- Coordinate Descent FCI can be categorized as one of the SCI+PT methods.
- It can be extended to a multi-coordinate version with higher scalability.

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Thanks for Your Attention!