Master Thesis Presentation
STOCHASTIC APPROACH TO MANY-BODY PROBLEMS

Anna Gribkovakaya

December 17, 2018

University of Oslo

Introduction

Outline

- Main Objectives
- Many-body problem formulation and Size of the Hilbert Space
- Many body *Ab initio* methods: deterministic and stochastic
- Coupled Cluster Theory
- Coupled Cluster Quantum Monte Carlo
- Results
- Summary

Objectives

The main objectives:

- Implement numerical methods to solve the Time Independent Schrödinger equation for N electrons
- Develop a Coupled Cluster Doubles code capable of handling relatively large systems
- The code should be general and can be applied to other systems
- Develop a Stochastic Coupled Cluster Doubles code
- Benchmarking with other methods

Main Part

Many-body: problem formulation

The Hamiltonian for quantum mechanical system consisting of N particles can be written as

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i<j}^{N}\frac{1}{r_{ij}} + \sum_{i=1}^{N}\hat{V}_{\text{external}}(r_i),$$

r_{ij} relative distance between the particles,
$\hat{V}_{\text{external}}(r_i)$external one-body potential.
Stationary Schrödinger equation can be written as:

$$\hat{H}\Psi_n(\vec{\mathbf{R}}) = E_n\Psi_n(\vec{\mathbf{R}}),$$

$\vec{\mathbf{R}}$ - vector representing both coordinates and spins for all particles.

$$\vec{\mathbf{R}} = \{\vec{R_n}\} = \{(\vec{r},\sigma)_n\},$$

For fermions the wave function must be antisymmetric:

$$\Psi_n(\ldots,\vec{R}_p,\ldots,\vec{R}_q,\ldots) = -\Psi_n(\ldots,\vec{R}_q,\ldots,\vec{R}_p,\ \ldots),$$

Many-body: Slater Determinant Space

- Slater Determinant (SD) Space is a Hilbert space for fermions
- Each SD is constructed from N orthonormal single particle wavefunctions
- SD for reference vacuum state :

$$|D_0\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \dots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \dots & \psi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(x_1) & \psi_N(x_2) & \dots & \psi_N(x_N) \end{vmatrix}$$

- Every SD is anti-symmetric by construction

Many-body: Size of the Slater Determinant Space

An orthonormal set of 2M spin-orbitals, where N are occupied.

$$\binom{2M}{N} = \frac{(2M)!}{N!(2M-N)!},$$

For the electron gas, N=14:

$2M$=38 (N_s=3) $\rightarrow 10^{10}$

$2M$=246 (N_s=10) $\rightarrow 10^{22}$

$2M$=730 (N_s=20) $\rightarrow 10^{29}$

For Quantum Dot, N=20:

$2M$=110 (N_s=10) $\rightarrow 10^{21}$

$2M$=420 (N_s=20) $\rightarrow 10^{33}$

$2M$=930 (N_s=30) $\rightarrow 10^{40}$,

here N_s is shell number.

Many-body: Ab initio quantum many body methods

Deterministic or Wave Function Methods

- Hartree-Fock Method
- Many Body Perturbation Theory
- Full Configuration Interaction
- Coupled Cluster Method

Many-body: Ab initio quantum many body methods

Deterministic or Wave Function Methods

- Hartree-Fock Method
- Many Body Perturbation Theory
- Full Configuration Interaction
- Coupled Cluster Method

Stochastic or Monte Carlo (MC) Methods

- Variational MC
- Diffusion MC
- Full Configuration MC
- Coupled Cluster MC

Many-body: Ab initio quantum many body methods

Deterministic or Wave Function Methods

- Hartree-Fock Method
- Many Body Perturbation Theory
- Full Configuration Interaction
- Coupled Cluster Method

Stochastic or Monte Carlo (MC) Methods

- Variational MC
- Diffusion MC
- Full Configuration MC
- Coupled Cluster MC

Density Functional Theory - widely used, but has issues

Coupled Cluster Theory

Coupled cluster theory: Exponential ansatz

The Coupled Cluster approximation for wavefunction is:

$$\Psi_{CC} = e^{\hat{T}}|D_0\rangle,$$

$$\hat{T} = \sum_i^N \hat{T}_i = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N,$$

Each excitation operator can be written in terms of creation and annihilation operators:

$$\hat{T}_1 = \sum_i \hat{t}_i = \sum_{ia} t_i^a c_a^\dagger c_i, \;\; \hat{T}_2 = \sum_{i<j} \hat{t}_{ij}^{ab} = \frac{1}{2!^2} \sum_{ijab} t_{ij}^{ab} c_a^\dagger c_b^\dagger c_j c_i,$$

$$\hat{T}_3 = \sum_{i<j<k} \hat{t}_{ijk}^{abc} = \frac{1}{3!^2} \sum_{ijkabc} t_{ijk}^{abc} c_a^\dagger c_b^\dagger c_c^\dagger c_k c_j c_i.$$

here i, j, k indexes denote the orbitals that are occupied in the reference determinant and a, b, c denote those that are not.

Coupled Cluster: Energy and Amplitudes

Insert the CC approximation for wave function into TISE:

$$\hat{H}e^{\hat{T}}|D_0\rangle = Ee^{\hat{T}}|D_0\rangle.$$

$$\langle D_0|\hat{H}|D_0\rangle + \langle D_0|\hat{H}\hat{T}|D_0\rangle + \langle D_0|\hat{H}\frac{1}{2!}\hat{T}^2|D_0\rangle = E.$$

In the energy equation is *naturally truncated* after $\hat{T}^2$. Equations for the amplitudes can be obtained from:

$$\langle D_{ij\ldots}^{ab\ldots}|\hat{H}e^{\hat{T}}|D_0\rangle = 0.$$

However for practical purposes we are using so-called similarly transformed Hamiltonian and the equations become:

$$\text{Energy} \Longrightarrow \langle D_0|e^{-\hat{T}}\hat{H}e^{\hat{T}}|D_0\rangle = E,$$

$$\text{Amplitudes} \Longrightarrow \langle D_{ij\ldots}^{ab\ldots}|e^{-\hat{T}}\hat{H}e^{\hat{T}}|D_0\rangle = 0.$$

Coupled Cluster Quantum Monte Carlo

Coupled Cluster Quantum Monte Carlo

CCQMC is a Projector Monte Carlo Method and can be introduced as follows:

- Perform Wick rotation for time dependent Schrödinger equation
$$-i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle \Longrightarrow -\frac{\partial}{\partial \tau}|\Psi(\tau)\rangle = \hat{H}|\Psi(\tau)\rangle,$$

Coupled Cluster Quantum Monte Carlo

CCQMC is a Projector Monte Carlo Method and can be introduced as follows:

- Perform Wick rotation for time dependent Schrödinger equation
$$-i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle \Longrightarrow -\frac{\partial}{\partial \tau}|\Psi(\tau)\rangle = \hat{H}|\Psi(\tau)\rangle,$$
- Express the wave function for arbitrary τ with a propagator:
$$|\Psi^{(\tau)}\rangle \propto e^{-\tau\hat{H}}|\Psi^{(\tau=0)}\rangle,$$

Coupled Cluster Quantum Monte Carlo

CCQMC is a Projector Monte Carlo Method and can be introduced as follows:

- Perform Wick rotation for time dependent Schrödinger equation

$$-i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \hat{H}|\Psi(t)\rangle \Longrightarrow -\frac{\partial}{\partial \tau}|\Psi(\tau)\rangle = \hat{H}|\Psi(\tau)\rangle,$$

- Express the wave function for arbitrary τ with a propagator:

$$|\Psi^{(\tau)}\rangle \propto e^{-\tau\hat{H}}|\Psi^{(\tau=0)}\rangle,$$

- Assume that initial wave function has nonzero overlap with the ground state of the Hamiltonian:

$$|\Psi_0\rangle = \lim_{\tau\to\infty} e^{-\tau(\hat{H}-S)}|\Psi^{(\tau=0)}\rangle,$$

Coupled Cluster Quantum Monte Carlo

- Approximate the exponential propagator by repeated application of the linear propagator:

$$|\Psi_0\rangle = \lim_{N\to\infty} \left[1 - \delta\tau(\hat{H} - S)\right]^N |\Psi^{(\tau=0)}\rangle,$$

Coupled Cluster Quantum Monte Carlo

- Approximate the exponential propagator by repeated application of the linear propagator:

$$|\Psi_0\rangle = \lim_{N\to\infty} \left[1 - \delta\tau(\hat{H} - S)\right]^N |\Psi^{(\tau=0)}\rangle,$$

- Introduce wave-function for the imaginary time $\tau + \delta\tau$:

$$|\Psi^{(\tau+\delta\tau)}\rangle = (1 - \delta\tau(\hat{H} - S))|\Psi^{(\tau)}\rangle.$$

Coupled Cluster Quantum Monte Carlo

- Approximate the exponential propagator by repeated application of the linear propagator:

$$|\Psi_0\rangle = \lim_{N\to\infty}\left[1 - \delta\tau(\hat{H} - S)\right]^N |\Psi^{(\tau=0)}\rangle,$$

- Introduce wave-function for the imaginary time $\tau + \delta\tau$:

$$|\Psi^{(\tau+\delta\tau)}\rangle = (1 - \delta\tau(\hat{H} - S))|\Psi^{(\tau)}\rangle.$$

- Introduce some new notations to simplify equations:

$$|D_{\boldsymbol{i}}\rangle = \hat{c}_{\boldsymbol{i}}|D_0\rangle,$$

here $\hat{c}_{\boldsymbol{i}}$ a string of creation and annihilation operators

Coupled Cluster Quantum Monte Carlo

- Insert a coupled cluster approximation for the wave function and project equation on the excited determinant $D_{\{\boldsymbol{i}\}}$:

$$\langle D_{\{\boldsymbol{i}\}}|e^{\hat{T}}D_0\rangle = \langle D_{\{\boldsymbol{i}\}}|e^{\hat{T}}D_0\rangle - \delta\tau\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)e^{\hat{T}}|D_0\rangle,$$

Coupled Cluster Quantum Monte Carlo

- Insert a coupled cluster approximation for the wave function and project equation on the excited determinant $D_{\{\boldsymbol{i}\}}$:

$$\langle D_{\{\boldsymbol{i}\}}|e^{\hat{T}}D_0\rangle = \langle D_{\{\boldsymbol{i}\}}|e^{\hat{T}}D_0\rangle - \delta\tau\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)e^{\hat{T}}|D_0\rangle,$$

- Express the RHS of the above equation in terms of amplitudes:

$$\langle D_{\boldsymbol{i}}|e^{\hat{T}^{(\tau)}}D_0\rangle = t_{\boldsymbol{i}}^{(\tau)} + \mathcal{O}(\hat{T}^2),$$

Coupled Cluster Quantum Monte Carlo

- Insert a coupled cluster approximation for the wave function and project equation on the excited determinant $D_{\{\boldsymbol{i}\}}$:

$$\langle D_{\{\boldsymbol{i}\}} | e^{\hat{T}} D_0 \rangle = \langle D_{\{\boldsymbol{i}\}} | e^{\hat{T}} D_0 \rangle - \delta\tau \langle D_{\{\boldsymbol{i}\}} | (\hat{H} - S) e^{\hat{T}} | D_0 \rangle,$$

- Express the RHS of the above equation in terms of amplitudes:

$$\langle D_{\boldsymbol{i}} | e^{\hat{T}^{(\tau)}} D_0 \rangle = t_{\boldsymbol{i}}^{(\tau)} + \mathcal{O}(\hat{T}^2),$$

- Derive the equation for the amplitudes for $\tau + \delta\tau$:

$$t_{\{\boldsymbol{i}\}}^{(\tau+\delta\tau)} + \mathcal{O}(\hat{T}^2) \;\; = t_{\{\boldsymbol{i}\}}^{(\tau)} + \mathcal{O}(\hat{T}^2) \;\; - \delta\tau \langle D_{\{\boldsymbol{i}\}} | (\hat{H} - S) e^{\hat{T}} | D_0 \rangle,$$

Coupled Cluster Quantum Monte Carlo

- Insert a coupled cluster approximation for the wave function and project equation on the excited determinant $D_{\{\boldsymbol{i}\}}$:

$$\langle D_{\{\boldsymbol{i}\}}|e^{\hat{T}}D_0\rangle = \langle D_{\{\boldsymbol{i}\}}|e^{\hat{T}}D_0\rangle - \delta\tau\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)e^{\hat{T}}|D_0\rangle,$$

- Express the RHS of the above equation in terms of amplitudes:

$$\langle D_{\boldsymbol{i}}|e^{\hat{T}^{(\tau)}}D_0\rangle = t_{\boldsymbol{i}}^{(\tau)} + \mathcal{O}(\hat{T}^2),$$

- Derive the equation for the amplitudes for $\tau + \delta\tau$:

$$t_{\{\boldsymbol{i}\}}^{(\tau+\delta\tau)} + \cancel{\mathcal{O}(\hat{T}^2)} = t_{\{\boldsymbol{i}\}}^{(\tau)} + \cancel{\mathcal{O}(\hat{T}^2)} - \delta\tau\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)e^{\hat{T}}|D_0\rangle,$$

Coupled Cluster Quantum Monte Carlo

- Insert a coupled cluster approximation for the wave function and project equation on the excited determinant $D_{\{\boldsymbol{i}\}}$:

$$\langle D_{\{\boldsymbol{i}\}}|e^{\hat{T}}D_0\rangle = \langle D_{\{\boldsymbol{i}\}}|e^{\hat{T}}D_0\rangle - \delta\tau\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)e^{\hat{T}}|D_0\rangle,$$

- Express the RHS of the above equation in terms of amplitudes:

$$\langle D_{\boldsymbol{i}}|e^{\hat{T}^{(\tau)}}D_0\rangle = t_{\boldsymbol{i}}^{(\tau)} + \mathcal{O}(\hat{T}^2),$$

- Derive the equation for the amplitudes for $\tau + \delta\tau$:

$$t_{\{\boldsymbol{i}\}}^{(\tau+\delta\tau)} = t_{\{\boldsymbol{i}\}}^{(\tau)} - \delta\tau\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)e^{\hat{T}}|D_0\rangle,$$

- Rewrite it to obtain CCQMC population dynamics equation:

$$\frac{\delta t_{\{\boldsymbol{i}\}}}{\delta\tau} = -\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)e^{\hat{T}}|D_0\rangle,$$

Coupled Cluster Quantum Monte Carlo

- Insert a coupled cluster approximation for the wave function and project equation on the excited determinant $D_{\{\boldsymbol{i}\}}$:

$$\langle D_{\{\boldsymbol{i}\}}|e^{\hat{T}}D_0\rangle = \langle D_{\{\boldsymbol{i}\}}|e^{\hat{T}}D_0\rangle - \delta\tau\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)e^{\hat{T}}|D_0\rangle,$$

- Express the RHS of the above equation in terms of amplitudes:

$$\langle D_{\boldsymbol{i}}|e^{\hat{T}^{(\tau)}}D_0\rangle = t_{\boldsymbol{i}}^{(\tau)} + \mathcal{O}(\hat{T}^2),$$

- Derive the equation for the amplitudes for $\tau+\delta\tau$:

$$t_{\{\boldsymbol{i}\}}^{(\tau+\delta\tau)} = t_{\{\boldsymbol{i}\}}^{(\tau)} - \delta\tau\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)e^{\hat{T}}|D_0\rangle,$$

- Rewrite it to obtain CCQMC population dynamics equation:

$$\frac{\delta t_{\{\boldsymbol{i}\}}}{\delta\tau} = -\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)e^{\hat{T}}|D_0\rangle,$$

Coupled Cluster Quantum Monte Carlo

The equation we obtained is very similar to a diffusion one. Now we need to introduce particles or walkers to simulate the population dynamics. We use random walkers to obtain amplitudes. In this case walkers are called $excips$.

$$\frac{\delta t_{\{\boldsymbol{i}\}}}{\delta\tau} = -\langle D_{\{\boldsymbol{i}\}}|(\hat{H} - S)e^{\hat{T}}|D_0\rangle,$$

Each amplitude corresponds to an excited determinant or $excitor$. The population of excips on a given excitor is proportional to the amplitude:

$$t_{\boldsymbol{i}} \propto N_{\boldsymbol{i}} = \sum_{\alpha} s_\alpha \delta_{\boldsymbol{i},\boldsymbol{i}_\alpha} \text{ and } N_{ex} = \sum_{\boldsymbol{i}} |N_{\boldsymbol{i}}|$$

here $s_\alpha = \pm 1$ is sign of excip, $t_{\boldsymbol{i}}$ is an amplitude corresponding to the determinant $\boldsymbol{i}_\alpha$.

CCQMC: Game of Life

CCQMC simulated equation:

$$\frac{\delta t_{\{\boldsymbol{i}\}}}{\delta \tau} = -\langle D_{\{\boldsymbol{i}\}}|(\hat{H} - S)e^{\hat{T}}|D_0\rangle,$$

Exponential ansatz:

$$\Psi_{cc} = \Big[1 + \sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}} + \frac{1}{2!}\sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}} + \frac{1}{3!}\sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}} + ...\Big]|D_0\rangle.$$

After the wave function collapse:

$$\frac{\delta t_{\{\boldsymbol{i}\}}}{\delta \tau} = -\langle D_n|(\hat{H} - S)|D_m\rangle,$$

These determinants are connected through the Hamiltonian.

CCQMC: Game of Life

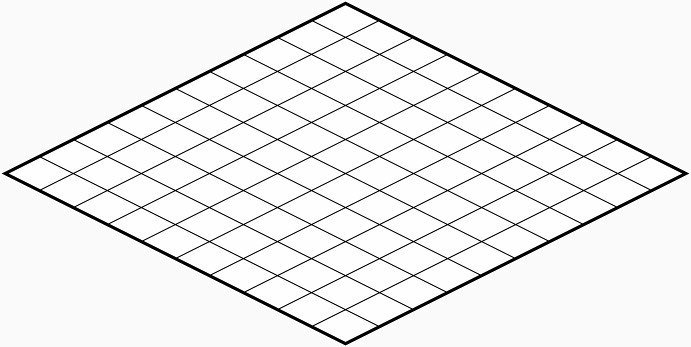
Probability to spawn:

$$P_{\mathsf{spawn}} = \delta\tau |AH_{nm}| \frac{1}{N}_a p_{size}(s) p_{clust}(e|s) \frac{1}{P_{gen}},$$

Probability do die:

$$P_{\mathsf{death}} = \delta\tau |A(H_{mm} - S)| \frac{1}{N_a p_{size}(s) p_{clust}(e|s)}.$$

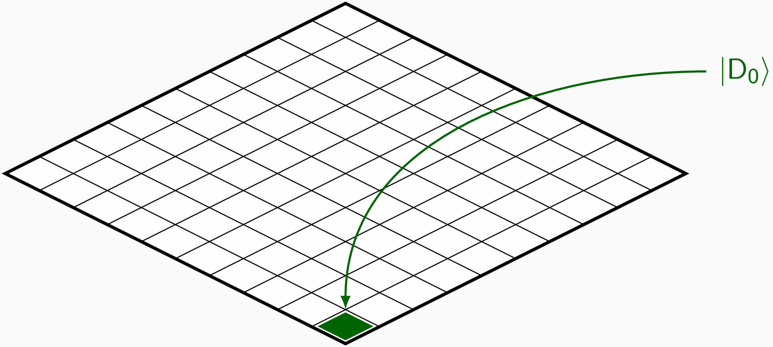
First Iteration



$$\Big[D_0 \mid \dots \Big]$$

$$\Big[N_0 \mid \dots \Big]$$

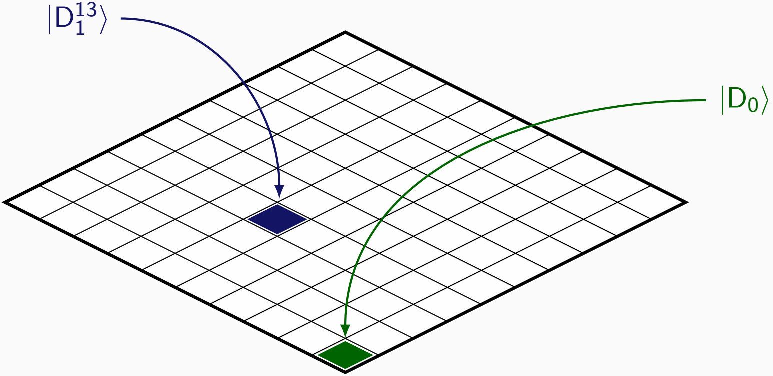
First Iteration



$$\left[D_0 \mid \ldots \right]$$

$$\left[N_0 \mid \ldots \right]$$

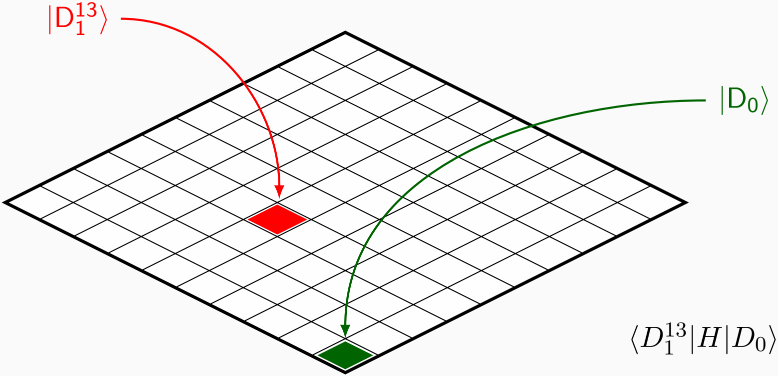
First Iteration



$$\left[D_0 \mid \ldots \right]$$

$$\left[N_0 \mid \ldots \right]$$

First Iteration

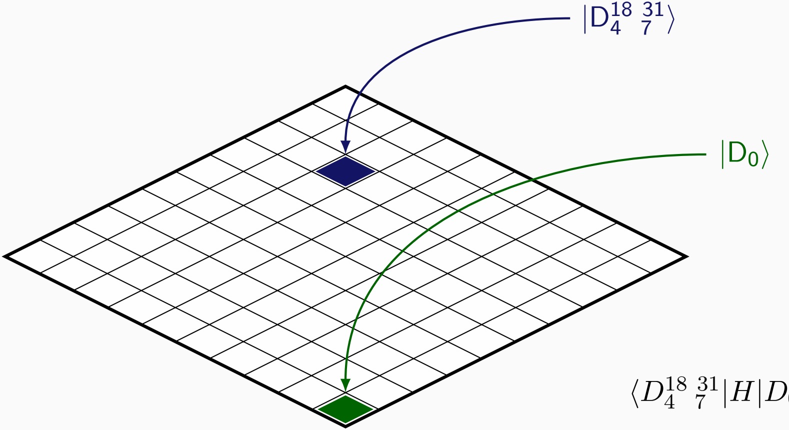


$$\langle D_1^{13}|H|D_0\rangle = 0$$

$$\left[D_0 \mid \dots \right]$$

$$\left[N_0 \mid \dots \right]$$

First Iteration

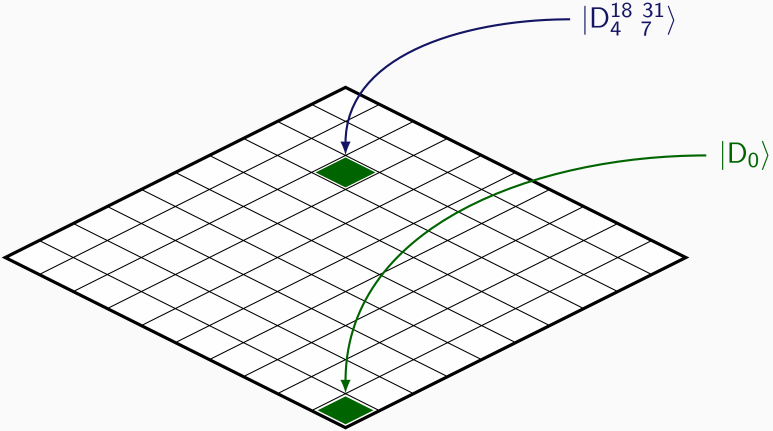


$$\langle D_{4\ 7}^{18\ 31}|H|D_0\rangle \neq 0$$

$$\left[D_0 \mid \ldots \right]$$

$$\left[N_0 \mid \ldots \right]$$

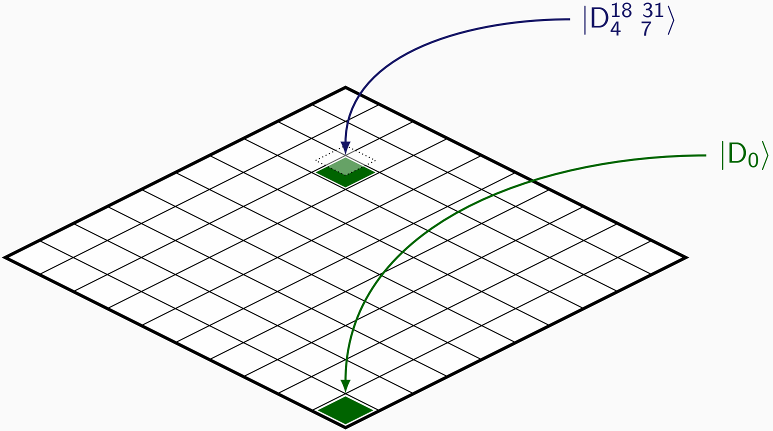
First Iteration



$$\left[D_0 \mid \ldots \right]$$

$$\left[N_0 \mid \ldots \right]$$

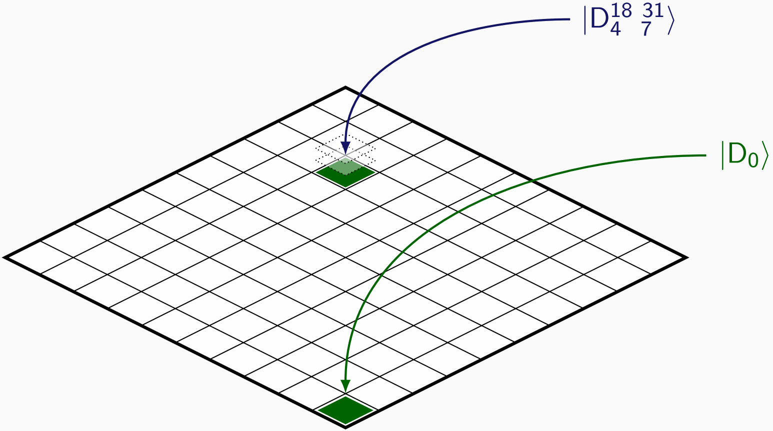
First Iteration



$$\left[D_0 \mid D^{18\ 31}_{4\ 7} \mid \ldots\right]$$

$$\left[N_0 \mid \quad +1 \quad \mid \ldots\right]$$

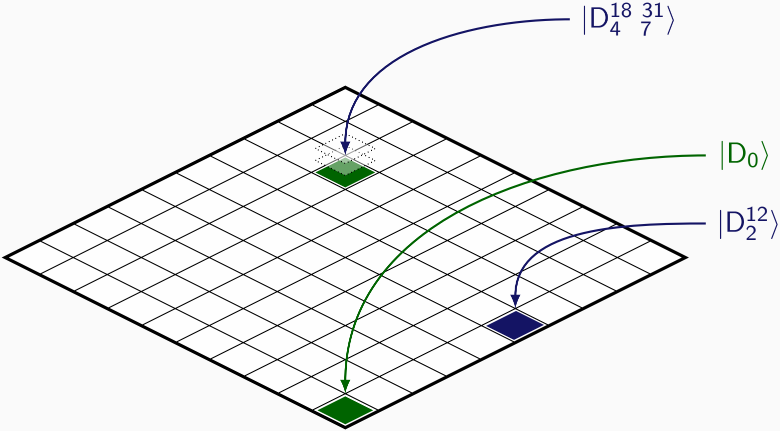
First Iteration



$$\left[D_0 \mid D^{18\ 31}_{4\ \ 7} \mid \ldots\right]$$

$$\left[N_0 \mid \quad +2 \quad \mid \ldots\right]$$

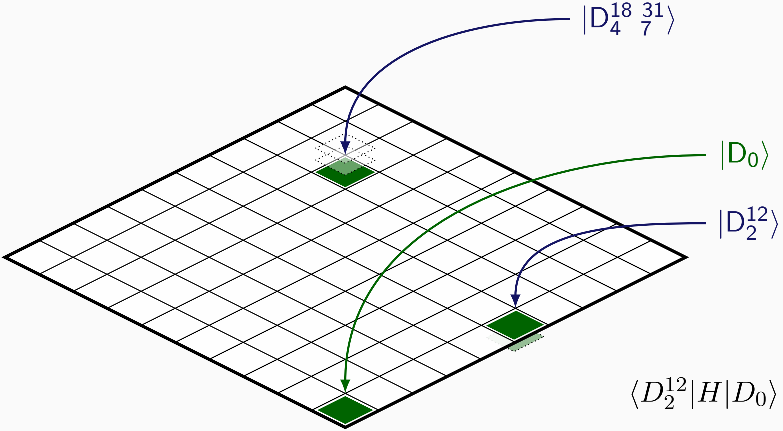
First Iteration



$$\left[D_0 \mid D_{4\ 7}^{18\ 31} \mid \ldots\right]$$

$$\left[N_0 \mid \quad +2 \quad \mid \ldots\right]$$

First Iteration



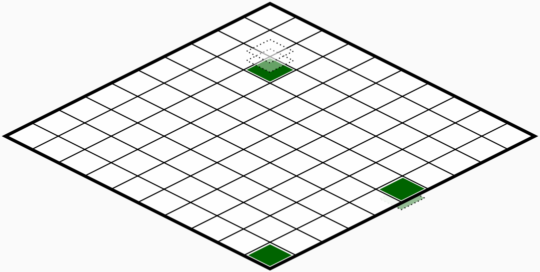
$$\langle D_2^{12}|H|D_0\rangle \neq 0$$

$$\left[D_0 \mid D_4^{18}\,{}_7^{31} \mid D_2^{12} \mid \dots \right]$$

$$\left[N_0 \mid \quad +2 \quad \mid -1 \quad \mid \dots \right]$$

Iteration

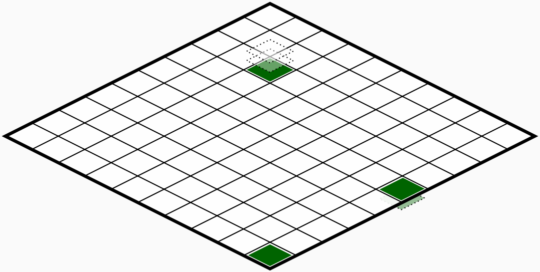
$$- \langle D_{\{\boldsymbol{i}\}} | (\hat{H} - S) | \Psi_{cc} \rangle$$



$$\Psi_{cc} = \Big[1 + \sum_{\boldsymbol{i}} t_{\boldsymbol{i}} \hat{a}_{\boldsymbol{i}} + \sum_{\boldsymbol{ij}} t_{\boldsymbol{i}} t_{\boldsymbol{j}} \hat{a}_{\boldsymbol{i}} \hat{a}_{\boldsymbol{j}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}} t_{\boldsymbol{j}} t_{\boldsymbol{k}} \hat{a}_{\boldsymbol{i}} \hat{a}_{\boldsymbol{j}} \hat{a}_{\boldsymbol{k}} + \dots \Big] | D_0 \rangle.$$

Iteration

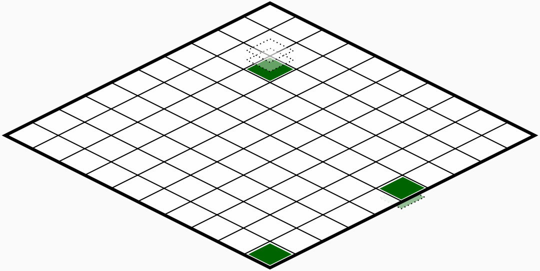
$$-\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)|\underline{\Psi_{cc}}\rangle$$



$$\Psi_{cc}=\Big[1+\sum_{\boldsymbol{i}}t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}+\sum_{\boldsymbol{ij}}t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}+\sum_{\boldsymbol{ijk}}t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}}+...\Big]|D_0\rangle.$$

Iteration

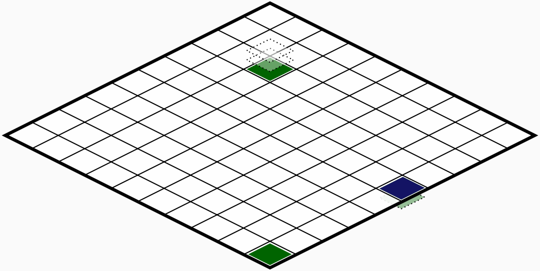
$$-\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)|\underline{\Psi_{cc}}\rangle$$



$$\Psi_{cc} = \left[1 + \underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}}_{\text{size one}} + \sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}} + \ldots\right]|D_0\rangle.$$

Iteration

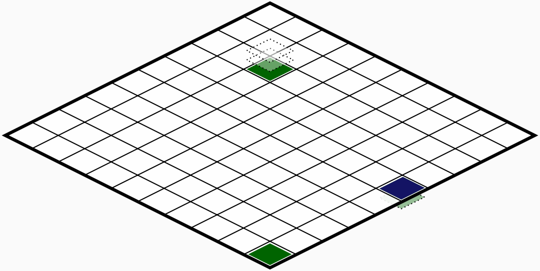
$$-\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)|D_n\rangle$$



$$\Psi_{cc} = \Big[1 + \underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}}_{\text{size one}} + \sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}} + ...\Big]|D_0\rangle.$$

Iteration

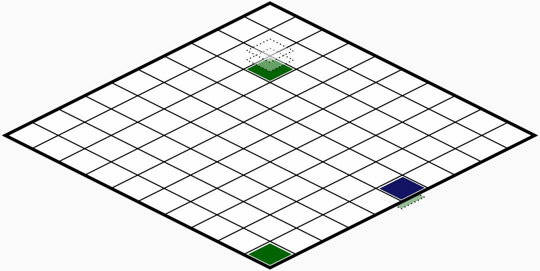
$$-\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)|D_n\rangle$$



$$\Psi_{cc}=\Big[1+\underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}}_{\text{size one}}+\sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}+\sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}}+\ldots\Big]|D_0\rangle.$$

Iteration

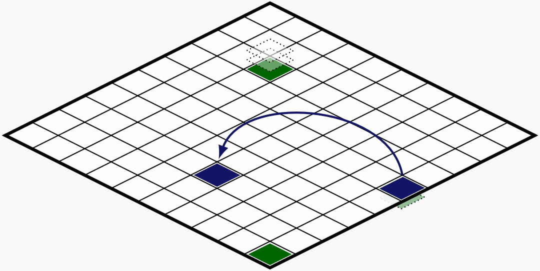
$$-\langle \underline{D_{\{\boldsymbol{i}\}}} |(\hat{H}-S)|D_n\rangle$$



$$\Psi_{cc} = \left[1 + \underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}}_{\text{size one}} + \sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}} + \ldots\right]|D_0\rangle.$$

Iteration

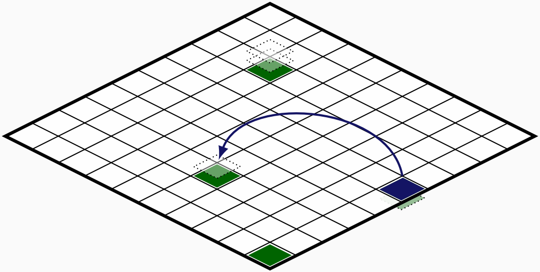
$$-\langle D_m|(\hat{H}-S)|D_n\rangle$$



$$\Psi_{cc} = \Big[1 + \underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}}_{\text{size one}} + \sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}} + \dots\Big]|D_0\rangle.$$

Iteration

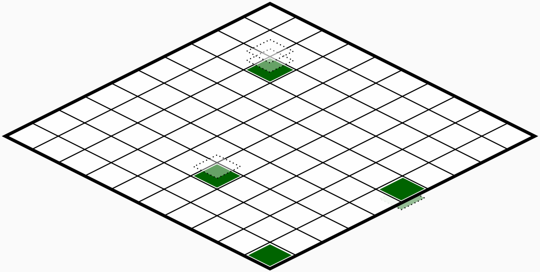
$$-\langle D_m|(\hat{H}-S)|D_n\rangle$$



$$\Psi_{cc}=\Big[1+\underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}}_{\text{size one}}+\sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}+\sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}}+\ldots\Big]|D_0\rangle.$$

Iteration

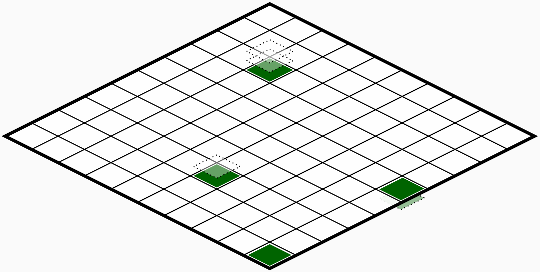
$$- \langle D_{\{\boldsymbol{i}\}} | (\hat{H} - S) | \Psi_{cc} \rangle$$



$$\Psi_{cc} = \Big[1 + \underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}} \hat{a}_{\boldsymbol{i}}}_{\text{size one}} + \sum_{\boldsymbol{ij}} t_{\boldsymbol{i}} t_{\boldsymbol{j}} \hat{a}_{\boldsymbol{i}} \hat{a}_{\boldsymbol{j}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}} t_{\boldsymbol{j}} t_{\boldsymbol{k}} \hat{a}_{\boldsymbol{i}} \hat{a}_{\boldsymbol{j}} \hat{a}_{\boldsymbol{k}} + \ldots\Big] | D_0 \rangle.$$

Iteration

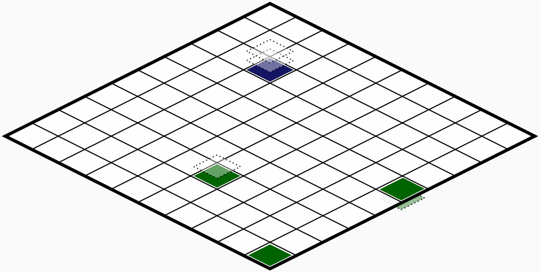
$$-\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)|\underline{\Psi_{cc}}\rangle$$



$$\Psi_{cc}=\Big[1+\underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}}_{\text{size one}}+\sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}+\sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}}+\ldots\Big]|D_0\rangle.$$

Iteration

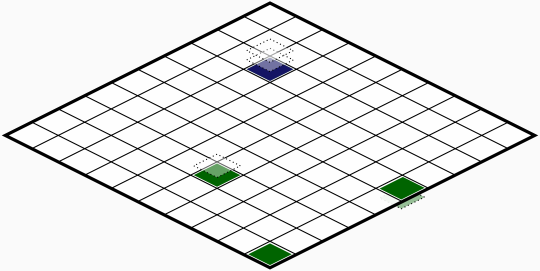
$$-\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)|D_{n'}\rangle$$



$$\Psi_{cc} = \Big[1 + \underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}}_{\text{size one}} + \sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}} + \ldots\Big]|D_0\rangle.$$

Iteration

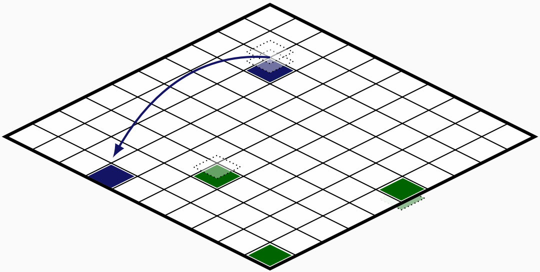
$$-\langle \underline{D_{\{\boldsymbol{i}\}}} | (\hat{H} - S) | D_{n'} \rangle$$



$$\Psi_{cc} = \Big[1 + \underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}} \hat{a}_{\boldsymbol{i}}}_{\text{size one}} + \sum_{\boldsymbol{ij}} t_{\boldsymbol{i}} t_{\boldsymbol{j}} \hat{a}_{\boldsymbol{i}} \hat{a}_{\boldsymbol{j}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}} t_{\boldsymbol{j}} t_{\boldsymbol{k}} \hat{a}_{\boldsymbol{i}} \hat{a}_{\boldsymbol{j}} \hat{a}_{\boldsymbol{k}} + \ldots\Big] |D_0\rangle.$$

Iteration

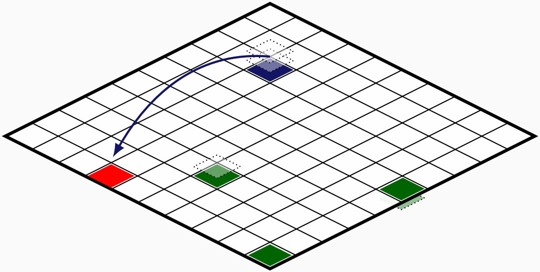
$$-\langle D_{m'}|(\hat{H}-S)|D_{n'}\rangle$$



$$\Psi_{cc}=\Big[1+\underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}}_{\text{size one}}+\sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}+\sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}}+...\Big]|D_0\rangle.$$

Iteration

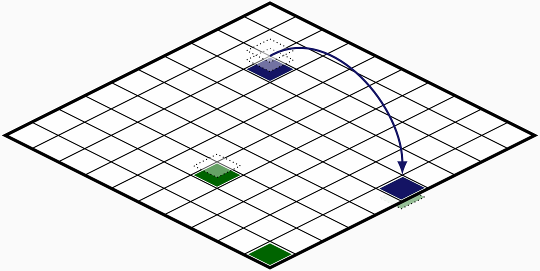
$$-\langle D_{m'}|(\hat{H}-S)|D_{n'}\rangle$$



$$\Psi_{cc} = \left[1 + \underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}}_{\text{size one}} + \sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}} + ...\right]|D_0\rangle.$$

Iteration

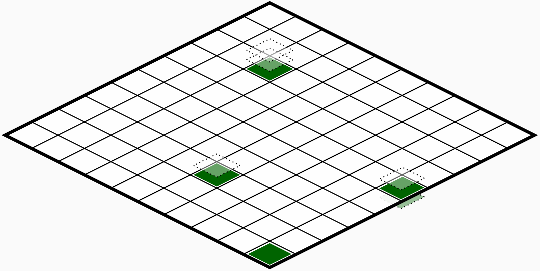
$$-\langle D_{m''}|(\hat{H}-S)|D_{n'}\rangle$$



$$\Psi_{cc} = \left[1 + \underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}}_{\text{size one}} + \sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}} + \ldots\right]|D_0\rangle.$$

Iteration

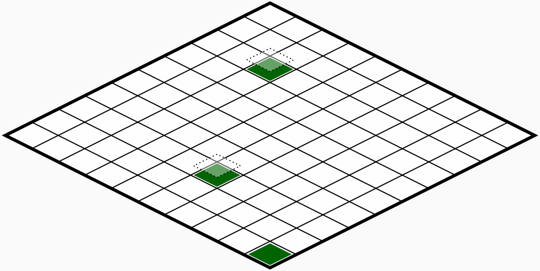
$$-\langle D_{m''}|(\hat{H}-S)|D_{n'}\rangle$$



$$\Psi_{cc}=\Big[1+\underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}}_{\text{size one}}+\sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}+\sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}}+\ldots\Big]|D_0\rangle.$$

Iteration

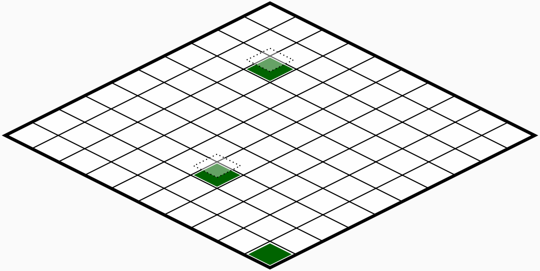
$$-\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)|\Psi_{cc}\rangle$$



$$\Psi_{cc}=\Big[1+\underbrace{\sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}}_{\text{size one}}+\sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}+\sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}}+\ldots\Big]|D_0\rangle.$$

Iteration

$$- \langle D_{\{\boldsymbol{i}\}}|(\hat{H} - S)|\underline{\Psi_{cc}}\rangle$$

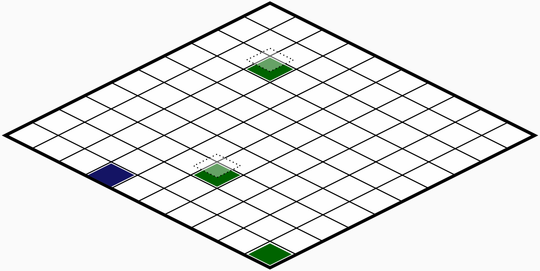


$$\Psi_{cc} = \Big[1 + \sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}} + \underbrace{\sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}}_{\text{size two}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}} + ...\Big]|D_0\rangle.$$

$$\hat{c}^{ac}_{ik} \;\; - \hat{c}^{b}_{j}$$

Iteration

$$-\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)|\underline{\Psi_{cc}}\rangle$$

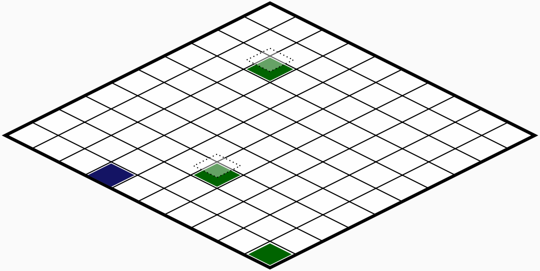


$$\Psi_{cc} = \Big[1 + \sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}} + \underbrace{\sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}}_{\text{size two}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}} + ...\Big]|D_0\rangle.$$

$$\hat{c}_{ik}^{ac} \ \ -\hat{c}_{j}^{b} \rightarrow -\hat{c}_{ijk}^{abc}$$

Iteration

$$-\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)|\underline{\Psi_{cc}}\rangle$$

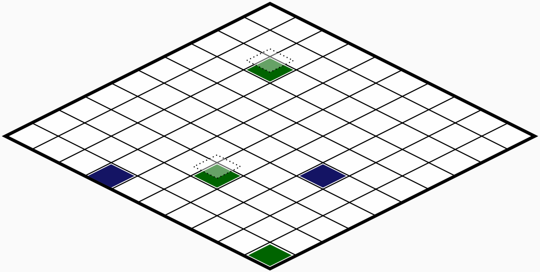


$$\Psi_{cc}=\Big[1+\sum_{\boldsymbol{i}}t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}}+\underbrace{\sum_{\boldsymbol{ij}}t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}}_{\text{size two}}+\sum_{\boldsymbol{ijk}}t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}}+...\Big]|D_0\rangle.$$

$$-\hat{c}_{ijk}^{abc}|D_0\rangle=-|D_{ijk}^{abc}\rangle$$

Iteration

$$-\langle D_{\{\boldsymbol{i}\}}|(\hat{H}-S)|\underline{\Psi_{cc}}\rangle$$

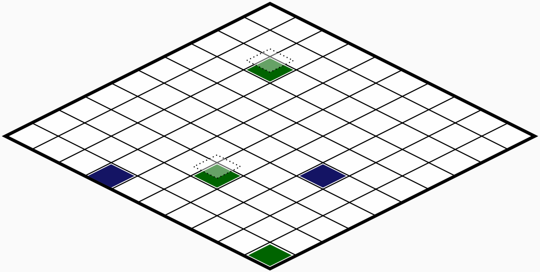


$$\Psi_{cc} = \Big[1 + \sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}} + \underbrace{\sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}}_{\text{size two}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}} + ...\Big]|D_0\rangle.$$

$$-\,|D_{ijk}^{abc}\rangle \rightarrow \quad {}_{i}^{c}$$

Iteration

$$- \langle D_i^c|\hat{H}|D_{ijk}^{abc}\rangle$$

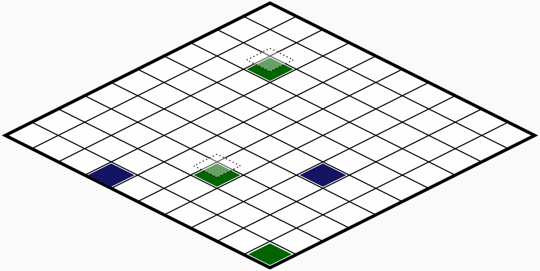


$$\Psi_{cc} = \Big[1 + \sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}} + \underbrace{\sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}}_{\text{size two}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}} + ...\Big]|D_0\rangle.$$

$$\delta\tau\langle D_i^c|\hat{H}|D_{ijk}^{abc}\rangle$$

Iteration

$$-\langle D_i^c|\hat{H}|D_{ijk}^{abc}\rangle$$



$$\Psi_{cc} = \left[1 + \sum_{\boldsymbol{i}} t_{\boldsymbol{i}}\hat{a}_{\boldsymbol{i}} + \underbrace{\sum_{\boldsymbol{ij}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}}_{\text{size two}} + \sum_{\boldsymbol{ijk}} t_{\boldsymbol{i}}t_{\boldsymbol{j}}t_{\boldsymbol{k}}\hat{a}_{\boldsymbol{i}}\hat{a}_{\boldsymbol{j}}\hat{a}_{\boldsymbol{k}} + ...\right]|D_0\rangle.$$

$$\delta\tau\langle D_{ijk}^{abc}|\hat{H} - S|D_{ijk}^{abc}\rangle$$

Results

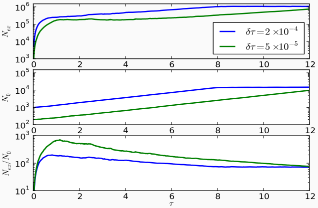
Benchmarking

CCD(deterministic) results for 14 electrons. Mixing parameter $\alpha = 0.8$ for Miller's results, and $\alpha = 0.3$ for our results. All energies are presented in Hartree units.

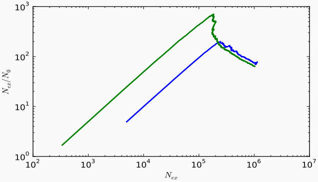
r_s	States	ΔE_{CCD} [1]	ΔE_{CCD}
1.0	54	-0.3178228436889338	-0.3178230699319593
1.0	66	-0.3926965898061968	-0.3926968074770886
1.0	114	-0.4479105961757175	-0.4479109389185165
1.0	162	-0.4805572589306421	-0.4805570782443642
1.0	186	-0.4855229317521320	-0.4855227418241649
1.0	246	-0.4929245740023971	-0.4929243692209991
1.0	294	-0.4984909094066806	-0.4984906939593084
1.0	342	-0.5019526761547777	-0.5019524529049425
1.0	358	-0.5025196736076414	-0.5025194488388953
0.5	114	-0.5120153541478306	-0.5120152296730573
0.5	342	-0.5729645498903680	-0.572964399507112
2.0	114	-0.3577968843144996	-0.3577955282575226
2.0	342	-0.4014136184665558	-0.4014117905655014

[1] Quantum Mechanical Studies of Infinite Matter by the Use of Coupled-Cluster Calculations, with an Emphasis on Nuclear Matter. Sean Bruce Sangolt Miller. 2017

Population dynamics



(a)

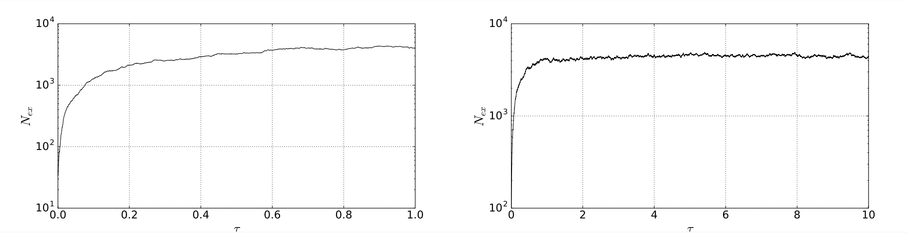


(b)

Ne CCSDTQ calculations starting with different initial particle numbers at the reference and different timesteps. (a): With a carefully chosen low timestep and initial population, a plateau is visible. An increased timestep and initial population overshoot the plateau but have a shoulder. The lower panel shows a maximum of the particle ratio at the position of the shoulder and plateau. (b): "Shoulder plots" allow shoulder height to be read off easily. [a]

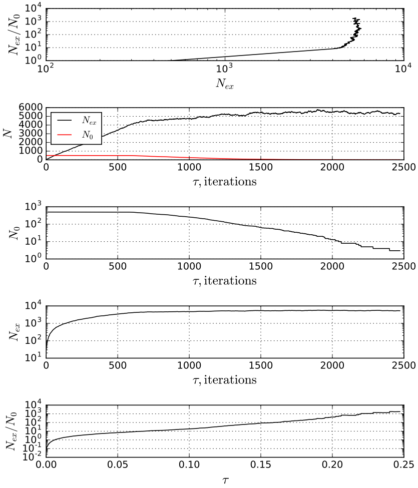
[a] James S. Spencer and Alex J. W. Thom. Developments in Stochastic Coupled Cluster Theory: The Initiator Approximation and Application to the Uniform Electron Gas. The Journal of Chemical Physics 144.8 (Feb. 2016)

Population dynamics



The population dynamics of the excited space for 14 electrons and 54 basis functions. $r_s = 0.5$, $\delta\tau = 0.0005$(left). The population dynamics of the excited space for 14 electrons and 54 basis functions with $r_s = 0.5$, $\delta\tau = 0.0005$ and the population control enabled after $5 \cdot 10^3$ iterations. Dampening parameter is $\gamma = 0.05$. The energy shift S is tuned every five iterations.(right)

Population dynamics



CBS energies

Summary of complete basis set extrapolated results for the correlation energy of the 14 electron uniform electron gas in hartree. $r_s = 1.0$

$-$	ΔE_{CCD}
dCCD	-0.514204
dCCD[2]	-0.5152(5)
qCCSD[3]	-0.51450(9)
qCCSDT[3]	-0.5307(2)
qCCSDTQ[3]	-0.5307(2)
FCIQMC[4]	-0.5325(4)

[2] J. J. Shepherd, A. Grneis, G. H. Booth, G. Kresse, and A. Alavi, Phys. Rev. B 86, 035111 (2012)

[3] Verena A. Neufeld and Alex J. W. Thom. "A Study of the Dense Uniform Electron Gas with High Orders of Coupled Cluster". The Journal of Chemical Physics 147.19 (Nov. 2017)

[4] J. J. Shepherd, G. H. Booth, and A. Alavi, J. Chem. Phys. 136, 244101 (2012)

Conclusion

Conclusion

- We have developed a CCD solver that reproduced published results for the homogeneous electron gas.
- This solver can also be applied to other systems.
- We have used this implementation to obtain a significant benchmark information to develop the CCQMC solver.
- We have developed a CCQMC solver and found that population of the reference state and truncation level play major roles for the CCQMC algorithm.
- The CCQMC method allows us to overcome the rapid growth of space size associated with deterministic methods even on a low truncation level.

Future work

Future work

- Implement the method for a higher truncation level (include triples)
- Investigate different sampling schemes
- Use optimization techniques, for example initiator approximation might be a very important topic for future work.
- The optimization of the implementation both numerically and algorithmically.
- Test solver on a not transitionally invariant systems, for example Quantum Dots.