

Introduction to quantum Monte Carlo

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Ab initio methods

- Quantum Monte Carlo belongs to category of *ab initio* methods.
- *Ab initio* electronic structure methods use **theory**, and **no experimental data**, to determine the properties of an electronic system.
- Basic theory:

Schrödinger equation for electronic system, static nuclei

$$\left(\sum_i^N \frac{1}{2} \nabla_i^2 + \sum_{i<j}^N \frac{1}{r_{ij}} - \sum_i^N \sum_I^{N_n} \frac{Z_I}{r_{iI}} \right) \Phi(\mathbf{R}) = E\Phi(\mathbf{R})$$

Hartree-Fock (HF)

- Use $\Psi = \det(\phi_i(\mathbf{r}_j))$
- Solve for $\{\phi_i\}$ that minimize $E_{HF} = \langle \Psi | \hat{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$
- E_{HF} is upper bound to ground-state energy
- Describes electronic exchange, but no electronic correlations

Density Functional Theory (DFT)

- Ground-state energy obtained by minimizing energy with respect to electronic density $n(\mathbf{r})$
- $E[n] = T[n] + V_H[n] + V_{ext}[n] + E_{xc}[n]$
- $E_{xc}[n]$ is unknown, must make (uncontrolled) approximation
- Very successful, scales as N^3

Post Hartree-Fock methods

- For example configuration interaction (CI), coupled cluster (CC)
- Expand $\Psi = \sum_k^{N_{det}} c_k \det \left(\phi_i^{(k)}(\mathbf{r}_j) \right)$
- Minimize E as function of $\{c_k\}$
- Converges to ground state since Slater determinants are basis for antisymmetric functions in \mathcal{R}^{3N}
- Standard in Quantum Chemistry, scales as N^7

Quantum Monte Carlo

- Wave-function based family of methods
- Solves Schrödinger equation by Monte Carlo integration
- Allows use of arbitrarily complex wave functions
- Intrinsically parallelizable at the random walker level
- No uncontrolled approximations
- Energy is variational
- Scales as N^3

Monte Carlo integration vs grid method

- Grid method:

- $\int_a^b f(x)dx \approx \frac{b-a}{M} \sum_{i=1}^M f(a + \frac{2i-1}{2} \frac{b-a}{M})$
- Error proportional to $M^{-2/d}$

- Monte Carlo method:

- $\int_a^b f(x)dx \approx \frac{1}{M} \sum_{i=1}^M f(x_i)$
- x_i are random numbers uniformly distributed in $[a, b]$
- Error proportional to $M^{-1/2}$

- Monte Carlo integration **scales better** for $d > 4$

Monte Carlo integration

- In general:

Monte Carlo integral with importance sampling

$$\langle f(\mathbf{x}) \rangle_{p(\mathbf{x})} = \int p(\mathbf{x}) f(\mathbf{x}) d\mathbf{x} \approx \frac{1}{M} \sum_i^M f(\mathbf{x}_i)$$

where:

- $p(\mathbf{x})$ is a probability distribution:
 - $p(\mathbf{x}) \geq 0$
 - $\int p(\mathbf{x}) d\mathbf{x} = 1$
- \mathbf{x}_i are vectors of random numbers distributed according to $p(\mathbf{x})$

Variational Monte Carlo

- Given a *trial* wave function Ψ ,

Variational principle

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\int \Psi(\mathbf{R}) \hat{H} \Psi(\mathbf{R}) d\mathbf{R}}{\int |\Psi(\mathbf{R})|^2 d\mathbf{R}} \geq E_0$$

- $E[\Psi] = E_0 \iff \Psi = \Phi_0$
- Combined with Monte Carlo integration:

$$E_{VMC} = \frac{1}{M} \sum_i^M \frac{\hat{H}(\mathbf{R}) \Psi(\mathbf{R})}{\Psi(\mathbf{R})}$$

- \mathbf{R} distributed according to $|\Psi(\mathbf{R})|^2 / \int |\Psi(\mathbf{R})|^2 d\mathbf{R}$ (Metropolis)
- Local energy: $E_L(\mathbf{R}) = \frac{\hat{H}(\mathbf{R}) \Psi(\mathbf{R})}{\Psi(\mathbf{R})}$

Wave function optimization

- VMC provides framework for wave function optimization:
 - Can minimize $E[\Psi(\boldsymbol{\alpha}; \mathbf{R})]$ with respect to parameters $\boldsymbol{\alpha}$
 - Can minimize variance of $E_L(\mathbf{R})$
- Typical wave function forms:

Slater

$$\Psi(\mathbf{R}) = \det[\phi_i(\mathbf{r}_j)]$$

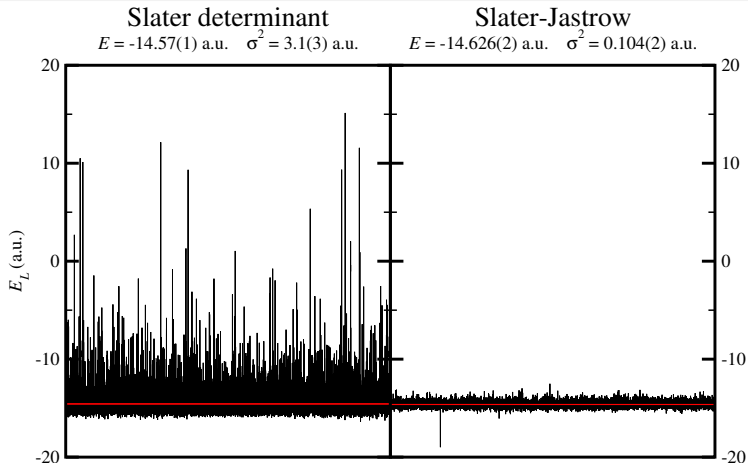
Slater-Jastrow

$$\Psi(\mathbf{R}) = \exp[J(\mathbf{R})] \det[\phi_i(\mathbf{r}_j)]$$

Slater-Jastrow-backflow

$$\Psi(\mathbf{R}) = \exp[J(\mathbf{R})] \det[\phi_i(\mathbf{r}_j + \boldsymbol{\xi}_j(\mathbf{R}))]$$

Wave function optimization



- Both mean energy and variance of local energies are good target functions to minimize

VMC in practice

- The quality of VMC results depend on the quality of the trial wave function
- VMC typically recovers 80–95% of the correlation energy
- VMC is usually used as a starting point for DMC

Diffusion Monte Carlo

Time-dependent Schrödinger equation

$$\hat{H}(\mathbf{R})\Phi(\mathbf{R},x) = i\frac{\partial\Phi(\mathbf{R},x)}{\partial x}$$

Imaginary time ($ix = t$) and energy shift

$$(\hat{H}(\mathbf{R}) - E_T)\Phi(\mathbf{R},t) = -\frac{\partial\Phi(\mathbf{R},t)}{\partial t}$$

Eigenstate expansion

$$\Phi(\mathbf{R},t) = \sum_{n=0}^{\infty} c_n \Phi_n(\mathbf{R}) e^{-(E_n - E_T)t}$$

If we adjust $E_T \sim E_0$, excited eigenstates **decay exponentially** as $t \rightarrow \infty$ and only **ground state** remains

Projection using discrete walkers

Let us consider the following generic equation

$$\hat{A}(\mathbf{R})f(\mathbf{R}, t) = -\frac{\partial f(\mathbf{R}, t)}{\partial t}$$

which we want to solve to obtain the evolution of f with t .

Given $f(\mathbf{R}, t)$ at time t and Green's function for operator \hat{A} at timestep T , $G(\mathbf{R}', T)$, we can compute f at time $t+T$ as

$$f(\mathbf{R}, t+T) = \int G(\mathbf{R}' \leftarrow \mathbf{R}, T)f(\mathbf{R}, t)d\mathbf{R}$$

Projection using discrete walkers

If $f(\mathbf{R}, t)$ is a probability distribution we can represent it discretely by a sufficiently large number of configurations P

$$f(\mathbf{R}, t) \approx \sum_{p=1}^P w_p(t) \delta[\mathbf{R} - \mathbf{R}_p(t)]$$

where $w_p(t)$ is the weight of configuration p at time t . Therefore

$$f(\mathbf{R}, t+T) \approx \sum_{p=1}^P w_p(t) G[\mathbf{R}' \leftarrow \mathbf{R}_p(t), T]$$

which we can re-represent as P' configurations

$$f(\mathbf{R}, t+T) \approx \sum_{p=1}^{P'} w_p(t+T) \delta[\mathbf{R} - \mathbf{R}_p(t+T)]$$

Diffusion Monte Carlo

- The DMC algorithm is derived by choosing $f(\mathbf{R}, t) = \Phi(\mathbf{R}, t)\Psi(\mathbf{R})$, where Ψ is the trial wave function and Φ is the *DMC wave function*
- Φ is forced to have the **same sign** as Ψ everywhere in configuration space so that $f(\mathbf{R}, t)$ is a probability distribution
- This is the **fixed-node approximation**
- Substituting $\Phi = f/\Psi$ into the imaginary time Schrödinger equation introduced earlier gives

Importance-sampled imaginary time Schrödinger equation

$$\sum_{i=1}^N \frac{1}{2} \left[-\nabla_i^2 f + 2\nabla_i \cdot \left(\frac{\nabla_i \Psi}{\Psi} f \right) \right] + (E_L - E_T)f = -\frac{\partial f}{\partial t}$$

Diffusion Monte Carlo

- Green's function for this equation at **small** T can be written as $G = G_D G_B$, where

Drift-diffusion Green's function

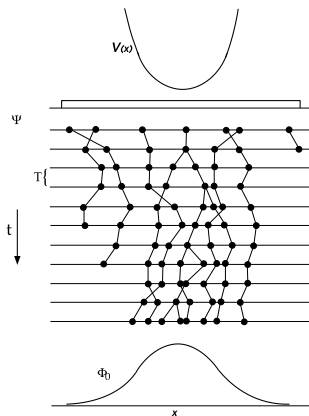
$$G_D(\mathbf{R} \leftarrow \mathbf{R}', T) = \frac{1}{(2\pi T)^{3N/2}} \exp \left[-\frac{1}{2T} \left(\mathbf{R} - \mathbf{R}' - T \frac{\nabla_{\mathbf{R}'} \Psi(\mathbf{R}')}{\Psi(\mathbf{R}')} \right)^2 \right]$$

Branching Green's function

$$G_B(\mathbf{R} \leftarrow \mathbf{R}', T) = \exp \left(-\frac{T}{2} [E_L(\mathbf{R}) + E_L(\mathbf{R}') - 2E_T] \right)$$

- The drift-diffusion term proposes configuration moves
- The branching factor causes configurations to be killed or multiplied; E_T is manipulated to control population

Diffusion Monte Carlo



- Schematic diagram of the DMC algorithm for a 1D harmonic oscillator starting from uniform distribution of walkers

Diffusion Monte Carlo

- Finite T approximation \rightarrow need to **extrapolate** to $T \rightarrow 0$
- Finite population of walkers \rightarrow usually no need to extrapolate, just **use several hundred** configurations
- The resulting Φ is the lowest energy wave function among those with the same nodal structure as Ψ
- Equivalently, the DMC wave function can be thought of as the VMC wave function with a perfect Jastrow factor
- Therefore DMC always gives a better answer than VMC
- The quality of DMC depends only on the **nodes** of the trial wave function

Where do we get orbitals from?

- We need one-particle orbitals to populate our Slater determinants
- Where do we obtain them from?
 - HF - a natural choice
 - DFT - some correlation effects in the orbitals (which may be a good thing or a bad thing!)
- How do we represent the orbitals?
 - Plane waves - natural choice for periodic systems
 - Blips - much better performance than plane waves, localizable
 - Gaussians - as used by quantum chemists for molecules
 - Numerical orbitals - feasible for small systems

Can excited states be handled by QMC?

- DMC converges to lowest-energy state of same symmetry as the wave function
- Can study excited states by using a wave function of the correct symmetry
- Excited state calculations are somewhat harder than ground state calculations, usually incur greater errors

Things we will cover during this week

- Sampling, Metropolis algorithm and statistics
- Periodic calculations, \mathbf{k} -point sampling
- Expectation values other than the energy
- Pseudopotentials