

Quantum Monte Carlo

Variational and Diffusion

Motivation

- So far we have seen Monte Carlo techniques that take advantage of probability – where quantum phenomena are probabilistic, Monte Carlo is a good candidate to solve quantum problems
- Many quantum problems may not be solved analytically due to difficulties in solving integrals or differential equations. This is often due to complicated potentials.
- Many real world systems are many-body problems, but cannot be solved analytically – Monte Carlo systems are developed to find approximate solutions.
- Quantities that may be found by Monte Carlo methods are ground state energy, ground state wavefunction, and ground state probability density. Other expectation values are possible for VMC
- Two examples of quantum Monte Carlo: Variational and Diffusion

Variational Monte Carlo

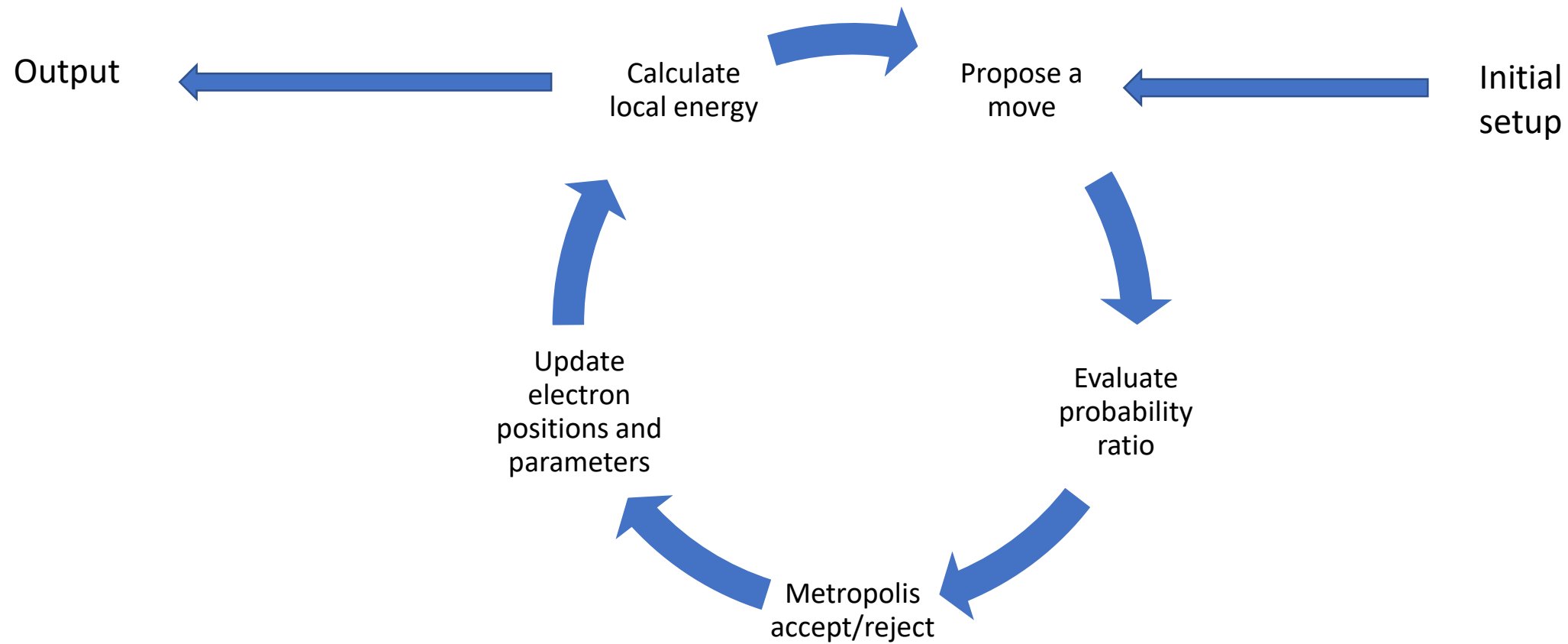
- Based on the variational principal:

$$E_0 \leq \langle \Psi | \hat{H} | \Psi \rangle$$

- This allows us to choose any wavefunction with any set of parameters and minimize the expectation value of this wavefunction
- The most obvious challenges and limitations is trying to find a good wavefunction and needing the Hamiltonian of the system
 - Trial wavefunction and its derivative must be continuous
 - The expectation value must exist:

$$\langle \Psi | \hat{H} | \Psi \rangle$$

VMC Algorithm



Diffusion

- Simulating a system with imaginary parameters is difficult – it would be easier to simulate something real
- Diffusion Monte Carlo relies on turning the Schrodinger equation into a diffusion equation
- The result of simulating a real differential equation will be the same as the Schrodinger equation
- Allows for the calculation of the ground state wavefunction and the ground state energy

$$\frac{du(r,t)}{dt} = D\nabla^2 u(r,t) + F(r,t)$$

PDEs

- To begin, the Schrodinger equation is transformed into a diffusion equation. Starting with the familiar 1D Schrodinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi$$

- Two substitutions need to be made: one to convert time to ‘imaginary time’ and another to define the diffusion term.

$$it = \tau \quad \frac{-\hbar}{2m} = D$$

- Performing the substitution, the result is

$$\hbar \frac{\partial \Psi(x, \tau)}{\partial \tau} = D\hbar \frac{d^2 \Psi(x, \tau)}{dx^2} + V(x)\Psi(x, \tau)$$

- In the 3 dimensional form used for diffusion Monte Carlo:

$$\frac{\partial \Psi(\vec{r}, t)}{\partial t} = D\nabla^2 \Psi(\vec{r}, t) + \frac{(V(\vec{r}) - E_R)}{\hbar} \Psi(\vec{r}, t)$$

Reference Eigenvalue

- In order to make diffusion monte carlo useful, the potential energy used needs to be re-defined. A 'reference energy' term is added to the potential, assuming that it is an eigenvalue of the quantum state of the system.

$$\hat{H} |\psi\rangle = E |\psi\rangle$$

$$\hat{H} |\psi\rangle + E_R |\psi\rangle = E |\psi\rangle + E_R |\psi\rangle$$

$$(\hat{H} - \hat{I}E_R) |\psi\rangle = (E - E_R) |\psi\rangle$$

- Hence, the modified value is also an eigen-energy of the system corresponding to a modified Hamiltonian operator

Time Evolution

- The reference energy is used in conjunction with the time evolution of a quantum system. When using imaginary time, all eigenstates except for the ground state will decay away as time approaches infinity. Recall the following

$$|\Psi(x, t)\rangle = e^{-i\omega t} |\Psi(x)\rangle$$

- Applying appropriate substitutions:

$$|\Psi(x)\rangle = \sum c_n |\psi_n(x)\rangle \quad it = \tau \quad \omega_n = \frac{E_n - E_R}{\hbar}$$

- When all the above are brought together at the limit:

$$|\Psi(x, \tau)\rangle = \sum c_n e^{-\omega_n \tau} |\psi_n(x)\rangle$$

$$\lim_{\tau \rightarrow \infty} |\Psi(x, \tau)\rangle = c_0 |\psi_0(x)\rangle$$

- The only term that survives is when omega is zero, meaning when the reference energy is the ground state

Diffusion Equation

$$\frac{\partial \Psi(\vec{r}, t)}{\partial t} = D \nabla^2 \Psi(\vec{r}, t) + \frac{(V(\vec{r}) - E_R)}{\hbar} \Psi(\vec{r}, t)$$

DIFFUSION

CREATION/DESTRUCTION

- Our original diffusion equation is a superposition of two equations: a diffusion term and a forcing term.
- By simulating each term sequentially, we may simulate the entire system.
- Each step in the simulation is a step in imaginary time
- After enough steps, the system will decay to the ground state system, with the reference energy E_0 and a wavefunction matching the ground state

Simulation 1

- Prior to this method other studies examined random diffusion
- Brownian motion, for instance, is also simulated by diffusion
- Diffusion may be simulated using random walks. A number of walkers are created, and are allowed to move some distance each time interval. The distance is normally distributed.
- Unlike other Monte Carlo methods, a random walk is always accepted, regardless of the potential in that region
- After each diffusion step, the second simulation takes place

Simulation 2

- After each diffusion step, the walkers are either created, destroyed, or multiply based on how likely a walker is to exist at that potential. In areas of low potential, more walkers will be created. In areas of high potential, walkers are destroyed.
- The simulation considers 4 possibilities:
 - Destruction: the walker is destroyed
 - Stasis: the walker remains
 - Growth: a new walker is created at the location
 - Extreme Growth: two new walkers are created at this location

Weighting

$$W(x_n) = \exp \left[- \frac{[V(x_n) - E_R] \Delta \tau}{\hbar} \right] \approx 1 - \frac{V(x_n) - E_R}{\hbar} \Delta \tau$$

- Whether particles are created, destroyed, or left alone is governed by the weighting function. This may be derived using Green's functions or Feynman path integrals.
- The weighting function is rounded to the nearest integer.
- A maximum value cap of $W=3$ is applied in the code to prevent occasional simulations with massive numbers of walkers

Ground Energy

- Like most Monte Carlo methods, an initial guess is used for the reference energy.
- After the first time step, the reference energy is guessed to be the expectation value of the potential from the previous walkers

$$E_R^{(1)} = \langle V \rangle_1$$

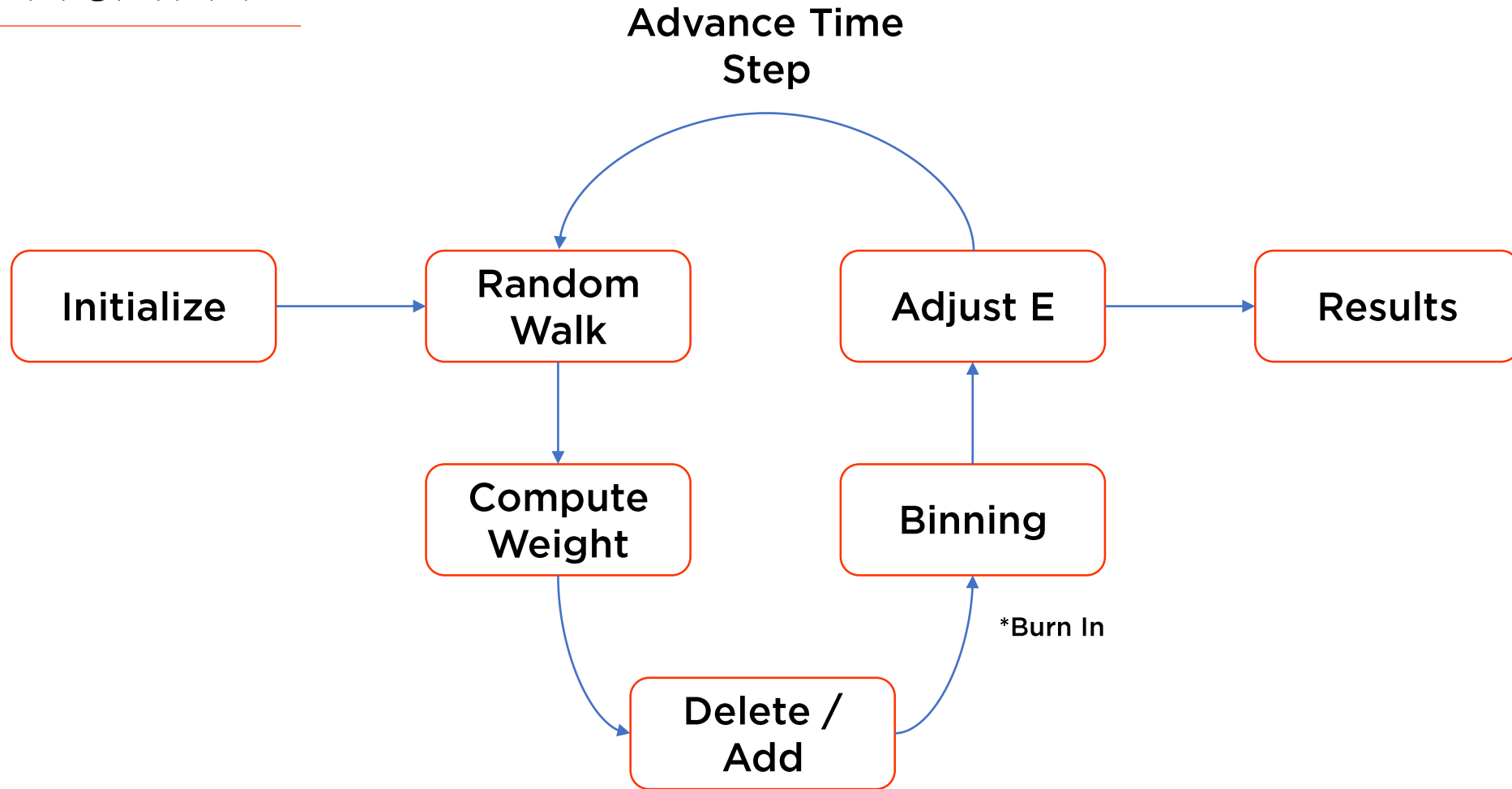
- We can hone in on the ground state by knowing that the system will eventually reach an equilibrium: the ground state.
- As we approach the ground state, the number of walkers should be constant.
- We may use this to find the ground state. If the number of walkers increases, the reference energy should increase to reduce the number of walkers and vice versa.

$$E_R^{(2)} = \langle V \rangle_1 + \frac{\hbar}{\Delta\tau} \left(1 - \frac{N_1}{N_0} \right)$$

$$E_0 = \lim_{n \rightarrow \infty} \langle V \rangle_n$$

- Over time, this yields an equilibrium

Algorithm



Why not QMC?

- QMC is more accurate, but there are more constraints on which systems can be used.
- QMC simulations are computationally expensive

A Common Alternative

- A more common substitute is Density-Functional Theory (DFT), which is generally less accurate, but faster and more flexible to apply to other fields
 - Increased efficiency comes from replacing the electron-electron Coulomb interaction with a single pseudopotential and other approximations
 - DFT also has problems, such as simulating van der Waals bonding, which is more accurate with QMC