Lecture 6

Quantum Monte Carlo methods

Variational Quantum Monte Carlo method

Consider a system of n particles $R = \{\vec{r}_1, \ldots, \vec{r}_n\}$ in n_d dimensions. It is described by the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i^n \nabla_i^2 + \sum_{i<j}^n V(r_{ij}) \tag{6.1}$$

where the behaviour of its ground state is described by the wave function $\psi_0(R)$. This wave function is found by solving the eigenvalue problem from the Schrödinger equation:

$$H\psi_0(R) = E_0\psi_0(R)$$

For atoms, the interaction potential has a strongly repulsive short distance behaviour, which means that perturbative calculations cannot be used in this case.

One alternative is to follow the **variational approach** which provides an upper bound to the ground state energy: Namely, for any given trial state ψ_T:

$$E_V = \frac{\int \psi_T^*(R)\hat{H}\psi_T(R)\,dR}{\int \psi_T^*(R)\psi_T(R)\,dR} \geq E_0 \tag{6.2}$$

where the inequality becomes exact only when ψ_T is equal to the ground state ψ_0. The method requires us to provide a trial wavefunction, that allows optimization of parameters in $\psi_T(R;\alpha)$.

For Monte Carlo calculations, it is recommended to write the expression for the mean energy in terms of the local energy:

$$E_L(R) \equiv \frac{\hat{H}\psi_T(R)}{\psi_T(R)}$$

so that the mean energy becomes

$$E_V = \frac{\int E_L(R)\psi_T^*(R)\psi_T(R)\,dR}{\int \psi_T^*(R)\psi_T(R)\,dR} = \int E_L(R)\rho(R)\,dR \tag{6.3}$$

$\rho(R)$ being the probability density of our trial wavefunction. Approximating the integral by discretizing the positions R_i, we obtain

$$E_V \simeq \frac{1}{N}\sum_i E_L(R_i) \tag{6.4}$$

We can also estimate the error of making such an approximation as

$$\epsilon(E_V) = \frac{1}{\sqrt{N-1}}\sqrt{\frac{1}{N}\sum_i E_L(R_i)^2 - E_V^2} \tag{6.5}$$

For the true ground state, this variance is zero, and any other $\psi_T(R;\alpha)$ will usually not satisfy this condition exactly. This way, we can find the optimal parameters α of our wavefunction by either minimizing $E_V(\alpha)$ or $\sigma^2[E_V(\alpha)]$.

Re-weighting technique to search optimal parameters

Suppose we are minimizing a function $f(\alpha)$ (e.g., the mean energy or variance, does not matter). If it is possible to analytically compute the expressions for $f'(\alpha)$ and $f''(\alpha)$ and sample them, then

$$f(\alpha+\delta) = f(\alpha) + f'(\alpha)\delta + f''(\alpha)\delta/2$$

the minimum of the function can be found iteratively with $f'(\alpha+\delta) = 0 \rightarrow \delta = -f'(\alpha)/f''(\alpha)$.

$$\alpha_{i+1} = \alpha_i - \frac{f'(\alpha_i)}{f''(\alpha_i)}$$

The Variational Monte Carlo method provides a starting point for a more powerful method: the Diffusion Monte Carlo method (DMC).

Diffusion Monte Carlo Method

The aim of this method is to make use of the trial wave function as the starting point, in order to get exact results for the energy of the ground state in addition to other properties. We start with the time-dependent Schrödinger equation:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\sum_i \nabla^2\psi + \sum_{i<j} V(r_{ij})\psi \tag{6.6}$$

The evolution in time of ψ is

$$\psi(t) = e^{-i\hat{H}t/\hbar}\psi(0)$$

we can compute the evolution towards imaginary time τ as

$$\psi(t=-i\tau) = e^{-\hat{H}\tau/\hbar}\psi(0)$$

re-writing equation 6.6 in imaginary (euclidean) time leads to

$$-\hbar\frac{\partial\psi}{\partial\tau} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2\psi + \sum_{i<j} V(r_{ij})\psi = \hat{H}\psi \tag{6.7}$$

Defining a diffusion coefficient as $D \equiv \frac{\hbar^2}{2m}$ and using $t = \tau/\hbar$ the expression becomes

$$-\frac{\partial\psi}{\partial t} = -D\sum_i \nabla_i^2\psi + \sum_{i<j} V(r_{ij})\psi \tag{6.8}$$

Equation 6.8 makes the evolution of any given initial state converge towards the ground state.

Proof:

Expanding ψ in terms of the eigenfunctions basis, we see

$$\psi(0) = \sum_i c_n \psi_n(R) \rightarrow \psi(t) = \sum_i c_n e^{-E_n t/\hbar} \psi_n(R)$$

here it is trivial to see that as $t \rightarrow \infty$ the only term that survives is precisely $c_0\psi_0(R)$.

The method

The DMC method consists in considering a stochastic process such that the probability distribution $p(R,t)$ evolves in time according to Equation 6.8. Introducing importance sampling by defining

$$f(R,t) = \psi_T(R)\psi(R,t)$$

where $\psi_T(R)$ is a static variational model wavefunction.

The goal is that when $t \rightarrow \infty$, $f(R, t \rightarrow \infty) = \psi_T(R)\psi_0(R)$ and we will get information regarding $\psi_0(R)$ via the knowledge of both $\psi_T(R)$ and $f(R, t \rightarrow \infty)$. The evolution of $f(R,t)$ is given by

$$-\frac{\partial \psi}{\partial t} = H\psi$$

or, in terms of $f(R,t)$:

$$-\frac{\partial f(R,t)}{\partial t} = -D\left(\sum_{i=1}^{n} \nabla_i^a \nabla_i^a f(R,t)\right) + D\sum_{i=1}^{n} \nabla_i^a \left(2\frac{(\nabla_i^a \psi_T(R))}{\psi_T(R)} f(R,t)\right) + E_L(R) f(R,t) \tag{6.9}$$

Some notes:

- $f(R,t)$ is more suited than $\psi(R,t)$ as a probability distribution.
- $f(R,t)$ is somewhat similar to ψ^2.
- $E_L(R)$ behaves better than $V(R)$, and for a good $\psi_T(R)$ it tends to a constant value E_0.
- We can write equation 6.9 as

$$-\frac{\partial f(R,t)}{\partial t} = (A_1 + A_2 + A_3) f(R,t) \tag{6.10}$$

with

$$A_1 f(R,t) = -D\left(\sum_{i=1}^{n} \nabla_i^a \nabla_i^a f(R,t)\right)$$
$$A_2 f(R,t) = D\sum_{i=1}^{n} \nabla_i^a \left(2\frac{(\nabla_i^a \psi_T(R))}{\psi_T(R)} f(R,t)\right)$$

introducing the drift force $F_i^a(R) \equiv 2\nabla_i^a \psi_T(R)/\psi_T(R)$

$$A_2 f(R,t) = D\sum_{i=1}^{n} \nabla_i^a \left(2F_i^a(R) f(R,t)\right)$$
$$A_3 f(R,t) = E_L(R) f(R,t)$$

Solving equation 6.10 for all A_i can only be worked out for small Δt, and leads to

$$f(R, t+\Delta t) = \int dR_0 \left(\exp\left(-\frac{(-R - \tilde{R}_0(\Delta t))^2}{4D\Delta t} \right) \exp\left(-(E_L(R_0) - E_0)\Delta t \right) \right) f(R_0, t) \tag{6.11}$$

which can be iterated indefinitely, so that the limit $t \to \infty$ can be reached eventually.

Summary of a DMC code

Starting from the Hamiltonian $\hat{H}$ and the trial model wave function ψ_T, we will work out the analytical expressions for the local energy and drift force:

$$E_L(R) \equiv \frac{\hat{H}\psi_T(R)}{\psi_T(R)} \qquad\qquad F_i^a(R) \equiv 2\frac{\nabla_i^a \psi_T(R)}{\psi_T(R)}$$

Then, we choose the desired number of walkers (N_w), the time step Δt and a starting energy reference E_0.

- Generate the initial configurations R_i, $i = 1, \ldots, N_w$.
- The random walkers will represent the initial state $f(R, t_0)$ of the system. For each walker R_i:
  1. Compute the new weight $w_i = \exp[-(E_L(R_i) - E_0)\Delta t]$.
  2. Compute the new position originated by the drift term $\tilde{R}_i = R_i + DF_i\Delta t$.
  3. Compute the new position originated by the diffusion term $R_i' = \tilde{R}_i + 2D\Delta t\zeta$, where ζ is a random gaussian distributed variable $\langle\zeta\rangle = 0$, $\langle\zeta^2\rangle = 1$.
  4. Replicate the walker R_i n_s times, with $n_s = \text{int}[w_i + \eta]$, where η is a uniformly distributed random variable in [0,1].
  5. Go to point 1 until completion of all walkers.
- This procedure implements the equivalent to one MC iteration ($t \to t + \Delta t$).
- Each configuration is highly correlated with the previous one, so a number of iterations has to be performed (a block) before new independent statistical information can be collected.
- At the end of a complete block, the parameter E_0 is adjusted as

  $$E_0 \leftarrow E_0 + a(N_w + N_w(\text{current}))$$

  where a is a proportionality factor.
- Whilst the steady state has not been reached, more updates of E_0 (smaller blocks) will result in a more stable behaviour.
- Once the steady state is reached the DMC code is providing samples of the ground state wavefunction.

  $$p(R) = \psi_T(R)\psi(R, t)$$