H3: Diffusion Monte Carlo

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Task Nº	Points	Avail. points
$\sum$		

Introduction

The *Diffusion Monte Carlo* (DMC) method is a way of obtaining the ground state of the Hamiltonian through diffusion-reaction processes. The method is based upon solving a rewritten Schrödinger equation where time is substituted to imaginary time, $t \to -i\tau$, and the Schrödinger equation turns into the imaginary time Schrödinger equation

$$\frac{\partial \Psi(\tau)}{\partial \tau} = -\mathcal{H}\Psi(\tau),$$

and its solution becomes

$$\Psi(\tau) = e^{-\mathcal{H}\tau}\Psi(0).$$

Additionally we shift the energy with E_T and write Ψ in terms of the eigenkets $\{\Phi_n\}$,

$$\Psi(\tau) = e^{-(\mathcal{H}-E_T)\tau}\Psi(0) = \sum_n e^{-(E_n-E_T)\tau}\Phi_n.$$

By propagating in time all terms with $E_T > E_0$ will diverge, terms with $E_T < E_0$ will decay and if $E_T = E_0$ the wavefunction converges to the ground state.

The wavefunction Ψ will now be represented by a ensemble of N random walkers, with

$$\mathcal{R}_i,\ i = 1, 2, 3, ..., N.$$

where $\mathcal{R}_i$ is the position of walker with index i.

Problem 1

We have a particle with mass m in a one-dimensional potential $V(x) = \frac{1}{2}[1 - e^x]^2$, using atomic units. The analytical solution for the ground state is

$$\Phi_0(x) = \sqrt{2}\exp\left[-e^{-x} - x/2\right],\ E_0 = \frac{3}{8}.$$

The Hamiltonian

$$\mathcal{L} = \frac{p^2}{2} + (V(x) - E_T) = \mathcal{K} + \mathcal{V},$$

where

$$\mathcal{K} = \frac{p^2}{2} = -\frac{\partial^2}{\partial x^2}\frac{1}{2}, \mathcal{V} = V(x) - E_T.$$

We can now use a Green's function as imaginary-time propagator

$$\Psi(x, \tau) = \int dx_0 G(x, x_0; \tau)\Psi(x_0, 0).$$

In order to obtain the stationary ground state we must iterate through small time steps $\Delta\tau$,

$$G(x, x_0; \tau) = \int dx_1 \dots dx_{M-1} \left\langle x \left| e^{-\mathcal{L}\Delta\tau} \right| x_{M-1} \right\rangle \left\langle x_{M-1} \left| e^{-\mathcal{L}\Delta\tau} \right| x_{M-2} \right\rangle$$
$$\dots \left\langle x_2 \left| e^{-\mathcal{L}\Delta\tau} \right| x_1 \right\rangle \left\langle x_1 \left| e^{-\mathcal{L}\Delta\tau} \right| x_0 \right\rangle.$$

The Green's function for the small time steps becomes

$$G(x, x_0; \Delta\tau) = \langle x| e^{-\mathcal{L}\delta\tau} |x_0\rangle.$$

If $\Delta\tau$ is small enough we may change the order of the operators,[1]

$$e^{-\mathcal{L}\Delta\tau} = e^{-(\mathcal{L}_D+\mathcal{L}_R)\Delta\tau} \approx e^{-\mathcal{L}_R\Delta\tau}e^{-\mathcal{L}_D\Delta\tau} + \mathcal{O}(\Delta\tau^2),$$

where $\mathcal{L}_D = \mathcal{K},\ \mathcal{L}_R = \mathcal{V}$.

The initial setup of the walkers will be, $N_0 = 200$ walkers placed equidistantly at $-5 \leq x \leq 5$ with the reference energy $E_T = 0.5$ and a timestep $\tau = 0.02$ (all in atomic units). The diffusive part with $\mathcal{L}_D$ represents the wavefunctions propagation due to its kinetic energy can be accounted by displacing each walker at every timestep with

$$x = x' + \Delta\tau G,$$

where G is a stochastic variable with a Gaussian distribution of zero mean and unit variance.

The reactive part with $\mathcal{L}_R$, is

$$e^{-\mathcal{L}_R \delta\tau} = e^{-(V(x)-E_T)\delta\tau} = W(x),$$

and can be accounted for using a branching method by either destroying or multiplying the walker based on $W(x)$. More precisely, all walkers will have m number copies of made where

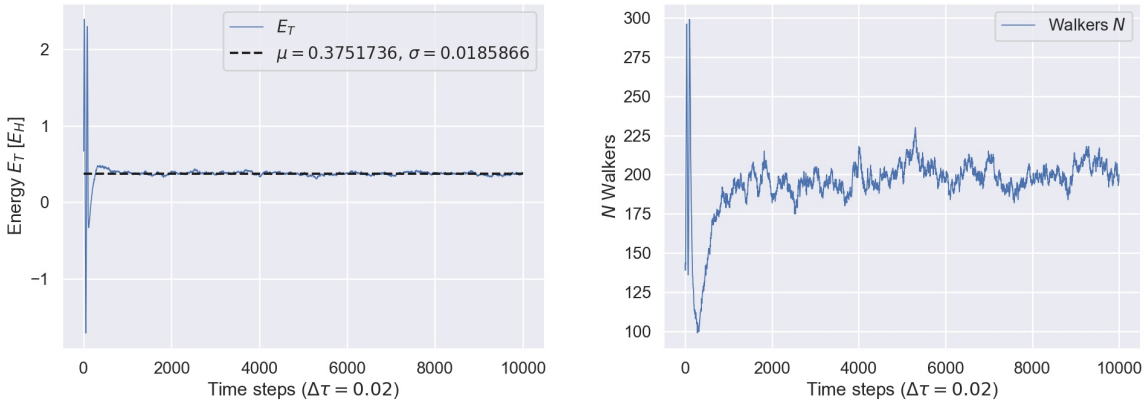
$$m = \text{Int}[W(x) + U],$$

where U is a stochastic variable with uniform distribution on $U \in [0, 1)$ and if $m = 0$ means the walker will be destroyed, $m = 2$ results in one copy made of the walker and so on.

If E_T is not adjusted during the time-propagation, the number of walkers will either go to zero or diverge towards infinity, unless $E_T = E_0$. Adjusting E_T based on the current number of walkers N_i with

$$E_T(i+1) = \langle E_T(i) \rangle - \gamma \frac{N_i}{N_0}$$

will eventually result in a stable number of walkers when E_T approaches E_0. In figures 1a, 1b, we see how the number of walkers varies during the DMC method as well as how energy converges towards the analytical ground state energy $E_0 = 3/8$.



(a) Reference energy E_T during DMC, converges to $E_0 \approx 3.75\, E_\text{H}$. In units of Hartree, atomic units.

(b) Amount of walkers during DMC, with $N_0 = 200$.

Figure 1: Energy E_T and number of walkers N during diffusion Monte Carlo method. The wavefunction stabilizes after approximately 1 000 timesteps.

In fig. 2 we the wavefunction probability density function from a collection of walkers at the end of the DMC method compared to the analytical pdf $|\Phi_0|^2$. Since their ground state energies were similar it is reasonable to expect their distributions to be similar as well.

Problem 2

We will now be solving for the helium atom with

$$\mathcal{H} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}},$$

with fundamentally the same method as in the previous one-dimensional problem. For efficiency the walkers are placed initially at likely positions and from the central-field approximation we know that the electrons should be around $r = 2/Z$, therefore we use the following positions for each walkers

$$\begin{aligned}
r_1 &= 0.7 + U_1, \\
\theta_1 &= \arccos\left(2U_2 - 1\right), \\
\varphi_1 &= 2\pi U_3, \\
r_2 &= 0.7 + U_4, \\
\theta_2 &= \arccos\left(2U_5 - 1\right), \\
\varphi_2 &= 2\pi U_6,
\end{aligned}$$

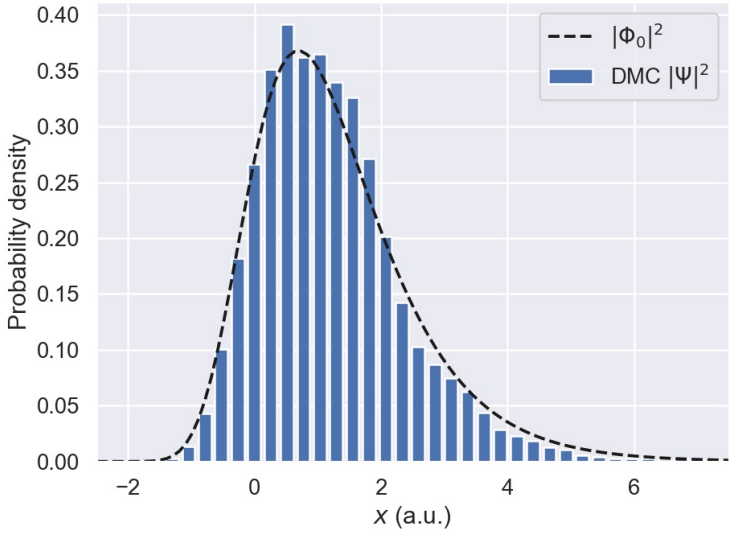
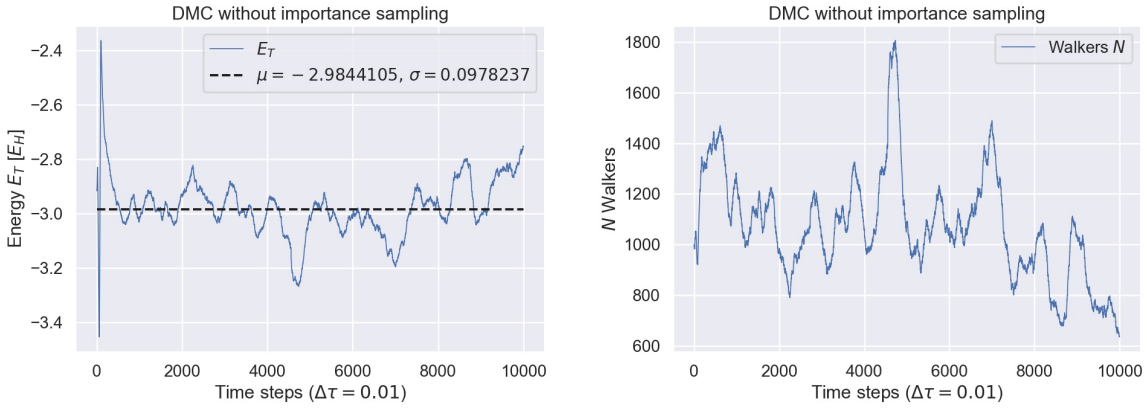


Figure 2: Ground state wavefunction pdf from DMC $|\Psi|^2$ and analytical solution pdf $|\Phi_0|^2$ (normalised).

where U_i is a random number from a uniform distribution $U \in [0, 1)$. Note that cartesian coordinates are used in the actual DMC method for convenience. Here we will be using $N_0 = 1\,000$ walkers , an initial refrence energy of $E_T = -3.0\,E_\mathrm{h}$ and a timestep $\Delta\tau = 0.01$.

In figures 3a, 3b, we see the reference energy E_T and the number of walkers N during the DMC method. Compared to the previous DMC simulation in figures 1a, 1b we see a much more unstable simulation here. The mean of E_T calculated in fig. 3a is from timesteps 2 000 and later, $\mu(E_T) = -2.9844(98)\,E_\mathrm{h}$.



(a) Reference energy E_T during DMC, converges to $E_0 \approx 3.75\,E_\mathrm{H}$. In units of Hartree, atomic units.

(b) Amount of walkers during DMC, with $N_0 = 1000$.

Figure 3: Energy E_T and number of walkers N during diffusion Monte Carlo method. The wavefunction stabilizes after approximately 1 000 timesteps.

Problem 3

Here we will incorperate importance sampling into the DMC method to improve stability. Importance sampling is done through using a trial wavefunction Ψ_T to then calculate the drift $\boldsymbol{v}_f$ to push the walkers towards the relevant regions.

We will now consider the function

$$f(x, \tau) = \Psi_T(x)\Psi(x, \tau),$$

and the local energy E_L,

$$E_L(x) \equiv \frac{\mathcal{H}\Psi_\mathrm{T}(x)}{\Psi_\mathrm{T}(x)} = -\frac{1}{2}\frac{1}{\Psi_\mathrm{T}(x)}\frac{d^2\Psi_\mathrm{T}(x)}{dx^2} + V(x).$$

By multiplying Ψ_T with the imaginary time Schrödinger equation we get

$$\frac{\partial}{\partial\tau}f(x,\tau) = \frac{1}{2}\left[\Psi_{\mathrm{T}}(x)\frac{\partial^2\Psi(x,\tau)}{\partial x^2} - \Psi(x,\tau)\frac{d^2\Psi_{\mathrm{T}}(x)}{dx^2}\right] - \left[E_L(x) - E_{\mathrm{T}}\right]f(x,\tau),$$

and can now let

$$v_F(x) = \frac{1}{\Psi_T(x)}\frac{\partial\Psi_T(x)}{\partial x}.$$

Which results in

$$\frac{\partial}{\partial\tau}f(x,\tau) = -\left[-\frac{1}{2}\frac{\partial^2}{\partial x^2} + \frac{\partial}{\partial x}v_F(x) + \left[E_L(x) - E_{\mathrm{T}}\right]\right]f(x,\tau),$$

and its solution can be written as

$$f(x,\tau) = e^{-(\mathcal{L}_R+\mathcal{L}_D+\mathcal{L}_F)\tau}f(x,0).$$

Once again, if we break τ down into small $\Delta\tau$ steps we can make the approximation

$$e^{-\mathcal{L}\Delta\tau} \approx e^{-\mathcal{L}_R\Delta\tau}e^{-\mathcal{L}_D\Delta\tau}e^{-\mathcal{L}_F\Delta\tau} + \mathcal{O}(\Delta\tau^2).$$

A more accurate decomposition is possible with

$$e^{-\mathcal{L}\Delta\tau} \approx e^{-\mathcal{L}_F/2\Delta\tau}e^{-\mathcal{L}_D/2\Delta\tau}e^{-\mathcal{L}_R\Delta\tau}e^{-\mathcal{L}_D/2}e^{-\mathcal{L}_F/2} + \mathcal{O}(\Delta\tau^3).$$

The drift part with $e^{-\mathcal{L}_F\Delta\tau}$ moves walkers' positon with $x = x' + v_F(x')\Delta\tau$ and is accurate to the first order of $\Delta\tau$. A second order accuracy is done by letting

$$x = x' + v_F(x_{1/2})\Delta\tau,\ x_{1/2} = x' + v_F(x')\Delta\tau/2.$$

The trial wavefunction used here for the helium atom is

$$\Psi_T(\mathcal{R}) = \exp\left[-2r_1\right]\exp\left[-2r_2\right]\exp\left[\frac{r_{12}}{2\left(1+\alpha r_{12}\right)}\right],$$

with $\alpha = 0.15$ and r_{12} is distance between $\boldsymbol{r}_1, \boldsymbol{r}_2$. The corresponding local energy becomes

$$E_L(\mathcal{R}) = -4 + \frac{(\hat{\boldsymbol{r}}_1 - \hat{\boldsymbol{r}}_2)\cdot(\boldsymbol{r}_1 - \boldsymbol{r}_2)}{r_{12}\left(1+\alpha r_{12}\right)^2} - \frac{1}{r_{12}\left(1+\alpha r_{12}\right)^3} - \frac{1}{4\left(1+\alpha r_{12}\right)^4} + \frac{1}{r_{12}},$$

and the drift velocity $\boldsymbol{v}_F$ for the first particle

$$\boldsymbol{v}_F(\mathcal{R}) = -2\hat{\boldsymbol{r}}_1 - \frac{1}{2\left(1+\alpha r_{12}\right)^2}\hat{\boldsymbol{r}}_{12}$$

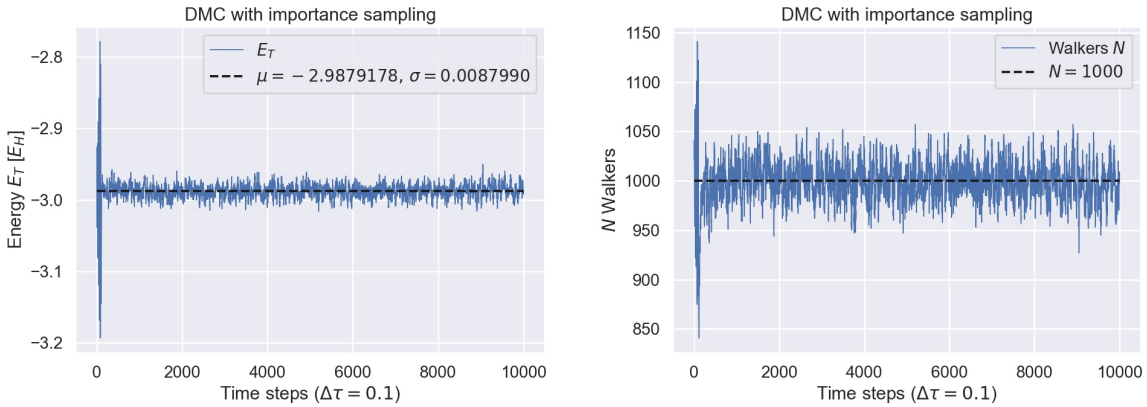
and for the second particle

$$\boldsymbol{v}_F(\mathcal{R}) = -2\hat{\boldsymbol{r}}_2 - \frac{1}{2\left(1+\alpha r_{12}\right)^2}\hat{\boldsymbol{r}}_{12}.$$

In figures 4a, 4b we see DMC with importance sampling and compared with figures in 3 it is considerably more stable but also uses a greater timestep. In figures 5a, 5b we see DMC with importance sampling using the second decomposition, quite similar to the first decomposition. Due to the fact that the two different decomposition gives very similar results, it is likely that the method using the second decomposition with second order accuracy is done incorrectly and warrants further testing.

Problem 4

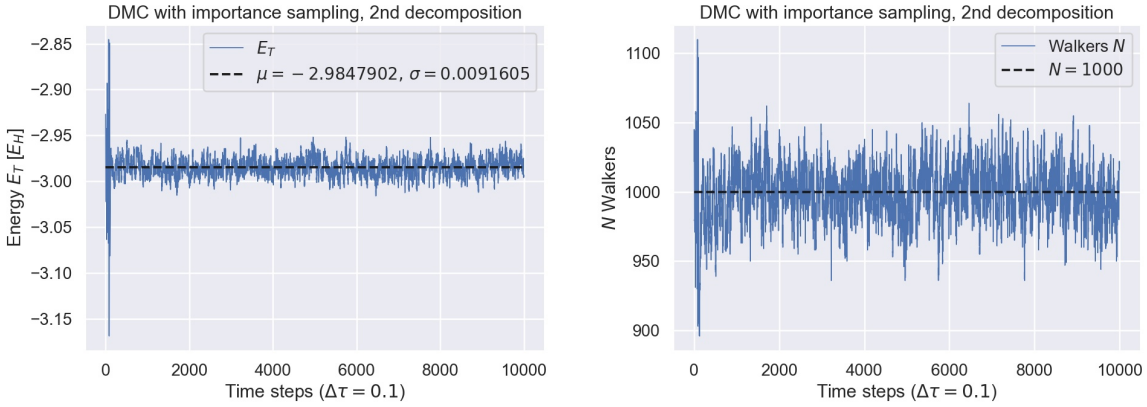
Since $\Delta\tau > 0$ the energy will slightly off, to counter act this we will calculate E_0 for a range of timesteps $\Delta\tau \in [0.01, 0.4]$, spaced linearly. Using the first decomposition with first order accuracy the relationship should be linear and using the second decomposition with second order accuracy its should quadratic. As seen in figure 6 both decompositions are quite similar and seemingly quadratic, where the linear fit of the first decomposition appears to diverge slightly as $\Delta\tau \to 0$. While the second decomposition is quadratic as expected, the first one deviates more from the fit than expected. The extrapolation of the first decomposition gives $E_0 \approx -2.9376\,E_{\mathrm{h}}$ and of the second gives $E_0 \approx -2.9425\,E_{\mathrm{h}}$. Both are relatively close to ground state, which is approximately[2] $-2.90\,E_{\mathrm{h}}$.



(a) Reference energy E_T during DMC, converges to $E_0 \approx 2.9879(88)\, E_\mathrm{H}$.

(b) Amount of walkers during DMC, with $N_0 = 1000$.

Figure 4: Energy E_T and number of walkers N during diffusion Monte Carlo method with importance sampling using the first decomposition.



(a) Reference energy E_T during DMC, converges to $E_0 \approx 2.9848(92)\, E_\mathrm{H}$.

(b) Amount of walkers during DMC, with $N_0 = 1000$.

Figure 5: Energy E_T and number of walkers N during diffusion Monte Carlo method with importance sampling using the second decomposition.

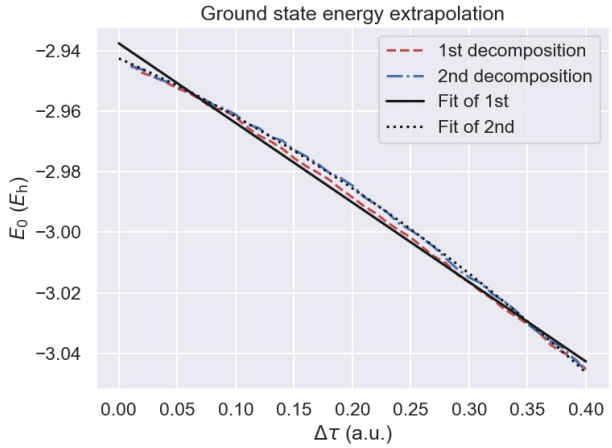


Figure 6: Ground state energy extrapolation using linear and polynomial regression.

References

[1] Göran Wahnström, (2021). Quantum Structure - Lecture notes. [Accessed 30th november 2022]

[2] Wikipedia contributors. (2022, September 30). Helium atom. In Wikipedia, The Free Encyclopedia. Retrieved January 5, 2023, from https://en.wikipedia.org/w/index.php?title=Helium_atom&oldid=1113243780