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H3a Diffusion Monte Carlo

Here you are asked to implement the Diffusion Monte Carlo (DMC) technique. You will first study the one-dimensional Morse potential and then the helium atom. Atomic units (a.u.) will be used, i.e. $\hbar = e = m_e = 4\pi\epsilon_0 = 1$. For information about the DMC technique, see Lecture notes "Quantum Structure".

Task

1. Consider first a particle with mass m moving in the one-dimensional Morse potential

$$V(x) = D\left[1 - e^{-ax}\right]^2 \ .$$

The well-depth is D and for small oscillations we have the frequency

$$\omega_0 = \sqrt{\frac{2a^2 D}{m}}$$

around the minimum. Assume that the particle is an electron ($m = m_e$), the well-depth is $D = E_H/2$ and $a = a_0^{-1}$. In atomic units the potential is then given by

$$V(x) = \frac{1}{2}\left[1 - e^{-x}\right]^2 \quad ; \quad \omega_0 = 1 \ ,$$

with the solution for the ground-state given by [1]

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

with the normalisation

$$\int_{-\infty}^{\infty} |\Phi_0(x)|^2 \, dx = 1 \ .$$

You should now determine the ground-state energy and wave function using diffusion Monte Carlo without importance sampling. Use the decomposition

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

Place $N_0 = 200$ walkers equidistant between $-5 < x < 5$. Choose the values $E_\mathsf{T} = 0.5$ and $\Delta\tau$=0.02.

- For all walkers:
  - displace each walker according to the diffusive part

- evaluate the weight factor $W(x)$ and eliminate or create walkers

- Update E_T so that the number of walkers eventually will stabilize around the value N_0. For the damping parameter use $\gamma = 0.5$.
- Repeat many times.

Plot your result for E_T and the number of walkers as function of time τ. Does the simulation result stabilize, equilibrate, when τ is increasing? It should approach the correct ground-state energy.

When the system is stabilized you can determine the ground-state energy and ground-state wave function. What value do you obtain for the ground-state energy? Compare with the exact result. Plot your result for the ground-state wave function and compare that with the analytical result. (6p)

2. Consider now the helium atom.

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

Use the same algorithm as above. However in this case the walkers are not moving in one-dimension. You have to generalize to 6 dimensions $\mathcal{R} = (x_1, y_1, z_1, x_2, y_2, z_2)$.

Initially it is efficient to place the random walkers at some likely positions. In the radial direction we have from the central-field approximation that the wave-function is proportional to $r^2 \exp -Zr$. This has a maximum at $r = 2/Z$, which implies that $r_{max} = 1$ for $Z = 2$ and $r_{max} = 1.2$ for $Z = 27/16$. Furthermore, to obtain a uniform distribution of points on the sphere the polar angle θ can not be chosen uniformly since the area element $d\Omega = \sin\theta \, d\theta \, d\varphi$ is a function of θ. Therefore, use the following initial values for each random walker:

$$\begin{aligned} r_1 &= 0.7 + \mathcal{U}_1 \\ \theta_1 &= \arccos(2\,\mathcal{U}_2 - 1) \\ \varphi_1 &= 2\pi\,\mathcal{U}_3 \\ r_2 &= 0.7 + \mathcal{U}_4 \\ \theta_2 &= \arccos(2\,\mathcal{U}_5 - 1) \\ \varphi_2 &= 2\pi\,\mathcal{U}_6 \end{aligned}$$

where $\mathcal{U}_i$ are 6 different independent uniform random numbers on [0,1]. The corresponding cartesian coordinates are

$$\begin{aligned} x_1 &= r_1 \sin\theta_1 \cos\varphi_1 \\ y_1 &= r_1 \sin\theta_1 \sin\varphi_1 \end{aligned}$$

$$
\begin{aligned}
z_1 &= r_1 \cos\theta_1 \\
x_2 &= r_2 \sin\theta_2 \cos\varphi_2 \\
y_2 &= r_2 \sin\theta_2 \sin\varphi_2 \\
z_2 &= r_2 \cos\theta_2
\end{aligned}
$$

Place $N_0 = 1000$ walkers according to the above scheme and choose the values $E_\mathsf{T} = -3.0$. A suitable number for the time-step is $\Delta\tau$=0.01. Without importance sampling the algorithm is quite inefficient and a short time-step is required to obtain reasonably stable results.

- For all walkers:
  - displace each walker according to the diffusive part
  - evaluate the weight factor $W(\mathcal{R})$ and eliminate or create walkers
- Update E_T so that the number of walkers eventually will stabilize around the value N_0. For the damping parameter use $\gamma = 0.5$.
- Repeat many times.

In this case you will find that the algorithm is less efficient. However, try to convince yourself that the program is working correctly in 6 dimensions. Plot your result for E_T and the number of walkers as function of time τ. If you want you can store your last configuration and use it in the next sub-task, no 3, as initial condition. (2 p)

3. The algorithm can be made more efficient by using **importance sampling**. One then introduces a trial wavefunction $\Psi_\mathsf{T}(\mathcal{R})$ that mimics the real wave function $\Psi(\mathcal{R})$.

   For helium we can use the trial wave-function

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

   which is parametrized with a single variational parameter α. The corresponding expression for the local energy is

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

   where $\hat{\boldsymbol{r}}_i$ denote a unit vector along $\boldsymbol{r}_i$, for $i = 1, 2$. This is the same trial wave-function as used in the homework problem H2b Variational Monte Carlo. More information can be found in the Lecture notes "Quantum structure".

The original Schrödinger equation is then transformed to a Fokker-Planck equation (see Lecture notes "Quantum structure") for the function $f(\mathcal{R},\tau) = \Psi_{\mathsf{T}}(\mathcal{R})\Psi(\mathcal{R},\tau)$. A drift part is then added that "pushes" the random walkers into more important regions. Using the trial wave-function above an expression for the drift velocity $\boldsymbol{v}_F(\mathcal{R})$ can be derived. For the first three components (x_1, y_1, z_1) we obtain the expression

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

and for the next three components (x_2, y_2, z_2)

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

where $\hat{\boldsymbol{r}}_{12}$ denote a unit vector along $\boldsymbol{r}_{12} \equiv \boldsymbol{r}_2 - \boldsymbol{r}_1$, i.e. $\hat{\boldsymbol{r}}_{12} = \boldsymbol{r}_{12}/r_{12}$ and $|\boldsymbol{r}_{12}| = r_{12}$. For more details, see the Lecture notes "Quantum structure".

Now perform a diffusion Monte Carlo (DMC) study of helium using importance sampling. For the α-value in the trial wave-function use $\alpha = 0.15$. This value can be obtained in a variational Monte Carlo (VMC) study of helium.

Use N_0=1000, $\Delta\tau$=0.1 and E_{T}=-3.0. For the damping parameter use γ=0.5. You can test to vary the damping parameter γ. As starting configuration use either the description in sub-task no 2, or the last configuration from the previous sub-task (no 2). This configuration should contain about N=1000 random walkers. In this case you could also use the last value for E_{T} from the previous sub-task (no 2) as your initial value for E_{T}.

First use the decomposition

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

To update the drift part use

$$\mathcal{R}(\Delta\tau) = \boldsymbol{v}_F(\mathcal{R}')\Delta\tau + \mathcal{R}'$$

Run and update E_{T} along the simulation. Verify that E_{T} stabilizes when τ is increasing and approaches a reasonable value for the ground-state energy. Plot your result for E_{T} and the number of walkers as function of time τ. What value do you obtain for the ground-state energy?

Change to the more accurate decomposition

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

and then update the drift part according to

$$\mathcal{R}(\Delta\tau) = v_F(\mathcal{R}_{1/2})\Delta\tau + \mathcal{R}' \quad , \quad \text{with} \quad \mathcal{R}_{1/2} = \boldsymbol{v}_F(\mathcal{R}')\Delta\tau/2 + \mathcal{R}'$$

Repeat the simulation and verify again that E_T stabilizes when τ is increasing and approach a reasonable value for the ground-state energy. Plot your result for E_T and the number of walkers as function of time τ. What value do you obtain for the ground-state energy? (6 p)

4. You should now have a working program for a diffusion Monte Carlo (DMC) study of the helium atom. Due to the finite size of the time step $\Delta\tau$ you do not obtain the exact result. You should now extrapolate your result and extract the exact value.

   Using the decomposition

$$e^{-\mathcal{L}\Delta\tau} \simeq e^{-\mathcal{L}_R\Delta\tau}e^{-\mathcal{L}_D\Delta\tau}e^{-\mathcal{L}_F\Delta\tau}$$

   the ground-state energy should scale linearly with the time step $\Delta\tau$ and by using

$$e^{-\mathcal{L}\Delta\tau} \simeq e^{-\mathcal{L}_F\Delta\tau/2}e^{-\mathcal{L}_D\Delta\tau/2}e^{-\mathcal{L}_R\Delta\tau}e^{-\mathcal{L}_D\Delta\tau/2}e^{-\mathcal{L}_F\Delta\tau/2}$$

   the scaling should become quadratic in $\Delta\tau$. Perform calculations for some $\Delta\tau$-values in the interval $0 < \Delta\tau \leq 0.4$ using the two different decompositions above. Notice, when you reduce the time-step $\Delta\tau$, increase the number of steps in the DMC algorithm, accordingly.

   Plot your final results for the ground-state energy as function of $\Delta\tau$ and extrapolate to zero. What is your best estimate of the ground-state energy for helium? (2 p)

References

[1] L. Infeld and T. E. Hull, Rev. Mod. Phys. **23**, 21 (1951).