University of Göttingen
Institute for Theoretical Physics
Methods of Computational Physics, WiSe 2022/23
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Project 5: Quantum Monte Carlo

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1. Variational Monte Carlo simulation of a Helium atom (30 points)

Implement a Variational Monte Carlo (VMC) simulation for the Helium atom. Use the following Padé–Jastrow ansatz for the trial wave function:

$$\Psi_T(\vec{r}_1, \vec{r}_2) = e^{-\kappa r_1} e^{-\kappa r_2} e^{\frac{\beta r_{12}}{1+\alpha r_{12}}}. \tag{1}$$

Note that this is identical to the form given in the lecture for $\kappa = 2$ and $\beta = \frac{1}{2}$, a choice that corresponds to the cusp conditions for $l = 0$. For the local energy, one finds

$$E_L = \frac{\kappa - 2}{r_1} + \frac{\kappa - 2}{r_2} + \frac{1}{r_{12}}\left(1 - \frac{2\beta}{u^2}\right) + \frac{2\beta\alpha}{u^3} - \kappa^2 - \frac{\beta^2}{u^4} + \frac{\kappa\beta}{u^2}\left(\frac{\vec{r}_1}{r_1} - \frac{\vec{r}_2}{r_2}\right)\frac{\vec{r}_1 - \vec{r}_2}{r_{12}}, \tag{2}$$

where $u = 1 + \alpha r_{12}$. For your Metropolis Monte Carlo step, update the position of one of the two electrons by adding to each position component a uniform random number in the range $[-\frac{s}{2}, \frac{s}{2})$. Use $M = 300$ random walkers, and initialise the three components of the electrons' position vectors using a random uniform distribution in the range $[-\frac{1}{2}, \frac{1}{2})$.

a) Define E_L^n to be the average of the local energy of a given walker over its last n Monte-Carlo steps. Plot the energy estimate $\langle E_L^n \rangle$ and its standard error $\sigma_{\langle E_L^n \rangle} = \sqrt{\mathrm{Var}(E_L^n)/(M-1)}$ versus the number of iterations for the step sizes $s = 0.1$, 1.0, and 10.0.[1] Use the cusp condition values for κ and β and set $\alpha = 0.15$. Run each simulation for $N = 30000$ steps and use $n = 1000$. It suffices to calculate and plot E_L^n only for every nth MC step. Quote the final value of $\sigma_{\langle E_L^n \rangle}$ after the simulation for each step size. Use this information to decide which step size to use in the following tasks. Explain your choice. (6 points)

b) Plot the energy estimate $\langle E_L^n \rangle$ for $n = 1000$, $N = 10000$ and $M = 300$ versus the number of iterations for $\alpha = 0.0, 0.1, 0.2, 0.3$, 0.4 and 0.5, and use the plot to choose a suitable number of Monte Carlo steps to reach equilibration, $n_{\text{equilibration}}$, for the following tasks. Quote your choice of $n_{\text{equilibration}}$. (2 points)

[1] Note that $\mathrm{Var}(X) = \langle X^2 \rangle - \langle X \rangle^2$ denotes the variance of the quantity X, and $\langle X \rangle$ denotes the ensemble average for X over all walkers.

c) Define $\bar{E}_L$ to be the average of the local energy of a given walker over *all* its Monte-Carlo steps excluding equilibration steps. Fix the cusp condition values $\beta = \frac{1}{2}$ and $\kappa = 2$ and plot the energy estimate $\langle \bar{E}_L \rangle$ and the standard error $\sigma_{\langle \bar{E}_L \rangle}$ versus α, varying α between 0.0 and 0.5. Choose N and the α binning such that you are able to give a reasonable estimate of the minima $E_{\min}$ and $\sigma_{E_{\min}}$ of $\langle \bar{E}_L \rangle$ and $\sigma_{\langle \bar{E}_L \rangle}$, respectively. Quote those two values and the corresponding values of α, and choose the one you will use in the following tasks. Give a reason for your choice. (4 points)

d) Now let us release the cusp condition on κ. Keep the cusp condition $\beta = \frac{1}{2}$ and use $\alpha = \alpha_{\min}$ as found in c). Plot the mean $\langle \bar{E}_L \rangle$ and the standard error $\sigma_{\bar{E}_L}$ for the energy versus κ, varying κ between 1.7 and 2.2. Use the same N as in c) and set the κ binning such that you can find the minima of $\langle \bar{E}_L \rangle$ and $\sigma_{\bar{E}_L}$ with respect to κ. Compare them to the values found when varying α in c). (2 points)

e) Confirm that $\beta = 0.38$, $\alpha = 0.18$ and $\kappa = 1.85$ gives a combined minimum of $\langle \bar{E}_L \rangle$. Quote the values of $E_{\min}$ and $\sigma_{E_{\min}}$ you obtain at this minimum. Compare it to the experimental value for the ground state energy of

$$E_g^{\text{exp}} = -2.90338583(13). \tag{3}$$

What does this tell us about the quality of Ψ_T? (4 points)

f) In the following, you will need the quantum force $\vec{F}(R) = 1/\rho(R)\nabla_R \rho(R)$. Calculate it analytically for our Helium model. (2 points)

g) Now implement the Fokker–Planck equation approach to VMC (FP-VMC), including the generalised Metropolis–Hasting accept/reject step to correct for the $\Delta\tau$ truncation error.[2] With that, run simulations using $\beta = 0.38$, $\alpha = 0.18$ and $\kappa = 1.85$, varying $\Delta\tau = 0.01, 0.05, 0.1, 0.2, 1.0$ to find the best value for $\Delta\tau$ (i.e. one with the lowest $\sigma_{\bar{E}_L}$). Quote the value of $\Delta\tau$ and the corresponding result for $\bar{E}_L$ and $\sigma_{\bar{E}_L}$ you obtain. Does it agree with the one obtained from your original VMC simulation? How do the errors obtained compare using the same number of MC steps? Explain this. (6 points)

h) Plot the density of the electrons given by the Fokker–Planck VMC walkers (after equilibration) in dependence of the radial distance r from the Helium nucleus. What should be the limiting behaviour of this quantity? Moreover, plot the probability distribution of the distances between the two electrons. (4 points)

2. Diffusion Monte Carlo simulation of a Helium atom (14 points)

With the knowledge gained by the implementation and the results of the VMC simulation of Helium, we are now ready to attempt one using the Guide Function approach to Diffusion Monte Carlo (GF-DMC) including the accept/reject step with the trial wave function Ψ_T. We will have to use the Ψ_T of Eq. (1), with both cusp conditions realised,

[2] Note that in contrast to the naive VMC described in the introduction of task 1, an FP-VMC step attempts to update the positions of *both* electrons, not just one of them.

i.e. $\kappa = 2$ and $\beta = \frac{1}{2}$, to ensure stability of the algorithm. Since it is crucial that Ψ_T is close to the exact ground state wave function Ψ, one should set the remaining parameter α to the value that minimises the ground state energy. Use your result of c) here.

Note that you can recycle most of the FP-VMC algorithm. The two necessary additions happen after the FP-VMC Metropolis–Hastings step.

The first is the death/birth procedure, which is applied to a walker only after its FP-VMC Metropolis–Hastings step has been accepted. Note that the newly birthed walkers should only be taken into account during the next Monte-Carlo loop over all walkers, not in the ongoing one when the birth has taken place.

The second is the adjustment of E_T as explained in the lecture. This happens after every n_{adjust} Monte-Carlo loops over all walkers. Here, we can use $n_{\text{adjust}} = 1$. Remember from the lecture that the update prescription is given by $E_T = E_0 + a/\Delta\tau \log\left(\tilde{M}/M\right)$, where M is the current number of walkers and $\tilde{M}$ is the desired number of walkers (which would usually be equal to M_0, the starting number of walkers). The parameter a (denoted by α in the lecture) is a free parameter of the algorithm. For the Helium simulation, set a such that $a/\Delta\tau = 1$. For E_0 (and the starting value of E_T), you can use the ground state energy estimate found in g).

a) Explain why one would use GF-DMC for Helium (instead of a plain DMC simulation), and why the cusp conditions should be fulfilled by the trial wave function Ψ_T. Discuss the error sources of the GF-DMC algorithm. (2 points)

b) Implement the FP-DMC algorithm extending the FP-VMC. Run a simulation for $\Delta\tau = 0.03$ for $N = 30000$ steps (after running 10000 equilibration steps), starting with $M_0 = 300$ walkers. Plot the evolution of E_T and quote the average of E_T over all after-equilibration MC steps. Is it close to the experimental value for the Helium ground state energy given in Eq. (3)? (You might want to plot only every 100th E_T value. Note that E_T is expected to fluctuate strongly.) (8 points)

c) Plot the electron density and the distance of the two electrons, comparing to the respective FP-VMC results. What should be the limiting behaviour of the density this time? (4 points)

3. Feynman Path Integral Quantum Mechanics (14 points)

Consider the action integral for the harmonic oscillator with potential

$$V(x) = \frac{1}{2} m\omega^2 x^2 \,. \tag{4}$$

Discretising the classical action, using Euler's forward rule for the derivative, leads to the following expression for the integrand:

$$\mathcal{S}[x] = \sum_{j=1}^{N} \left[\frac{m}{2} \left(\frac{x_j - x_{j-1}}{\Delta\tau} \right)^2 + V\left(\frac{x_j + x_{j-1}}{2} \right) \right] . \tag{5}$$

In the following, consider $m = 1$, $\omega = 1$.

a) Use the discretised action (5) to evaluate the quantum mechanical path integral numerically. Discretise time, starting from $\tau_0 = 0$ to $\tau = 100$ using $N = 400$ steps. To run the simulation, change a random position from $x(\tau_i)$ to $x'(\tau_i)$ and accept the change using the Metropolis algorithm with an acceptance probability $P = e^{-\Delta\tau\Delta\mathcal{S}}$, but keeping the boundary values $x(\tau = 0) = x(\tau = 100) = 0$ fixed. Compute the potential and kinetic parts of the energy separately and plot them together, what can you observe? Run the simulation long enough to equilibrate the energies. The virial theorem for this system states $\langle T \rangle = \langle V \rangle$, where T is the total kinetic energy and V is the total potential energy. Can you confirm this in your simulation? (6 points)

b) For the wave function, establish a histogram of positions $x(\tau_i)$ filling the histogram with the value of the changed position after each Metropolis step. Also use the values if the change was rejected by the Metropolis step. Start by running the simulation long enough to equilibrate, after this initial phase collect enough data, to sufficiently fill the histogram. Plot the normalised histogram. The normalised histogram values directly correspond to the squared wave function, can you qualitatively explain why? (4 points)

c) Repeat the above tasks for a 2D quantum mechanical harmonic oscillator, using a suitably generalised version of the action (5) and the asymmetric potential

$$V(x, y) = \frac{1}{2} m\omega_x^2 x^2 + \frac{1}{2} m\omega_y^2 y^2 \,, \tag{6}$$

with $\omega_x = 1$, $\omega_y = 10$. Plot the resulting squared wave function. (4 points)