Department of Physics, Chalmers, Göteborg
Göran Wahnström, 2018-12-17

H2b Variational Monte Carlo

Here you are asked to determine the ground state energy for the helium atom using the variational Monte Carlo technique. It is an application of the Metropolis algorithm. Atomic units (a.u.) are used, i.e. $\hbar = e = m_e = 4\pi\epsilon_0 = 1$.

The variational Monte Carlo method

The variational Monte Carlo mehod is based on the variation theorem. This theorem states that for some arbitrary (trial) wave function Ψ_T the expectation value of the energy

$$E[\Psi_T] = \frac{\langle \Psi_T \mid \mathcal{H} \mid \Psi_T \rangle}{\langle \Psi_T \mid \Psi_T \rangle} \geq E_0 \tag{1}$$

is always larger or equal to the ground state energy E_0. Only if Ψ_T is equal to the ground state wave function Ψ_0, the expectation value is equal to E_0.

If the system contains many electrons the calculation of the expectation value of the energy involves integrals over many degrees of freedom. It can be solved using Monte Carlo integration together with the Metropolis algorithm. The expression for the energy can be written as

$$E[\Psi_T] = \int d\mathcal{R} E_L(\mathcal{R}) \rho(\mathcal{R}) \tag{2}$$

where

$$E_L(\mathcal{R}) = \frac{\mathcal{H}\Psi_T(\mathcal{R})}{\Psi_T(\mathcal{R})} \tag{3}$$

is called the *local energy* and

$$\rho(\mathcal{R}) = \frac{\mid \Psi_T(\mathcal{R}) \mid^2}{\int d\mathcal{R} \mid \Psi_T(\mathcal{R}) \mid^2} \tag{4}$$

is a normalized probability distribution for the coordinate $\mathcal{R}$, which can be used as the weight function in the Metropolis algorithm. Here, $\mathcal{R}$ denotes the combined coordinate of all N electrons, $\mathcal{R} = (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$. If $\Psi_T(\mathcal{R})$ is parametrized with a set of S parameters $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, \ldots, \alpha_S)$, the expectation value becomes an ordinary function of $\boldsymbol{\alpha}$

$$E(\boldsymbol{\alpha}) = \frac{\langle \Psi_T \mid \mathcal{H} \mid \Psi_T \rangle}{\langle \Psi_T \mid \Psi_T \rangle} \tag{5}$$

The trial wave function

Use the trial wave-function

$$\Psi_T(\boldsymbol{r}_1, \boldsymbol{r}_2) = \exp\left[-2r_1\right] \exp\left[-2r_2\right] \exp\left[\frac{r_{12}}{2(1+\alpha r_{12})}\right] \tag{6}$$

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

$$\begin{aligned} E_L(\boldsymbol{r}_1, \boldsymbol{r}_2) = -4 + \frac{(\hat{\boldsymbol{r}}_1 - \hat{\boldsymbol{r}}_2)\cdot(\boldsymbol{r}_1 - \boldsymbol{r}_2)}{r_{12}(1+\alpha r_{12})^2} \\ -\frac{1}{r_{12}(1+\alpha r_{12})^3} - \frac{1}{4(1+\alpha r_{12})^4} + \frac{1}{r_{12}} \end{aligned} \tag{7}$$

where $\hat{\boldsymbol{r}}$ denote a unit vector along $\boldsymbol{r}$. More information can be found in the lecture notes "Quantum structure".

Task

1. Consider the helium atom. Implement the Metropolis algorithm and use the ansatz in eqn (6) for the trial wave function. Use the value $\alpha = 0.1$.

   You have to define how to generate a new configuration. The simpliest is to choose one of the six coordinates $(\boldsymbol{r}_1, \boldsymbol{r}_2)$ at random and displace it symmetrically. You can also choose to displace all six coordinates at each step. Introduce a parameter d to control the size of the symmetric displacement(s). Determine an appropriate value for d by monitoring the acceptance-rejection ratio.

   To convince yourself that the program is working correctly, it is instructive to investigate the distribution of the sampled points. Determine the probability $\rho(r)$ to find an electron at a distance r from origo based on the sampled points from the Monte Carlo simulation. Compare with the result

   $$\rho(r) = Z^3 4r^2 e^{-2Zr}$$

   from the central field approximation, both with an unscreened nucleus $Z = 2$ and the variationally optimized value Z=27/16. Do you obtain what you expect?

   You should also try to investigate how correlated the two electrons are. Denote the position of the two electrons with $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, respectively, and determine the angle

   $$\theta = \cos^{-1}\left(\frac{\boldsymbol{r}_1 \cdot \boldsymbol{r}_2}{|\boldsymbol{r}_1|\,|\boldsymbol{r}_2|}\right)$$

If the two electrons are uncorrelated the angle θ should be uniformly distributed over the unit sphere, i.e.

$$P(\theta) = \frac{1}{2}\sin\theta \quad 0 < \theta < \pi$$

where $P(\theta)$ is the probability to obtain the value θ. If you introduce

$$x = \cos\theta$$

the probability for x is given by

$$P(x) = \frac{1}{2} \quad -1 < x < 1$$

Determine the distribution for x based on the sampled points from the Monte Carlo simulation. What do you obtain? Can you understand the result?

Determine also the ground state energy by averaging the local energy along the Markov chain. You should obtain about $E_0 = -3$ a.u.. Do you obtain a reasonable number? (4p)

2. In a Monte Carlo calculation using the Metropolis algorithm a large number of steps, $N_{tot} = N_{eq} + N$, are generated. The first N_{eq} steps is discarded, the system has to equilibrate, and the subsequent N steps are used to compute different quantities. The configurations are correlated and the statistical inefficiency, the correlation length, has to be determined in order to be able to make a proper estimate of the error.

   Consider again the case $\alpha = 0.1$ and determine the local energy at each step. Start with some unlikely initial configuration and investigate the number of steps N_{eq} required to equilibrate the system by monitoring the variation of the local energy. When N_{eq} is reached no direct drift of the local energy should be observable.

   Determine next the statistical inefficiency using both the correlation function method and block averaging. (3p)

3. You should now have a correct working program. Perform simulations for several different α-values in the range $0.05 < \alpha < 0.25$. Determine the energy with error bars. For the latter, you may use the statistical inefficency you obtained above, i.e. you may neglect the (weak) α-dependence of the statistical inefficiency.

   You may also perform several independent calculations (for the same α-value) to verify that you get results independent on the starting configuration. In some cases one can get stuck in local minima, favourable regions in configuration space, and the sampling of configuration space

will not be correct. Independent runs are then a useful test. The information from the different runs can also be used to reduce the error bars.

What optimum value do you obtain for the energy? What is the corresponding α-value? (4p)

4. Variational Monte Carlo is an optimization method. It is possible to adjust the parameter α directly in the simulation. In the case of a large set of variational parameters $\boldsymbol{\alpha}_p$ this becomes essential.

   Perform such a study using the method described in the lecture notes "Quantum structure", Sec. 5.2. Use the damped steepest descent method, according to

   $$\boldsymbol{\alpha}_{p+1} = \boldsymbol{\alpha}_p - \gamma_p \nabla_{\boldsymbol{\alpha}} E(\boldsymbol{\alpha}_p) \tag{8}$$

   and for γ_p use the expression

   $$\gamma_p = A p^{-\beta} \tag{9}$$

   with A=1 and investigate a few different values for the exponent β. Do you converge to the same α value? Is your result for α consistent with what you obtained above? (4p)

5. You should now have obtained an optimum value for α. Perform a careful simulation using this α-value and compare your result with the Hartree value -2.862 a.u. and the experimental number -2.9033 a.u. (1p)