FYS4411

Part a, Variational Monte Carlo studies of atoms

The final aim of this project is to develop a variational Monte Carlo program which can be used to obtain ground state properties of atoms like He, Be, O, Ne, Si etc. If possible (time allowing) the hope is to be to be able to perform calculations for important molecules.

The aim of the part (a) of this project is to use the Variational Monte Carlo (VMC) method and evaluate the ground state energy of the helium, beryllium and neon atoms. Although we confine ourselves to atoms and molecules, you should however make your code flexible enough to run for two-dimensional systems like electrons confined in quantum dots or other fermionic systems in one, two and three dimensions.

We expect to finalize this part on March 22. Only a short report and a link to your Git repository is required.

Exercise 1: Variational Monte Carlo calculations of the helium atom

We will start with the simplest possible system beyond hydrogen, namely the helium atom. We label r_1 the distance from electron 1 to the nucleus and similarly r_2 the distance between electron 2 and the nucleus. The contribution to the potential energy from the interactions between the electrons and the nucleus is

$$\widehat{\mathbf{V}}_{nuc}(\mathbf{r}_1,\mathbf{r}_2) = -\frac{Z}{r_1} - \frac{Z}{r_2}, \tag{1}$$

and if we add the electron-electron repulsion with $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, the total potential energy $\widehat{\mathbf{V}}(\mathbf{r}_1,\mathbf{r}_2)$ is

$$\widehat{\mathbf{V}}(\mathbf{r}_1,\mathbf{r}_2) = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \tag{2}$$

yielding the total Hamiltonian

$$\widehat{\mathbf{H}}(\mathbf{r}_1,\mathbf{r}_2) = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \tag{3}$$

where $Z = 2$ for Helium. The Schrödinger equation reads

$$\widehat{\mathbf{H}}\psi = E\psi. \tag{4}$$

All equations are in so-called atomic units. The distances r_i and r_{12} are dimensionless. To have energies in electronvolt you need to multiply all results with $2E_0$, where $E_0 = 13.6$ eV. The experimental binding energy for helium in atomic units a.u. is $E_{\mathrm{He}} = -2.9037$ a.u.. See chapter 14 of the lecture notes[3] for more details.

1a) We want to perform a Variational Monte Carlo calculation of the ground state of the helium atom. In our first attempt we will use a brute force Metropolis sampling with a trial wave function which has the following form

$$\psi_T(\mathbf{r}_1,\mathbf{r}_2) = \exp\left(-\alpha(r_1+r_2)\right)\exp\left(\frac{r_{12}}{2(1+\beta r_{12})}\right), \tag{5}$$

with α and β as variational parameters.

Your task is to perform a Variational Monte Carlo calculation using the Metropolis algorithm to compute the integral

$$\langle E\rangle = \frac{\int \psi_T^*(\mathbf{r_1},\mathbf{r_2})\widehat{\mathbf{H}}(\mathbf{r_1},\mathbf{r_2})\psi_T(\mathbf{r_1},\mathbf{r_2})d\mathbf{r_1}d\mathbf{r_2}}{\int \psi_T^*(\mathbf{r_1},\mathbf{r_2})\psi_T(\mathbf{r_1},\mathbf{r_2})d\mathbf{r_1}d\mathbf{r_2}}. \tag{6}$$

Parallelize your program. Find the energy minimum by plotting the energy surface as a function of the variational parameters. Using the optimal parameters compute the mean distance r_{12} between the two electrons. A sample code for doing a VMC calculation for the helium atom can be found at https://github.com/ComputationalPhysics under the project 'fys4411' and navigate to '/examples/vmc-simple/'.

Your Monte Carlo moves are determined by

$$\mathbf{R}' = \mathbf{R} + \mathbf{r}\delta, \tag{7}$$

where $\mathbf{r}$ is a random vector where each of the components are drawn from a uniform distribution, and δ a chosen step length. In solving this exercise you need to devise an algorithm which finds an optimal value of δ so that roughly 50% of the moves are accepted, for example Newtons method. Note that the optimal value of δ depends on the variational parameters α and β.

Give a physical interpretation of the best value of α. Make a plot of the variance as a function of the number of Monte Carlo cycles.

1b) Find closed form expressions for the local energy

$$E_{L2} = \frac{1}{\Psi_T}\widehat{\mathbf{H}}\Psi_T \tag{8}$$

for the above trial wave function and explain shortly how this trial function satisfies the cusp condition when $r_1 \to 0$ or $r_2 \to 0$ or $r_{12} \to 0$. Show that the closed-form expression for the trial wave function is

$$E_{L2} = E_{L1} + \frac{1}{2(1+\beta r_{12})^2}\left\{\frac{\alpha(r_1+r_2)}{r_{12}}(1-\frac{\mathbf{r}_1\mathbf{r}_2}{r_1 r_2}) - \frac{1}{2(1+\beta r_{12})^2} - \frac{2}{r_{12}} + \frac{2\beta}{1+\beta r_{12}}\right\},$$

where

$$E_{L1} = (\alpha - Z)\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \frac{1}{r_{12}} - \alpha^2.$$

Compare the results of with and without the closed-form expressions (in terms of CPU time).

1c) Introduce importance sampling and study the dependence of the results as a function of the time step Δt. Compare the results with those obtained under 1a) and comment eventual differences. In performing the Monte Carlo analysis you should use blocking[1] as a technique to make a statistical analysis of the numerical data. The code has to run in parallel.

1d) With the optimal parameters for the ground state wave function, compute the onebody density and the charge density. Discuss your results and compare the results with those obtained with a pure hydrogenic wave functions. Run a Monte Carlo calculations without the Jastrow factor as well and compute the same quantities. How important are the correlations induced by the Jastrow factor?

1e) Repeat step 1c) and minimize the energy by finding the optimal variational parameters. This can be done using methods like the stochastic gradient descent[2], conjugate gradient, or some other algorithm of your choice.

Exercise 2: Variational Monte Carlo calculations of the Beryllium and Neon atoms

The previous exercise has prepared you for extending your calculational machinery to other systems. Here we will focus on the neon and beryllium atoms. It is convenient to make classes of

trial wave functions, both many-body wave functions and single-particle wave functions and the quantum numbers involved, such as spin, orbital momentum and principal quantum numbers.

The new item you need to pay attention to is the calculation of the Slater Determinant. This is an additional complication to your VMC calculations. If we stick to hydrogen-like wave functions, the trial wave function for Beryllium can be written as

$$\psi_T(\mathbf{r_1},\mathbf{r_2},\mathbf{r_3},\mathbf{r_4}) = Det\left(\phi_{1s}^{\uparrow},\phi_{1s}^{\downarrow},\phi_{2s}^{\uparrow},\phi_{2s}^{\downarrow}\right)\prod_{i<j}^{4}\exp\left(\frac{r_{ij}}{2(1+\beta r_{ij})}\right), \tag{9}$$

where Det is a Slater determinant

$$Det\left(\phi_1,\phi_2,\phi_3,\phi_4\right) \propto \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \phi_3(\mathbf{r}_1) & \phi_4(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \phi_3(\mathbf{r}_2) & \phi_4(\mathbf{r}_2) \\ \phi_1(\mathbf{r}_3) & \phi_2(\mathbf{r}_3) & \phi_3(\mathbf{r}_3) & \phi_4(\mathbf{r}_3) \\ \phi_1(\mathbf{r}_4) & \phi_2(\mathbf{r}_4) & \phi_3(\mathbf{r}_4) & \phi_4(\mathbf{r}_4) \end{vmatrix}, \tag{10}$$

and the single-particle wave functions are the hydrogen wave functions for the $1s$ and $2s$ orbitals. Their form within the variational ansatz are given by

$$\phi_{1s}(\mathbf{r_i}) = e^{-\alpha r_i}, \tag{11}$$

and

$$\phi_{2s}(\mathbf{r_i}) = (1-\alpha r_i/2)\, e^{-\alpha r_i/2}. \tag{12}$$

For neon, the trial wave function can take the form

$$\psi_T(\mathbf{r_1},\mathbf{r_2},\ldots,\mathbf{r_{10}}) = Det\left(\phi_1,\phi_2,\ldots,\phi_{10}\right)\prod_{i<j}^{10}\exp\left(\frac{r_{ij}}{2(1+\beta r_{ij})}\right), \tag{13}$$

In this case you need to include the $2p$ wave function as well. It is given as

$$\phi_{2p}(\mathbf{r_i}) = \alpha \mathbf{r_i} e^{-\alpha r_i/2}. \tag{14}$$

Observe that $r_i = \sqrt{r_{i_x}^2 + r_{i_y}^2 + r_{i_z}^2}$.

You can approximate the ground state of the Beryllium atom by writing it out as the Slater determinant

$$\psi_T(\mathbf{r_1},\mathbf{r_2},\mathbf{r_3},\mathbf{r_4}) \propto \left(\phi_{1s}^{\uparrow}(\mathbf{r_1})\phi_{2s}^{\uparrow}(\mathbf{r_2}) - \phi_{1s}^{\uparrow}(\mathbf{r_2})\phi_{2s}^{\uparrow}(\mathbf{r_1})\right)\left(\phi_{1s}^{\downarrow}(\mathbf{r_3})\phi_{2s}^{\downarrow}(\mathbf{r_4}) - \phi_{1s}^{\downarrow}(\mathbf{r_4})\phi_{2s}^{\downarrow}(\mathbf{r_3})\right). \tag{15}$$

Here you can see a simple code example which implements the above expression

```
for(int i = 0; i < numberParticles; i++) {
   arg[i] = 0.0;
   rSingleParticle = 0;
   for(int j = 0; j < dimension; j++) {
     rSingleParticle  += r(i,j)*r(i,j);
   }
   arg[i] = sqrt(rSingleParticle);
 }

// Slater determinant, no factors as they vanish in the Metropolis ratio
wf  = ( psi1s(arg[0])*psi2s(arg[1]) - psi1s(arg[1])*psi2s(arg[0]))*
      ( psi1s(arg[2])*psi2s(arg[3]) - psi1s(arg[3])*psi2s(arg[2]));
```

For beryllium we can easily implement the explicit evaluation of the Slater determinant. The above will serve as a useful check for your function which computes the Slater determinat. The derivatives of the single-particle wave functions can be computed analytically and you should consider using

the closed form expression for the local energy (not mandatory, you can use numerical derivatives as well although a closed form expressions speeds up your code).

For the correlation part

$$\Psi_C = \prod_{i<j} g(r_{ij}) = \exp\left\{\sum_{i<j} \frac{a r_{ij}}{1+\beta r_{ij}}\right\},$$

we need to take into account whether electrons have equal or opposite spins since we have to obey the electron-electron cusp condition as well. For Beryllium, as an example, you can fix electrons 1 and 2 to have spin up while electrons 3 and 4 have spin down. When the electrons have equal spins

$$a = 1/4,$$

while for opposite spins (as for the ground state of helium)

$$a = 1/2.$$

2a) Write a function which sets up the Slater determinant for beryllium and neon and can be generalized to handle larger systems as well. Compute the ground state energies of neon and beryllium as you did for the helium atom in 1d). The calculations should include parallelization, blocking, importance sampling and energy minimization.

2b) With the optimal parameters for the ground state wave function, compute again the onebody density and the charge density. Discuss your results and compare the results with those obtained with a pure hydrogenic wave functions. Run a Monte Carlo calculations without the Jastrow factor as well and compute the same quantities. How important are the correlations induced by the Jastrow factor?

Brief summary on how to write a report

Here follows a brief recipe and recommendation on how to write a report for each project.

- Give a short description of the nature of the problem and the eventual numerical methods you have used.
- Describe the algorithm you have used and/or developed. Here you may find it convenient to use pseudocoding. In many cases you can describe the algorithm in the program itself.
- Include the source code of your program. Comment your program properly.
- If possible, try to find analytic solutions, or known limits in order to test your program when developing the code.
- Include your results either in figure form or in a table. Remember to label your results. All tables and figures should have relevant captions and labels on the axes.
- Try to evaluate the reliabilty and numerical stability/precision of your results. If possible, include a qualitative and/or quantitative discussion of the numerical stability, eventual loss of precision etc.
- Try to give an interpretation of you results in your answers to the problems.
- Critique: if possible include your comments and reflections about the exercise, whether you felt you learnt something, ideas for improvements and other thoughts you've made when solving the exercise. We wish to keep this course at the interactive level and your comments can help us improve it. We do appreciate your comments.

- Try to establish a practice where you log your work at the computerlab. You may find such a logbook very handy at later stages in your work, especially when you don't properly remember what a previous test version of your program did. Here you could also record the time spent on solving the exercise, various algorithms you may have tested or other topics which you feel worthy of mentioning.

Format for electronic delivery of report and programs

The preferred format for the report is a PDF file and a link to your online Git repository, see the course web-page for more information. As programming language we prefer that you use C++.

Finally, we recommend that you work together. Optimal working groups consist of 2-3 students, but more people can collaborate. You can then hand in a common report.

Literature

1. B. L. Hammond, W. A. Lester and P. J. Reynolds, Monte Carlo methods in Ab Inition Quantum Chemistry, World Scientific, Singapore, 1994, chapters 2-5 and appendix B.
2. B.H. Bransden and C.J. Joachain, Physics of Atoms and molecules, Longman, 1986. Chapters 6, 7 and 9.
3. S.A. Alexander and R.L. Coldwell, Int. Journal of Quantum Chemistry, **63** (1997) 1001. This article is available at the webpage of the course as the file jastrow.pdf under the project 1 link.
4. C.J. Umrigar, K.G. Wilson and J.W. Wilkins, Phys. Rev. Lett. **60** (1988) 1719.

References

[1] H. Flyvbjerg and H. G. Petersen. "Error estimates on averages of correlated data". In: *J. Chem. Phys.* 91 (1989), pp. 461–466.

[2] A. Harju. *Stochastic gradient approximation method applied to Hubbard model*. Jan. 2001. arXiv:cond-mat/0101465v1 [cond-mat.str-el]. URL: http://arxiv.org/abs/cond-mat/0101465v1;http://arxiv.org/pdf/cond-mat/0101465v1.

[3] Morten Hjorth-jensen. *COMPUTATIONAL PHYSICS*. 2012.