Introduction to numerical projects

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.

- 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. You can also use DOC or postscript formats. As programming language we prefer that you choose between C/C++ and Fortran90/95. You could also use Java or Python as programming languages. Matlab/Maple/Mathematica/IDL are not allowed as programming languages for the handins, but you can use them to check your results where possible. The following prescription should be followed when preparing the report:

- Use Classfronter to hand in your projects, log in at blyant.uio.no and choose 'fellesrom fys3150 og fys4150'. Thereafter you will see an icon to the left with 'hand in' or 'innlevering'. Click on that icon and go to the given project. There you can load up the files within the deadline.

- Upload **only** the report file and the source code file(s) you have developed. The report file should include all of your discussions and a list of the codes you have developed. Do not include library files which are available at the course homepage, unless you have made specific changes to them.

- Comments from us on your projects, approval or not, corrections to be made etc can be found under your Classfronter domain and are only visible to you and the teachers of the course.

Finally, we do prefer that you work two and two together. Optimal working groups consist of 2-3 students. You can then hand in a common report.

Project 4, Variational Monte Carlo studies of light atoms, deadline 12 november 12am (midnight)

For this project you can build upon program programs/chapter11/program1.cpp (or the f90 version). You will need to parallelize exercises b-e and you should therefore use parts of project 2.

The aim of this project is to investigate the variational Monte Carlo method applied to light atoms such as helium and litium. Various trial wave functions are to be tested and compared. The aim is to find wave functions which reproduce the experimental energies as best as possible.

Ground state energy of helium

Helium consists of two electrons and a nucleus with charge $Z = 2$. We are going to use the Born-Oppenheimer approximation in modelling the system, assuming thereby that we can neglect nucleonic degrees of freedom. The nucleus, whose extension is on the order of $\sim 10^{-15}$ m (roughly six order of magnitude smaller than interatomic distances), is taken to be a point charge with mass much larger than that of the electrons. Electrostatic forces constitute then the essential contribution to the potential energy, given in this case by the attraction experienced by every electron from the nucleus and the repulsion between the two electrons.

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

$$-\frac{2}{r_1} - \frac{2}{r_2},\tag{1}$$

and if we add the electron-electron repulsion with $r_{12} = |\mathbf{r_1} - \mathbf{r_2}|$, the total potential energy $V(r_1, r_2)$ is

$$V(r_1, r_2) = -\frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}, \tag{2}$$

yielding the total Hamiltonian

$$\widehat{\mathbf{H}} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}, \tag{3}$$

and Schrödinger's 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 $2 \times E_0$, where $E_0 = 13.6$ eV. The experimental binding energy for helium in atomic units is a.u. is $E_{\mathrm{He}} = -2.9037$ a.u.. The basic wave functions we will employ in this exercise are

$$\psi_{T1}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}}) = \exp\left(-\alpha(r_1 + r_2)\right), \tag{5}$$

and

$$\psi_{T2}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}}) = \exp\left(-\alpha(r_1 + r_2)\right) \exp\left(\frac{r_{12}}{2(1 + \beta r_{12})}\right), \tag{6}$$

with β as a new variational parameter. Your task is to perform a Variational Monte Carlo calculation using the Metropolis algorithm to compute the integral

$$\langle H \rangle = \frac{\int d\mathbf{R}\psi_T^*(\mathbf{R})H(\mathbf{R})\psi_T(\mathbf{R})}{\int d\mathbf{R}\psi_T^*(\mathbf{R})\psi_T(\mathbf{R})}, \tag{7}$$

with the above trial wave functions.

a) Find analytic expressions for the local energy for the above two trial wave functions and explain shortly how these trial functions satisfy the cusp condition when $r_1 \to 0$ or $r_2 \to 0$ or $r_{12} \to 0$.

b) Compute

$$\langle H \rangle = \frac{\int d\mathbf{R}\Psi_T^*(\mathbf{R})H(\mathbf{R})\Psi_T(\mathbf{R})}{\int d\mathbf{R}\Psi_T^*(\mathbf{R})\Psi_T(\mathbf{R})}, \tag{8}$$

for the helium atom using a variational Monte Carlo method employing the Metropolis algorithm to sample over different states. You will have to calculate

$$\langle H \rangle = \int P(\mathbf{R})E_L(\mathbf{R})d\mathbf{R}, \tag{9}$$

where E_L is the local energy. Here all calculations are performed with the trial wave function $\psi_{T1}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}})$ only. Study the stability of your calculation as function

of the number of Monte Carlo samples and compare these results with the exact variational result

$$\langle H \rangle = \alpha^2 - 2\alpha \left(Z - \frac{5}{16} \right). \tag{10}$$

Your Monte Carlo moves are determined by

$$\mathbf{R}' = \mathbf{R} + \delta \times r, \tag{11}$$

where r is a random number from the 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 for each variational parameter α, resulting in roughly 50% accepted moves.

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. You should parallelize your code.

c) Use thereafter the optimal value for α as a starting point for computing the ground state energy of the helium atom using the trial wave functions $\psi_{T2}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}})$. In this case you need to vary both α and β. The strategy here is to use α from the previous exercise, [1b)] and then vary β in order to find the lowest energy as function of β. Thereafter you change α in order to see whether you find an even lower energy and so forth.

Which one of the wave functions $\psi_{T1}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}})$ and $\psi_{T2}(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}})$ would you prefer? Give arguments for your choices.

Excited states of the helium atom and the ground state of the litium atom

Now we will only use trial wave functions of the form

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}) = Det\left(\phi_1(\mathbf{r_1}), \phi_2(\mathbf{r_2})\right) \prod_{i<j}^{2} \exp\left(\frac{r_{ij}}{2(1 + \beta r_{ij})}\right), \tag{12}$$

for helium and

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}) = Det\left(\phi_1(\mathbf{r_1}), \phi_2(\mathbf{r_2}), \phi_3(\mathbf{r_3})\right) \prod_{i<j}^{3} \exp\left(\frac{r_{ij}}{2(1 + \beta r_{ij})}\right), \tag{13}$$

for litium where Det is a determinant and the single-particle wave functions are the hydrogen wave functions for the $1s$ and $2s$ orbitals. Their form within the variational ansatz is given by

$$\phi_{1s}(\mathbf{r_i}) = e^{-\alpha r_i}, \tag{14}$$

and

$$\phi_{2s}(\mathbf{r_i}) = (2 - \alpha r_i) e^{-\alpha r_i/2}. \tag{15}$$

The variational parameters are still α and β only. Observe that $r_i = \sqrt{r_{i_x}^2 + r_{i_y}^2 + r_{i_z}^2}$. Here you will need to employ the best optimization result from the previous exercise, that is the results from exercise [c)]. The experimental binding energy for litium is $E_{\mathrm{Li}} = -7.4781$ a.u. while the two first excited states of helium have energies of -2.1752 a.u. and -2.1460.

d) The first two excited states of the helium atom can be thought of, within a single-particle picture, as consisting of an electron in the $1s$ orbital and one in the $2s$ orbital. There are two possibilities for the total trial wave function

$$\psi_{Tas}(\mathbf{r_1}, \mathbf{r_2}) = (\phi_{1s}(\mathbf{r_1})\phi_{2s}(\mathbf{r_2}) - \phi_{1s}(\mathbf{r_2})\phi_{2s}(\mathbf{r_1})) \prod_{i<j}^{2} \exp\left(\frac{r_{ij}}{2(1 + \beta r_{ij})}\right), \qquad (16)$$

where the subscript as stands for antisymmetric and

$$\psi_{Ts}(\mathbf{r_1}, \mathbf{r_2}) = (\phi_{1s}(\mathbf{r_1})\phi_{2s}(\mathbf{r_2}) + \phi_{1s}(\mathbf{r_2})\phi_{2s}(\mathbf{r_1})) \prod_{i<j}^{2} \exp\left(\frac{r_{ij}}{2(1 + \beta r_{ij})}\right), \qquad (17)$$

where s means symmetric. You can think of $\mathbf{r_1}$ and $\mathbf{r_2}$ as the positions of electrons 1 and 2, respectively. Which wave function do you expect to give the lowest energy (most bound)? Perform a variational Monte Carlo calculation and see if your arguments are correct. Compare your results with the experimental values.

e) For litium we assume that a possible trial wave function for the ground state is given by

$$\begin{aligned} \psi_T(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}) &= (\phi_{1s}(\mathbf{r_1})\phi_{2s}(\mathbf{r_2}) - \phi_{1s}(\mathbf{r_2})\phi_{2s}(\mathbf{r_1})) \phi_{1s}(\mathbf{r_3}) \\ &\times \prod_{i<j}^{3} \exp\left(\frac{r_{ij}}{2(1 + \beta r_{ij})}\right). \end{aligned} \qquad (18)$$

Compute the ground state energy and compare with experiment. Comment your results.