

Project 3, Variational Monte Carlo studies of helium and beryllium

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 as well as diatomic molecules. for important molecules

The final project builds on project 1 and 2 and adds the optimization procedure for the variational parameter β using for example Newton's methods, the steepest descent method or the conjugate gradient method. Furthermore, the single-particle wave functions used in the computation of the Slater determinant will be replaced by Gaussian type orbitals (GTO) using already optimized parameters.

Thus, in addition to these ingredients, the final project contains all the elements you have included in projects 1 and 2. This means that you can include all results you have obtained in projects 1 and 2 in the wrap-up of the final report. It is the final report which counts for the final mark.

You will thus see that this report contains much of the same text as included in projects 1 and 2.

The deadline for project 3 is May 31, at noon. See below for delivery format.

Part 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

$$-\frac{2}{r_1} - \frac{2}{r_2}, \quad (1)$$

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

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

yielding the total Hamiltonian

$$\hat{\mathbf{H}} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}, \quad (3)$$

and Schrödinger's equation reads

$$\hat{\mathbf{H}}\psi = E\psi. \quad (4)$$

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 a.u. is $E_{\text{He}} = -2.9037$ a.u..

- 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

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

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

$$\langle E \rangle = \frac{\int d\mathbf{r}_1 d\mathbf{r}_2 \psi_T^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) \hat{H}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) \psi_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12})}{\int d\mathbf{r}_1 d\mathbf{r}_2 \psi_T^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) \psi_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12})}. \quad (6)$$

You should parallelize your program. Find the energy minimum and compute also the mean distance r_{12} between the two electrons for the optimal set of the variational parameters. A code for doing a VMC calculation for the helium atom can be found on the webpage of the course, see under programs.

Your Monte Carlo moves are determined by

$$\mathbf{R}' = \mathbf{R} + \delta \times r, \quad (7)$$

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 the variational parameters α and β , 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.

- 1b) Find closed form expressions for the local energy (see below) for the above trial wave function and explain shortly how this trial function satisfies the cusp condition when $r_1 \rightarrow 0$ or $r_2 \rightarrow 0$ or $r_{12} \rightarrow 0$. Show that closed-form expression for the trial wave function is

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

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 now 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 as a technique to make the 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. 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) by varying the energy using the conjugate gradient method or similar methods to obtain the best possible parameter β . Replace now the hydrogen-like single-particle wave functions with the 3-21G basis defined at the EMSL website <https://bse.pnl.gov/bse/portal>.

Part 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 modules or 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

$$\psi_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \text{Det}(\phi_1(\mathbf{r}_1), \phi_2(\mathbf{r}_2), \phi_3(\mathbf{r}_3), \phi_4(\mathbf{r}_4)) \prod_{i < j}^4 \exp\left(\frac{r_{ij}}{2(1 + \beta r_{ij})}\right), \quad (8)$$

where Det is a Slater determinant 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

$$\phi_{1s}(\mathbf{r}_i) = e^{-\alpha r_i}, \quad (9)$$

and

$$\phi_{2s}(\mathbf{r}_i) = (1 - \alpha r_i/2) e^{-\alpha r_i/2}. \quad (10)$$

For neon, the trial wave function can take the form

$$\psi_T(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{10}) = \text{Det}(\phi_1(\mathbf{r}_1), \phi_2(\mathbf{r}_2), \dots, \phi_{10}(\mathbf{r}_{10})) \prod_{i < j}^{10} \exp\left(\frac{r_{ij}}{2(1 + \beta r_{ij})}\right), \quad (11)$$

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

$$\phi_{2p}(\mathbf{r}_i) = \alpha \mathbf{r}_i e^{-\alpha r_i/2}. \quad (12)$$

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

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

$$\psi_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \propto (\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2) - \phi_{1s}(\mathbf{r}_2)\phi_{2s}(\mathbf{r}_1))(\phi_{1s}(\mathbf{r}_3)\phi_{2s}(\mathbf{r}_4) - \phi_{1s}(\mathbf{r}_4)\phi_{2s}(\mathbf{r}_3)). \quad (13)$$

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

```
for (i = 0; i < number_particles; i++) {
    argument[i] = 0.0;
    r_single_particle = 0;
    for (j = 0; j < dimension; j++) {
        r_single_particle += r[i][j]*r[i][j];
    }
    argument[i] = sqrt(r_single_particle);
}
// Slater determinant, no factors as they vanish in Metropolis ratio
wf = (psils(argument[0])*psi2s(argument[1])
      -psils(argument[1])*psi2s(argument[0]))*
      (psils(argument[2])*psi2s(argument[3])
      -psils(argument[3])*psi2s(argument[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 determinant. 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

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

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 using the conjugate gradient approach or related approaches like the steepest descent method or Newton's method. You should also replace the hydrogen-like single-particle wave functions with the 3-21G basis set defined at the EMSL website <https://bse.pnl.gov/bse/portal>. If you get time, you should also try the 6-311G basis set from the same website.
- 2b) With the optimal parameters for the ground state wave function, compute again the onebody 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?

Part 3 Variational Monte Carlo studies of molecules

The H_2 molecule consists of two protons and two electrons with a ground state energy $E = -1.17460$ a.u. and equilibrium distance between the two hydrogen atoms of $r_0 = 1.40$ Bohr radii. We define our systems using the following variables. Origo is chosen to be halfway between the two protons. The distance from proton 1 is defined as $-\mathbf{R}/2$ whereas proton 2 has a distance $\mathbf{R}/2$. Calculations are performed for fixed distances \mathbf{R} between the two protons.

Electron 1 has a distance r_1 from the chose origo, while electron 2 has a distance r_2 . The kinetic energy operator becomes then

$$-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2}. \quad (14)$$

The distance between the two electrons is $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The repulsion between the two electrons results in a potential energy term given by

$$+\frac{1}{r_{12}}. \quad (15)$$

In a similar way we obtain a repulsive contribution from the interaction between the two protons given by

$$+\frac{1}{|\mathbf{R}|}, \quad (16)$$

where \mathbf{R} is the distance between the two protons. To obtain the final potential energy we need to include the attraction the electrons feel from the protons. To model this, we need to define the distance between the electrons and the two protons. If we model this along a chosen z -akse with electron 1 placed at a distance \mathbf{r}_1 from a chose origo, one proton at $-\mathbf{R}/2$ and the other at $\mathbf{R}/2$, the distance from proton 1 to electron 1 becomes

$$\mathbf{r}_{1p1} = \mathbf{r}_1 + \mathbf{R}/2, \quad (17)$$

and

$$\mathbf{r}_{1p2} = \mathbf{r}_1 - \mathbf{R}/2, \quad (18)$$

from proton 2. Similarly, for electron 2 we obtain

$$\mathbf{r}_{2p1} = \mathbf{r}_2 + \mathbf{R}/2, \quad (19)$$

and

$$\mathbf{r}_{2p2} = \mathbf{r}_2 - \mathbf{R}/2. \quad (20)$$

These four distances define the attractive contributions to the potential energy

$$-\frac{1}{r_{1p1}} - \frac{1}{r_{1p2}} - \frac{1}{r_{2p1}} - \frac{1}{r_{2p2}}. \quad (21)$$

We can then write the total Hamiltonian as

$$\hat{\mathbf{H}} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{1}{r_{1p1}} - \frac{1}{r_{1p2}} - \frac{1}{r_{2p1}} - \frac{1}{r_{2p2}} + \frac{1}{r_{12}} + \frac{1}{|\mathbf{R}|}, \quad (22)$$

and if we choose $\mathbf{R} = 0$ we obtain the helium atom.

In this part we will use a trial wave function of the form

$$\psi_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}) = \psi(\mathbf{r}_1, \mathbf{R})\psi(\mathbf{r}_2, \mathbf{R}) \exp\left(\frac{r_{12}}{2(1 + \beta r_{12})}\right), \quad (23)$$

with the following trial wave function

$$\psi(\mathbf{r}_1, \mathbf{R}) = (\exp(-\alpha r_{1p1}) + \exp(-\alpha r_{1p2})), \quad (24)$$

for electron 1 and

$$\psi(\mathbf{r}_2, \mathbf{R}) = (\exp(-\alpha r_{2p1}) + \exp(-\alpha r_{2p2})). \quad (25)$$

The variational parameters are α and β .

One can show that in the limit where all distances approach zero that

$$\alpha = 1 + \exp(-R/\alpha), \quad (26)$$

resulting in β as the only variational parameter.

1. Set up an algorithm and write a program which computes the expectation value of $\langle \hat{\mathbf{H}} \rangle$ using the best variational Monte Carlo method you developed for parts 1 and 2. For each inter-proton distance R you must find the parameter β which minimizes the energy. Plot the corresponding energy as function of the distance R between the protons.
2. Use thereafter the optimal parameter sets to compute the average distance $\langle r_{12} \rangle$ between the electrons where the energy as function of R exhibits its minimum. Comment your results.
3. We modify now the approximation for the wave functions of electrons 1 and 2 by subtracting the two terms instead of adding up, viz

$$\psi(\mathbf{r}_1, \mathbf{R}) = (\exp(-\alpha r_{1p1}) - \exp(-\alpha r_{1p2})), \quad (27)$$

for electron 1

$$\psi(\mathbf{r}_2, \mathbf{R}) = (\exp(-\alpha r_{2p1}) - \exp(-\alpha r_{2p2})), \quad (28)$$

for electron 2. Mathematically, this approach is equally viable as the previous one. Repeat your calculations and see if you can obtain an energy minimum as function of R . Comment your results.

4. Using your Slater determinants and Jastrow factors from part a, our final step consists in estimating the binding energy of the H_2 and Be_2 molecules using the optimal Jastrow factor and the 3-21G basis set. The last two references in the reference list may be useful.

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 reliability 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 your 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. You can also use DOC or postscript formats. As programming language we prefer that you choose between C++, Fortran2008 or Python. 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

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4. C.J. Umrigar, K.G. Wilson and J.W. Wilkins, Phys. Rev. Lett. **60** (1988) 1719.
5. Moskowitz and Kalos, Int. Journal of Quantum Chemistry **XX**, 1107 (1981). Results for He and H₂.

6. Filippi, Singh and Umrigar, J. Chemical Physics **105**, 123 (1996). Useful results on Be₂ to which you can benchmark your results against.