

VARIATIONAL MONTE CARLO SIMULATIONS OF ATOMIC SYSTEMS

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**Part I**

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FYS4411  
COMPUTATIONAL PHYSICS II

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# 1 Introduction

This is part 1 of a 3 part project to evaluate the ground state properties of some single atoms and diatomic molecules, using variational Monte Carlo simulations.

A compulsory part of doing this is using expandable programs that can handle systems of increasing particles and complexity. This poses many challenges; implementational, statistical, numerical and mathematical. The atoms studied here are Helium and Beryllium, and the ground state energies and one-body densities are the properties we are interested in. The computational methods to do this is a main focus of part 1.

We are interested in the ground state energies, because the results are more easily verifiable. One aim of the project is to see how effective our numerical methods are in computing these quantities, and compare the methods to each other, by applying statistical tools.

As stated, there are several challenges. Here basic mathematical, computational, statistical models are dealt with, and applied to the second most simple system, Helium.

All results displayed in this article are gathered from our variational Monte Carlo program.

Github:

<https://github.com/lastis/FYS4411>

# 2 Methods

## 2.1 Definitions

The Helium atom consists of two electrons orbiting a nucleus, where the distance between electron 1 and the nucleus, and electron 2 and the nucleus are labeled as  $r_1 = \sqrt{x_1^2 + y_1^2 + z_1^2}$  and  $r_2 = \sqrt{x_2^2 + y_2^2 + z_2^2}$ .

The total potential energy of the system is modelled as

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

where the interaction between each electron and the nucleus is given by the two first terms. The mutual electron-electron repulsion is given by the last. The distance between the electrons is  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ .

The Hamiltonian of the system is thusly,

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

The radii  $\{r_1, r_2, r_{12}\}$  are scaled, and are dimensionless.

The Laplace operator of a function  $f$  in three dimensions,  $\nabla^2 f$ , can be represented as

$$\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}\right)f + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta}\right)f + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} f$$

in spherical coordinates, and as

$$\left(\frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}\right)f$$

in cartesian coordinates.

## 2.2 The Variational Principle

The Variation Principle states that if we have a Hamiltonian  $\hat{\mathbf{H}}$  and a trial wavefunction  $\psi_T$ , an upper bound for the ground state energy is given by equation (1).

The principle is that the given integral is a value of the energy of a given wave function and when the wave function is variated, the according values of the energy is the output. If we then record the lowest energy, the ground state, we also have the wave function of the ground state.

$$E_0 \leq \langle H \rangle = \frac{\int d\mathbf{r}_1 d\mathbf{r}_2 \psi_{Ti}^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) \hat{\mathbf{H}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) \psi_{Ti}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12})}{\int d\mathbf{r}_1 d\mathbf{r}_2 \psi_{Ti}^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) \psi_{Ti}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12})} \quad (1)$$

## 2.3 Variational Monte Carlo (VMC)

The integrals to be solved in the variational method, does not scale well with traditional integral methods when increasing the number of particles and dimensions and using more complex wave functions.

Therefore, we introduce the brute-force Monte Carlo method to solve the integrals.

### 2.3.1 VMC Algorithm

- Initialization.
  - Set a fixed number of MC steps.
  - Choose initial position  $\mathbf{R}$  and variational parameters  $\alpha$ .
  - Calculate  $|\psi_T(\mathbf{R})|^2$
- Set energy and variance and start the MC calculation.
  - Find the trial position  $\mathbf{R}' = \mathbf{R} + \delta \times r$ , where  $r \in [0, 1]$  is randomly selected.
  - Use the Metropolis algorithm to determine if the move  $w = \frac{P(\mathbf{R}')}{P(\mathbf{R})}$  is accepted or rejected.
  - Given that the move is accepted, set  $\mathbf{R} = \mathbf{R}'$ .
  - Update averages.
- Compute final averages.

## 2.4 The Metropolis Algorithm

The Metropolis algorithm samples a normalized probability distribution by a stochastic process. In other words, it is a method for simulating random walks, which we can use to do brute-force Monte Carlo computations.

Define  $P_i^{(n)}$  as the probability for finding the system in state  $i$  at some step  $n$ .

- Sample a possible new state  $j$  with a probability  $T_{i \rightarrow j}$ .
- With probability  $A_{i \rightarrow j}$ , accept  $j$  as a new state. Set it as the new sample. The move is rejected with probability  $1 - A_{i \rightarrow j}$ . set  $i$  as the sample again.

## 2.5 Importance Sampling

A random walker is the most efficient way to sample where the wave function is large. To increase this we can implement importance sampling where the walk in space is effected by the trial wave function.

The results are based on the Fokker-Planck equation and the Langevin equation. This makes the step look similar to a diffusion process where the new position is given by,

$$y = x + DF(x)\delta t + \xi\sqrt{\Delta t}.$$

$\xi$  is a gaussian random variable and  $\Delta t$  is a chosen timestep. For atomic units  $D$  is  $1/2$  and  $\Delta t$  is a variable for the simulation. In our plots  $\Delta t = 0.01$ .

An important part of this result is that the walker is effected by  $F(x)$  which contains the trial wavefunction. This has been named the quantum force.

$$\mathbf{F} = 2\frac{1}{\Psi_T}\nabla\Psi_T.$$

This also has the result of changing the random number check in the Metropolis algorithm from :  $q(y, x) = |\Psi_T(y)|^2/|\Psi_T(x)|^2$  to:

$$q(y, x) = \frac{G(x, y, \Delta t)|\Psi_T(y)|^2}{G(y, x, \Delta t)|\Psi_T(x)|^2}.$$

Where  $G$  is the Green function given by,

$$G(y, x, \Delta t) = \frac{1}{(4\pi D\Delta t)^{3N/2}} \cdot \exp\left(-(y - x - D\Delta t F(x))^2/4D\Delta t\right).$$

## 2.6 Statistical Analysis

The MC calculation are a set of computational *experiments*, with statistical errors. In the experiments we are interested in the mean value of the ground energies and the density distribution. The individual samples are not as interesting to us and we would rather like to look in the variance of the mean value.

The variance of the mean value is closely connected with the correlation in the individual samples. This can

be shown mathematically, but the result is this:

$$\sigma^2(m) = \frac{1}{n^2} \sum_{i,j=1}^n \text{Cov}(x_i, x_j)$$

Both our random walker and walking with importance sampling gives correlated samples. In our case, blocking is the technique of finding out how many steps the walker has to go to be as uncorrelated as possible with its first step. If we then plot the variance in mean as a function of block size we will see that the variance reaches a plateau.

This plateau means that increasing the sample length will no longer change the variance in the mean significantly. This makes us able to more easily calculate variance in the mean because we know how short block sizes we can use. This is used to make the standard deviation interval around our densities.

### 2.6.1 Blocking Implementation

- Compute MC calculation, store samples in array.
- Loop over a set of block sizes  $n_b$ .
- For each  $n_b$ , calculate the mean of the block and store these values in a new array.
- Take the mean and variance of this array.
- Store results.

## 2.7 The Trial Wavefunctions for Helium

To conclude if the computational methods are implemented correctly, we should check that the results are reasonable. We do this by finding a mathematical approximation of the closed form expression.

Given the trial wavefunction  $\psi_T(\mathbf{R}, \alpha)$ , we define a new quantity

$$E_L = \frac{1}{\psi_T} \hat{\mathbf{H}} \psi_T$$

where  $\alpha$  is a set of variational parameters.  $E_{L1}$  is called the local energy

### 2.7.1 The first trial wavefunction

We first model the variational solution with a trial function of one variation parameter  $\alpha$ . It has the form

$$\psi_{T1}(\mathbf{r}_1, \mathbf{r}_2) = \exp(-\alpha(r_1 + r_2))$$

The only part of the operator  $\hat{\mathbf{H}}$  that affects the wavefunction are the Laplace operators.

Since  $\psi_{T1}$  is only spatially dependent on  $r_1$  and  $r_2$ , the Laplaces of  $\psi_{T1}$  reduces to

$$\nabla_i^2 \psi_{T1} = \left( \frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial}{\partial r_i} \right) \psi_{T1} = \left( \alpha^2 - \alpha \frac{2}{r_i} \right) \psi_{T1}$$

for  $i = 1, 2$ , since

$$\begin{aligned} \frac{\partial}{\partial r_i} e^{-\alpha(r_1+r_2)} &= -\alpha e^{-\alpha(r_1+r_2)} \\ \frac{\partial^2}{\partial r_i^2} e^{-\alpha(r_1+r_2)} &= \alpha^2 e^{-\alpha(r_1+r_2)} \end{aligned}$$

This gives us the following trial energy

$$\begin{aligned} E_{L1} &= \frac{1}{\psi_{T1}} \left( -\alpha^2 + \alpha \left( \frac{1}{r_1} + \frac{1}{r_2} \right) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right) \psi_{T1} \\ &= (\alpha - 2) \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_{12}} - \alpha^2 \end{aligned}$$

The 2 in the  $\alpha - 2$  term is the number of protons,  $Z$ .

### 2.7.2 The second trial wavefunction

To approximate the closed-form solution even better, we assume another trial wavefunction based on  $\psi_{T1}$ , namely

$$\psi_{T2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) = \exp(-\alpha(r_1 + r_2)) \exp\left(\frac{r_{12}}{2(1 + \beta r_{12})}\right)$$

The second part is dependent on the distance between the electrons, and is called the correlation part, which accounts for the effect between the electrons.

One can then in the same way as for  $\psi_{T1}$  calculate the local energy. The correlations part will give us some trouble when we try to calculate the Laplacian. This is due to the distance between  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , since this quantity is dependent on the angles  $\varphi$  and  $\theta$ . It has the form

$$\begin{aligned} E_{L2} &= E_{L1} + \frac{1}{2(1 + \beta r_{12})^2} \left( \frac{\alpha(r_1 + r_2)}{r_{12}} \left( 1 - \frac{\mathbf{r}_1^T \mathbf{r}_2}{r_1 r_2} \right) \right. \\ &\quad \left. - \frac{1}{2(1 + \beta r_{12})^2} - \frac{2}{r_{12}} + \frac{2\beta}{1 + \beta r_{12}} \right) \end{aligned}$$

## 2.8 The Trial Wavefunction for Beryllium

We can use a trial wavefunction on the same form as for Hydrogen and Helium

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

where we approximate the Slater determinant *Det* as

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

where the hydrogenic wavefunctions for the two spin orbitals are given by

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

and

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

## 2.9 Onebody Density and Charge Density

The one-body density is computed from the form

$$\rho(\mathbf{R}) = |\psi(\mathbf{R})|^2$$

This is implemented as NOTE: ... in our program.

## 2.10 Implementation

The methods described above are implemented in an object oriented C++ program which is simple to use, and does not have any dependencies.

Most of the code is contained in the class VMC-Solver.cpp and VMC-Solver.h. These were created to contain the full system and parameters for a single run.

To start a simulation one must instantiate the solver and initialize the system, either by file and/or manually. After this the integration can be run and all data will be contained in the solver object. The last step is to collect data from the solver.

All plot data are generated by individual programs using the mentioned solver. Plots are generated using python.

## 3 Results

### 3.1 Helium: Estimating $\alpha$ and $\beta$

These parameters decide the minimal ground energy for the system, and both should be adjusted simultaneously to reach the most optimal value of the energy. First we sample the parameterspace of the first trial wave function. This function had a minimum of 1.66. This was the first value of  $\alpha$  that was used in sampling the parameterspace with beta in the second trial wavefunction. This can be seen in Figure 2 with mean error. Using the computed  $\beta$ -value we again sampled the energy as a function of  $\alpha$ , which we concluded was the same as before.  $\alpha$  is plotted in Figure 1

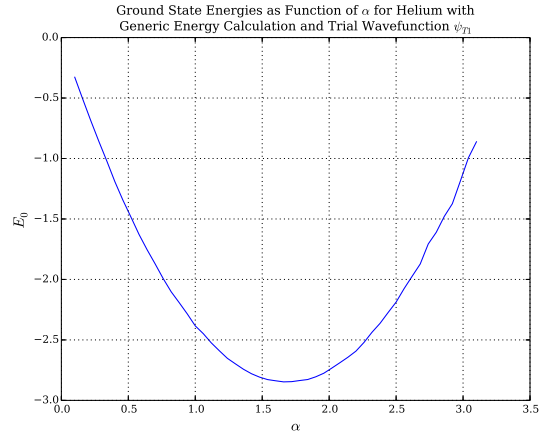


Figure 1:

### 3.2 Helium: $\psi_{T1}$ and $\psi_{T2}$

Firstly we want to compare the first and second trial wavefunctions for Helium. The difference between these two are that there are no correlation term in the first wavefunction. This makes computations much faster, but we would expect that our results are farther away from the experimental value of the ground state. This is done using a numerical approximation of the local energy of the particles. The mean value of  $\psi_{T1} = -2.84264$  and  $\psi_{T2} = -2.87105$ . The experimental value of the ground

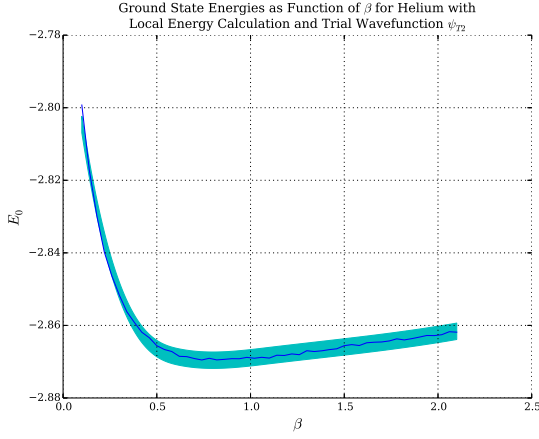


Figure 2:

state is about  $-2.903$ , thus we conclude that the second wavefunction is a better approximation.

### 3.3 Helium: Closed Form Local Energy

The local energy has a closed form solution for Helium, this has been implemented in Figure 3. The closed-form solution should give use a lower standard deviation than the numerical approximation of the local energy because it is a closer approximation.

### 3.4 Helium: Importance Sampling

Now we would like to see how the program does with importance sampling instead of static steplength. Importance sampling should also lower the standard deviation because it makes the walker sample the wavefunction in a better way. The downside of importance sampling is that it takes about twice as long time as the random walker. This is also shown in Figure 3.

### 3.5 Helium: Evaluating Ground State and Density

With our optimal parameters, we calculated the ground state and the density function of Helium, Figure 4. The standard deviation has been added as a error bar along the curve.

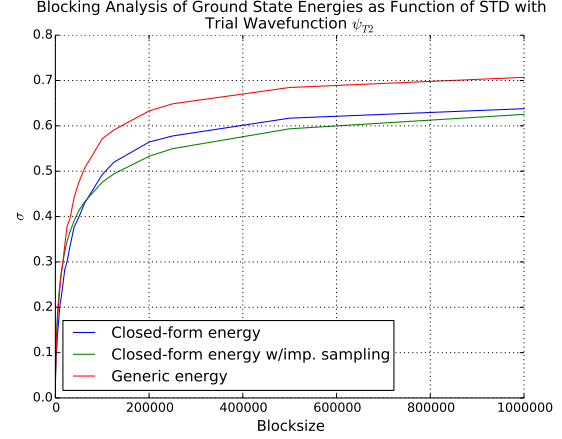


Figure 3:

Here we can see how the correlation factor effects the density. When the Jastrow factor is added the electrons are repelled a bit farther away from the nucleus and the mean radius between the electrons increases slightly. The mean distance increased from 1.316 to 1.414.

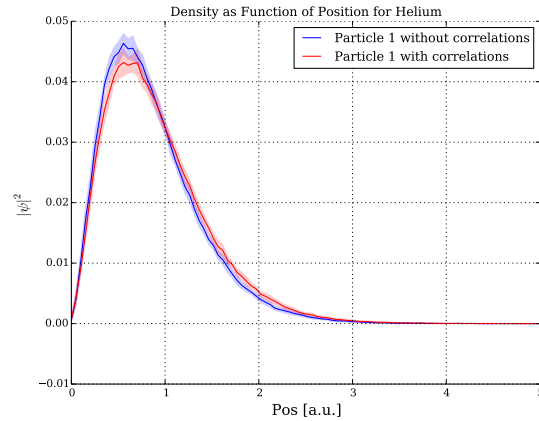


Figure 4:

### 3.6 Beryllium: Estimating $\alpha$ and $\beta$

In Figure 5 a wide range of the parameter space has been sampled. As can be seen this area have an energy mean

that are quite similar. Because of this the parameters have been chosen to be  $\alpha = 3.75$  and  $\beta = 0.8$ .

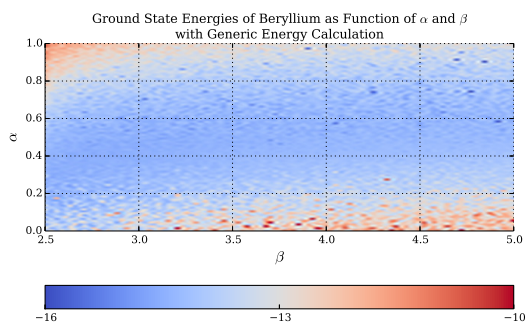


Figure 5:

### 3.7 Beryllium: Comparing $\psi_{T1}$ and $\psi_{T2}$

In Figure 6 we see the difference the Jastrow factor makes for Beryllium. We also notice the two clear peaks in the distribution. These are the electron orbitals for 1s and 2s. Again this correlation makes the electrons repel each other and pushes the distributions farther apart. The mean distance increased from 1.669 to 1.804. The mean energy were  $-19.9325$  and  $-14.340$  respectively. A value around  $-14$  is the experimental value of Beryllium and the value without the Jastrow factor is supposed to be  $-20$ .

## 4 Discussion

### 4.1 Parameter Space

After estimating the parameters  $\alpha$  and  $\beta$  for Helium, we didn't adjust them in the late comparative trials. The reason for this was that small changes in the parameters did not effect our results considerably because the mean energies as well as the variance of the mean energies are similar. Our results was always close to  $-2.89$ . The

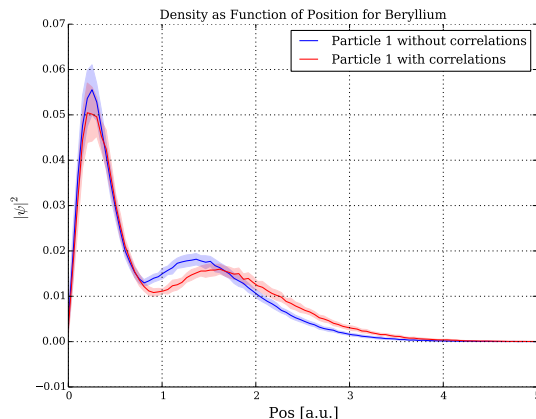


Figure 6:

same conclusion was made for Beryllium, which showed even harder to locate exact values of the paramters.

The standard deviation of the mean was not considered when estimating the values of  $\alpha$  and  $\beta$ . Performing blocking with our program would require full sampling of every step which stores about 10 mb for every value of  $\alpha$  and  $\beta$ .

### 4.2 Testing of the Solver

To varify that the solver works as intended, several unit tests using UnitTest++ were created. The most important tests are those that estimate the one-body hamiltonian. this has an analytical solution for both Helium and Beryllium, which is  $-4$  and  $-20$  respectively.

The solutions for Hydrogen are also easy to calculate, and was estimated to be  $-0.5$  correctly.

## 5 References

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