

# Computational Physics II

## FYS-4411

Gullik Vetvik Killie  
Håkon S.B. Mørk  
Jose Emeilio Ruiz Navarro

March 2, 2015

### Abstract

Fill in abstract

## 1 Introduction

## 2 Methods

### 2.1 Monte Carlo of the Helium Atom

In a quantum mechanical system the energy is given by the expectation value of the Hamiltonian, let  $\Psi_T$  be a proposal for a wavefunction that can describe the system.

$$E[\hat{H}] = \langle \Psi_T | \hat{H} | \Psi_T \rangle = \frac{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) \hat{H} \Psi_T(\mathbf{R})}{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R})} \quad (1)$$

Let us introduce a local energy:

$$E_L(\hat{H}) = \frac{1}{\Psi_T(\mathbf{R})} \hat{H} \Psi_T(\mathbf{R}) \quad (2)$$

$$E[\hat{H}] = \frac{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R}) E_L(\mathbf{R})}{\int d\mathbf{R} \Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R})} \quad (3)$$

Since the denominator is a scalar constant after integrating it we can put it inside the integral in the numerator

$$E[\hat{H}] = \int d\mathbf{R} \frac{\Psi_T^*(\mathbf{R}) \Psi_T(\mathbf{R})}{\int d\mathbf{R}' \Psi_T^*(\mathbf{R}') \Psi_T(\mathbf{R}')} E_L(\mathbf{R}) \quad (4)$$

$$E[\hat{H}] = \int d\mathbf{R} P(\mathbf{R}) E_L(\mathbf{R}) \quad (5)$$

This probability function with  $P(\mathbf{R})$  as the pdf, and we can use monte carlo integration to solve the integral.

1. Initialise system. Give particles a random position and decide how many Monte Carlo Cycles to run.
2. Start Monte Carlo Calculations
  - (a) Propose a move of the particles according to an algorithm, for example  $\mathbf{R}_{\text{new}} = \mathbf{R}_{\text{old}} + \delta * r$ , where  $r$  is a random number in  $[0, 1]$
  - (b) Accept or reject move according to  $P(\mathbf{R}_{\text{new}})/P(\mathbf{R}_{\text{old}}) \geq r$ , where  $r$  is a new number. Update position values if accepted.
  - (c) Calculate energy for this cycle.

## 2.2 Helium atom

The dimensionless hamiltonian for the Helium atom consists of a kinetic energy part and a potential energy part and is given by

$$\hat{H} = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \quad (6)$$

For the energy to be finite the wavefunction must be constructed so the local energy is finite at all points.

$$E_L(r_i, r_{12}) = \frac{1}{\Psi_T} \hat{H} \Psi_T \quad (7)$$

If we consider the case where  $r_i \rightarrow 0$  then the  $-\frac{\nabla_i^2}{2} - \frac{Z}{r_i}$  terms of the hamiltonian could cause the energy to blow up, so we need to make sure that those terms stay finite in the limit.

$$\lim_{r_i \rightarrow 0} E_L(r_1, r_{12}) = \frac{1}{R_i(r_i)} \left( -\frac{1}{2} \frac{\partial^2}{\partial x_k^2} - \frac{Z}{r_i} \right) R_i(r_i) + G(r_i, r_{ij}) \quad (8)$$

$$\lim_{r_i \rightarrow 0} E_L(r_1, r_{12}) = \frac{1}{R_i(r_i)} \left( -\frac{1}{2} \frac{\partial^2}{\partial r_k^2} - \frac{1}{r_i} \frac{\partial}{\partial r_i} - \frac{Z}{r_i} \right) R_i(r_i) + G(r_i, r_{ij}) \quad (9)$$

Derivatives of the wavefunction does not diverge since the wavefunction is finite at all points. so the following terms dominate when the particles approach the center.

$$\lim_{r_i \rightarrow 0} E_L(r_1, r_{12}) = \frac{1}{R_i(r_i)} \left( -\frac{1}{r_i} \frac{\partial}{\partial r_i} - \frac{Z}{r_i} \right) R_i(r_i) \quad (10)$$

$$\frac{1}{R_i(r_i)} \frac{\partial}{\partial r_i} R_i(r_i) = -Z \quad \text{With solution} \quad R_i(r_i) = Ae^{-Z} \quad (11)$$

A similar calculation applies for  $r_{12} \rightarrow 0$  and a trialfunction of the form

$$\Psi_T(r_1, r_2, r_{12}) = e^{-\alpha(r_1+r_2)} e^{\beta r_{12}}$$

should fulfill the condition that the wavefunction is finite everywhere.

## 2.3 Derivation of local energies

The local energy of is dependant on the Hamiltonian and the wavefunction describing the system, the Hamiltonian incorporates both a kinetic energy part given by  $\frac{\nabla^2}{2}$  for each particle and a potential energy part given by  $\frac{Z}{r_i}$  and  $\frac{1}{r_{ij}}$ , where  $Z$  is the charge of the center,  $r_i$  is the distance for electron  $i$  to the atom center and  $r_{ij}$  is the distance between electron  $l$  and  $m$ . Then the local energy is given by the following:

$$E_L = \sum_{i,i < j} \frac{1}{\Psi_T(\mathbf{r}_i, \mathbf{r}_{ij})} \hat{H} \Psi_T(\mathbf{r}_i, \mathbf{r}_{ij}) \quad (12)$$

$$= \sum_{i,i < j} \frac{1}{\Psi_T(\mathbf{r}_i, \mathbf{r}_{ij})} \left( -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \right) \Psi_T(\mathbf{r}_i, \mathbf{r}_{ij}) \quad (13)$$

$$= \sum_{i,i < j} -\frac{1}{2\Psi_T} (\nabla_i^2 \Psi_T) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \quad (14)$$

Let us change derivation variables:

$$-\frac{1}{2\Psi_T} (\nabla_i^2 \Psi_T) = \sum_{m=1}^3 -\frac{1}{2\Psi_T} \left( \frac{\partial^2 \Psi_T}{\partial x_m^2} \right)_i \quad (15)$$

$$= \sum_{m=1}^3 -\frac{1}{2\Psi_T} \left( \frac{\partial}{\partial x_m} \left( \frac{\partial \Psi_T}{\partial r_i} \frac{\partial r_i}{\partial x_m} \right) \right)_i \quad (16)$$

Since  $r_i = (x_1^2 + x_2^2 + x_3^2)^{1/2}$  then  $\frac{\partial r_i}{\partial x_m} = \frac{\partial (x_1^2 + x_2^2 + x_3^2)^{1/2}}{\partial x_m} = \frac{x_m}{r_i}$

$$= \sum_{m=1}^3 -\frac{1}{2\Psi_T} \left( \frac{\partial}{\partial x_m} \left( \frac{\partial \Psi_T}{\partial r_i} \frac{x_m}{r_i} \right) \right)_i \quad (17)$$

$$= \sum_{m=1}^3 -\frac{1}{2\Psi_T} \left( \frac{\partial^2 \Psi_T}{\partial x_m \partial r_i} \frac{x_m}{r_i} + \frac{\partial \Psi_T}{\partial r_i} \frac{\partial}{\partial x_m} \left( \frac{x_m}{r_i} \right) \right)_i \quad (18)$$

The term  $\frac{\partial}{\partial x_m} \left( \frac{x_m}{r_i} \right)$  becomes for the different values for  $m$ ,  $\frac{\partial}{\partial x_1} \left( \frac{x_1}{(x_1^2 + x_2^2 + x_3^2)^{1/2}} \right) = \frac{x_2^2 + x_3^2}{r_i^3}$  so all the values for  $m$  term it should sum up to  $\frac{2(x_1^2 + x_2^2 + x_3^2)}{r_i^3}$

$$= -\frac{1}{2\Psi_T} \left( \frac{\partial^2 \Psi_T}{\partial r_i^2} \frac{x_1^2 + x_2^2 + x_3^2}{r_i^2} + \frac{\partial \Psi_T}{\partial r_i} \frac{2(x_1^2 + x_2^2 + x_3^2)}{r_i^3} \right)_i \quad (19)$$

$$= -\frac{1}{2\Psi_T} \left( \frac{\partial^2 \Psi_T}{\partial r_i^2} + \frac{\partial \Psi_T}{\partial r_i} \frac{2}{r_i} \right) \quad (20)$$

Then the local energy becomes:

$$E_L = \sum_{i,i < j} -\frac{1}{2\Psi_T} \left( \frac{\partial^2 \Psi_T}{\partial r_i^2} + \frac{\partial \Psi_T}{\partial r_i} \frac{2}{r_i} \right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \quad (21)$$

### 2.3.1 Helium: Simple trialfunction

The simple version of the trial function is only dependant on one parameter  $\alpha$  and does not take into account interaction between the two electrons, it is of the form

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

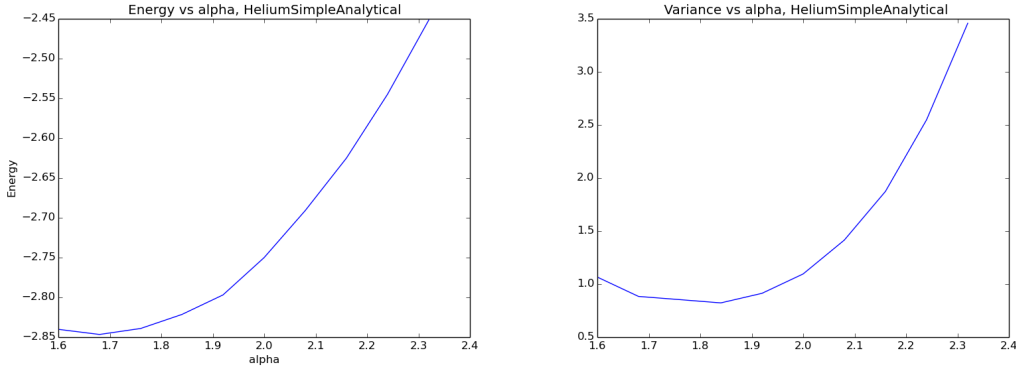


Figure 1: To be filled in

Let us set this trialfunction into the equation for the local energy (21).

$$E_L = \sum_{i,i < j} -\frac{1}{2\Psi_T} \left( \frac{\partial^2 e^{-\alpha(r_i+r_j)}}{\partial r_i^2} + \frac{\partial e^{-\alpha(r_i+r_j)}}{\partial r_i} \frac{2}{r_i} \right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \quad (22)$$

$$E_L = -\frac{1}{2\Psi_T} \sum_{i=1}^2 \left( \alpha^2 - \alpha \frac{2}{r_i} \right) \Psi_T - \frac{Z}{r_i} + \frac{1}{r_{ij}} \quad (23)$$

$$E_L = -\alpha^2 + (\alpha - Z) \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_{12}} \quad (24)$$

### 3 Results and discussion

As a first attempt to solve the ground state energy for the helium atom we perform Variational Monte Carlo calculation with a brute force Metropolis sampling. We do this with two trial wave functions

$$\psi_{T1}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) = \exp\{(-\alpha(r_1 + r_2))\}$$

and

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

using  $\alpha$  and  $\beta$  as variational parameters. Energy values for the simple wave function,  $\psi_{T1}$ , using only one variational parameter  $\alpha$ , are shown in figure 1. We run the Variational Monte Carlo calculation with  $10^7$  cycles. As we see in the figures, the energy minimum occurs when we use  $\alpha = 1.65$ . Using this value for  $\alpha$  we get an energy of  $-2.8442934$ .

We now look at our second trial function,  $\psi_{T2}$ . Running over different values for the two variables  $\alpha$  and  $\beta$ , again with  $10^7$  cycles in the Monte Carlo simulation, we get the results presented in figure 3. From this run we find that the optimal values are  $\alpha = 1.8$  and  $\beta = 0.94$ , and we get a minimum energy of  $-2.8979105$ , which is considerably better than without the Jastrow factor.

From research papers we find the value for energy in the ground state of helium to be  $-2.9037$  [Toichiro Kinoshita] and the value for energy in the ground state of beryllium to be  $-14.667$  [Jacek Koput]

#### 3.1 Alpha and Beta Values

Table 2 shows the values, for  $\alpha$  and  $\beta$  values, we got from running several Monte Carlo cycles with different values. As an algorithm to pick out the best values we minimized

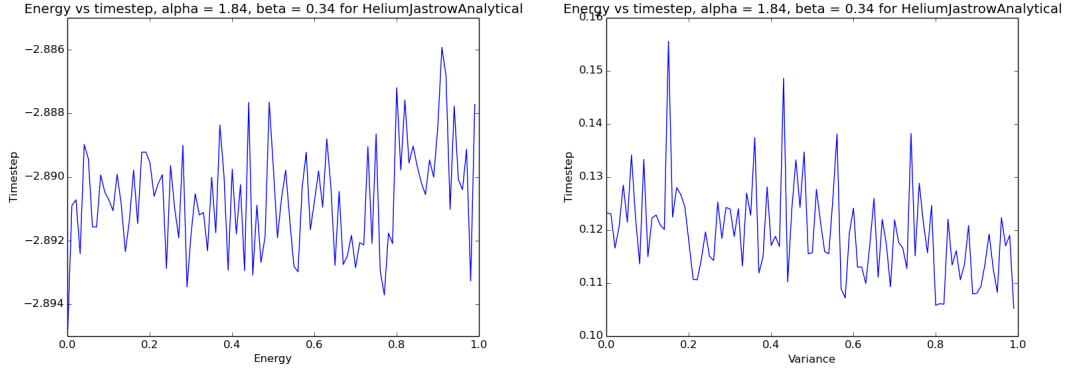


Figure 2: To be filled in

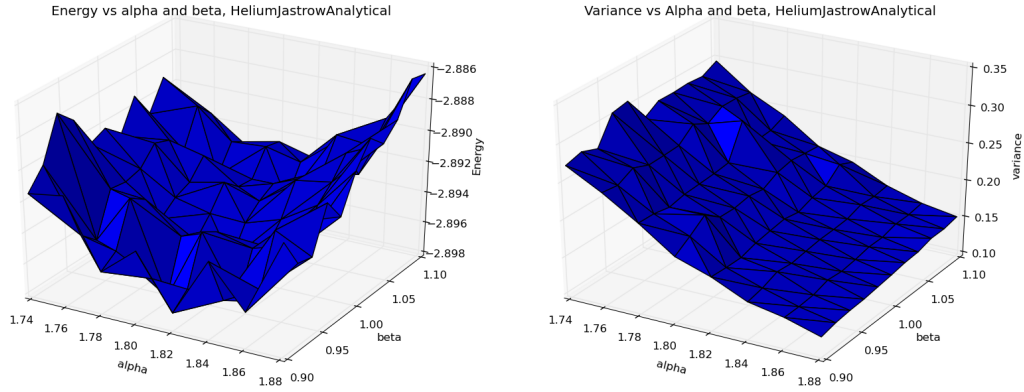


Figure 3: To be filled in

| Atom               | VMC     | References |
|--------------------|---------|------------|
| Helium $\psi_{T1}$ | -2.8442 | -2.9037    |
| Helium $\psi_{T2}$ | -2.8979 | -2.9037    |
| Beryllium          |         | -14.667    |

Table 1: Comparison of energies found with Variational Monte Carlo method and energies found in research papers.

| Trialfunction         | $\alpha$ | $\beta$ |
|-----------------------|----------|---------|
| Helium $\psi_{T1}$    | 1.65     | -       |
| Helium $\psi_{T2}$    | 1.8      | 0.94    |
| Beryllium $\psi_{T2}$ | 3.8      | 0.293   |

Table 2: The values for  $\alpha$  and  $\beta$  where found by doing running Monte Carlo calculation with over a mesh of different  $\alpha$  and  $\beta$  values, with stepssize 0.02. Each Monte Carlo run went over 10000000, using importance sampling. Then the run with the lowest energy gave the  $\alpha$  and  $\beta$  values

| <b>Trialfunction</b>  | Numerical (s) | Analytical (s) | Ratio |
|-----------------------|---------------|----------------|-------|
| Helium $\psi_{T1}$    | 61.75         | 14.34          | 4.307 |
| Helium $\psi_{T2}$    | 86.76         | 19.98          | 4.342 |
| Beryllium $\psi_{T2}$ |               |                |       |

Table 3: The time to run a Monte Carlo run with  $10^7$  cycles. The closed expression for the local energy increased the computation time by a significant degree for each trialfunction

the energy found in the Monte Carlo runs. The values found are quite uncertain since the variance of the energy was quite high compared to the difference caused by varying the parameters. The variance was more smooth as a function of the parameters, see fig 3 and should have been used.

### 3.2 Computational speed gain by using an analytical local energy

By using an analytical expression for the local energy instead of using a numerical derivation in the calculation a speed up of approximately factor 4 was achieved, see table 3.

19.98 86.76  
4.342

## 4 Conclusions and perspectives

### 4.1 Parameter grid and values

The algorithm by just minimizing the energy to find the best fits for  $\alpha$  and  $\beta$  could be improved since both the energy and it's variance should be minimized with a correct wavefunction. So the algorithm should take into account that and find the combined lowest energy and variance and use that to find the best values for the parameters. A homogeneous is used to search through the different  $\alpha$  and  $\beta$  and by improving this the speed of the program would be greatly improved. If for example it first did a coarse run, then found the best value searched in the vicinity of that point with a higher resolution it would be improved.

## A Testing the VMC

### A.1 Hydrogen Atom

The wavefunction for the Helium atom can be found exactly and can be used to test our Variational Monte Carlo Calculation since an exact wavefunction should return the exact energy, 0.5 atomic units with 0 variance.

$$\Psi(\mathbf{R}) = r_1 e^{-r_1} \quad E_L(r_1) = -\frac{1}{r_1} - \frac{\alpha}{2} \left( \alpha - \frac{2}{r_1} \right)$$

The unit test a unit named Helium tests the VMC claculation with a hydrogen wavefunction and returns the correct values.