

Computational Physics II

FYS-4411

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Abstract

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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 Ψ_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 α and does not take into account interaction between the two electrons, it is of the form

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

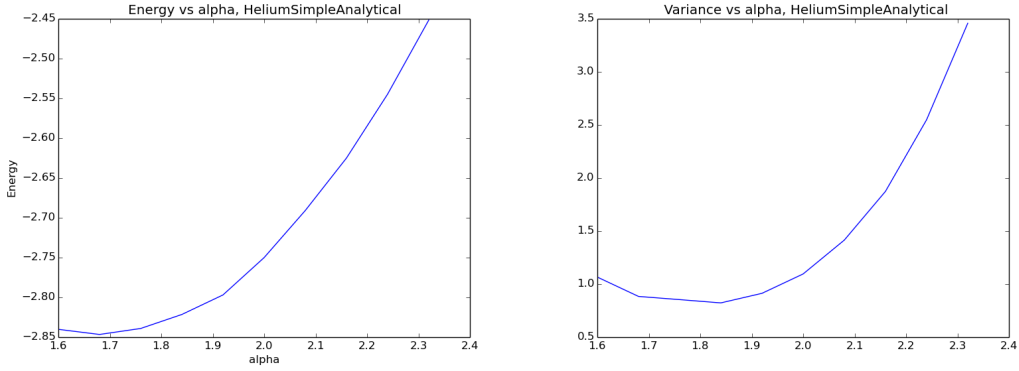


Figure 1: To be filled in

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 α and β as variational parameters. Energy values for the simple wave function, ψ_{T1} , using only one variational parameter α , 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 α we get an energy of -2.8442934 .

We now look at our second trial function, ψ_{T2} . Running over different values for the two variables α and β , 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 $\beta = 1.05$.

3.1 Alpha and Beta Values

Table 1 shows the values we got from

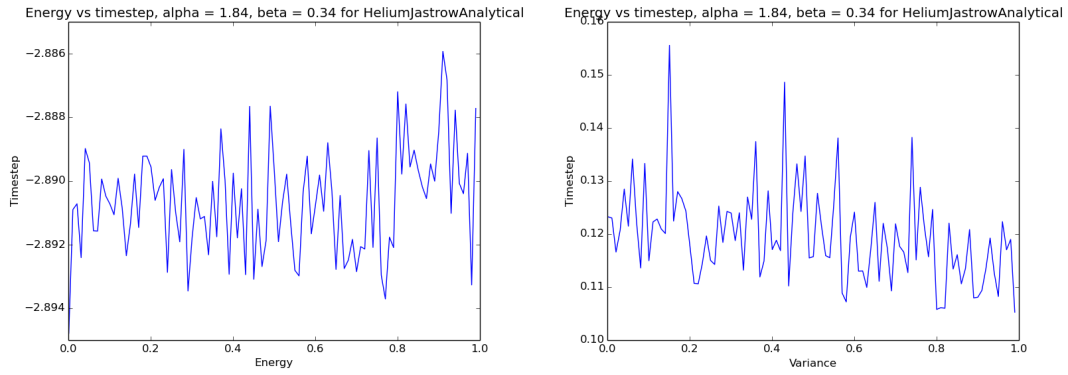


Figure 2: To be filled in

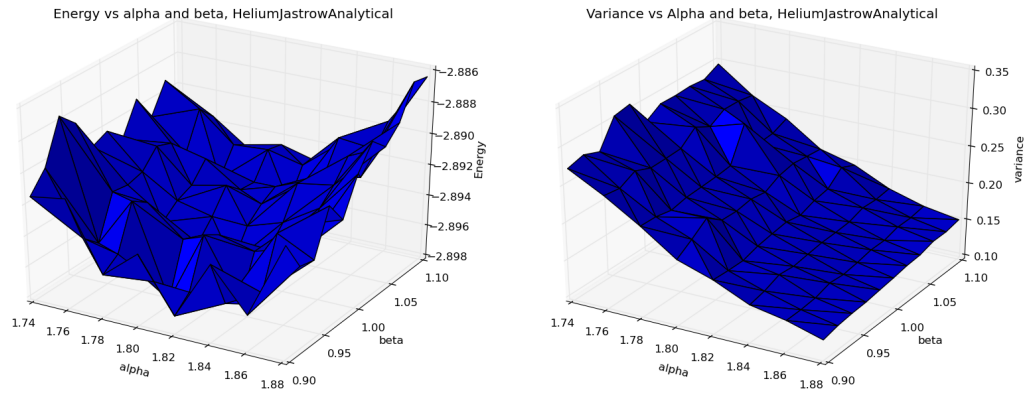


Figure 3: To be filled in

| Trialfunction | α | β |
|----------------------|----------|---------|
| Helium Simple | 1.65 | - |
| Helium Jastrow | 1.8 | 0.94 |
| Beryllium | 3.8 | 0.293 |

Table 1: The values we got from running the

4 Conclusions and perspectives

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.