Computational Physics II
FYS-4411

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

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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 Ψ_T be a proposal for a wavefunction that can describe the system.

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

Let us introduce a local energy:

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

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

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

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

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

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 $\mathbf{R_{new}} = \mathbf{R_{old}} + \delta * r$, where r is a random number in $[0, 1]$
   (b) Accept or reject move according to $P(\mathbf{R_{new}})/P(\mathbf{R_{old}}) \geq r$, 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

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

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

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

If we consider the case where $r_i \to 0$ 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.

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

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

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.

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

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 $\frac{\nabla_i^2}{2}$ 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:

$$E_L = \sum_{i,i<j} \frac{1}{\Psi_T(\mathbf{r_i}, \mathbf{r_{ij}})} \hat{H} \Psi_T(\mathbf{r_i}, \mathbf{r_{ij}}) \tag{11}$$

$$= \sum_{i,i<j} \frac{1}{\Psi_T(\mathbf{r_i}, \mathbf{r_{ij}})} \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \right) \Psi_T(\mathbf{r_i}, \mathbf{r_{ij}}) \tag{12}$$

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

Let us change derivation variables:

$$-\frac{1}{2\Psi_T} \left(\nabla_i^2 \Psi_T \right) = \sum_{m=1}^{3} -\frac{1}{2\Psi_T} \left(\frac{\partial^2 \Psi_T}{\partial x_m^2} \right)_i \tag{14}$$

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

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

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

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

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

$$= -\frac{1}{2\Psi_T} \left(\frac{\partial^2 \Psi_T}{\partial r_i^2} \frac{x_1^2 + x_2^2 + x_3^2}{r_i^2} + \frac{\partial \Psi_T}{\partial r_i} \frac{2(x_1^2 + x_2^2 + x_3^2)}{r_i^3} \right)_i \tag{18}$$

$$= -\frac{1}{2\Psi_T} \left(\frac{\partial^2 \Psi_T}{\partial r_i^2} + \frac{\partial \Psi_T}{\partial r_i} \frac{2}{r_i} \right) \tag{19}$$

Then the local energy becomes:

$$E_L = \sum_{i,i<j} -\frac{1}{2\Psi_T} \left(\frac{\partial^2 \Psi_T}{\partial r_i^2} + \frac{\partial \Psi_T}{\partial r_i} \frac{2}{r_i} \right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \tag{20}$$

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

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

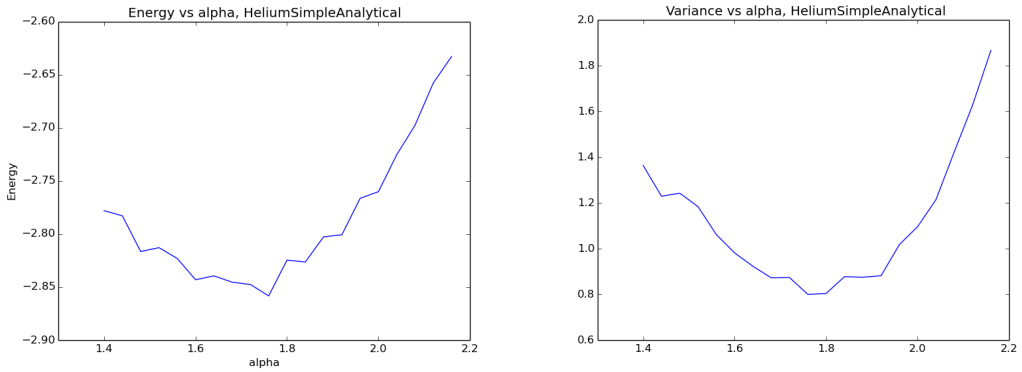

Figure 1: To be filled in

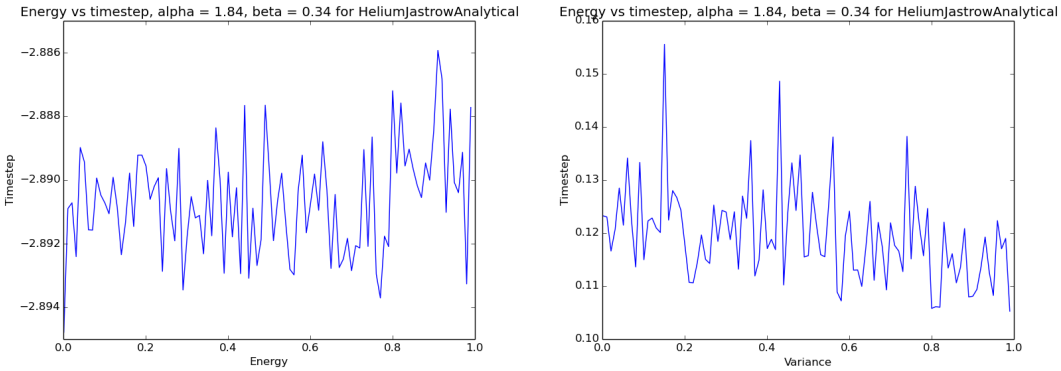

Figure 2: To be filled in

Let us set this trialfunction into the equation for the local energy (20).

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

$$E_L = -\frac{1}{2\Psi_T}\sum_{i=1}^{2}\left(\alpha^2 - \alpha\frac{2}{r_i}\right)\Psi_T - \frac{Z}{r_i} + \frac{1}{r_{ij}} \tag{22}$$

$$E_L = -\alpha^2 + (\alpha - Z)\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} \tag{23}$$

3 Results and discussion

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

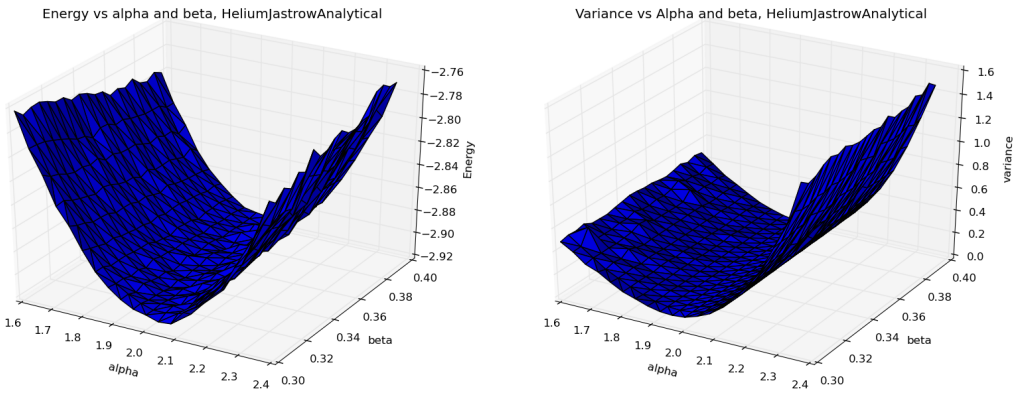

Figure 3: To be filled in

energy, 0.5 atomic units with 0 variance.

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

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