# Computational Physics II
# FYS-4411

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

March 1, 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.

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

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 consists of a kinetic energy part and a potential energy part and is given by

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

## 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:

$$E_L = \sum_{i,i<j} \frac{1}{\Psi_T(\mathbf{r_i}, \mathbf{r_{ij}})} \hat{H} \Psi_T(\mathbf{r_i}, \mathbf{r_{ij}}) \tag{7}$$

$$= \sum_{i,i<j} \frac{1}{\Psi_T(\mathbf{r_i}, \mathbf{r_{ij}})} \left( -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \right) \Psi_T(\mathbf{r_i}, \mathbf{r_{ij}}) \tag{8}$$

$$= \sum_{i,i<j} -\frac{1}{2\Psi_T} \left( \nabla_i^2 \Psi_T \right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \tag{9}$$

Let us change derivation variables:

$$-\frac{1}{2\Psi_T} \left( \nabla_i^2 \Psi_T \right) = \sum_{m=1}^{3} -\frac{1}{2\Psi_T} \left( \frac{\partial^2 \Psi_T}{\partial x_m^2} \right)_i \tag{10}$$

$$= \sum_{m=1}^{3} -\frac{1}{2\Psi_T} \left( \frac{\partial}{\partial x_m} \left( \frac{\partial \Psi_T}{\partial r_i} \frac{\partial r_i}{\partial x_m} \right) \right)_i \tag{11}$$

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

$$= \sum_{m=1}^{3} -\frac{1}{2\Psi_T} \left( \frac{\partial}{\partial x_m} \left( \frac{\partial \Psi_T}{\partial r_i} \frac{x_m}{r_i} \right) \right)_i \tag{12}$$

$$= \sum_{m=1}^{3} -\frac{1}{2\Psi_T} \left( \frac{\partial^2 \Psi_T}{\partial x_m \partial r_i} \frac{x_m}{r_i} + \frac{\partial \Psi_T}{\partial r_i} \frac{\partial}{\partial x_m} \left( \frac{x_m}{r_i} \right) \right)_i \tag{13}$$

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 $\frac{2(x_1^2+x_2^2+x_3^2)}{r_i^3}$

$$= -\frac{1}{2\Psi_T}\left(\frac{\partial^2\Psi_T}{\partial r_i^2}\frac{x_1^2+x_2^2+x_3^2}{r_i^2} + \frac{\partial\Psi_T}{\partial r_i}\frac{2(x_1^2+x_2^2+x_3^2)}{r_i^3}\right)_i \tag{14}$$

$$= -\frac{1}{2\Psi_T}\left(\frac{\partial^2\Psi_T}{\partial r_i^2} + \frac{\partial\Psi_T}{\partial r_i}\frac{2}{r_i}\right) \tag{15}$$

Then the local energy becomes:

$$E_L = \sum_{i,i<j} -\frac{1}{2\Psi_T}\left(\frac{\partial^2\Psi_T}{\partial r_i^2} + \frac{\partial\Psi_T}{\partial r_i}\frac{2}{r_i}\right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \tag{16}$$

### 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

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

Let us set this trialfunction into the equation for the local energy (16).

$$E_L = \sum_{i,i<j} -\frac{1}{2\Psi_T}\left(\frac{\partial^2 e^{-\alpha(r_i+r_j)}}{\partial r_i^2} + \frac{\partial e^{-\alpha(r_i+r_j)}}{\partial r_i}\frac{2}{r_i}\right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \tag{17}$$

$$E_L = -\frac{1}{2\Psi_T}\sum_{i=1}^{2}\left(\alpha^2 - \alpha\frac{2}{r_i}\right)\Psi_T - \frac{Z}{r_i} + \frac{1}{r_{ij}} \tag{18}$$

$$E_L = -\alpha^2 + (\alpha - Z)\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} \tag{19}$$

## 3  Results and discussion

## 4  Conclusions and perspectives

The local energy for the simple trialfunct

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