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# FYS-4411: Computational Physics II
# Project 3

Gullik Vetvik Killie
Håkon Sebastian Bakke Mørk
Jose Emilio Ruiz Navarro

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### Abstract

In this work, a simple Variational Monte Carlo (VMC) method has been used to calculate the values of the energies of the ground states of two atoms: Beryllium and Neon. The program uses importance sampling to improve efficiency and make the results more precise. To further improve the efficiency, MPI has been implemented as well. We provide a statistical analysis by the means of blocking so as to not understimate the error of our results. The one-body and charge densities were obtained to compare the effects of the Jastrow factor and provide insight into the electronic structure of the atoms.

# Contents

# 1    Introduction

VMC methods pose a very attractive alternative to other more complex ways of finding the ground state energies of simple atoms and molecules, like configuration-interaction calculations. The price to be paid in exchange for this simplicity is the sensitivity to the trial wave functions that are used, a VMC algorithm is very sensitive to how these are constructed, so they are one of the most important aspects to be considered (in this work, given the simple nature of the atoms which we will be working with, it's not so important to worry about the quality of the trial wave functions because very simple and basic ones are more than enough to reproduce the actual results). It shouldn't be forgotten that it is a variational method, and this implies that finding the optimal set of variational parameters is going to be the most important part of the calculation itself because it would create a lot of problems if the search range for the parameters was illy defined and not close enough to the variational minimum, namely, the results would have a poor quality in this case. This means that the parameters need to be chosen very carefully, or a recursive search with decreasingly coarse spacing in the space of variational parameters is required if there is no deep knowledge about the system in question.

Instead of evaluating a very complex multidimensional integral to compute the expectation value of an operator, like the hamiltonian in this case, a VMC calculation exploits the fact that the majority of the configuration space where the wave function belongs can be regarded as much less important than other parts, the values of the wave function are too small there and can be mostly ignored during the integration of the algorithm. To capitalize this, the Metropolis algorithm is added to the VMC method, as well as importance sampling.

# 2    Theory

## 2.1 Monte Carlo method with simple Metropolis sampling

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 denumerator 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 Atoms and Molecules

The dimensionless hamiltonian for the case of electrons around a nucleus is given by

$$\hat{H} = \sum_{i=1}^{N} -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} + \sum_{i<j} \frac{1}{r_{ij}} \tag{6}$$

where $r_i$ is the distance from electron $i$ to the nucleus, $Z$ is the nucleus charge, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The kinetic energy for electron $i$ is represented by $-\frac{\nabla_i^2}{2}$, $-\frac{Z}{r_i}$ the potential energy with respect to the nucleus and $\frac{1}{r_{ij}}$ the repulsive energy between the electrons $i$ and $j$.

In the VMC calculation the local energy, $E_L$ is a useful quantity and needs to be finite at all points to be normalizable. So by looking at the limits where the $E_L$ diverges we can guess the form the wavefunctions should follow.

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

In the cases where $r_i \to 0$ or $r_{ij} \to 0$ we need to make sure that the local energy does not diverge.

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

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

Given a well behaved wavefunction $\frac{1}{2} \frac{\partial^2}{\partial r_k^2}$ is finite.

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

This is finite given when the following differential equation is fulfilled.

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

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

$$\Psi_T(r_i, r_j, r_{ij}) = e^{-\alpha \sum_N r_i} \prod_{i<j}^{N} e^{\beta r_{ij}} = e^{-\alpha \sum_N r_i} \prod_{i<j}^{N} e^{\frac{a r_{ij}}{1 + \beta r_{ij}}}$$

should fulfill the condition that the local energy is finite.

### 2.2.1 Hydrogenic wavefunctions

A hydrogen atom is analytically solvable and we have exact wavefunctions corresponding to the electron being in the different shells. When we are building atoms containing more electrons turning it into a many body problem we base our guess at the trialfunction on the solutions to the hydrogen atom. So we need the wavefunctions for the five lowest states to calculate up to the 10 electron big neon atom. The hydrogenic wavefunctions along with their gradients and laplacians is contained in table .

| | $\psi_i$ | $\nabla \psi_i$ | $\nabla^2 \psi_i$ |
|---|---|---|---|
| $\psi_{1S}$ | $e^{-\alpha ri}$ | $-\frac{\alpha}{r_i}\mathbf{r_i}e^{-\alpha r_i}$ | $\frac{\alpha}{r_i}\left(\alpha r_i - 2\right)e^{-\alpha r_i}$ |
| $\psi_{2S}$ | $\left(-\frac{\alpha r_i}{2}+1\right)e^{-\frac{\alpha r_i}{2}}$ | $\frac{\alpha}{4r_i}\left(\alpha r_i - 4\right)\mathbf{r_i}e^{-\frac{\alpha r_i}{2}}$ | $-\frac{\alpha}{8r_i}\left(\alpha^2 r_i^2 - 10\alpha r_i + 16\right)e^{-\frac{\alpha r_i}{2}}$ |
| $\psi_{2Px}$ | $\alpha x_i e^{-\frac{\alpha r_i}{2}}$ | $-\frac{\alpha x_i}{2r_i}\left(\alpha \mathbf{r_i} - 2r_i\hat{\mathbf{i}}\right)e^{-\frac{\alpha r_i}{2}}$ | $\frac{\alpha^2 x_i}{4r_i}\left(\alpha r_i - 8\right)e^{-\frac{\alpha r_i}{2}}$ |
| $\psi_{2Py}$ | $\alpha x_i e^{-\frac{\alpha r_i}{2}}$ | $-\frac{\alpha y_i}{2r_i}\left(\alpha \mathbf{r_i} - 2r_i\hat{\mathbf{i}}\right)e^{-\frac{\alpha r_i}{2}}$ | $\frac{\alpha^2 x_i}{4r_i}\left(\alpha r_i - 8\right)e^{-\frac{\alpha r_i}{2}}$ |
| $\psi_{2Pz}$ | $\alpha x_i e^{-\frac{\alpha r_i}{2}}$ | $-\frac{\alpha z_i}{2r_i}\left(\alpha \mathbf{r_i} - 2r_i\hat{\mathbf{i}}\right)e^{-\frac{\alpha r_i}{2}}$ | $\frac{\alpha^2 x_i}{4r_i}\left(\alpha r_i - 8\right)e^{-\frac{\alpha r_i}{2}}$ |

Table 1: The different hydrogenic wavefunctions along with the gradients and laplacians. The derivatives is computed in the program derivatives.py

### 2.2.2 Helium atom

We wanted to do our Variational Monte Carlo, VMC, computations on helium first since it was a simpler system that the larger atoms and molecules. The hamiltonian for the helium atom is given by equation (6) and a trialfunction that fulfills the cusp conditions discussed earlier is

$$\Psi_{T2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) = e^{-\alpha(r_1 + r_2)}e^{\frac{r_{12}}{2(1+\beta r_{12})}} \tag{12}$$

We have also done calculations for a simplified version of the trialfunction by taking out electron-electron interaction from the trialfunction so we end up with the trialfunction

$$\Psi_{T1}(\mathbf{r}_1, \mathbf{r}_2) = e^{-\alpha(r_1 + r_2)} \tag{13}$$

We calculated the local energies for these two trialfunctions, **(NB!!!! Add link to localEnergy.py)**, and they are for $\Psi_{T1}$ and $\Psi_{T2}$.

$$E_{L1} = (\alpha - Z)\left(\frac{1}{r_2} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} - \alpha^2 \tag{14}$$

$$E_{L2} = E_{L1} + \frac{1}{2\left(1 + \beta r_{12}\right)}\left[\frac{\alpha(r_1 + r_2)}{r_{12}}\left(1 - \frac{\mathbf{r_1 r_2}}{r_1 r_2}\right) - \frac{1}{2\left(1 + \beta r_{12}\right)} - \frac{2}{r_{12}} + \frac{2\beta}{\left(1 + \beta r_{12}\right)}\right] \tag{15}$$

### 2.2.3 Beryllium atom

It is fairly simple to extend the calculational machinery of Variational Monte Carlo to other systems than the Helium atom. To show this we want to perform calculations on the beryllium atom. As beryllium has four electrons compared to the 2 of helium, we need to calculate a Slater determinant. Sticking to hydrogen-like wave functions, we can write the trial wave function for beryllium as

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \mathbf{r_4}) = Det\left(\phi_1(\mathbf{r_1}), \phi_2(\mathbf{r_2}), \phi_3(\mathbf{r_3}), \phi_4(\mathbf{r_4})\right)\prod_{i<j}^{4}\exp\left\{\left(\frac{ar_{ij}}{(1 + \beta r_{ij})}\right)\right\}, \tag{16}$$

where $Det$ is a Slater determinant and the single-particle wave functions are the hydrogen wave functions for the 1s and 2s orbitals. With the variational ansatz these are

$$\phi_{1s}(\mathbf{r_i}) = e^{-\alpha r_i}, \tag{17}$$

and

$$\phi_{2s}(\mathbf{r_i}) = (1 - \alpha r_i/2)\,e^{-\alpha r_i/2}. \tag{18}$$

The Slater determinant is calculated using these ansatzes, and can for Beryllium be written out as

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$$|D| \propto [\psi_{1s}(\mathbf{r_1})\psi_{2s}(\mathbf{r_2}) - \psi_{1s}(\mathbf{r_2})\psi_{2s}(\mathbf{r_1})] [\psi_{1s}(\mathbf{r_3})\psi_{2s}(\mathbf{r_4}) - \psi_{1s}(\mathbf{r_4})\psi_{2s}(\mathbf{r_3})] \qquad (19)$$

Furthermore, for the Jastrow factor,

$$\Psi_C = \prod_{i<j} g(r_{ij}) = \exp\left\{ \sum_{i<j} \frac{ar_{ij}}{1 + \beta r_{ij}} \right\}, \qquad (20)$$

we need to take into account the spins of the electrons. We fix electrons 1 and 2 to have spin up, and electron 3 and 4 to have spin down. This means that when the electrons have equal spins we get a factor

$$a = \frac{1}{4}, \qquad (21)$$

and if they have opposite spins we get a factor

$$a = \frac{1}{2}. \qquad (22)$$

### 2.2.4 Neon atom

Wishing to extend our variational Monte Carlo machinery further we implement Neon. Neon has ten electrons, so it is a big jump from Helium and Beryllium. Now we need better methods to handle the Slater determinant and is described in subsection 2.3. The trial wave function for Neon can be written as

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \ldots, \mathbf{r_{10}}) = Det\left(\phi_1(\mathbf{r_1}), \phi_2(\mathbf{r_2}), \ldots, \phi_{10}(\mathbf{r_{10}})\right) \prod_{i<j}^{10} \exp\left\{ \left( \frac{r_{ij}}{2(1 + \beta r_{ij})} \right) \right\}, \qquad (23)$$

Now we need to include the $2p$ wave function as well. It is given as

$$\phi_{2p}(\mathbf{r_i}) = \alpha \mathbf{r_i} e^{-\alpha r_i/2}. \qquad (24)$$

where $r_i = \sqrt{r_{i_x}^2 + r_{i_y}^2 + r_{i_z}^2}$.

### 2.2.5 Hydrogen molecule

The VMC machinery can also handle simple molecules with some modifications considering that we now have two nuclei. So we need a slightly different Hamiltonian, where we we need include a few more terms in the potential energy of the system. If we let $\mathbf{R}$ be the vector between the nuclei we can write the positions, $\mathbf{r_{ip1}}$, of electron $i$ in relation to nucleus 1.

$$\mathbf{r_{ip1}} = \mathbf{r_i} + \frac{\mathbf{R}}{2} \qquad (25)$$

$$\mathbf{r_{ip2}} = \mathbf{r_i} - \frac{\mathbf{R}}{2} \qquad (26)$$

Then we add all the terms for the potential energy with the kinetic energy and get the Hamiltonian

$$\hat{H} = \sum_{i=1}^{2} -\frac{\nabla_i^2}{2} - \frac{Z_1}{r_{ip1}} - \frac{Z_2}{r_{ip2}} + \sum_{i<j} \frac{1}{r_{ij}} + \frac{Z_1 Z_2}{|\mathbf{R}|} \qquad (27)$$

Here $Z_1$ and $Z_2$ is given by the charge of the respective nuclei. If we base our guess for the trialfunction on the assumption that the wavefunction for an electron should be a linear combination of the two hydrogenic wavefunctions around each nuclei. Disregarding factors, since they disappear in the VMC computation, and assuming symmetry about the nuclei we end up with

$$\Psi_T(\mathbf{r_1}, \mathbf{r_2}, \mathbf{R}) = \psi(\mathbf{r_1}, \mathbf{R})\psi(\mathbf{r_2}, \mathbf{R}) \exp\left\{ \frac{r_{12}}{2(1 + \beta r_{12})} \right\} \qquad (28)$$

## 2.3 Calculating the Slater determinant

To describe the wavefunction of multiple fermions we use a Slater determinant. The Slater determinant has the form

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \alpha, \beta, \gamma, \delta) = \frac{1}{\sqrt{4!}} \begin{vmatrix} \psi_{100\uparrow}(\mathbf{r}_1) & \psi_{100\uparrow}(\mathbf{r}_2) & \psi_{100\uparrow}(\mathbf{r}_3) & \psi_{100\uparrow}(\mathbf{r}_4) \\ \psi_{100\downarrow}(\mathbf{r}_1) & \psi_{100\downarrow}(\mathbf{r}_2) & \psi_{100\downarrow}(\mathbf{r}_3) & \psi_{100\downarrow}(\mathbf{r}_4) \\ \psi_{200\uparrow}(\mathbf{r}_1) & \psi_{200\uparrow}(\mathbf{r}_2) & \psi_{200\uparrow}(\mathbf{r}_3) & \psi_{200\uparrow}(\mathbf{r}_4) \\ \psi_{200\downarrow}(\mathbf{r}_1) & \psi_{200\downarrow}(\mathbf{r}_2) & \psi_{200\downarrow}(\mathbf{r}_3) & \psi_{200\downarrow}(\mathbf{r}_4) \end{vmatrix} \tag{29}$$

for a four-fermionic system. Because the spatial wave functions for spin up and spin down states are equal, this Slater determinant equals zero. We can rewrite the Slater determinant as a product of two Slater determinants, one for spin up and one for spin down. This gives us

$$\begin{aligned} \Phi(\mathbf{r}_1, \mathbf{r}_2, , \mathbf{r}_3, \mathbf{r}_4, \alpha, \beta, \gamma, \delta) \quad = \quad & \det\uparrow(1, 2) \det\downarrow(3, 4) - \det\uparrow(1, 3)\det\downarrow(2, 4) \\ & - \det\uparrow(1, 4)\det\downarrow(3, 2) + \det\uparrow(2, 3)\det\downarrow(1, 4) \\ & - \det\uparrow(2, 4)\det\downarrow(1, 3) + \det\uparrow(3, 4)\det\downarrow(1, 2) \end{aligned}$$

Here we have defined the Slater determinant for spin up as

$$\det\uparrow(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{100\uparrow}(\mathbf{r}_1) & \psi_{100\uparrow}(\mathbf{r}_2) \\ \psi_{200\uparrow}(\mathbf{r}_1) & \psi_{200\uparrow}(\mathbf{r}_2) \end{vmatrix} \tag{30}$$

and the Slater determinant for spin down as

$$\det\downarrow(3, 4) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{100\downarrow}(\mathbf{r}_3) & \psi_{100\downarrow}(\mathbf{r}_4) \\ \psi_{200\downarrow}(\mathbf{r}_3) & \psi_{200\downarrow}(\mathbf{r}_4) \end{vmatrix} \tag{31}$$

And the total determinant is of course still zero.

Further, it can be shown that for the variational energy we can approximate the Slater determinant as

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_N) \propto \det\uparrow \det\downarrow \tag{32}$$

We now have the Slater determinant as a product of two determinants, one containing the electrons with only spin up, and one containing the electrons of spin down. This approach has certain limits as the ansatz isn't antisymmetric under the exchange of electrons with opposite spins, but it gives the same expectation value for the energy as the full Slater determinant as long as the Hamiltonian is spin independent. We thus avoid summing over spin variables.

Now we have the Slater determinant written as a product of a determinant for spin up and a determinant for spin down. The next step is to invert the matrices using LU decomposition. We can thus rewrite a matrix $\hat{A}$ as a product of two matrices, $\hat{B}$ and $\hat{C}$

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ b_{21} & 1 & 0 & 0 \\ b_{31} & b_{32} & 1 & 0 \\ b_{41} & b_{42} & b_{43} & 1 \end{pmatrix} \begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} \\ 0 & c_{22} & c_{23} & c_{24} \\ 0 & 0 & c_{33} & c_{34} \\ 0 & 0 & 0 & c_{44} \end{pmatrix}$$

LU factorization exists for $\hat{A}$ if the determinant is nonzero. If $\hat{A}$ also is non-singular, then the LU factorization is unique and the determinant is given by

$$|\hat{A}| = c_{11}c_{22}\dots c_{nn} \tag{33}$$

Using this we can calculate the spin up determinant, the spin down determinant, and by putting them together, the Slater determinant.

## 2.4 Optimization

Since the raw computational cost of the VMC computation scales up very fast with the increase of particles considered we have implemented several different methods to achieve a faster speed allowing us to compute longer and with more precision. The optimization is done along three paths importance sampling, multithreaded computation and improvements to computing the ratios and local energy. Importance sampling improves the convergence speed of the algorithm, multithreaded computation while allowing several processors to compute at the same time and the algorithmic improvements to reduce computing saving time in computing the Slater determinants and removing the need for slow numerical derivations. Here we will go through the algorithmic optimizations first.

**NB!!!!!!!!!!!!!!!!!!11 Should probably add all the information about the computational savings**

### 2.4.1 Metropolis-Hastings-Ratio

In the Metropolis-Hasting algorithm a ratio of the new probability and the old probability is calculated to evaluate if a suggested move is accepted or rejected.

$$\frac{P(\mathbf{r_{new}})}{P(\mathbf{r_{old}}} \geq r \tag{34}$$

For our probability function it can be written as

$$\frac{|D_\uparrow^{new}|}{|D_\uparrow^{old}|} \frac{|D_\downarrow^{new}|}{|D_\downarrow^{old}|} \frac{\Psi_C^{new}}{\Psi_C^{old}} \geq r \tag{35}$$

### 2.4.2 Slater-Determinant-Ratio

The Slater-Determinants ratios are slow to calculate by brute force, for example by LU-decomposition, but recalculation it after each move can be done in a computationally easier way.

To tackle the determinant ratios we need to introduce some notation. Let an element in the determinant matrix, $|D|$, be described by

$$D_{ij} = \phi_j(\mathbf{r}_i) \tag{36}$$

where $\phi_j$ is the j'th single particle wavefunction and $\mathbf{r}_i$ is the position of the i'th particle.

The inverse of a matrix is given by transposing it and dividing by the determinant, so the determinant can be written as

$$|D| = \frac{\mathbf{D}^T}{\mathbf{D^{-1}}} = \sum_{j=1}^{N} \frac{C_{ji}}{D_{ij}^{-1}} = \sum_{j=1}^{N} D_{ij} C_{ji} \tag{37}$$

This gives the ratio of the new and old Slater determinants the following

$$R_{SD} = \frac{|\mathbf{D}^{new}|}{|\mathbf{D}^{old}|} = \frac{\sum_{j=0}^{N} D_{ij}^{new} C_{ji}^{new}}{\sum_{j=0}^{N} D_{ij}^{old} C_{ji}^{old}} \tag{38}$$

Since we are only moving one particle at a time and the cofactor term relies on the other rows it doesn't change, $C_{ij}^{new} = C_{ij}^{old}$ in one movement. Combining this with equation (37) we get

$$R_{SD} = \frac{\sum_{j=0}^{N} D_{ij}^{new} (D_{ji}^{old})^{-1} |D^{old}|}{\sum_{j=0}^{N} D_{ij}^{old} (D_{ji}^{old})^{-1} |D^{old}|} \tag{39}$$

Since $\mathbf{D}$ is invertible, $\mathbf{DD}^{-1} = \mathbf{1}$, the ratio becomes

$$R_{SD} = \sum_{j=0}^{N} D_{ij}^{new}(D_{ji}^{old})^{-1} = \sum_{j=0}^{N} \phi_j(\mathbf{x}_i^{new})D_{ji}^{-1}(\mathbf{x}^{old}) \tag{40}$$

### 2.4.3 Correlation-to-correlation ratio

We have $N(N-1)/2$ relative distances $r_{ij}$. We can write these in a matrix storage format, where they form a strictly upper triangular matrix

$$\mathbf{r} \equiv \begin{pmatrix} 0 & r_{1,2} & r_{1,3} & \dots & r_{1,N} \\ \vdots & 0 & r_{2,3} & \dots & r_{2,N} \\ \vdots & \vdots & 0 & \ddots & \vdots \\ \vdots & \vdots & \vdots & \ddots & r_{N-1,N} \\ 0 & 0 & 0 & \dots & 0 \end{pmatrix}$$

This upper triangular matrix form also applies to $g = g(r_{ij})$.

The correlation-to-correlation ratio, or ratio between Jastrow factors is given by

$$R_C = \frac{\Psi_C^{new}}{\Psi_C^{cur}} = \prod_{i=1}^{k-1} \frac{g_{ik}^{new}}{g_{ik}^{cur}} \prod_{i=k+1}^{N} \frac{g_{ki}^{new}}{g_{ki}^{cur}} \tag{41}$$

or in the Padé-Jastrow form

$$R_C = \frac{\Psi_C^{new}}{\Psi_C^{cur}} = \frac{\exp(U_{new})}{\exp(U_{cur})} = \exp(\Delta U) \tag{42}$$

where

$$\Delta U = \sum_{i=1}^{k-1} \left( f_{ik}^{new} - f_{ik}^{cur} \right) + \sum_{i=k+1}^{N} \left( f_{ki}^{new} - f_{ki}^{cur} \right) \tag{43}$$

### 2.4.4 Efficient calculation of derivatives

Calculating the derivatives involved in the VMC calculation numerically is slow in that they entail several calls to the wavefunctions in addition to introducing an extra numerical error. Here we will show how to divide up the derivatives and how to find analytical expressions for all the parts using the derivatives found in table 1.

The trialfunction can be factorized as

$$\Psi_T(\mathbf{x}) = \Psi_D \Psi_C = |D_\uparrow||D_\downarrow|\Psi_C \tag{44}$$

where $D_\uparrow$, $D_\downarrow$ and $\Psi_C$ is the spin up and down part of the Slater determinant and the Jastrow factor respectively.

### 2.4.5 Gradient-Ratio

For the quantum force, and in the final expression for the local energy, we need to calculate the gradient ratio of the trialfunction which is given by

$$\frac{\nabla \Psi_T}{\Psi_T} = \frac{\nabla(\Psi_D \Psi_C)}{\Psi_D \Psi_C} = \frac{\nabla \Psi_D}{\Psi_D} + \frac{\nabla \Psi_C}{\Psi_C} \tag{45}$$

$$= \frac{\nabla|D_\uparrow|}{|D_\uparrow|} + \frac{\nabla|D_\downarrow|}{|D_\downarrow|} + \frac{\nabla \Psi_C}{\Psi_C} \tag{46}$$

### 2.4.6 Laplacian-Ratio

From the Hamiltonians and the expression for the local energy the local kinetic energy of electron $i$ is given by the following

$$K_i = -\frac{1}{2}\frac{\nabla_i^2\Psi}{\Psi} \tag{47}$$

Using the factorization of the trialfunction from (44) we can calculate the ratio needed for the kinetic energy.

$$\frac{1}{\Psi_T}\frac{\partial^2\Psi_T}{\partial x_k^2} = \frac{1}{\Psi_D\Psi_C}\frac{\partial^2(\Psi_D\Psi_C)}{\partial x_k^2} = \frac{1}{\Psi_D\Psi_C}\frac{\partial}{\partial x_k}\left(\frac{\partial\Psi_D}{\partial x_k}\Psi_C + \Psi_D\frac{\partial\Psi_C}{\partial x_k}\right) \tag{48}$$

$$= \frac{1}{\Psi_D\Psi_C}\left(\frac{\partial^2\Psi_D}{\partial x_k^2}\Psi_C + 2\frac{\partial\Psi_D}{\partial x_k}\frac{\partial\Psi_C}{\partial x_k} + \Psi_D\frac{\partial^2\Psi_C}{\partial x_k^2}\right) \tag{49}$$

$$= \frac{1}{\Psi_D}\frac{\partial^2\Psi_D}{\partial x_k^2} + 2\frac{1}{\Psi_D}\frac{\partial\Psi_D}{\partial x_k}\cdot\frac{1}{\Psi_C}\frac{\partial\Psi_C}{\partial x_k} + \frac{1}{\Psi_C}\frac{\partial^2\Psi_C}{\partial x_k^2} \tag{50}$$

Since the Slater determinant part of the trialfunction is separable into a spin up and down part we can simplify it further.

$$\frac{1}{\Psi_D}\frac{\partial^2\Psi_D}{\partial x_k^2} = \frac{1}{|D_\uparrow||D_\downarrow|}\frac{\partial^2|D_\uparrow||D_\downarrow|}{\partial x_k^2} = \frac{1}{|D_\uparrow|}\frac{\partial^2|D_\uparrow|}{\partial x_k^2} + \frac{1}{|D_\downarrow|}\frac{\partial^2|D_\downarrow|}{\partial x_k^2} \tag{51}$$

$$\frac{1}{\Psi_D}\frac{\partial\Psi_D}{\partial x_k} = \frac{1}{|D_\uparrow||D_\downarrow|}\frac{\partial|D_\uparrow||D_\downarrow|}{\partial x_k} = \frac{1}{|D_\uparrow|}\frac{\partial|D_\uparrow|}{\partial x_k} + \frac{1}{|D_\downarrow|}\frac{\partial|D_\downarrow|}{\partial x_k} \tag{52}$$

Inserting equations (52) and (51) into (50) we get

$$\frac{\nabla^2\Psi_T}{\Psi_T} = \frac{\nabla^2|D_\uparrow|}{|D_\uparrow|} + \frac{\nabla^2|D_\downarrow|}{|D_\downarrow|} + 2\left(\frac{\nabla|D_\uparrow|}{|D_\uparrow|} + \frac{\nabla|D_\downarrow|}{|D_\downarrow|}\right)\cdot\frac{\nabla\Psi_C}{\Psi_C} + \frac{\nabla^2\Psi_C}{\Psi_C} \tag{53}$$

So to calculate the laplacian-ratio and the gradient-ratio we need to find expressions for $\frac{\nabla|D|}{|D|}$, $\frac{\nabla^2|D|}{|D|}$, $\frac{\nabla\Psi_C}{\Psi_C}$ and $\frac{\nabla^2\Psi_C}{\Psi_C}$.

### 2.4.7 The $\nabla|D|/|D|$ ratio

By the same argument as in section 2.4.2 the the gradient-slater-ratio can be written as

$$\frac{\nabla|D|}{|D|} = \sum_{j=0}^{N}\nabla(D_{ij})D_{ji}^{-1} = \sum_{j=0}^{N}\nabla\phi_j(\mathbf{x}_i)D_{ji}^{-1}(\mathbf{x}) \tag{54}$$

### 2.4.8 The $\nabla^2|D|/|D|$ ratio

As in the previous section the laplacian can be calculated by a similar method to the one used in section 2.4.2, and we end up with

$$\frac{\nabla^2|D|}{|D|} = \sum_{j=0}^{N}\nabla^2(D_{ij})D_{ji}^{-1} = \sum_{j=0}^{N}\nabla^2\phi_j(\mathbf{x}_i)D_{ji}^{-1}(\mathbf{x}) \tag{55}$$

### 2.4.9 The $\nabla\Psi_C/\Psi_C$ ratio

We continue by finding a useful expression for the quantum force and kinetic energy, the ratio $\nabla\Psi_C/\Psi_C$. It has, for all dimensions, the form

$$\frac{\nabla_i\Psi_C}{\Psi_C} = \frac{1}{\Psi_C}\frac{\partial\Psi_C}{\partial x_i} \tag{56}$$

where $i$ runs over all particles. Since the g-terms aren't differentiated they cancel with their corresponding terms in the denominator, so only $N-1$ terms survive the first derivative. We get

$$\frac{1}{\Psi_C}\frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1}\frac{1}{g_{ik}}\frac{\partial g_{ik}}{\partial x_k} + \sum_{i=k+1}^{N}\frac{1}{g_{ki}}\frac{\partial g_{ki}}{\partial x_k} \tag{57}$$

For the exponential form we get almost the same, by just replacing $g_{ij}$ with $\exp(f_{ij})$ and we get

$$\frac{1}{\Psi_C}\frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1}\frac{\partial g_{ik}}{\partial x_k} + \sum_{i=k+1}^{N}\frac{\partial g_{ki}}{\partial x_k} \tag{58}$$

We now use the identity

$$\frac{\partial}{\partial x_i}g_{ij} = -\frac{\partial}{\partial x_j}g_{ij} \tag{59}$$

and get expressions where the derivatives that act on the particle are represented by the second index of $g$

$$\frac{1}{\Psi_C}\frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1}\frac{1}{g_{ik}}\frac{\partial g_{ik}}{\partial x_k} - \sum_{i=k+1}^{N}\frac{1}{g_{ki}}\frac{\partial g_{ki}}{\partial x_i} \tag{60}$$

and for the exponential case

$$\frac{1}{\Psi_C}\frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1}\frac{\partial g_{ik}}{\partial x_k} - \sum_{i=k+1}^{N}\frac{\partial g_{ki}}{\partial x_i} \tag{61}$$

Since we have that the correlation function is depending on the relative distance we use the chain rule

$$\frac{\partial g_{ij}}{\partial x_j} = \frac{\partial g_{ij}}{\partial r_{ij}}\frac{\partial r_{ij}}{\partial x_j} = \frac{x_j - x_i}{r_{ij}}\frac{\partial g_{ij}}{\partial r_{ij}} \tag{62}$$

After substitution we get

$$\frac{1}{\Psi_C}\frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1}\frac{1}{g_{ik}}\frac{\mathbf{r_{ik}}}{r_{ik}}\frac{\partial g_{ik}}{\partial r_{ik}} - \sum_{i=k+1}^{N}\frac{1}{g_{ki}}\frac{\mathbf{r_{ki}}}{r_{ki}}\frac{\partial g_{ki}}{\partial r_{ki}} \tag{63}$$

For the Padé-Jastrow form we set $g_{ij} \equiv g(r_{ij}) = e^{f(r_{ij})} = e^{f_{ij}}$ and

$$\frac{\partial g_{ij}}{\partial r_{ij}} = g_{ij}\frac{\partial f_{ij}}{\partial r_{ij}} \tag{64}$$

and arrive at

$$\frac{1}{\Psi_C}\frac{\partial \Psi_C}{\partial x_k} = \sum_{i=1}^{k-1}\frac{\mathbf{r_{ik}}}{r_{ik}}\frac{\partial f_{ik}}{\partial r_{ik}} - \sum_{i=k+1}^{N}\frac{\mathbf{r_{ki}}}{r_{ki}}\frac{\partial f_{ki}}{\partial r_{ki}} \tag{65}$$

where we have the relative vectorial distance

$$\mathbf{r}_{ij} = |\mathbf{r}_j - \mathbf{r}_i| = (x_j - x_i)\mathbf{e}_1 + (y_j - y_i)\mathbf{e}_2 + (z_j - z_i)\mathbf{e}_3 \tag{66}$$

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With a linear Padé-Jastrow we set

$$f_{ij} = \frac{ar_{ij}}{(1 + \beta r_{ij})} \tag{67}$$

with the corresponding closed form expression

$$\frac{\partial f_{ij}}{\partial r_{ij}} = \frac{a}{(1 + \beta r_{ij})^2} \tag{68}$$

### 2.4.10 The $\nabla^2 \Psi_C / \Psi_C$ ratio

For the kinetic energy we also need the second derivative of the Jastrow factor divided by the Jastrow factor. We start with this

$$\left[ \frac{\nabla^2 \Psi_C}{\Psi_C} \right]_x = 2 \sum_{k=1}^{N} \sum_{i=1}^{k-1} \frac{\partial^2 g_{ik}}{\partial x_k^2} + \sum_{k=1}^{N} \left( \sum_{i=1}^{k-1} \frac{\partial g_{ik}}{\partial x_k} - \sum_{i=k+1}^{N} \frac{\partial g_{ki}}{\partial x_i} \right)^2 \tag{69}$$

But we have another, simpler form for the function

$$\Psi_C = \prod_{i<j} \exp f(r_{ij}) = \exp \left\{ \sum_{i<j} \frac{ar_{ij}}{1 + \beta r_{ij}} \right\} \tag{70}$$

and for particle $k$ we have

$$\frac{\nabla_k^2 \Psi_C}{\Psi_C} = \sum_{ij \neq k} \frac{(\mathbf{r}_k - \mathbf{r}_i)(\mathbf{r}_k - \mathbf{r}_j)}{r_{ki} r_{kj}} f'(r_{ki}) f'(r_{kj}) + \sum_{j \neq k} \left( f''(r_{kj}) + \frac{2}{r_{kj}} f'(r_{kj}) \right) \tag{71}$$

We use

$$f(r_{ij}) = \frac{ar_{ij}}{1 + \beta r_{ij}} \tag{72}$$

and with

$$g'(r_{kj}) = dg(r_{kj})/dr_{kj} \qquad \text{and} \qquad g''(r_{kj}) = d^2 g(r_{kj})/dr_{kj}^2 \tag{73}$$

we find that for particle $k$ we have

$$\frac{\nabla_k^2 \Psi_C}{\Psi_C} = \sum_{ij \neq k} \frac{(\mathbf{r}_k - \mathbf{r}_i)(\mathbf{r}_k - \mathbf{r}_j)}{r_{ki} r_{kj}} \frac{a}{(1 + \beta r_{ki})^2} \frac{a}{(1 + \beta r_{kj})^2} + \sum_{j \neq k} \left( \frac{2a}{r_{kj}(1 + \beta r_{kj})^2} - \frac{2a\beta}{(1 + \beta r_{kj})^3} \right) \tag{74}$$

And for the linear Padé-Jastrow we get the closed form result

$$\frac{\partial^2 f_{ij}}{\partial r_{ij}^2} = -\frac{2a_{ij}\beta_{ij}}{(1 + \beta_{ij} r_{ij})^3} \tag{75}$$

### 2.4.11    Importance sampling

We now want to make the code more efficient, so we replace the brute force Metropolis algorithm with a walk in coordinate space biased by the trial wave function, an approach based on the Fokker-Planck equation and the Langevin equation for generating a trajectory in coordinate space.

For one particle or walker, a diffusion process characterized by a time-dependent probability density $P(x, t)$ in one dimension we have the Fokker-Planck equation

$$\frac{\partial P}{\partial t} = D\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x} - F\right)P(x, t), \tag{76}$$

where $F$ is a drift term and $D$ is the diffusion coefficient.

The new positions in coordinate space are found using the Langevin equation with Euler's method. We go from the Langevin equation

$$\frac{\partial x(t)}{\partial t} = DF(x(t)) + \eta \tag{77}$$

where $\eta$ is a random variable. This gives us a new position

$$y = x + DF(x)\Delta t + \xi\sqrt{\Delta t}. \tag{78}$$

Here $\xi$ is gaussian random variable and $\Delta t$ is a chosen time step. $D$ comes from the factor $1/2$ in the kinetic energy operator, and is therefore equal to $1/2$ in atomic units.

The process of isotropic diffusion characterized by a time-dependent probability density $P(\mathbf{x}, t)$ will, as an approximation, obey the Fokker-Planck equation

$$\frac{\partial P}{\partial t} = \sum_i D\frac{\partial}{\partial \mathbf{x_i}}\left(\frac{\partial}{\partial \mathbf{x_i}} - \mathbf{F_i}\right)P(\mathbf{x}, t), \tag{79}$$

where $\mathbf{F}_i$ is component number $i$ of the drift term caused by an external potential, and $D$ is the diffusion coefficient. We set the left hand side equal to zero and obtain the convergence to a stationary probability density

$$\frac{\partial^2 P}{\partial \mathbf{x_i}^2} = P\frac{\partial}{\partial \mathbf{x_i}}\mathbf{F_i} + \mathbf{F_i}\frac{\partial}{\partial \mathbf{x_i}}P. \tag{80}$$

Inserting the drift vector, $\mathbf{F} = g(\mathbf{x})\frac{\partial P}{\partial \mathbf{x}}$, we get

$$\frac{\partial^2 P}{\partial \mathbf{x_i}^2} = P\frac{\partial g}{\partial P}\left(\frac{\partial P}{\partial \mathbf{x}_i}\right)^2 + Pg\frac{\partial^2 P}{\partial \mathbf{x}_i^2} + g\left(\frac{\partial P}{\partial \mathbf{x}_i}\right)^2 \tag{81}$$

To meet the condition of stationary density the left hand side has to be zero. This means that the terms containing first and second order derivatives has to cancel each other, which is only possible if $g = \frac{1}{P}$. This yields

$$\mathbf{F} = 2\frac{1}{\Psi_T}\nabla\Psi_T, \tag{82}$$

known as the quantum force. This so-called force pushes the walker towards regions of configuration space where the trial wave function is large, thus increasing the efficiency of the simulation. This is a great improvement on the Metropolis algorithm where the walker has the same probability to move in every direction.

From the Fokker-Planck equation we get a transition probability given by Green's function

$$G(y, x, \Delta t) = \frac{1}{(4\pi D\Delta t)^{3N/2}}\exp\left(-\frac{(y - x - D\Delta t F(x))^2}{4D\Delta t}\right) \tag{83}$$

This means that the Metropolis algorithm

$$A(y, x) = \min(1, q(y, x))), \tag{84}$$

where

$$q(y, x) = \frac{|\Psi_T(y)|^2}{|\Psi_T(x)|^2}, \tag{85}$$

is replaced by the Metropolis-Hastings algorithm,

$$q(y, x) = \frac{G(x, y, \Delta t)|\Psi_T(y)|^2}{G(y, x, \Delta t)|\Psi_T(x)|^2} \tag{86}$$

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## 2.5 Implementation of MPI

As the calculations now become increasingly complex and heavy we implement MPI to make use of multiple processors. Personal computers today usually have two, four or sometimes eight processors, which will give a fairly good speedup to our calculations. With bigger atoms or systems it is crucial to implement a way to distribute calculation to multiple processors.

Implementing MPI in the Monte Carlo method is very easy. As we deal with statistical values we can easily split up the problem. Each process will run its own set of samples. The number of samples used by each process is simply $n/p$, where $n$ is the total number of samples we want to do, and $p$ is the number of processes. In the end all processors send their results to the master process, which sums up the values and takes the average over all processes.

## 2.6 Blocking

Blocking refers to a method to more accurately estimate the error of the values obtained by the VMC algorithm. It's actually a completely separate and independent process. The basic idea lies on the correlations between all the measurements. If these are important enough, they will produce an increase in the error that needs to be taken into account. The reason behind this is related to the effective amount of measurements, if there are correlations there will be measurements that will contain less information, so these won't be as valuable as the rest and it will be as if there are *less* measurementes than we actually have. Obviously this is a problem, the usual identification of the error with $\sqrt{\frac{\sigma}{n}}$ will be overly optimistic and a correction is needed.

$$f_d = \frac{1}{n-d} \sum_{k=1}^{n-d} (x_k - \bar{x}_n)(x_{k+d} - \bar{x}_n) \tag{87}$$

Where $f_d$ is the correlation between measurements separated by a distance of $d$. This can be used to give an actual form to the correction factor:

$$\tau = 1 + 2 \sum_{d=1}^{n-1} \frac{f_d}{var(x)} \tag{88}$$

This is the autocorrelation time and it relates the error with the variance:

$$err^2 = \frac{\tau}{n} var(x) \tag{89}$$

And the inverse of the first factor is actually the number of effective measurements (that are actually useful since they contain information):

$$n_{eff} = \frac{n}{\tau} \tag{90}$$

The expression that relates the standard deviation with this correlation time is thus:

$$\sigma = \sqrt{\left( \frac{1 + 2\tau/\Delta t}{n} \left( \bar{x^2} - \bar{x}^2 \right) \right)} \tag{91}$$

Where $\Delta t$ is the time between samples, and it's commonly smaller than $\tau$. The main problem is that to compute $\tau$ a lot of time is needed, and this is not feasible in most cases.

The solution is to use blocking, and the algorithm to do this is actually quite simple. The total amount of measurements is divided into blocks (hence the name) of a certain size,
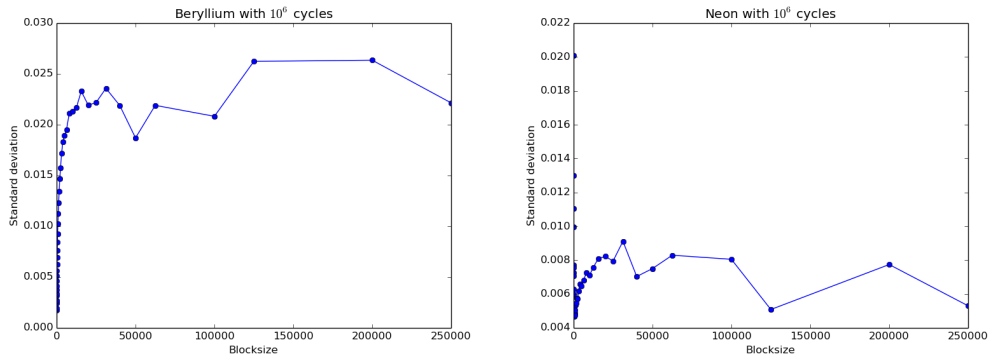
Figure 1: STD vs. blocksize with $10^6$ MC cycles. The STD should have a plateauing trend as the blocksize increases.

and for each block the standard deviation is obtained. When the standard deviation stops increasing as the block size does, the correlations are irrelevant and the value for it is ready.

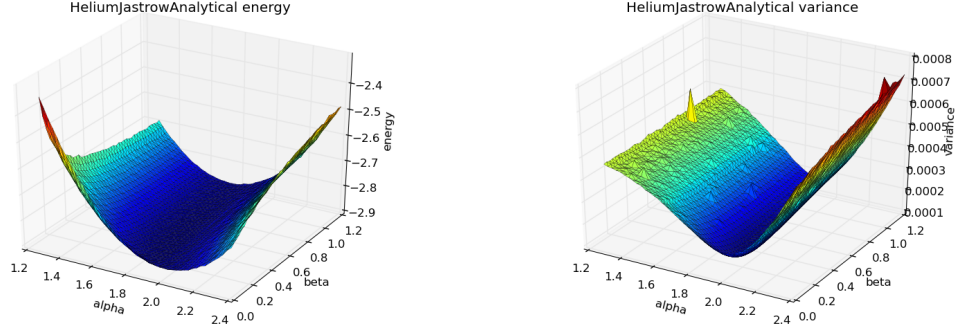**NB!!!!!!!!!!!! NEEDS TO BE MOVED TO RESULTS PART**

# 3   Results

Figure 2: Using $\psi_T$, plot of the energy versus alpha and beta, and plot of the variance versus $\alpha$ and $\beta$.

| Atom **UPDATE ME** | VMC | References |
|---|---|---|
| Helium $\psi_T$ | $-2.8979$ | $-2.9037$ |
| Beryllium | $-14.4127$ | $-14.667$ |
| Neon | $-$ | $-128.928$ |

Table 2: Comparison of energies found with Variational Monte Carlo method and energies found in research papers. [1] [3]

## 3.1 Variational Monte Carlo calculations of the helium atom

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

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{12}}) = \exp\{(-\alpha(r_1 + r_2))\} \exp\left\{\left(\frac{r_{12}}{2(1 + \beta r_{12})}\right)\right\},$$

using $\alpha$ and $\beta$ as variational parameters. We run the Variational Monte Carlo calculation over different values for the two variables $\alpha$ and $\beta$, with $2 \times 10^7$ cycles in the Monte Carlo simulation, we get the results presented in figure 2. We find the optimal values to be $\alpha = 1.8$ and $\beta = 0.94$ CHECK THIS, as we can see in the figures. With these values for $\alpha$ and $\beta$ we get an energy of $-2.8979105$ CHECK THIS. The parameter $\alpha$ can be interpreted as a parameter for the force pulling the electron to the nucleus.

### 3.1.1 Alpha and Beta Values

Table 3 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 the energy found in the Monte Carlo runs. The values found are quite uncertain since the variance of

| Trialfunction **UPDATE ME** | $\alpha$ | $\beta$ |
|---|---|---|
| Helium $\psi_T$ | 1.8 | 0.94 |
| Beryllium $\psi_T$ | 3.8 | 0.293 |
| Neon $\psi_T$ | - | - |

Table 3: 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.

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| Trialfunction UPDATE ME | Numerical (s) | Analytical (s) | Ratio |
|---|---|---|---|
| Helium $\psi_T$ | 86.76 | 19.98 | 4.342 |
| Beryllium $\psi_{T2}$ | 1918.34 | | |

Table 4: 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.
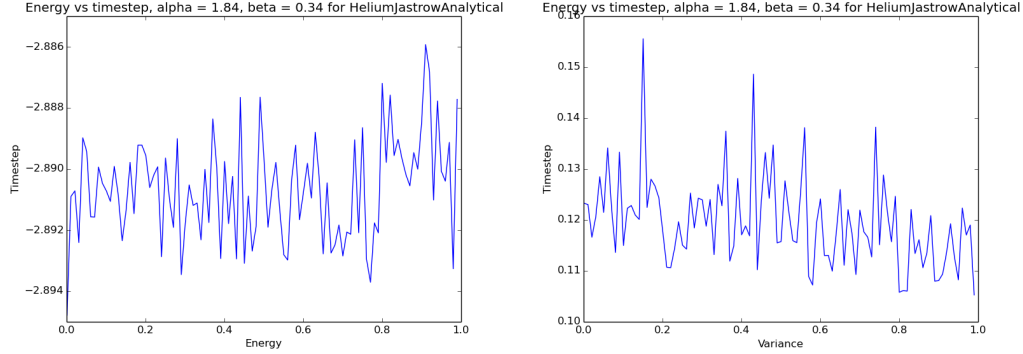


Figure 3: Plots for Helium $\psi_T$ for the energy versus the timestep, and the variance versus the timestep.

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 2 and should have been used.

### 3.1.2  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 4.

### 3.1.3  Calculations using importance sampling

We now introduce importance sampling to our calculations. We search for the optimal variables and find them to be $\alpha = FILLME$ and $\beta = FILLME$, which gives an energy of $-FILLME$. The energy and variance as a function of the timestep, $\delta t$ is shown in figure 3. BLOCKING. COMPARISON AND COMMENTS.

### 3.1.4  Onebody density

### 3.1.5  Conjugate gradient with GTOs

| Atom | VMC | References |
|---|---|---|
| Beryllium | $-14.3888$ | $-14.667$ |
| Neon | $-127.961$ | $-128.928$ |

Table 5: Comparison of energies found with Variational Monte Carlo method and energies found in research papers [3] [1]

| **Trialfunction** | $\alpha$ | $\beta$ |
|---|---|---|
| Beryllium $\psi_{T2}$ | 3.8 | 0.293 |
| Neon $\psi_{T2}$ | 10.22 | 0.091 |

Table 6: The values for $\alpha$ and $\beta$ where found by doing running Monte Carlo calculation with over a mesh of different $\alpha$ and $\beta$ values. For Beryllium each Monte Carlo run went over 10000000, using importance sampling. For Neon each run went over 5000, also with importance sampling. Then the run with the lowest energy gave the $\alpha$ and $\beta$ values.

## 3.2 Variational Monte Carlo calculations of the Beryllium and Neon atoms

We attempt to solve the ground state energy for the Beryllium atom and Neon atom using a Variational Monte Carlo calculation with importance sampling. We have used the trial functions (16) for Beryllium and (23) for Neon which uses $\alpha$ and $\beta$ as variational parameters.

**NEED TO CALCULATE VALUES AGAIN**

For Beryllium we have the Alpha and Beta values $\alpha = 4.0$ and $\beta = 0.31$. We use $10^6$ cycles and find the energy to be $-14.3795$, with a variance of 0.0020. For Neon, with $5 \times 10^5$ cycles we get an energy of $-127.936$ with a variance of 0.0548.

From reseach papers we find the value for energy in the ground state of Beryllium to be $-14.667$ [3] and the value for energy in the ground state of Neon to be $-128.928$ [1]. In table 5 we compare results obtained with our Variational Monte Carlo method with results from various research papers.

### 3.2.1 Alpha and Beta Values

To find optimal Alpha and Beta values for the atoms we run VMC with ranges of different values for $\alpha$ and $\beta$. The resulting plots of variance and energy for different combinations are given in figure 4 for Beryllium and figure 5 for Neon. The optimal values are shown in table 6. As VMC runs slowly for Neon, because it has 10 electrons, we were only able to run over the range of Alpha and Beta values with $10^5$ cycles. This is reflected in the higher variance, and the spikes in the variance plot.
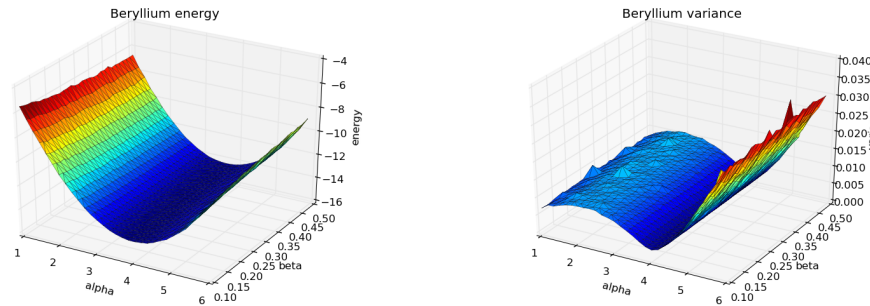


Figure 4: Energy (left) and variance (right) for different Alpha and Beta values for Beryllium, using $10^6$ cycles.
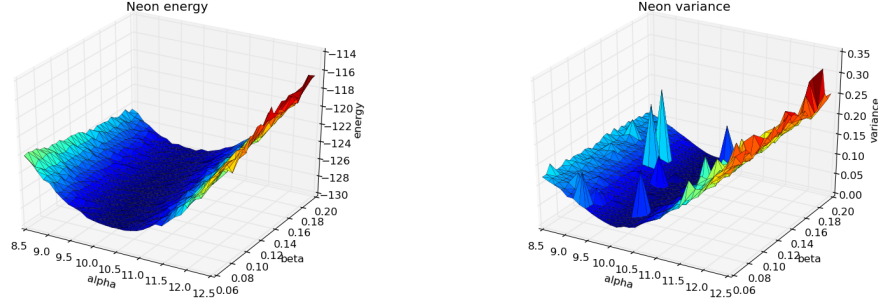
Figure 5: Energy (left) and variance (right) for different Alpha and Beta values for Neon, using $10^5$ cycles.

| Num. of processes | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Speedup | 1.0 | 1.97 | 2.90 | 3.35 |

Table 7: MPI speedup

### 3.2.2   Speedup with MPI

It is desirable to have a speedup as close as possible to the number of processors used. The speedup measured by our VMC program running 1, 2, 3 and 4 is shown in table 7 and figure 6. We see that the speedup is good for 2 and 3 processes, but for 4 processes suffers somewhat because it also have to run the OS and other programs.

### 3.2.3   Onebody densities / Comparisons / Without Jastrow

As we see in the verification section, without interaction the energies behave like hydrogen like wave functions. Comparing with the energies we obtain when also using interaction in the calculations we see that the Jastrow factor offers a good improvement on the energy, especially for larger systems.

### 3.2.4   Charge Density

The charge density gives measure of how often the electrons occupies certain area in the Monte Carlo simulation, in figure 7 the square of the norm of the distance is plotted. On the
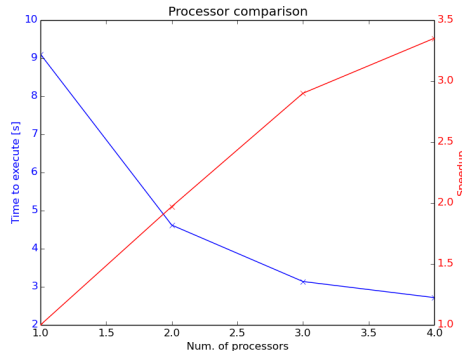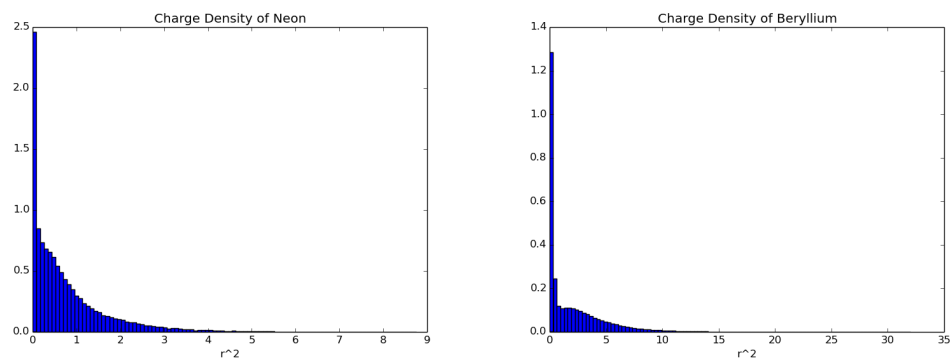


Figure 6: MPI speedup

Figure 7: Charge densities for Neon and Beryllium with the x-axis representing how far away from the atomcenter the electrons are.

Neon atom the electrons have a closer distribution to the center that is caused by the more electrically charged core of Neon compared to Beryllium.

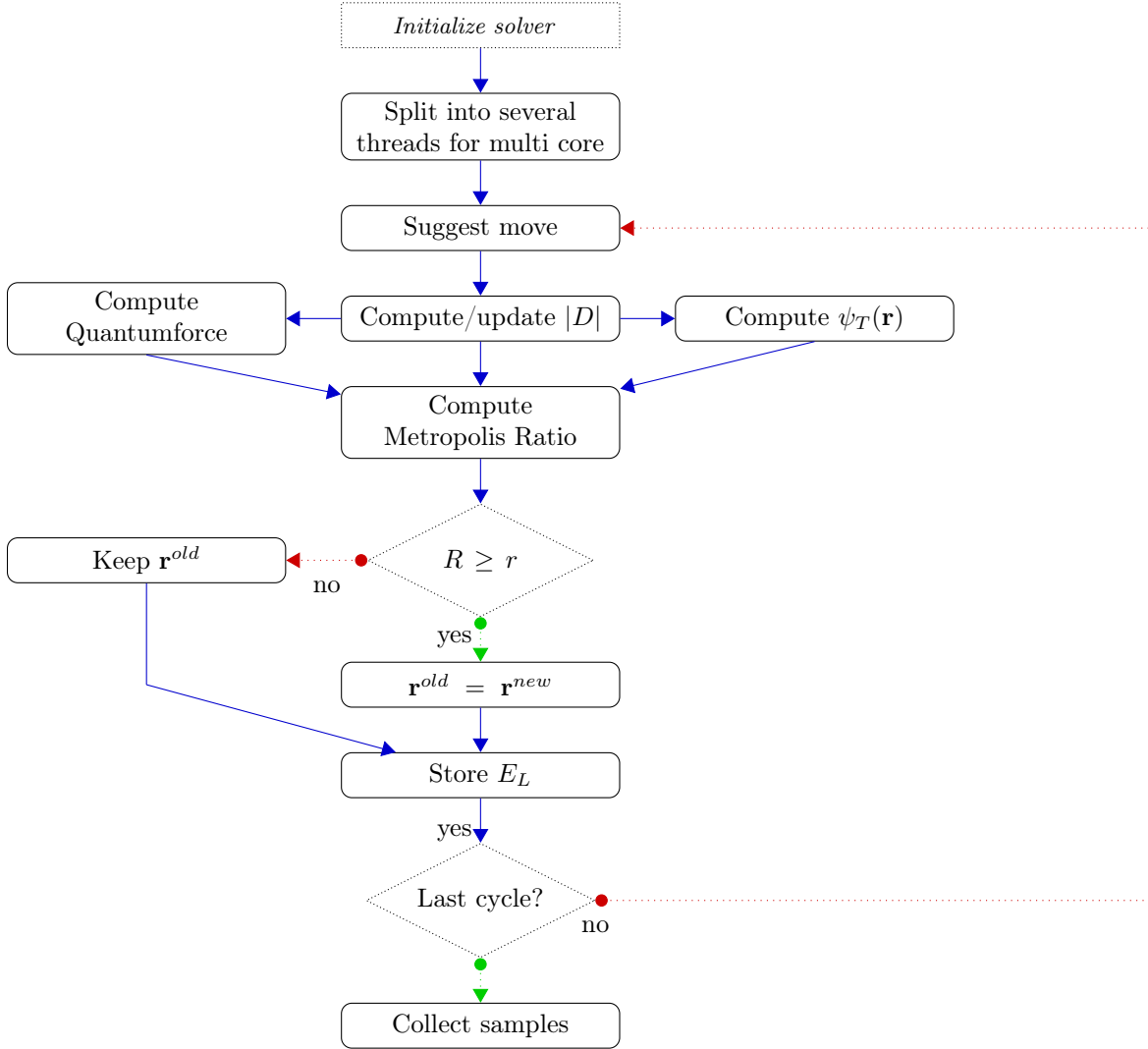# 4 Conclusions and discussion

## 4.1 Critique on the exercise

Figure 8: Schematic overview over the workflow of the VMC solver

# A    Program overview

# B    Class structure

# C    Closed expression for noncorrelation Helium trial-function

## C.1    Derivation of local energies, using radial coordinates

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:
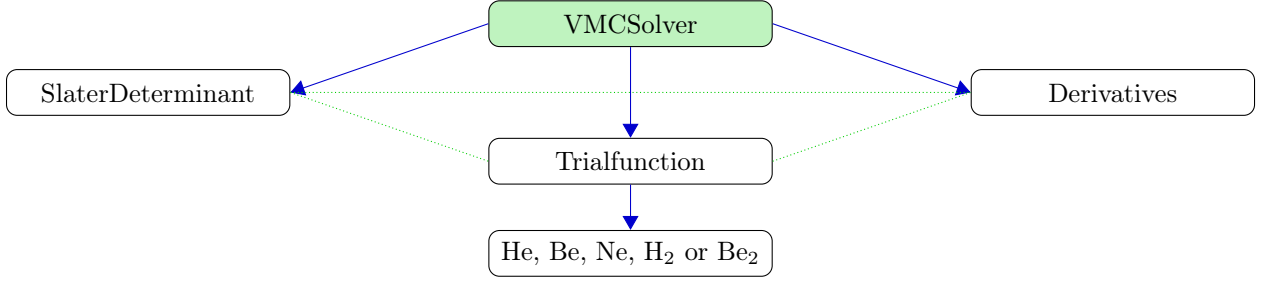
Figure 9: Class and subclass structure used by the program

$$E_L = \sum_{i,i<j} \frac{1}{\Psi_T(\mathbf{r_i}, \mathbf{r_{ij}})} \hat{H} \Psi_T(\mathbf{r_i}, \mathbf{r_{ij}}) \tag{92}$$

$$= \sum_{i,i<j} \frac{1}{\Psi_T(\mathbf{r_i}, \mathbf{r_{ij}})} \left( -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \right) \Psi_T(\mathbf{r_i}, \mathbf{r_{ij}}) \tag{93}$$

$$= \sum_{i,i<j} -\frac{1}{2\Psi_T} \left( \nabla_i^2 \Psi_T \right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \tag{94}$$

Let us change derivation variables:

$$-\frac{1}{2\Psi_T} \left( \nabla_i^2 \Psi_T \right) = \sum_{m=1}^{3} -\frac{1}{2\Psi_T} \left( \frac{\partial^2 \Psi_T}{\partial x_m^2} \right)_i \tag{95}$$

$$= \sum_{m=1}^{3} -\frac{1}{2\Psi_T} \left( \frac{\partial}{\partial x_m} \left( \frac{\partial \Psi_T}{\partial r_i} \frac{\partial r_i}{\partial x_m} \right) \right)_i \tag{96}$$

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

$$= \sum_{m=1}^{3} -\frac{1}{2\Psi_T} \left( \frac{\partial}{\partial x_m} \left( \frac{\partial \Psi_T}{\partial r_i} \frac{x_m}{r_i} \right) \right)_i \tag{97}$$

$$= \sum_{m=1}^{3} -\frac{1}{2\Psi_T} \left( \frac{\partial^2 \Psi_T}{\partial x_m \partial r_i} \frac{x_m}{r_i} + \frac{\partial \Psi_T}{\partial r_i} \frac{\partial}{\partial x_m} \left( \frac{x_m}{r_i} \right) \right)_i \tag{98}$$

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

$$= -\frac{1}{2\Psi_T} \left( \frac{\partial^2 \Psi_T}{\partial r_i^2} \frac{x_1^2 + x_2^2 + x_3^2}{r_i^2} + \frac{\partial \Psi_T}{\partial r_i} \frac{2(x_1^2 + x_2^2 + x_3^2)}{r_i^3} \right)_i \tag{99}$$

$$= -\frac{1}{2\Psi_T} \left( \frac{\partial^2 \Psi_T}{\partial r_i^2} + \frac{\partial \Psi_T}{\partial r_i} \frac{2}{r_i} \right) \tag{100}$$

Then the local energy becomes:

$$E_L = \sum_{i,i<j} -\frac{1}{2\Psi_T} \left( \frac{\partial^2 \Psi_T}{\partial r_i^2} + \frac{\partial \Psi_T}{\partial r_i} \frac{2}{r_i} \right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \tag{101}$$

We can apply this to the simple helium trialfunction with no electronic interaction to obtain the local energy.

### C.1.1 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 (101).

$$E_L = \sum_{i,i<j} -\frac{1}{2\Psi_T} \left( \frac{\partial^2 e^{-\alpha(r_i+r_j)}}{\partial r_i^2} + \frac{\partial e^{-\alpha(r_i+r_j)}}{\partial r_i} \frac{2}{r_i} \right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \tag{102}$$

$$E_L = -\frac{1}{2\Psi_T} \sum_{i=1}^{2} \left( \alpha^2 - \alpha \frac{2}{r_i} \right) \Psi_T - \frac{Z}{r_i} + \frac{1}{r_{ij}} \tag{103}$$

$$E_L = -\alpha^2 + (\alpha - Z) \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_{12}} \tag{104}$$

| Atom | Energy |
|-----------|------------------------|
| Hydrogen | $E_{min} = -\frac{1}{2}$ |
| Helium | $E_{min} = -4$ |
| Beryllium | $E_{min} = -20$ |
| Neon | $E_{min} = -200$ |

Table 8: Ground states for the different atoms without electron-electron interaction

# D    Verification of the model

To ensure that the program produces valid results as it gets more complicated we have implemented several different tests of smaller parts of the program that all should be met if the VMC solver is functioning properly. This section consists of a list of the different tests.

## D.1    Verification of the general Monte Carlo method

Since the wavefunction for a Hydrogen atom can be calculated analytically, see equation (105), a Monte Carlo calculation with that wavefunction should return an exact value for the energy.

$$\Psi(\rho) = \alpha \rho e^{-\alpha \rho} \qquad \text{With local energy:} \qquad E_L(\rho) = -\frac{1}{\rho} - \frac{\alpha}{2}\left(\alpha - \frac{2}{\rho}\right) \qquad (105)$$

So a VMC calculation runrun with a Hydrogen atom with $\alpha = 1$ it should produce an energy of exactly $-0.5$ with 0 variance.

## D.2    Verification of the Slater determinant and the laplacian Slaterdeterminant ratio

To verify the Slater determinant part of the trialfunctions we consider the atoms without any electron-electron interactions. Then it is a one-body system like hydrogen and can be calculated analytically, see [2], and we get exact wavefunctions and energy with 0 variance.

In this case, where the correlation derivatives disappear, the kinetic part of the local energy gets simplified, from (53), to the following

$$\frac{\nabla^2 \Psi_T}{\Psi_T} = \frac{\nabla^2 |D_\uparrow|}{|D_\uparrow|} + \frac{\nabla^2 |D_\downarrow|}{|D_\downarrow|}$$

To reproduce the correct results both the Slater determinant and it's laplacian needs to be correct.

## D.3    The gradient

The gradient is used in the calculation of the quantum force, and all it's components is used in the calculation of the so by testing that this is correctly reproduced we get an inclination several terms are correct, $\frac{\nabla |D_\uparrow|}{|D_\uparrow|}$, $\frac{\nabla |D_\downarrow|}{|D_\downarrow|}$ and $\frac{\nabla \Psi_C}{\Psi_C}$.

The wavefunctions should be correct due to the earlier test, D.2, so a numerical derivation of the trialfunction should produce a correct gradient, which is then used to test the analytical version against.

**NB!!!!!!!!!!!!!!!! Does not pass at the moment...... Not sure why**

## D.4    The correlation laplacian

Due to the earlier two tests, D.2 and D.3, we can be fairly certain that all the terms except the laplacian-correlation-ratio, $\frac{\nabla^2 \Psi_C}{\Psi_C}$ in the local energy equation (53) is correct. So by then comparing the analytical version of the local energy to the numerical version we can verify that the last term is also correct.

## D.5 Local Energy in Helium

For Helium we have a complete closed expression for the local energy, $E_l$ (104), we use this to check that the local energy calculation, see "Efficient calculation of stuff chapters"!!!!!!!!!, used on the more complicated atoms also replicates the local energy for the simpler atom which it does.

## D.6 Verification of correlation gradient

The correlation gradient ratio is checked by calculating what calculating it directly for Helium, and then comparing this value against value produced by the program.

Let us consider the gradient ratio of the Padè-Jastrow factor in Helium, $\frac{\nabla \psi_C(\mathbf{r_{12}})}{\psi_C(\mathbf{r_{12}})}$ with $\psi_C(\mathbf{r_{12}}) = e^{\frac{r_{12}}{2(1+\beta r_{12})}}$. Using the results from equation (65) on Helium for the first electron we get

$$\left[ \frac{\nabla \Psi_C}{\Psi_C} \right]_1 = \frac{1}{\Psi_c} \frac{\partial \Psi_C}{\partial x_k} = \frac{\mathbf{r_{12}}}{r_{12}} \frac{\partial}{\partial r_{12}} \left( \frac{r_{12}}{2(1+\beta r_{12})} \right) - \frac{\mathbf{r_{21}}}{r_{21}} \frac{\partial}{\partial r_{21}} \left( \frac{r_{21}}{2(1+\beta r_{21})} \right) \tag{106}$$

$$= 2 \frac{\mathbf{r_{12}}}{r_{12}} \frac{\partial}{\partial r_{12}} \left( \frac{r_{12}}{2(1+\beta r_{12})} \right) \tag{107}$$

$$= \frac{\mathbf{r_{12}}}{r_{12}} \frac{1}{(1+\beta r_{12})^2} \tag{108}$$

Testing that the program reproduces this for the helium atom indicates the $\frac{\nabla \Psi_C}{\Psi_C}$ is being calculated correctly.

## D.7 Hydrogen Molecule

**NB!!!!!!!!!!!!!!! Write this**

# References

[1] J. S. Binkley and J. A. Pople. Møller–plesset theory for atomic ground state energies. *International Journal of Quantum Chemistry*, 9(2):229–236, 1975.

[2] David J Griffiths. *Introduction to Quantum Mechanics*. Pearson, 2005.

[3] Jacek Koput. *The ground-state potential energy function of a beryllium dimer determined using the single-reference coupled-cluster approach*. July 2011.