

Abstract

Write something interesting about the main findings of the project.

1 Introduction

This is part 1 of a 3 part project to evaluate the ground state properties of some single atoms and diatomic molecules, using variational Monte Carlo simulations.

A compulsory part of doing this is using expandable programs that can handle systems of increasing particles and complexity. This poses many challenges; implementational, statistical, numerical and mathematical. The atoms studied here are Helium and Beryllium, and the ground state energies and one-body densities are the properties we are interested in. The computational methods to do this is a main focus of part 1.

We are interested in the ground state energies, because the results are more easily verifiable. One aim of the project is to see how effective our numerical methods are in computing these quantities, and compare the methods to each other, by applying statistical tools.

As stated, there are several challenges. Here basic mathematical, computational, statistical models are dealt with, and applied to the second most simple system, Helium.

All results displayed in this article are gathered from our variational Monte Carlo program.

2 Methods

The Helium atom consists of two electrons orbiting a nucleus, where the distance between electron 1 and the

nucleus, and electron 2 and the nucleus are labeled as $r_1 = \sqrt{x_1^2 + y_1^2 + z_1^2}$ and $r_2 = \sqrt{x_2^2 + y_2^2 + z_2^2}$.

The total potential energy of the system is modelled as

$$V(r_1, r_2) = -\frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

where the interaction between each electron and the nucleus is given by the two first terms. The mutual electron-electron repulsion is given by the last. The distance between the electrons is $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$.

The Hamiltonian of the system is thusly,

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

The radii $\{r_1, r_2, r_{12}\}$ are scaled, and are dimensionless.

The Laplace operator of a function f in three dimensions, $\nabla^2 f$, can be represented as

$$\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}\right)f + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta}\right)f + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} f$$

in spherical coordinates, and as

$$\left(\frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}\right)f$$

in cartesian coordinates.

2.1 The Variational Principle

The Variation Principle states that if we have a Hamiltonian $\hat{\mathbf{H}}$ and a trial wavefunction ψ_T , an upper bound for the ground state energy is given by equation (1)

$$E_0 \leq \langle H \rangle = \frac{\int d\mathbf{r}_1 d\mathbf{r}_2 \psi_{T_i}^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) \hat{\mathbf{H}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) \psi_{T_i}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12})}{\int d\mathbf{r}_1 d\mathbf{r}_2 \psi_{T_i}^*(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12}) \psi_{T_i}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_{12})} \quad (1)$$

2.2 Variational Monte Carlo (VMC)

The integrals to be solved in the variational method, are often too large to be solved by traditional integral methods.

Therefore, we introduce the brute-force Monte Carlo method to solve the integrals.

2.2.1 VMC Algorithm

- Initialization.
 - Set a fixed number of MC steps.
 - Choose initial position \mathbf{R} and variational parameters α .
 - Calculate $|\psi_T(\mathbf{R})|^2$
- Set energy and variance and start the MC calculation.
 - Find the trial position $\mathbf{R}' = \mathbf{R} + \delta \times r$, where $r \in [0, 1]$ is randomly selected.
 - Use the Metropolis algorithm to determine if the move $w = \frac{P(\mathbf{R}')}{P(\mathbf{R})}$ is accepted or rejected.
 - Given that the move is accepted, set $\mathbf{R} = \mathbf{R}'$.
 - Update averages.
- Compute final averages.

2.3 The Metropolis Algorithm

2.4 Importance Sampling

2.5 Statistical Analysis

The MC calculation are a set of computational *experiments*, and to evaluate the results we need to implement statistical analysis of these experiments to find *statistical* errors.

For this purpose, we implement the *blocking technique*.

2.5.1 Blocking Implementation

- Compute MC calculation, store samples in array.
- Loop over a set of block sizes n_b .
- For each n_b , calculate the mean of the block and store these values in a new array.
- Take the mean and variance of this array.
- Store results.

2.6 The Trial Wavefunctions for Helium

To conclude if the computational methods are implemented correctly, we should check that the results are reasonable. We do this by finding a mathematical approximation of the closed form expression.

Given the trial wavefunction $\psi_T(\mathbf{R}, \alpha)$, we define a new quantity

$$E_L = \frac{1}{\psi_T} \hat{H} \psi_T$$

where α is a set of variational parameters. E_{L1} is called the local energy

2.6.1 The first trial wavefunction

We first model the variational solution with a trial function of one variation parameter α . It has the form

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

The only part of the operator \hat{H} that affects the wavefunction are the Laplace operators.

Since ψ_{T1} is only spatially dependent on r_1 and r_2 , the Laplaces of ψ_{T1} reduces to

$$\nabla_i^2 \psi_{T1} = \left(\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial}{\partial r_i} \right) \psi_{T1} = \left(\alpha^2 - \alpha \frac{2}{r_i} \right) \psi_{T1}$$

for $i = 1, 2$, since

$$\begin{aligned} \frac{\partial}{\partial r_i} e^{-\alpha(r_1+r_2)} &= -\alpha e^{-\alpha(r_1+r_2)} \\ \frac{\partial^2}{\partial r_i^2} e^{-\alpha(r_1+r_2)} &= \alpha^2 e^{-\alpha(r_1+r_2)} \end{aligned}$$

This gives us the following trial energy

$$\begin{aligned} E_{L1} &= \frac{1}{\psi_{T1}} \left(-\alpha^2 + \alpha \left(\frac{1}{r_1} + \frac{1}{r_1} \right) - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \right) \psi_{T1} \\ &= (\alpha - 2) \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_{12}} - \alpha^2 \end{aligned}$$

The 2 in the $\alpha - 2$ term is the number of protons, Z .

2.6.2 The second trial wavefunction

To approximate the closed-form solution even better, we assume another trial wavefunction based on ψ_{T1} , namely

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

The second part is dependent on the distance between the electrons, and is called the correlation part, which accounts for the effect between the electrons.

One can then in the same way as for ψ_{T1} calculate the local energy. The correlations part will give us some trouble when we try to calculate the Laplacian. This is due to the distance between \mathbf{r}_1 and \mathbf{r}_2 , since this quantity is dependent on the angles φ and θ . It has the form

$$E_{L2} = E_{L1} + \frac{1}{2(1 + \beta r_{12})^2} \left(\frac{\alpha(r_1 + r_2)}{r_{12}} \left(1 - \frac{\mathbf{r}_1^T \mathbf{r}_2}{r_1 r_2} \right) - \frac{1}{2(1 + \beta r_{12})^2} - \frac{2}{r_{12}} + \frac{2\beta}{1 + \beta r_{12}} \right)$$

2.7 The Trial Wavefunction for Beryllium

We can use a trial wavefunction on the same form as for Hydrogen and Helium

$$\psi_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \text{Det}(\phi_1(\mathbf{r}_1), \phi_2(\mathbf{r}_2), \phi_3(\mathbf{r}_3), \phi_4(\mathbf{r}_4)) \cdot \prod_{i < j}^4 \exp\left(\frac{r_{ij}}{2(1 + \beta r_{ij})}\right)$$

where we approximate the Slater determinant *Det* as

$$\psi_T(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \propto (\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2) - \phi_{1s}(\mathbf{r}_2)\phi_{2s}(\mathbf{r}_1)) \cdot (\phi_{1s}(\mathbf{r}_3)\phi_{2s}(\mathbf{r}_4) - \phi_{1s}(\mathbf{r}_4)\phi_{2s}(\mathbf{r}_3))$$

where the hydrogenic wavefunctions for the two spin orbitals are given by

$$\phi_{1s}(\mathbf{r}_i) = e^{-\alpha r_i}$$

and

$$\phi_{2s}(\mathbf{r}_i) = (1 - \alpha r_i/2) e^{-\alpha r_i/2}$$

2.8 Onebody Density and Charge Density

The one-body density is computed from the form

$$\rho(\mathbf{R}) = |\psi(\mathbf{R})|^2$$

This is implemented as NOTE: ... in our program.

2.9 Implementation

The methods described above are implemented in an object oriented C++ program which is simple to use, and does not have any dependencies.

Most of the code is contained in the class VMC-Solver.cpp and VMCSolver.h. These were created to contain the full system and parameters for a single run.

To start a simulation one must instantiate the solver and initialize the system, either by file and/or manually. After this the integration can be run and all data will be contained in the solver object. The last step is to collect data from the solver.

All plot data are generated by individual programs using the mentioned solver. Plots are generated using python.

3 Results

3.1 Helium: Estimating α and β

These parameters decide the minimal ground energy for the system, and both should be adjusted simultaneously to reach the most optimal value of the energy. First we sample the parameterspace of the first trial wave function. This function had a minimum of about NOTE: () + statistical inaccuracy here??? This was the first value of α that was used in sampling the parameterspace with beta in the second trial wavefunction. Using the computed β -value we again sampled the energy as a function of α . NOTE: This can be seen in ...

FOOTNOTE¹

3.2 Helium: Comparing ψ_{T1} and ψ_{T2}

Firstly the first and second trial wavefunctions for Helium are compared. The difference between these two are that there are no correlation term in the first wavefunction. This makes computations much faster, but we would expect that our results are farther away from the experimental value of the ground state. This is done using a numerical approximation of the local energy of the particles.

¹Finding the statistically most optimal values of β is challenging, because the mean variance is substantial compared to the energies around the flat region.

3.3 Helium: Closed Form Local Energy

The local energy has a closed form solution for Helium, this has been implemented in fig.... Here we can see something.

3.4 Helium: Importance Sampling

Now we would like to see how the program does with importance sampling instead of static steplength. This we can see in NOTE: fig ...

3.5 Helium: Evaluating Ground State and Density

With our optimal parameters, we see that using NOTE: something something gives the lowest variance of the mean and the lowest mean energy. Compared to experimental values, this result is statistically significant.

4 Discussion

4.1 Parameter Space

After estimating the parameters in the start of Helium, we didn't adjust them anymore. The standard deviation of the mean was not considered when estimating the values of alpha and beta. Performing blocking with our program would require full sampling of every step which stores about 10 mb for every value of alpha and beta.

4.2 Testing of the Solver

Here we did unittests.