Computational Physics II
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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 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   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.

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

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

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

$$\Psi_T(r_1, r_2, r_{12}) = e^{-\alpha(r_1+r_2)} e^{\beta r_{12}}$$

should fulfill the condition that the wavefunction is finite everywhere.

2.3 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. However the computation of the Slater determinant can be simplified for beryllium. Sticking to hydrogen-like wave functions, we can write the trial wave function for beryllium as

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \mathbf{r_4}) = Det\left(\phi_1(\mathbf{r_1}), \phi_2(\mathbf{r_2}), \phi_3(\mathbf{r_3}), \phi_4(\mathbf{r_4})\right) \prod_{i<j}^{4} \exp\left\{\left(\frac{r_{ij}}{2(1 + \beta r_{ij})}\right)\right\}, \quad (12)$$

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

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

and

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

The Slater determinant for the ground state of the Beryllium atom can be approximated as

$$\psi_T(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_3}, \mathbf{r_4}) \propto (\phi_{1s}(\mathbf{r_1})\phi_{2s}(\mathbf{r_2}) - \phi_{1s}(\mathbf{r_2})\phi_{2s}(\mathbf{r_1}))\,(\phi_{1s}(\mathbf{r_3})\phi_{2s}(\mathbf{r_4}) - \phi_{1s}(\mathbf{r_4})\phi_{2s}(\mathbf{r_3})).$$

Furthermore, for the Jastrow factor,

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

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

$$a = \frac{1}{4},$$

and if they have opposite spins, we get

$$a = \frac{1}{2}.$$

2.4 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:

$$E_L = \sum_{i,i<j} \frac{1}{\Psi_T(\mathbf{r_i}, \mathbf{r_{ij}})} \hat{H}\Psi_T(\mathbf{r_i}, \mathbf{r_{ij}}) \tag{13}$$

$$= \sum_{i,i<j} \frac{1}{\Psi_T(\mathbf{r_i}, \mathbf{r_{ij}})} \left(-\frac{\nabla_i^2}{2} - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}}\right) \Psi_T(\mathbf{r_i}, \mathbf{r_{ij}}) \tag{14}$$

$$= \sum_{i,i<j} -\frac{1}{2\Psi_T}\left(\nabla_i^2 \Psi_T\right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \tag{15}$$

Let us change derivation variables:

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

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

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

$$= \sum_{m=1}^{3} -\frac{1}{2\Psi_T}\left(\frac{\partial}{\partial x_m}\left(\frac{\partial\Psi_T}{\partial r_i}\frac{x_m}{r_i}\right)\right)_i \tag{18}$$

$$= \sum_{m=1}^{3} -\frac{1}{2\Psi_T}\left(\frac{\partial^2\Psi_T}{\partial x_m\partial r_i}\frac{x_m}{r_i} + \frac{\partial\Psi_T}{\partial r_i}\frac{\partial}{\partial x_m}\left(\frac{x_m}{r_i}\right)\right)_i \tag{19}$$

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

$$= -\frac{1}{2\Psi_T}\left(\frac{\partial^2\Psi_T}{\partial r_i^2}\frac{x_1^2+x_2^2+x_3^2}{r_i^2} + \frac{\partial\Psi_T}{\partial r_i}\frac{2(x_1^2+x_2^2+x_3^2)}{r_i^3}\right)_i \tag{20}$$

$$= -\frac{1}{2\Psi_T}\left(\frac{\partial^2\Psi_T}{\partial r_i^2} + \frac{\partial\Psi_T}{\partial r_i}\frac{2}{r_i}\right) \tag{21}$$

Then the local energy becomes:

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

2.4.1   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

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

Let us set this trialfunction into the equation for the local energy (22).

$$E_L = \sum_{i,i<j} -\frac{1}{2\Psi_T}\left(\frac{\partial^2 e^{-\alpha(r_i+r_j)}}{\partial r_i^2} + \frac{\partial e^{-\alpha(r_i+r_j)}}{\partial r_i}\frac{2}{r_i}\right) - \frac{Z}{r_i} - \frac{Z}{r_j} + \frac{1}{r_{ij}} \tag{23}$$

$$E_L = -\frac{1}{2\Psi_T}\sum_{i=1}^{2}\left(\alpha^2 - \alpha\frac{2}{r_i}\right)\Psi_T - \frac{Z}{r_i} + \frac{1}{r_{ij}} \tag{24}$$

$$E_L = -\alpha^2 + (\alpha - Z)\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} \tag{25}$$

2.5 Verification of the model

The wavefunction for a Hydrogen atom is known, see equation (26), a Monte Carlo calculation for an exact wavefunction will give a exact result.

$$\Psi(\rho) = \alpha\rho e^{-\alpha\rho} \qquad \text{With local energy:} \qquad E_L(\rho) = -\frac{1}{\rho} - \frac{\alpha}{2}\left(\alpha - \frac{2}{\rho}\right) \qquad (26)$$

If the VMC calculation is run with a Hydrogen atom with $\alpha = 1$ it should produce an energy of exactly -0.5 with 0 variance. A check for this is implemented as a unit test in the program.

The closed expressions of the local energy has also been verified by comparing them to numerical versions and checked that they produced similar values.

2.6 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 generation 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

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

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

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

where η is a random variable. This gives us a new position

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

Here ξ is gaussian random variable and Δt 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

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

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

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

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

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

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

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

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 fiven by the Green's function

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

This means that the Metropolis algorithm

$$A(y, x) = \min(1, q(y, x))),$$

where

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

is replaced by the Metropolis-Hastings algorithm,

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

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 $\beta = 0.94$, and we get a minimum energy of -2.8979105, which is considerably better than without the Jastrow factor.

Finally we use our Variational Monte Carlo machinery to find the ground state energy for a beryllium atom. Since beryllium has 4 electrons, compared to the 2 in helium, the computation is much slower and we only had time to run it for 10^6 cycles. We then find the lowest energy to be -14.4127 with $\alpha = 3.8$ and $\beta = 0.293$.

From reseach papers we find the value for energy in the ground state of helium to be -2.9037 [Toichiro Kinoshita] and the value for energy in the ground state of beryllium to be -14.667 [Jacek Koput]. In table ?? we compare results obtained with our Variational Monte Carlo method with results from various research papers.
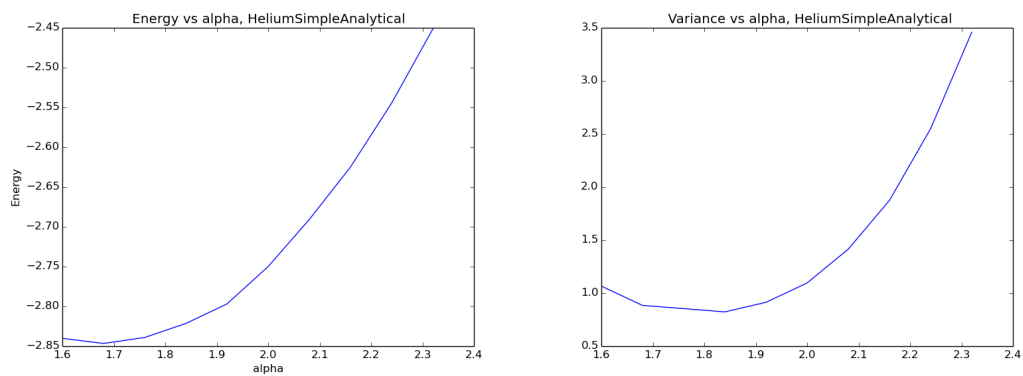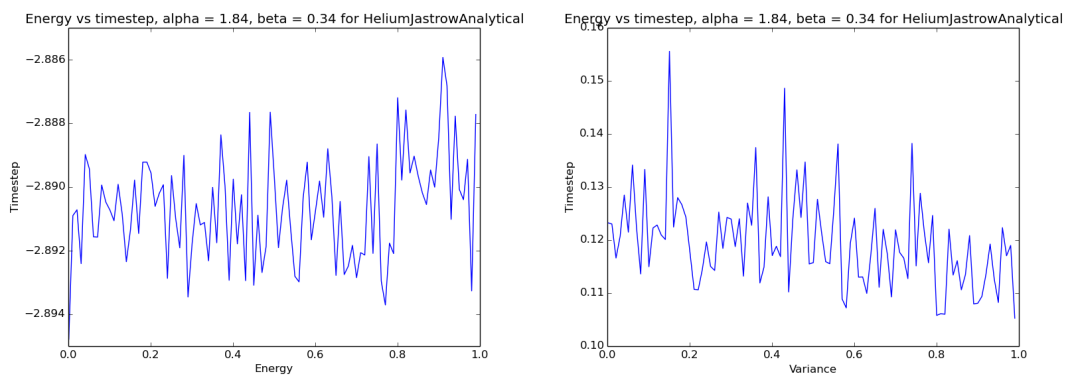
Figure 1: To be filled in
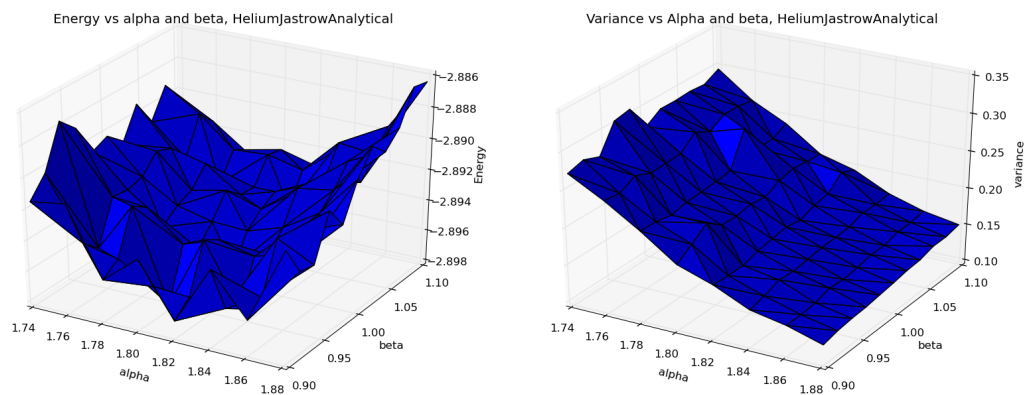

Figure 2: To be filled in

Figure 3: To be filled in

Atom	VMC	References
Helium ψ_{T1}	-2.8442	-2.9037
Helium ψ_{T2}	-2.8979	-2.9037
Beryllium	-14.4127	-14.667

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

Trialfunction	α	β
Helium ψ_{T1}	1.65	-
Helium ψ_{T2}	1.8	0.94
Beryllium ψ_{T2}	3.8	0.293

Table 2: The values for α and β where found by doing running Monte Carlo calculation with over a mesh of different α and β values, with stepssize 0.02. Each Monte Carlo run went over 10000000, using importance sampling. Then the run with the lowest energy gave the α and β values

3.1 Alpha and Beta Values

Table 2 shows the values, for α and β 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 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 3 and should have been used.

3.2 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 3.

4 Conclusions and perspectives

4.1 Parameter grid and values

The algorithm by just minimizing the energy to find the best fits for α and β could be improved since both the energy and it's variance should be minimized with a correct wavefunction. So the algorithm should take into account that and find the combined lowest energy and variance and use that to find the best values for the parameters. A homogeneous is used to search through the different α and β and by improving this the

Trialfunction	Numerical (s)	Analytical (s)	Ratio
Helium ψ_{T1}	61.75	14.34	4.307
Helium ψ_{T2}	86.76	19.98	4.342
Beryllium ψ_{T2} 1918.34			

Table 3: 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

speed of the program would be greatly improved. If for example it first did a coarse run, then found the best value searched in the vicinity of that point with a higher resolution it would be improved.

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.

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

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