

## Variational Monte Carlo Method

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**Abstract:** Scope of this term paper is to look into Quantum monte carlo methods, specifically *Variational monte carlo methods*. A description of the method would be given supplemented by code and some applications

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# 1 Variational Principle

Variational principle in quantum mechanics is an approximate method to find ground state energy of a system, generally of many body quantum systems. The main idea of variational method is that we take an ansatz find the expectation value of energy with that ansatz. If the ansatz depend on some set of parameters, the calculates energy value would also depend on those set of parameters. It can be shown that, the calculated expectation value would be an upper bound for the ground state energy. Hence, in principle if we try to minimize the calculated expectation value of energy with respect to the parameters, we should hit the ground state energy[3].

The method is given below step by step:

1. We need to come up with an ansatz for finding the expectation value. This ansatz is found by looking at the symmetry of the problem. We can include some parameters to tune the ansatz. Let us call such ansatz  $|\psi_0\rangle = |\psi_0(\alpha_1, \alpha_2, \dots, \alpha_n)\rangle$
2. Next, calculate the expectation value of the energy. This value will depend on the parameters  $\alpha_1, \alpha_2, \dots, \alpha_n$ .

$$E_0(\alpha_1, \alpha_2, \dots, \alpha_n) = \frac{\langle \psi_0(\alpha_1, \alpha_2, \dots, \alpha_n) | \hat{H} | \psi_0(\alpha_1, \alpha_2, \dots, \alpha_n) \rangle}{\langle \psi_0(\alpha_1, \alpha_2, \dots, \alpha_n) | \psi_0(\alpha_1, \alpha_2, \dots, \alpha_n) \rangle} \quad (1)$$

. The denominator is to make sure that the ansatz is normalized.

3. The next step is to find  $\alpha_i$ s such that  $\frac{\partial E_0}{\partial \alpha_i} = 0$
4. Finally substitute the values of  $\alpha_i$ s found from step 3 in the expectation value defined by eq (1) to get approximate ground state energy.

This method can very well be applied to excited state as well. For example, for first excited state all we need to do is to make sure that the ansatz chosen is orthogonal to the ground state wavefunction so that while minimizing the expectation value, we hit the first excited state energy.

The calculation of the expectation value, we need to evaluate an integral. That integral is most of the time high dimensional and hence, evaluating them is in general difficult. Variational monte carlo method is one of such method to evaluate higher order integrals.

# 2 Monte Carlo Integration and sampling technique

Before going further, let us take a look at monte carlo integration and the sampling techniques.

## 2.1 Monte Carlo Integration

The main idea of monte carlo integration is numerically computing an integral by using random numbers within the volume of integration. The approximation of the integral happens in the following way,

$$\int_a^b f(x)dx = (b-a) \int_a^b p(x)f(x)dx \approx \frac{b-a}{N} \sum_{i=1}^{i=N} f(x_i) \quad (2)$$

where,  $x_i$ s are random numbers in the interval  $[a, b]$  that follows the distribution  $p(x)$ . In this case,  $p(x)$  is just  $\frac{1}{b-a}$  i.e., a uniform distribution. However, this might not be the case as the "importance" of the function might not be equal everywhere in the volume of integration. This would mean only a few points would contribute significantly to the integral. We solve this by using a sampling algorithm called *importance sampling*.

## 2.2 Importance Sampling

This is a technique for choosing the points  $x_i$  where we evaluate the function. At these points the function's absolute value is large and those points will contribute more towards the integral. We can write the integral as,

$$\int_a^b f(x) = \int_a^b dx \rho(x) \left( \frac{f(x)}{\rho(x)} \right) \quad (3)$$

where  $\rho(x)$  is the distribution that samples the points  $x_i$  so that they are concentrated where  $f(x)$  is relevant. Let us call  $\frac{f(x)}{\rho(x)}$  as  $F(x)$ . The integral can now be written as,

$$\int_a^b F(x)dx \approx \frac{1}{N} \sum_{i=1}^N f(x_i) \quad (4)$$

Now, we will look at a way to sample  $\rho$ . This algorithm is called *Metropolis Algorithm*.

## 2.3 Metropolis Algorithm

When performing monte carlo integration it is important to sample the random points in a proper way, which we might know *a-priori*. The *metropolis algorithm* is a way to sample points, not randomly, but in a way such that the new sampled point depends on the previously chosen point. It uses a *Markov chain* for this.

We start with a Markov chain starting from the interior of the integration volume. The next element of that chain will be correlated to the this point and so on. While doing this, we need to keep in mind that the probability of going from one point one to point 2 is the same as probability of going from point 2 to point 1. This is called the *detailed balance*. The fate of the new generated point is decided by the following rules:

- If  $\rho(x_{i+1}) \geq \rho(x_i)$ , the point is accepted.
- $\rho(x_{i+1}) < \rho(x_i)$ , we accept the point with a likelihood of  $\frac{\rho(x_{i+1})}{\rho(x_i)}$

The result of this activity is a collection of random points that follow  $\rho(x)$ .

### 3 Variational Monte Carlo

Now we have to use the techniques described above to find the ground state energy. Writing down eq (1) explicitly in the integral form, we have

$$\langle E[\alpha] \rangle = \frac{\int d\vec{r} \psi_T^\dagger(\vec{r}, \alpha) H \psi_T(\vec{r}, \alpha)}{\int d\vec{r} \psi_T^\dagger(\vec{r}, \alpha) \psi_T(\vec{r}, \alpha)} \quad (5)$$

This equation can be written as,

$$\langle E[\alpha] \rangle = \frac{\int d\vec{r} \psi_T^\dagger(\vec{r}, \alpha) \psi_T(\vec{r}, \alpha) \left( \frac{H \psi_T(\vec{r}, \alpha)}{\psi_T(\vec{r}, \alpha)} \right)}{\int d\vec{r} \psi_T^\dagger(\vec{r}, \alpha) \psi_T(\vec{r}, \alpha)} \quad (6)$$

We now define, *Local Energy* and the probability distribution as,

$$E_L = \frac{H \psi_T(\vec{r}, \alpha)}{\psi_T(\vec{r}, \alpha)} \quad (7)$$

$$\rho(\vec{r}, \alpha) = \frac{\psi_T^\dagger(\vec{r}, \alpha) \psi_T(\vec{r}, \alpha)}{\int |\psi_T(\vec{r}, \alpha)|^2 d\vec{r}} = \frac{|\psi_T(\vec{r}, \alpha)|^2}{\int |\psi_T(\vec{r}, \alpha)|^2 d\vec{r}}$$

and,

Since metropolis compares two instances of the same distribution at two different points, the denominator can be ignored as it will be cancelled off during the comparison. Hence, the final distribution is

$$\rho(\vec{r}, \alpha) = \psi_T^\dagger(\vec{r}, \alpha) \psi_T(\vec{r}, \alpha) = |\psi_T(\vec{r}, \alpha)|^2 \quad (8)$$

With these definitions and the earlier definition of  $\rho$ , eq (5) can be written as,

$$\langle E[\alpha] \rangle = \int d\vec{r} \rho(\vec{r}, \alpha) E_L(\vec{r}, \alpha) \quad (9)$$

Note the similarity between eq (3) and eq (9). We convert this to a sum like eq (4). We get,

$$\langle E[\alpha] \rangle = \frac{1}{N} \sum_{i=1}^N E_L(\vec{r}_i) \quad (10)$$

where, N is the number of elements in the markov chain and  $r_i$  are sampled from the distribution eq (10)

## 4 Implementation

This section is to talk about implementing the algorithm. The code was written in Julia language<sup>[1]</sup> and the packages Pluto.jl and Plots.jl were used as a coding environment and the plotting packages.

### 4.1 The metropolis Algorithm

The code for the metropolis algorithm as function named "metropolis" was written as per the theory written in section 2.3. In order to build the markov chain, the length used for the two examples are given below,

1. **Harmonic Oscillator:** Since the ansatz is a gaussian, the length was chosen to be  $\frac{3}{\sqrt{2\alpha}}$ . This is to increase the efficiency as the probability distribution, which is square of gaussian dies out faster at higher lengths and that would mean, at larger points, the wavefunction is not much relevant.
2. **Hydrogen Atom:** For hydrogen atom the length was taken as  $\frac{1}{\sqrt{2\alpha}}$ . The length scale is in the units of *bohr's radius* which was set to be one for the calculations.
3. **Helium Atom:** For Helium atom the typical length was chosen to be 1 and all the constants are chosen to be one to simplify the calculations and theory.

### 4.2 Minimization

The main aim of variational principle is to give the value of parameters  $\alpha$  such that the expectation value of energy hits the ground state. Instead of choosing a gradient descent algorithm, the minimization algorithm involves finding the derivative of the population of the walkers and using that to find the next value of alpha according to the formula<sup>[2]</sup>,

$$\frac{dE}{d\alpha} = 2(\langle E_L \frac{d\ln(\psi_T)}{d\alpha} \rangle - E \langle \frac{d\ln(\psi_T)}{d\alpha} \rangle)$$

and the new alpha was chosen by,

$$\alpha_{n+1} = \alpha_n - \gamma \frac{dE}{d\alpha}$$

This expression can be found by differentiating eq (6).

## 5 Application

In this section, The two standard examples are considered for the algorithm.

## 5.1 1D Harmonic oscillator

The hamiltonian of the harmonic oscillator is given by,

$$\hat{H} = -\frac{1}{2}\nabla^2 + \frac{x^2}{2} \quad (11)$$

Let us choose one variational parameter  $\alpha$  and the trial wave function to be simply a gaussian,

$$\psi_T(x, \alpha) = e^{-\alpha x^2}$$

Using this as the ansatz, we can find the local energy and the distribution function to be,

$$\rho(x, \alpha) = e^{-2x^2} \quad (12)$$

$$E_L = \alpha + x^2\left(\frac{1}{2} - 2\alpha^2\right)$$

One reason why harmonic oscillator problem was chosen is that it is exactly solvable system and we can get the value of analytical expression for energy. From eq (9), if the ansatz and the probability is substituted, we can get the analytical value to be,

$$E_{Analytical} = \frac{1}{8\alpha}(4\alpha^2 + 1)$$

and similarly, for the variance, we have the analytical expression,

$$V_{Analytical} = \frac{(1 - 4\alpha^2)^2}{32\alpha}$$

## 5.2 Hydrogen Atom

The hydrogen atom is a problem of two particles. we can write the hamiltonian as,

$$\hat{H} = \frac{-1}{2}\nabla^2 - \frac{1}{r} \quad (13)$$

Working in the spherical coordinates, we can write this hamiltonian as,

$$\hat{H} = -\frac{1}{2}\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right] - \frac{1}{r} \quad (14)$$

The ansatz we shall choose would be a gaussian,

$$\psi_T(r, \alpha) = e^{-\alpha r^2} \quad (15)$$

With this ansatz we can get the local energy and the distribution function to be,

$$E_L = -\frac{1}{2}\left[\alpha^2 - \frac{2\alpha}{r}\right] - \frac{1}{r} \quad (16)$$

$$\rho(r, \alpha) = |\psi_T(r, \alpha)|^2 = e^{-2\alpha r^2}$$

### 5.3 Helium Atom

Helium atom is an atom with two electrons and will have an interaction term in the hamiltonian. This makes the problem non solvable analytically and hence we need to apply approximations and numerical technique to solve this. Let us have a look at the hamiltonian in detail first.

The hamiltonian of the helium atom is given by,

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

Here, the subscript 1 and 2 are for the two electrons involved. One important point to note about this hamiltonian is that, it only has terms that would affect the radial and the angular part of the wavefunction and nothing happens to the spin of the electron.

Now, since this is a two electron system we know that the join wave function is going to be anti-symmetric. Hence, we can write the trial wave function as a slater determinant,

$$\psi_T = \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) \\ \phi_1(r_2) & \phi_2(r_2) \end{vmatrix} \quad (17)$$

where the subscripts as usual denote the two electrons. The wavefunction  $\phi$  is the full wavefunction i.e., with the spatial part and the spin part. The aim of this report is to find the energy of the  $1s_2$  orbital where both the electrons are in the  $1s$  orbital and for the approximation we shall be using the hydrogen atom wavefunction for  $1s$  as the ansatz.

Now,  $\phi$  can be written as a product of the spatial wavefunction and the spin wavefunction,  $\psi_{1s}\alpha_1$  and  $\psi_{1s}\alpha_2$ . Here,  $\psi_{1s}$  is the hydrogen atom  $1s$  orbital which is,  $e^{\frac{Z}{r}}$  where the normalisation constant is ignored as it does not really matter in the calculations involved in the variational monte carlo.

Substituting in the slater determinant,

$$\psi_T = \begin{vmatrix} \psi_{1s}(r_1)\alpha_1(r_1) & \psi_{1s}(r_1)\alpha_2(r_1) \\ \psi_{1s}(r_2)\alpha_1(r_2) & \psi_{1s}(r_2)\alpha_2(r_2) \end{vmatrix} \quad (18)$$

By the property of the determinant the hydrogen wave functions can be pulled out and we would get a determinant only containing the spin part. Now, as we noted earlier the hamiltonian does nothing to the spin part and while solving TISE, that part can be pulled out of the hamiltonian and would get cancelled with the spin part on the RHS in the eigen value equation. Notice also in the starting expression for expectation of energy eq (5), the spin part can be pulled out and it would cancelled from the numerator and the denominator. Thus, we can just ignore this part. Finally we have the ansatz for the variational principle,

$$\psi_T(r_1, r_2) = \psi_{1s}(r_1) \cdot \psi_{1s}(r_2) = e^{\frac{Z}{r_1}} e^{\frac{Z}{r_2}}$$



For helium atom,  $Z = 2$ . We shall also include a correlation term to compensate for the electron-electron interaction. The correlation function that shall be considered here is the Pade-Jastro correlation function which is,

$$f(r_1, r_2) = e^{\frac{r_{12}}{2(1+\alpha r_{12})}}$$

where  $r_{12} = |r_2 - r_1|$  and  $\alpha$  is the variational parameter. This gives us the full ansatz as,

$$\psi_T = e^{-2r_1} e^{-2r_2} e^{\frac{r_{12}}{2(1+\alpha r_{12})}} \quad (19)$$

With this ansatz, now we can find the probability density and the local energy and proceed with the variational monte carlo algorithm. The local energy and the probability density is obtained as,

$$E_L = -4 + (\hat{r}_1 - \hat{r}_2)(\vec{r}_1 - \vec{r}_2) \frac{1}{r_{12}(1 + \alpha r_{12})^2} - \frac{1}{r_{12}(1 + \alpha r_{12})^3} - \frac{1}{4(1 + \alpha r_{12})^4} + \frac{1}{r_{12}}$$

## 6 Results

Here are the results that are obtained from the simulations of the systems according to the details mentioned in the previous sections.

### 6.1 Harmonic Oscillator

This system is an excellent test for the algorithm and the code as the solutions are known exactly. Hence, we can compare the simulation result with the actual result.

From figure 2, we can see the minimization process. At  $\alpha = 0.5$ , we have the minimum energy of  $E = 0.5$  which is expected as for a harmonic oscillator,

$$E_n = (n + \frac{1}{2})\hbar\omega$$

With the units,  $\hbar = \omega = 1$ , the ground state energy is indeed  $E_0 = \frac{1}{2}$ . Hence, the algorithm is works.

### 6.2 Hydrogen Atom

Now that we have applied and checked the code against harmonic oscillator, it can now be applied to the hydrogen atom case. Figure 3, shows how the energy expectation varies with the iteration timestep and we can see that it settles at a constant value of  $-0.5$ . Is this the correct ground state energy? Check, the ground state energy,  $E_0 = -\frac{Z^2 e^4 m}{2\hbar^2}$ . With the reduced units  $e = m = \hbar = 1$  and  $Z = 1$  (for hydrogen,  $Z = 1$ ),  $E_0 = -\frac{1}{2}$ . Hence, VMC gives the correct ground state energy.

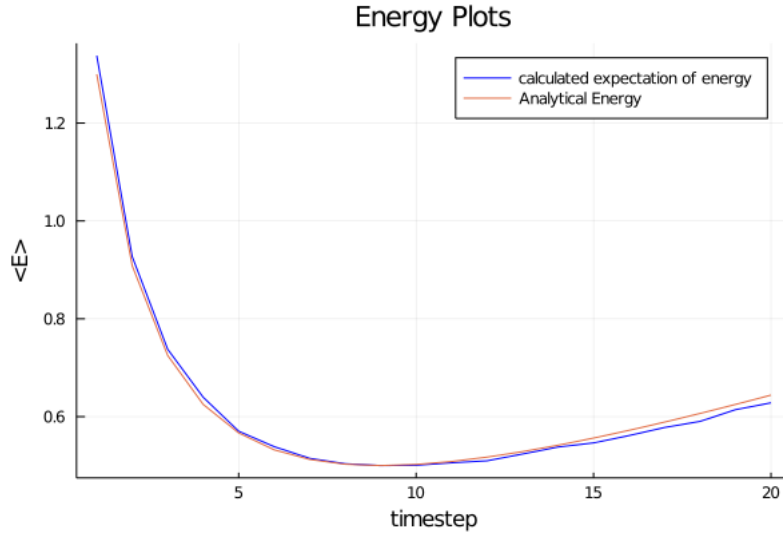


Figure 1: Harmonic Oscillator: plot of energy vs iteration timestep

Figure 5, shows how the variance in the energy expectation evolves over the iteration. We can see that after only 20 or so iterations, the variance falls to zero. Figure 4, shows how the energy expectation varies with the variation parameter  $\alpha$ . We can see that as  $\alpha$  varies, the energy decreases upto -0.5 and those points are all located near  $\alpha = 1$  that is to say that the variational parameter has settled to the minimizing value.

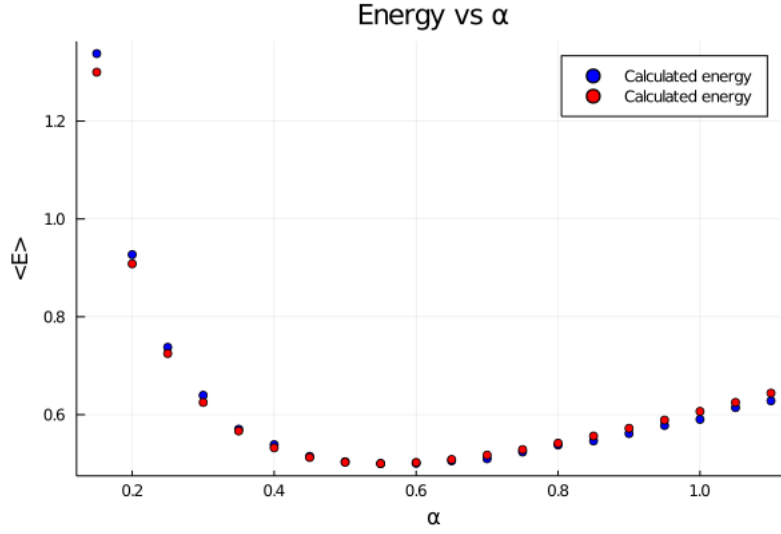


Figure 2: Harmonic Oscillator: plot of energy vs the variation parameter  $\alpha$

### 6.3 Helium Atom

The plots for helium atom are made to show the how the energy varies with the variation parameter  $\alpha$ . As can be seen in figure 6, there is a minimum of energy at  $\alpha = 0.2$  and the minimum energy obtained by calculations is around  $-2.87$  which is very close to the energy obtained by using much more accurate simulations like Density Functional Theory<sup>[2]</sup>. The value of  $\alpha$  was varied from 0 at the steps of 0.05 in 15 steps. One other point in helium atom is that in the monte carlo integration, 5000 steps were used to find the energy expectation but only the last 500 were used. If all the steps are used, there is some noise in the data and not all the runs give a good enough result.

## 7 Conclusion

In this report, the ground state energy is estimated using the variational principle and the integration is carried out by using monte carlo integration technique. For harmonic oscillator, where finding analytical solution is easy, the technique is in good agreement with the analytical case. For hydrogen atom, the analytical solution might be a bit difficult to find, however, this technique was successful in estimating the ground state energy. However, since randomness is built into this, the results are bound to contain some spikes. But this technique is easily scalable to very large systems and is known to give nearly accurate results.

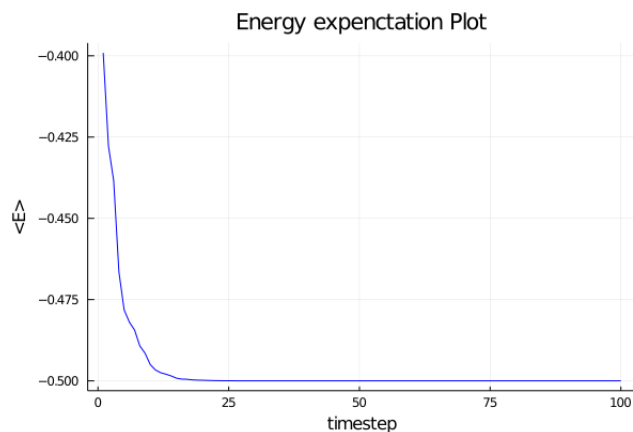


Figure 3: Hydrogen atom: plot of energy vs iteration timestep

## 8 Supplements

All the codes written in Julia language using Pluto as the platform are available on my GitHub (<https://github.com/Ved-Mahajan/VMC>) with MIT license. The data points used to make the plots are stored in the folder named **data** as .csv files and all the plots are stored in the folder named **plots**. In the README.md, there is instruction to run the codes online in the browser on Binder.

## References

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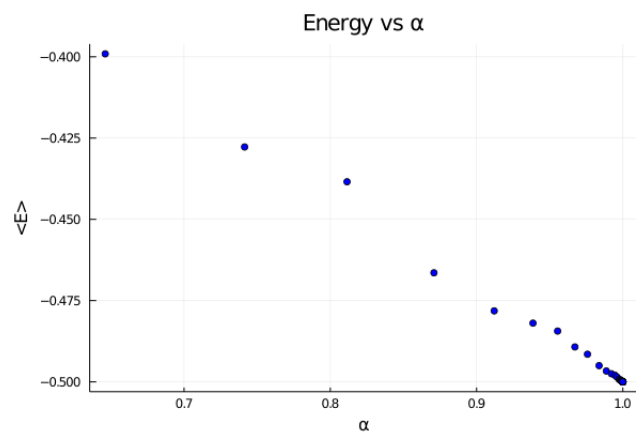


Figure 4: Hydrogen atom: plot of energy vs variation parameter  $\alpha$

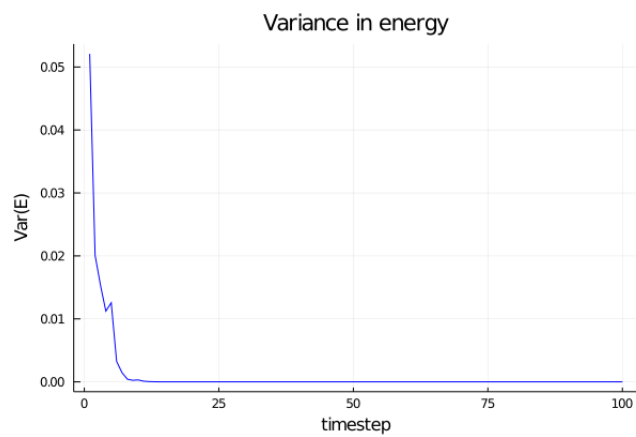


Figure 5: Hydrogen atom: plot of variance vs iteration timestep

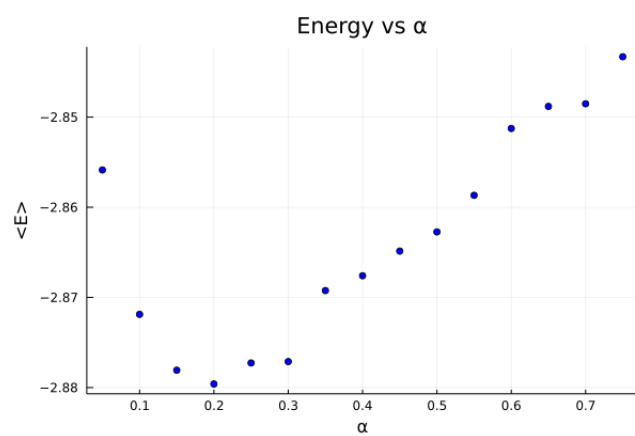


Figure 6: Helium atom: plot of energy expectation vs variation parameter  $\alpha$