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

Contents

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[2].

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 $|\psi_0 >= |\psi_0(\alpha_1, \alpha_2, ...\alpha_n) >$

2. Next, calculate the expectation value of the energy. This value will depend on the parameters $\alpha_1, \alpha_2, ...\alpha_n$.

$$E_0(\alpha_1, \alpha_2, ...\alpha_n) = \frac{< \psi_0(\alpha_1, \alpha_2, ...\alpha_n)|\hat{H}|\psi_0(\alpha_1, \alpha_2, ...\alpha_n) >}{< \psi_0(\alpha_1, \alpha_2, ...\alpha_n)|\psi_0(\alpha_1, \alpha_2, ...\alpha_n) >} \quad (1)$$

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

3. The next step is to find α_is such that $\frac{\partial E_0}{\partial \alpha_i} = 0$

4. Finally substitute the values of α_is 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 dimentional 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,

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

where, x_is 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,

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

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,

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

Now, we will look at a way to sample ρ. 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

$$< E[\boldsymbol{\alpha}] >= \frac{\int d\vec{r}\psi_T^\dagger(\vec{r},\boldsymbol{\alpha})H\psi_T(\vec{r},\boldsymbol{\alpha})}{\int d\vec{r}\psi_T^\dagger(\vec{r},\boldsymbol{\alpha})\psi_T(\vec{r},\boldsymbol{\alpha})} \tag{5}$$

This equation can be written as,

$$< E[\boldsymbol{\alpha}] >= \frac{\int d\vec{r}\psi_T^\dagger(\vec{r},\boldsymbol{\alpha})\psi_T(\vec{r},\boldsymbol{\alpha})(\frac{H\psi_T(\vec{r},\boldsymbol{\alpha})}{\psi_T(\vec{r},\boldsymbol{\alpha})})}{\int d\vec{r}\psi_T^\dagger(\vec{r},\boldsymbol{\alpha})\psi_T(\vec{r},\boldsymbol{\alpha})} \tag{6}$$

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

$$\begin{aligned} E_L &= \frac{H\psi_T(\vec{r},\boldsymbol{\alpha})}{\psi_T(\vec{r},\boldsymbol{\alpha})} \\ \rho(\vec{r},\boldsymbol{\alpha}) &= \frac{\psi_T^\dagger(\vec{r},\boldsymbol{\alpha})\psi_T(\vec{r},\boldsymbol{\alpha})}{\int |\psi_T(\vec{r},\boldsymbol{\alpha})|^2 d\vec{r}} = \frac{|\psi_T(\vec{r},\boldsymbol{\alpha})|^2}{\int |\psi_T(\vec{r},\boldsymbol{\alpha})|^2 d\vec{r}} \end{aligned} \tag{7}$$

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

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

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

$$< E[\boldsymbol{\alpha}] >= \int d\vec{r}\rho(\vec{r},\boldsymbol{\alpha})E_L(\vec{r},\boldsymbol{\alpha}) \tag{9}$$

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

$$< E[\boldsymbol{\alpha}] >= \frac{1}{N}\sum_{i=1}^{N} E_L(\vec{r_i}) \tag{10}$$

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[1] 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.

4.2 Minimization

The main aim of variational principle is the give the value of parameters $\boldsymbol{\alpha}$ such that the 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,

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

and the new alpha was chosen by,

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

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,

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

Let us choose one variational parameter α 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,

$$\begin{aligned} \rho(x,\alpha) &= e^{-2^2} \\ E_L &= \alpha + x^2(\tfrac{1}{2} - 2\alpha^2) \end{aligned} \tag{12}$$

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,

$$\hat{H} = \frac{-1}{2}\nabla^2 - \frac{1}{r} \tag{13}$$

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

$$\hat{H} = -\frac{1}{2}[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}] - \frac{1}{r} \tag{14}$$

The ansatz we shall choose would be a gaussian,

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

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

$$\begin{aligned} E_L &= -\tfrac{1}{2}[\alpha^2 - \tfrac{2\alpha}{r}] - \tfrac{1}{r} \\ \rho(r,\alpha) &= |\psi_T(r,\alpha)|^2 = e^{-2\alpha r^2} \end{aligned} \tag{16}$$

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 the theory we know that the ground state of the harmonic oscillator is

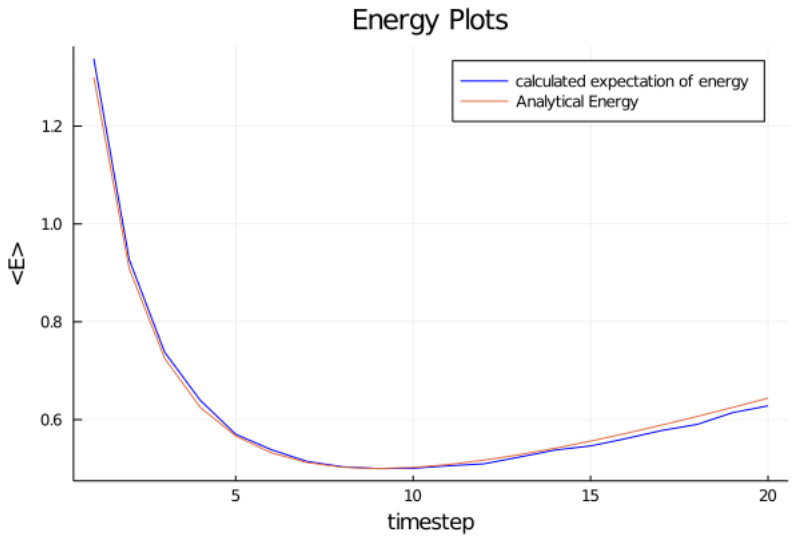

Figure 1: Harmonic Oscillator: plot of energy vs iteration timestep

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), $E_0 = 1\frac{1}{2}$. Hence, VMC gives the correct ground state energy.

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.

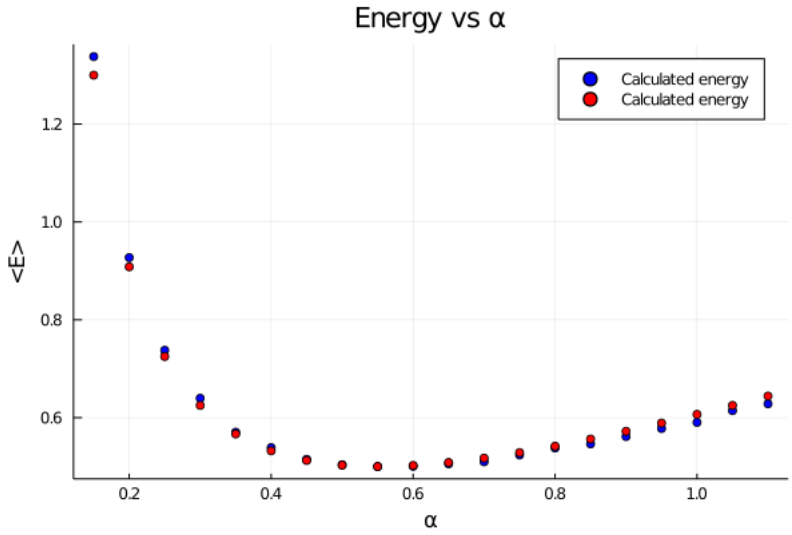

Figure 2: Harmonic Oscillator: plot of energy vs the variation parameter α

Figure 4, shows how the energy expectation varies with the variation parameter α. We can see that as α 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.

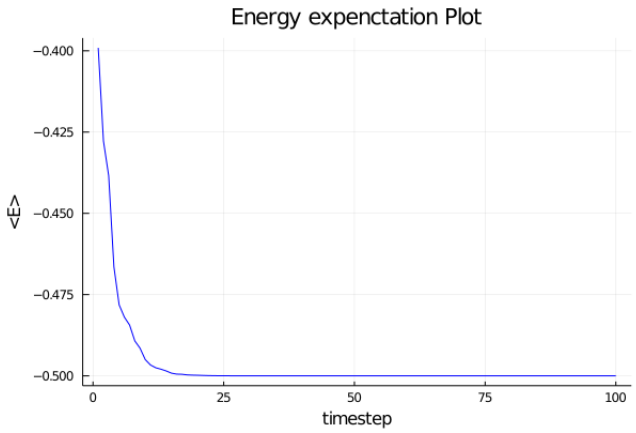

Figure 3: Hydrogen atom: plot of energy vs iteration timestep

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 in built into this, the results are bound to contain to some spikes. But this technique is easily scalable to very large systems and is known to give nearly accurate results.

References

[1] Jeff Bezanson, Alan Edelman, Stefan Karpinski, and Viral B Shah. Julia: A fresh approach to numerical computing. *SIAM review*, 59(1):65–98, 2017.

[2] Nouredine Zettili. Quantum mechanics: concepts and applications, 2003.

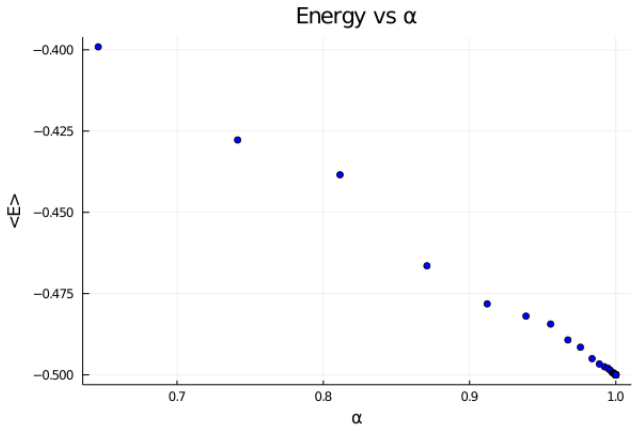

Figure 4: Hydrogen atom: plot of energy vs variation parameter α

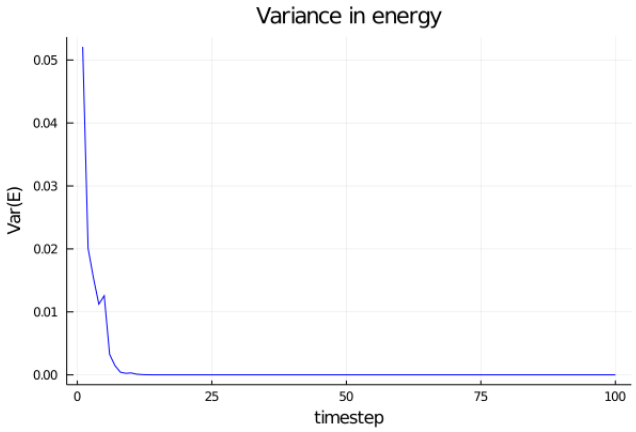

Figure 5: Hydrogen atom: plot of variance vs iteration timestep