Quantum Monte Carlo Methods: Solving the Time-independent Schrödinger Equation

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This paper introduces the variational Monte Carlo (VMC) method, and implements it in Python to solve some simple quantum mechanical systems. It was found that the VMC method can find exact solutions to the simple harmonic oscillator and the Hydrogen atom with Pade-Jastrow variational parameters $\alpha = 0.5$ and $\alpha = 1.0$ respectively. Exact solutions for the Helium atom are not clear, although the VMC solution seems to converge to the exact solution for greater α.

I. INTRODUCTION

In a quantum system with a large number of interacting particles, similar to the n-body problem in classical mechanics, quantum Monte Carlo methods are often used because of the multi-dimensional integrals. The quantum Monte Carlo methods allow us to solve the time-independent Schrödinger Equation generalised to $\mathbb{R}^3$,

$$H\psi(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + U(\boldsymbol{r})\right]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \tag{1}$$

The variational principle states that the average value, or the expectation value, of the total energy is given by $\langle E\rangle$. Following the derivation from [2],

$$\langle E\rangle = \frac{\int \Psi_T^\dagger(\boldsymbol{r}) H \Psi_T(\boldsymbol{r}) \mathrm{d}\boldsymbol{r}}{\int |\Psi_T(\boldsymbol{r})|^2 \mathrm{d}\boldsymbol{r}} \tag{2}$$

where Ψ_T is the trial wave-function which is the linear combination of the eigenstates $\psi_n(\boldsymbol{r})$,

$$\Psi_T(\boldsymbol{r}) = \sum_n c_n \psi_n(\boldsymbol{r}) \tag{3}$$

Note that the trial wave function depends on a parameter α known as the Pade-Jastrow variational parameter [2]. $\boldsymbol{r}$ is the positions of all the N particles in the system. Therefore the integral in [Eq. 2] is multidimensional, which is why the Monte Carlo method is used in the first place.

$\rho(\boldsymbol{r})$ is the probability distribution,

$$\rho(\boldsymbol{r}) = \frac{|\Psi_T(\boldsymbol{r})|^2}{\int |\Psi_T(\boldsymbol{r})|^2 \mathrm{d}\boldsymbol{r}} \tag{4}$$

Combining the probability distribution and [Eq. 2], we define a new operator $\hat{E}_L$ as the local energy

$$\hat{E}_L(\boldsymbol{r}) = \frac{\hat{H}\Psi_T(\boldsymbol{r})}{\Psi_T(\boldsymbol{r})} \tag{5}$$

and subsequently the expectation value of the local energy $\langle E_L\rangle$,

$$\langle E_L\rangle = \int \rho(\boldsymbol{r}) \hat{E}_L(\boldsymbol{r}) \mathrm{d}\boldsymbol{r} \tag{6}$$

The integral in [Eq. 6] is computed for a range of values of α. We want to find the minimum of E_L and the value of α_{min} at which it is minimum. α_{min} gives us the closest trial wave-function to the exact wave-function of the problem. Thus, at α_{min}, $\langle E_L\rangle$ should approach the expectation value of the Hamiltonian $\langle H\rangle$.

II. VARIATIONAL MONTE CARLO

Variational Monte Carlo (VMC) finds the ground state energy of the system using the variational method.

The algorithm, from [4], is as follows:

Define the number of Monte Carlo steps and step-size h. Choose an initial position $\boldsymbol{r}$ and Pade-Jastrow variational parameter α. Choose a trial wave-function $\Psi_T(\boldsymbol{r}) = e^{-\alpha \boldsymbol{r}}$ and calculate the probability density $\rho = |\Psi_T(\boldsymbol{r})|^2$. Initialise energy and variance. Begin the Monte Carlo simulation over the number of steps.

1. Calculate the trial position $\boldsymbol{r}_{trial} = \boldsymbol{r}$ + h*z where z is a random number between 0 and 1.
2. Calculate the ratio between the probability densities associated with the trial and original positions.

$$\omega = \frac{\rho(\boldsymbol{r}_{trial})}{\rho(\boldsymbol{r})}$$

Using the Metropolis algorithm, we accept the trial position unconditionally iff $\omega \geq 1$. If $\omega < 1$, we only accept it if $\omega \geq P$, where P is a random number between 0 and 1.

3. If the Metropolis algorithm accepts the position, set $\boldsymbol{r} = \boldsymbol{r}_{trial}$. If not, stay at the old position.
4. Calculate the new local energies and variances.

A. VMC for the Simple Harmonic Oscillator

The trial wave-function for the harmonic oscillator [2] is,

$$\Psi_T(\boldsymbol{x}) = e^{-\alpha \boldsymbol{x}^2} \tag{7}$$

with local energy E_L,

$$E_L(\boldsymbol{x}) = \alpha + \boldsymbol{x}^2\left(\frac{1}{2} - 2\alpha^2\right) \tag{8}$$

Analytically, this local energy loses its dependence on the position $\boldsymbol{x}$ when $\alpha = 1/2$. The exact solution at this value

is $E_0 = \frac{1}{2}$. The Monte Carlo simulation for the harmonic oscillator is shown in VMC_SHO.py.

B. VMC for the Hydrogen Atom

The trial wave-function for the ground state of a Hydrogen atom is,

$$\Psi_T(\boldsymbol{r}) = e^{-\alpha \boldsymbol{r}} \tag{9}$$

with local energy E_L,

$$E_L(\boldsymbol{r}) = (\alpha - 1)\frac{1}{\boldsymbol{r}} - \frac{\alpha^2}{2} \tag{10}$$

Analytically, the local energy loses its dependence on the radius $\boldsymbol{r}$ when $\alpha = 1$. When $\alpha \neq 1$, there is a single singularity at $\boldsymbol{r} = 0$. However, the code bypasses this because NumPy's rand() function excludes 0.

This simulation is shown in VMC_H.py. As one can see, at $\alpha = 1$ where the energy plot is supposed to be minimum, the ground state energy is $E_0 = -\frac{1}{2}$ which is the exact solution.

C. VMC for the Helium Atom

The trial wave-function for the ground state of a Helium atom is,

$$\Psi_T(\boldsymbol{r}_1, \boldsymbol{r}_2) = e^{-2\boldsymbol{r}_1} e^{-2\boldsymbol{r}_2} e^{\frac{\boldsymbol{r}_{12}}{2(1+\alpha \boldsymbol{r}_{12})}} \tag{11}$$

where $\boldsymbol{r}_{12} = |\boldsymbol{r}_1 - \boldsymbol{r}_2|$. Note that this trial wave-function uses a cusp condition to restrict values of α so that we do not have any singularities. The local energy E_L,

$$\begin{aligned} E_L(\boldsymbol{r}_1, \boldsymbol{r}_2) = -4 + \frac{\alpha}{1+\alpha \boldsymbol{r}_{12}} + \frac{\alpha}{(1+\alpha \boldsymbol{r}_{12})^2} \\ + \frac{\alpha}{(1+\alpha \boldsymbol{r}_{12})^3} - \frac{\alpha}{4(1+\alpha \boldsymbol{r}_{12})^4} + \frac{\hat{\boldsymbol{r}}_{12} \cdot (\hat{\boldsymbol{r}}_1 - \hat{\boldsymbol{r}}_2)}{(1+\alpha \boldsymbol{r}_{12})^2} \end{aligned} \tag{12}$$

The exact solution is given by E(Z),

$$E(Z) = Z^2 - 4Z + \frac{5}{8}Z \tag{13}$$

where Z = α [4]. The VMC simulation for the Helium atom is in VMC_He.py.

III. RESULTS

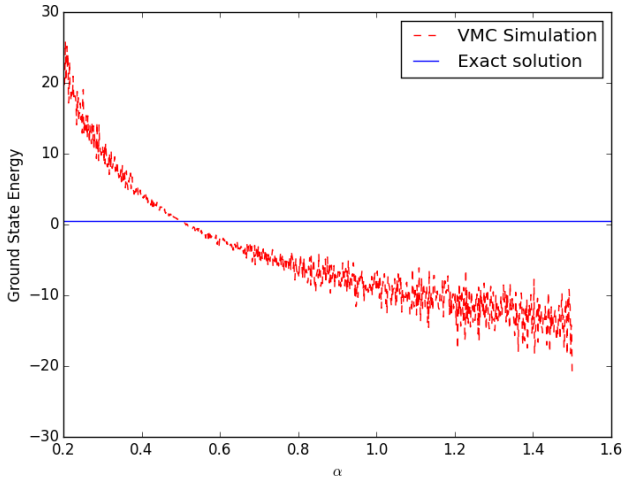

FIG. 1: Variational Monte Carlo simulation of the simple harmonic oscillator with N = 1000 steps. ($\alpha = 0.5$)

The exact solution of the simple harmonic oscillator is $E_0 = 0.5$. $\alpha = 0.5$ gives the exact wave-function so that the solutions match.

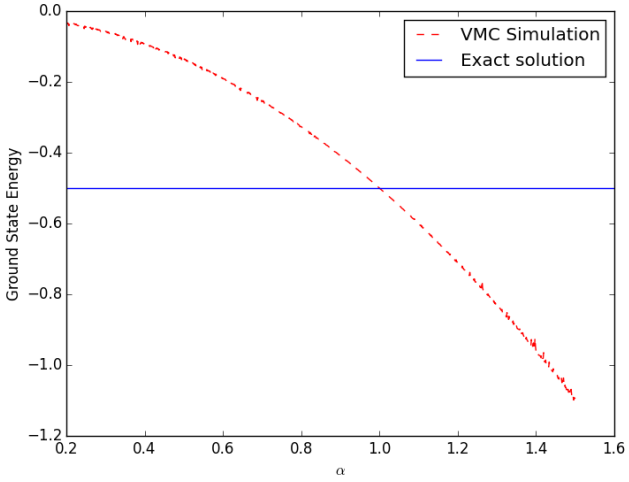

FIG. 2: Variational Monte Carlo simulation of the Hydrogen atom with N = 1000 steps. ($\alpha = 1$)

The exact solution of the Hydrogen atom is $E_0 = -0.5$. $\alpha = 1$ gives the exact wave-function so that the solutions match as well.

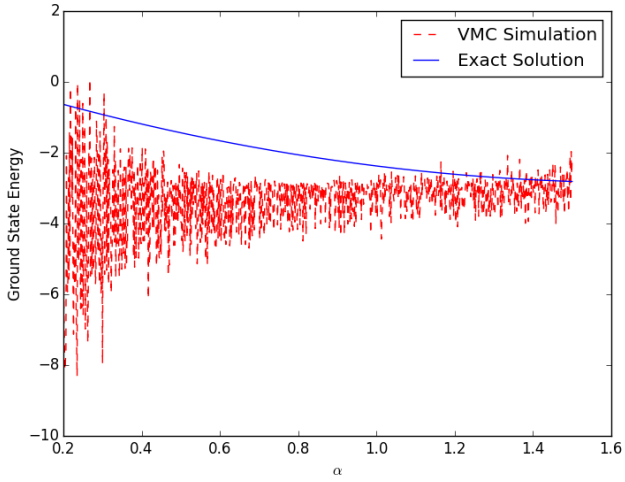

FIG. 3: Variational Monte Carlo simulation of the Helium atom with N = 1000 steps. ($\alpha = 0.2, \alpha = 1.5$)

The exact solution of the Helium atom is $E(\alpha) = \alpha^2 - 4\alpha + \frac{5}{8}\alpha$. In the VMC simulation, the endpoint $\alpha = 1.5$ gives the closest trial wave-function.

IV. DISCUSSION

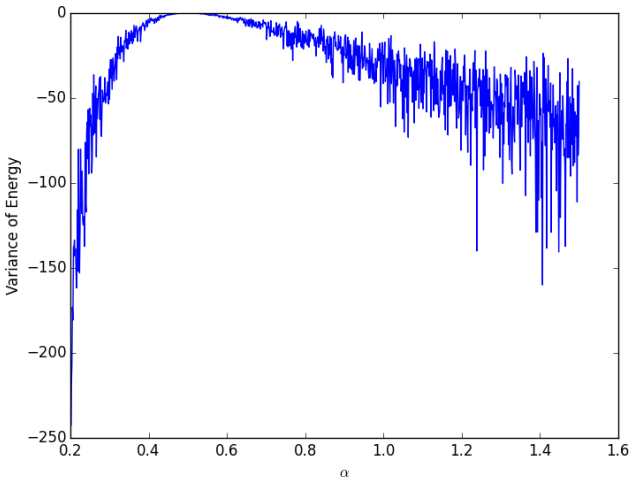

FIG. 4

As one can see, the variance $\sigma^2 = \langle E_0 \rangle^2 - \langle E_0^2 \rangle$ for the SHO is 0 at $\alpha = 0.5$, where the Monte Carlo result matches the exact solution $\langle E \rangle = 0.5$.

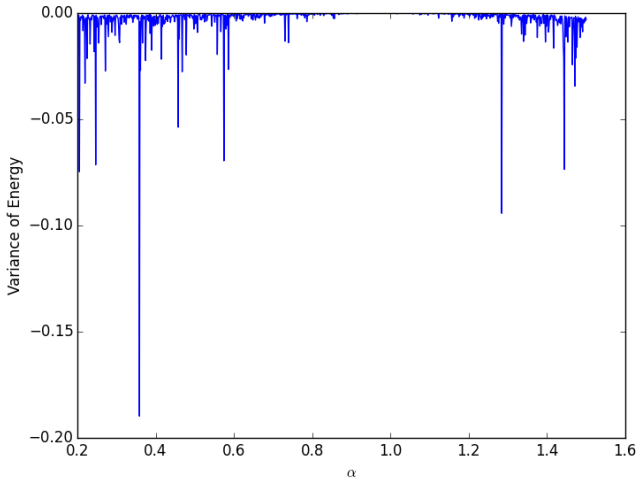

FIG. 5

For the Hydrogen atom, the variance is 0 at $\alpha = 1.0$, where the Monte Carlo result matches the exact solution $\langle E \rangle = -0.5$.

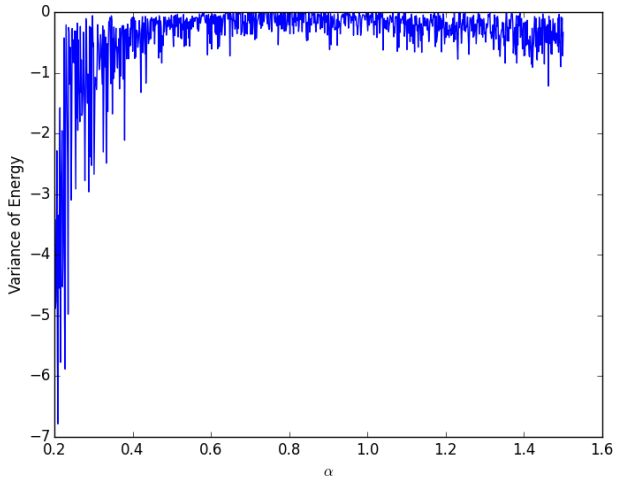

FIG. 6

For the Helium atom, the variance is close to 0 in the entire range. The exact solution is given by [Eq. 13], and it seems like the VMC simulation matches up best at the endpoint $\alpha = 1.5$.

Although my results for α agree with other literature [2], [4], it is not the minimum energy. The energy keeps decreasing for the simple harmonic oscillator and hydrogen atom case. The ground state energy plots do not agree with previously done studies [2], [4]. This large source of error may be caused by an incorrect choice of step size h. Gonsalves suggests that the step size should be a value such that the acceptance ratio is around 50%.

The expected graphs of the ground states for the three cases from [4] is shown in Appendix a.

The sampling of points in the VMC method is not very efficient since the trial wave-function is not used in determining the move $r \rightarrow r_{trial}$. The trial wave-function is only used in determining the ratio of the probability densities. The efficiency can be improved by importance sampling and can also be improved by using the diffusion Monte Carlo method.

Furthermore, there are many other quantum Monte Carlo methods not mentioned in this paper. The diffusion Monte Carlo (DMC) method lets us solve the Schrödinger for many particles exactly. It is a very efficient, accurate method that uses Green's functions to solve the Schrödinger equation.

V. CONCLUSION

This report explored the variational quantum Monte Carlo method for the time-independent Schrödinger equation. The examples of simple quantum systems explored were the simple harmonic oscillator, the Hydrogen atom, and the Helium atom. For the simple harmonic oscillator, it was found that Pade-Jastrow variational parameter $\alpha = 0.5$ gave the exact solution. For the Hydrogen atom, it was found that $\alpha = 1.0$ gave the exact solution. For the Helium atom, the endpoint $\alpha = 1.5$ gave the closest solution. Quantum Monte Carlo is an excellent tool at solving many-body quantum systems. There also exists the time-dependent variational Monte Carlo method which can be used to solve the time-dependent Schrödinger equation.

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[3] M. P. Nightingale C et al, *A diffusion Monte Carlo algorithm with very small time-step errors*, J. Chem. Phys. **99**, 2865, 1993

[4] M.H. Jensen, *Computational Physics Lecture Notes*, (University of Oslo, Oslo, 2012)

[5] B. L. Hammond et al., *Monte Carlo Methods in Ab Initio Quantum Chemistry*, (World Scientific, 1994).

VI. APPENDIX A

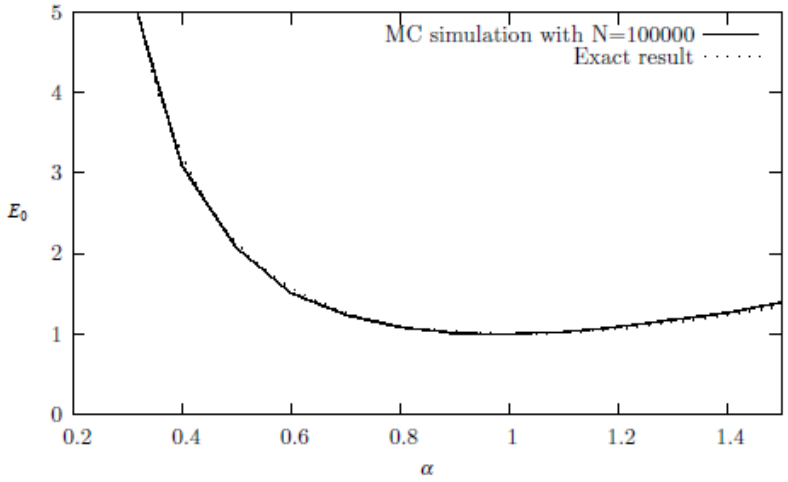

FIG. 7: Expected simple harmonic oscillator ground state energy [4].

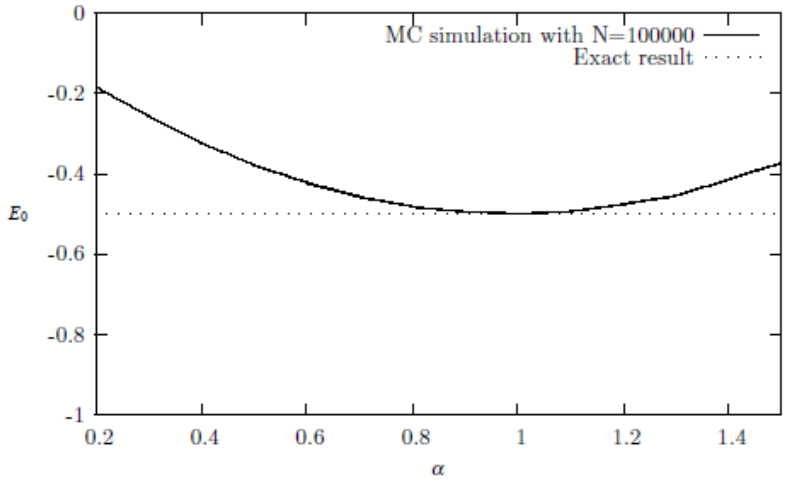

FIG. 8: Expected Hydrogen ground state energy [4].

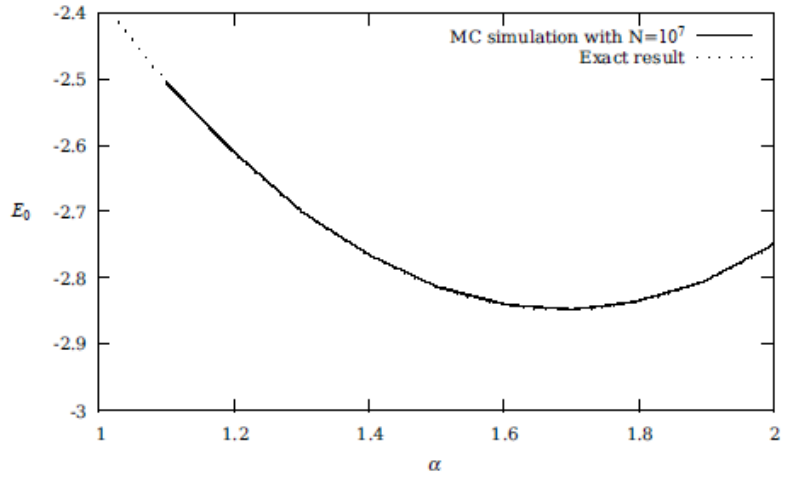

FIG. 9: Expected Helium ground state energy [4].