Quantum Monte Carlo

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April 24, 2024

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Monte Carlo

Monte Carlo methods are a broad class of computational algorithms that rely on repeated random sampling to obtain numerical results. The underlying concept is to use randomness to solve problems that might be deterministic in principle. The name comes from the Monte Carlo Casino in Monaco, where the primary developer of the method, physicist Stanislaw Ulam, was inspired by his uncle's gambling habits.

Figure 1: Casino Monte Carlo

Quantum Monte Carlo

Quantum Monte Carlo encompasses a large family of computational methods whose common aim is the study of complex quantum systems. One of the major goals of these approaches is to provide a reliable solution (or an accurate approximation) of the quantum many-body problem. The diverse flavors of quantum Monte Carlo approaches all share the common use of the Monte Carlo method to handle the multi-dimensional integrals that arise in the different formulations of the many-body problem.(1)

Quantum Monte Carlo

Two Methods

1. Diffusion Monte Carlo (DMC)
2. Variational Monte Carlo (VMC)

Diffusion Monte Carlo

The time-dependent Schrödinger equation :

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$$

The diffusion equation:

$$\frac{\partial\psi}{\partial t} = D\nabla^2\psi$$

If we let $i = 1,\ \frac{1}{\hbar} = D,\ \hat{H} = \nabla^2$, these two equations are same!

For

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} + V(x), \quad \tau = \frac{it}{\hbar}$$

We have Schrödinger equation:

$$\frac{\partial \psi}{\partial \tau} = \frac{\hbar^2}{2\mu}\frac{\partial^2 \psi}{\partial x^2} - V(x)\psi$$

We could add a chemical reaction item $k(x)C$.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - k(x)C$$

We could use random walk to solve diffusion equation, so it's reasonably to solve Schrödinger equation using random walk. And we call it diffusion Monte Carlo.(2)

How to treat chemical reaction item $k(x)$ or potential $V(x)$?

Birth - Death Process

See $V(x)$ as a probability to "kill" a old particle or "create" a new particle.

For example: let $0.02V(x)$ be the probability of "kill" particle, let $1 - 0.02V(x)$ be the probability of "create" particle.

So the particles at the edge are easy to dead, and in the centre it's easy to get a new particle.(3)

Warning

At centre $V(x) \approx 0$, so the probability of "create" particle is almost 1.

This means the number of particle will become infinite!

We need some limits for this part.

Using DMC get ground energy

The solution of TDSE could be written as:

$$\Psi(x,t) = \sum_{n=0}^{\infty} c_n \phi_n(x) e^{-\frac{i}{\hbar} E_n t}$$

Change potential $V(x)$ to $V(x) - E_R$:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + [V(x) - E_R]\,\Psi$$

$$\Psi(x,t) = \sum_{n=0}^{\infty} c_n \phi_n(x) e^{-i\frac{E_n - E_R}{\hbar} t}$$

Change $\frac{it}{\hbar}$ to τ:

$$\frac{\partial \Psi}{\partial \tau} = \frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} - [V(x) - E_R]\,\Psi$$

$$\Psi(x,\tau) = \sum_{n=0}^{\infty} c_n \phi_n(x) e^{-(E_n - E_R)\tau}$$

- For E_R values less then the ground state energy the distribution $\psi(x, \tau)$ decays asymptotically to zero, i.e., the particles eventually all die.
- For E_R values larger than the ground state energy, the distribution will increase indefinitely, i.e., the number N_n will exceed all bounds.
- Only for $E_R = E_0$ can one expect a stable asymptotic distribution such that the number of particles fluctuates around an average value N_0.

The spatial distribution and increases/decreases of the number of particles allow one to adjust the value of E_R as to keep the total number of particles approximately constant.
Finally we could know the ground state energy

Variational Monte Carlo

Guess a wave function Ψ_T, the energy could be written as:

$$E_v = \frac{\int \Psi_T^* \hat{H} \Psi_T dR}{\int \Psi_T^* \Psi_T dR} = \frac{\int |\Psi_T|^2 \left[\Psi^{-1} \hat{H} \Psi\right] dR}{\int |\Psi_T|^2 dR}$$

$$P(R) = \frac{|\Psi_T|^2}{\int |\Psi_T|^2 dR}$$

Randomly choose m particles and calculate energy:

$$E_L = \Psi_T^{-1} \hat{H} \Psi_T \approx \frac{1}{M} \sum E_L(R_m)$$

nature communications

Article

https://doi.org/10.1038/s41467-023-37609-3

Towards the ground state of molecules via diffusion Monte Carlo on neural networks

Received: 24 May 2022

Accepted: 20 March 2023

Published online: 03 April 2023

Check for updates

Weiluo Ren [1,4], Weizhong Fu [1,2,4], Xiaojie Wu [1] & Ji Chen [2,3]

Diffusion Monte Carlo (DMC) based on fixed-node approximation has enjoyed significant developments in the past decades and become one of the go-to methods when accurate ground state energy of molecules and materials is needed. However, the inaccurate nodal structure hinders the application of DMC for more challenging electronic correlation problems. In this work, we apply the neural-network based trial wavefunction in fixed-node DMC, which allows accurate calculations of a broad range of atomic and molecular systems of different electronic characteristics. Our method is superior in both accuracy and efficiency compared to state-of-the-art neural network methods using variational Monte Carlo (VMC). We also introduce an extrapolation scheme based on the empirical linearity between VMC and DMC energies, and significantly improve our binding energy calculation. Overall, this computational framework provides a benchmark for accurate solutions of correlated electronic wavefunction and also sheds light on the chemical understanding of molecules.

Figure 2: NNDMC (4)

nature machine intelligence

Article

https://doi.org/10.1038/s42256-024-00794-x

A computational framework for neural network-based variational Monte Carlo with Forward Laplacian

Received: 26 July 2023

Accepted: 10 January 2024

Published online: 13 February 2024

Check for updates

Ruichen Li[1,2,7], Haotian Ye[3,7], Du Jiang[1,2], Xuelan Wen[2], Chuwei Wang[4], Zhe Li[2], Xiang Li[2], Di He[1] ✉, Ji Chen[5] ✉, Weiluo Ren[2] ✉ & Liwei Wang[1,6] ✉

Neural network-based variational Monte Carlo (NN-VMC) has emerged as a promising cutting-edge technique of ab initio quantum chemistry. However, the high computational cost of existing approaches hinders their applications in realistic chemistry problems. Here we report a development of NN-VMC that achieves a remarkable speed-up rate, thereby greatly extending the applicability of NN-VMC to larger systems. Our key design is a computational framework named Forward Laplacian, which computes the Laplacian associated with neural networks, the bottleneck of NN-VMC, through an efficient forward propagation process. We then demonstrate that Forward Laplacian can further facilitate more developments of acceleration methods across various aspects, including optimization for sparse derivative matrix and efficient network design. Empirically, our approach enables NN-VMC to investigate a broader range of systems, providing valuable references to other ab initio methods. The results demonstrate a great potential in applying deep learning methods to solve general quantum mechanical problems.

Figure 3: NNVMC (5)

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Q & A

Simulation Results of DMC

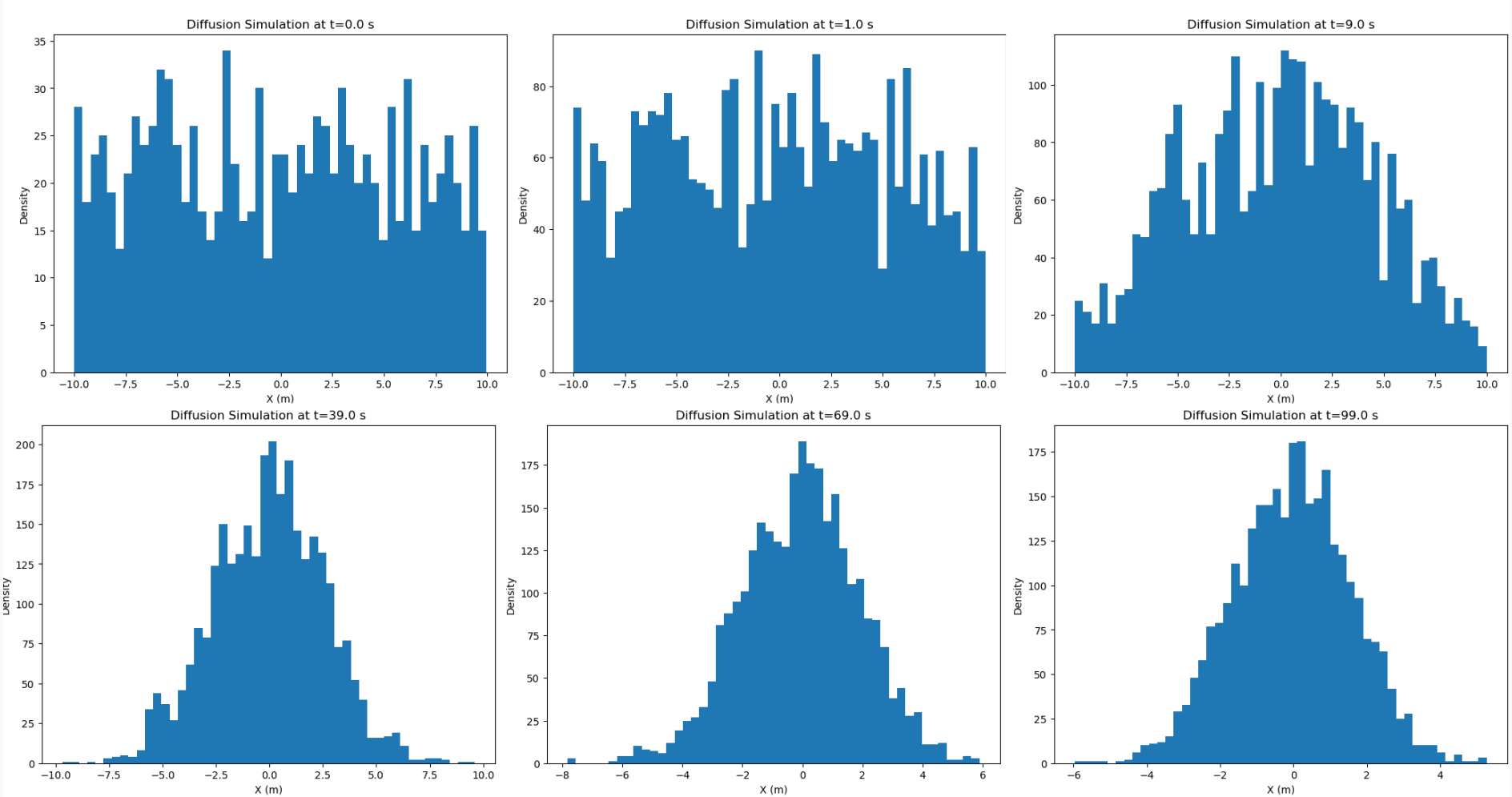

Figure 4: Simulation Results of 1D-DMC

Simulation Results of DMC

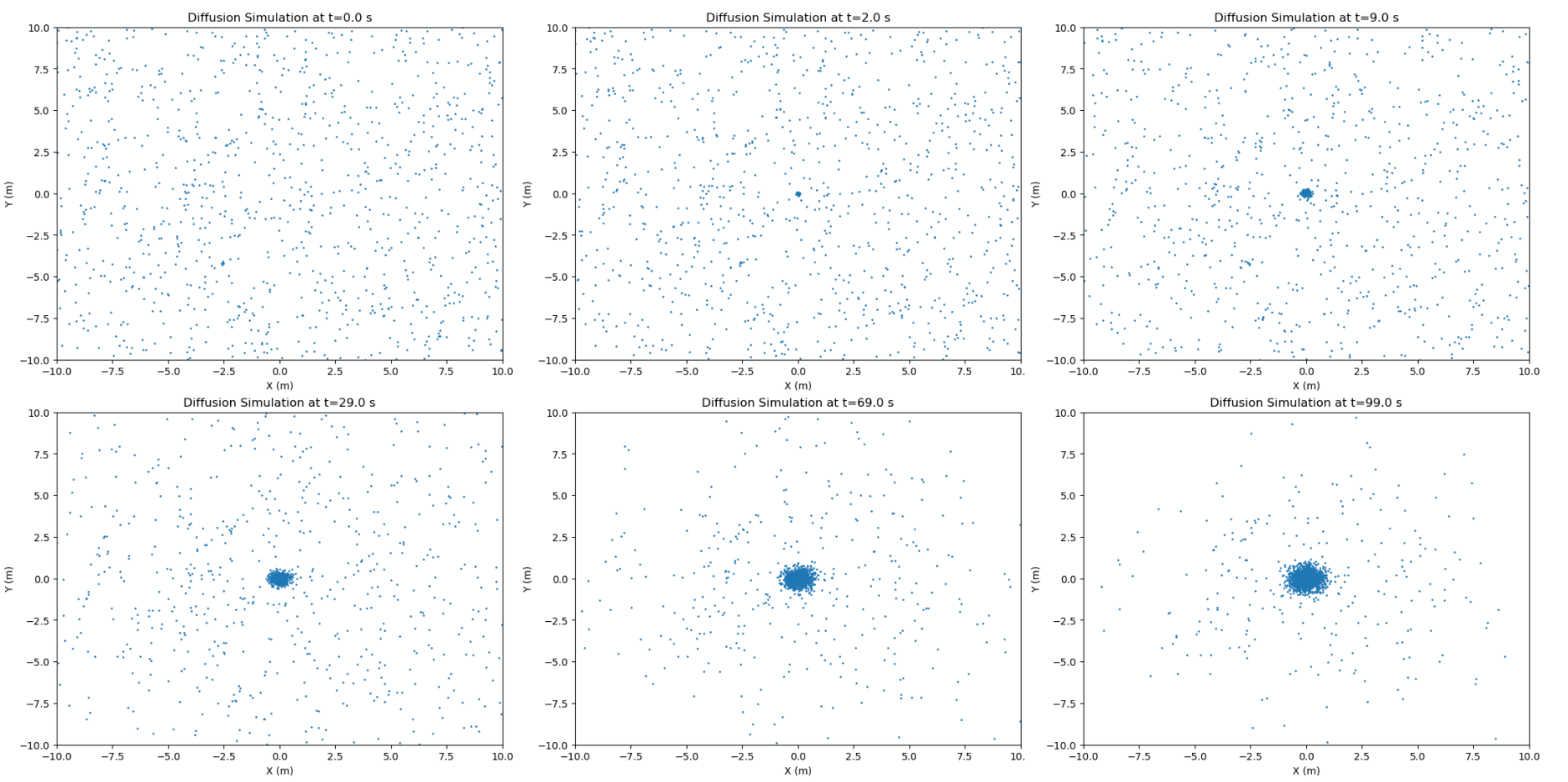

Figure 5: Simulation Results of 2D-DMC

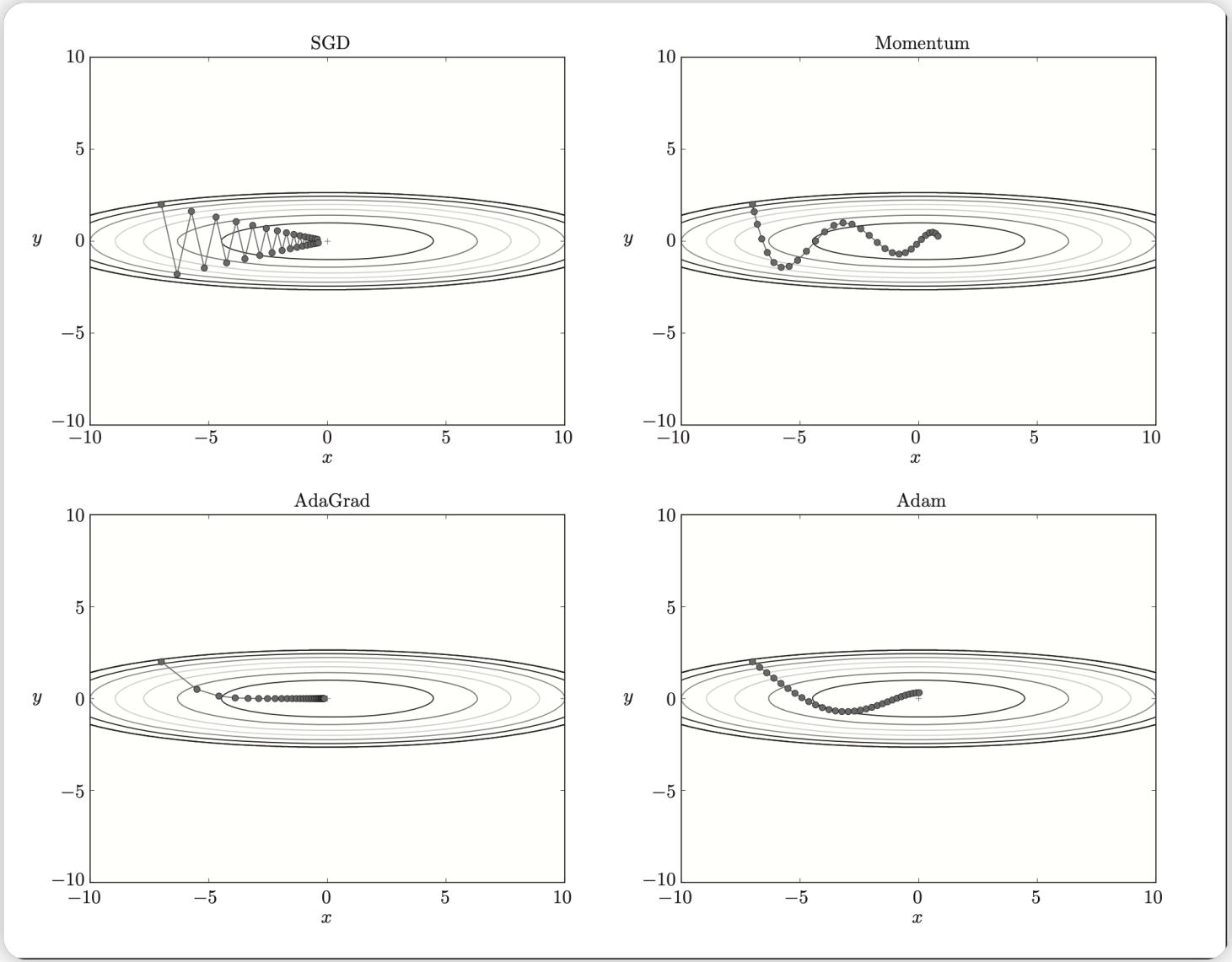

Figure 6: Four different optimiser in Machine Learning

Simulation Results of VMC

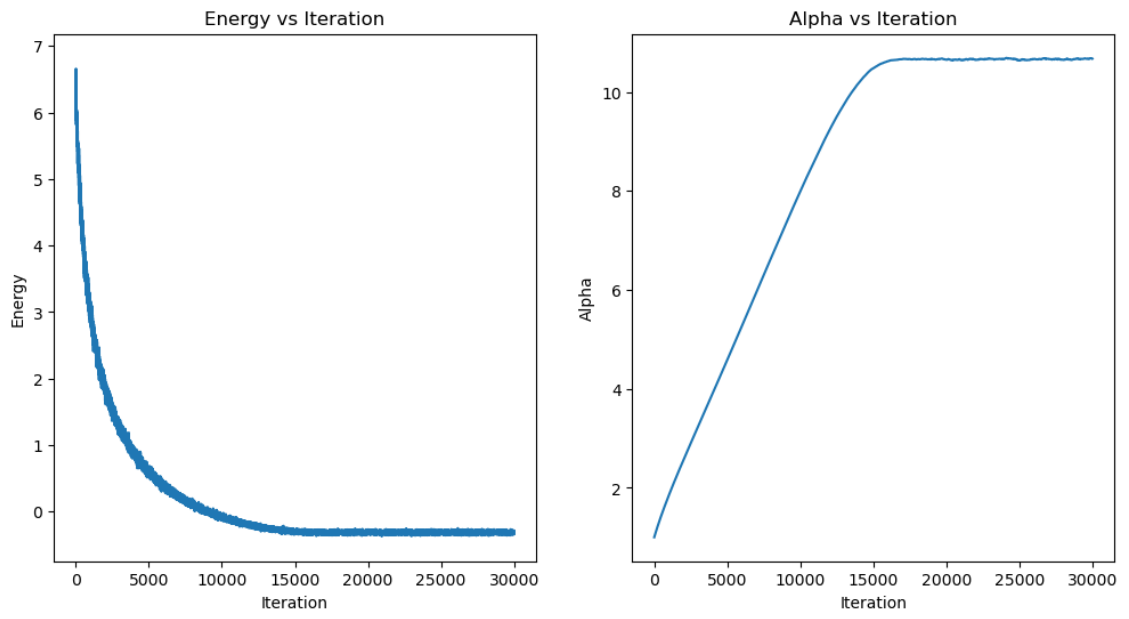

Figure 7: Energy and α

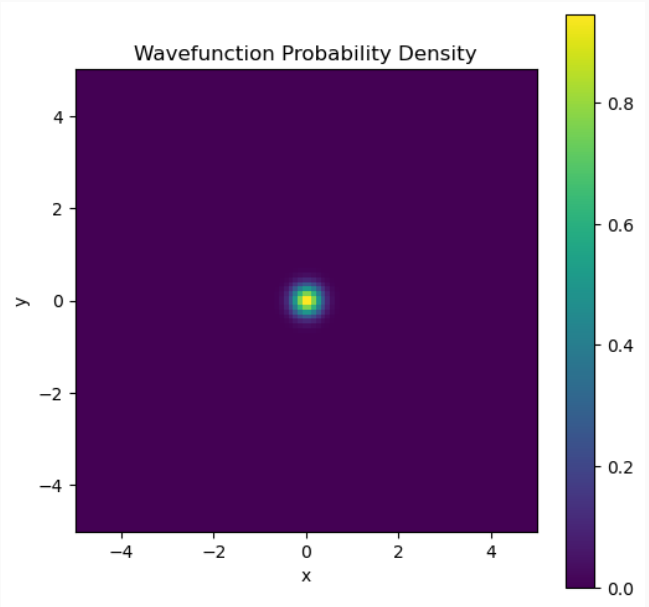

Figure 8: $|\psi|^2$