Research Article

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Particle diffusion Monte Carlo (PDMC)

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Abstract: General expressions for anisotropic particle diffusion Monte Carlo (PDMC) in a d-dimensional space are presented. The calculations of ground state energy of a helium atom for solving the many-body Schrödinger equation is carried out by the proposed method. The accuracy and stability of the results are discussed relative to other alternative methods, and our experimental results within the statistical errors agree with the quantum Monte Carlo methods. We also clarify the benefits of the proposed method by modeling the quantum probability density of a free particle in a plane (energy eigenfunctions). The proposed model represents a remarkable improvement in terms of performance, accuracy and computational time over standard MCMC method.

Keywords: Monte Carlo methods, quantum many-body systems

MSC 2010: 65Cxx

1 Introduction

Probability distributions over many variables occur frequently in Bayesian inference, statistical physics and simulation studies [14]. Computational methods for dealing with these large and complex distributions remain an active area of research. As a canonical example, we consider a statistical model $\theta \to x$ for data x generated using parameters θ. The predictive distribution over new data $x^{(N+1)}$ given observations of N previous settings $\{x^{(n)}\}_{n=1}^{N}$ is an average under the posterior distribution $p(\theta|\{x^{(n)}\}_{n=1}^{N}r)$ as

$$p(x^{n+1})|\{x^{(n)}\}_{n=1}^{N} = \int p(x^{N+1}|\theta)p(\theta|\{x^{(n)}\}_{n=1}^{N})\,d\theta = \mathbb{E}_{p(\theta|\{x^{(n)}\}_{n=1}^{N})}[p(x^{N+1})|\theta],$$

where the posterior distribution is given by the Bayes rule

$$p(\theta|\{x^{(n)}\}_{n=1}^{N}) = \frac{p((\theta|\{x^{(n)}\}_{n=1}^{N})|\theta)p(\theta)}{\int p((\theta|\{x^{(n)}\}_{n=1}^{N})|\acute{\theta})p(\acute{\theta})\,d\acute{\theta}}.$$

Given a parameter space, we can specify the target distribution as a smooth probability density function $p(\theta)$, while expectations reduce to integrals over parameter space $\mathbb{E}_p[f] = \int d\theta p(\theta)f(\theta)$. Unfortunately, we will not be able to evaluate these integrals analytically for any nontrivial target distribution. The predominant methodology for sampling from such a probability density is Markov chain Monte Carlo (MCMC) [16]. Despite the potential efficiency gains to be obtained in MCMC sampling, the tuning of the MCMC methods remains a major issue especially for challenging inference problems. This paper seeks to address these issues by proposing an adapting method based on the Langevin diffusion algorithm for the overall development of MCMC methods. Major steps forward in this regard were made in a proposal process based on the gradient

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information of the target density. A brief review of the proposed method is provided in the following section, and general concepts with certain extensions and a description of the formalism in terms of gradient flows of the target density which contains all the relevant information are also considered. Finally, the new methodology is demonstrated and assessed on a number of interesting statistical problems.

2 Adaptive proposal distribution

For an unnormalized probability density function $\tilde{p}(\theta)$, where $\theta \in \mathbb{R}^d$, the normalized density follows as $p(\theta) = \tilde{p}(\theta)/\int \tilde{p}(\theta)\, d\theta$, which is analytically intractable for many statistical models. Monte Carlo estimation of integrals with respect to $p(\theta)$ are therefore required. The predominant methodology for sampling from such a probability density is Markov chain Monte Carlo (MCMC). Consider $p(\theta)$ a probability density function on $\mathbb{R}^d$, from which we desire to draw an ensemble of independent and identically distributed samples. We consider the Langevin diffusion equation $\dot{\theta} = \nabla_\theta \log(p(\theta)) + \sqrt{2}\dot{W}$ driven by the time derivative of a standard Brownian motion W. In the limit as $t \to \infty$, the probability distribution $p(\theta)$ approaches a stationary distribution, which is also invariant under the diffusion; in fact, it turns out that $p_\infty = p(\theta)$. If we consider the random vector $\theta \in \mathbb{R}^d$ with density $p(\theta)$ and the log density denoted as $L(\theta) \equiv \log(p(\theta))$, then the Metropolis adjusted Langevin algorithm (MALA) [27] is based on a Langevin diffusion, with stationary distribution $p(\theta)$, defined by the stochastic differential equation (SDE) as

$$p(\theta(t)) = \frac{1}{2}\nabla_\theta L(\theta(t))\, dt + dW(t), \tag{2.1}$$

where W denotes n-dimensional Brownian motion [7, 21, 33]. In case of Brownian motion, a particle of mass m suspended in a fluid experiences two type of forces: a frictional force F_{f} that dissipates the kinetic energy of the particle and a random force $F_{\mathrm{r}}(t)$ that pushes the particle in an erratic way. The random force $F_{\mathrm{r}}(t)$ has zero mean and is uncorrelated at different time. Its statistics is Gaussian, and its strength is related to the temperature T_{e} of the fluid.

$$\langle F_{\mathrm{r}}(t)\rangle = 0,$$
$$\langle F_{\mathrm{r}}(t)F_{\mathrm{r}}(s)\rangle = 2\gamma K_{\mathrm{B}} T_{\mathrm{e}}\delta(t-s),$$

where γ is the friction constant and K_{B} is the Boltzmann factor. This simple model has been extended, modified and generalized in many different ways. For example, one may allow for potential forces that act on the considered particle in an external field of force [22]. Other generalization concern the random and the frictional forces. For example, the surrounding medium may undergo slow processes that result in long-lived correlation of the fluctuating force. Other generalization concerns the statistical character of the noise, which may be non-Gaussian. In this article, we pursue the idea that the friction coefficient may be a fluctuating quantity that randomly changes its value in space and time. In the following, we formulate our model and derive the expression of the diffusion tensor in terms of the time-ordered directional derivative of the fluctuating friction tensor. This approach is based on the Fokker–Planck equation [5, 12, 20, 24, 34] and the Langevin equation for generating a trajectory in coordinate space. Lets consider the d-dimensional Brownian motion of a massive particle in an external potential $U(\theta)$ under influence of a spatially constant and in time fluctuating friction tensor $\gamma(t)$. The motion of the particle with a function of all the position coordinates

$$\theta = \begin{bmatrix} \theta_1 \\ \theta_2 \\ \vdots \\ \theta_d \end{bmatrix} \quad \text{and} \quad v = \begin{bmatrix} v_1 \\ v_2 \\ \vdots \\ v_d \end{bmatrix}$$

is governed by the Langevin equations as

$$\dot{\theta}(t) = v(t),$$
$$m \times \dot{v} = -\nabla U(\theta) - \gamma(t)v(t) + \sqrt{2K_{\mathrm{B}}T_{\mathrm{e}}}\, b(t)W(t),$$

where $\nabla U(\theta)$ is the gradient of the potential and $b(t)$ is related to the friction tensor $\gamma(t)$

$$\gamma(t) = b(t)b(t)^T,$$

and

$$W(t) = \begin{bmatrix} w_1(t) \\ w_2(t) \\ \vdots \\ w_d(t) \end{bmatrix}$$

is a vector of independent, identical Gaussian white noise with

$$\langle w_i(t) \rangle = 0,$$
$$\langle w_i(t) w_j(s) \rangle = \delta_{i,j}\delta(t-s),$$

where T is the matrix transposition. However, it turns out that the probability density of the Brownian particle approaches the Maxwell–Boltzmann distribution [13, 17, 18] defined as

$$Z^{-1} \exp[-(mv^2 + U(\theta))/K_B T_e]$$

in the limit as $t \to \infty$ provided the potential $U(\theta)$ is confirming such that the partition function

$$Z = \iint d^d\theta \, d^d v \exp[-(mv^2 + U(\theta))/K_B T_e]$$

is finite. For a diffusion process characterized by a time-dependent probability density $p(\theta, t)$, the Fokker–Planck equation is defined as

$$\frac{\partial p}{\partial t} = \sum_i D \times \frac{\partial}{\partial x_i}\Big(\frac{\partial}{\partial \theta_i} - \mu_i\Big)p(\theta, t),$$

where μ_i is the i-th component of the drift term caused by an external potential, and D is the diffusion tensor. In one spatial dimension θ with drift term $\mu(\theta_t, t)$ and diffusion coefficient $D(\theta_t, t) = \sigma^2(\theta_t, t)/2$, the Fokker–Planck equation for the probability density $p(\theta, t)$ of the random variable θ_t is

$$\frac{\partial}{\partial t}p(\theta, t) = -\frac{\partial}{\partial \theta}[\mu(\theta, t)p(\theta, t)] + \frac{\partial^2}{\partial \theta^2}[D(\theta, t)p(\theta, t)],$$

where the zero-drift equation with constant diffusion can be considered as a model of classical Brownian motion. A first-order Euler discretization of equation (2.1) gives the proposal mechanism

$$\theta^{n+1} = \theta^n + \frac{\epsilon^2}{2}L(\theta^n) + \epsilon z^n,$$

where z comes from a normal distribution $N(z|0, I)$ and ϵ is the integration step size. An apparent problem with this method is that the resulting proposal is no longer a Markov process (resulting in a non-standard MCMC), and the convergence to the invariant distribution, $p(\theta)$, is no longer guaranteed for finite step size ϵ, due to the first-order integration error. Instead, it is still possible to obtain a valid algorithm by viewing the chain as a d-dimensional Markov process. This discrepancy can be corrected by employing a Metropolis acceptance probability after each integration step, thus ensuring convergence to the invariant measure. We would like to mention that the isotropic diffusion will be inefficient to draw independent and identically distributed samples from target density without correlation. As an example, MALA incorporates an independent draw from isotropic multivariate normal distribution on $\mathbb{R}^d$ with mean $\mu(\theta^n, \epsilon) = \theta^n + \frac{\epsilon^2}{2}L(\theta^n)$; then the discrete form of the SDE defines a proposal density $q(\theta^\star|\theta^n) = N(\theta^\star|\mu(\theta^n, \epsilon), \epsilon^2 I)$ with acceptance probability of $\min[1, p(\theta^\star)q(\theta^n|\theta^\star)/p(\theta^n)q(\theta^\star|\theta^n)]$ and covariance matrix equal to a $d \times d$ identity matrix scaled by step size ϵ [27]. In contrast to the standard MALA algorithm, we would like to have an adaptive proposal mechanism which satisfies the Markov property. To complete our algorithm, we need to specify a proposal q from

which we sample $\theta^\star$, and to this aim we make use of the gradient information and the last accepted θ. The way to alleviate this problem, by generating proposals based on the drift term (transition kernel), is the following:

$$\begin{aligned} p(\theta(t)) &= \frac{1}{2}\nabla_\theta L(\theta(t))\,dt + dW(t), \\ W(t) &= N\big(\mu(\theta^n, \epsilon), \Sigma(\theta^n, \epsilon)\big), \\ \mu(\theta^{n+1}, \epsilon|\theta^n) &= \theta^n + \frac{\epsilon^2}{2}L(\theta^n), \\ \Sigma(\theta^n, \epsilon|\theta^n, \Sigma^n, \nabla_\theta L(\theta^{n-1})) &= \epsilon \times \frac{[\beta + \psi(\Sigma, n) \times (\|\frac{\theta^n}{\theta^{n-1}} - (\|\frac{\nabla_\theta L(\theta^n)^2}{\nabla_\theta L(\theta^{n-1})}\|)\|)^\xi]}{[1 + \exp[-\|\frac{\nabla_\theta L(\theta_n)^2}{\nabla_\theta L(\theta^{n-1})}\|]]}, \\ \psi(\Sigma, n) &= \sqrt{2\pi} + \Sigma^n, \end{aligned} \tag{2.2}$$

where $\|\cdot\|$ is the Euclidean norm, β is a constant scalar value, $\psi(\cdot)$ is a uniform random variable between $[0, \sqrt{2\pi} + \Sigma^n]$ and $0 \ll x < 1$.

In this manner, we build up the complete path of diffusion, but, as a step size $\epsilon \to 0$, we recover the solution path of the continuous SDE, and the target distribution would be the solution of the equation. As mentioned before, if ϵ is a finite value, then the distribution of the path is biased and Markov properties are modified. We can correct the biases by use of $\theta(t + \epsilon)$ as a proposal mechanism with a mean of $\theta(t)$ and the non-isotropic covariance, scaled by ϵ. Therefore, the covariance matrix is encountered by the gradient information of the posterior distribution. Up to this stage, we use the directional gradient of the posterior distribution to accommodate the small variance. Then, to correct the bias, we have to enforce the acceptance probability to ensure detailed balances as

$$p(\theta^\star|\theta) = \min\Big[1, \frac{p(\theta^\star)p(\theta|\theta^\star)}{p(\theta)p(\theta^\star|\theta)}\Big].$$

Therefore, the interesting question here could be: can geometric structures be employed in the proposed methodology? The concept we proposed is not far from the notion of metric tensor and the curvature in Riemannian manifold. Here we have a probability distribution which is completely a function of the directional derivative of the target density. Our proposed method captures the notion of similarities in a tangent space defined by the metric tensor which is associated with the Fisher information matrix. So we can see that the proposed methodology shares relevant structure with the Fisher information matrix defined as

$$X^2(\delta\theta) = \int \frac{|p(y;\theta + \delta\theta) - p(y;\theta)|^2}{p(y;\theta)}\,dy \approx \delta\theta^T G(\theta)\delta\theta,$$

where the Fisher information may also be written as

$$X(\theta) = \mathbb{E}\Big[\Big(\frac{\partial}{\partial\theta}\log f(y;\theta)\Big)^2|\theta\Big] = \int\Big(\frac{\partial}{\partial\theta}\log f(y;\theta)\Big)^2 f(y;\theta)\,dy.$$

Fisher information has a lot of impact on a target density $f(\cdot)$ and defines the overall geometry of the space.

3 Numerical simulations

In the following, we are going to describe the proposed technique to approximates the ground state energy of a helium atom by means of refining a trial wave function dependent on a set of parameters, $\Psi(\theta, t)$. The helium atom consists of two electrons and a nucleus with charge $z = 2$. For this two-electron problem, the Schrödinger equation has the form

$$\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2)\Psi - \frac{ze^2}{r_1}\Psi - \frac{ze^2}{r_2}\Psi = E\Psi,$$

where m is the mass of an electron, and the subscripts refer to electron 1 and 2, respectively, and $\hbar$ is the

reduced Planck constant. Here

$$\nabla_1 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}, \quad \nabla_2 = \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}.$$

Then, cross-multiplying, we have

$$-(\nabla_1^2 + \nabla_2^2)\Psi - \frac{2m}{\hbar^2}\frac{ze^2}{r_1}\Psi - \frac{2m}{\hbar^2}\frac{ze^2}{r_2}\Psi = E\frac{2m}{\hbar^2}\Psi.$$

Assuming infinite nuclear masses, the Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{ze^2}{r_1} - \frac{ze^2}{r_2} + \frac{e^2}{r_{12}}.$$

We start with the idea of expressing the kinetic energy part of the Hamiltonian in a form appropriate for this problem. That operator surely has the form

$$-\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2).$$

The contribution to the potential energy due to the attraction from the nucleus is

$$-\frac{2ze^2}{r_1} - \frac{2ze^2}{r_2},$$

and if we add the repulsion arising from the two interacting electrons, we obtain the potential energy

$$V(r_1, r_2) = -\frac{2ze^2}{r_1} - \frac{2ze^2}{r_2} + \frac{ze^2}{r_{12}}$$

with the electrons separated at a distance $r_{12} = |r_1 - r_2|$. Then the Hamiltonian becomes

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

and the Schrödinger equation is $\hat{H}\Psi = E\Psi$ with the corresponding probability density

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

generated by the trial wave function. The choice of the trial wave function used in the computations for helium (assuming $r_1 \to 0$) is

$$E_L(R) = \frac{1}{\Psi_T(R)} H\Psi_T(R) = \frac{1}{\Psi_T(R)}\left(-\frac{1}{2}\nabla_1^2 - \frac{z}{r_1}\right)\Psi_T(R) + \text{finite terms},$$
$$E_L(R) = \frac{1}{R_T(r_1)}\left(-\frac{1}{2}\frac{d^2}{dr_1^2} - \frac{1}{r_1}\frac{d}{dr_1} - \frac{z}{r_1}\right)R_T(r_1) + \text{finite terms}.$$

For small values of r_1, the terms which dominate are

$$\lim_{r_1 \to 0} E_L(R) = \frac{1}{R_T(r_1)}\left(-\frac{1}{r_1}\frac{d}{dr_1} - \frac{z}{r_1}\right)R_T(r_1).$$

This results in

$$\frac{1}{R_T(r_1)}\frac{dR_T(r_1)}{dr_1} = -z \quad \text{and} \quad R_T(r_1) \propto \exp[-zr_1].$$

A similar condition applies to electron 2 as well. For orbital momenta $l > 0$, we have

$$\frac{1}{R_T(r)}\frac{dR_T(r)}{dr} = -\frac{z}{l+1}.$$

Similarly, by the case $r_{12} \to 0$, we can write a possible trial wave function for a system with N electrons or particles as

$$\Psi_{\mathrm{T}}(R) = \Phi(r_1)\Phi(r_2)\cdots\Phi(r_N)\prod_{i<j} f(r_{i,j}).$$

During the development of our benchmark, helium, the wave function is

$$\Psi_{\mathrm{T}}(r_1, r_2) = \exp[-\alpha(r_1 + r_2)] + \exp\left[\frac{r_{12}}{2(1+\beta r_{12})}\right]$$

with α and β as variational parameters. The local energy for this case is defined as

$$E_{\mathrm{L2}} = E_{\mathrm{L1}} + \frac{1}{2(1+\beta r_{12})^2}\left[\frac{\alpha(r_1+r_2)}{r_{12}}\left[1 - \frac{r_1 r_2}{r_1 r_2}\right] - \frac{1}{2(1+\beta r_{12})^2} - \frac{2}{r_{12}} + \frac{2\beta}{1+\beta r_{12}}\right].$$

Various quantum Monte-Carlo methods have in fact been used extensively in the calculation of the ground state energy and wave function for the Schrödinger equation. The basic simulation technique of the various quantum Monte-Carlo methods has been described in detail several times in the literature [1–4, 6, 10, 19, 26, 28, 29, 35], and only a brief description follows here: given a Hamiltonian $\hat{H}$ and a trial wave function Ψ_{T}, the variational principle states that the expectation value of $\langle H \rangle$, defined as

$$E[\hat{H}] = \langle \hat{H} \rangle = \frac{\int dR \Psi_{\mathrm{T}}^{*}(R)\hat{H}(R)\Psi_{\mathrm{T}}(R)}{\int dR \Psi_{\mathrm{T}}^{*}(R)\Psi_{\mathrm{T}}(R)},$$

where the trial wave function can be expanded in the eigenstates of the Hamiltonian

$$\Psi_{\mathrm{T}}(R) = \sum_i \alpha_i \Psi_i(R).$$

The basic procedure in our numerical simulation is as follows:

- Choose a trial wave function $\Psi_{\mathrm{T}}(R, \alpha, \beta)$ for a many-body system consisting of N particles located at positions

$$\bar{R} = \begin{bmatrix} R_1 \\ R_2 \\ \vdots \\ R_N \end{bmatrix},$$

with variational parameters

$$\bar{\alpha} = \begin{bmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_N \end{bmatrix} \quad \text{and} \quad \bar{\beta} = \begin{bmatrix} \beta_1 \\ \beta_2 \\ \vdots \\ \beta_N \end{bmatrix}.$$

- Choose an initial $\bar{R}$ and variational parameters $\bar{\alpha}$ and $\bar{\beta}$ and calculate $|\Psi_{\mathrm{T}}^{\bar{\alpha}\bar{\beta}}(\bar{R})|^2$ with probability density of the wave function defined as

$$p(\bar{R}) = \frac{|\Psi_{\mathrm{T}}(\bar{R})|^2}{\int |\Psi_{\mathrm{T}}(\bar{R})|^2 \, d\bar{R}}.$$

- Define a local energy

$$E_{\mathrm{L}}(\bar{R}, \bar{\alpha}, \bar{\beta}) = \frac{1}{\Psi_{\mathrm{T}}(\bar{R}, \bar{\alpha}, \bar{\beta})}\hat{H}\Psi_{\mathrm{T}}(\bar{R}, \bar{\alpha}, \bar{\beta}).$$

- The local energy together with the trial PDF yields

$$E[\hat{H}(\bar{\alpha}, \bar{\beta})] = \int p(\bar{R}) E_{\mathrm{L}}(\bar{R}) \, d\bar{R} \approx \frac{1}{N}\sum_{i=1}^{N} p(\bar{R}_i, \bar{\alpha}, \bar{\beta}) E_{\mathrm{L}}(\bar{R}_i, \bar{\alpha}, \bar{\beta}).$$

- Initialize the energy and the variance, and start the Monte Carlo calculation.
- Propose a new position vector based on equation (2.2), and calculate a trial position R_{p}.

Method	E_0 (a.u.)	E_0 (eV)
PDMC	−2.903385	−79.0052
MHMC	−2.37401	−64.6
VMC	−2.84609	−77.446
GFMC	−2.37906	−64.7376
VGFMC	−2.85129	−77.5876

Table 1: Ground state energy of helium atom. Comparison between particle diffusion Monte Carlo (PDMC), Metropolis–Hastings Monte Carlo (MHMC) [16], variational Monte Carlo (VMC) [9, 23], Green function Monte Carlo (GFMC) and variational Green function Monte Carlo (VGFMC) [8, 31, 32]. The iterations were performed with a sample of approximately 10^6 points. The total ground state energy of the helium atom is −79.005151042 eV, or −2.90338583 a.u. [37].

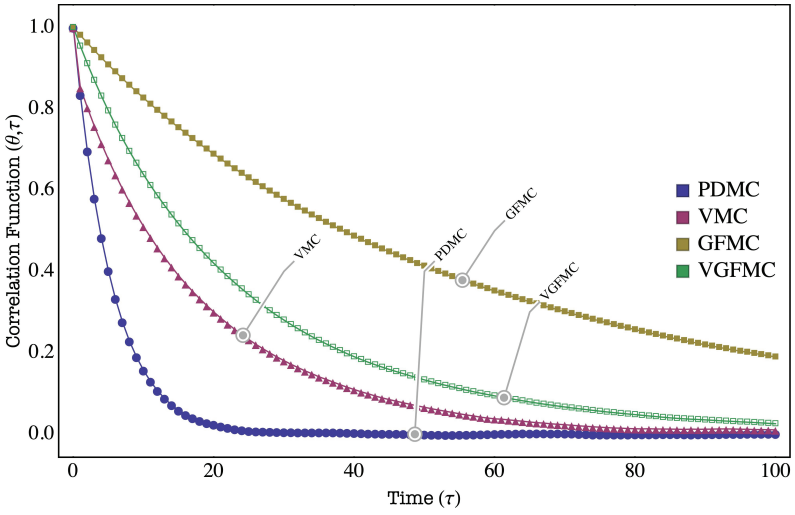

Figure 1: Comparative correlation function in our simulation for a helium atom, which provides a useful way of characterizing the fast convergence with respect to other quantum Monte Carlo methods [8–23, 31, 32].

- Apply the Metropolis-Hastings proposal algorithm to accept or reject this move $p(R_\mathrm{p})/p(R)$.
- If the step is accepted, then set $R = R_\mathrm{p}$.
- Evaluate the expectation value of the Hamiltonian $\hat{H}$.

In Table 1, we report the ground state energy obtained by some of the method in the literature and the proposed described in this work.

For the second benchmark, we evaluate the performance of our method, which involves sampling from the probability density function of a free particle in a plane of dimension L_x and L_y. The time-independent Schrödinger equation for this system, as a wave function $|\Psi\rangle$, can be written as [30]

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}\right]=E\Psi,$$

where the permitted energy values are

$$E_{n_x,n_y}=\frac{\rho^2\hbar^2}{2m}\left[\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}\right],$$

where ρ is a momentum and $\hbar$ is the reduced Planck constant, while the normalized wave function is defined as

$$\Psi_{n_x,n_y}(x,y)=\frac{2}{\sqrt{L_xL_y}}\sin\left[\frac{n_x\pi x}{L_x}\right]\sin\left[\frac{n_y\pi y}{L_y}\right].$$

where $n_xn_y = 1, 2, 3, \ldots$. We evaluate the performances of the proposed method by comparing it to the pure Hamiltonian Monte Carlo (HMC) [11, 15, 25] and the classic Metropolis-adjusted Langevin algorithm

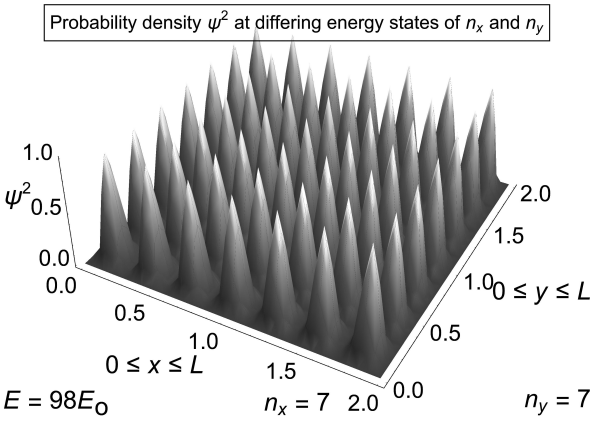

Figure 2: Probability distribution wave function for a free particle.

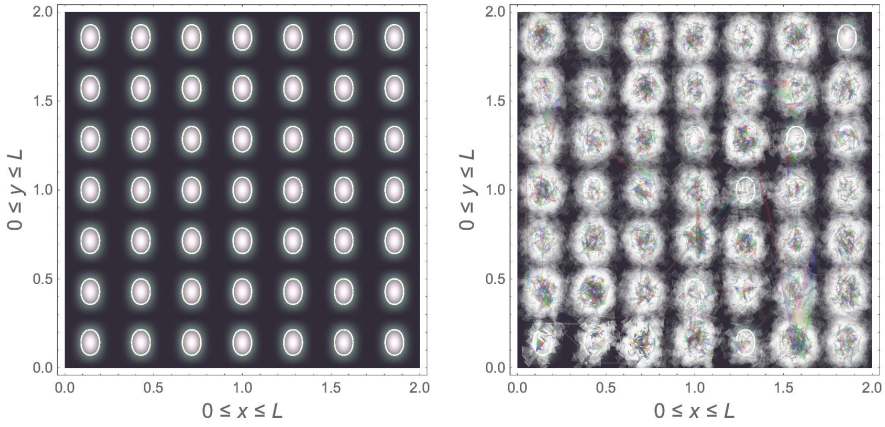

Figure 3: Sampling trajectory of the proposed method, indicating a robust mixing property and fast convergence to the theoretical reference values. Left and right panels are contour plots for target density and estimated posterior probability distribution in order.

(MALA) [27]. In order to evaluate the performance of the above models, we run the Monte Carlo simulation to obtain $N = 50000$ samples. In Figure 3, we represent the posterior estimation of the probability density function for a particle from our method (PDMC).

It is interesting to conclude that HMC and MALA failed in sampling from the probability density function of a free particle because of the complexity of spaces where modes are isolated, small and hard to hit. Instead, the proposed method defines precisely high density regions around the modes and results in a more efficient exploration of the posterior probability density (Figure 3). Table 2 demonstrates the overall performance of the proposed method in comparison with the other two algorithms. The computational test in this study is done on a 2.3 GHz quad-core Intel Core i5-based MacBook Pro system with 8 GB of RAM. We would also like to mention that, for the numerical simulations, we use a pseudo-random number generator armed with special features and carefully designed for use in high performance computation based on cellular automata [36].

Method	CPU (s)	Speed
HMC	No convergence	—
MALA	No convergence	—
PDMC	115	t_{10}

Table 2: Comparison of sampling methods from the probability density function of a free particle with $N = 50000$ samples for every Monte Carlo simulation, where the average CPU time is measured in seconds for the whole run.

4 Discussion and conclusion

In this paper, we proposed a new Monte Carlo method (PDMC), to resolve the problem of existing Monte Carlo algorithms. We have discussed a possible method for the numerical solution of the many-body Schrödinger equation and described the computational procedures required for our solution. Therefore, we evaluated the performance of proposed method to compare upon existing MCMC methodologies. We also provide a probabilistic approach to model stochastic diffusion processes. Through experiments, we visualize the estimated densities between most probable regions, which leads to smoother and more coherent results in contrast to other Monte Carlo sampling methods.

References

[1] N. Aquino, The role of correlation in the ground state energy of confined helium atom, *AIP Conf. Proc.* **1579** (2014), no. 1, 136–140.
[2] N. Aquino, A. Flores-Riveros and J. F. Rivas-Silva, The compressed helium atom variationally treated via a correlated Hylleraas wave function, *Phys. Lett. A* **307** (2003), no. 5–6, 326–336.
[3] N. Aquino, J. Garza, A. Flores-Riveros, J. F. Rivas-Silva and K. D. Sen, Confined helium atom low-lying S states analyzed through correlated Hylleraas wave functions and the Kohn–Sham model, *J. Chem. Phys.* **124** (2006), no. 5, Article ID 054311.
[4] A. Banerjee, C. Kamal and A. Chowdhury, Calculation of ground-and excited-state energies of confined helium atom, *Phys. Lett. A* **350** (2006), no. 1–2, 121–125.
[5] E. Barkai, R. Metzler and J. Klafter, From continuous time random walks to the fractional Fokker–Planck equation, *Phys. Rev. E* **61** (2000), no. 1, Article ID 132.
[6] C. F. Bunge, J. A. Barrientos and A. V. Bunge, Roothaan–Hartree–Fock ground-state atomic wave functions: Slater-type orbital expansions and expectation values for Z= 2-54, *At. Data Nuclear Data Tables* **53** (1993), no. 1, 113–162.
[7] A. O. Caldeira and A. J. Leggett, Path integral approach to quantum Brownian motion, *Phys. A* **121** (1983), no. 3, 587–616.
[8] J. Carlson, Green's function Monte Carlo study of light nuclei, *Phys. Rev. C* **36** (1987), no. 5, Article ID 2026.
[9] D. Ceperley, G. V. Chester and M. H. Kalos, Monte carlo simulation of a many-fermion study, *Phys. Rev. B* **16** (1977), no. 7, Article ID 3081.
[10] G. W. F. Drake and Z. C. Van, Variational eigenvalues for the S states of helium, *Chem. Phys. Lett.* **229** (1994), no. 4–5, 486–490.
[11] S. Duane, A. D. Kennedy, B. J. Pendleton and D. Roweth, Hybrid Monte Carlo, *Phys. Lett. B* **195** (1987), no. 2, 216–222.
[12] T. D. Frank, *Nonlinear Fokker–Planck Equations: Fundamentals and Applications*, Springer, Berlin, 2005.
[13] A. L. Garcia and B. J. Alder, Generation of the Chapman–Enskog distribution, *J. Comput. Phys.* **140** (1998), no. 1, 66–70.
[14] A. Gelman, H. S. Stern, J. B. Carlin, D. B. Dunson, A. Vehtari and D. B. Rubin, *Bayesian Data Analysis*, Chapman and Hall/CRC, Boca Raton, 2013.
[15] M. Girolami and B. Calderhead, Riemann manifold Langevin and Hamiltonian Monte Carlo methods, *J. Roy. Statist. Soc. Ser. B* **73** (2011), no. 2, 123–214.
[16] W. K. Hastings, Monte Carlo sampling methods using markov chains and their applications, *Biometrika* **57** (1970), no. 1, 97–109.
[17] X. He and L. S. Luo, A priori derivation of the lattice Boltzmann equation, *Phys. Rev. E* **55** (1997), no. 6, Article ID R6333.
[18] R. H. Heist, F. K. Fong, Maxwell–Boltzmann distribution of $M^{3+} - F^{-}$ interstitial pairs in fluorite-type lattices, *Phys. Rev. B* **1** (1970), no. 7, Article ID 2970.
[19] C. Huiszoon and W. J. Briels, The static dipole polarizabilities of helium and molecular hydrogen by differential diffusion Monte Carlo, *Chem. Phys. Lett.* **203** (1993), no. 1, 49–54.
[20] R. Jordan, D. Kinderlehrer and F. Otto, The variational formulation of the Fokker–Planck equation, *SIAM J. Math. Anal.* **29** (1998), no. 1, 1–17.
[21] H. A. Kramers, Brownian motion in a field of force and the diffusion model of chemical reactions, *Physica* **7** (1940), no. 4, 284–304.
[22] B. H. Lavenda, *Nonequilibrium Statistical Thermodynamics*, Wiley, New York, 1985.
[23] W. L. McMillan, Ground state of liquid He 4, *Phys. Rev.* **138** (1965), no. 2A, 442–451.
[24] R. Metzler, E. Barkai and J. Klafter, Anomalous diffusion and relaxation close to thermal equilibrium: A fractional Fokker–Planck equation approach, *Phys. Rev. Lett.* **82** (1999), no. 18, Article ID 3563.
[25] R. M. Neal, Mcmc using Hamiltonian dynamics, in: *Handbook of Markov Chain Monte Carlo*, Chapman & Hall/CRC, Boca Raton (2011), 113–162.

[26] S. H. Patil, Wavefunctions for the confined hydrogen atom based on coalescence and inflexion properties, *J. Phys. B* **35** (2002), no. 2, Article ID 255.
[27] G. Roberts and O. Stramer, Langevin diffusions and metropolis-Hastings algorithms, *Methodol. Comput. Appl. Probab.* **4** (2003), no. 4, 337–358.
[28] M. Rodriguez-Bautista, C. Diaz-Garcia, A. M. Navarrete-Lopez, R. Vargas and J. Garza, Roothaan's approach to solve the Hartree–Fock equations for atoms confined by soft walls: Basis set with correct asymptotic behavior, *J. Chem. Phys.* **143** (2015), no. 3, Article ID 034103.e.
[29] K. K. Sabelfeld, *Monte Carlo Methods in Boundary Value Problems*, Springer, Berlin, 1991.
[30] E. Schrödinger, An undulatory theory of the mechanics of atoms and molecules, *Phys. Rev.* **28** (1926), no. 6, Article ID 1049.
[31] N. Trivedi and D. M. Ceperley, Green-function Monte Carlo study of quantum antiferromagnets, *Phys. Rev. B* **40** (1989), no. 4, Article ID 2737.
[32] N. Trivedi and D. M. Ceperley, Ground-state correlations of quantum antiferromagnets: A green-function monte carlo study, *Phys. Rev. B* **41** (1990), no. 7, Article ID 4552.
[33] G. E. Uhlenbeck and L. S. Ornstein, On the theory of the Brownian motion, *Phys. Rev.* **36** (1930), no. 5, Article ID 823.
[34] W. Wagner, A random walk model for the Schrödinger equation, *Math. Comput. Simulation* **143** (2018), 138–148.
[35] T. D. Young, R. Vargas and J. Garza, A Hartree–Fock study of the confined helium atom: Local and global basis set approaches, *Phys. Lett. A* **380** (2016), no. 5–6, 712–717.
[36] Z. Zarezadeh, Cellular automaton-based pseudorandom number generator, *Complex Systems* **26** (2017), no. 4, 373–389.
[37] NIST, Atomic Spectra Database Ionization Energies Data (2018).