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## Diffusion Monte Carlo: A powerful tool for studying quantum many-body systems

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Diffusion quantum Monte Carlo is introduced at an elementary level. We highlight the strengths of the method in addressing important issues associated with quantum many-body systems, such as those associated with the ground-state energy and pair-distribution function. <sup>4</sup>He clusters trapped on a graphite surface are simulated as an example of the method. A sample program and documentation for developing simulation projects are provided. © 2014 American Association of Physics Teachers.  
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### I. INTRODUCTION

Understanding quantum many-body systems usually means solving the Schrödinger equation of a system of many interacting particles. However, there is no panacea for solving the many-body Schrödinger equation. Different approximations must be made to understand the roles played by the interactions between the particles in different systems under various conditions.

The diffusion Monte Carlo method<sup>1</sup> is a stochastic scheme that can extract important information about the ground state and sometimes excited states of many-body systems. The method maps the Schrödinger equation onto a diffusion equation under an imaginary-time transformation and guides the system toward its ground state over time. In principle, it is an exact method for calculating the ground-state properties of a many-boson system.

There is a major hurdle in applying the method to a many-fermion system because of the statistics of fermions. A typical wavefunction of a many-fermion system has a complex nodal structure which prevents an easy stochastic process from driving the system to its ground state. This problem is called the *fermion sign problem*,<sup>2</sup> because crossing a node of the wavefunction changes its sign.

Quantum effects in helium atoms can become very important when the temperature is below a few kelvins. A helium droplet is a fascinating many-body system that can have many different collective states, which are formed from the interplay of quantum fluctuations and the strong interaction between atoms,<sup>3</sup> including recent observations of <sup>3</sup>He puddles<sup>4</sup> and quantum vortices in a superfluid helium droplet.<sup>5</sup>

The paper is structured as follows. We first discuss the Metropolis algorithm, which forms the backbone of most Monte Carlo methods. Then we introduce the variational Monte Carlo method, which utilizes the Metropolis algorithm and the variational principle. It provides an initialization and some key elements for a diffusion quantum Monte

Carlo simulation. The importance-sampling diffusion quantum Monte Carlo method is then introduced. To illustrate both methods, we show how to implement them for <sup>4</sup>He clusters trapped on the surface of graphite. We will assume that readers have some familiarity with quantum physics and statistical mechanics.

### II. THE METROPOLIS ALGORITHM

We first discuss a sampling scheme devised by Metropolis *et al.*<sup>6</sup> to evaluate multivariable integrals under a distribution function. For example, a typical problem in classical statistical mechanics requires the evaluation of integrals with many variables under the Boltzmann distribution.

Consider a system of  $N$  particles, such as the atoms in a classical liquid, with  $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ , the  $3N$ -dimensional position vector of the particles. In the canonical ensemble, we want a statistical process that leads the system to the equilibrium distribution of the particles given by

$$W(\mathbf{R}) = \frac{e^{-U(\mathbf{R})/kT}}{\int e^{-U(\mathbf{R}')/kT} d\mathbf{R}'}, \quad (1)$$

where  $U(\mathbf{R})$  is the potential energy of the system for a given configuration  $\mathbf{R}$ . Here  $k$  is the Boltzmann constant and  $T$  is the temperature of the system. Note that

$$\int W(\mathbf{R}) d\mathbf{R} = 1. \quad (2)$$

The average of a physical quantity  $A$  of the system is given by

$$\langle A \rangle = \int A(\mathbf{R}) W(\mathbf{R}) d\mathbf{R} \simeq \frac{1}{M} \sum_{i=1}^M A(\mathbf{R}_i), \quad (3)$$

where  $M$  is the number of configurations sampled according to the distribution function  $W(\mathbf{R})$ .

In equilibrium, the values of the distribution function at different points of the configuration space must satisfy the condition

$$W(\mathbf{R})T(\mathbf{R} \rightarrow \mathbf{R}') = W(\mathbf{R}')T(\mathbf{R}' \rightarrow \mathbf{R}), \quad (4)$$

where  $T(\mathbf{R} \rightarrow \mathbf{R}')$  is the transition rate from configuration  $\mathbf{R}$  to configuration  $\mathbf{R}'$ . This condition is usually referred to as *detailed balance*.

The *Metropolis algorithm*<sup>6</sup> samples the configurations such that the move from one configuration  $\mathbf{R}$  to another  $\mathbf{R}'$  is accepted if the ratio of the transition rates satisfies the condition

$$\frac{T(\mathbf{R} \rightarrow \mathbf{R}')}{T(\mathbf{R}' \rightarrow \mathbf{R})} = \frac{W(\mathbf{R}')}{W(\mathbf{R})} > \eta, \quad (5)$$

where  $\eta \in [0, 1]$  is a uniform random number. To evaluate the integral  $\langle A \rangle$ , we first randomly select an allowable and, if possible, likely configuration  $\mathbf{R}$  and evaluate  $W(\mathbf{R})$ . A new configuration  $\mathbf{R}'$  is attempted with

$$\mathbf{R}' = \mathbf{R} + \Delta\mathbf{R}, \quad (6)$$

where  $\Delta\mathbf{R}$  is a  $3N$ -dimensional vector with a component chosen from a uniform distribution between  $[-h, h]$ . For example,

$$\Delta x_i = h(2\eta - 1), \quad (7)$$

for the  $x$  component of  $\mathbf{r}_i$ . If the length scale in one direction, for example, the  $z$  direction, is different from the others, we can choose  $h_z$  to be different from  $h_x$  or  $h_y$ . The value chosen for the step size  $h$  is determined from the desired acceptance probability (the ratio of the accepted to the attempted steps). Larger  $h$  results in a smaller acceptance probability. To optimize the sampling, the acceptance probability times  $h^2$  is maximized. In practice,  $h$  is commonly chosen so that the acceptance probability of the moves is less than or close to 50%. The attempted change in the configuration is usually made by moving one particle at a time. However, moving all particles at once can speed up the exploration of configuration space if  $N$  is not too large. In the program provided all the components of  $\mathbf{R} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  are attempted at each Metropolis move.

The ratio of the distribution function at the attempted new configuration to that of the old configuration is computed and the new configuration is accepted using Eq. (5). If the ratio is greater than  $\eta$ , the new configuration is accepted; otherwise, the old configuration is assumed to be the new configuration. The desired quantity  $A(\mathbf{R}_i)$  is evaluated at  $\ell = n_1 + n_0, n_1 + 2n_0, \dots, n_1 + Mn_0$ , and the integral is approximated by

$$\langle A \rangle \simeq \frac{1}{M} \sum_{\ell=1}^M A(\mathbf{R}_{n_1+\ell n_0}). \quad (8)$$

Note that  $n_1 + n_0$  moves are used to remove the influence of the initial configuration. The thermodynamic data are taken  $n_0$  moves apart to avoid correlations between the data because they are generated consecutively and a reasonable number of attempted moves, typically on the order of ten,<sup>7</sup> should be skipped before the next data point is used.

In most cases, the distribution function  $W(\mathbf{R})$  varies by several orders of magnitude, whereas  $A(\mathbf{R})$  remains smooth or is nearly constant. The sampling scheme that we have outlined yields the average of a physical quantity according to the distribution  $W(\mathbf{R})$ . In other words, configurations with a greater value of  $W(\mathbf{R})$  will occur more often. Importance sampling is the essence of the Metropolis algorithm and is much more efficient than a random sampling of an integrand with a large number of variables.

### III. VARIATIONAL MONTE CARLO

In the following, we outline the most direct application of the Metropolis algorithm to quantum many-body systems using the variational principle. Consider a quantum system of  $N$  interacting particles with the Hamiltonian  $H$ . The corresponding time-independent Schrödinger equation can be written symbolically as

$$H\Psi_n(\mathbf{R}) = E_n\Psi_n(\mathbf{R}), \quad (9)$$

where  $\Psi_n(\mathbf{R})$  and  $E_n$  are the  $n$ th eigenstate and the corresponding eigenvalue of  $H$ , respectively.

Usually we cannot obtain an analytical or exact solution of the Schrödinger equation of a system with more than two particles. Therefore approximate methods are important tools for studying quantum systems. It is easiest to study the ground state of a many-body system.

Based on the variational principle, we can use a trial state  $\Phi(\mathbf{R})$  to approximate the ground-state wavefunction. The parameters or functions in  $\Phi(\mathbf{R})$  can be optimized according to the variational principle:

$$E[\alpha_i] = \frac{\langle \Phi | H | \Phi \rangle}{\langle \Phi | \Phi \rangle} \geq E_0, \quad (10)$$

where  $E_0$  is the ground-state energy of the system and  $\alpha_i$  is a set of linearly independent variational parameters or functions. This inequality can be shown by expanding  $\Phi(\mathbf{R})$  in terms of the eigenstates of the Hamiltonian with

$$\Phi(\mathbf{R}) = \sum_{n=0}^{\infty} a_n \Psi_n(\mathbf{R}). \quad (11)$$

The expansion in Eq. (11) is a generalization of the Fourier theorem because the  $\Psi_n(\mathbf{R})$  form a complete basis set. The variational principle results if we substitute the expansion for  $\Phi(\mathbf{R})$  into the expectation value with the understanding that  $E_n \geq E_0$  for  $n > 0$  and  $\langle \Psi_n | \Psi_m \rangle = \delta_{nm}$ .

To simplify our discussion, we assume that the space hosting the system is a continuum and that  $\alpha_i$  is a set of variational parameters. Hence, we can write the expectation value in the form of an integral

$$E[\alpha_i] = \frac{\int \Phi^\dagger(\mathbf{R}) H \Phi(\mathbf{R}) d\mathbf{R}}{\int |\Phi(\mathbf{R}')|^2 d\mathbf{R}'} = \int W(\mathbf{R}) E(\mathbf{R}) d\mathbf{R}, \quad (12)$$

where

$$W(\mathbf{R}) = \frac{|\Phi(\mathbf{R})|^2}{\int |\Phi(\mathbf{R}')|^2 d\mathbf{R}'} \quad (13)$$

can be interpreted as a distribution function and

$$E(\mathbf{R}) = \frac{H\Phi(\mathbf{R})}{\Phi(\mathbf{R})} \quad (14)$$

can be viewed as a local energy, a physical quantity of the system at configuration  $\mathbf{R}$ . The expectation value  $E[\alpha_i]$  can be evaluated if the expressions for  $E(\mathbf{R})$  and  $W(\mathbf{R})$  for a specific set of parameters  $\alpha_i$  are available. In practice,  $\Phi(\mathbf{R})$  can be parameterized to include the relevant physics. The variational parameters  $\alpha_i$  in the trial wavefunction  $\Phi(\mathbf{R})$  can then be optimized by minimizing  $E[\alpha_i]$ .

Each evaluation of the expectation value in the variational quantum Monte Carlo method for a given set of variational parameters is equivalent to the evaluation of an average of a physical quantity of a classical system with the same Metropolis algorithm for a given temperature. During the sampling process, we can either update the entire configuration or just the coordinates associated with a particular particle at each step. If the variational wavefunction  $\Phi(\mathbf{R})$  is sufficiently simple, for example, it contains a small number of parameters, we can search for the optimal state by varying each parameter in the simulation. If the form of the wavefunction is more complicated, or there are more than a few parameters, a systematic scheme can be designed to optimize the wavefunction based on the Euler–Lagrange equation

$$\frac{\delta E[\alpha_i]}{\delta \alpha_j} = 0, \quad (15)$$

for  $j = 1, 2, 3, \dots$ . Good examples of performing a systematic search of variational parameters are available.<sup>9</sup>

It is important to include in the variational wavefunction a way to cope with the divergence of the interaction when two particles approach each other. It is common to have this divergence canceled by the relative kinetic energy of the two particles when their separation goes to zero. Such a constraint on the wavefunction is called the *cusp condition*<sup>10</sup> and can be found by solving the two-body problem analytically for a vanishing separation distance. If the cusp condition is built into the variational wavefunction, fluctuations of the results are significantly reduced, and we can simulate a system with a larger number of particles and greater accuracy. We will demonstrate this point in the example of <sup>4</sup>He clusters trapped on the surface of graphite.

The kinetic energy of the  $i$ th particle,  $K_i$ , can be written in two parts as

$$K_i = -\frac{\hbar^2}{2m} \frac{\nabla_i^2 \Phi(\mathbf{R})}{\Phi(\mathbf{R})} = 2T_i - |\mathbf{F}_i|^2, \quad (16)$$

where

$$T_i = -\frac{\hbar^2}{4m} \nabla_i^2 \ln|\Phi(\mathbf{R})| \quad (17)$$

and

$$\mathbf{F}_i = \frac{\hbar}{\sqrt{2m}} \nabla_i \ln|\Phi(\mathbf{R})|. \quad (18)$$

In principle, both  $T_i$  and  $|\mathbf{F}_i|^2$  converge to the kinetic energy  $K_i$ , which can be shown by integration by parts.<sup>11</sup> In practice, each term fluctuates during sampling. The combination minimizes the fluctuations because the two terms have opposite signs. The separate evaluation of  $T_i$  and  $|\mathbf{F}_i|^2$  also provides

an independent check on the convergence and validity of the average kinetic energy through the combination.

#### IV. THE DIFFUSION QUANTUM MONTE CARLO METHOD

The limitation of the variational quantum Monte Carlo method is obvious. Unless we know the exact form of the ground-state wavefunction, the simulation will never approach the ground state. In many cases, we may not even have enough information to construct a decent variational wavefunction. Is there still a way to simulate a many-body system if we have limited knowledge?

We can rewrite the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi(\mathbf{R}, t)}{\partial t} = H\Psi(\mathbf{R}, t) \quad (19)$$

in the imaginary-time form

$$\frac{\partial \Psi(\mathbf{R}, \tau)}{\partial \tau} = -(H - E_R)\Psi(\mathbf{R}, \tau), \quad (20)$$

where  $E_R$  is a reference energy that can be interpreted as the zero point of the system's energy at the given moment and  $\tau = it/\hbar$ , with  $t$  equal to the real time from the original Schrödinger equation.  $E_R$  is adjusted so that the simulation will converge faster. We have absorbed Planck's constant  $\hbar$  into the time for convenience. The solution of the diffusion equation (20) can be written symbolically as

$$\Psi(\mathbf{R}, \tau) = e^{-(H-E_R)\tau} \Psi(\mathbf{R}, 0) \quad (21)$$

if we start from an initial state  $\Psi(\mathbf{R}, 0)$ .

A good choice for the initial state of configuration is  $\Psi(\mathbf{R}, 0) = \Phi(\mathbf{R})$ , the trial wavefunction that we have already found from the variational Monte Carlo simulation. We can multiply the imaginary-time Schrödinger equation by  $\Phi(\mathbf{R})$  and rewrite it as a diffusion equation for  $f(\mathbf{R}, \tau) = \Phi(\mathbf{R})\Psi(\mathbf{R}, \tau)$ :

$$\begin{aligned} \frac{\partial f(\mathbf{R}, \tau)}{\partial \tau} = & \frac{\hbar^2}{2m} \nabla^2 f(\mathbf{R}, \tau) - \mathbf{V} \cdot [\mathbf{V}(\mathbf{R})f(\mathbf{R}, \tau)] \\ & - [E(\mathbf{R}) - E_R]f(\mathbf{R}, \tau), \end{aligned} \quad (22)$$

where the local energy  $E(\mathbf{R})$  was defined earlier and  $f(\mathbf{R}, \tau)$  can be interpreted as a distribution function of the system with configuration  $\mathbf{R}$  at time  $\tau$  if  $f(\mathbf{R}, \tau)$  is always positive. The vector

$$\mathbf{V}(\mathbf{R}) = \frac{\hbar^2}{m} \nabla \ln|\Phi(\mathbf{R})| = \sqrt{\frac{2\hbar^2}{m}} \mathbf{F} \quad (23)$$

can be interpreted as a drift velocity of the distribution in configuration space.

It is clear from the form of Eq. (22) that the time evolution of  $f(\mathbf{R}, \tau)$  is influenced by three contributions, a pure diffusion term involving  $\nabla^2$ , a drift term involving  $\mathbf{V}$ , and a source/sink term involving  $E - E_R$ .

The short-time evolution of  $f(\mathbf{R}, \tau)$  is given by

$$f(\mathbf{R}', \tau + \Delta\tau) = \int G(\mathbf{R}', \mathbf{R}; \Delta\tau) f(\mathbf{R}, \tau) d\mathbf{R}, \quad (24)$$



where the propagator

$$G(\mathbf{R}', \mathbf{R}; \Delta\tau) = \left(\frac{1}{2\pi\chi^2}\right)^{3N/2} e^{-[\mathbf{R}' - \mathbf{R} - \Delta\tau\mathbf{V}(\mathbf{R})]^2/2\chi^2 - \Delta\tau[E(\mathbf{R}) - E_R]} \quad (25)$$

carries the system from configuration  $\mathbf{R}$  at time  $\tau$  to the new configuration  $\mathbf{R}'$  at time  $\tau + \Delta\tau$ .

The three contributions can be clearly identified in  $G(\mathbf{R}', \mathbf{R}; \Delta\tau)$ . The first is a random walk, following a Gaussian distribution with variance  $\chi^2 = \hbar^2 \Delta\tau/m$ . The second is a drift process that moves the mean value of the configuration by  $\Delta\tau\mathbf{V}(\mathbf{R})$ . To include these two contributions, the configuration is updated according to

$$\mathbf{R}' = \mathbf{R} + \Delta\tau\mathbf{V}(\mathbf{R}) + \xi, \quad (26)$$

where  $\xi$  is a 3  $N$ -dimensional Gaussian random number with a variance of  $\chi^2$  in each component.

What is left in the propagator is a contribution which either lowers or raises the population of configurations in the ensemble according to the birth/death rate

$$W_B(\mathbf{R}) \propto e^{-\Delta\tau[E(\mathbf{R}) - E_R]}. \quad (27)$$

The lower the value of the local energy  $E(\mathbf{R})$ , the higher the rate. This part of the contributions in the propagator can be sampled by a *branching* process:  $M_B \propto W_B(\mathbf{R})$  copies of the configuration  $\mathbf{R}$  are created to be part of the new ensemble and a mechanism, which does not influence the relative weight of each configuration, needs to be devised to control the overall number of configurations in the ensemble. Usually this control is done by adjusting the reference energy

$$E_R \rightarrow E_R + \kappa \ln \frac{N_P}{N_E} \quad (28)$$

during the simulation with  $N_P$  being the preferred population targeted from a current population of  $N_E$ . The small parameter  $\kappa$  is selected to control the speed of adjustment. The adjusted reference energy approaches the ground-state energy of the system as the simulation progresses.

The sampling process starts from a selected trial wavefunction,  $\Phi(\mathbf{R})$ , which evolves through the diffusion process by the propagator to the ground state of the system. For a boson system, the function  $f(\mathbf{R}, \tau)$  can always be made real and positive and behaves as a true distribution. Simulation errors still arise from the finite size of the system, the finite time step, and the finite number of samples. In principle, the guide wavefunction does not affect the outcome of the simulation if the simulation is performed for a long time and if the guide wavefunction has a finite overlap with the actual ground state of the system. In practice, the overlap between the guide wavefunction and the true ground state impacts the speed of convergence of the simulation, and therefore is an important aspect to consider. For a fermion system, the wavefunction has a nodal structure that is usually unknown and further approximations have to be made because of the fermion sign problem.

Although the reference energy approaches the ground-state energy of the system if the simulation converges, we do not use it to estimate the ground-state energy because it is adjusted during the simulation. Instead the ground-state

energy is sampled from the distribution function  $f(\mathbf{R}, \tau)$  at large time  $\tau$ . Because

$$\lim_{\tau \rightarrow \infty} f(\mathbf{R}, \tau) = \Phi(\mathbf{R})\Psi_0(\mathbf{R}), \quad (29)$$

the ground-state energy can be obtained from the time-dependent variational energy

$$E(\tau) = \frac{\langle \Phi | H | \Psi \rangle}{\langle \Phi | \Psi \rangle} = \frac{\int E(\mathbf{R}) f(\mathbf{R}, \tau) d\mathbf{R}}{\int f(\mathbf{R}, \tau) d\mathbf{R}}, \quad (30)$$

which can be interpreted as an average sampled over the distribution function  $f(\mathbf{R}, \tau)$ . For example, if we have an ensemble of configurations  $\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_E}$ , distributed according to  $f(\mathbf{R}, \tau)$ , the average energy is given by

$$E(\tau) = \frac{\sum_{i=1}^{N_E} E(\mathbf{R}_i) W_B(\mathbf{R}_i)}{\sum_{i=1}^{N_E} W_B(\mathbf{R}_i)}, \quad (31)$$

which approaches the exact ground-state energy  $E_0$  at infinite time as  $f(\mathbf{R}, \tau)$  approaches its limiting value given by Eq. (29).

Our discussion forms the basis of the diffusion Monte Carlo for a boson system and can be refined by some other steps. The update in the drift part is accurate only up to the linear term in  $\Delta\tau$  and can be improved with a better approximation of the short-time propagator.<sup>12</sup> For example, the second-order approximation of the propagator replaces  $\Delta\tau\mathbf{V}(\mathbf{R})$  by  $\Delta\tau\mathbf{V}(\mathbf{R}_t)$ ,<sup>13</sup> where

$$\mathbf{R}_t = \mathbf{R} + \frac{\Delta\tau}{4} \left\{ \mathbf{V}(\mathbf{R}) + \mathbf{V} \left[ \mathbf{R} + \frac{\Delta\tau}{2} \mathbf{V}(\mathbf{R}) \right] \right\}. \quad (32)$$

To reduce the branching fluctuations, we can replace the local energy  $E(\mathbf{R})$  in  $W_B(\mathbf{R})$  by the average energy of the old and new configurations,  $[E(\mathbf{R}) + E(\mathbf{R}')]/2$ , resulting in a smoother propagator. Also, a Metropolis move can be inserted between the configuration update and branching with the acceptance probability

$$p = \min \left\{ 1, \frac{|\Phi(\mathbf{R}')|^2 G(\mathbf{R}, \mathbf{R}'; \Delta\tau)}{|\Phi(\mathbf{R})|^2 G(\mathbf{R}', \mathbf{R}; \Delta\tau)} \right\} > \eta \quad (33)$$

for the new configuration  $\mathbf{R}'$ . This additional step ensures detailed balance between  $\mathbf{R}$  and  $\mathbf{R}'$  in configuration space.

For a fermion system, a boson-equivalent approach, called the *fixed-node approximation*,<sup>14</sup> can be introduced to reject any attempt that would cross a node in the trial wavefunction. Several methods have been introduced to relax the nodes of the guide wavefunction, with only limited success, due in part to the intrinsic complexity of the fermion sign problem.<sup>2</sup>

## V. STRUCTURAL ANALYSIS

We can analyze the structural properties of a many-body system from the behavior of its distribution functions. Suppose that a system has  $N$  particles and is in its ground state described by the wavefunction  $\Psi_0(\mathbf{R})$ . The  $n$ -body distribution function is given by

$$\rho_n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \frac{1}{Z(N-n)} \int |\Psi_0(\mathbf{R})|^2 d\mathbf{r}_{n+1} d\mathbf{r}_{n+2} \dots d\mathbf{r}_N, \quad (34)$$

where

$$Z = \int |\Psi_0(\mathbf{R})|^2 d\mathbf{R} \quad (35)$$

is the normalization factor. One of the most interesting distribution functions is the pair distribution function  $g(\mathbf{r}, \mathbf{r}')$ , which is defined by

$$\rho_1(\mathbf{r})g(\mathbf{r}, \mathbf{r}')\rho_1(\mathbf{r}') = \rho_2(\mathbf{r}, \mathbf{r}') \quad (36)$$

and contains information about long-range order in the system.

For a uniform system,  $\rho_1(\mathbf{r})$  is the density of the system,  $\rho = N/V$ , where  $V$  is the volume of the system, and  $g(\mathbf{r}, \mathbf{r}') = g(|\mathbf{r}' - \mathbf{r}|)$ . The radial distribution function  $g(r)$  can be interpreted as the probability of finding another particle a distance  $r$  away from a given particle. If we know  $g(r)$ , we can find the corresponding structure function,  $S(k)$ , which is measured in a typical scattering experiment. Formally  $S(k) - 1$  is the Fourier transform of  $g(r) - 1$ , that is,

$$\begin{aligned} S(k) - 1 &= \rho \int [g(r) - 1] e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} \\ &= 4\pi\rho \int_0^\infty \frac{\sin kr}{kr} [g(r) - 1] r^2 dr. \end{aligned} \quad (37)$$

To perform a numerical evaluation of  $g(r)$ , we count the average number of particles in the spherical shell between  $r$  and  $r + dr$  around any given particle in the system and then divide this number by the number of particles in the same spherical shell of the corresponding ideal gas of the same density,  $4\pi\rho[(r + dr)^3 - r^3]/3$ . If the system is two-dimensional or has a layered structure, we can introduce the two-dimensional radial distribution function, which is useful for characterizing a system trapped on a surface. For a two-dimensional system, the number of particles in the spherical shell is replaced by the number of particles in the ring between  $r$  and  $r + dr$ . For an ideal gas with area density  $\rho$ , the number of particles in the ring is  $\pi\rho[(r + dr)^2 - r^2]$ .

## VI. $^4\text{He}$ CLUSTERS ON A GRAPHITE SURFACE

The best known variational quantum Monte Carlo application is by McMillan for the ground state of liquid  $^4\text{He}$ .<sup>8</sup> Over the years, many interesting quantum phenomena have been observed for a collection of helium atoms. We will consider a cluster of  $^4\text{He}$  atoms on the surface of graphite.

### A. The model Hamiltonian

The Hamiltonian for  $N$   $^4\text{He}$  atoms on the surface of graphite can be written as

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N U_{\text{ext}}(\mathbf{r}_i) + \sum_{i>j=1}^N V(r_{ij}), \quad (38)$$

where  $U_{\text{ext}}$  represents the interaction between a helium atom and the graphite surface and  $V$  is the interaction between helium atoms. We use a simple, parameterized surface potential introduced by Joly, Lhuillier, and Bami.<sup>15</sup> The latter potential is given by

$$U_{\text{ext}}(z) = \epsilon U^*(y), \quad (39)$$

where

$$U^*(y) = u_0 e^{-\gamma y} - \frac{a_3}{y^3} - \frac{a_4}{y^4}, \quad (40)$$

with  $y = z/r_m$ . The parameters for a helium atom on the surface of graphite are  $r_m = 2.9683 \text{ \AA}$ ,  $\epsilon/k = 10.956 \text{ K}$ ,  $u_0 = 206875.0$ ,  $\gamma = 11.027235$ ,  $a_3 = 6.386763$ , and  $a_4 = 12.116816$ .<sup>15</sup>

The interaction between two helium atoms is taken to be the Aziz potential and is given by<sup>16</sup>

$$V(r) = \epsilon V^*(x), \quad (41)$$

with

$$V^*(x) = v_0 e^{-\alpha x - \beta x^2} - \left[ \frac{c_6}{x^6} + \frac{c_8}{x^8} + \frac{c_{10}}{x^{10}} \right] F(x), \quad (42)$$

and

$$F(x) = \begin{cases} e^{-(d/x-1)^2} & x < d \\ 1 & x \geq d, \end{cases} \quad (43)$$

with  $x = r/r_m$ . The parameters in Eq. (42) are  $v_0 = 186924.404$ ,  $\alpha = 10.5717543$ ,  $\beta = 2.07758779$ ,  $d = 1.438$ ,  $c_6 = 1.35186623$ ,  $c_8 = 0.41495143$ , and  $c_{10} = 0.17151143$ . Note that we have used  $r_m$ , the separation distance of the minimum interaction between two helium atoms, to scale all the lengths and  $\epsilon/k$  to scale all the energies.

We have used certain combinations of constants to simplify the units used in the simulation. For  $^4\text{He}$  with atomic mass  $m = 4.002602 \text{ u}$ , we have  $\hbar^2/mk = 12.119232 \text{ K \AA}^2$ . Dropping the units in this combination leads to lengths measured in  $\text{\AA}$  and energies in  $\text{K}$ . The imaginary time  $\tau = it/\hbar$  is measured in  $\text{K}^{-1}$ , which makes  $\tau E$ , with  $E$  the energy, dimensionless.

### B. The guide/trial wavefunction

We have constructed a guide/trial wavefunction to have the typical Jastrow form<sup>10</sup> with

$$\Phi(\mathbf{R}) = e^{-J(\mathbf{R})} \prod_{i=1}^N \phi(\mathbf{r}_i), \quad (44)$$

where  $\phi(\mathbf{r}_i)$  is a single-particle wavefunction for the  $i$ th particle, and

$$J(\mathbf{R}) = \sum_{i>j} u(r_{ij}) \quad (45)$$

is the two-body Jastrow factor. Because we are considering a system of  $^4\text{He}$  atoms bound to the surface of graphite, all of the single-particle states are bound to the surface in the same manner, for example, a Gaussian function in the direction perpendicular to the surface. Furthermore, we imagine that the atoms are spread out along the surface close to a close-packed lattice of lattice constant  $a_x$  with  $L$  sites, located at  $\mathbf{s}_l$ . We have

$$\phi(\mathbf{r}_i) = e^{-(z_i - z_e)^2/z_0^2} \sum_{j=1}^L e^{-|\mathbf{r}_i - \mathbf{s}_j|^2/r_0^2}, \quad (46)$$

where  $z_e$  and  $z_0$  are variational parameters that are on the order of the average distance between the surface and atoms in the cluster,  $r_0$  is a variational parameter that is on the order of  $a_x$ . Both  $a_x$  and  $L$  are variational parameters of the guide/trial wavefunction.

We choose the form of the two-particle function  $u(r_{ij})$  as

$$u(r) = \left(\frac{a}{r}\right)^5 + \frac{b^2}{c^2 + r^2}, \quad (47)$$

where the first term is from the cusp condition which forces the kinetic energy to cancel the divergent potential energy when the separation between any two particles approaches zero. The second term comes from the phonon contribution in the long-wavelength limit. These parameters can be roughly estimated, for example,<sup>10,17,18</sup>  $a \simeq 1.05 \text{ \AA}$  and  $\sigma \simeq 2.77 \text{ \AA}$ .

Symbolically, we can write the guide/trial wavefunction as a pure exponential function with

$$\Phi(\mathbf{R}) = e^{-J(\mathbf{R}) - X(\mathbf{R})}, \quad (48)$$

where

$$X(\mathbf{R}) = - \sum_{i=1}^N \ln \phi(\mathbf{r}_i). \quad (49)$$

The ratio of the distributions from two different configurations in the Metropolis algorithm is

$$\frac{W'}{W} = \frac{|\Phi(\mathbf{R}')|^2}{|\Phi(\mathbf{R})|^2} = e^{-2[J(\mathbf{R}') - J(\mathbf{R})] - 2[X(\mathbf{R}') - X(\mathbf{R})]}. \quad (50)$$

### C. The initial configuration

We want to choose an initial configuration that is close to the final configuration and also sufficiently flexible so that any number of atoms can be chosen in the simulation. One way to do so is to place the particles in a plane in a close-packed lattice, such as a hexagonal lattice. We first construct lines with particles on each line a distance  $a_x$  apart. We can arrange the lines  $a_y = a_x \sin \pi/3 = \sqrt{3}a_x/2$  apart, shifting every other line along the  $x$  axis back and forth by  $a_x/2$ . The lattice constant  $a_x$  is chosen from the density of a large system and is a little larger than the minimum interaction separation between two atoms,  $r_m$ , because of quantum zero-point motion. We do not impose any boundary conditions on the cluster, and  $a_x$  is used only to set up the initial configuration and in principle has no bearing on the shape or extent of the cluster when it is in equilibrium.

In this simulation, we have chosen a cluster of  $N$  atoms that matches the number of sites of the lattice used in the guide/trial wavefunction, that is,  $N = L = L_x \times L_y$ . This choice allows the program to run with different number of atoms in the cluster without making a significant change in the program. The distance between the surface and the initial layer of He atoms can be chosen to be the average distance between the surface and the location of the minimum surface potential of a helium atom,  $z_e \simeq 2.85 \text{ \AA}$ .<sup>19</sup> If the cluster is a liquid, we expect that its final shape to be close to a disk; otherwise, the particles will form a two-dimensional lattice.

## VII. SOME PRELIMINARY SIMULATION RESULTS

We did both variational and diffusion Monte Carlo simulations for  $^4\text{He}$  clusters on a graphite surface with different values of  $N$ . We have searched the parameter space for a reasonable set of parameters in the variational wavefunction to achieve a good start for diffusion Monte Carlo but have not done an exhaust search of the parameters because we want to use the wavefunction as a guide for the more powerful diffusion Monte Carlo method. However, a poor guide wavefunction can cause the diffusion Monte Carlo method to converge slowly.

The system that we used to search for a reasonable set of variational parameters in the guide/trial wavefunction had  $N = 3 \times 4 = 12$  atoms. The parameters were varied one after another until we reached a point that any further change of the parameters did not produce a noticeable change in the ground-state energy. To remove the dependence on the initial configuration, 15000 initial Metropolis updates were made before taking any data for averaging. To avoid any significant correlation among the data, 15 additional Metropolis moves were made before taking another value of data for the average. A total of 50000 energy values were gathered for calculating the average. The data were sorted in two different ways, treating each value or the average of 100 values independently, to ensure the accuracy of the error estimate. The two estimated errors should be about the same if the data are not correlated.

The parameters found using the variational Monte Carlo method are taken to be  $a_x = 4.257601 \text{ \AA}$ ,  $z_0 = 0.521 \text{ \AA}$ ,  $r_0 = 15 \text{ \AA}$ ,  $a = 2.770844 \text{ \AA}$ , and  $b = c = 0$ . Here  $a_x$  is based on a known commensurate two-dimensional  $\sqrt{3} \times \sqrt{3}$  lattice of density<sup>20</sup>  $\rho = 0.0636 \text{ \AA}^{-2}$ ;  $z_e$  is taken as the minimum surface potential position,<sup>15</sup> which equals the value found from the variational calculation,  $a$  is taken from Ref. 21, and  $z_0$  and  $r_0$  were found from the variational calculation.

To keep the acceptance probability of the Metropolis moves in the variational Monte Carlo calculations at about 50%,  $h_x = h_y = h_z = 0.35 \text{ \AA}$  was used for  $N = 12$  and a smaller value was used for larger  $N$ . The variational ground-state energy per particle obtained from our simulation is  $E_0/12 \leq -140.40(4) \text{ K}$ , which decreases slightly with increasing  $N$ . A good comparison is the single-particle ground-state energy for this surface potential,  $-142.2 \text{ K}$ .<sup>15</sup>

We then calculated the ground-state energy of each of the clusters with diffusion Monte Carlo. As expected, the major contribution to the energy comes from the confinement potential of the graphite surface, the same as in the variational Monte Carlo calculations. The parameter  $\kappa = 0.1 \text{ K}$  was used in the simulation to achieve the desired ensemble population of 300. We used 2500 data points, each of which contains a weighted-average energy of Eq. (31) from about 300 configurations in an ensemble, taken  $15 \Delta\tau$  apart, and computed the error for 2500 data points as well as for 50 data points each averaged over 50 of the original data points. Three to nine independent runs were done for each value of  $\Delta\tau$ . Each run is started from a different initial configuration (with each particle randomly displaced from its lattice site). We summarize our simulation results for the ground-state energies of  $N = 12$  and  $N = 6 \times 7 = 42$  atoms with different time steps in Table I. The  $\Delta\tau = 0$  results are obtained from the extrapolation of the simulation data using

Table I. The ground-state energies calculated with different time steps and the corresponding extrapolated values with  $N=12$  and  $N=42$ . Each time step is given in  $1/(1000\text{ K})$  and energy is given in K. The variances from the simulation with the shortest time step are assumed for the extrapolated values.

$\Delta\tau$	2	1	0.5	0.25	0
$E_0/12$	-145.5(2)	-143.12(2)	-142.81(1)	-142.67(2)	-142.46(2)
$E_0/42$	-147.4(1)	-143.55(2)	-143.01(2)	-142.90(1)	-142.82(1)

$$\frac{E_0(\Delta\tau)}{N} = \frac{E_0(0)}{N} + \beta_1\Delta\tau + \beta_2\Delta\tau^2 + \beta_3\Delta\tau^3 + \cdots, \quad (51)$$

where  $E_0(0)$  and  $\beta_i$  can be found from  $E_0(\Delta\tau)$ , the simulated values for different values of  $\Delta\tau$ .

We have to ensure that the system has evolved long enough to be in the ground state before any data are taken. The data shown in Table I are taken after 15000 diffusion time steps.

From Table I, we see that each cluster is in a bound state with the ground-state energy per particle is lower than the non-interacting single particle energy. We also see that the ground-state energy per particle decreases slightly with increasing  $N$ .

We can make a better variational Monte Carlo calculation by a more careful, systematic search of the parameters in the variational wavefunction, or by introducing more terms in the variational wavefunction to improve the representation of the variational wavefunction to the true ground state of the system. The time-step dependence is clearly noticeable. The simulations exhibit significantly less fluctuations from independent runs and within each run for  $\Delta\tau \leq 0.001\text{ K}^{-1}$ , as indicated by the much smaller statistical variance.

We have tested the program with cluster sizes ranging from  $N=12$  to  $N=13 \times 15 = 195$ . Although there is a small cluster size dependence on the energy per particle, the increase of the binding energy (the difference between the single-particle ground-state energy and the energy per particle in the cluster) is small.<sup>22</sup> The binding energy per particle is less than  $0.3\text{ K}$  for  $N=12$  and does not go beyond twice this value for a very large cluster. Thus a droplet of  $^4\text{He}$  formed on the surface of graphite can break up unless the temperature is sufficiently low, for example, much less than  $1\text{ K}$ .

The behavior of the radial distribution function  $g(r)$  yields information about whether the clusters are in a liquid or a solid phase. The computed  $g(r)$  for a three-dimensional cluster with  $N=11 \times 13 = 143$  is shown in Fig. 1. Because the particles are not contained in a fixed volume, the number density of the system is not well-defined. We have used the bulk density  $\rho = 0.024494\text{ \AA}^{-3}$  to scale  $g(r)$ , and thus only relative values of the plotted  $g(r)$  are physically meaningful. The first peak of  $g(r)$  shows that the atoms are spread out uniformly with the nearest-neighbor distance roughly the same everywhere. If the cluster were a solid, the peaks in  $g(r)$  would be of roughly equal height and spaced according to its lattice structure. Hence, our simulation results show that the clusters are likely in a liquid state.

We also considered the projection of the particle coordinates onto a two-dimensional surface. In Fig. 2, we show the two-dimensional radial distribution function taken from another simulation with the same cluster size of  $N=143$ .

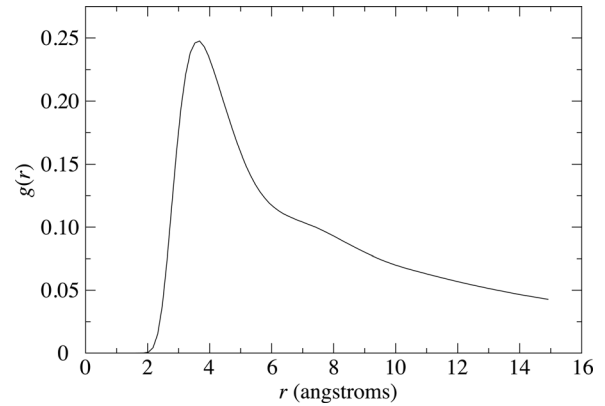


Fig. 1. The computed three-dimensional radial distribution function for  $N=143$ .

The features of  $g_{2D}(r)$  are similar to those in  $g_{3D}(r)$ , indicating that the positions of the particles are close to a plane near the minimum of the surface potential. The values of  $g_{2D}(r)$  are also relative because they are scaled with a uniform density,  $0.0636\text{ \AA}^{-2}$ .

## VIII. DISCUSSION

We have described the diffusion Monte Carlo and associated variational Monte Carlo methods. These methods were demonstrated for the example of  $^4\text{He}$  clusters trapped on the surface of graphite. Readers can download the sample program used to create the results that we have discussed.<sup>23</sup>

The algorithm that we have implemented in the program to do the calculations involves diffusion, drifting, and branching processes. From the data presented in Table I with different values of  $\Delta\tau$ , we see that a time step of  $\Delta\tau = 0.0005\text{ K}^{-1}$  yields meaningful data. The time step is chosen so that the binding energy per particle is accurate to within  $0.01\text{ K}$ . If we want to use the code to do calculations for clusters with larger  $N$ , or find the binding energy per particle with an error on the order of  $0.01\text{ K}$ , the time step should be  $\Delta\tau \leq 0.0005\text{ K}^{-1}$ . A smaller time step would yield higher accuracy, but would require longer runs to reach the ground state.

If we wish to reduce the time-step dependence in the simulation, we can improve the algorithm with a higher-order correction, such as the iteration scheme for the drift step discussed earlier. This higher-order correction scheme requires

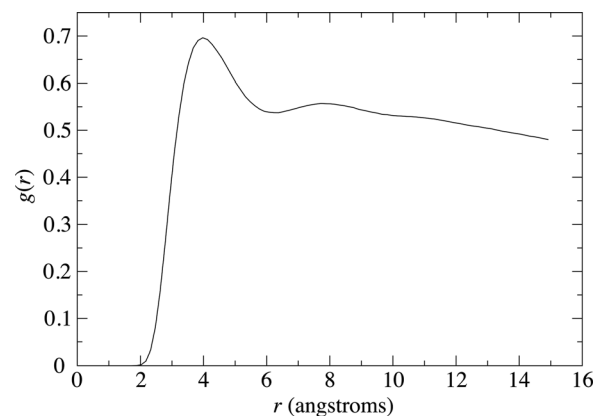


Fig. 2. The two-dimensional radial distribution function for  $N=143$ .



two additional evaluations of the drift velocity for each time step but makes the algorithm accurate up to  $\Delta\tau^2$  instead of  $\Delta\tau$  in the simplest algorithm. Another way to reduce the time-step dependence is to enforce detailed balance at each time step via the Metropolis algorithm, and replace the local energy in the birth/death rate by an average of those of the old and new configurations, and estimate an effective diffusion time step for branching. This estimate requires an additional evaluation of the drift velocity and tracking the attempted moves and accepted moves separately. Both the high-order correction and detailed balance enforcement are implemented separately in a code.

## IX. SUGGESTED PROBLEMS

1. Derive the relation (16) by calculating the expectation values of all the terms and show that the expectation values of both  $T_i$  and  $|\mathbf{F}_i|^2$  converge to that of  $K_i$  after performing an integration by parts.<sup>11</sup>
2. Find the ground-state energy of a three-dimensional harmonic oscillator with the Hamiltonian  $H = -(\hbar^2/2m)\nabla^2 + kr^2/2$ , using both the variational and diffusion Monte Carlo methods. Use the trial/guide wavefunction  $\phi(\mathbf{r}) = e^{-r^2/2}$  and natural units of  $m = k = \hbar = 1$ . Compare your simulation results with the exact result,  $E_0 = 3/2$ .
3. Find the ground-state energy of the hydrogen molecule using the variational and diffusion Monte Carlo methods. Assume that the protons are stationary with a fixed separation of 0.741 Å. A possible choice of the trial/guide wavefunction of the two electrons is  $\Phi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)e^{r_{12}/(2a_0)}$ , with  $\phi(\mathbf{r})$  a linear combination of the 1s atomic orbitals from the two protons and  $a_0$  the Bohr radius. Show that the cusp condition is satisfied between the two electrons and between an electron and a proton. Improve the trial wavefunction with variational parameters or variations of the functional form while maintaining the cusp condition. Compare the calculated result with the observed dissociation energy of the molecule, 4.52 eV.<sup>24</sup>
4. Estimate the ground-state energy of the lithium atom using the variational and diffusion Monte Carlo methods. One choice of the trial/guide wavefunction is to combine the 1s and 2s atomic orbitals and a Jastrow factor. Use a Slater determinant for the two electrons with the same spin and reject any time step that causes the system to cross a node of the wavefunction. Compare the calculated result with the observed ground-state energy of the atom, -203.4860 eV.<sup>25</sup>
5. Calculate the ground-state energy per atom and pair distribution function of bulk  $^4\text{He}$  using the variational and diffusion Monte Carlo methods. Enforce periodic boundary conditions on the system by moving a particle back to the simulation box on the opposite side when a move takes it to the outside of the box. Use the Aziz potential given in the article for the interaction between the atoms,  $\rho = 0.024494 \text{ \AA}^{-3}$  for the density, and  $N = 32$  atoms in the simulation box with the starting positions on a face-centered cubic lattice.
6. Simulate a system of hard-sphere bosons in a three-dimensional harmonic potential well  $V(r) = kr^2/2$ . The model can be viewed as a simple model of cold atoms in a trap. Use  $\Phi(\mathbf{R}) = \prod_{i=1}^N e^{-r_i^2}$  as the trial/guide wavefunction and reject any move that would cause the separation

of any two particles  $r_{ij}$  to be less than  $d$ , where  $d$  is the diameter of the hard spheres. Calculate  $E_0/N$  for various values of  $N$  with natural units of  $m = k = \hbar = 1$ . Check your result in the limit  $d \rightarrow 0$  against  $E_0/N = 3/2$ . Start the simulation with  $N$  on the order of 10 and increase it to 1000. What is the  $N$  dependence of the computation time if the same accuracy of calculation is sought?

7. Use diffusion Monte Carlo to simulate  $^3\text{He}$  clusters on a graphite surface with the surface potential and interaction used in this article. Construct a guide/trial wavefunction for which the single-particle wavefunction in a Slater determinant of the Gaussian orbitals from the virtual lattice sites. Reject any move that causes crossing a node of the wavefunction. Do the clusters form quantum liquids?

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### Water-Powered Centrifuge

This is listed at \$16.00 in the 1909 catalogue of the Scientific Materials Company of Pittsburgh. By comparison, the hand-powered model was \$10.00 and the electric ones were \$32 and up. In the early part of the twentieth century, electricity was not always available, but city water at sufficient pressure to run a water motor was always installed in the lab. It is in the Greenslade Collection, and was given to me by a chemistry student at a college who rescued it from the trash heap thirty years ago. (Notes and photograph by Thomas B. Greenslade, Jr., Kenyon College)