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A variational path integral molecular dynamics study of a solid helium-4

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Abstract

In the present study, a variational path integral molecular dynamics method developed by the author [*Chem. Phys. Lett.* **482** (2009) 165] is applied to a solid helium-4 in the ground state. The method is a molecular dynamics algorithm for a variational path integral method which can be used to generate the exact ground state numerically. The solid state is shown to successfully be realized by the method, although a poor trial wavefunction that can not describe the solid state is used.

Key words: quantum Monte Carlo, variational path integral, molecular dynamics, solid helium-4
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1. Introduction

Quantum Monte Carlo (QMC) methods provide computational tools for accurately calculating ground state properties of many body systems [1, 2, 3, 4]. Variational Monte Carlo (VMC) method [5], for example, is used to calculate expectation values of physical quantities using a trial wavefunction of the target system. The more sophisticated diffusion Monte Carlo (DMC) method [6] is a projector approach in which a stochastic imaginary time evolution is used to improve a starting trial wavefunction. The QMC methods including the VMC and DMC methods have successfully been applied to various quantum systems ranging from quantum liquids like helium to electronic structure of atoms and molecules [1, 4].

Recently, we have developed a molecular dynamics algorithm [7] for a variational path integral method [1, 8] that is closely related to the diffusion Monte Carlo method. The variational path integral method [1], which is also called path integral ground state [8], is a method to numerically generate exact ground state of many body systems. We have constructed the molecular dynamics algorithm to carry out the variational path integral calculations on the basis of path integral molecular dynamics method developed for finite temperature quantum systems [9, 10]. We call it a variational path integral molecular dynamics (V-PIMD) method. In the present study, we apply the V-PIMD method to a solid helium-4 for showing the reliability and the robustness of the method even when we use a trial wavefunction that can not describe the solid state.

2. Method

In this section, we briefly describe the variational path integral molecular dynamics method. N-particle systems are considered; particle coordinates are collectively represented to be R. It is known that the exact ground state of the system, $|\Psi_0\rangle$, can be obtained using a trial wavefunction $|\Phi_T\rangle$ by the following relation [1, 4]:

$$|\Psi_0\rangle = \lim_{\beta\to\infty} e^{-\frac{\beta}{2}\hat{H}}|\Phi_T\rangle, \tag{1}$$

where $\hat{H}$ is a Hamiltonian of the system and β is an imaginary time [1]. Here, we refer to a scalar product of the above exact wavefunction as a pseudo partition function $Z_0 = \langle\Psi_0|\Psi_0\rangle$ [11]. This function plays a central role to construct a variational path integral [1]:

$$\begin{aligned} Z_0 &= \langle\Phi_T|e^{-\beta\hat{H}}|\Phi_T\rangle \\ &= \int\cdots\int\{\prod_{s=0}^{M} dR^{(s)}\}\Phi_T(R^{(0)})e^{-S(\{R^{(s)}\};\Delta\tau)}\Phi_T(R^{(M)}), \end{aligned} \tag{2}$$

where $\Delta\tau = \beta/M$ and $S(\{R^{(s)}\};\Delta\tau)$ is a discretized imaginary time action. Explicit expression of the action is dependent on an approximation on a short time propagator $\langle R|e^{-\Delta\tau\hat{H}}|R'\rangle$. In the present study, the primitive approximation [1] is adopted. As in the standard path integral method for finite temperature systems [12], the pseudo partition function can be regarded as a configurational integral of classical polymers. In the variational path integral, however, the classical isomorphic systems consist of open chain polymers. Furthermore, distributions of endpoint coordinates at $s = 0$ and M are affected by the trial wavefunction $\Phi_T(R^{(0)})$ and $\Phi_T(R^{(M)})$, respectively. Then, a molecular dynamics method can be constructed to sample configurations of the above isomorphic polymers on the basis of the path integral molecular dynamics method for finite temperature systems [9, 10]. We introduce the following classical Hamiltonian:

$$\begin{aligned} H_{\text{V-PIMD}} &= \sum_{s=0}^{M}\sum_{i=1}^{N}\frac{(\mathbf{p}_i^{(s)})^2}{2m_i'} + \frac{S(\{R^{(s)}\})}{\beta} \\ &\quad -\frac{\ln\Phi_T(R^{(0)})}{\beta} - \frac{\ln\Phi_T(R^{(M)})}{\beta}, \end{aligned} \tag{3}$$

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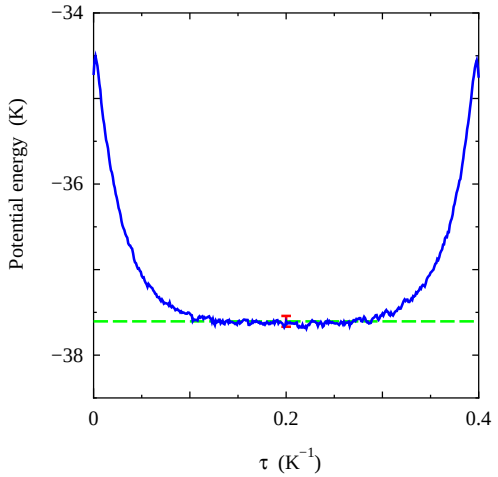

Figure 1: Averaged potential energy of the liquid helium-4 per atom as a function of the imaginary time τ. Blue solid line is for the variational path integral molecular dynamics result and blue dashed line indicates the averaged potential energy at $\tau = 0.2$. The error bar is expressed at 95 % confidence level for the potential energy at $\tau = 0.2$.

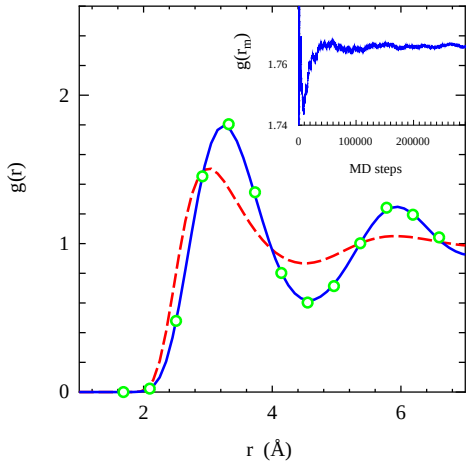

Figure 2: Radial distribution function of the solid helium-4, $g(r)$. Blue solid line is for the variational path integral molecular dynamics result and red dashed line is for the variational molecular dynamics result with the variational parameter $b = 3.07$ Å. Green open circles are for Green's-function Monte Carlo results [18] using the HFDHE2 pair potentials [19]. The inset shows the cumulative average of the first peak height of $g(r)$ as a function of V-PIMD steps

where $\mathbf{p}_i^{(s)}$ denotes a fictitious momentum of an i-th particle at an s-th time slice and m_i' is a fictitious mass of the i-th particle. Using the above Hamiltonian, we can derive equations of motion based on the Hamilton equation. Then, to generate the distribution compatible with Eq. (2), we attach a single Nosé-Hoover chain thermostat [13] to each degree of freedom. The resulting equations of motion are basic equations for the variational path integral molecular dynamics (V-PIMD) method. In the present study, we use staging coordinates [9] to describe the polymer configurations for enhancing sampling efficiency. The standard definition [10, 14] on the staging variables and associated staging masses $m^{(s)}$ are adopted.

3. Results

We consider a solid helium-4 at the ground state. The following trial wavefunction is employed:

$$\Phi_T(R) = \prod_{i<j}^{N} e^{-\frac{1}{2}(\frac{b}{r_{ij}})^5}, \tag{4}$$

where b is a variational parameter. In the present study, $b = 3.07$ Å was adopted. To describe a solid state, Eq. (4) is usually multiplied by one body term which localizes the particles in a crystalline order. In this sense, the above trial wavefunction is a poor choice to describe the solid state. The density of the system was set to be $\rho = 0.0353$ Å^{-3}. The system consisted of $N = 108$ helium atoms in a cubic box under the periodic boundary condition. The interatomic interaction was represented by the pair interaction developed by Aziz and coworkers [15]. For the V-PIMD calculation, the imaginary time increment was set to be $\Delta\tau = 0.001$ K^{-1} and $M = 400$. Then, the total imaginary time was $\beta = 0.4$ K^{-1}. It has been shown [16] that the present choice of $\Delta\tau$ is short enough to yield numerically accurate results with the primitive approximation for the condensed helium. As will be shown below, the present total projection time β is long enough to obtain the ground-state distribution. As noted in Sec. 2, the V-PIMD calculation was performed using the staging variables. The fictitious masses for the staging variables $m^{(s)\prime}$ were set to be equal to the corresponding staging masses except end-point coordinates (at $s = 0$ and M) where $m^{(0)\prime} = m^{(M)\prime} = \gamma m$. The parameter $\gamma = 0.02$ was used. The V-PIMD calculation was performed 300000 steps with a time increment $\Delta t = 8.0$ fs. The computational time of the present calculation was 63 hours using a single intel Xeon processor of 3.33 GHz. For comparison, a variational molecular dynamics (VMD) calculation, which is compatible with a corresponding variational Monte Carlo calculation, was performed using the trial wavefunction Eq. (4). Details on the VMD method can be found elsewhere [7].

Figure 1 shows the potential energy of the helium per atom as a function of the imaginary time τ by the V-PIMD calculation. After an initial transient regime, the potential energy is found to relax to a plateau value around $\tau = 0.1$ K^{-1} where the energy can be expected to be the exact ground-state potential energy for the given Hamiltonian. Then, in the imaginary time interval $\tau = 0.1 \sim 0.3$ K^{-1}, the system is in the ground state of the solid helium-4. Using the mixed estimator, the total energy was calculated to be -2.99 ± 0.01 K, which is in good agreement with the experimental value -2.70 ± 0.05 K [17]. Here, we added tail corrections to the energy to account for the finite size of the system by assuming the homogeneity of the medium beyond the half of the cell dimension. To see atomistic structural correlation in the ground state, the radial distribution function $g(r)$ is presented in Fig. 2. It is also shown that the cumulative average of the first peak height of $g(r)$ as a function of MD steps to confirm the convergence of the present calculation; the convergence is found to be attained around 50000 steps. The radial distribution function is defined using the ground state

wavefunction as follows:

$$g(r_{12}) = \frac{N(N-1)}{\rho^2} \frac{\int d\mathbf{r}_3 \cdots d\mathbf{r}_N |\Psi_0(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2}{\int d\mathbf{r}_1 \cdots d\mathbf{r}_N |\Psi_0(\mathbf{r}_1, \ldots, \mathbf{r}_N)|^2}. \quad (5)$$

The function $g(r)$ calculated by the VMD method is also presented for comparison. Since the VMD method provides $g(r)$ for the trial wavefunction used in the V-PIMD calculation, it is helpful to see the quality of the trial wavefuntion by comparing it with the V-PIMD result that is numerically exact for the given interatomic interaction. As seen in Fig. 2, the VMD result shows less structured $g(r)$ compared with the V-PIMD counterpart, indicating the present trial wavefunction is a poor choice to describe the solid state. On the other hand, the V-PIMD result is found to be in good agreement with the $g(r)$ calculated by Green's-function Monte Carlo (GFMC) method for the same density [18], which is an another method to obtain numerically exact ground state; in the GFMC calculation, HFDHE2 pair potentials by Aziz and coworkers [19] were used. Although the interatomic interaction employed in the present study is slightly different from the HFDHE2 potentials, the radial distribution function is not so sensitive to the precise difference of the potentials. Thus, the comparison presented above provides a good guide to see the improvement of the initial trial wavefunction. It is worthwhile to note that the GFMC calculation used an importance function which localizes the particles on the lattice sites, while the trial wavefunction, Eq. (4), does not contain the information regarding the crystalline order.

4. Concluding remarks

In the present study, the variational path integral molecular dynamics method (V-PIMD) has been applied to the solid helium-4. The solid state is successfully realized by the method although the adopted trial wavefunction is a poor to describe the crystalline order, which demonstrates the robustness of the variational path integral method. The important feature of the variational path integral method compared with other quantum Monte Carlo methods like diffusion Monte Carlo (DMC) and Green's function Monte Carlo (GFMC) methods is that a variety of ground state properties can be calculated without extrapolation which is sometimes used in DMC and GFMC calculations [8]. Although, using either DMC or GFMC, the ground state energy can be calculated accurately, expectation values of operators which do not commute with Hamiltonian, for example, the potential energy and the radial distribution function, are harder to calculate. The present method is the molecular dynamics algorithm for the variational path integral method. In V-PIMD, the force calculations at each time slice can almost be performed independently. Also, the computational cost for each time slice is almost the same as that of classical molecular dynamics calculations with the same N and the potentials, t_{CMD}. Thus, the computational time of one V-PIMD step can be estimated to be about $t_{\mathrm{CMD}} \times M$. The V-PIMD method can fully enjoy the independency on the force calculations when the method is implemented in parallel computations.

For large scale quantum simulations, methodological improvements are important for the V-PIMD method. For example, higher order factorization schemes of the density matrix [16, 20, 21] may be useful to reduce the number of time slices. In the higher order schemes, however, we need derivatives of the interaction potential; the use of the higher order approximations is computationally more expensive than that of the primitive approximation (PA). It has been suggested [20] that using the molecular dynamics method, computational cost can be reduced close to that by PA using multiple time step algorithms, in which the higher order terms by the derivatives do not have to be evaluated at every time step. The hybrid Monte Carlo algorithm [9, 22], which can be easily constructed by the present MD method, also may provide an efficient way to perform variational path integral simulations with the higher order approximations; short MD runs to generate trial configurations are performed without the higher order terms, which are included in the Metropolis criterion. The work on these issues is in progress in our group.

Acknowledgments

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