Variational path integral molecular dynamics study of a water molecule

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Abstract. In the present study, a variational path integral molecular dynamics method developed by the author [Chem. Phys. Lett. 482, 165 (2009)] is applied to a water molecule on the adiabatic potential energy surface. The method numerically generates an exact wavefunction using a trial wavefunction of the target system. It has been shown that even if a poor trial wavefunction is employed, the exact quantum distribution is numerically extracted, demonstrating the robustness of the variational path integral method.

1. Introduction
Quantum Monte Carlo (QMC) methods provide computational tools for accurately calculating ground state properties of many body systems [1, 2, 3, 4]. The 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, 7] 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 for a variational path integral method [1, 8] that is closely related to the diffusion Monte Carlo method [9, 10, 11, 12, 13]. 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 [14, 15]. We call it a variational path integral molecular dynamics (VPIMD) method. In the present study, we apply the VPIMD method to vibrational fluctuation of a water molecule on an adiabatic potential energy surface.

2. Methods

2.1. Variational molecular dynamics
We start to consider a system consisting of \( N \) particles whose coordinates are collectively represented to be \( R \). The ground state of the system is described using a trial wavefunction \( \Phi_T(R, A) \) where \( A \) denotes a set of variational parameters. Expectation value of a Hamiltonian...
Using the trial wavefunction reads \[1, 4\]

\[
\langle H \rangle = \frac{\int dR \Phi_T^* \hat{H} \Phi_T}{\int dR |\Phi_T|^2} = \frac{\int dR |\Phi_T|^2 E_L(R)}{\int dR |\Phi_T|^2},
\]

where \(E_L(R)\) represents a local energy defined by

\[
E_L(R) = \Phi^{-1}_T(R) \hat{H} \Phi_T(R).
\]

The variational Monte Carlo method is designed so as to generate coordinates \(R\) according to a distribution function \(\rho(R) \propto |\Phi_T|^2\). Then, the expectation value of the Hamiltonian (1) can be calculated by the local energy averaged along a Monte Carlo trajectory. Here, we consider a molecular dynamics method to generate the distribution function \(\rho(R)\). First, we define an effective potential \(V_{VMC}(R)\) using the distribution function \(\rho(R)\):

\[
\rho(R) = e^{-\beta V_{VMC}(R)},
\]

where a parameter \(\beta\) is a fictitious inverse temperature. The distribution function \(\rho(R)\) can be regarded as a canonical distribution at the fictitious \(\beta\). To sample the distribution, we introduce the following classical Hamiltonian:

\[
H_{VMC} = \sum_{i=1}^{N} \frac{p_i^2}{2m'_i} + V_{VMC}(R),
\]

where \(p_i\) is a fictitious momentum of an \(i\)-th particle and \(m'_i\) is an associated fictitious mass. Then, we can obtain equations of motion based on the Hamilton equation. In the present study, we attach a single Nosé-Hoover chain thermostat [16] to each degrees of freedom for generating the canonical distribution compatible with (3). The resulting thermostatted equations of motion are basic equations of the variational molecular dynamics method [9]. Then, as in the variational Monte Carlo method, we can obtain quantum mechanical expectation values of various physical quantities using a molecular dynamics trajectory.

2.2. Variational path integral molecular dynamics

In this subsection, a method to systematically improve the description of the system is considered. The exact ground state of the system, \(|\Psi_0\rangle\), can be obtained using a trial wavefunction \(\Phi_T\) by the following relation: \[1, 4\]

\[
|\Psi_0⟩ = \lim_{\beta \to \infty} e^{-\frac{\beta}{2} \hat{H}} |\Phi_T⟩,
\]

where \(\beta\) is an imaginary time \[1\]. Here, we refer to a scalar product of the above exact wavefunction as a pseudo partition function \(Z_0\) \[17\], which plays a central role to construct a variational path integral:

\[
Z_0 = \langle \Psi_0 | \Psi_0 \rangle = \langle \Phi_T | e^{-\beta \hat{H}} | \Phi_T \rangle = \int \int dR dR' \langle \Phi_T | R \rangle \langle R | e^{-\beta \hat{H}} | R' \rangle \langle R' | \Phi_T \rangle,
\]
where we use the closure relation for the coordinate basis: $\int dR |R\rangle\langle R| = 1$. A matrix element $\langle R | e^{-\beta H} | R' \rangle$ in (6) is found to be the same as a density matrix at the inverse temperature $\beta$, $\rho(R, R'; \beta)$. The density matrix can be written on the basis of the discretized path integral as [1]

$$
\rho(R, R'; \beta) = \langle R | e^{-\Delta \tau \hat{H}} | M | R' \rangle
$$

$$
= \int \cdots \int \{ \prod_{s=1}^{M-1} dR^{(s)} \} \prod_{s=0}^{M-1} \langle R^{(s)} | e^{-\Delta \tau \hat{H}} | R^{(s+1)} \rangle
$$

$$
\propto \int \cdots \int \{ \prod_{s=1}^{M-1} dR^{(s)} \} e^{-S\{R^{(s)}; \Delta \tau\}},
$$

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. Then, the pseudo partition function can be written by

$$
Z_0 \propto \int \cdots \int \{ \prod_{s=0}^{M} dR^{(s)} \} \Phi_T(R^{(0)}) e^{-S\{R^{(s)}; \Delta \tau\}} \Phi_T(R^{(M)}).
$$

As in the standard path integral method for finite temperature systems [18], the pseudo partition function can be regarded as a configurational integral of classical polymers. However, in the variational path integral, the classical isomorphic systems consist of open chain polymers. Furthermore, distributions of end-point coordinates at $s = 0$ and $M$ are affected by the trial wavefunction $\Phi_T(R^{(0)})$ and $\Phi_T(R^{(M)})$, respectively. Here, we consider a molecular dynamics method to sample configurations of the above isomorphic polymers. First, we define the following classical Hamiltonian:

$$
H_{VPiMD} = \sum_{s=0}^{M} \sum_{i=1}^{N} \frac{(p_i^{(s)})^2}{2m_i'} + \frac{S\{R^{(s)}\}}{\beta} - \frac{\ln \Phi_T(R^{(0)})}{\beta} - \frac{\ln \Phi_T(R^{(M)})}{\beta},
$$

where $p_i^{(s)}$ 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 (8), we attach a single Nosé-Hoover chain thermostat to each degree of freedom. The resulting equations of motion are basic equations for the variational path integral molecular dynamics (VPiMD) method [9]. In the present study, we use staging coordinates [14] to describe the polymer configurations for enhancing sampling efficiency. The standard definition [15, 19] on the staging variables and associated staging masses $m^{(s)}$ are adopted.

3. Results

In the present study, a trial wavefunction is constructed using a local mode $S_\nu$ representing the distance between a pair of atoms in a molecule [20]. The local modes are defined for a molecule consisting of $N$ atoms by

$$
S_\nu = |r_i - r_j|, \quad 1 \leq i < j \leq N, \quad 1 \leq \nu \leq N_{\text{pair}} = \frac{N(N-1)}{2}
$$

where $r_i$ is an $i$-th atomic coordinate. Then, the trial wavefunction is written by [20]

$$
\Phi_T(R) = \exp \left\{ \sum_{\mu=1}^{N_{\text{pair}}} \sum_{\nu=1}^{N_{\text{pair}}} \Delta S_\mu A_{\mu \nu} \Delta S_\nu \right\}
$$
Let us define the variational parameters. For a water molecule, four parameters are needed for the trial wavefunction (11). Let us define $S_1 = r_{OH_1}$, $S_2 = r_{OH_2}$, and $S_3 = r_{H_1H_2}$. For the water molecule, the matrix $A$ has the following symmetry: $A_{ij} = A_{ji}$, $A_{11} = A_{22}$, and $A_{13} = A_{23}$. Then, the following four parameters are independent: $A_{11}$, $A_{12}$, $A_{13}$, and $A_{33}$. In the present study, two sets of the variational parameters have been tested. The set 1 is given by $A_{11} = -19.61$, $A_{12} = -6.11$, $A_{13} = 4.32$, and $A_{33} = -8.60$ in units of Bohr$^{-2}$ [21], and the set 2 by $A_{11} = -19.61$, $A_{12} = 12.20$, $A_{13} = 8.63$, and $A_{33} = -8.60$ in units of Å$^{-2}$ [20].

Regarding the interatomic interaction for the water molecule, we have used a potential derived from experimental data by Carney, Curtiss and Langhoff [22]. It involves an expansion in Simons-Parr-Finlan coordinates about the equilibrium geometry and consists 19 terms. Then, the variational molecular dynamics and the variational path integral molecular dynamics calculations for the H$_2$O molecule have been performed. Here, we comment that the variational MD results presented in the paper are all with the parameter set 2, since the variational MD with the set 1 causes unphysical behavior of the water molecule; actually, the water molecule dissociated in the course of the VMD calculation. The variational PIMD calculations have been performed for various $eta$; both sets of the parameters, 1 and 2 have been tested. The imaginary time increment is fixed to be $\Delta \tau = 2.5\times10^{-5}$ K$^{-1}$ for all the VPIMD calculations. Here and hereafter, the inverse temperature $\beta$ and the associated $\Delta \tau$ is represented to be in units of K$^{-1}$, corresponding to the $\beta$ multiplied by the Boltzmann constant.

In Fig. 1, we show the projection time dependence of the total energy. The total energy was calculated using the mixed estimator derived by the following relation [4]:

$$E_0 = \frac{\langle \Phi_T | \hat{H} e^{-\beta \hat{H}} | \Phi_T \rangle}{\langle \Phi_T | e^{-\beta \hat{H}} | \Phi_T \rangle},$$

where $E_0$ is the ground state energy. We first discuss the results by the parameter set 1. Using the variational MD method, the total energy by the trial wave function with the set 1 was calculated to be 4930 $\pm$ 15 cm$^{-1}$. With increasing $\beta$, the variational PIMD energy decreases quickly and reaches the exact ground state energy. For the parameter set 1, $\beta = 5.0 \times 10^{-4}$ K$^{-1}$ is found to be large enough to obtain the exact ground state energy. On the other hand, the energy using the set 2 also decreases with increasing $\beta$. As seen in the figure, we need twice larger $\beta$ to obtain the exact ground state energy. This is due to the fact that the set 1 is
Figure 2. O-H bond length distribution $f(r_{\text{OH}})$ by the variational PIMD calculations. Vermilion dashed line, green twin dot line, orange dot dashed line, and pink solid line indicate the results with the projection time $\beta = 2.5, 5.0, 10, \text{ and } 20 \times 10^{-4} \text{ K}^{-1}$, respectively. Blue dotted line indicates the variational MD result. All the calculations are performed using the trial wavefunction with the parameter set 1.

Figure 3. H-O-H bond angle distribution $f(\theta)$ by the variational PIMD calculations. Vermilion dashed line, green twin dot line, orange dot dashed line, and pink solid line indicate the results with the projection time $\beta = 2.5, 5.0, 10, \text{ and } 20 \times 10^{-4} \text{ K}^{-1}$, respectively. Blue dotted line indicates the variational MD result. All the calculations are performed using the trial wavefunction with the parameter set 1.

much better variational parameters than the set 2. As mentioned above, we could not obtain the total energy by the VMD, since the water molecule was dissociated in the course of the simulation. Similarly, the VPIMD calculations could not be performed stably in the range of $\beta < 5.0 \times 10^{-4} \text{ K}^{-1}$. For such a poor set of the parameters, we could obtain the exact ground state energy, demonstrating the robustness of the variational path integral method.

Figure 2 shows the structural fluctuation of the water molecule at the ground state. Quantum expectation values of observables diagonal in the coordinate space can straightforwardly be obtained using the variational path integral, since the system coordinates at the time slices around $\tau = \beta/2$ are distributed according to the exact wavefunction with $\beta$ large enough. In Fig. 2, O-H bond length and H-O-H bond angle distributions are presented. For each VPIMD calculation, the distributions are evaluated using the coordinates at $\tau = \beta/2$. In both distributions, trial wavefunction describes well the structural correlation in the exact wavefunction. This is due to the trial wavefunction with the set 1 provides the good trial wavefunction for the water molecule. With increasing $\beta$, the structural correlations approach those for the exact wavefunction.

4. Concluding remarks

In the present study, the variational path integral molecular dynamics (VPIMD) method has been applied to quantum vibrational fluctuation of a water molecule on the adiabatic potential energy surface. To perform the VPIMD calculations, we need to prepare a trial wavefunction of the water molecule. The VPIMD method numerically extracts the exact ground state from the trial wavefunction. In the present study, we have tested two sets of variational parameters for a vibrational wavefunction. It is demonstrated that the VPIMD method generates the same results for the different sets of the parameters, when the projection time is long enough. It
is worthwhile to remark that one parameter set is so poor that the bound state of the water molecule could not be reproduced; even for such a poor set of parameters, the VPIMD method is found to generate the exact ground state, demonstrating the robustness of the variational path integral.

An important direction on further methodological development regarding the VPIMD is on systematically improving the description of adiabatic potential energy surfaces of atoms and molecules. This can be achieved by combining the variational path integral with electronic structure calculations as in the case of the finite temperature path integral molecular dynamics [23, 24]. Since this method needs to perform electronic structure calculations at each VPIMD step, computational cost is expected to be rather expensive. As demonstrated in this paper, we can reduce the projection time $\beta$ directly related with the computational cost if we adopt a good trial wavefunction. This indicates that the variational parameter optimization is crucial for efficient VPIMD calculations combined with \textit{ab initio} electronic structure theory. These issues will be addressed in the near future.

Acknowledgments
This work was partially supported by the Grant-in-Aid for Scientific Research (C) (No. 23550011) from the Japan Society for the Promotion of Science and by the Strategic Programs for Innovative Research (SPIRE), MEXT, and the Computational Materials Science Initiative (CMSI), Japan.

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