Path Integral Brownian Chain Molecular Dynamics: A Simple Approximation of Quantum Vibrational Dynamics

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Abstract

An approximate approach to quantum vibrational dynamics, "Brownian Chain Molecular Dynamics (BCMD)", is proposed to alleviate the chain resonance and curvature problems in the imaginary time-based path integral (PI) simulation. Here the non-centroid velocity is randomized at each step when solving the equation of motion of path integral molecular dynamics. This leads to a combination of the Newton equation and the overdamped Langevin equation for the centroid and non-centroid variables, respectively. BCMD shares the basic properties of other PI approaches such as centroid and ring polymer molecular dynamics: It gives the correct Kubo-transformed correlation function at short times, conserves the time symmetry, has the correct high-temperature/classical limits, gives exactly the position and velocity autocorrelations of harmonic oscillator systems, and does not have the zero-point leakage problem. Numerical tests were done on simple molecular models and liquid water. On-the-fly ab initio BCMD simulations were performed for the protonated water cluster, $H_5O_2^+$, and its isotopologue, $D_5O_2^+$.

Keywords: path integral simulations, molecular dynamics, vibrational dynamics, semiclassical theory, ab initio simulations   ∎

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1 INTRODUCTION

Various semiclassical methods have been proposed as approximate solutions to quantum vibrational dynamics of many-body systems.[1–12] Centroid molecular dynamics (CMD)[1,13] and the ring polymer molecular dynamics (RPMD)[5,14] are among such representative methods in the framework of path integral (PI) simulations. They could be categorized as an extension of path integral molecular dynamics (PIMD) simulations that utilize the isomorphism between the quantum fluctuation of a particle and that of a cyclic chain of its classical replica (beads). The family of PI simulations is based on quantum statistical mechanics and is rigorous for time-independent physical properties in the limit of infinite number of beads. In the CMD and RPMD methods, the time correlation function from the classical dynamics of cyclic chains is regarded as an approximation of the Kubo-transformed quantum correlation function. These CMD and RPMD correlation functions are correct at short times, preserves time symmetry, follows basic conservation laws, and has the correct high temperature/classical limits. In addition, the position and velocity autocorrelation functions are exact for harmonic oscillators. Since the thermodynamic equilibrium is maintained in the CMD and RPMD trajectories, so-called the "zero-point leakage" problem in semiclassical methods is not present in CMD and RPMD. Accordingly, the CMD and RPMD methods have been applied successfully in a variety of systems.

However, the semiclassical methods always have some limitations. A common drawback of CMD and RPMD is in the vibrational spectra of high frequency modes. As the temperature is lower, the CMD curvature problem[15,16] and the RPMD chain resonance problem[15,17] become more prominent. The former arises from a spurious coupling between rotations and vibrations due to the adiabatic separation of the centroid variable and the non-centroid variables. The latter is due to spurious resonance between the vibrations of the physical mode and the vibrations of the cyclic chain. These problems appear, for example, as peak shifts and peak splits in the OH and CH vibrations of water and methane, respectively, which do not go away even at room temperature. The thermostatted RPMD (TRPMD) method was later proposed to suppress chain resonances, where the RPMD equation of motion is coupled to the Langevin thermostats.[18] The path integral Liouville dynamics

(PILD) was also proposed to solve these problems at a cost of computing the Hessian matrix.[9]

In this study, we propose a simple method that completely eliminates the chain resonance problem of RPMD. This method does not eliminate the curvature problem, but it does reduce the severity of the problem with respect to spurious frequency shifts over CMD. It uses the same type of equation of motion used in the family of path integral simulation techniques (PIMD, CMD, RPMD). The main difference from other methods is that the non-centroid velocities are randomized at each step according to the Maxwell-Boltzmann distribution. It turns out that this is equivalent to solving the Newtonian dynamics for centroid variables and the Brownian (overdamped Langevin) dynamics for non-centroid variables at the same time. For this reason, this method is named here as "Brownian Chain Molecular Dynamics (BCMD)". While randomization of the non-centroid velocities can eliminate the chain resonance problem, the nonadiabaticity between the centroid and non-centroid variables can alleviate the curvature problem. Yet BCMD shares the basic nature of CMD and RPMD; the Kubo-transformed correlation function is correct at short times, has the correct time symmetry, has the correct high-temperature/classical limits, provides exact results for the position and velocity autocorrelations for harmonic oscillators, and does not have the zero-point leakage problem.

In Section 2, the theory and numerical algorithm of the BCMD method are described. In Section 3, the short-time behavior of BCMD is tested for one-dimensional oscillator model. The vibrational spectra of BCMD are tested for gaseous OH molecule, and H_2O molecule and its isotopologues and liquid water isotopologues. BCMD results are compared with the available data for MD, CMD, RPMD and TRPMD. The ab initio BCMD simulations are demonstrated for $H_5O_2^+$ and $D_5O_2^+$ with the on-the-fly electronic structure calculations based on the second-order Møller-Plesset perturbation theory (MP2). The infrared spectra obtained from the dipole autocorrelation function are compared with experimental results. In Section 4, the conclusive remarks are given.

2 THEORY

2.1 Equation of motion in PI methods

The imaginary time path integral theory is a formulation for the statistical mechanics of quantum many-body systems.[19–21] Let us consider the simple case of a single quantum particle moving in a one-dimensional potential energy surface, $V(x)$, with mass m. Extension to multidimensional systems is described in Section 2.6. The quantum partition function of the canonical ensemble at temperature T can be expressed as

$$Z = \lim_{P \to \infty} \left(\frac{mP}{2\pi\beta\hbar^2} \right)^{\frac{P}{2}} \int d\mathbf{x} \exp\left(-\frac{S[\mathbf{x}]}{\hbar} \right) \tag{1}$$

where $\beta \equiv \frac{1}{k_B T}$ and $\hbar \equiv \frac{h}{2\pi}$ with the Boltzmann constant k_B and the Planck constant h. The functional $S[\mathbf{x}] \equiv \beta\hbar V_{\text{eff}}(\mathbf{x})$ represents the action with respect to a cyclic path $\mathbf{x} = (x_1, \cdots, x_P)^T$ along the imaginary time $\tau_j = \frac{\beta\hbar(j-1)}{P}$, and

$$V_{\text{eff}}(\mathbf{x}) = \frac{1}{2} m\omega_P^2 \mathbf{x}^T \mathbf{A} \mathbf{x} + \phi(\mathbf{x}). \tag{2}$$

Equation (1) is isomorphic to the classical partition function of a system of P replicated particles (beads) with the effective potential of $V_{\text{eff}}(\mathbf{x})$.[22–24] In the rhs of Equation (2), the first term is the harmonic interaction between the adjacent beads with the characteristic frequency $\omega_P \equiv \frac{\sqrt{P}}{\beta\hbar}$. The elements of the matrix $\mathbf{A}$ is defined as $A_{ij} = 2\delta_{i,j} - \delta_{i,j+1} - \delta_{i,j-1}$ according to a cyclic boundary condition, $0 \to P$ and $P + 1 \to 1$. The second term is the bead average of the physical potential,

$$\phi(\mathbf{x}) \equiv \frac{1}{P} \sum_{j=1}^{P} V(x_j). \tag{3}$$

The equations of motion for PI methods (PIMD, CMD, and RPMD) can be commonly derived from the Hamiltonian in normal mode space where the first term of Equation (2) is diagonalized.[15] This is used in the BCMD method as well. The normal mode transformation is obtained from the diagonalization of the $\mathbf{A}$ matrix, $P\mathbf{A}\mathbf{U} = \boldsymbol{\lambda}\mathbf{U}$, which can be solved analytically. The eigenvalues are

$$\lambda_{2k} = 4P \sin^2\left(\frac{\pi k}{P} \right) \quad (k \neq 0),$$

$$\lambda_{2k+1} = 4P \sin^2\left(\frac{\pi k}{P} \right) \quad (k \leq \tfrac{P-1}{2}), \tag{4}$$

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and the eigenvectors are

$$U_{j,2k} = \sqrt{\frac{2}{P}} \cos\left(\frac{2\pi jk}{P}\right) \qquad (k \neq 0),$$

$$U_{j,2k+1} = \begin{cases} \sqrt{\frac{1}{P}} & (k = 0) \\ \sqrt{\frac{2}{P}} \sin\left(\frac{2\pi jk}{P}\right) & (k \leq \frac{P-1}{2}). \end{cases} \qquad (5)$$

Using the normal modes

$$\mathbf{q} = \frac{1}{\sqrt{P}} \mathbf{U}^T \mathbf{x} \qquad (6)$$

and its momentum conjugate $\mathbf{p}$, the Hamiltonian is constructed as

$$H(\mathbf{p}, \mathbf{q}) = \frac{1}{2} \mathbf{p}^T \boldsymbol{\mu}^{-1} \mathbf{p} + \frac{1}{2} m\omega_P^2 \mathbf{q}^T \boldsymbol{\lambda} \mathbf{q} + \phi(\mathbf{x}(\mathbf{q})), \qquad (7)$$

where $\boldsymbol{\mu}$ is a diagonal matrix, each of whose element corresponds to the fictitious mass of the normal mode, $\mathrm{diag}(\boldsymbol{\mu}) = (m, \mu_2, \cdots, \mu_P)$. The canonical equation of motion derived from Equation (7) is obtained as

$$\dot{\mathbf{q}} = \boldsymbol{\mu}^{-1} \mathbf{p}, \qquad \dot{\mathbf{p}} = -m\omega_P^2 \boldsymbol{\lambda} \mathbf{q} - \nabla_{\mathbf{q}} \phi(\mathbf{x}(\mathbf{q})). \qquad (8)$$

The first mode is the centroid variable, $q_1 = \frac{1}{P} \sum_{j=1}^{P} x_j$, and $\lambda_1 = 0$. Thus, Equation (8) is a set of equations for the centroid variable,

$$\dot{q}_1 = \frac{p_1}{m} = v_1, \qquad \dot{p}_1 = -\frac{\partial \phi}{\partial q_1}, \qquad (9)$$

and the non-centroid variables,

$$\dot{q}_\alpha = \frac{p_\alpha}{\mu_\alpha} = v_\alpha, \qquad \dot{p}_\alpha = f_\alpha, \qquad (10)$$

where the non-centroid forces are

$$f_\alpha = -m\omega_P^2 \lambda_\alpha q_\alpha - \frac{\partial \phi}{\partial q_\alpha}. \qquad (11)$$

In Eqs.(9) and (11), the normal mode forces with respect to ϕ can be obtained using the relation,

$$\frac{\partial \phi}{\partial q_\beta} = \sqrt{P} \sum_{j=1}^{P} U_{j,\beta} \frac{\partial \phi}{\partial x_j} \qquad (1 \leq \beta \leq P). \qquad (12)$$

The non-centroid fictitious masses are set to $\mu_\alpha = \lambda_\alpha m$ in PIMD, $\mu_\alpha = \gamma_{\mathrm{cmd}}^{-2}\lambda_\alpha m$ in CMD (where $\gamma_{\mathrm{cmd}} > 0$ is the adiabaticity parameter, which should be sufficiently large for a convergence), and $\mu_\alpha = m$ for all $\alpha \geq 2$ in RPMD. Temperature control also depends on the PI method. Thermostats are used to control the temperature of both centroid and non-centroid variables in PIMD, only to the non-centroid variables in CMD and TRPMD, but thermostats are not used in RPMD.

2.2 BCMD

The BCMD method is based on the set of equations of motion, Eq.(9) and a similar one to Eq.(10) but with randomization of the non-centroid velocity, $v_\alpha(t) = v'_\alpha(t)$ for $\alpha \geq 2$. In other words, at each step interval of Δt, $v'_\alpha(t)$ is randomly sampled according to the Maxwell distribution with a variance of

$$\left\langle [v'_\alpha(t)]^2 \right\rangle = \frac{1}{\beta\mu_\alpha}. \tag{13}$$

Now let us show that this leads to Brownian dynamics, which is a generator of the canonical ensemble. Applying the velocity-Verlet algorithm to Eq.(10) with the initial non-centroid velocities $v'_\alpha(t)$, the short-time evolution of the non-centroid modes from t to $t + \Delta t$ is given by

$$q_\alpha(t + \Delta t) = q_\alpha(t) + v'_\alpha(t)\Delta t + \frac{f_\alpha(t)}{\mu_\alpha}\frac{(\Delta t)^2}{2}. \tag{14}$$

Introducing the notations

$$\gamma \equiv \frac{2}{\Delta t} \tag{15}$$

and

$$\xi_\alpha(t) \equiv \mu_\alpha \gamma v'_\alpha(t), \tag{16}$$

Eq.(14) can be rewritten in the form of the Brownian dynamics (overdamped Langevin equation),

$$\mu_\alpha \gamma \dot{q}_\alpha(t) = f_\alpha(t) + \xi_\alpha(t), \tag{17}$$

where

$$\dot{q}_\alpha = \frac{q_\alpha(t + \Delta t) - q_\alpha(t)}{\Delta t}. \tag{18}$$

Combining to Eqs.(13) and (16), one obtains

$$\langle [\xi_\alpha(t)]^2 \rangle = \frac{2\mu_\alpha\gamma}{\beta}\frac{1}{\Delta t}, \tag{19}$$

indicating that $\xi_\alpha(t)$ corresponds to a random force subject to the fluctuation-dissipation theorem,

$$\xi_\alpha(t) = \sqrt{\frac{2\mu_\alpha\gamma}{\beta}}\zeta(t), \tag{20}$$

with the white noise $\langle \zeta(t)\zeta(t') \rangle = \delta(t - t')$. Therefore, the BCMD is the combination between the Newtonian dynamics with respect to the centroid variables, Eq.(9), and the Brownian dynamics with respect to the non-centroid variables, Eq.(17).

The major difference between BCMD and (T)RPMD is that the inertia term of (T)RPMD, i.e., $m\ddot{q}_\alpha$ where m is the atomic mass, is not present in the non-centroid equation of motion, Eq.(17). The presence of the inertia term together with the spring force in the first term of the right-hand side of Eq.(17) is the source of the chain resonance problem. In TRPMD the resonance can be diminished by applying a random force with the damping parameter being carefully optimized. On the other hand, BCMD has no inertia term, so it can be used safely avoiding any resonant behavior from the outset, and this is of great advantage in the calculation of vibrational spectra using BCMD. Comparing BCMD with RPMD and CMD, they are derived from the same equation of motion, Eq.(10), and there is a clear correspondence among them in theory and numerical algorithm. As discussed in Section 2.5, BCMD has also a close relationship with path integral hybrid Monte Carlo (PIHMC) in terms of the numerical algorithm.

Eq.(10) has turned into Eq.(17) simply by randomizing the non-centroid velocities with the Maxwell-Boltzmann distribution at each step in the velocity-Verlet algorithm; Randomizing v_α every step has changed a deterministic second-order differential equation of q_α (i.e., $\mu_\alpha\ddot{q}_\alpha = f_\alpha$) into a stochastic first-order differential equation of q_α with respect to t (i.e., Eq.(17)). As described in Eqs.(16) and (20), the random generation of velocities is

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the origin of the random force, ξ_α, with a white noise that obeys the fluctuation-dissipation theorem. Thus it is guaranteed in the BCMD method thermal equilibrium of the system is maintained. It is stressed once again that it is the nature of stochastic first-order differential equation of the BCMD method that ensures the system being completely free of the chain resonance behavior, in contrast to the case of the (T)RPMD method.

Now the mass of the non-centroid variables, μ_α, has to be determined. The smaller the μ_α value, the shorter the time scale of non-centroid variables would become, and the larger the adiabatic separation would be from the centroid variable. The limiting case of $\mu_\alpha \to 0$ would simply correspond to CMD-like adiabatic dynamics. Instead, let us herein determine the μ_α value from the short-time behavior of free particle system. For the case of $V(x) = 0$, Eq.(17) becomes

$$\mu_\alpha \gamma \dot{q}_\alpha = -\kappa_\alpha q_\alpha + \xi_\alpha, \tag{21}$$

where

$$\kappa_\alpha \equiv m\omega_P^2 \lambda_\alpha. \tag{22}$$

Equation (21) corresponds exactly to the Ornstein-Uhlenbeck process.[25] Thus, the mean square displacement (MSD) is

$$\left\langle |q_\alpha(t) - q_\alpha(0)|^2 \right\rangle = \frac{2}{\kappa_\alpha \beta} \left[1 - \exp\left(-\frac{\kappa_\alpha |t|}{\mu_\alpha \gamma} \right) \right], \tag{23}$$

indicating that the non-centroid position will be uncorrelated after the relaxation time, $\tau_\alpha = \frac{\mu_\alpha \gamma}{\kappa_\alpha}$. Since it is expected that the imaginary time path integrals are not able to describe the quantum interference effects beyond the thermal time $\beta\hbar$, it should be natural to set the relaxation time as $\tau_\alpha = \beta\hbar$. Accordingly, in BCMD, μ_α is determined as

$$\mu_\alpha = \frac{\kappa_\alpha \tau_\alpha}{\gamma}. \tag{24}$$

Note that with this setting the friction term, $\mu_\alpha \gamma \dot{q}_\alpha$, in the lhs of Eqs.(17) and (21) does not depend on Δt. As explained in the Appendix 5, $\beta\hbar$ corresponds to the time scale that free particle wavepacket persists at temperature $T = \frac{1}{k_B \beta}$. Thus, BCMD maintains the shape of the free particle ring polymer, which is determined by the set of non-centroid variables, on

the same time scale. It seems that $\tau_\alpha = \beta\hbar$ is a reasonable choice, at least, for the vibrational spectrum of OH molecule tested in Section 3.2. In this case, Eq.(24) combined with Eqs.(15) and (22) becomes $\mu_\alpha = \frac{1}{2}m\omega_P^2\lambda_\alpha\Delta t(\beta\hbar)$.

In BCMD, one computes the correlation function

$$C_{AB}(t) = \langle \overline{A}(0)\overline{B}(t) \rangle \tag{25}$$

where $\overline{A}(0)$ and $\overline{B}(t)$ is the bead average of the observable $X = A$ at time 0 and the observable $X = B$ at time t, respectively, which are given by

$$\overline{X}(t) = \frac{1}{P}\sum_{j=1}^{P} X(x_j(t), p_j(t)). \tag{26}$$

In Sections 2.3 and 2.4, it will be shown that Eq.(25) is an approximation of the Kubo-transformed correlation function, whose exact expression is

$$C_{AB}^{\text{kubo}}(t) = \frac{\frac{1}{\beta\hbar}\int_0^{\beta\hbar} d\tau\,\text{Tr}\left(e^{-\beta\hat{H}}\hat{A}(0)\hat{B}(t+i\tau)\right)}{\text{Tr}\left(e^{-\beta\hat{H}}\right)}, \tag{27}$$

where $\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}$ is the Hamiltonian operator of the system. Since BCMD does not disturb the thermal equilibria and is time reversible, the BCMD correlation function, Eq.(25), is invariant under time origin shifts and time sign inversions. Thus, $C_{AB}(t) = C_{BA}(t)$ is even function of t. This is consistent with the exact correlation function, Eqs.(27), which is real-valued and even function of t with the same symmetry, $C_{AB}^{\text{kubo}}(t) = C_{BA}^{\text{kubo}}(t)$.[5]

2.3 Short time correlations

Let us see how accurate $C_{xx}(t)$ of Eq.(25) is compared with $C_{xx}^{\text{kubo}}(t)$ of Eq.(27) at short times. Since $C_{xx}(t)$ is an even function of t, the Taylor expansion of the position and velocity correlation functions near $t = 0$ are described as

$$C_{xx}(t) = C_{xx}^{(0)} + \frac{t^2}{2}C_{xx}^{(2)} + \frac{t^4}{24}C_{xx}^{(4)} + \cdots, \tag{28}$$

and

$$C_{vv}(t) = -\ddot{C}_{xx}(t) = -C_{xx}^{(2)} - \frac{t^2}{2}C_{xx}^{(4)} - \cdots, \tag{29}$$

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respectively. In Eq.(28), the zeroth-order coefficient is

$$C_{xx}^{(0)} = \langle \bar{x}^2 \rangle = \langle q_1^2 \rangle, \tag{30}$$

the second-order coefficient is

$$C_{xx}^{(2)} = -\langle \dot{\bar{x}}^2 \rangle = -\langle \dot{q}_1^2 \rangle = -\frac{1}{m^2} \langle p_1^2 \rangle = -\frac{1}{m\beta}, \tag{31}$$

and the fourth-order coefficient is

$$\begin{aligned}
C_{xx}^{(4)} &= -\langle \dot{\bar{x}} \dddot{\bar{x}} \rangle = -\frac{1}{m} \langle \dot{q}_1 \dddot{p}_1 \rangle = \left\langle \frac{\dot{q}_1}{m} \frac{d}{dt} \frac{\partial \phi}{\partial q_1} \right\rangle \\
&= \frac{1}{mP} \left\langle \sum_{j=1}^{P} \frac{\partial^2 V}{\partial x_j} \dot{x}_j \dot{q}_1 \right\rangle = \frac{1}{\beta m^2} \left\langle \frac{1}{P} \sum_{j=1}^{P} \frac{\partial^2 V}{\partial x_j^2} \right\rangle,
\end{aligned} \tag{32}$$

where the principle of equipartition, $\frac{p_1^2}{m} = \frac{1}{\beta}$, has been used. Eqs.(30), (31), and (32), on the other hand, exactly match the zeroth, second, and fourth-order coefficients, respectively, in the Taylor expansion of the exact correlation function, $C_{xx}^{\text{kubo}}(t)$.[14] Therefore, $C_{xx}(t)$ and $C_{vv}(t)$ are accurate up to the fifth order in t, and the third order in t, respectively.

2.4 Harmonic system

Let us consider the case of harmonic system with a potential energy function, $V(x) = \frac{K}{2}x^2$, where K is the force constant. In this case, Eq.(3) becomes

$$\phi = \frac{K}{2P} \sum_{j=1}^{P} x_j^2 = \frac{K}{2} \sum_{\alpha=1}^{P} q_\alpha^2. \tag{33}$$

where Eq.(6) is used with the relation $\mathbf{U}^T = \mathbf{U}^{-1}$ in Eq.(5). For the CMD and RPMD equations of motion, Eqs.(9) and (10) become

$$m\ddot{q}_1 = -Kq_1, \quad \text{and} \quad \mu_\alpha \ddot{q}_\alpha = -\kappa'_\alpha q_\alpha, \tag{34}$$

respectively, where

$$\kappa'_\alpha \equiv m\omega_P^2 \lambda_\alpha + K. \tag{35}$$

For the BCMD equations of motion, Eqs.(21) and (32) become

$$m\ddot{q}_1 = -Kq_1, \quad \text{and} \quad \mu_\alpha \gamma \dot{q}_\alpha = \xi_\alpha - \kappa'_\alpha q_\alpha \tag{36}$$

respectively.

In both cases of Eq.(34) and (36), the motion of the centroid variable is uncoupled from that of the non-centroid variables. The time evolution of centroid variable is

$$q_1(t) = q_1(0)\cos(\omega t) + \dot{q}_1(0)\omega^{-1}\sin(\omega t) \tag{37}$$

where $\omega = \sqrt{\frac{K}{m}}$. From Eq.(37) the centroid position correlation function becomes

$$C_{xx}(t) = \langle \overline{x}(0)\overline{x}(t) \rangle = \langle q_1(0)q_1(t) \rangle = \frac{\cos(\omega t)}{\beta m \omega^2}, \tag{38}$$

where the principle of equipartition for harmonic oscillators, $\langle q_1^2 \rangle = \frac{1}{\beta m \omega^2}$, has been used. From Eq.(38) the centroid velocity correlation function is

$$C_{vv}(t) = -\ddot{C}_{xx}(t) = \frac{\cos(\omega t)}{\beta m}. \tag{39}$$

Eqs.(38) and (39) are exactly the same as $C_{xx}^{\text{kubo}}(t)$ and $C_{vv}^{\text{kubo}}(t)$, respectively, for the harmonic system.[5]

2.5   Numerical algorithm

Generally, overdamped Langevin dynamics can be considered as short-time case of the hybrid Monte Carlo (HMC).[26] The HMC algorithm[24,26–28] is composed of the velocity randomization, the integration of Hamilton's equation of motion with a time reversible and area preserving algorithm, and the Metropolis acceptance/rejection. The Metropolis acceptance/rejection can be skipped for the short-time case because the energy is conserved.[26] An application of HMC to Eqs.(9) and (10) corresponds to path integral hybrid Monte Carlo (PIMHC).[29,30] Thus the integration of the BCMD equation of motion can be built in a way similar to that of the PIHMC method based on the Reversible System Propagator Algorithm (RESPA),[24] which is time reversible and area preserving. In fact, BCMD could be thought of as a special class of PIHMC applied only to the non-centroid variables where the trial move consists of a single step, and thus the velocity randomization of the non-centroid variables is applied each step. This leads to a pseudo-code for the BCMD

cycle as follows:

$$v_\alpha \leftarrow v'_\alpha \text{ (randomized for } \alpha \geq 2)$$

$$v_1 \leftarrow v_1 - \frac{\partial \phi}{\partial q_1} \frac{\Delta t}{2m}, \quad v_\alpha \leftarrow v_\alpha - \frac{\partial \phi}{\partial q_\alpha} \frac{\Delta t}{2\mu_\alpha} \quad (\alpha \geq 2)$$

$$q_1 \leftarrow q_1 + v_1 \Delta t$$

$$q_\alpha \leftarrow q_\alpha \cos(\omega_\alpha \Delta t) + v_\alpha \omega_\alpha^{-1} \sin(\omega_\alpha \Delta t) \quad (\alpha \geq 2),$$

$$v_\alpha \leftarrow v_\alpha \cos(\omega_\alpha \Delta t) - q_\alpha \omega_\alpha \sin(\omega_\alpha \Delta t) \quad (\alpha \geq 2)$$

$$\text{calculate } \frac{\partial \phi}{\partial x_j}, \text{ obtain } \frac{\partial \phi}{\partial q_1}, \frac{\partial \phi}{\partial q_\alpha} \text{ from Eq.(12)}$$

$$v_1 \leftarrow v_1 - \frac{\partial \phi}{\partial q_1} \frac{\Delta t}{2m}, \quad v_\alpha \leftarrow v_\alpha - \frac{\partial \phi}{\partial q_\alpha} \frac{\Delta t}{2\mu_\alpha} \quad (\alpha \geq 2) \tag{40}$$

where

$$\omega_\alpha = \sqrt{\frac{m\lambda_\alpha}{\mu_\alpha}} \omega_P. \tag{41}$$

In Eq.(40), line 1 corresponds to the velocity randomization, while the rest corresponds to the time integration of Eqs.(9) and (10). To ensure time reversibility, the time integration for the force contributions from the first and second terms in the rhs of Eq.(2) are divided into lines (4,5) and lines (2,3,7), respectively, and the analytic expression for the harmonic oscillator is adopted for the former, which corresponds to taking the number of steps infinite for the reference forces in the RESPA technique. The force for the second term (ϕ) is calculated at line 6. The velocity update at Line 7 is necessary not only for the centroids but also for the non-centroids in order to assess the energy conservation of $E'(t)$, see Section 2.7.

BCMD gives rise to the canonical ensemble as in PIHMC, but it has access to the time dependence via Kubo-transformed correlation function in contrast to PIHMC. A notable difference of the BCMD algorithm from the PIHMC algorithm is that the Metropolis acceptance/rejection step can be omitted. This is because in BCMD a small step size Δt is chosen such that the energy is conserved within a single step. In other words, H defined in Eq.(7) is almost constant when Eq.(8) is solved for a single step excluding the velocity randomization part (as in the case of PIHMC algorithm), which corresponds to Lines 2–7 in Eq.(40). This is in contrast to the case of PIHMC where a large step size Δt is used such that H is no longer conserved, and Eq.(40) is regarded as a trial move. In PIHMC, a set

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of the cycle(s) of Eq.(40) is accepted with the probability $P = \min(1, e^{-\beta \Delta H})$ where ΔH is the change in H upon the trial move. In BCMD, meanwhile, $P \approx 1$ if $H \ll \beta^{-1}$, and thus the trial move is always accepted. The BCMD algorithm is similar to the RPMD algorithm, except for the velocity randomization and the values for μ_α.

The "partially adiabatic" CMD (PACMD) using a non-large adiabaticity parameter, γ_{cmd}, would have an aspect similar to BCMD in that the adiabatic separation between centroid and noncentroid variables becomes incomplete. However, PACMD is difficult to establish without ambiguity in setting up the non-centroid masses and the system-thermostat coupling. Thus the results of PACMD should strongly depend on such setups. In contrast, BCMD is uniquely defined by Eqs.(9) and (17) [Eqs.(45) and (48) for the multidimensional case], and the degree of nonadiabaticity is determined unambiguously.

The simple algorithm Eq.(40) works correctly as long as the step size is small enough. It is required that the energy is conserved, which could be checked numerically by monitoring the energy conservation of $E'(t)$, as mentioned in Section 2.7. It may also be useful to confirm that the non-centroid MSD in the absence of physical potential, Eq.(23), is reproduced with the step size chosen. A modern algorithmic development of the Langevin equation,[31–33] especially those beyond the simple "pxpT" algorithm,[33] may help making it more efficient and accurate by enabling the use of increased step sizes.

2.6 Multidimensional extension

Let us consider a system composed of N atoms in 3-dimensional space with Cartesian coordinates $(\mathbf{R}_1, \cdots, \mathbf{R}_N)$, and the potential energy function $V(\mathbf{R}_1, \cdots, \mathbf{R}_N)$. Following Section 2.1, the cyclic path of the I-th atom, $\mathbf{R}_I = \left(\mathbf{R}_I^{(1)}, \cdots, \mathbf{R}_I^{(P)} \right)^T$, can be represented in normal modes $\mathbf{Q}_I = \left(\mathbf{Q}_I^{(1)}, \cdots, \mathbf{Q}_I^{(P)} \right)^T$, using the linear transformation

$$\mathbf{Q}_I = \frac{1}{\sqrt{P}} \mathbf{U}^T \mathbf{R}_I. \tag{42}$$

With the set $\{\mathbf{Q}\}$ and its momentum conjugate $\{\mathbf{P}\}$, the Hamiltonian is constructed as

$$H(\{\mathbf{P}, \mathbf{Q}\}) = \sum_{I=1}^{N} \left(\frac{1}{2} \mathbf{P}_I^T \boldsymbol{\mu}_I^{-1} \mathbf{P}_I + \frac{1}{2} M_I \omega_P^2 \mathbf{Q}_I^T \boldsymbol{\lambda} \mathbf{Q}_I \right) + \phi(\{\mathbf{Q}\}), \tag{43}$$

where M_I is the physical atomic mass of the I-th atom, $\boldsymbol{\mu}_I$ is a diagonal matrix whose elements are the fictitious normal mode masses, and

$$\phi(\{\mathbf{Q}\}) \equiv \frac{1}{P} \sum_{j=1}^{P} V\left(\mathbf{R}_1^{(j)}(\mathbf{Q}_1), \cdots, \mathbf{R}_N^{(j)}(\mathbf{Q}_N)\right) \tag{44}$$

is the average physical potential. The canonical equation of motion derived from Eq.(43) is as follows. For the centroid variables,

$$\dot{\mathbf{Q}}_I^{(1)} = \frac{\mathbf{P}_I^{(1)}}{M_I} = \mathbf{V}_I^{(1)}, \quad \dot{\mathbf{P}}_I^{(1)} = -\frac{\partial \phi}{\partial \mathbf{Q}_I^{(1)}}, \tag{45}$$

and for the non-centroid variables $\alpha \geq 2$,

$$\dot{\mathbf{Q}}_I^{(\alpha)} = \frac{\mathbf{P}_I^{(\alpha)}}{\mu_I^{(\alpha)}} = \mathbf{V}_I^{(\alpha)}, \quad \dot{\mathbf{P}}_I^{(\alpha)} = \mathbf{F}_I^{(\alpha)}, \tag{46}$$

with

$$\mathbf{F}_I^{(\alpha)} = -M_I \omega_P^2 \lambda^{(\alpha)} \mathbf{Q}_I^{(\alpha)} - \frac{\partial \phi}{\partial \mathbf{Q}_I^{(\alpha)}}. \tag{47}$$

In BCMD, the non-centroid velocities are randomized at each step ($\mathbf{V}_I^{(\alpha)'}$). Then, following Section 2.2, one obtains the Brownian equation

$$\mu_I^{(\alpha)} \gamma \dot{\mathbf{Q}}_I^{(\alpha)}(t) = \boldsymbol{\xi}_I^{(\alpha)}(t) + \mathbf{F}_I^{(\alpha)}(t), \tag{48}$$

where

$$\boldsymbol{\xi}_I^{(\alpha)} = \sqrt{\frac{2\mu_I^{(\alpha)}\gamma}{\beta}} \boldsymbol{\zeta}(t) \tag{49}$$

is the random force. Eqs.(48) and (49) are the working BCMD equation of motion for multidimension systems. The masses are set to $\mu_I^{(1)} = M_I$ for the centroids, and

$$\mu_I^{(\alpha)} = \frac{1}{2} M_I \omega_P^2 \lambda^{(\alpha)} (\Delta t) \tau_\alpha, \tag{50}$$

with $\tau_\alpha = \beta\hbar$ for the non-centroids ($\alpha \geq 2$), which is obtained by combining Eq.(24) with Eqs.(15) and (22).

2.7 Conservation laws

To calculate the vibrational spectrum, it is useful to remove the total momentum. In the case of gaseous systems in the free boundary condition, it is also useful to remove the full angular momentum. If the potential V has the translation symmetry, BCMD conserves the total centroid momentum, $\mathbf{P}_{\text{cent}} \equiv \sum_{I=1}^{N} M_I \dot{\mathbf{Q}}_I^{(1)}$, because

$$\dot{\mathbf{P}}_{\text{cent}} = \sum_{I=1}^{N} M_I \ddot{\mathbf{Q}}_I^{(1)} = -\sum_{I=1}^{N} \frac{\partial \phi}{\partial \mathbf{Q}_I^{(1)}} = -\frac{1}{P} \sum_{k=1}^{P} \left(\sum_{I=1}^{N} \frac{\partial V}{\partial \mathbf{R}_I^{(k)}} \right) = 0. \tag{51}$$

Thus, $\mathbf{P}_{\text{cent}} = 0$ is satisfied by setting at the initial step,

$$\dot{\mathbf{Q}}_I^{(1)} \leftarrow \dot{\mathbf{Q}}_I^{(1)} - \frac{\sum_{J=1}^{N} M_J \dot{\mathbf{Q}}_J^{(1)}}{\sum_{J=1}^{N} M_J}. \tag{52}$$

On the other hand, BCMD does not conserve by itself the total angular momentum of the centroid variables, $\mathbf{L}_{\text{cent}} \equiv \sum_{I=1}^{N} \left(\mathbf{Q}_I^{(1)} \times M_I \dot{\mathbf{Q}}_I^{(1)} \right)$. However, $\mathbf{L}_{\text{cent}} = 0$ can be imposed in BCMD using the rotational correction technique, as done in CMD and RPMD as well.[15] This technique removes at each step the rotational component of the centroid velocities by

$$\dot{\mathbf{Q}}_I^{(1)} \leftarrow \dot{\mathbf{Q}}_I^{(1)} - \left(\mathbf{I}_{\text{cent}}^{-1} \mathbf{L}_{\text{cent}} \right) \times \mathbf{Q}_I^{(1)}, \tag{53}$$

and the rotational component of the centroid forces by

$$\mathbf{F}_I^{(1)} \leftarrow \mathbf{F}_I^{(1)} - \left(\mathbf{I}_{\text{cent}}^{-1} \mathbf{N}_{\text{cent}} \right) \times \mathbf{Q}_I^{(1)}, \tag{54}$$

where $\mathbf{I}_{\text{cent}}$ is a 3×3 matrix for the centroid moment of inertia, and $\mathbf{N}_{\text{cent}}$ is a $3N$-dimensional vector for the centroid torque.

The energy conservation of the classical isomorph is useful in determining a reasonable step size, Δt. In the BCMD algorithm, the energy conservation for $H(\{\mathbf{P}, \mathbf{Q}\})$ defined in Eq.(43) is kept in the time integration part, but is broken in the velocity randomization part. For this reason, one can introduce a modified energy for BCMD as

$$E'(t) = H(\{\mathbf{P}, \mathbf{Q}\}) - \sum_{s<t} \sum_{I=1}^{N} \sum_{\alpha=2}^{P} \frac{\mu_I^{(\alpha)}}{2} \left(\left| \mathbf{V}_I^{(\alpha)\prime}(s) \right|^2 - \left| \mathbf{V}_I^{(\alpha)}(s) \right|^2 \right), \tag{55}$$

where the second term in the rhs corrects the jumps in the kinetic energy due to the velocity randomization. $E'(t)$ is conserved for small step size Δt in the absence of the rotational

correction. When the rotational correction is applied, $E'(t)$ is not strictly conserved. However, the energy shift due to the rotational correction is small, as was experienced in CMD and RPMD as well. Thus the conservation error of $E'(t)$ is acceptable within tens of picoseconds of BCMD trajectories required in the computation of vibrational spectra.

3 CALCULATIONS

All the calculations in this study were performed using the in-house version of the `PIMD` software,[30,34,35] with the BCMD method newly implemented.

3.1 One dimensional models

The BCMD method was first tested on one-dimensional models, as done in previous studies of the CMD and RPMD methods.[5,13,36,37] Figures 1 and 2 show the Kubo-transformed correlation functions $C_{xx}(t)$ for mildly anharmonic and quartic potentials, respectively. Figure 3 shows the function $C_{aa}(t)$ for a harmonic potential, where $a = x^2$. The BCMD results were compared with the results of MD, CMD, RPMD, and the exact solution. The CMD and RPMD results are consistent with earlier works such as Figures 1–2 in Reference[5], Figures 7–8 in Reference[37], and Figure 1 of Reference[38]. Note in Figure 3 of this paper that the correlation functions where nonlinear operators are involved are not necessarily exact in BCMD as well as CMD and (T)RPMD even for a harmonic system.

In general, the performance of BCMD shown in Figures 1–3 of this paper is similar to those of CMD and RPMD. However, there is a slight difference in the low temperatures case of quartic potential shown in the bottom panel of Figure 2. Here it can be seen that the BCMD captures the amplitude of long-time vibrations better than RPMD, but worse than CMD. The stronger the anharmonicity and the lower the temperature, the faster the deviation from the exact solution will be. BCMD, like CMD and RPMD, cannot describe long-time quantum interference in anharmonic oscillations, as expected from theory. This means that this method is more suitable for condensed phase systems where the interference effects are expected to be rapidly quenched.

3.2 OH molecule

Next, the BCMD method was tested on the vibrational spectra for the harmonic and Morse models of gaseous OH molecule. These models were used in previous studies to test the CMD, RPMD and TRPMD methods.[15,18] The harmonic model is not a quadratic function with respect to the Cartesian coordinates of the O and H atoms, but a quadratic function with respect to the shift of the beadwise OH distance in three dimensional space from the equilibrium distance. For this reason, BCMD, CMD, and RPMD do not provide the exact results for this model.

The BCMD, CMD, and RPMD simulations were performed at temperatures 100, 200, 300 and 600 K with $P = 96$, 48, 32 and 16 beads, respectively. Starting from the equilibrated structures of the PIMD simulations, 100–300 trajectories of 2.5 ps long were computed for each case. For CMD, the adiabaticity parameter was set to $\gamma_{\mathrm{cmd}} = 10$. The rotational correction was applied to fix the molecular orientation. The MD simulations were performed in the same way as above, but with a single bead, $P = 1$.

Previous studies pointed out that there are chain resonance and curvature problems in the RPMD and CMD vibrational spectra, respectively. When P is large, the chain resonance is found at the RPMD normal mode frequencies, $\omega_n = \frac{2n\pi}{\beta\hbar}$ where n is a natural number. At 300 K, $\omega_n = 1310 \times n$ cm^{-1}, are within the frequency range of physical vibrations (0–5000 cm^{-1}). As the temperature decreases, the amount of resonant modes in this region increases, making the spurious peak splittings become more noticeable. This is shown in the bottom right panel of Figures 4 and 5. TRPMD diminishes the chain resonance, but it does not completely remove it even with the optimal damping parameter. On the other hand, the curvature problem arises from the spurious coupling between the rotation and vibration of the system. The coupling is amplified by the adiabaticity between the centroid and non-centroid variables which is assumed in the CMD equation of motion. This leads to an unnatural red shift and broadening of the spectra as the temperature decreases, as shown in the bottom-left panel of Figures 4 and 5.

The results of BCMD are shown in the top-left panels of Figures 4 and 5. The peak positions from Figure 5 were plotted in the left panel of Figure 6. An advantage of BCMD

is in the complete absence of peak splitting due to spurious resonances, which is often a fundamental requirement in vibrational spectroscopy. On the other hand, the peak shift due to the curvature problem of BCMD does not seem to be as severe as CMD. The reason is that BCMD breaks the adiabaticity between the centroid and non-centroid variables, and thus weakens the spurious coupling between rotation and vibration. Still, in this case, the peak shift of BCMD cannot be ignored, especially at temperatures below 200 K in this case. The BCMD peak positions reasonably matches the exact frequency of the $(v, r) = (0, 0) \rightarrow (1, 0)$ transition in both the harmonic and Morse models. For the Morse model, the peak position in BCMD (top-left panel) shows a redshift relative to that of MD (top-right panel), improving the agreement with the exact result. This shows that BCMD properly considers the nuclear quantum effects of anharmonic vibrations.

The peak width for the Morse model are shown in the right panel of Figure 6. Here the full-width at half minimum (FWHM) values were evaluated by fitting the spectrum to the Lorenzian function. This result shows the limitation of BCMD that unphysical broadening of the spectrum becomes noticeable at low temperatures, especially below 200 K in this case. CMD and TRPMD also show more or less unphysical broadening at low temperatures as well.

Further tests on the vibrational spectra of methane molecule is shown in Appendix B. As a general trend, the performance of BCMD shown in Figure 10 and 11 was similar to those seen in Figures 4 and 5. The unphysical peak shift and broadening were found to decrease for the vibrational modes with lower frequency. They are generally smaller for the HOH and HCH bending modes than in the OH and CH stretching modes, and they are smaller in the D isotopologues than in the H isotopologues.

3.3   Gaseous water

The BCMD, CMD, RPMD, and MD simulations of gaseous water molecule and its isotopologues were carried out at 300 K using the q-TIP4P/F model.[39] The simulation settings were the same as those described in Section 3.2. In Figure 7, the results are compared to the solution of vibrational Schrödinger equation based on the full vibrational configuration interaction (VCI) method[40] using the SINDO code,[41] with a 3-mode representation and 11

grid points per mode. Since the q-TIP4P/F potential is quartic with respect to the OH bonds, the exact peak frequencies in the spectra are red-shifted from the harmonic frequencies.

In all cases studied for H_2O, D_2O, HDO and HTO molecules, the BCMD vibrational spectra were significantly improved compared to the MD vibrational spectra. This indicates that the nuclear quantum effects on the vibrational spectra were properly taken into account in the BCMD method. Assuming that the VCI frequencies are correct, the mean absolute error and the maximum absolute error of the BCMD peaks were 22 and 41 cm^{-1}, respectively. These values are lower than the mean absolute error and the maximum absolute error of the CMD peaks (44 and 129 cm^{-1}, respectively), the RPMD peaks (52 and 156 cm^{-1}, respectively), the MD peaks (77 and 151 cm^{-1}, respectively), and the harmonic frequencies (85 and 166 cm^{-1}, respectively). In this respect, the BCMD method outperforms the CMD and RPMD methods in these cases. However, the spectral broadening of the BCMD method remains a problem when dealing with vibrational spectra of the gas phase molecules at the low temperature, and it seems that PILD outperforms BCMD in this sense.[9]

3.4   Liquid water

As a typical example of condensed phase systems, the BCMD method was tested on the vibrational spectra of liquid water and its isotopologues at a temperature of 300 K. TIP3P and modified TIP3P (mTIP3P) models were used for comparison with previous studies on MD and CMD simulations.[16] In addition, the q-TIP4P/F model was used for comparison with previous studies on MD and (T)RPMD simulations.[18] The BCMD simulations of liquid H_2O were performed using $P = 32$ beads, for a system of 256 H_2O molecules contained in a cubic box with a side length of 19.7 Å. Ewald sum technique was used to compute the electrostatic interaction under the periodic boundary condition. Starting from the equilibrated structures of the PIMD simulations, 100 independent BCMD trajectories were run for 2.5 ps each with a step size of $\Delta t = 0.25$ fs. The same procedure was repeated for the BCMD simulations of liquid D_2O and HDO. The intensity of the vibrational spectra was computed by the formula

$$\alpha(\omega) \propto \beta\omega^2 \int_{-\infty}^{\infty} C_{\mathbf{MM}}(t) \exp(-\mathrm{i}\omega t)dt \tag{56}$$

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where $C_{\mathbf{MM}}(t)$ is the Kubo-transformed dipole autocorrelation function. In this case, the dipole trajectories were computed by

$$\mathbf{M}^{(j)}(t) = \sum_{I=1}^{N} \rho_I \mathbf{R}_I^{(j)}(t) \tag{57}$$

where $\mathbf{R}_I(t)$ and ρ_I are the Cartesian coordinates (in the expanded space of periodic boundary) and the TIP3P charge, respectively, of the I-th atom.

Figure 8 shows the BCMD results compared with the MD, CMD, and (T)RPMD results. Here, the spectral peaks correspond respectively to intermolecular vibrations (0-1000 cm^{-1}), DOD bending (1200–1300 cm^{-1}), HOD bending (1500–1600 cm^{-1}), HOH bending (1700–1800 cm^{-1}), the OD stretching (2200–2500 cm^{-1}), and the OH stretching (2900–3400 cm^{-1}). It was pointed out that CMD shows a significant redshift in the spectra compared to MD, partly due to the curvature problem.[16] It is expected that the correct peak positions is somewhere between those of MD and CMD, when the physical redshifts due to the nuclear quantum effects were taken into account. In this respect, the results of BCMD are indeed convincing, since the peak positions are found systematically between those of MD and CMD. Thus it seems that BCMD is capable of improving CMD with respect to the vibrational spectra of liquid water. Comparing the results of BCMD and TRPMD, the peaks of the OH stretching and HOH bending were found similar to each other, but the peak of intermolecular vibrations in BCMD were found at higher frequency than that in TRPMD.[18]

3.5   Protonated water: Ab initio BCMD

The final test is on the applicability of ab initio BCMD simulations where the electronic structure calculations are performed on the fly. Here the infrared spectra of the protonated water dimer (Zundel ion), $H_5O_2^+$, and its isotopologue, $D_5O_2^+$, were taken as an example. In this system, the anharmonicity in vibration due to quantum and thermal fluctuations is important.[42]

Electronic structure calculations were performed using the `SMASH` code[43] which was built into the `PIMD` software.[44] Potential energy (V) and force ($-\nabla V$) were calculated by the MP2 method with the 6-31G(d) basis set.[45,46] The infrared spectrum was calculated from

the dipole correlation function, Eq.(56). In this case the dipole trajectories were computed by the Hartree-Fock (HF) theory using the 6-31G(d) basis set,

$$\mathbf{M}^{(j)}(t) = \sum_{I=1}^{N} Z_I \mathbf{R}_I^{(j)}(t) - \langle \phi^{(j)}(t)| \sum_{i=1}^{n} e\hat{\mathbf{r}}_i |\phi^{(j)}(t)\rangle, \tag{58}$$

where e, n, $\hat{\mathbf{r}}_i$, Z_I, and $\phi^{(j)}(t)$ represent the elementary charge, the number of electrons, the position operator of the i-th electron, the nuclear charge of the I-th nucleus, and the HF wavefunction of the j-th bead at time t, respectively. Ab initio PIMD and BCMD simulations with $P = 24$ beads were performed at the temperature 300 K. After the equilibration with the ab initio PIMD simulation, ab initio BCMD simulations were run for 50 trajectories, each with the length of 2.5 ps. The rotational correction was applied to fix the orientation of the system. The step size was set to $\Delta t = 0.25$ fs. The ab initio MD simulations were performed in the same way but using a single bead, at the temperature 300 K.

The results are shown in Figure 9. It can be seen that the infrared spectra calculated from ab initio BCMD are overall in good agreement with the experimental results[47] for both $H_5O_2^+$ and $D_5O_2^+$. The spectra of $H_5O_2^+$ is also in reasonable agreement with the optimally-damped TRPMD calculations based on ab initio-based force field.[18] For the OD and OH stretching peaks near 2600 cm^{-1} and 3600 cm^{-1}, respectively, the BCMD peak positions are redshifted compared to the MD peak positions, and are closer to the experimental peak positions. Also for the DOD and HOH bending peaks near 1300 cm^{-1} and 1800 cm^{-1}, respectively, the BCMD peak positions are redshifted compared to the MD peak positions, and are closer to the experimental peak positions. For the peaks of the shared hydrogen vibrational modes of $D_5O_2^+$ and $H_5O_2^+$ near 800 cm^{-1} and 1100 cm^{-1}, respectively, the BCMD peak positions are blueshifted compared to the MD peak positions, and are higher than the experimental peak positions. However, because this peak is temperature sensitive, it may not be fair to directly compare theory and experiments with different temperature settings. In fact, it was experimentally observed that the peak in the Ar-tagged $H_5O_2^+$ is blueshifted compared to the Ne-tagged $H_5O_2^+$.[47] Further research should be necessary to verify this issue.

4 CONCLUSIVE REMARKS

In this paper, the BCMD method was proposed as a new approximation of quantum vibrational dynamics. BCMD is similar to CMD and RPMD in its accuracy in the short-time correlation, in the classical/high temperature limits, and in the harmonic oscillator systems. However, in the computation of vibrational spectra, BCMD eliminates the chain resonance problem of RPMD, and it alleviates the curvature problem of CMD. The BCMD causes spectral broadening at low temperatures, which one should be most cautious of. BCMD requires about the same computational effort as RPMD and CMD. The ab initio BCMD simulation can be run in parallel computing, and should be useful for a wide range of applications.

5 APPENDIX

A: Wavepacket propagation

Following the textbook by Schatz and Ratner,[48] a free particle wavepacket is expressed by the superposition of plane waves

$$\Psi(x,t) = N_0 \int_{-\infty}^{\infty} c(p) \exp\left(-\frac{p^2}{2m}\frac{\mathrm{i}t}{\hbar} + \frac{\mathrm{i}px}{\hbar}\right) dp, \tag{59}$$

where N_0 is a normalization constant, and $c(p)$ is a function describing the distribution of momentum, p, in the wavepacket. Assuming the Maxwell-Boltzmann distribution at temperature $T = \frac{1}{k_\mathrm{B}\beta}$, $c(p) = \sqrt{w(p)}$ and

$$w(p) = \sqrt{\frac{\beta}{2\pi m}} e^{-\beta\frac{p^2}{2m}}, \tag{60}$$

the probability distribution of the wavepacket is

$$|\Psi(x,t)|^2 = \sqrt{\frac{\pi}{a(t)}} \exp\left(-a(t)x^2\right), \tag{61}$$

where $a(t) = \frac{2\beta m}{(2t)^2 + (\hbar\beta)^2}$ and $N_0 = \frac{1}{\sqrt{2\pi\hbar}}$. Thus, the wavepacket starts changing its shape after about $t = \frac{\beta\hbar}{2}$, and it is broadened by $\sqrt{5} \approx 2.2$ times at $t = \beta\hbar$.

B: Gaseous methane

Figures 10 and 11 show the infrared spectra of gaseous CH_4 and CD_4 molecules, respectively, of a harmonic force field used in Reference[15]. The potential energy function of this model is given by

$$V = \sum_{j \in CH}^{4} \frac{K_r}{2}(r_j - R)^2 + \sum_{j \in HCH}^{6} \frac{K_\theta}{2}(\theta_j - \Theta)^2 \tag{62}$$

where r_j is the j-th CH bond length, θ_j is the j-th HCH bond angle, $R = 2.0598$ bohr, $K_r = 0.3035$ hartree·bohr^{-2} $\Theta = 107.8$ deg. $K_\theta = 3.1068 \times 10^{-5}$ hartree·deg.$^{-2}$. The BCMD, CMD, RPMD, and MD simulations were carried out in the same manner as done for gaseous OH molecule in Section 3.2.

ACKNOWLEDGMENTS

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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6 FIGURE CAPTIONS

- Figure 1: Kubo-transformed correlation function $C_{xx}(t)$ of a mild anharmonic potential, $V(x) = \frac{1}{2}x^2 + \frac{1}{10}x^3 + \frac{1}{10}x^4$ with $m = 1$ and $\hbar = 1$. The results are shown for BCMD (solid blue lines), MD (black double-dotted-dashed lines), CMD (violet single-dotted-dashed lines), RPMD (green dashed lines), and the exact results $C_{xx}^{\text{kubo}}(t)$ (grey dotted lines) at a high temperature, $\beta = 1$ (top panel) and at a low temperature, $\beta = 8$ (bottom panel). The number of beads is set to $P = \frac{1}{4\beta}$ for BCMD.

- Figure 2: Kubo-transformed correlation function $C_{xx}(t)$ of a quartic potential, $V(x) = \frac{1}{2}x^4$, otherwise the same as Figure 1.

- Figure 3: Kubo-transformed correlation function $C_{aa}(t)$ with $a = x^2$ of a harmonic potential $V(x) = \frac{1}{2}x^2$, otherwise the same as Figure 1. For CMD, the result of the effective classical operator[13,38] is shown.

- Figure 4: Vibrational spectra of OH molecule obtained from the BCMD (top left), MD (top right), CMD (bottom left), RPMD (bottom right), and optimally-damped TRPMD (bottom right) methods for harmonic model, $V = \frac{K}{2}(r - R)^2$, where r is the OH bond length. The parameters are $K = 0.49536$ hartree·bohr^{-2} and $R = 1.8897$ bohr. The black line represents the exact frequency of $(v, r) = (0, 0) \to (1, 0)$ transition of this model. The dotted lines in BCMD, RPMD and TRPMD are the magnified views.

- Figure 5: Vibrational spectra of OH molecule obtained in the same way as Figure 4, but for Morse model, $V = D\left(1 - e^{-A(r-R)}\right)^2$, where r is the OH bond length. The parameters are $R = 1.8324$ bohr, $D = 0.1875$ hartree, and $A = 1.1562$ bohr^{-1}. The black solid line represents the exact frequency of $(v, r) = (0, 0) \to (1, 0)$ transition, while the black dashed line represents the harmonic frequency of this model. The results of TRPMD using the same Morse model were reproduced from Reference[18]. The dotted lines in BCMD and RPMD are the magnified views.

- Figure 6: The temperature dependence on the position (left) and the FWHM value

(right) of the spectral peak shown in Figure 5. The results of TRPMD using the same Morse model were reproduced from Reference[18].

- Figure 7: Vibrational spectra of gaseous H_2O (top-left), D_2O (top-right), HDO (bottom-left), and HTO (bottom-right) at 300 K using the q-TIP4P/F model. The results of BCMD, MD, CMD, RPMD are shown along with the frequencies of $(v, r) = (0,0) \rightarrow (1,0)$ transitions obtained by the VCI calculations, and those in the harmonic approximation (HAR). The peak positions were obtained by fitting the spectrum to the sum of Lorentzian functions.

- Figure 8: Vibrational spectra of liquid H_2O (top-left), D_2O (top-right) and HDO (bottom-left) obtained from the MD and BCMD methods using the TIP3P and mTIP3P models, and vibrational spectra of liquid H_2O obtained from the MD and BCMD methods using the q-TIP4P/F model (bottom-right). The results of the CMD method were reproduced from Reference[16], and the results of the RPMD and the optimally-damped TRPMD methods were reproduced from Reference[18]. The experimental infrared spectrum was reproduced from Reference[49]. The peak positions were obtained by fitting the spectrum to the sum of Lorentzian functions.

- Figure 9: The infrared spectra of $H_5O_2^+$ (top) and $D_5O_2^+$ (bottom) obtained from the ab initio MD and BCMD methods at 300 K. The peak positions were obtained by fitting the spectrum to the sum of Lorentzian functions. The result of the optimally-damped TRPMD methods using ab initio-based force field were reproduced from Reference[18]. The experimental results were reproduced from Reference[47], for those of $H_5O_2^+ \cdot$Ne and $D_5O_2^+ \cdot$Ar.

- Figure 10: Vibrational spectra of CH_4 molecule obtained from the BCMD (top left), MD (top right), CMD (bottom left), RPMD and optimally-damped TRPMD (bottom right) methods using the harmonic force field in Reference[15]. The black lines represent the harmonic frequencies of this model for the infrared active modes (solid) and inactive modes (dotted).

- Figure 11: The same as Figure 10, but for CD_4 molecule.

An approximate approach to quantum vibrational dynamics, "Brownian Chain Molecular Dynamics", is proposed to alleviate the chain resonance and curvature problems in the imaginary time-based path integral simulation. Here the non-centroid velocity is randomized at each step when solving the equation of motion of path integral molecular dynamics. This leads to a combination of the Newton equation and the overdamped Langevin equation for the centroid and non-centroid variables, respectively.

Figure 1: Shiga, submitted to JCC.

Figure 2: Shiga, submitted to JCC.

Figure 3: Shiga, submitted to JCC.

Figure 4: Shiga, submitted to JCC.

Figure 5: Shiga, submitted to JCC.

Figure 6: Shiga, submitted to JCC.

Figure 7: Shiga, submitted to JCC.

Figure 8: Shiga, submitted to JCC.

Figure 9: Shiga, submitted to JCC.

Figure 10: Shiga, submitted to JCC.

Figure 11: Shiga, submitted to JCC.