Equilibrium-nonequilibrium ring-polymer molecular dynamics for nonlinear spectroscopy

Tomislav Begušić, a) Xuecheng Tao, and Thomas F. Miller III

Division of Chemistry and Chemical Engineering, California Institute of Technology,
Pasadena, California 91125, USA

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Two-dimensional Raman and hybrid terahertz/Raman spectroscopic techniques provide invaluable insight into molecular structure and dynamics of condensed-phase systems. However, corroborating experimental results with theory is difficult due to the high computational cost of incorporating quantum-mechanical effects in the simulations. Here, we present the equilibrium-nonequilibrium ring-polymer molecular dynamics (RPMD), a practical computational method that can account for nuclear quantum effects on the two-time response function of nonlinear optical spectroscopy. Unlike a recently developed approach based on the double Kubo transformed (DKT) correlation function, our method is exact in the classical limit, where it reduces to the established equilibrium-nonequilibrium classical molecular dynamics method. Using benchmark model calculations, we demonstrate the advantages of the equilibrium-nonequilibrium RPMD over classical and DKT-based approaches. Importantly, its derivation, which is based on the nonequilibrium RPMD, obviates the need for identifying an appropriate Kubo transformed correlation function and paves the way for applying real-time path-integral techniques to multidimensional spectroscopy.

a)Electronic mail: tbegusic@caltech.edu
I. INTRODUCTION

Two-dimensional vibrational spectroscopy is a versatile technique to study microscopic interactions at their natural, femtosecond time scales.\textsuperscript{1} Recently, a series of hybrid spectroscopic experiments\textsuperscript{2–5} involving mid-infrared, far-infrared (or terahertz), and visible (Raman) pulses have been developed to study electrical and mechanical anharmonicities,\textsuperscript{6–9} structural heterogeneities of liquids,\textsuperscript{10–12} and the couplings between intermolecular and intramolecular vibrational modes.\textsuperscript{13,14} However, the interpretation of such spectra is still an open question and requires adequate simulation methods.\textsuperscript{12,15}

Several computational methods have been proposed for simulating two-dimensional Raman and hybrid terahertz–Raman spectra. Model-based approaches aim at constructing simplified, few-dimensional model systems that can be solved fully quantum mechanically in the presence of a harmonic oscillator bath.\textsuperscript{16,17} These approaches can disentangle different contributions to spectra and relate them to different physical effects encoded in the model parameters. The parameters can be obtained by fitting to the existing experiment\textsuperscript{8} or molecular dynamics (MD) simulations.\textsuperscript{18} Alternatively, MD can be used to simulate spectra directly,\textsuperscript{6,19–26} as a way to cross-validate the simplified model and further test the molecular mechanics force field or ab initio quantum chemistry method used for describing the forces between atoms, dipole moments, and polarizabilities.\textsuperscript{27–29} However, one improvement of MD is highly desired—MD simulations are based on classical atomic nuclei and neglect nuclear quantum effects, which can significantly modify the spectra. Indeed, recent two-dimensional Raman–THz–THz spectra of H\textsubscript{2}O and D\textsubscript{2}O revealed the effect of isotopic substitution beyond what would be expected from classical mechanics, pointing at nuclear quantum effects of the light hydrogen atoms.\textsuperscript{12}

Quantum simulations in the condensed phase were enabled by various semiclassical methods based on the classical MD framework, including linearized semiclassical initial value representation (LSC-IVR),\textsuperscript{30,31} path-integral Liouville dynamics,\textsuperscript{32} centroid molecular dynamics (CMD),\textsuperscript{33} and ring-polymer molecular dynamics (RPMD).\textsuperscript{34} These methods have proven useful for the computation of one-time correlation functions\textsuperscript{35} related to various dynamical properties, including reaction rates,\textsuperscript{30,36–40} diffusion coefficients,\textsuperscript{41,42} and one-dimensional vibrational spectra.\textsuperscript{43–48} In contrast, their application to multi-time correlation functions, which would be needed for multidimensional spectroscopy, has been limited. Recently, the
group of Batista\textsuperscript{49,50} proposed a set of methods that approximate the symmetric contribution to the so-called double Kubo transformed (DKT) correlation function, which is a two-time extension of the original one-time Kubo transformed correlation function.\textsuperscript{35} However, the relation between the symmetrized DKT correlation function and the spectroscopic response function is only approximate.

Here, we present an alternative RPMD approach to two-dimensional spectroscopy, which directly approximates the two-time response function and does not rely on the additional approximation related to the DKT correlation function. To derive the proposed method, we start from the recently developed nonequilibrium RPMD\textsuperscript{51–55} and employ classical response theory. We then explore its validity and limitations both theoretically and numerically.

II. THEORY

In two-dimensional Raman\textsuperscript{56,57} and hybrid terahertz–Raman spectroscopies,\textsuperscript{3–5} the signal is measured as a function of two delay times between three ultrashort light pulses, whose specific sequence determines the type of spectroscopy. To keep the discussion general, we consider the time-dependent Hamiltonian

\[
\hat{H}_{\text{tot}} = \hat{H} - \hat{A}F_1(t) - \hat{B}F_2(t)
\]

comprised of the system’s field-free Hamiltonian $\hat{H}$ and two interactions with the first two ultrashort pulses, controlled, respectively, by coordinate-dependent operators $\hat{A}$ and $\hat{B}$ and by time-dependent functions $F_{1,2}(t)$ representing the pulse shapes. For terahertz pulses, the interaction operators are the system’s dipole moments and functions $F(t)$ are the electric fields of the light, whereas for the visible or near-infrared (Raman) pulses, the operators are the system’s polarizabilities and the time-dependent functions correspond to the squares of the electric fields. $F_1$ is centered at $t = -t_1$, $F_2$ is centered at $t = 0$, and the signal is measured at $t = t_2$, where $t_1$ and $t_2$ represent the time delays between the three light pulses. The recorded signal is proportional to the expectation value\textsuperscript{7}

\[
\langle \hat{C}(t_2) \rangle = \text{Tr}[\hat{C}\hat{\rho}(t_2)]
\]

of another coordinate-dependent operator $\hat{C}$, which is again either the polarizability or dipole moment operator of the system. In Eq. (2), system’s equilibrium density operator
\( \hat{\rho} = \exp(-\beta \hat{H})/\text{Tr}[\exp(-\beta \hat{H})] \) evolves under the time-dependent Hamiltonian (1), i.e.,

\[
\hat{\rho}(t) = \hat{U}_{\text{tot}}(t, -\infty)\hat{\rho}(t, -\infty),
\]

\[
\hat{U}_{\text{tot}}(t_f, t_i) = \mathcal{T} \exp \left[ -\frac{i}{\hbar} \int_{t_i}^{t_f} d\tau \hat{H}_{\text{tot}}(\tau) \right],
\]

\( \beta \) is the inverse temperature, and \( \mathcal{T} \) is the time ordering operator. In practice, the experiments are designed to extract the components of the signal that are proportional to \( F_1 \) and \( F_2 \), which can be accounted for by evaluating the signal as

\[
S(t_2) = \langle \hat{C}(t_2) \rangle_{++} - \langle \hat{C}(t_2) \rangle_{+-} - \langle \hat{C}(t_2) \rangle_{-+} + \langle \hat{C}(t_2) \rangle_{--},
\]

where \( \langle \cdot \rangle_{jk} \) represents the expectation value (2) of the system evolved under the Hamiltonian (1) with \( F_1(t) \rightarrow (j/2)F_1(t) \) and \( F_2(t) \rightarrow (k/2)F_2(t) \). For weak enough external fields, we can further invoke the second-order time-dependent perturbation theory and recover the well-known result

\[
S(t_2) = \int_0^{t_2} d\tau_2 \int_0^{\tau_2} d\tau_1 R(\tau_2, \tau_1)F_2(t_2 - \tau_2)F_1(t_2 - \tau_2 - \tau_1),
\]

where

\[
R(\tau_2, \tau_1) = -\frac{1}{\hbar^2} \text{Tr} \left\{ \hat{C}(\tau_2 + \tau_1)[\hat{B}(\tau_1), [\hat{A}, \hat{\rho}]] \right\}
\]

is the corresponding response function, which depends only on system’s properties. Because it can be easily convolved with different experimental pulses to recover the observed experimental signals (6), the response function is often the direct target of many theoretical studies. Here, we also intend to focus on the response function, but take a slightly different route in developing the computational approach. Namely, we note that for delta pulses, \( F_1(t) = \varepsilon_1 \delta(t + t_1) \) and \( F_2(t) = \varepsilon_2 \delta(t) \), the signal measured after the second time delay \( t_2 \) is proportional to the response function,

\[
S(t_2) = \varepsilon_1 \varepsilon_2 R(t_2, t_1),
\]

where \( \varepsilon_{1,2} \) control the amplitude of the external fields. In the following, we derive an approximation to \( S(t_2) \) under weak delta pulses and relate it to \( R(t_2, t_1) \) using Eq. (8).

To develop a tractable theory for condensed-phase simulations of spectra, we replace the exact quantum-mechanical expression (2) by its nonequilibrium RPMD approximation

\[
\langle \hat{C}(t) \rangle_{jk} \approx \langle C(t) \rangle_{jk}^{\text{RP}} = \int dq \int dp \ C_N(q_{jk,t})\rho_N(q,p),
\]
where $q$ and $p$ are the positions and momenta of the extended system comprised of $N$ replicas of the original $D$-dimensional system,

$$\rho_N(q, p) = \frac{e^{-\beta_N H_N(q, p)}}{\int dq \int dp \ e^{-\beta_N H_N(q, p)}}$$

(10)

is the corresponding phase-space distribution,

$$H_N(q, p) = \sum_{i=1}^{N} \frac{1}{2} p_i^T \cdot m^{-1} \cdot p_i + \frac{1}{2(\beta_N \hbar)^2} (q_i - q_{i-1})^T \cdot m \cdot (q_i - q_{i-1}) + V(q_i)$$

(11)

is the system’s field-free ring-polymer Hamiltonian,$^{35} \beta_N = \beta/N,$

$$C_N(q) = \frac{1}{N} \sum_{i=1}^{N} C(q_i)$$

(12)

$m$ is the symmetric mass matrix of the system, and $q_0 = q_N$. The classical time evolution of $q_{jk,t}$ and $p_{jk,t}$ is governed by the time-dependent ring-polymer Hamiltonian

$$H_{jk,N}(q, p, t) = H_N(q, p) + jV_{A,N}(q)\delta(t + t_1) + kV_{B,N}(q)\delta(t),$$

(13)

$$V_{A,N}(q) = -\frac{\varepsilon_1}{2} NA_N(q), \quad V_{B,N}(q) = -\frac{\varepsilon_2}{2} NB_N(q),$$

(14)

with $j, k \in \{+, -\}$. Nonequilibrium RPMD, in which the dynamics and initial distribution depend on different Hamiltonians [see Eqs. (9)–(11) and (13)], has been rigorously justified as an approximation to the more general real-time nonequilibrium Matsubara dynamics.$^{51}$ Although its original derivation involved only time-independent Hamiltonians, this assumption was not used explicitly at any step of the derivation, justifying the use of nonequilibrium RPMD even in the time-dependent setting. At this point, we recognize that the equations above already formulate a valid computational technique for evaluating the response function, which, in the limit of $N = 1$, is equivalent to the finite-field nonequilibrium MD method of Jansen, Snijders, and Duppen.$^{19,20}$ In contrast to their classical approach, the nonequilibrium RPMD theory can include, at least approximately, the nuclear quantum effects on two-dimensional spectra when the path-integral continuum limit is reached. However, these nonequilibrium (RP)MD methods are impractical because a different set of trajectories is needed for each choice of the delay time $t_1$. To address this problem, we employ the equilibrium-nonequilibrium approach, originally developed by Hasegawa and Tanimura$^{23}$ in the context of classical MD simulations, in which one of the two pulses is treated perturbatively, and combine it with the RPMD to account for nuclear quantum effects.
We start by rewriting Eq. (9) as

$$\langle C(t) \rangle_{jk}^{RP} = \int dq \int dp \ C_N(q) U_{jk,N}(t, -\infty) \rho_N(q, p),$$

(15)

where

$$U_{jk,N}(t_f, t_i) = \mathcal{T} \exp \left[ - \int_{t_i}^{t_f} d\tau L_{jk,N}(\tau) \right]$$

(16)

governs the time evolution under the Hamiltonian $H_{jk,N}$,

$$L_{jk,N}(t) = \{\cdot, H_{jk,N}(t)\} = L_N + j\delta(t + t_1)L_{A,N} + k\delta(t)L_{B,N}$$

(17)

is the corresponding Liouvillian, $L_N = \{\cdot, H_N\}$, $L_{A,N} = \{\cdot, V_{A,N}\}$, $L_{B,N} = \{\cdot, V_{B,N}\}$, and $\{\cdot, \cdot\}$ denotes the Poisson bracket. Next, we expand\textsuperscript{58,59}

$$U_{jk,N}(t, -\infty) \approx U_{k,N}(t, -\infty) - j \int_{-\infty}^{t} d\tau U_{k,N}(t, \tau) L_{A,N}\delta(\tau + t_1) U_{k,N}(\tau, -\infty)$$

(18)

$$= U_{k,N}(t, -\infty) - j U_{k,N}(t, -t_1) L_{A,N} U_N(-t_1, -\infty)$$

(19)

to the first order in $\varepsilon_1$ to obtain

$$\langle C(t) \rangle_{jk}^{RP} \approx \langle C(t) \rangle_{k}^{RP, (0)} + \langle C(t) \rangle_{jk}^{RP, (1)},$$

(20)

where

$$\langle C(t) \rangle_{k}^{RP, (0)} = \int dq \int dp \ C_N(q) U_{k,N}(t, -\infty) \rho_N(q, p)$$

(21)

and

$$\langle C(t) \rangle_{jk}^{RP, (1)} = - j \int dq \int dp \ C_N(q) U_{k,N}(t, -t_1) L_{A,N} U_N(-t_1, -\infty) \rho_N(q, p).$$

(22)

In Eq. (18) we introduced a short-hand notation

$$U_{k,N}(t_f, t_i) = \mathcal{T} \exp \left\{ - \int_{t_i}^{t_f} d\tau [L_N + k\delta(\tau)L_{B,N}] \right\}$$

(23)

for the evolution operator that involves only the second pulse. In going from Eq. (18) to Eq. (19), we assumed that $t, t_1 > 0$ and used

$$U_{k,N}(t_f, t_i) = \begin{cases} U_N(t_f, t_i), & 0 \notin (t_i, t_f), \\ U_{k,N}(t_f, 0) U_N(0, t_i), & \text{otherwise}, \end{cases}$$

(24)

with

$$U_N(t_f, t_i) = e^{-L_N(t_f - t_i)}.$$
Then, we derive
\[
\langle C(t) \rangle^{\text{RP,(1)}}_{jk} = \frac{j \beta \varepsilon_1}{2} \int dq \int dp \ C_N(q_{k,t}) \dot{A}_N(q_{-t_1}) \rho_N(q, p)
\] (26)
from Eq. (22) by applying \( U_N(-t_1, -\infty) \rho_N(q, p) = \rho_N(q, p) \),

\[
L_{A,N} \rho_N(q, p) = -\frac{\partial V_{A,N}(q)}{\partial q} \cdot \frac{\partial}{\partial p} \rho_N(q, p)
\] (27)

\[
= -\beta_N \frac{\varepsilon_1}{2} \sum_{i=1}^{N} \left[ \frac{\partial A(q_i)}{\partial q_i} \right]^T \dot{q}_i \rho_N(q, p)
\] (28)

\[
= -\beta \frac{\varepsilon_1}{2} \dot{A}_N(q) \rho_N(q, p),
\] (29)
where \( \dot{f} = \partial f / \partial t \) denotes the time derivative, and Eq. (24) in combination with \( C_N(q_{k,t}) = C_N(q) U_{k,N}(t, 0) \) and \( \dot{A}_N(q_{-t_1}) = U_N(0, -t_1) \dot{A}_N(q) \). \( q_{-t_1} \) is the position along a backward equilibrium trajectory. \( q_{k,t_2} \) corresponds to a nonequilibrium trajectory evolved under the Hamiltonian that involves the interaction with the second pulse, which is equivalent to the field-free evolution with the initial conditions \( q_{k,0} = q \) and \( p_{k,0} = p + (k \varepsilon_2/2) N[\partial B_N(q) / \partial q] \).

Combining Eq. (26) with Eqs. (5), (8), and (20) yields the final result

\[
R(t_2, t_1) \approx \frac{\beta}{\varepsilon_2} \int dq \int dp [C_N(q_{+,t_2}) - C_N(q_{-,t_2})] \dot{A}_N(q_{-t_1}) \rho_N(q, p),
\] (30)
assuming \( \varepsilon_2 \) is small enough to guarantee the validity of the perturbative expression (8). It follows that the response function \( R(t_2, t_1) \) can be evaluated as an equilibrium ensemble average of an estimator based on two nonequilibrium trajectories (\( q_{\pm,t_2} \)) and one backward equilibrium trajectory (\( q_{-t_1} \)). In the high-temperature limit \( \beta \to 0 \) or for \( N = 1 \), Eq. (30) reduces to the equilibrium-nonequilibrium classical MD approach. In contrast to the classical approach, the RPMD method captures nuclear quantum effects, in accordance with the well-known advantages and limitations of the RPMD for one-time correlation functions. Furthermore, in the Supplementary Material, we show that the RPMD is exact for the harmonic oscillator when two out of three operators \( \hat{A}, \hat{B}, \) and \( \hat{C} \) are linear functions of position. Finally, the proposed equilibrium-nonequilibrium RPMD method always satisfies \( R(t_2 = 0, t_1) = 0 \) (because \( q_{+,0} = q_{-,0} \)), which holds for the exact quantum response function (7), but is not guaranteed by some other approximate methods (as discussed below).

Before demonstrating these properties numerically, we briefly review the only other RPMD-based method proposed to date for simulating two-dimensional vibrational spectra. In 2018, Jung, Videla, and Batista showed that the response function (7) is related
to the DKT correlation function\textsuperscript{60}

\[ K(t_2, t_1) = \frac{1}{\beta^2} \int_0^\beta d\lambda_1 \int_0^{\lambda_1} d\lambda_2 \text{Tr} \left[ \rho \hat{A}(\lambda_1) \hat{B}(t_1 - i\lambda_2) \hat{C}(t_1 + t_2) \right] \]  

(31)

through the frequency-domain expression

\[ R(\omega_2, \omega_1) = Q_+(\omega_2, \omega_1) K^{\text{sym}}(\omega_2, \omega_1) + Q_-(\omega_2, \omega_1) K^{\text{asym}}(\omega_2, \omega_1), \]  

(32)

where

\[ K^{\text{sym}}(t_2, t_1) = 2\text{Re}[K(t_2, t_1)], \quad K^{\text{asym}}(t_2, t_1) = 2i\text{Im}[K(t_2, t_1)], \]  

(33)

\[ f(\omega_1, \omega_2) = \int_{-\infty}^\infty dt_1 \int_{-\infty}^\infty dt_2 f(t_2, t_1) e^{-i\omega_1 t_1 - i\omega_2 t_2}, \]  

(34)

and \( Q_\pm \) are some known functions of \( \omega_1 \) and \( \omega_2 \).\textsuperscript{60} Although Eq. (32) is exact, an additional approximation is needed before \( K(t_2, t_1) \) can be evaluated using the RPMD. Specifically, the authors employed the symmetrized DKT approximation

\[ R(\omega_2, \omega_1) \approx Q_+(\omega_2, \omega_1) K^{\text{sym}}(\omega_2, \omega_1), \]  

(35)

neglecting the asymmetric contribution to the DKT correlation function, to make use of the RPMD approximation

\[ K^{\text{sym}}(t_2, t_1) \approx \int dq \int dp A_N(q) B_N(q_{t_1}) C_N(q_{t_1+t_2}) \rho_N(q, p). \]  

(36)

Because the symmetrized DKT approximation is not exact in any known limit, the RPMD DKT response function is not zero at \( t_2 = 0 \) and is not exact in the classical limit.\textsuperscript{60}

III. RESULTS AND DISCUSSION

Above considerations about the classical, RPMD, and RPMD DKT methods for simulating two-dimensional vibrational spectra are demonstrated numerically on an anharmonic model system determined by the Hamiltonian

\[ H(q, p) = \frac{1}{2}(p^2 + q^2) + aq^3 + a^2q^4, \]  

(37)

where \( a \) is a tunable parameter that controls the degree of anharmonicity. This system can be solved numerically exactly in a finite basis and was used before with \( a = 0.1 \) for evaluating the accuracy of RPMD and nonequilibrium RPMD methods.\textsuperscript{34,51} Details of exact
FIG. 1. Errors of approximate methods (columns 2–4) for evaluating the two-time response function (shown in the left-most column): New equilibrium-nonequilibrium RPMD method (labeled “RPMD”), RPMD DKT approximation, and the exact quantum symmetrized DKT correlation function (“Symmetrized DKT”). Results are shown at both high ($\beta = 1$, top) and low ($\beta = 8$, bottom) temperatures, with the anharmonicity parameter $a = 0.1$ [Eq. (37)], and operators $\hat{A} = \hat{B} = \hat{q}$, $\hat{C} = \hat{q}^2/2$.

quantum and approximate trajectory-based simulations can be found in the Supplementary Material.

Figure 1 shows that the equilibrium-nonequilibrium RPMD approach performs better than the RPMD DKT method at both low and high temperatures. Notably, the newly proposed RPMD approach exhibits the expected short-time accuracy, while most of the error in the RPMD DKT method can be attributed to the neglect of the asymmetric part of the full DKT correlation function (compare columns 3 and 4 of Fig. 1).

Figure 2 shows the time slices of $R(t_2, t_1)$ along $t_2$ (left panels) and $t_1$ (right panels). At low temperature (Fig. 2, bottom), equilibrium-nonequilibrium RPMD is more accurate than the classical method due to the inclusion of nuclear quantum effects, while the two are similar at high temperature (Fig. 2, top). In this example, the classical simulation is more accurate than the RPMD DKT method, showing that the uncontrolled error of the
FIG. 2. Cuts along $t_1 = 10$ (left) and $t_2 = 10$ (right) of the two-dimensional response function at $\beta = 1$ (top) and $\beta = 8$ (bottom) evaluated with the exact quantum approach, with the RPMD and classical equilibrium-nonequilibrium methods, and with the RPMD DKT approach. System’s parameters and operators were same as in Fig. 1.

Symmetrized DKT approximation can outweigh the benefits of including nuclear quantum effects. In fact, similar findings were implied, even if not explicitly discussed, by the earlier reports on the symmetrized DKT approximation. In addition, both classical and RPMD equilibrium-nonequilibrium methods are exact (zero) at $t_2 = 0$ (see left panels of Fig. 2), which does not hold for the RPMD DKT approach (see also Figs. 6e and 8e of Ref. 60).

To demonstrate numerically that the proposed approach inherits some well-known properties of RPMD, we choose to quantify the error of an approximate response function $R_{\text{approx}}$ as

$$\text{Error} = \frac{\| R_{\text{approx}} - R_{\text{exact}} \|}{\max(\| R_{\text{approx}} \|, \| R_{\text{exact}} \|)},$$

where $\| R \| = \int dt_1 \int dt_2 |R(t_2, t_1)|^2$ and $R_{\text{exact}}$ is the exact response function. Figure 3 shows that the equilibrium-nonequilibrium RPMD consistently outperforms the classical approach for systems of different anharmonicities (a), at different temperatures (b), and for different combinations of operators (c). As discussed earlier, the RPMD method is exact for the harmonic oscillator ($a = 0$, see Fig. 3a) and certain combinations of operators $\hat{A}, \hat{B},$ and $\hat{C}$. Interestingly, the classical approach is also exact in some of those limiting
FIG. 3. Errors based on Eq. (38) of the approximate two-time response functions for systems with different degree of anharmonicity (a), at different temperatures (b), and for different combinations of linear and quadratic operators $\hat{A}$, $\hat{B}$, and $\hat{C}$ (c). Apart from the parameters that are being varied or explicitly indicated in each plot, the default parameters are $a = 0.1$ [Eq. (37)], $\beta = 8$, $\hat{A} = \hat{B} = \hat{q}$, $\hat{C} = \hat{q}^2/2$. In panel (c), “1” denotes linear operator $\hat{q}$, “2” denotes quadratic operator $\hat{q}^2/2$. For example, “122” means $\hat{A} = \hat{q}$ and $\hat{B} = \hat{C} = \hat{q}^2/2$. Operator combinations are ordered according to the error of the RPMD simulation at $\beta = 8$.

cases (see Supplementary Material). Nevertheless, as soon as the system is even weakly anharmonic, RPMD is clearly superior to the classical approach. As expected, both RPMD and classical methods perform worse as the anharmonicity increases. Furthermore, the equilibrium-nonequilibrium RPMD method converges to the exact (classical) result in the high-temperature limit ($\beta \to 0$, Fig.3b). Again, as the temperature decreases, the RPMD
approach becomes less accurate. Finally, the proposed RPMD approach is more accurate for linear compared to nonlinear operators (Fig. 3c).

IV. CONCLUSION

To conclude, we introduced an RPMD-based method that captures nuclear quantum effects on three-pulse two-dimensional vibrational spectra at the cost of classical MD simulations. The proposed approach was shown to perform better than the classical and recently developed RPMD DKT methods. Although our discussion focused only on RPMD, the overall scheme could be extended to the more general Matsubara dynamics and to its efficient approximations, including thermostated RPMD, CMD, and quasi-CMD. It would be interesting to see how these approximations perform when applied to multidimensional spectroscopy, because it is expected to provide a more stringent test for dynamical approximations compared to linear spectroscopy, for which similar studies exist. Because two-dimensional Raman and hybrid THz–Raman spectra vanish for harmonic potentials with linear dipole moment or polarizability operators, adequate computational approaches must capture the effect of electrical and mechanical anharmonicities, which poses a challenge for RPMD and the above-mentioned methods.

To derive the equilibrium-nonequilibrium RPMD, we did not invoke the concept of the Kubo transformation, which is done traditionally for one-time correlation functions, but instead combined nonequilibrium RPMD with classical response theory. This new way of deriving real-time path-integral methods will be of special interest for simulating time-resolved spectroscopic experiments, but also in other contexts where multi-time correlation or response functions appear, or if a derivation of the appropriate Kubo transformed correlation function is not obvious. The theory is general and enables new applications of established quantum dynamical methods.

SUPPLEMENTARY MATERIAL

See the supplementary material for the computational details and for the analytical expressions in the harmonic limit.
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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supplementary material for: Equilibrium-nonequilibrium ring-polymer molecular
dynamics for nonlinear spectroscopy

Tomislav Begušić,a) Xuecheng Tao, and Thomas F. Miller III

Division of Chemistry and Chemical Engineering, California Institute of Technology,
Pasadena, California 91125, USA

(Dated: 3 February 2022)

a)Electronic mail: tbegusic@caltech.edu
I. COMPUTATIONAL DETAILS

Response function $R(t_2,t_1)$ was computed for 120 steps along both time coordinates with a time step of 0.25. Exact result was obtained by solving the time-independent Schrödinger equation on a position grid (see Fig. 1) ranging from -10 to 10 with a step of 0.01 and transforming the operators $\hat{A}$, $\hat{B}$, and $\hat{C}$ to the eigenstate basis. Depending on the temperature, between 10 and 60 states were used in the evaluation of the response function. Same approach was used for computing the exact DKT correlation function. Since the relation between the DKT correlation function $K(t_2,t_1)$ and $R(t_2,t_1)$ assumes a Fourier transform involving both positive and negative $t_1$ and $t_2$, DKT correlation functions were computed for positive and negative times, i.e., from -30 to 30. In addition, the Fourier transform assumes infinite integral boundaries, which can be replaced by final times only if the integrand is zero beyond some time. This is usually the case because correlation functions are typically damped by the environment. In our simple system, no damping is applied to the correlation functions, which is why the relation between the computed $K(t_2,t_1)$ and $R(t_2,t_1)$ holds only approximately. To avoid artefacts due to boundary effects, the Fourier transform of the DKT correlation function, $K(\omega_2,\omega_1)$ was multiplied by $\exp[-0.02(\omega_1^2 + \omega_2^2)]$. For the same reason, only $t_1,t_2 < 27.5$ are used to offer a fair comparison between DKT-based and other methods. Figure 2 shows that the numerical error introduced in this way is negligible.

![Graph of potentials](image)

FIG. 1. Potentials $V(q) = 0.5q^2 + aq^3 + a^2q^4$ of varying degree of anharmonicity, controlled by the parameter $a$, plotted on the position grid used in quantum calculations.

To obtain classical and RPMD results, $K = 2^{17} \approx 10^5$ initial conditions $(q^{(k)}, p^{(k)})$ were
FIG. 2. Same as Fig. 2 of the main text, but comparing two exact quantum simulations of the response function, using either the direct evaluation or the DKT correlation function, and two approximate calculations based on the symmetrized DKT correlation function and its RPMD approximation.

sampled from a thermal trajectory computed using the Andersen thermostat\(^1\). Then, four trajectories were run for each initial condition: two nonequilibrium trajectories starting from \((q^{(k)}, p^{(k)} \pm (\varepsilon_2/2) N[\partial B_N(q^{(k)})/\partial q^{(k)}])\) with \(\varepsilon = 0.01\), a forward trajectory starting from \((q^{(k)}, p^{(k)})\), and a backward trajectory that is computed by propagating \((q^{(k)}, -p^{(k)})\) forward in time. Trajectories were propagated using a second-order symplectic algorithm\(^2\) with a time step of 0.05 for 600 steps, while the observables were evaluated every 5 steps of the dynamics. Classical results were obtained by setting the number of beads \(N = 1\), while \(N = 64\) was used for the converged RPMD results. The nonequilibrium and backward trajectories were used for evaluating the equilibrium-nonequilibrium response function according to

\[
R(t_2, t_1) = -\frac{\partial}{\partial t_1} \left\{ \frac{\beta}{K \varepsilon_2} \sum_{k=1}^{K} [C_N(q^{(k)}_{+,t_2}) - C_N(q^{(k)}_{-,t_2})] A_N(q^{(k)}_{-,t_1}) \right\},
\]  

(1)

where the time derivative was computed numerically. The forward and backward equilibrium trajectories were used for evaluating the RPMD DKT response function for positive and negative \(t_1\) and \(t_2\) times.
II. HARMONIC LIMIT

In this Section, we show that the RPMD method proposed in the main text is exact in the limit \( N \to \infty \) for the harmonic oscillator,

\[
V(q) = \frac{1}{2}m\omega^2q^2, \tag{2}
\]

and when two of the operators \( \hat{A}, \hat{B}, \) and \( \hat{C} \) are linear in position.

A. Quantum response functions

To derive the exact quantum results, we first rewrite

\[
R(t_2,t_1) = -\frac{1}{\hbar^2} \text{Tr} \left\{ \hat{C}(t_2 + t_1)[\hat{B}(t_1), [\hat{A}, \hat{\rho}]] \right\} \tag{3}
\]

\[
= -\frac{1}{\hbar^2} \text{Tr} \left\{ [[\hat{C}(t_2 + t_1), \hat{B}(t_1)], \hat{A}][\hat{\rho}] \right\} \tag{4}
\]

\[
= -\frac{1}{\hbar^2} \left\langle [[\hat{C}(t_2 + t_1), \hat{B}(t_1)], \hat{A}] \right\rangle \tag{5}
\]

and note that

\[
[\hat{q}(t), f(\hat{q})] = \frac{1}{m\omega}[\hat{p}, f(\hat{q})] = -\frac{i\hbar}{m\omega} f'(\hat{q}) \sin \omega t, \tag{6}
\]

where \( f'(q) = \frac{\partial f}{\partial q} \).

Then, for \( \hat{A} = \hat{B} = \hat{q} \) and \( \hat{C} = C(\hat{q}) \), we have

\[
R(t_2,t_1) = -\frac{1}{\hbar^2} \left\langle [[C(\hat{q}), \hat{q}(-t_2)], \hat{q}(-t_1 - t_2)] \right\rangle \tag{7}
\]

\[
= -\frac{1}{\hbar^2} \left( -\frac{i\hbar}{m\omega} \right) \sin \omega t_2 \left\langle [C'(\hat{q}), \hat{q}(-t_1 - t_2)] \right\rangle \tag{8}
\]

\[
= \frac{i}{m\hbar \omega} \sin \omega t_2 \left( -\frac{i\hbar}{m\omega} \right) \sin \omega(t_1 + t_2) \left\langle C''(\hat{q}) \right\rangle \tag{9}
\]

\[
= \frac{\langle C''(\hat{q}) \rangle}{(m\omega)^2} \sin \omega t_1 \sin \omega t_2. \tag{10}
\]

where we applied Eq. (6) twice. For \( \hat{A} = \hat{C} = \hat{q} \) and \( \hat{B} = B(\hat{q}) \):

\[
R(t_2,t_1) = -\frac{1}{\hbar^2} \left\langle [[\hat{q}(t_2), B(\hat{q})], \hat{q}(-t_1)] \right\rangle \tag{11}
\]

\[
= -\frac{1}{\hbar^2} \left( -\frac{i\hbar}{m\omega} \right) \sin \omega t_2 \left\langle [B'(\hat{q}), \hat{q}(-t_1)] \right\rangle \tag{12}
\]

\[
= \frac{\langle B''(\hat{q}) \rangle}{(m\omega)^2} \sin \omega t_1 \sin \omega t_2. \tag{13}
\]
For \( \hat{B} = \hat{C} = \hat{q} \) and \( \hat{A} = A(\hat{q}) \):

\[
R(t_2, t_1) = -\frac{1}{\hbar^2} \left\langle \left[ [\hat{q}(t_2), \hat{q}], \hat{A}(-t_1) \right] \right\rangle 
= -\frac{1}{\hbar^2} \left\langle \left( -\frac{i \hbar}{m \omega} \sin \omega t_2, \hat{A}(-t_1) \right) \right\rangle 
= 0,
\]

because scalars commute with operators.

**B. RPMD response functions**

Assuming \( \epsilon_2 \) is small, we can derive the fully equilibrium RPMD from the equilibrium-nonequilibrium RPMD:

\[
R(t_2, t_1) = \frac{\beta}{\epsilon_2} \langle [C_N(q_{+t_2}) - C_N(q_{-t_2})] \dot{A}_N(q_{-t_1}) \rangle,
\]

\[
= N \beta \left\langle \left[ \frac{\partial C_N(q_{t_2})}{\partial q_{t_2}} \right]^T M_{q_p,t_2} \cdot \frac{\partial B_N(q)}{\partial q} \dot{A}_N(q_{-t_1}) \right\rangle,
\]

where we used

\[
C_N(q_{\pm t_2}) \approx C_N(q_{t_2}) \pm \frac{\epsilon_2}{2} \left[ \frac{\partial C_N(q_{t_2})}{\partial p} \right]^T N \frac{\partial B_N(q)}{\partial q}
\]

\[
\approx C_N(q_{t_2}) \pm \frac{\epsilon_2}{2} N \left[ \frac{\partial C_N(q_{t_2})}{\partial q_{t_2}} \right]^T \frac{\partial q_{t_2}}{\partial p} \cdot \frac{\partial B_N(q)}{\partial q}
\]

and defined \( M_{xy,t} = \partial x_t / \partial y \). Equation (18) provides yet another way for employing RPMD in the simulation of two-time response function \( R(t_2, t_1) \). Similar to the hybrid equilibrium-nonequilibrium approach, the equilibrium method also reduces to its classical MD analogue.\(^3\)\(^-\)\(^5\) However, this method is less practical due to the need for computing and converging the stability matrix element \( M_{q_p,t_2} \), which has been deemed difficult even in the classical MD setting. Finally, we note that the equilibrium-nonequilibrium and the fully equilibrium methods give equal results when \( \epsilon_2 \) is small.

Before continuing with specific cases, we rewrite Eq. (18)

\[
R(t_2, t_1) = N \beta \left\langle \left[ \frac{\partial C_N(q_{t_2})}{\partial q_{t_2}} \right]^T M_{\tilde{q}_p,t_2} \dot{\tilde{B}}_N(\tilde{q}) \dot{\tilde{A}}_N(\tilde{q}_{-t_1}) \right\rangle,
\]

in terms of the ring-polymer normal mode coordinates \( \tilde{q} = O \cdot q \), where \( O \) is an orthogonal \( N \times N \) matrix that diagonalizes the ring-polymer force-constant and \( \tilde{f}(\tilde{q}) = f(q) \). Specifically,
the first normal mode $\tilde{q}_1 = \sqrt{N} q_c$ is a scalar multiple of the ring-polymer centroid $q_c = \frac{1}{N} \sum_{i=1}^{N} q_i$ and evolves according to

$$\tilde{q}_{1,t} = \tilde{q}_1 \cos \omega t + \frac{1}{m\omega} \tilde{p}_1 \sin \omega t.$$  \hspace{1cm} (22)

Then, for $A(q) = B(q) = q$ and arbitrary $C(q)$, we have:

$$R(t_2, t_1) = N\beta \left\langle \frac{\partial \tilde{C}_N(\tilde{q}_{t_2})}{\partial \tilde{q}_{1, t_2}} M_{\tilde{q}_{1, t_2}} \frac{1}{\sqrt{N}} \hat{A}_N(\tilde{q}_{t_1}) \right\rangle$$

$$= \frac{\sqrt{N} \beta}{m\omega} \sin \omega t_2 \left\langle \frac{\partial \tilde{C}_N(\tilde{q}_{t_2})}{\partial \tilde{q}_{1, t_2}} \hat{A}_N(\tilde{q}_{t_1}) \right\rangle$$

$$= \frac{\sqrt{N} \beta}{m\omega} \sin \omega t_2 \left\langle \frac{\partial \tilde{C}_N(q)}{\partial \tilde{q}_1} \hat{A}_N(\tilde{q}_{t_1}) \right\rangle$$

$$= \frac{\beta}{m} \sin \omega t_2 \sin \omega (t_1 + t_2) \left\langle \frac{\partial \tilde{C}_N(q)}{\partial \tilde{q}_1} \tilde{q}_1 \right\rangle$$

$$= \frac{N}{(m\omega)^2} \left\langle \frac{\partial^2 \tilde{C}_N(q)}{\partial \tilde{q}_1^2} \right\rangle \sin \omega t_2 \sin \omega (t_1 + t_2)$$

$$= \frac{1}{(m\omega)^2} \left\langle \frac{1}{N} \sum_{i=1}^{N} \frac{\partial^2 C(q_i)}{\partial q_i^2} \right\rangle \sin \omega t_2 \sin \omega (t_1 + t_2),$$

$$= \left\langle \frac{C''_{\text{RP}}}{(m\omega)^2} \right\rangle \sin \omega t_2 \sin \omega (t_1 + t_2),$$

where we used $\hat{A}_N(\tilde{q}) = \hat{B}_N(\tilde{q}) = q_c$, $\partial q_c/\partial \tilde{q}_1 = 1/\sqrt{N}$, and $\partial q_{i,t}/\partial \tilde{q}_1 = \delta_{i1} \sin \omega t/(m\omega)$ in Eqs. (23) and (24), $\hat{A}_N(\tilde{q}_t) = -(\omega/\sqrt{N}) \tilde{q}_1 \sin \omega t + (1/m\sqrt{N}) \tilde{p}_1 \cos \omega t$ to derive Eq. (26), in which we immediately dropped the second term that vanishes because $\langle p_1 \rangle = 0$, and $\tilde{q}_1 \exp(-\beta_N H_N) = -(N/\beta m\omega^2)(\partial/\partial \tilde{q}_1) \exp(-\beta_N H_N)$ together with the integration by parts to obtain Eq. (27). Finally, Eq. (28) follows from Eq. (27) because

$$\frac{\partial^2 \tilde{C}_N(q)}{\partial \tilde{q}_1^2} = \left( \frac{\partial q}{\partial \tilde{q}_1} \right)^T \cdot \frac{\partial^2 C_N(q)}{\partial q^2} \cdot \frac{\partial q}{\partial \tilde{q}_1} = \frac{1}{N} e^T \cdot \frac{\partial^2 C_N(q)}{\partial q^2} \cdot e = \frac{1}{N^2} \sum_{i=1}^{N} \frac{\partial^2 C(q_i)}{\partial q_i},$$

where we used $\partial q/\partial \tilde{q}_1 = e/\sqrt{N}$ and defined the $N$-dimensional vector $e = (1 \ldots 1)^T$. In the limit of $N \to \infty$, Eq. (28) converges to the quantum result (10). Similarly, for $A(q) =
\( C(q) = q \) and arbitrary \( B(q) \):

\[
R(t_2, t_1) = N \beta \left\langle \frac{1}{\sqrt{N}} \frac{1}{m \omega} \sin \omega t_2 \frac{\partial \tilde{B}_N(\tilde{q})}{\partial \tilde{q}_1} \frac{\omega}{\sqrt{N}} \tilde{q}_1 \sin \omega t_1 \right\rangle \tag{31}
\]

\[
= \frac{\beta}{m} \left\langle \frac{\partial \tilde{B}_N(\tilde{q})}{\partial \tilde{q}_1} \tilde{q}_1 \right\rangle \sin \omega t_1 \sin \omega t_2 \tag{32}
\]

\[
= \frac{\langle B'' \rangle_{\text{RP}}}{(m \omega)^2} \sin \omega t_1 \sin \omega t_2, \tag{33}
\]

which reduces to the corresponding quantum expression (13) when converged with respect to the number of beads \( N \). Finally, for \( B(q) = C(q) = q \),

\[
R(t_2, t_1) = N \beta \left\langle \frac{1}{\sqrt{N}} \frac{1}{m \omega} \sin \omega t_2 \frac{1}{\sqrt{N}} \dot{\tilde{A}}_N(\tilde{q}_{-t_1}) \right\rangle \tag{34}
\]

\[
= \frac{1}{m \omega} \sin \omega t_2 \left\langle \dot{\tilde{A}}_N(\tilde{q}_{-t_1}) \right\rangle = 0, \tag{35}
\]

because equilibrium expectation values are time-independent.

Interestingly, in certain cases, even the classical method (\( N = 1 \)) is exact. This is trivially true for the last studied case \([B(q) = C(q) = q]\), but also for certain non-trivial cases, e.g., for \( C(q) \propto q^2 \) in the first studied example \([A(q) = B(q) = q]\) and \( B(q) \propto q^2 \) in the second studied case \([A(q) = C(q) = q]\) because the corresponding final expressions are independent of temperature. This can be seen in Fig. 3a of the main text for the anharmonicity parameter \( a = 0, A(q) = B(q) = q, \) and \( C(q) = q^2/2, \) where both classical and RPMD results are exact.

REFERENCES