Inclusion of nuclear quantum effects for simulations of nonlinear spectroscopy

Kenneth A. Jung, Pablo E. Videla,a) and Victor S. Batista
Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107, USA

(Received 18 April 2018; accepted 7 June 2018; published online 26 June 2018)

The computation and interpretation of nonlinear vibrational spectroscopy is of vital importance for understanding a wide range of dynamical processes in molecular systems. Here, we introduce an approach to evaluate multi-time response functions in terms of multi-time double symmetrized Kubo transformed thermal correlation functions. Furthermore, we introduce a multi-time extension of ring polymer molecular dynamics to evaluate these Kubo transforms. Benchmark calculations show that the approximations are useful for short times even for nonlinear operators, providing a consistent improvement over classical simulations of multi-time correlation functions. The introduced methodology thus provides a practical way of including nuclear quantum effects in multi-time response functions of non-linear optical spectroscopy. Published by AIP Publishing. https://doi.org/10.1063/1.5036768

I. INTRODUCTION

Recent developments in nonlinear spectroscopy are of vital importance for understanding and interpreting intricate dynamic processes in liquids, including mode-coupling and mechanisms of energy transfer commonly masked by spectral broadening.1,2 The advantage of nonlinear optical spectroscopies is to decongest the spectrum by dispersing different components along multiple spectroscopic axes. However, the complexity of the systems often precludes a straightforward interpretation of the spectral features. Computations thus provide a valuable approach for the correct assignment of the spectroscopic signals.

Under the perturbative formalism, the different forms of non-linear spectroscopy are cast in terms of response functions which are multi-time correlation functions (multi-TCF’s) of operators evaluated at different times.3 Although recent work on tensor decomposition schemes4–6 has been encouraging for the exact quantum mechanical evaluation of small coupled systems, the full quantum mechanical calculations of TCF’s are still intractable for large systems comprising many degrees of freedom.7 Therefore, there is great interest in the development and implementation of approximate methods based on classical molecular dynamics.

Significant advances have been made to formulate classical theories of nonlinear spectroscopy using the quantum-classical correspondence between commutators and Poisson brackets.8–11 However, these methods often rely upon computing a stability matrix that can be numerically challenging to obtain for complex systems since they involve a measure of the sensitivity of dynamical variables to the initial conditions. As an alternative, Keyes et al. developed an approach based on a classical multi-TCF,12–14 making use of the connection between the real and imaginary parts of the TCF for a harmonic system in the classical limit. These methodologies have been successfully applied to the description of different types of non-linear spectroscopies,8–15 but they address only the classical limit.

It is well established that nuclear quantum effects (NQE) due to zero-point energy fluctuations and tunneling can play crucial roles, even at room temperature, and modulate a wide variety of thermodynamic and dynamical properties of polyatomic systems.16–20 Therefore, incorporation of NQE along with dynamics based on accurate potential energy surfaces is essential for proper descriptions of the infrared, Raman, and sum frequency generation spectra.21–24

Semiclassical methodologies such as the Herman-Klucy (HK) semiclassical initial value representation (SC-IVR)25 have been applied to computations of nonlinear spectroscopy based on linear response theory.22 Furthermore, the linearized SC-IVR (LSC-IVR) approach,23 obtained as the linearized approximation of the SC-IVR 22 has been used for simulations of infrared spectroscopy,23,24 although the method neglects interference effects and does not in general preserve quantum statistics. Methods based on the path-integral formalism that preserve the quantum Boltzmann distribution, such as Centroid Molecular Dynamics (CMD),25,26 Ring Polymer Molecular Dynamics (RPMD),27,28 or the planetary model,29 provide a balance between accuracy and computational overhead.30 Very recently, it has been shown that these methods are approximations of the general Boltzmann conserving Matsubara dynamics.31 Another promising methodology is the path integral Liouville dynamics of Liu45 that gave good results for the linear IR spectra of several gas phase systems.46 An outstanding challenge is to extend these methodologies for computation of non-linear response functions.

In this paper, we address multi-time response functions evaluated in terms of multi-time Kubo transforms.2 We focus on second-order responses that can be expressed as differences of two-time correlation functions of the form \( \langle A(0)B(t)C(t') \rangle \)

a)Electronic mail: pablo.videla@yale.edu
b)Electronic mail: victor.batista@yale.edu
(see Sec. II B), which are relevant to vibrational spectroscopy such as 2D-Raman and 2D-THz-Raman spectroscopy. By expressing the response functions in the frequency domain, it is possible to rewrite them in terms of the real (symmetric) and imaginary (asymmetric) parts of the corresponding double Kubo transformed (DKT) correlation functions. The main contribution to the response can be expressed only in terms of the symmetric DKT, invoking a harmonic reference potential with operators expanded to second order in the harmonic variable. An advantage of this approach is that the symmetric DKT exhibits the same symmetries as those of classical two-time correlation functions and, hence, is amenable to semiclassical approximations that preserve the Boltzmann distribution. Here, we show that the evaluation of the symmetrized DKT by a multi-time extension of Ring Polymer Molecular Dynamics (RPMD) provides a consistent improvement over classical simulations of multi-time correlation functions at short times even for nonlinear operators. The resulting extension of RPMD for evaluation of these multi-time correlation functions provides an approximate way of including NQE in calculations of the second-order response function. Hence, we anticipate it might be valuable for simulations of non-linear spectroscopy of condensed phase systems.

The paper is organized as follows: Sec. II A introduces the DKT along with its symmetries. Section II B presents the relation of the DKT to the second-order response in the frequency domain. The extension of the RPMD methodology for the evaluation of the two-time symmetrized DKT is presented in Sec. II C. The accuracy of the proposed approximations is numerically tested on model potentials in Sec. III. In Sec. IV, we summarize the most important conclusions, potential applications, and future work.

II. MULTI-TIME CORRELATION FUNCTIONS

A. The double Kubo transform

The DKT of three Hermitian position-dependent operators $\hat{A}$, $\hat{B}$, and $\hat{C}$ is defined as

$$\langle A; B(t); C(t') \rangle = \frac{1}{Z} \int_0^\beta d\lambda \int_0^\lambda d\lambda' \text{Tr}[e^{-i\lambda H} \hat{A} e^{-i\lambda' H} \hat{B}(t) e^{-i\lambda' H} \hat{C}(t')]$$

(1)

where $\hat{O}(t) = e^{i\lambda t/H} \hat{O} e^{-i\lambda t/H}$ represents a Heisenberg-evolved operator, $Z$ is the partition function,

$$Z = \text{Tr}[e^{-\beta H}]$$

(2)

and $\beta = 1/kT$ is the inverse temperature.

The standard TCF of three operators,

$$\langle AB(t)C(t') \rangle = \frac{1}{Z} \text{Tr}[e^{-\beta H} \hat{A} \hat{B}(t) \hat{C}(t')]$$

(3)

can be obtained from the DKT, according to the following relation in the frequency domain:

$$\langle A; B(\omega); C(\omega') \rangle = F_1(\omega, \omega') \langle AB(\omega)C(\omega') \rangle$$

(4)

where

$$\langle A; B(\omega); C(\omega') \rangle = \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} dt' e^{-i\omega t} e^{-i\omega' t'} \langle A; B(t); C(t') \rangle$$

(5)

is the double Fourier transform of the DKT (with a similar definition for the standard TCF $\langle AB(\omega)C(\omega') \rangle$ and

$$F_1(\omega, \omega') = \frac{1}{\beta^2 \hbar^2} \left( e^{-\beta \omega} - e^{-\beta \omega'} \frac{1}{\omega' - \omega} \right)$$

(6)

with $\omega = \omega + \omega'$ (see the supplementary material).

Equation (4) shows that the standard and Kubo correlation functions are indeed quantum mechanically equivalent. However, the DKT has considerably more symmetry than the standard TCF. In particular, by exploiting the symmetry of the integration limits in Eq. (1) and cyclic properties of the trace, it can be shown that (see the supplementary material)

$$\langle A; B(t); C(t') \rangle = \langle B(t); C(t'); A \rangle$$

(7)

$$\langle A; B(t); C(t') \rangle^* = \langle B(t); A; C(t') \rangle$$

(8)

and

$$\langle A; B(t); C(t') \rangle^* = \langle A; B(-t); C(-t') \rangle$$

(9)

We note that only the symmetry property described by Eq. (9) holds for the standard correlation function.

The DKT is a complex function with real and imaginary parts related to symmetrized and asymmetric linear combinations as follows:

$$K_{ABC}^{\text{sym}}(t, t') \equiv \langle A; B(t); C(t') \rangle^{\text{sym}}$$

$$\equiv \langle A; B(t); C(t') \rangle + \langle B(t); A; C(t') \rangle$$

$$\equiv \frac{1}{Z \beta^2} \int_0^\beta d\lambda \int_0^\lambda d\lambda' \text{Tr}[e^{-i\lambda H} \hat{A} e^{-i\lambda H} \hat{B}(t) e^{-i\lambda H} \hat{C}(t')]$$

$$= 2 \Re\{\langle A; B(t); C(t') \rangle\}$$

(10)

and

$$K_{ABC}^{\text{asy}}(t, t') \equiv \langle A; B(t); C(t') \rangle^{\text{asy}}$$

$$\equiv \langle A; B(t); C(t') \rangle - \langle B(t); A; C(t') \rangle$$

$$\equiv \frac{1}{Z \beta^2} \int_0^\beta d\lambda \int_0^\lambda d\lambda' \text{Tr}[e^{-i\lambda H} \hat{A} e^{-i\lambda H} \hat{B}(t) e^{-i\lambda H} \hat{C}(t')]$$

$$= 2 \Im\{\langle A; B(t); C(t') \rangle\}$$

(11)

Interestingly, the symmetrized DKT defined by Eq. (10) shares the formal properties and symmetries with classical two-time correlation functions.

We focus on the symmetrized DKT that is a real even function of time and satisfies the following time domain version of detailed balance (see the supplementary material for the proof):

$$\langle A(0); B(t); C(t') \rangle^{\text{sym}} = \langle B(0); A(-t); C(t' - t) \rangle^{\text{sym}}$$

(12)
When any of the operators $\hat{A}$, $\hat{B}$, or $\hat{C}$ is the unity operator, $\hat{1}$, the symmetrized DKT reduces to the single Kubo transform of linear response theory (see the supplementary material for the proof),\textsuperscript{51}

$$\langle \hat{A}; B(t); \hat{1} \rangle_{\text{sym}} = \frac{1}{Z\beta} \int_0^\beta d\lambda Tr[e^{-\beta-\lambda\hat{H}} \hat{A}e^{-\lambda\hat{H}} \hat{B}(t)].$$ \hspace{1cm} (13)

The symmetrized DKT [Eq. (10)] has been discussed in the context of CMD, as a way of computing one-time correlations functions of non-linear operators,\textsuperscript{50} and has been related to a path-integral expression of the vibrational energy relaxation for single-mode excitations.\textsuperscript{52} In Sec. II B, we will show that it is also related to the second-response function of nonlinear spectroscopy.

### B. Double Kubo transform and second-order response

We focus on the second-order response function,

$$R(t, t') = -\frac{1}{\hbar^2} Tr\left\{ \hat{C}(t') \left[ \hat{B}(t), \hat{A} e^{-\beta \hat{H}} \right] \right\},$$ \hspace{1cm} (14)

which is related to several forms of nonlinear vibrational spectroscopy.\textsuperscript{47-49} For example, when $\hat{A} = \hat{B} = \hat{C} = \hat{1}$, with $\hat{1}$ being a component of the polarizability tensor, the response $R(t, t')$ is relevant to two-dimensional Raman spectroscopy.\textsuperscript{12,15,47-53} If, on the other hand, $\hat{A} = \hat{1}$ and $\hat{B} = \hat{C} = \hat{\mu}$ ($\hat{\mu}$ being a component of the dipole operator), then Eq. (14) reduces to a particular scheme of two-dimensional terahertz-Raman spectroscopy.\textsuperscript{47-49,60}

Expanding the commutators of Eq. (14), we find that $R(t, t')$ involves a linear combination of four two-time standard correlation functions. Thus, it can be written in the frequency domain as follows:

$$\tilde{R}(\omega, \omega') = -\frac{1}{\hbar^2} \left\{ \langle AB(\omega)C(\omega') \rangle + \langle C(\omega')B(\omega)A \rangle - \langle AC(\omega')B(\omega) \rangle - \langle B(\omega)C(\omega')A \rangle \right\}.$$ \hspace{1cm} (15)

Using the Fourier relations between the different standard TCF’s (see the supplementary material),\textsuperscript{12} the previous result can be re-expressed as follows:

$$\tilde{R}(\omega, \omega') = -\frac{1}{\hbar^2} (1 - e^{-\beta \omega}) \left\{ \langle AB(\omega)C(\omega') \rangle + e^{-\beta \omega} \langle B(\omega)AC(\omega') \rangle \right\},$$ \hspace{1cm} (16)

where $\omega' = \omega + \omega'$. Now, using Eq. (4), we can substitute the standard TCF’s by their corresponding DKT’s to obtain

$$\tilde{R}(\omega, \omega') = Q_1(\omega, \omega') \langle A; B(\omega); C(\omega') \rangle + Q_2(\omega, \omega') \langle B(\omega); A; C(\omega') \rangle,$$ \hspace{1cm} (17)

where

$$Q_1(\omega, \omega') = -\frac{1}{\hbar^2} \left( 1 - e^{-\beta \omega} \right) \frac{1}{F_1(\omega, \omega')} = -\beta^2 \frac{1}{e^{-\beta \omega} e^{-\beta \omega'} - 1} (1 - e^{-\beta \omega} e^{-\beta \omega'}).$$ \hspace{1cm} (18)

and

$$Q_2(\omega, \omega') = \frac{1}{\hbar^2} \left( 1 - e^{-\beta \omega} \right) \frac{e^{-\beta \omega}}{F_2(\omega, \omega')} = \beta^2 \frac{1}{e^{-\beta \omega} e^{-\beta \omega'} + 1} (1 - e^{-\beta \omega} e^{-\beta \omega'}).$$ \hspace{1cm} (19)

It is straightforward to show that Eqs. (18) and (19) are related through $Q_1(\omega, \omega') = Q_2(-\omega, -\omega')$. Using Eqs. (8) and (9), Eq. (17) gives

$$\tilde{R}(\omega, \omega') = Q_1(\omega, \omega') \langle A; B(\omega); C(\omega') \rangle + Q_1(-\omega, -\omega') \langle A; B(-\omega); C(-\omega') \rangle.$$ \hspace{1cm} (20)

By further decomposing the double Kubo transform and the $Q$ factors into their even and odd contributions, Eq. (20) can be recast as

$$\tilde{R}(\omega, \omega') = Q_+(\omega, \omega') \tilde{R}_{ABC}(\omega, \omega') + Q_-(\omega, \omega') \tilde{R}_{ABC}(\omega, \omega'),$$ \hspace{1cm} (21)

where

$$Q_+(\omega, \omega') = \frac{1}{2} \left[ Q_1(\omega, \omega') + Q_1(-\omega, -\omega') \right]$$ \hspace{1cm} (22)

and

$$Q_-(\omega, \omega') = \frac{1}{2} \left[ Q_1(\omega, \omega') - Q_1(-\omega, -\omega') \right].$$ \hspace{1cm} (23)

Equation (21) and equivalently Eq. (20) express the second-order response function $\tilde{R}(\omega, \omega')$ in terms of DKT’s and are equivalent to Eq. (15) since no approximations have yet been introduced. Equation (21) is thus a quantum mechanically exact equation (within second-order perturbation theory) and one of the main results of this paper. It provides a novel approach for the evaluation of the nonlinear response as well as a starting point to explore semiclassical approximations. The full quantum-mechanical evaluation of the double Kubo transform is no easier than the evaluation of the standard TCF. Hence, for practical applications of Eq. (21) to real condensed-phase systems, approximations need to be made.

Interestingly, the classical limits ($\hbar \rightarrow 0$) of the prefactors in Eq. (21), $Q_+ \rightarrow \beta^2 \omega^2$ and $Q_- \rightarrow -2\beta \omega / \hbar$, imply that the symmetric and asymmetric DKT’s must have a leading order of $\hbar^0$ and $\hbar^1$.\textsuperscript{12} This result, along with the symmetry properties found in Sec. II A, suggests that the symmetrized DKT could be well approximated by using a semiclassical methodology, whereas no simple (semi)classical-like analog might exist for the asymmetric part. In fact, Sec. II C shows that the symmetrized DKT can be evaluated by RPMD. Therefore, if one can find an approximate relation between the symmetrized and asymmetric DKT, Eq. (21) could be applied for atomistic simulations of nonlinear vibrational spectroscopy.

Recalling the definitions of the symmetric and asymmetric DKT’s [Eqs. (10) and (11)], the problem at hand is equivalent to finding a relation between the real and imaginary parts of a two-time correlation function. For the single Kubo transform, introduced by Eq. (13), a simple relation exists between the real and imaginary parts since the single Kubo
transformed TCF is real. For multi-time correlation functions, however, no exact relationship is known.\textsuperscript{12,61} Nevertheless, an approximate connection can be established by expanding the operators to second order for a harmonic reference potential, which is the simplest non-trivial system that produces a second-order response, as shown in Ref. 12 (see the supplementary material). Briefly, the operators $\hat{A}$, $\hat{B}$, and $\hat{C}$ are expanded to second order in the harmonic coordinate and all the resulting terms of $K_{ABC}^{\text{sym}}(\omega, \omega')$ and $K_{ABC}^{\text{pure}}(\omega, \omega')$ are compared.

For a harmonic potential, it can be shown that the first-order contributions yield six terms. For $K_{ABC}^{\text{sym}}(\omega, \omega')$, all six of these terms contribute, while for $K_{ABC}^{\text{pure}}(\omega, \omega')$, three out of six terms are zero. When considering the full asymmetric term $Q_+(\omega, \omega')K_{ABC}^{\text{sym}}(\omega, \omega')$, an additional term vanishes giving only two non-zero contributions to the response function. Therefore, for harmonic or nearly harmonic potentials, $Q_+(\omega, \omega')K_{ABC}^{\text{sym}}(\omega, \omega')$ gives the dominate contribution to the second-order response. Hence, as a simple and practical approximation, it is possible to express the Fourier transform of the second-order response as

$$\tilde{R}(\omega, \omega') \approx Q_+(\omega, \omega')\tilde{K}_{ABC}^{\text{sym}}(\omega, \omega').$$

The approximation introduced by Eq. (24) expresses the response function solely in terms of the symmetrized DKT, providing the second important result of this paper. Note that in this expression, $K_{ABC}^{\text{sym}}(\omega, \omega')$ is still a full quantum mechanical object but for practical applications semi-classical approximations need to be made.

**C. RPMD approximation of the symmetrized double Kubo transform**

RPMD\textsuperscript{37,62} is a real time extension of the path integral formulation of the partition function to evaluate thermal correlation functions by classically evolving the ring polymer construction of the Boltzmann operator.\textsuperscript{63} Formally, RPMD approximates the Kubo transformed thermal correlation function\textsuperscript{51} [Eq. (13)] by\textsuperscript{37,62}

$$\langle A(0); B(t) \rangle \sim \lim_{N \to \infty} \langle A(0)B(t) \rangle_{N}^{\text{RP}},$$

(25)

where

$$\langle A(0)B(t) \rangle_{N}^{\text{RP}} = \frac{1}{Z_N(2\pi \hbar)^N} \int d\mathbf{x}_0 \int d\mathbf{p}_0 e^{-\beta_N H_N(\mathbf{x}_0, \mathbf{p}_0)} \times A_N(\mathbf{x}_0)B_N(\mathbf{x}_t).$$

(26)

Here, $N$ is the number of beads used to discretize the Boltzmann operator, $\beta_N = \beta N$, and $\mathbf{x} = \{x_i\}$ and $\mathbf{p} = \{p_i\}$ ($1 \leq i \leq N$) represent the position and momenta of the $i$th bead.\textsuperscript{64} $Z_N$ is the $N$-bead path-integral representation of the partition function,

$$Z_N = \frac{1}{(2\pi \hbar)^N} \int d\mathbf{x}_0 \int d\mathbf{p}_0 e^{-\beta_N H_N(\mathbf{x}_0, \mathbf{p}_0)},$$

(27)

$O_N$ is the ring polymer representation of observable $\hat{O}$,

$$O_N(\mathbf{x}) = \frac{1}{N} \sum_{i=1}^{N} O(x_i),$$

(28)

and

$$H_N(\mathbf{x}, \mathbf{p}) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} m \omega_N^2 (x_{i+1} - x_i)^2 + V(x_i)$$

(29)

is the ring polymer Hamiltonian, where $m$ is the physical mass of the particle and $\omega_N = 1/(\beta_N \hbar)$.

The exact path-integral representation of the Kubo transform [Eq. (13)] is recovered by Eq. (25) in the limit of $t \to 0$.\textsuperscript{35} Also, for correlations of the form $\langle \hat{A}(\mathbf{x}), \hat{\chi}(\mathbf{y}) \rangle$ with $\hat{A}(\mathbf{x})$, RPMD gives the exact result in the limit of harmonic potentials as $N \to \infty$.\textsuperscript{31} For general potentials, it is possible to show that the accuracy of the approximation is of order $t^2$ for linear and of order $t^3$ for nonlinear operators.\textsuperscript{65,66} Finally, the dynamics generated by the RPMD approximation preserve the initial Boltzmann distribution, which is an appealing feature for any semiclassical approximation to avoid leakage of energy between different modes.\textsuperscript{67}

The RPMD methodology has been successfully applied to a wide range of problems including rate theory,\textsuperscript{68–76} simulations of linear spectroscopy in water clusters,\textsuperscript{77–80} and bulk water,\textsuperscript{39,40,81,82} and in describing diffusion dynamics of liquid systems,\textsuperscript{21,83–85} to name a few examples. In recent years, different efforts have been made to extend RPMD to describe nonadiabatic dynamics\textsuperscript{64–89} and non-equilibrium conditions.\textsuperscript{80} Very recently, Althorpe and co-workers have shown that RPMD can be viewed as an approximation to a more general type of quantum Boltzmann preserving classical dynamics, known as Matsubara dynamics.\textsuperscript{42,43}

However, so far, the formulation of RPMD has been restricted to the evaluation of the single-time Kubo transform.\textsuperscript{37} To compute the second-order response, given by Eq. (24), an approximation to the two-time symmetrized DKT is necessary. Here, we propose to approximate the two-time symmetrized DKT by using the “natural” extension of RPMD to two-times,

$$\langle A(0); B(t); C(t') \rangle_{N}^{\text{RP}} \sim \lim_{N \to \infty} \langle A(0)B(t)C(t') \rangle_{N}^{\text{RP}},$$

(30)

with

$$\langle A(0)B(t)C(t') \rangle_{N}^{\text{RP}} = \frac{1}{Z_N(2\pi \hbar)^N} \int d\mathbf{x}_0 \int d\mathbf{p}_0 e^{-\beta_N H_N(\mathbf{x}_0, \mathbf{p}_0)} \times A_N(\mathbf{x}_0)B_N(\mathbf{x}_t)C_N(\mathbf{x}_{t'}),$$

(31)

where $C_N(\mathbf{x}_{t'})$ corresponds to a third position-dependent observable evaluated at time $t'$.

In the short time limit (i.e., $t \to 0$ and $t' \to 0$), the expression in Eq. (31) corresponds to the exact path-integral representation of a symmetrized DKT correlation function, as shown in Appendix A,

$$\langle A(0)B(0)C(0) \rangle_{N}^{\text{RP}} = \lim_{t, t' \to 0} \langle A(0); B(t); C(t') \rangle_{N}^{\text{sym}},$$

(32)

i.e., the RPMD expression is exact in this limit. Note also that Eq. (31) reduces to the standard RPMD approximation in the case of one of the operators equaling unity, just as Eq. (10) reduces to the single Kubo transform in this case. It is straightforward to verify that the two-time extension of RPMD holds the same symmetries as Eq. (10) and that classical dynamics generated from Eq. (29) preserve the quantum Boltzmann distribution.
The approximation proposed in this paper is, then, to use the classically evolved phase-space of ring polymers at time \(t, t' > 0\) to evaluate Eq. (31) as a short-time approximation to the symmetrized DKT function which, in turn, can be related to the second-order response function. A justification for this approximation is the fact that RPMD is exact in two limiting cases for two-time correlations. For a harmonic potential, it is possible to prove that Eq. (31) is exact for all \(t\) and \(t'\) for correlations of the form \(\langle A_1(t)x(t)x(t')\rangle\) as \(N \to \infty\) (Appendix B). On the other hand, in the high temperature (i.e., classical) limit, the intrapolymer harmonic spring forces in Eq. (29) become so large that the polymer collapses to a single point and Eq. (31) reduces to a classical two-time correlation function.

In this classical limit, the operators in Eq. (10) become classical dynamical variables that commute with the Hamiltonian and, after rearranging the exponentials and upon performing the integrals, the classical two-time correlation function is obtained from Eq. (10). Hence, the proposed approximation gives the correct results in the classical and harmonic limit, a fact that is certainly encouraging. In Sec. III, we numerically test this approximation for a series of benchmark model systems for which we can make direct comparisons to the exact results.

We note that a similar connection, as the one introduced by Eq. (32), has been recognized by Reichman et al. in the context of CMD for the case of \(\hat{A} = \hat{B} = \hat{x}\) and was used for the computation of single-time correlation functions of nonlinear operators.\(^{30}\) However, to the best of our knowledge, this is the first time that an explicit connection has been made between a higher-order Kubo-transform and RPMD. This is also the first time this formalism has been used to compute two-time correlation functions in relation with the second-order response function.

III. NUMERICAL TESTS

We report numerical calculations for simple one-dimensional model potentials for both linear and non-linear operators and direct comparisons to the corresponding exact results to test the accuracy and capabilities of the two main approximations proposed in this paper [i.e., Eqs. (24) and (31)]. The results support that the response can be approximated by the symmetrized DKT [Eq. (24)] and that RPMD provides a reasonable approximation to the symmetrized DKT [Eq. (31)].

The model systems include the harmonic potential \(V(x) = \frac{1}{2} \lambda x^2\), the weakly anharmonic potential \(V(x) = \frac{1}{2} \lambda^2 + \frac{3}{10} \lambda^3 + \frac{1}{120} \lambda^4\), and the quartic potential \(V(x) = \frac{1}{2} \lambda x^4\) previously used to test CMD and RPMD.\(^{36,37}\) In all cases, \(m = 1\) and atomic units are used.

The RPMD simulations were performed using the standard PIMD techniques\(^{49,92}\) in the normal mode representation,\(^{49}\) employing \(N = 32\) beads for both \(\beta = 1\) and \(\beta = 8\) and using a time step of 0.05 a.u. The results correspond to averages of a large number of simulations, resampling the momenta between trajectories from a Maxwell-Boltzmann distribution. We also test the performance of the thermostatted version of RPMD (TRPMD) to model multi-time correlation functions where Eq. (31) is evaluated using a Langevin thermostat for the non-centroid degrees of freedom.\(^{40}\) Classical results were obtained by setting \(N = 1\) in Eq. (31). Exact results corresponding to the DKT were obtained by the direct evaluation of the trace of the DKT in a finite harmonic basis set. All results were checked to be converged with respect to the basis set size.

To perform the double Fourier transform, the TCF’s were damped by the function \(f(t, t') = e^{-(t^2 + t'^2)/\tau^2}\) with \(\tau = 13\) to avoid numerical ripples due to the finite time Fourier transform. Tests were performed to ensure that the results were qualitatively insensitive to the choice of \(\tau\).

A. Response function

Figure 1, left panel, shows contour plots of the double Fourier transform of the exact response function and the approximate response function given by the symmetrized DKT [Eq. (24)] for \(\hat{A} = \hat{B} = \hat{x}\) and \(\hat{C} = \hat{x}^2\) in an anharmonic potential at low temperatures (\(\beta = 8\)). As can be appreciated from the figure, the spectrum obtained from the approximation is in reasonably good agreement with the exact result, both in terms of the position as well as in terms of the sign of the peaks.

In order to get a more quantitative estimate of the accuracy of the approximations, the right panels of Fig. 1 represent comparisons between cuts along \(\omega = 0\) (top panel) and \(\omega = 1\) (bottom panel). Note that, although the approximation correctly captures the sign and position of each peak at each frequency, the intensity is either overestimated or underestimated. This result is not surprising, taking into consideration that in our proposed approximation to the response, we are neglecting contributions from the asymmetric DKT, which can be either positive or negative. Nevertheless, the overall performance is reasonable and should allow for a

![Fig. 1. Top left: Exact response function Eq. (21). Bottom left: The approximate response as given in Eq. (24). Top right: A projection at \(\omega = 0\) comparing the exact and approximate response. Bottom right: A projection at \(\omega = 1\) comparing the exact and approximate response. The potential is defined as \(V(x) = \frac{1}{2} \lambda x^2 + \frac{3}{10} \lambda^3 + \frac{1}{120} \lambda^4\) with a temperature \(\beta = 8\) with \(\hat{A} = \hat{B} = \hat{x}\) and \(\hat{C} = \hat{x}^2\).](image)
qualitative interpretation of the spectra. Incorporating the contributions from the asymmetric DKT is the subject of future work which might enable quantitative comparisons with exact results.

The previous analysis also holds for simulations of the spectrum at high temperatures ($\beta = 1$). In general, the qualitative features of the spectrum are reproduced by the approximate response Eq. (24), but the intensities of the peaks are overestimated/underestimated. For example, in Fig. 2, we show the results for the same system as in Fig. 1 but for $\beta = 1$. As can be seen for $\omega = 0$, the approximated response overlaps with the exact result, but at $\omega = 1$, the intensity is not as well reproduced, although all the qualitative features are exhibited in the approximated spectrum.

Similar results also hold for different correlation functions of harmonic/mildly anharmonic potentials, as shown in the supplementary material. Note that the approximation gives reasonable spectra even for a nonlinear correlation function such as $\langle x^2 x^2 x^2 \rangle$ in a harmonic potential. For the quartic oscillator, a very strongly anharmonic potential, the approximation proposed in Eq. (24), starts to break down for nonlinear correlation functions, as shown in Fig. S7 of the supplementary material for $\langle x^2 x^2 x^2 \rangle$. Interestingly, at low temperatures, the approximation seems to still be valid, though at high temperatures the line shape is not fully reproduced. These results are not surprising since Eq. (24) was derived from a harmonic reference potential and highlights the limitation of the methodology to treat strongly anharmonic potentials. Note, however, that since the proposed methodology is intended to be used in condensed phases, these scenarios with highly nonlinear potentials are not likely to be encountered.

B. Two-time RPMD

In Sec. III A, we have shown that the symmetrized DKT provides a reasonable approximation to the exact second-order response function of the model systems investigated. Here, we test the approximation of evaluating the DKT by the two-time RPMD expression introduced by Eq. (31). From the derivation discussed in Sec. II C and Appendix B, it is clear that the RPMD approximation is exact for $t = t' = 0$ and in the harmonic limit for $\hat{B} = \hat{C} = \hat{x}$, so we now turn our attention to investigating how well this approximation works for finite times and anharmonic potentials.

Figure 3 shows the results for the exact symmetrized DKT [Eq. (10)] of the position auto-correlation for the weakly anharmonic potential at $\beta = 1$ (left panel). We also present heat maps of the difference between the exact and RPMD (top right panel) and classical (bottom right panel) results. In this high-temperature regime, both RPMD and classical results are in good agreement with the exact results, as can be appreciated from the small scale of the heat map in comparison to the magnitude of the exact TCF. Moreover, RPMD and classical results agree with each other, as expected in this high-temperature limit (see the discussion at the end of Sec. II C).
At lower temperatures ($\beta = 8$), the differences between classical and RPMD are more significant, as can be appreciated from the heat maps shown in Fig. 4 (note the scale in comparison with the magnitude of the exact result). Nevertheless, it is worth noting that the RPMD results are in much better agreement with the exact results than the classical results which are off by $\sim 60\%$ in the zero time limit ($t = t' = 0$). Hence, it is clear that RPMD provides an improvement over the purely classical results in the low temperature regime.

Figure 5 shows a $t' = 0$ cut of the symmetrized DKT position auto-correlation for both $\beta = 1$ and $\beta = 8$ that further highlights the comparison of the RPMD approximation and the classical results for the weakly anharmonic potential. As already seen in Fig. 3, there is good agreement between all methods for $\beta = 1$, being almost indiscernible from the exact results. For the low temperature case, RPMD performs much better than the classical simulations both in terms of peak amplitudes and frequency of the oscillations for several periods, until the thermal time $t_\beta = \beta = 8$ beyond which there is dephasing and amplitude decay. In Fig. 5, we also include the results obtained using the TRPMD methodology. For this particular potential and correlation function, we found that both RPMD and TRPMD perform equally well, with small discrepancies at longer times probably due to insufficient sampling. These results show that TRPMD also provides a satisfactory description of the DKT.

Figure 6 shows the results for the position auto-correlation function evaluated at $t' = 3$, which allow for analysis of performance along the $t'$ axis. Here, it is also clear that RPMD and
TRPMD perform better than classical simulations and provide good approximations to the exact results at high temperatures, although the accuracy slightly degrades at lower temperatures. Note that at time $t = 0$, the RPMD results do not necessarily have to agree with $K^{sym}(t = 0, t' \neq 0)$ although they are close in this case.

Figure 7 shows the results of calculations of the correlation function $K^{sym}_{x^2x^2x^2}(t, t')$ for the harmonic potential at $t' = 0$, allowing us to assess the capabilities of the method as applied to non-linear operators. When evaluated at low temperatures, this correlation function involving three non-linear operators provides a difficult test for semiclassical methodologies. At high temperatures ($\beta = 1$), both classical and RPMD results agree reasonably well as compared to benchmark full quantum calculations. At lower temperatures ($\beta = 8$), the classical calculations show significant disagreement with full quantum results, while the RPMD provides a better description of the short time behavior. It is worth remarking that the RPMD approximation captures the correct quantum Boltzmann statistics even for this non-linear case, whereas other methodologies are expected to fail.\textsuperscript{43} Note, however, that the RPMD results exhibit contamination from the intrapolymer frequencies at low temperatures, a well-known problem of RPMD known as “spurious contamination.”\textsuperscript{40} The use of TRPMD “washes out” the contamination, providing some improvement over non-thermostatted RPMD.

For strongly anharmonic potentials, such as the quartic oscillator, where coherences are important to describe the dynamics, the performance and accuracy of the RPMD approximation are expected to be poor since the methodology completely neglects any quantum phase information.\textsuperscript{37} As an example of this phenomena, in the supplementary material, we present results for $K^{sym}_{x^2x^2x^2}(t, t')$ for the quartic potential (Fig. S9 of the supplementary material). Even at high temperatures, it can be appreciated that the RPMD and classical results differ from the exact one after the first two oscillations. At low temperatures, RPMD captures the correct zero-time value and short time limit; although after the second oscillation, it is completely decorrelated. Note, however, that the methodology proposed here is tailored to be applied to condensed phase systems where quantum coherences are expected to rapidly be quenched by the environment and do not play a significant role.

The results presented so far deal with the performance of two-time RPMD to approximate the symmetrized DKT. Results of the overall performance of RPMD to approximate the response function, namely, the combination of both Eqs. (24) and (30), are presented in Figs. S10 and S11 of the supplementary material for the correlation $\hat{A} = \hat{B} = \hat{C} = x^2$ in the harmonic potential and in Figs. S12 and S13 of the supplementary material for $\hat{A} = \hat{B} = \hat{x}$ and $\hat{C} = \hat{x}^2$ in the weakly anharmonic potential. For the case of the anharmonic potential, the results at high temperatures are indistinguishable from the one presented in Fig. 2, whereas at low temperatures the RPMD response is slightly less intense than the symmetrized DKT response (Fig. 1). For the case of the non-linear correlation in the harmonic potential, the spectra are perfectly reproduced by the RPMD approximation at high temperatures, whereas the intensity of the peaks is underestimated at low temperatures (as expected from the poor performance of RPMD presented in Fig. 7). The overall conclusion of this analysis is that the proposed RPMD approximation to the response function works reasonably well when applied to harmonic or weakly anharmonic potentials.

IV. CONCLUSIONS AND FINAL REMARKS

We have shown that multi-time response functions $\langle A(t_0)B(t)C(t') \rangle$ of interest in simulations of nonlinear optical spectroscopy can be evaluated as linear combinations of multi-time Kubo transforms. By using a harmonic reference potential with operators expanded to second order in the harmonic coordinate, we have shown that the main contributions to the second-order response result from the symmetrized real parts of the DKT’s.

We found that the evaluation of the symmetrized DKT by using Ring Polymer Molecular Dynamics (RPMD) provides results in better agreement with full quantum mechanical calculations than the corresponding classical calculations, even for non-linear operators. The improvement is significant in the short-time limit, until the thermal time. Numerical tests and comparisons to the exact response functions have shown that the approximate approach correctly reproduces the qualitative features found in the spectra in terms of peak position and signs for harmonic/weakly anharmonic potentials, although the intensities of the peaks are not fully reproduced likely due to the neglect of the asymmetric contributions. The resulting methodology thus provides a practical approximate approach to include nuclear quantum effects in the description of multi-time response functions.

**FIG. 7.** $t' = 0$ cut of the symmetrized DKT $x^2$ auto-correlation for the harmonic potential. Black line: exact result, $K^{sym}_{x^2x^2x^2}(t, 0)$. Red line: Classical result. Green line: RPMD result. Blue line: TRPMD result.
It is important to point out that, while the two-time RPMD extension introduced in this study does inherit all of the properties that make the RPMD methodology attractive, it also has all the same flaws as the original formulations of RPMD. Particularly, its performance for nonlinear operators and/or highly nonlinear potentials is quite poor except at very short times. We also point out that the results reported in this paper are based on simple model potentials for which exact quantum mechanical results can be computed. It would be interesting in future work to see how well the proposed methodology performs when applied to calculations of spectra of condensed phase systems. In particular, it would be interesting to study the 2D Raman or terahertz-Raman spectrum of liquid water where nuclear quantum effects are known to be of vital importance.

We have provided a practical approach for the incorporation of nuclear quantum effects in the calculation of second-order response functions. However, there is certainly room for improvements. For example, the approximation proposed in Eq. (24) neglects the contribution of the asymmetric part of the double Kubo transform. We anticipate incorporating the asymmetric part would improve the intensities of the peaks and would thus bring the approximation in semi-quantitative agreement with full quantum calculations for the model systems investigated. On the other hand, one could seek to improve the approximation to the symmetrized DKT rather than using the RPMD approximation of Eq. (31). In addition, it would be worth exploring the multi-time formulation of Matsubara dynamics and the corresponding multi-time approximations that stem from it. Finally, while the work presented here deals only with the second-order response, this framework could, in principle, be extended to higher orders of the response function and generalized to the simulation of other types of spectroscopies. Work on all of these directions is currently underway.

SUPPLEMENTARY MATERIAL

See supplementary material for a detailed description of the derivation of Eq. (24) and additional figures comparing the performance of this approximation with the exact response. Also included are the Fourier relationships of both the standard and Kubo transformed two-time TCF’s.

ACKNOWLEDGMENTS

V.S.B. acknowledges support from the NSF Grant No. CHE-1465108 and high-performance computing time from the National Energy Research Scientific Computing Center (NERSC) and the Yale High Performance Computing Center.

APPENDIX A: PROOF OF EQ. (32)

To prove the relation given in Eq. (32), it is useful to rewrite the integrand of Eq. (31) (in the $t, t' \to 0$ limit) as

\[
A_N(x)B_N(x)C_N(x) = \frac{1}{N^3} \sum_{i,j} \sum_{N} A(x_i)B(x_j)C(x_k) \quad (A1)
\]

\[
= \frac{1}{N^2} \sum_{i,j} \sum_{j} A(x_i)B(x_j)C(x_1) \quad (A2)
\]

\[
= \frac{1}{N^2} \sum_{i,j} \sum_{j} [A(x_i)B(x_j) + B(x_j)A(x_i)] C(x_1), 
\]

where we have used the invariance of the beads to cyclic permutation within the integral.

The RPMD approximation now reads

\[
\langle A(0)B(0)C(0) \rangle_{\text{RP}}^N = \frac{1}{Z_N N^2} \sum_{i,j} \int \frac{1}{(2\pi \hbar)^N} dx \delta_0 e^{-\beta N H_N(x_0, \theta_0)} 
\times \left(A(x_i)B(x_j) + B(x_j)A(x_i)\right) C(x_1) \quad (A3)
\]

Upon performing the momentum integrals, it follows that

\[
\langle A(0)B(0)C(0) \rangle_{\text{RP}}^N = \frac{1}{Z_N N^2} \sum_{i,j} \int \frac{1}{(2\pi \hbar)^N} dx \delta_0 e^{-\beta N U_N(x)} 
\times \left(A(x_i)B(x_j) + B(x_j)A(x_i)\right) C(x_1) \quad (A5)
\]

where

\[
U_N(x) = \sum_{i} \frac{m}{2} \omega_i^2 (x_{i+1} - x_i)^2 + V(x_i). \quad (A6)
\]

The Boltzmann factor can be discretized according to the indices of the summations to give

\[
\langle A(0)B(0)C(0) \rangle_{\text{RP}}^N
= \frac{1}{Z_N N^2} \sum_{i,j} \int \frac{1}{(2\pi \hbar)^N} dx \delta_0 e^{-(N-i)\beta U_N(x)} 
\times \left(A(x_i)B(x_j) + B(x_j)A(x_i)\right) C(x_1) \quad (A7)
\]

Taking the infinite bead limit, undoing the path integral discretization, and relabeling the beads indices, it is possible to express the previous equation as

\[
\langle A(0)B(0)C(0) \rangle_{\text{RP}}^N
= \frac{1}{Z_N^2} \sum_{i,j} \int d\lambda \langle x_1 | e^{-(N-i)\beta H} \hat{A} e^{-(i-j)\beta H} \hat{B} e^{-(j-1)\beta H} \hat{C} \rangle \langle x_1 | C(x_1) \quad (A8)
\]

\[
= \frac{1}{Z_N^2} \sum_{i,j} \text{Tr} \left\{ e^{-(N-i)\beta H} \hat{A} e^{-(i-j)\beta H} \hat{B} e^{-(j-1)\beta H} \hat{C} \right\} \quad (A9)
\]
where it is understood that the operators $\hat{A}$, $\hat{B}$, and $\hat{C}$ are functions solely of $\hat{x}$.

Realizing that the sums in Eq. (A9) are simply the Riemann approximations of an iterated integral, we have that

$$\langle A(0) B(0) C(0) \rangle_{N}^{\text{RP}} = \langle A(0); B(0); C(0) \rangle + \langle B(0); A(0); C(0) \rangle$$

(A10)

$$= \langle A(0); B(0); C(0) \rangle_{\text{sym}},$$

(A11)

which completes the proof of Eq. (32).

**APPENDIX B: HARMONIC LIMIT OF THE TWO-TIME RPMD**

Hamilton’s equations of motion applied to Eq. (29) yield the classical equation of motion for the centroid for the harmonic potential $V = \frac{1}{2} m \omega^2 x^2$, namely, $x_N(t) = x_N(0) \cos(\omega t) + \frac{m \omega(0)}{m \omega} \sin(\omega t)$. Taking $\hat{A}$ as an arbitrary function of $x$, the RPMD approximation to $\langle A(0); x(t); x(t') \rangle_{\text{sym}}$

$$\langle A(0) x(t) x(t') \rangle_{N}^{\text{RP}} = \frac{1}{Z_N(2 \pi \hbar)^N} \int d x_0 \int d p_0 e^{\beta N H_0(x_0, p_0)}$$

$$\times A_N(x_0) x_N(x, t) x_N(x', t'),$$

(B1)

can be shown to be

$$\frac{1}{2} \langle A(0) x(0) \rangle_{N}^{\text{RP}} \left[ \cos[\omega(t + t')] + \cos[\omega(t - t')] \right] + \frac{1}{2m^2 \omega^2}$$

$$\times \langle A(0) p(0) \rangle_{N}^{\text{RP}} \left[ \cos[\omega(t - t')] - \cos[\omega(t + t')] \right]$$

(B2)

$$= \frac{B_1 - B_2}{2} \cos[\omega(t + t')] + \frac{B_1 + B_2}{2} \cos[\omega(t - t')],$$

(B3)

where $B_1 = \langle A(0) x(0) \rangle_{N}^{\text{RP}}$ and $B_2 = \langle A(0) p(0) \rangle_{N}^{\text{RP}} / (m^2 \omega^2)$.

The exact correlation function $\langle A(0); x(t); x(t') \rangle_{\text{sym}}$ can be cast in similar form through the use of

$$\hat{x}(t) = \sqrt{\frac{\hbar}{2m \omega}} (\hat{a}^\dagger e^{i \omega t} + \hat{a} e^{-i \omega t}),$$

(B4)

where $\hat{a}^\dagger (\hat{a})$ is the creation (annihilation) operator in the harmonic oscillator basis and the time dependence of these operators comes from solving $\dot{\hat{a}} = i/\hbar [\hat{H}, \hat{a}]$. The result is

$$\langle \hat{A}; \hat{x}(0); \hat{x}(0) \rangle_{\text{sym}} = \left\{ \langle \hat{A}; \hat{x}(0) \rangle_{\text{sym}} - \frac{1}{m^2 \omega^2} \langle \hat{A}; \hat{p}(0); \hat{p}(0) \rangle_{\text{sym}} \right\}$$

(B11)

$$= \left\{ \frac{1}{2} \left( \langle \hat{A}; \hat{x}(0) \rangle_{\text{sym}} - \frac{1}{m^2 \omega^2} \langle \hat{A}; \hat{p}(0); \hat{p}(0) \rangle_{\text{sym}} \right) \right\}$$

(B12)

$$= \frac{1}{2} \left\{ \langle A(0) x(0) \rangle_{N \rightarrow \infty}^{\text{RP}} - \langle A(0) p(0) \rangle_{N \rightarrow \infty}^{\text{RP}} \right\},$$

(B13)

which proves $C_1 + C_4 = \frac{1}{2} (B_1 - B_2)$ as $N \rightarrow \infty$. Using similar steps, it is easy to show that $C_2 + C_3 = \frac{1}{2} (B_1 + B_2)$. This completes the proof that two-time RPMD is exact for correlations of the form $\langle A(0); x(t); x(t') \rangle_{\text{sym}}$. 

---

\[
\frac{\hbar}{m \omega Z^2} \mathcal{R}\left\{ \int_{0}^{\beta} d \lambda \int_{0}^{1} d \lambda' \mathcal{R}\left[ e^{-(\beta-\lambda)\hat{A}} e^{-(\lambda-x')\hat{B}} \hat{A} \hat{B} e^{x' \hat{B}} \hat{B} e^{-x' \hat{B}} \right] + \mathcal{R}\left[ e^{-(\beta-\lambda)\hat{A}} e^{-(\lambda-x')\hat{B}} \hat{A} \hat{B} e^{x' \hat{B}} \hat{B} e^{-x' \hat{B}} \right] \right\}
\]

with

\[
C_1 = \frac{\hbar}{m \omega} \left\langle \hat{A}; \hat{a}^\dagger; \hat{a} \right\rangle,
\]

(B6)

\[
C_2 = \frac{\hbar}{m \omega} \left\langle \hat{A}; \hat{a}; \hat{a}^\dagger \right\rangle,
\]

(B7)

\[
C_3 = \frac{\hbar}{m \omega} \left\langle \hat{A}; \hat{a}; \hat{a} \right\rangle,
\]

(B8)

\[
C_4 = \frac{\hbar}{m \omega} \left\langle \hat{A}; \hat{a}; \hat{a} \right\rangle.
\]

(B9)

To prove that the RPMD correlation function is exact in this limit, it is now a matter of proving that $\frac{1}{2} (B_1 - B_2) = C_1 + C_4$ and $\frac{1}{2} (B_1 + B_2) = C_2 + C_3$ for $N \rightarrow \infty$.

It is straightforward to show that

\[
C_1 + C_4 = \frac{\hbar}{m \omega Z^2} \mathcal{R}\left\{ \int_{0}^{\beta} d \lambda \int_{0}^{1} d \lambda' \mathcal{R}\left[ e^{-(\beta-\lambda)\hat{A}} e^{-(\lambda-x')\hat{B}} \hat{A} \hat{B} e^{x' \hat{B}} \hat{B} e^{-x' \hat{B}} \right] \right\}
\]

where

\[
\hat{a} = \sqrt{\frac{m \omega}{2 \hbar}} + \frac{i}{\sqrt{2m \omega}} \hat{p}
\]

can be rewritten as

$$\langle \hat{A}; \hat{x}(0); \hat{x}(0) \rangle_{\text{sym}} \quad \text{sym},$$

(B10)

\[
\langle A(0) x(0) \rangle_{N \rightarrow \infty}^{\text{RP}} - \langle A(0) p(0) \rangle_{N \rightarrow \infty}^{\text{RP}}.
\]

(B14)