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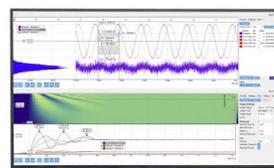
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ABSTRACT

We present the non-adiabatic Matsubara dynamics, a general framework for computing the time-correlation function (TCF) of electronically non-adiabatic systems. This new formalism is derived based on the generalized Kubo-transformed TCF using the Wigner representation for both the nuclear degrees of freedom and the electronic mapping variables. By dropping the non-Matsubara nuclear normal modes in the quantum Liouvillian and explicitly integrating these modes out from the expression of the TCF, we derived the non-adiabatic Matsubara dynamics approach. Further making the approximation to drop the imaginary part of the Matsubara Liouvillian and enforce the nuclear momentum integral to be real, we arrived at the non-adiabatic ring-polymer molecular dynamics (NRPMD) approach. We have further justified the capability of NRPMD for simulating the non-equilibrium TCF. This work provides the rigorous theoretical foundation for several recently proposed state-dependent RPMD approaches and offers a general framework for developing new non-adiabatic quantum dynamics methods in the future.

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I. INTRODUCTION

Accurately simulating the quantum dynamics of the molecular system remains a central challenge in theoretical chemistry due to the difficulties of accurately describing electronically non-adiabatic dynamics and nuclear quantum dynamics. Directly performing exact quantum dynamics simulations is computationally demanding, despite exciting recent progress.[1–11] To accurately describe the non-adiabatic dynamics, a large number of approximate approaches are developed, including the popular trajectory surface-hopping method [based on the mixed quantum–classical (MQC) approximation],[12–15] the linearized path-integral approaches,[16–23] and the mixed quantum–classical Liouville equation.[24–28] Despite providing accurate electronic non-adiabatic dynamics, these approaches often rely on the Wigner sampling of the initial nuclear distribution and a classical dynamics for propagation. Thus, in general, they do not preserve quantum Boltzmann distribution (QBD)[29,30] or zero-point energy (ZPE) associated with the nuclear degrees of freedom (DOF). In fact, they often suffer from numerical issues such as ZPE leakage,[31,32] although significant improvements were accomplished through recent developments.[33–36]

To accurately describe nuclear quantum dynamics for electronically adiabatic systems, imaginary-time path integral based approaches[37–39] are developed, including the centroid molecular dynamics (CMD)[40–42] and the ring-polymer molecular dynamics (RPMD).[43,44] In particular, RPMD resembles the classical MD in the extended phase space, providing a convenient way to compute approximate quantum time-correlation functions (TCFs).[43] The classical evolution of RPMD preserves its initial quantum

distribution captured by the ring-polymer Hamiltonian, and it is free of the zero-point energy leaking problem.[31,43] Despite its success on describing quantum effects in the condensed phase, RPMD is limited to one-electron non-adiabatic dynamics[45–49] or nuclear quantization,[43,50–53] as well as the lack of real-time electronic coherence effects.[45,46]

Recently emerged state-dependent RPMD approaches provide a unified description of both the electronically non-adiabatic dynamics and nuclear quantum effects. These state-dependent RPMD methods, such as non-adiabatic RPMD (NRPMD),[54–56] mapping variable RPMD (MV-RPMD),[57–59] ring-polymer Ehrenfest dynamics,[60] kinetically constrained RPMD (KC-RPMD),[48,61,62] coherent state RPMD (CS-RPMD),[63] and ring-polymer surface hopping (RPSH),[64–68] are promising to provide both accurate non-adiabatic dynamics with an explicit description of electronic states, as well as a reliable treatment of nuclear quantum dynamics through the ring-polymer path-integral quantization.

Despite the initial success, all of the above state-dependent RPMD approaches are currently viewed as the model dynamics. The Hamiltonians associated with some of these approaches (such as MV-RPMD) are derived from the quantum partition function, and these Hamiltonians are directly used for dynamics propagation as well as the initial sampling. Thus, the fundamental and crucial theoretical question is that can these methods be rigorously justified. If so, not only it will explain the numerical success of these state-dependent RPMD approaches but also it will offer a general theoretical framework to understand the limitations of these approaches and further improving them. Recent theoretical work on the Matsubara dynamics[69–72] by Hele, Althorpe, and others indeed provide the hope for this because RPMD (as well as CMD) can be derived as an approximation of the Matsubara dynamics,[70,73] which itself can be rigorously derived.[69] Along this direction, it has been recently shown[74] that one can use the Matsubara approximation to derive a state-dependent Matsubara dynamics for a golden-rule type of the time-correlation function (TCF), which contains two different electronic surfaces for the forward and backward propagators, However, this formalism does not provide the time-dependent electronic state information during the quantum dynamics propagation.

In this paper, we present the non-adiabatic Matsubara dynamics, a general framework for computing the time-correlation function of electronically non-adiabatic systems. This new formalism is derived based on the generalized Kubo-transformed time-correlation function (TCF) formalism[42,69] using the Wigner representation for both the nuclear DOF and electronic mapping variables.[75–77] By dropping the non-Matsubara nuclear normal modes in the quantum Liouvillian,[69] we derived the non-adiabatic Matsubara dynamics, which can be viewed as a generalization of the original (electronically adiabatic) Matsubara dynamics.[69] Further making the approximation that drops the imaginary part of the Matsubara Liouvillian,[73] we arrived at the non-adiabatic RPMD (NRPMD) approach, where the initial distribution coincides with the one in Mapping-Variable (MV)-RPMD,[57] whereas the Liouvillian coincides with the Liouvillian used in the originally proposed NRPMD.[54] We have further justified the capability of NRPMD for simulating the non-equilibrium time correlation function.[56]

II. EXACT KUBO-TRANSFORMED TIME-CORRELATION FUNCTION

We begin by introducing the generalized Kubo-transformed time-correlation function for a state-dependent Hamiltonian. We start by expressing the total Hamiltonian operator as follows:

$$\hat{H} = \hat{T} + \hat{V}_0 + \hat{V}_e = \frac{\hat{P}^2}{2m} + V_0(\hat{R}) + \sum_{i,j=1}^{\mathcal{K}} \mathcal{V}_{ij}(\hat{R})|i\rangle\langle j|, \quad (1)$$

where $\{|i\rangle\}$ is the *diabatic* basis, $\hat{T}$ is the nuclear kinetic energy operator, and $\hat{R}$ is the nuclear position operator with the corresponding conjugate momentum operator $\hat{P}$. To simplify our discussion, we have assumed that there is only one nuclear DOF in the system. Generalizing the discussion with many nuclear DOF is straightforward.

Furthermore, $V_0(\hat{R})$ is the state-independent potential operator, whereas $\hat{V}_e = \sum_{ij} \mathcal{V}_{ij}(\hat{R})|i\rangle\langle j| \equiv \mathcal{V}(R)$ is the state-dependent potential operator with $\mathcal{K}$ total diabatic electronic states. We assume that $\mathcal{V}_{ij}(\hat{R})$ is real and symmetric throughout this work.

A. Mapping representation of electronic states

For the electronic part of the Hamiltonian, the $\mathcal{K}$ diabatic electronic states can be mapped into $\mathcal{K}$ harmonic oscillators' ground and excited states, with $(\mathcal{K}-1)$ oscillators in the ground state and the ith oscillator in the first excited state. This is commonly referred to as the single excited oscillator (SEO) subspace of the mapping oscillators. It can be formally written as

$$|i\rangle \rightarrow |0_1,\ldots,1_i\ldots,0_{\mathcal{K}}\rangle = \hat{a}_i^{\dagger}|0_1,\ldots,0_i\ldots,0_{\mathcal{K}}\rangle, \quad (2)$$

where $\hat{a}_i^{\dagger} = \frac{1}{\sqrt{2\hbar}}(\hat{q}_i - i\hat{p}_i)$ and $\hat{a}_j = \frac{1}{\sqrt{2\hbar}}(\hat{q}_j + i\hat{p}_j)$, and $\hat{\mathbf{q}} = \{\hat{q}_1,\ldots,\hat{q}_i,\ldots,\hat{q}_{\mathcal{K}}\}$ and $\hat{\mathbf{p}} = \{\hat{p}_1,\ldots,\hat{p}_i,\ldots,\hat{p}_{\mathcal{K}}\}$ are the mapping position and momentum operators, respectively. This mapping formalism is often referred to as the Meyer–Miller–Stock–Thoss (MMST)[75–77] mapping representation. With this mapping relation, the electronic part of the Hamiltonian is expressed as

$$\sum_{i,j=1}^{\mathcal{K}} \mathcal{V}_{ij}(\hat{R})|i\rangle\langle j| \rightarrow \sum_{i,j=1}^{\mathcal{K}} \mathcal{V}_{ij}(\hat{R})\hat{a}_i^{\dagger}\hat{a}_j, \quad (3)$$

and the electronic part of the Hamiltonian in Eq. (1) can be represented as

$$\hat{V}_e = \frac{1}{2\hbar} \sum_{i,j=1}^{\mathcal{K}} \mathcal{V}_{ij}(\hat{R})(\hat{q}_i\hat{q}_j + \hat{p}_i\hat{p}_j - \delta_{ij}\hbar). \quad (4)$$

This is known as the MMST[75–77] mapping Hamiltonian.

B. Generalized Kubo-transformed time-correlation functions

We begin by writing the generalized Kubo-transformed time-correlation function (TCF). The conventional Kubo-transformed correlation function is defined as

$$C_{AB}^{\mathrm{K}}(t) = \frac{1}{\mathcal{Z}\beta} \int_0^{\beta} d\lambda \mathrm{Tr}\left[e^{-(\beta-\lambda)\hat{H}} \hat{A} e^{-\lambda\hat{H}} e^{\frac{i}{\hbar}\hat{H}t} \hat{B} e^{-\frac{i}{\hbar}\hat{H}t} \right]$$

$$= \frac{1}{\mathcal{Z}N} \sum_{k=1}^{N} \mathrm{Tr}\left[e^{-\beta_N(N-k)\hat{H}} \hat{A} e^{-\beta_N k\hat{H}} e^{\frac{i}{\hbar}\hat{H}t} \hat{B} e^{-\frac{i}{\hbar}\hat{H}t} \right], \quad (5)$$

where $\beta = 1/k_B T$ is the inverse temperature, $\beta_N = \beta/N$, $\mathcal{Z} = \text{Tr}[e^{-\beta \hat{H}}]$ is the canonical partition function, $\hat{H}$ is defined in Eq. (1), and Tr $= \text{Tr}_n \text{Tr}_e$ represents the trace over both electronic and nuclear DOFs. From the first to the second expression in Eq. (5), we have converted a definite integral into the discrete Riemann sum through $\int_a^b f(\lambda) d\lambda = \lim_{N \to \infty} \sum_{k=1}^N f(a + k \cdot \Delta\lambda) \cdot \Delta\lambda$, where $a = 0$, $b = \beta$, and $\Delta\lambda = \beta/N = \beta_N$. Note that the second line of Eq. (5) is equivalent to the first line under the limit of $N \to \infty$.

We further insert $N-1$ identities of the form $e^{i\hat{H}t/\hbar} e^{-i\hat{H}t/\hbar} = \hat{\mathbb{1}}$ in Eq. (5) (see details in the supplementary material), resulting in

$$C_{AB}^{[N]}(t) = \frac{1}{\mathcal{Z}} \frac{1}{N} \sum_{k=1}^N \text{Tr}\Big[\left(e^{-\beta_N \hat{H}} e^{\frac{i}{\hbar}\hat{H}t} e^{-\frac{i}{\hbar}\hat{H}t}\right)^{N-k-1}$$
$$\times e^{-\beta_N \hat{H}} \hat{A} e^{\frac{i}{\hbar}\hat{H}t} e^{-\frac{i}{\hbar}\hat{H}t} \left(e^{-\beta_N \hat{H}} e^{\frac{i}{\hbar}\hat{H}t} e^{-\frac{i}{\hbar}\hat{H}t}\right)^{k-1}$$
$$\times e^{-\beta_N \hat{H}} e^{\frac{i}{\hbar}\hat{H}t} \hat{B} e^{-\frac{i}{\hbar}\hat{H}t}\Big]. \tag{6}$$

Note that Eq. (6) has a symmetric block structure of the form $e^{-\beta_N \hat{H}} e^{\frac{i}{\hbar}\hat{H}t} e^{-\frac{i}{\hbar}\hat{H}t}$, where the operator $\hat{A}$ is evaluated inside a particular block depending on the value of the k index. This type of *generalized* Kubo-transformed time-correlation function was first introduced in the work connecting the linearized path-integral approach and CMD[42] and later used for the development of the Matsubara dynamics.[69–72]

A path integral representation of Eq. (6) can be obtained by inserting the following identities:

$$\hat{\mathbb{1}}_{R_l', \mathbf{q}_l'} = \int dR_l' \int d\mathbf{q}_l' \hat{\mathcal{P}} |R_l', \mathbf{q}_l'\rangle \langle R_l', \mathbf{q}_l'|, \tag{7}$$

$$\hat{\mathbb{1}}_{R_l'', \mathbf{q}_l''} = \int dR_l'' \int d\mathbf{q}_l'' |R_l'', \mathbf{q}_l''\rangle \langle R_l'', \mathbf{q}_l''| \hat{\mathcal{P}}, \tag{8}$$

where the bead index $l = 1, \ldots, N$ and $\{R_l'', R_l'\}$ and $\{\mathbf{q}_l'', \mathbf{q}_l'\}$ are the nuclear and mapping variable positions, respectively, with

$\mathbf{q}_l' = \{[q_l']_1, \ldots, [q_l']_i, \ldots, [q_l']_{\mathcal{K}}\}$ and similarly for $\mathbf{q}_l''$. Furthermore, in both of the above identities, the electronic projection operator

$$\hat{\mathcal{P}} = \sum_{i=1}^{\mathcal{K}} |i\rangle\langle i| \tag{9}$$

is used to confine the mapping DOFs within the correct SEO subspace.[78] Inserting Eqs. (7) and (8) into the bead-specific positions of Eq. (6), one arrives at the formal mathematical description of the generalized Kubo correlation function[69,79] as follows:

$$C_{AB}^{[N]}(t) = \frac{1}{\mathcal{Z}} \int d\mathbf{R}'' \int d\mathbf{R}' \int d\mathbf{q}' \int d\mathbf{q}''$$
$$\times \frac{1}{N} \sum_{k=1}^N \prod_{l \neq k}^N \langle R_{l-1}'', \mathbf{q}_{l-1}'' | \hat{\mathcal{P}} e^{-\beta_N \hat{H}} \hat{\mathcal{P}} |R_l', \mathbf{q}_l'\rangle$$
$$\times \langle R_{k-1}'', \mathbf{q}_{k-1}'' | \hat{\mathcal{P}} e^{-\beta_N \hat{H}} \hat{\mathcal{P}} \hat{A} |R_k', \mathbf{q}_k'\rangle$$
$$\times \frac{1}{N} \sum_{k'=1}^N \prod_{l \neq k'}^N \langle R_l', \mathbf{q}_l' | e^{\frac{i}{\hbar}\hat{H}t} e^{-\frac{i}{\hbar}\hat{H}t} |R_l'', \mathbf{q}_l''\rangle$$
$$\times \langle R_{k'}', \mathbf{q}_{k'}' | e^{\frac{i}{\hbar}\hat{H}t} \hat{B} e^{-\frac{i}{\hbar}\hat{H}t} |R_{k'}'', \mathbf{q}_{k'}''\rangle, \tag{10}$$

where we introduce the notation $\int d\mathbf{x} = \prod_{l=1}^N \int dx_l$ for $\mathbf{x} = \{\mathbf{R}', \mathbf{R}'', \mathbf{q}', \mathbf{q}''\}$, and we have used the cyclic-symmetric property to write operator $\hat{B}$ in a bead-averaged fashion. A detail derivation of Eq. (10) is provided in the supplementary material.

Next, we change the variables $(R_l', R_l'', \mathbf{q}_l', \mathbf{q}_l'')$ into the mean (R_l and $\mathbf{q}_l$) and difference coordinates (D_l and Δ_l) as follows:[42,79]

$$R_l = \frac{1}{2}\left(R_l' + R_l''\right), \quad \mathbf{q}_l = \frac{1}{2}\left(\mathbf{q}_l' + \mathbf{q}_l''\right), \tag{11}$$

$$D_l = R_l' - R_l'', \quad \Delta_l = \mathbf{q}_l' - \mathbf{q}_l''. \tag{12}$$

Note that the Jacobian of the above transformation is unity for each bead index l. With this, one can re-express Eq. (10) as follows:

$$C_{AB}^{[N]}(t) = \frac{1}{\mathcal{Z}} \int d\mathbf{R} \int d\mathbf{D} \int d\mathbf{q} \int d\mathbf{\Delta} \frac{1}{N} \sum_{k=1}^N \prod_{l \neq k}^N \langle \mathbf{q}_{l-1} - \frac{1}{2}\Delta_{l-1}, R_{l-1} - \frac{1}{2}D_{l-1} | \hat{\mathcal{P}} e^{-\beta_N \hat{H}} \hat{\mathcal{P}} |\mathbf{q}_l + \frac{\Delta_l}{2}, R_l + \frac{D_l}{2}\rangle$$
$$\times \langle \mathbf{q}_{k-1} - \frac{1}{2}\Delta_{k-1}, R_{k-1} - \frac{1}{2}D_{k-1} | \hat{\mathcal{P}} e^{-\beta_N \hat{H}} \hat{\mathcal{P}} \hat{A} |q_k + \frac{\Delta_k}{2}, R_k + \frac{D_k}{2}\rangle \frac{1}{N} \sum_{k'=1}^N \prod_{l \neq k'}^N \langle \mathbf{q}_l - \frac{\Delta_l}{2}, R_l - \frac{D_l}{2} | e^{\frac{i}{\hbar}\hat{H}t}$$
$$\times e^{-\frac{i}{\hbar}\hat{H}t} |\mathbf{q}_l + \frac{\Delta_l}{2}, R_l + \frac{D_l}{2}\rangle \langle \mathbf{q}_{k'} - \frac{\Delta_{k'}}{2}, R_{k'} - \frac{D_{k'}}{2} | e^{\frac{i}{\hbar}\hat{H}t} \hat{B} e^{-\frac{i}{\hbar}\hat{H}t} |\mathbf{q}_{k'} + \frac{\Delta_{k'}}{2}, R_{k'} + \frac{D_{k'}}{2}\rangle. \tag{13}$$

Next, inserting the following identities

$$1 = \int dD_l' \delta(D_l + D_l') = \frac{1}{(2\pi\hbar)} \int dD_l' \int dP_l e^{\frac{i}{\hbar}P_l(D_l+D_l')},$$

$$1 = \int d\Delta_l' \delta(\Delta_l + \Delta_l') = \frac{1}{(2\pi\hbar)^{\mathcal{K}}} \int d\Delta_l' \int d\mathbf{p}_l e^{\frac{i}{\hbar}\mathbf{p}_l \cdot (\Delta_l+\Delta_l')}$$

into Eq. (13) for all l blocks, we have

$$C_{AB}^{[N]}(t) = \frac{\alpha_N}{\mathcal{Z}} \int d\mathbf{R} \int d\mathbf{P} \int d\mathbf{q} \int d\mathbf{p} [e^{-\beta\hat{H}} \hat{A}]_{\bar{N}} [\hat{B}(t)]_N, \tag{14}$$

with the constant $\alpha_N = 1/(2\pi\hbar)^{(k+1)N}$, and the operator $[e^{-\beta\hat{H}} \hat{A}]_{\bar{N}}$ is expressed as

$$[e^{-\beta \hat{H}} \hat{A}]_{\bar{N}} = \frac{1}{N} \sum_{k=1}^{N} \int d\mathbf{D} \int d\mathbf{\Delta} \prod_{l=1}^{N} e^{\frac{i}{\hbar} P_l D_l} e^{\frac{i}{\hbar} \mathbf{p}_l \Delta_l}$$

$$\times \prod_{l \neq k}^{N} \langle \mathbf{q}_{l-1} - \frac{1}{2}\mathbf{\Delta}_{l-1}, R_{l-1} - \frac{1}{2}D_{l-1}|$$

$$\times \hat{\mathcal{P}} e^{-\beta_N \hat{H}} \hat{\mathcal{P}} |\mathbf{q}_l + \frac{\mathbf{\Delta}_l}{2}, R_l + \frac{D_l}{2}\rangle$$

$$\times \langle \mathbf{q}_{k-1} - \frac{1}{2}\mathbf{\Delta}_{k-1}, R_{k-1} - \frac{1}{2}D_{k-1}|$$

$$\times \hat{\mathcal{P}} e^{-\beta_N \hat{H}} \hat{\mathcal{P}} \hat{A} |\mathbf{q}_k + \frac{\mathbf{\Delta}_k}{2}, R_k + \frac{D_k}{2}\rangle, \tag{15}$$

and $[\hat{B}(t)]_N$ is expressed as follows:

$$[\hat{B}(t)]_N = \frac{1}{N} \sum_{k=1}^{N} \int d\mathbf{D}' \int d\mathbf{\Delta}' \prod_{l=1}^{N} e^{\frac{i}{\hbar} P_l D_l'} e^{\frac{i}{\hbar} \mathbf{p}_l \Delta_l'}$$

$$\times \prod_{l \neq k}^{N} \langle \mathbf{q}_l - \frac{1}{2}\mathbf{\Delta}_l', R_l - \frac{1}{2}D_l'|e^{\frac{i}{\hbar}\hat{H}t} e^{-\frac{i}{\hbar}\hat{H}t}|\mathbf{q}_l$$

$$+ \frac{1}{2}\mathbf{\Delta}_l', R_l + \frac{1}{2}D_l'\rangle$$

$$\times \langle \mathbf{q}_k - \frac{1}{2}\mathbf{\Delta}_k', R_k - \frac{1}{2}D_k'|e^{\frac{i}{\hbar}\hat{H}t}\hat{B}e^{-\frac{i}{\hbar}\hat{H}t}|\mathbf{q}_k$$

$$+ \frac{1}{2}\mathbf{\Delta}_k', R_k + \frac{1}{2}D_k'\rangle, \tag{16}$$

where we have changed the dummy variable from $\sum_{k'}$ to $\sum_k$. Integrals over $\mathbf{R}$, $\mathbf{P}$, $\mathbf{D}$, are N dimensional, whereas integrals over $\mathbf{q}$, $\mathbf{p}$, and $\mathbf{\Delta}$ are $(N \times \mathcal{K})$ dimensional. Note that $[e^{-\beta \hat{H}} \hat{A}]_{\bar{N}}$ in Eq. (15) contains a complicated structure of the Wigner transform involving the couplings with adjacent beads l and $l + 1$, whereas $[\hat{B}(t)]_N$ in Eq. (16) is a simple bead average of the Wigner transform.

We want to remind the reader that $C_{AB}^{[N]}(t)$ in Eq. (14) should be viewed as a generalized Kubo-transformed time-correlation function such that under the $N \to \infty$ limit, it returns to the original definition of the Kubo-transformed time-correlation function $C_{AB}^{K}(t)$ defined in Eq. (5). With a finite N, even though it is no longer equivalent to $C_{AB}^{K}(t)$, it is still an quantum mechanically exact time-correlation function.

C. The quantum Liouvillian

For a Wigner transform of an operator $[\hat{A}]_W = \int dD e^{\frac{i}{\hbar}PD} \langle R - \frac{D}{2}|\hat{A}|R + \frac{D}{2}\rangle$, one can formally write down its time-dependent average as $[\hat{A}(t)]_W = [e^{\frac{i}{\hbar}\hat{H}t}\hat{A}e^{-\frac{i}{\hbar}\hat{H}t}]_W = e^{\mathcal{L}^{[1]}t}[\hat{A}(0)]_W$, where $\mathcal{L}^{[1]}$ is the quantum Liouvillian (see the supplementary material for detail derivation), and is commonly referred to as the Wigner–Moyal series.[80,81]

Note that $[\hat{B}(t)]_N$ [Eq. (16)] is expressed as the bead-averaged $(\mathcal{K} + 1)$-dimensional Wigner transform as follows:

$$[\hat{B}(t)]_N = \frac{1}{N} \sum_k \int dD_k \int d\mathbf{\Delta}_k e^{\frac{i}{\hbar}P_k D_k} e^{\frac{i}{\hbar}\mathbf{p}_k \mathbf{\Delta}_k}$$

$$\times \langle \mathbf{q}_k - \frac{1}{2}\mathbf{\Delta}_k, R_k - \frac{1}{2}D_k|\hat{B}(t)|\mathbf{q}_k + \frac{1}{2}\mathbf{\Delta}_k, R_k + \frac{1}{2}D_k\rangle$$

$$\equiv \frac{1}{N} \sum_k [\hat{B}_k(t)]_W, \tag{17}$$

where $\hat{B}(t) = e^{\frac{i}{\hbar}\hat{H}t}\hat{B}e^{-\frac{i}{\hbar}\hat{H}t}$ and $[\hat{B}_k(t)]_W$ is the Wigner transform of $\hat{B}(t)$ associated with the kth bead, defined in the above equation. In Eq. (17), we have also changed the dummy variables from D' and Δ' to D and Δ. When $t = 0$, $[\hat{B}(0)]_N = \frac{1}{N}\sum_k[\hat{B}_k]_W$, with $[\hat{B}_k]_W = \int dD_k \int d\mathbf{\Delta}_k e^{\frac{i}{\hbar}P_k D_k} e^{\frac{i}{\hbar}\mathbf{p}_k \mathbf{\Delta}_k} \langle \mathbf{q}_k - \frac{1}{2}\mathbf{\Delta}_k, R_k - \frac{1}{2}D_k|\hat{B}|\mathbf{q}_k + \frac{1}{2}\mathbf{\Delta}_k, R_k + \frac{1}{2}D_k\rangle$.

With the above information, we can formally write $[\hat{B}(t)]_N$ as follows:

$$[\hat{B}(t)]_N = e^{\mathcal{L}^{[N]}t}[\hat{B}(0)]_N. \tag{18}$$

The quantum Liouvillian $\mathcal{L}^{[N]}$ has the following form:

$$\mathcal{L}^{[N]} = \sum_l \frac{2}{\hbar}[\hat{H}_l]_W \cdot \sin\left(\frac{\hbar}{2}\hat{\Lambda}_l\right), \tag{19}$$

where $\hat{\Lambda}_l \equiv -\{\ ,\ \}$ is the negative Poisson operator associated with the lth bead expressed as

$$\hat{\Lambda} = \begin{pmatrix} \hat{\Lambda}_l^n \\ \hat{\Lambda}_l^e \end{pmatrix} = \begin{pmatrix} \frac{\overleftarrow{\partial}}{\partial P_l}\frac{\overrightarrow{\partial}}{\partial R_l} - \frac{\overleftarrow{\partial}}{\partial R_l}\frac{\overrightarrow{\partial}}{\partial P_l} \\ \overleftarrow{\nabla}_{\mathbf{p}_l} \cdot \overrightarrow{\nabla}_{\mathbf{q}_l} - \overleftarrow{\nabla}_{\mathbf{q}_l} \cdot \overrightarrow{\nabla}_{\mathbf{p}_l} \end{pmatrix}, \tag{20}$$

with the mapping variables related derivatives defined as

$$\nabla_{\mathbf{q}} = \begin{pmatrix} \frac{\partial}{\partial q_1} \\ \vdots \\ \frac{\partial}{\partial q_\mathcal{K}}, \end{pmatrix} \tag{21}$$

where $\nabla_{\mathbf{q}}^T = (\frac{\partial}{\partial q_1}, \ldots, \frac{\partial}{\partial q_\mathcal{K}})$, and likewise for $\nabla_{\mathbf{p}}$.

Furthermore, $[\hat{H}_l]_W$ in Eq. (19) is the Wigner transform of the MMST mapping Hamiltonian [Eq. (1)] associated with the lth bead, which can be shown[25,56,82] as

$$[\hat{H}_l]_W = \frac{P_l^2}{2m} + V_0(R_l) + V_e(R_l, \mathbf{q}_l, \mathbf{p}_l). \tag{22}$$

The detailed proof of the above Wigner transform is provided in the supplementary material. In the above equation, $V_0(R_l)$ is the state-independent potential evaluated at the lth nuclear bead position R_l, and $V_e(R_l, \mathbf{q}_l, \mathbf{p}_l)$ is the state-dependent potential that parametrically depends on R_l, $\mathbf{q}_l = ([q_l]_1, [q_l]_2, \ldots, [q_l]_\mathcal{K})$, and $\mathbf{p}_l = ([p_l]_1, [p_l]_2, \ldots, [p_l]_\mathcal{K})$, with the following expression:

$$V_e(R_l, \mathbf{q}_l, \mathbf{p}_l) = \frac{1}{2\hbar} \sum_{i,j=1}^{\mathcal{K}} \mathcal{V}_{ij}(R_l)([p_l]_i[p_l]_j + [q_l]_i[q_l]_j - \delta_{ij}\hbar). \tag{23}$$

The above expression is the classical limit of Eq. (4) (when replacing the mapping position and momentum operators with the corresponding values).

Now, using Eq. (19) with the detailed expressions of $\hat{\Lambda}_l$ [Eq. (20)] and $[\hat{H}_l]_W$ [Eq. (22)], the full Liouvillian[79] can be explicitly expressed as follows:

$$
\mathcal{L}^{[N]} = \sum_{l=1}^{N}\left[\frac{P_l}{m}\frac{\overrightarrow{\partial}}{\partial R_l} - \left[V_0(R_l) + V_e(R_l, \mathbf{q}_l, \mathbf{p}_l)\right]\frac{2}{\hbar}\sin \right.
$$
$$
\times \left(\frac{\hbar}{2}\frac{\overleftarrow{\partial}}{\partial R_l}\frac{\overrightarrow{\partial}}{\partial P_l}\right) + \frac{1}{\hbar}\left[\mathbf{p}_l^{\mathrm{T}}\mathcal{V}(R_l)\overrightarrow{\nabla}_{\mathbf{q}_l} - \mathbf{q}_l^{\mathrm{T}}\mathcal{V}(R_l)\overrightarrow{\nabla}_{\mathbf{p}_l}\right]
$$
$$
\times \cos\left(\frac{\hbar}{2}\frac{\overleftarrow{\partial}}{\partial R_l}\frac{\overrightarrow{\partial}}{\partial P_l}\right) + \frac{1}{4}\left[\overrightarrow{\nabla}_{\mathbf{q}_l}^{\mathrm{T}}\mathcal{V}(R_l)\overrightarrow{\nabla}_{\mathbf{q}_l}\right.
$$
$$
\left. + \overrightarrow{\nabla}_{\mathbf{p}_l}^{\mathrm{T}}\mathcal{V}(R_l)\overrightarrow{\nabla}_{\mathbf{p}_l}\right]\sin\left(\frac{\hbar}{2}\frac{\overleftarrow{\partial}}{\partial R_l}\frac{\overrightarrow{\partial}}{\partial P_l}\right)\right]. \tag{24}
$$

The above Liouvillian was first derived in Ref. 79, and the details of the derivation are also provided in Appendix A as well as in the supplementary material. In Eq. (24), $V_0(R_l)$ and $V_e(R_l, \mathbf{q}_l, \mathbf{p}_l)$ are defined in $[\hat{H}_l]_{\mathrm{W}}$ [Eq. (22)], and $\nabla_{\mathbf{q}_l}$ and $\nabla_{\mathbf{p}_l}$ are the gradient operators corresponding to the lth mapping bead's position and momentum, respectively, defined in Eq. (21). Furthermore, $\mathcal{V}(R_l)$ is the $(\mathcal{K}\times\mathcal{K})$ state-dependent potential energy matrix, which parametrically depends on the lth nuclear bead's position as follows:

$$
\mathcal{V}(R_l) = \begin{pmatrix} \mathcal{V}_{11}(R_l) & \mathcal{V}_{12}(R_l) & \cdots & \mathcal{V}_{1\mathcal{K}}(R_l) \\ \vdots & \vdots & & \vdots \\ \mathcal{V}_{\mathcal{K}1}(R_l) & \mathcal{V}_{\mathcal{K}2}(R_l) & \cdots & \mathcal{V}_{\mathcal{K}\mathcal{K}}(R_l) \end{pmatrix}. \tag{25}
$$

This generalized Liouvillian $\mathcal{L}^{[N]}$ governs the time evolution of N individual replicas connected through the zero-time quantum Boltzmann distribution. The exact Liouvillian $\mathcal{L}^{[N]}$ in Eq. (24) has three components. The first term $\mathcal{L}_{\mathrm{n}}^{[N]} = \sum_{l=1}^{N}\frac{P_l}{m}\frac{\overrightarrow{\partial}}{\partial R_l} - [V_0(R_l) + V_e(R_l, \mathbf{q}_l, \mathbf{p}_l)]\frac{2}{\hbar}\sin\left(\frac{\hbar}{2}\frac{\overleftarrow{\partial}}{\partial R_l}\frac{\overrightarrow{\partial}}{\partial P_l}\right)$ corresponds to an Ehrenfest-type evolution of the nuclear DOF,[83] with higher-order nuclear derivatives inside the sine function. The second term $\mathcal{L}_{\mathrm{e}}^{[N]} = \sum_{l=1}^{N}\frac{1}{\hbar}[\mathbf{p}_l^{\mathrm{T}}\mathcal{V}(R_l)\overrightarrow{\nabla}_{\mathbf{q}_l} - \mathbf{q}_l^{\mathrm{T}}\mathcal{V}(R_l)\overrightarrow{\nabla}_{\mathbf{p}_l}]\cos\left(\frac{\hbar}{2}\frac{\overleftarrow{\partial}}{\partial R_l}\frac{\overrightarrow{\partial}}{\partial P_l}\right)$ describes the electronic–nuclear couplings. The third term $\mathcal{L}_{\mathrm{h}}^{[N]} = \frac{1}{4}[\overrightarrow{\nabla}_{\mathbf{q}_l}^{\mathrm{T}}\mathcal{V}(R_l)\overrightarrow{\nabla}_{\mathbf{q}_l} + \overrightarrow{\nabla}_{\mathbf{p}_l}^{\mathrm{T}}\mathcal{V}(R_l)\overrightarrow{\nabla}_{\mathbf{p}_l}]\sin\left(\frac{\hbar}{2}\frac{\overleftarrow{\partial}}{\partial R_l}\frac{\overrightarrow{\partial}}{\partial P_l}\right)$ contains coupled higher-order derivatives of nuclear and electronic DOFs.[25,82,84] Note that there are no cross-bead interaction terms between electronic DOF and nuclear DOF in Eq. (24). The nuclear and mapping beads with the same bead index l interact with each other through $\mathcal{V}(R_l)$ [Eq. (25)]. If the system evolves on a single surface (electronically adiabatic regime), then Eq. (24) reduces to the conventional Wigner–Moyal series[79–81] for N independent replicas as follows:

$$
\mathcal{L}^{[N]} = \sum_{l=1}^{N}\left[\frac{P_l}{m}\frac{\overrightarrow{\partial}}{\partial R_l} - \frac{2}{\hbar}V_0(R_l)\cdot\sin\left(\frac{\hbar}{2}\frac{\overleftarrow{\partial}}{\partial R_l}\frac{\overrightarrow{\partial}}{\partial P_l}\right)\right]. \tag{26}
$$

On the other hand, if there is no nuclear DOF, then the Liouvillian [Eq. (24)] becomes

$$
\mathcal{L}^{[N]} = \sum_{l=1}^{N}\frac{1}{\hbar}[\mathbf{p}_l^{\mathrm{T}}\mathcal{V}\overrightarrow{\nabla}_{\mathbf{q}_l} - \mathbf{q}_l^{\mathrm{T}}\mathcal{V}\overrightarrow{\nabla}_{\mathbf{p}_l}]. \tag{27}
$$

It has been rigorously proved that the above Liouvillian in Eq. (27) preserves the electronic Rabi oscillations.[79]

D. Time-correlation function

With the detail expression of Liouvillian in Eq. (24), one can formally rewrite Eq. (14) as

$$
C_{AB}^{[N]}(t) = \frac{\alpha_N}{\mathcal{Z}}\int d\mathbf{R}\int d\mathbf{P}\int d\mathbf{q}\int d\mathbf{p}
$$
$$
\times [e^{-\beta\hat{H}}\hat{A}]_{\bar{N}}e^{\mathcal{L}^{[N]}t}[\hat{B}(0)]_N, \tag{28}
$$

where $\mathcal{L}^{[N]}$ is the Liouvillian in Eq. (24), $[e^{-\beta\hat{H}}\hat{A}]_{\bar{N}}$ is expressed in Eq. (15), and $[\hat{B}(0)]_N = \frac{1}{N}\sum_k[\hat{B}_k]_{\mathrm{W}}$ as shown in Eq. (17). Up to this point, there is no approximation in the expression of $C_{AB}^{[N]}(t)$ in Eq. (28).

We can further write $[e^{-\beta\hat{H}}\hat{A}]_{\bar{N}}$ [Eq. (15)] in the symmetric form as

$$
[e^{-\beta\hat{H}}\hat{A}]_{\bar{N}} = \frac{1}{2}\left[\hat{A}e^{-\beta\hat{H}} + e^{-\beta\hat{H}}\hat{A}\right]_{\bar{N}}
$$
$$
= \frac{1}{N}\sum_{k=1}^{N}\int d\mathbf{D}\int d\Delta\prod_{l=1}^{N}e^{\frac{i}{\hbar}P_lD_l}e^{\frac{i}{\hbar}\mathbf{p}_l\Delta_l}
$$
$$
\times\prod_{l\neq k}^{N}\langle\mathbf{q}_{l-1} - \tfrac{1}{2}\Delta_{l-1}, R_{l-1} - \tfrac{1}{2}D_{l-1}|\hat{\mathcal{P}}e^{-\beta_N\hat{H}}\hat{\mathcal{P}}
$$
$$
\times|\mathbf{q}_l + \tfrac{\Delta_l}{2}, R_l + \tfrac{D_l}{2}\rangle\langle\mathbf{q}_{k-1} - \tfrac{1}{2}\Delta_{k-1}, R_{k-1} - \tfrac{1}{2}D_{k-1}|
$$
$$
\times\tfrac{1}{2}(\hat{\mathcal{P}}e^{-\beta_N\hat{H}}\hat{\mathcal{P}}\hat{A} + \hat{A}\hat{\mathcal{P}}e^{-\beta_N\hat{H}}\hat{\mathcal{P}})|\mathbf{q}_k + \tfrac{\Delta_k}{2}, R_k + \tfrac{D_k}{2}\rangle. \tag{29}
$$

Using the property of the Wigner transform,[80,85] $[\hat{O}_1\hat{O}_2]_{\mathrm{W}} = [\hat{O}_1]_{\mathrm{W}}e^{-i\hat{\Lambda}\hbar/2}[\hat{O}_2]_{\mathrm{W}}$, with $\hat{\Lambda}$ defined in Eq. (20), we can rewrite Eq. (29) as

$$
[e^{-\beta\hat{H}}\hat{A}]_{\bar{N}} = [\hat{A}]_N\left[\sum_{l=1}^{N}\cos(\hat{\Lambda}_l\hbar/2)\right][e^{-\beta\hat{H}}]_{\bar{N}}, \tag{30}
$$

where $[\hat{A}]_N = \frac{1}{N}\sum_k[\hat{A}_k]_{\mathrm{W}}$, with

$$
[\hat{A}_k]_{\mathrm{W}} = \int dD_k\int d\Delta_k e^{\frac{i}{\hbar}P_kD_k}e^{\frac{i}{\hbar}\mathbf{p}_k\Delta_k}
$$
$$
\times\langle\mathbf{q}_k - \tfrac{1}{2}\Delta_k, R_k - \tfrac{1}{2}D_k|\hat{A}|\mathbf{q}_k + \tfrac{1}{2}\Delta_k, R_k + \tfrac{1}{2}D_k\rangle, \tag{31}
$$

and $\hat{\Lambda}_l$ is defined previously in Eq. (20). The multi-dimensional Wigner transformed Boltzmann operator $[e^{-\beta\hat{H}}]_{\bar{N}}$ is expressed as

$$
[e^{-\beta\hat{H}}]_{\bar{N}} = \int d\mathbf{D}\int d\Delta\prod_{l=1}^{N}e^{\frac{i}{\hbar}P_lD_l}e^{\frac{i}{\hbar}\mathbf{p}_l\Delta_l}
$$
$$
\times\langle q_{l-1} - \tfrac{1}{2}\Delta_{l-1}, R_{l-1} - \tfrac{1}{2}D_{l-1}|\hat{\mathcal{P}}e^{-\beta_N\hat{H}}\hat{\mathcal{P}}
$$
$$
\times|\mathbf{q}_l + \tfrac{1}{2}\Delta_l, R_l + \tfrac{1}{2}D_l\rangle. \tag{32}
$$

The detail derivation of Eq. (30) is provided in the supplementary material. Equation (30) can be further simplified under special cases, which are also elaborated in the supplementary material.

From this point and below, we assume that both operators $\hat{A}$ and $\hat{B}$ are linear functions of the nuclear position (R) such that Eq. (30) becomes $[e^{-\beta\hat{H}}\hat{A}]_{\tilde{N}} = [\hat{A}]_N \cdot [e^{-\beta\hat{H}}]_{\tilde{N}}$. With this simplification, we can write Eq. (28) as

$$C_{AB}^{[N]}(t) = \frac{\alpha_N}{\mathcal{Z}} \int d\mathbf{R} \int d\mathbf{P} \int d\mathbf{q} \int d\mathbf{p} [e^{-\beta\hat{H}}]_{\tilde{N}}[\hat{A}]_N e^{\mathcal{L}^{[N]}t}[\hat{B}]_N. \quad (33)$$

III. NORMAL MODE REPRESENTATION

We briefly introduced the normal mode coordinates of the free ring-polymer. The advantage of using normal modes is that with this set of global coordinates, one can conveniently describe the collective motion of individual beads.

A. Definition of the normal modes

The free ring-polymer Hamiltonian is defined as

$$H_{\text{rp}} = \sum_{l=1}^{N} \frac{P_l^2}{2m} + \frac{m}{2\beta_N^2\hbar^2}(R_l - R_{l-1})^2, \quad (34)$$

without an external potential. Normal modes are defined as the eigenvectors of the Hessian matrix of H_{rp}. Diagonalizing the Hessian matrix of H_{rp}, one obtains the eigenvalues ω_n^2, which are the square of following normal mode frequency:

$$\omega_n = \frac{2}{\beta_N\hbar} \sin\left(\frac{n\pi}{N}\right), \quad (35)$$

where $n = 0, \ldots, \pm(N-1)/2$ is the index of normal modes. The same diagonalization process also gives the eigenvectors T_{ln} of the Hessian matrix, which provides the relation between the primitive variables R_l, P_l and the normal mode variables $\mathcal{Q}_n, \mathcal{P}_n$ as follows:

$$\mathcal{Q}_n = \sum_{l=1}^{N} \frac{T_{ln}}{\sqrt{N}}R_l, \quad \mathcal{P}_n = \sum_{l=1}^{N} \frac{T_{ln}}{\sqrt{N}}P_l,$$

$$R_l = \sum_{n=-(N-1)/2}^{(N-1)/2} \sqrt{N}T_{ln}\mathcal{Q}_n, \quad P_l = \sum_{n=-(N-1)/2}^{(N-1)/2} \sqrt{N}T_{ln}\mathcal{P}_n. \quad (36)$$

Similar transformation should also apply to $\{\mathcal{D}_n\}$ and $\{D_l\}$. The extra $\sqrt{N}$ factor in Eq. (36) ensures that the $\mathcal{Q} = \{\mathcal{Q}_n\}$ converges in the limit of $N \to \infty$. For an odd N (to simplify our algebra), the transformation matrices are

$$T_{ln} = \begin{cases} \sqrt{\frac{1}{N}}, & n = 0 \\ \sqrt{\frac{2}{N}}\sin(2\pi ln/N), & n = 1, \ldots, (N-1)/2 \\ \sqrt{\frac{2}{N}}\cos(2\pi ln/N), & n = -1, \ldots, -(N-1)/2. \end{cases} \quad (37)$$

Under the normal mode representation, the free ring-polymer Hamiltonian [Eq. (34)] becomes

$$H_{\text{rp}} = \sum_{n=-(N-1)/2}^{(N-1)/2} \frac{\mathcal{P}_n^2}{2m} + \frac{1}{2}m\omega_n^2\mathcal{Q}_n^2. \quad (38)$$

Note that the ring-polymer spring terms are now simplified to uncoupled quadratic potentials; hence, the normal modes of the

free-ring polymer can be evolved analytically by simple harmonic motions.[86]

B. Time-correlation function with normal modes

It is straightforward to transform Eq. (33) into the normal mode coordinates by using the orthonormal transformations defined in Eq. (36), leading to

$$C_{AB}^{[N]}(t) = \frac{\alpha_N}{\mathcal{Z}} \int d\mathcal{Q} \int d\mathcal{P} \int d\mathbf{q} \int d\mathbf{p} [\hat{A}(0)]_N [e^{-\beta\hat{H}}]_{\tilde{N}} e^{\mathcal{L}^{[N]}t}[\hat{B}(0)]_N, \quad (39)$$

where we used the shorthand notation $\int d\mathcal{Q} = \prod_{n=-(N-1)/2}^{(N-1)/2} \int d\mathcal{Q}_n$ and likewise for $\int d\mathcal{P}$. Here, both the $\int d\mathbf{q}$ and $\int d\mathbf{p}$ are defined as before in bead's representation, such as $\int d\mathbf{q} = \prod_{l=1}^{N} \int d\mathbf{q}_l$ and likewise for $\int d\mathbf{p}$. Only nuclear coordinates $\mathbf{R}$ and $\mathbf{P}$ are transformed to their corresponding normal mode coordinates $\mathcal{Q}$ and $\mathcal{P}$, respectively.

Using new coordinates $\xi_l^{\pm}$ defined as

$$\xi_l^{\pm} = \sum_{n=-(N-1)/2}^{(N-1)/2} \sqrt{N}T_{ln}\mathcal{Q}_n \pm \sum_{n=-(N-1)/2}^{(N-1)/2} \frac{1}{2}\sqrt{N}T_{ln}\mathcal{D}_n \quad (40)$$

$[e^{-\beta\hat{H}}]_{\tilde{N}}$ is expressed in these normal mode coordinates as

$$[e^{-\beta\hat{H}}]_{\tilde{N}} = \int d\mathcal{D} \int d\Delta \left[\prod_{n=-(N-1)/2}^{(N-1)/2} e^{\frac{i}{\hbar}NP_n\mathcal{D}_n}\right]\prod_{l=1}^{N} e^{\frac{i}{\hbar}p_l\Delta_l}$$
$$\times \langle \mathbf{q}_{l-1} - \frac{1}{2}\Delta_{l-1}, \xi_{l-1}^{-}|\hat{\mathcal{P}}e^{-\beta_N\hat{H}}\hat{\mathcal{P}}|\mathbf{q}_l + \frac{\Delta_l}{2}, \xi_l^{+}\rangle. \quad (41)$$

Providing the operators $\hat{A} = \hat{B} = \hat{R}$, $[\hat{A}]_N$ can be expressed in normal mode coordinates as

$$[\hat{A}]_N = \frac{1}{N}\sum_{k=1}^{N}[\hat{A}_k]_{\text{W}} = \frac{1}{N}\sum_{k=1}^{N}R_k = \frac{1}{N}\sum_{k=1}^{N}\sum_n \sqrt{N}T_{kn}\mathcal{Q}_n, \quad (42)$$

and the same for $[\hat{B}]_N$.

Finally, we decompose the total Liouvillian $\mathcal{L}^{[N]}$ [Eq. (24)] into the following terms:

$$\mathcal{L}^{[N]} = \mathcal{L}_n^{[N]} + \mathcal{L}_e^{[N]} + \mathcal{L}_h^{[N]}, \quad (43)$$

and express each term with the normal mode coordinates as

$$\mathcal{L}_n^{[N]} = \sum_{n=-(N-1)/2}^{(N-1)/2}\left(\frac{\mathcal{P}_n}{m}\frac{\overrightarrow{\partial}}{\partial\mathcal{Q}_n}\right) - \frac{2N}{\hbar}\left[U_0^{[N]}(\mathcal{Q}) + U_e^{[N]}(\mathcal{Q},\mathbf{q},\mathbf{p})\right]$$
$$\times \sin\left(\frac{\hbar}{2N}\sum_{n=-(N-1)/2}^{(N-1)/2}\frac{\overleftarrow{\partial}}{\partial\mathcal{Q}_n}\frac{\overrightarrow{\partial}}{\partial\mathcal{P}_n}\right), \quad (44)$$

$$\mathcal{L}_e^{[N]} = \frac{1}{\hbar}\sum_{l=1}^{N}\left[\mathbf{p}_l^{\text{T}}\mathcal{V}(R_l(\mathcal{Q}))\overrightarrow{\nabla}_{\mathbf{q}_l} - \mathbf{q}_l^{\text{T}}\mathcal{V}(R_l(\mathcal{Q}))\overrightarrow{\nabla}_{\mathbf{P}_l}\right]$$
$$\times \cos\left(\frac{\hbar}{2N}\sum_{n=-(N-1)/2}^{(N-1)/2}\frac{\overleftarrow{\partial}}{\partial\mathcal{Q}_n}\frac{\overrightarrow{\partial}}{\partial\mathcal{P}_n}\right), \quad (45)$$

$$\mathcal{L}_{\mathrm{h}}^{[N]} = \frac{1}{4} \sum_{l=1}^{N} \left[\vec{\nabla}_{\mathbf{q}_l}^{\mathrm{T}} \mathcal{V}(R_l(\boldsymbol{\mathcal{Q}})) \vec{\nabla}_{\mathbf{q}_l} + \vec{\nabla}_{\mathbf{P}_l}^{\mathrm{T}} \mathcal{V}(R_l(\boldsymbol{\mathcal{Q}})) \vec{\nabla}_{\mathbf{P}_l} \right]$$

$$\times \sin\left(\frac{\hbar}{2N} \sum_{n=-(N-1)/2}^{(N-1)/2} \frac{\overleftarrow{\partial}}{\partial \mathcal{Q}_n} \frac{\overrightarrow{\partial}}{\partial \mathcal{P}_n} \right). \quad (46)$$

Here, the normal mode representation of $U_0^{[N]}(\boldsymbol{\mathcal{Q}})$, $U_e^{[N]}(\boldsymbol{\mathcal{Q}}, \mathbf{q}, \mathbf{p})$, and $\mathcal{V}(R_l(\boldsymbol{\mathcal{Q}}))$ is defined as

$$U_0^{[N]}(\boldsymbol{\mathcal{Q}}) = \frac{1}{N} \sum_{l=1}^{N} V_0 \left(\sum_{n=-(N-1)/2}^{(N-1)/2} \sqrt{N} T_{ln} \mathcal{Q}_n \right), \quad (47)$$

$$U_e^{[N]}(\boldsymbol{\mathcal{Q}}, \mathbf{q}, \mathbf{p}) = \frac{1}{N} \sum_{l=1}^{N} \sum_{i,j=1}^{\mathcal{K}} \mathcal{V}_{ij} \left(\sum_{n=-(N-1)/2}^{(N-1)/2} \sqrt{N} T_{ln} \mathcal{Q}_n \right)$$

$$\times \frac{1}{2\hbar} ([p_i]_l [p_j]_l + [q_i]_l [q_j]_l - \delta_{ij}\hbar), \quad (48)$$

$$\mathcal{V}(R_l(\boldsymbol{\mathcal{Q}})) = \begin{pmatrix} \mathcal{V}_{11}(R_l(\boldsymbol{\mathcal{Q}})) & \mathcal{V}_{12}(R_l(\boldsymbol{\mathcal{Q}})) & \cdots & \mathcal{V}_{1\mathcal{K}}(R_l(\boldsymbol{\mathcal{Q}})) \\ \vdots & \vdots & & \vdots \\ \mathcal{V}_{\mathcal{K}1}(R_l(\boldsymbol{\mathcal{Q}})) & \mathcal{V}_{\mathcal{K}2}(R_l(\boldsymbol{\mathcal{Q}})) & \cdots & \mathcal{V}_{\mathcal{K}\mathcal{K}}(R_l(\boldsymbol{\mathcal{Q}})) \end{pmatrix}, \quad (49)$$

where each $\mathcal{V}_{ij}(R_l(\boldsymbol{\mathcal{Q}}))$ term in Eq. (49) is expressed as

$$\mathcal{V}_{ij}(R_l(\boldsymbol{\mathcal{Q}})) = \mathcal{V}_{ij} \left(\sum_{n=-(N-1)/2}^{(N-1)/2} \sqrt{N} T_{ln} \mathcal{Q}_n \right). \quad (50)$$

Note that in Eq. (50), the $\mathcal{V}_{ij}(R_l(\boldsymbol{\mathcal{Q}}))$ term corresponds to the diabatic potential $\mathcal{V}_{ij}(R)$ evaluated at the lth bead position R_l in terms of the normal mode coordinate $R_l = \sum_n \sqrt{N} T_{ln} \mathcal{Q}_n$. Also note that each nuclear derivative term $\frac{\overleftarrow{\partial}}{\partial \mathcal{Q}_n} \frac{\overrightarrow{\partial}}{\partial \mathcal{P}_n}$ in the above Liouvillian does not couple to each other. They only couple to each other through the sine or cosine function in the Liouvillian.

IV. NON-ADIABATIC MATSUBARA DYNAMICS

A. Matsubara modes

We now consider the M lowest frequency normal modes for $M \ll N$ under the limit $N \to \infty$. They are commonly referred to as the Matsubara modes[38,69] of distinguishable particles, with the corresponding Matsubara frequency $\tilde{\omega}_n$ as follows:

$$\tilde{\omega}_n = \lim_{N \to \infty} \omega_n = \frac{2n\pi}{\beta\hbar}, \quad |n| \le (M-1)/2. \quad (51)$$

Figure 1 presents the normal mode frequency of the ring-polymer and the Matsubara region (blue box).

The superposition of these M Matsubara modes produces a smooth and differentiable function[69,87–89] in imaginary time $\tau = \beta_N \hbar l$ with $l = 1, \ldots, N$. On the other hand, if one considers both the Matsubara (M) and non-Matsubara (N-M) modes, then the imaginary-time path is not necessarily differentiable because the latter gives rise to non-smooth, non-differentiable distribution with respect to τ. It is a well-known fact that the Boltzmann operator guarantees that only
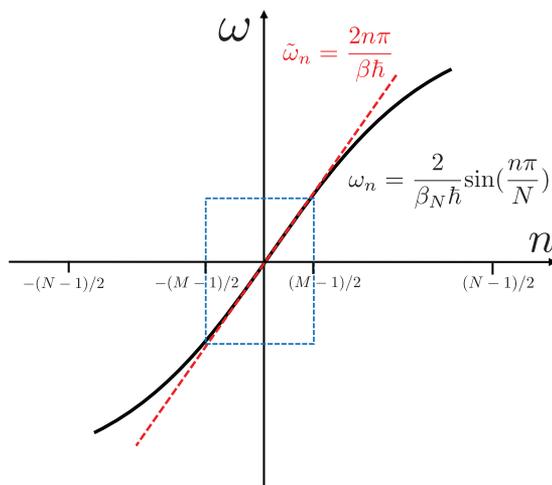
FIG. 1. The red dashed line presents the Matsubara frequency $\tilde{\omega}_n$ with $|n| \le (M-1)/2$, and the black line corresponds to the ring-polymer frequency ω_n with $|n| \le (N-1)/2$, where $M \ll N$. The blue dotted line corresponds to the "Matsubara" regime.

the Matsubara modes contribute to the initial Quantum Boltzmann Distribution (QBD)[38,90–92] (for electronically adiabatic systems). The previous work on Matsubara dynamics[69,73] has suggested that there is a close connection between the smoothness in imaginary-time and the dynamics that preserves the QBD.

Similar to the previous work of the Matsubara dynamics[69] (in Sec. IV C), we shall prove that one can integrate out all of the non-Matsubara modes from Eq. (39), giving rise to the exact initial quantum statistics, which corresponds to the generalized Kubo-transformed correlation function at $t = 0$ in the limit $M \to \infty$, $M \ll N$.[69,90–92] This suggests that only the smooth and imaginary-time differentiable Matsubara modes contribute to the initial quantum statistics for the electronically non-adiabatic systems as well.

B. Matsubara approximation

We separate each term in Eq. (43) into two parts, one contains the lowest M Matsubara modes and the other contains $(N - M)$ non-Matsubara modes,

$$\mathcal{L}^{[N]} = \mathcal{L}^{[M]} + \mathcal{L}^{[N-M]}, \quad (52)$$

where the Matsubara Liouvillian is $\mathcal{L}^{[M]}$ and the non-Matsubara Liouvillian $\mathcal{L}^{[N-M]}$ is expressed in Appendix A. Note that the non-Matsubara Liouvillian $\mathcal{L}^{[N-M]}$ does couple the non-Matsubara modes with the Matsubara modes, and both the Matsubara and non-Matsubara modes couple to the mapping DOFs through $\mathcal{L}^{[M]}$ and $\mathcal{L}^{[N-M]}$. Since the non-Matsubara modes do not contribute to the initial quantum statistics, it should be a good approximation (at least in short time) to ignore their presence in the quantum Liouvillian.[69] This approximation is achieved by neglecting the non-Matsubara modes in the derivatives of the corresponding Liouvillian terms

$\mathcal{L}^{[N]} \approx \mathcal{L}^{[M]} + \mathcal{O}(\mathcal{L}^{[N-M]})$, which effectively produces the decoupling between non-Matsubara modes from the Matsubara modes during the time evolution.

Similar to $\mathcal{L}^{[N]}$ in Eq. (43), we further decompose $\mathcal{L}^{[M]}$ into the following three terms:

$$\mathcal{L}^{[M]} = \mathcal{L}_n^{[M]} + \mathcal{L}_e^{[M]} + \mathcal{L}_h^{[M]}, \qquad (53)$$

where the detailed expressions for each term are

$$\mathcal{L}_n^{[M]} = \sum_{n=-(M-1)/2}^{(M-1)/2} \left(\frac{\mathcal{P}_n}{m} \frac{\overrightarrow{\partial}}{\partial \mathcal{Q}_n} \right) - \frac{2N}{\hbar} \left[U_0^{[N]}(\mathcal{Q}) + U_e^{[N]}(\mathcal{Q}, \mathbf{q}, \mathbf{p}) \right]$$
$$\times \sin\left(\frac{\hbar}{2N} \sum_{n=-(M-1)/2}^{(M-1)/2} \frac{\overleftarrow{\partial}}{\partial \mathcal{Q}_n} \frac{\overrightarrow{\partial}}{\partial \mathcal{P}_n} \right), \qquad (54)$$

$$\mathcal{L}_e^{[M]} = \frac{1}{\hbar} \sum_{l=1}^{N} \left[\mathbf{p}_l^{\mathrm{T}} \mathcal{V}(R_l(\mathcal{Q})) \overrightarrow{\nabla}_{\mathbf{q}_l} - \mathbf{q}_l^{\mathrm{T}} \mathcal{V}(R_l(\mathcal{Q})) \overrightarrow{\nabla}_{\mathbf{p}_l} \right]$$
$$\times \cos\left(\frac{\hbar}{2N} \sum_{n=-(M-1)/2}^{(M-1)/2} \frac{\overleftarrow{\partial}}{\partial \mathcal{Q}_n} \frac{\overrightarrow{\partial}}{\partial \mathcal{P}_n} \right), \qquad (55)$$

$$\mathcal{L}_h^{[M]} = \frac{1}{4} \sum_{l=1}^{N} \left[\overrightarrow{\nabla}_{\mathbf{q}_l}^{\mathrm{T}} \mathcal{V}(R_l(\mathcal{Q})) \overrightarrow{\nabla}_{\mathbf{q}_l} + \overrightarrow{\nabla}_{\mathbf{p}_l}^{\mathrm{T}} \mathcal{V}(R_l(\mathcal{Q})) \overrightarrow{\nabla}_{\mathbf{p}_l} \right]$$
$$\times \sin\left(\frac{\hbar}{2N} \sum_{n=-(M-1)/2}^{(M-1)/2} \frac{\overleftarrow{\partial}}{\partial \mathcal{Q}_n} \frac{\overrightarrow{\partial}}{\partial \mathcal{P}_n} \right). \qquad (56)$$

In Eqs. (54)–(56), we re-express $\mathcal{L}_n^{[N]}$, $\mathcal{L}_e^{[N]}$ and $\mathcal{L}_h^{[N]}$ in Matsubara modes under the $N \to \infty$ and $M \ll N$ limit. It is worth mentioning that the full Matsubara Liouvillian in Eq. (53) contains potential terms $U_0^{[N]}(\mathcal{Q})$, $U_e^{[N]}(\mathcal{Q}, \mathbf{q}, \mathbf{p})$, and $\mathcal{V}(R_l(\mathcal{Q}))$, which still depend on all N normal modes. On the other hand, all derivatives *only* involve M Matsubara modes.

C. Matsubara time-correlation function

Explicitly applying the Matsubara approximation for the Liouvillian $\mathcal{L}^{[N]} \approx \mathcal{L}^{[M]} + \mathcal{O}(\mathcal{L}^{[N-M]})$, the exact correlation function in Eq. (39) becomes an approximate correlation function $C_{AB}^{[N]}(t) \approx C_{AB}^{[M]}(t)$, whereas $C_{AB}^{[N]}(0) = C_{AB}^{[M]}(0)$ such that the initial QBD is exactly captured (see Sec. IV D). This approximate TCF, which is commonly referred to as the Matsubara TCF, is expressed as follows:

$$C_{AB}^{[M]}(t) = \lim_{N \to \infty} \frac{\alpha_N}{\mathcal{Z}} \int d\mathcal{Q} \int d\mathcal{P} \int d\mathbf{q} \int d\mathbf{p}$$
$$\times [\hat{A}(0)]_N [e^{-\beta \hat{H}}]_{\bar{N}} e^{\mathcal{L}^{[M]} t} [\hat{B}(0)]_N. \qquad (57)$$

Note that the above expression still depends on the non-Matsubara modes through the potentials in $\mathcal{L}^{[M]}$ and the QBD term $[e^{-\beta \hat{H}}]_{\bar{N}}$, and the integrals $\int d\mathcal{Q}$ and $\int d\mathcal{P}$ still include all normal modes (Matsubara and non-Matsubara). However, as non-Matsubara modes are decoupled from the Matsubara modes (because we have

dropped $\mathcal{L}^{[N-M]}$ in the Liouvillian), one can analytically integrate out all of the non-Matsubara modes under the limit of $N \to \infty$, $M \to \infty$, and $M \ll N$. The detailed derivation of this procedure is provided in Appendix C.

After integrating out the non-Matsubara modes in Eq. (57), we reach to the *first key result* of this paper as follows:

$$C_{AB}^{[M]}(t) = \frac{\alpha_N \cdot \alpha_M}{\mathcal{Z}_M} \int d\mathcal{Q}_M \int d\mathcal{P}_M \int d\mathbf{q} \int d\mathbf{p} A(\mathcal{Q}_M)$$
$$\times \Gamma(\mathcal{Q}_M, \mathbf{q}, \mathbf{p}) e^{-\beta(H_M(\mathcal{P}_M, \mathcal{Q}_M) - i\theta_M(\mathcal{P}_M, \mathcal{Q}_M))} e^{\mathcal{L}^{[M]} t} B(\mathcal{Q}_M), \qquad (58)$$

where the shorthand notations for the integrals are $\int d\mathcal{Q}_M = \prod_{n=-(M-1)/2}^{(M-1)/2} d\mathcal{Q}_n$, $\int d\mathbf{q} = \prod_{l=1}^{N} d\mathbf{q}_l$, and analogously for $\int d\mathcal{P}_M$ and $\int d\mathbf{p}$, and α_M is the following constant:

$$\alpha_M = \frac{\hbar^{(1-M)}}{[(M-1)/2]!^2}. \qquad (59)$$

Note that $C_{AB}^{[M]}(t)$ explicitly depends on the Matsubara modes $\mathcal{Q}_M$ and $\mathcal{P}_M$. The mapping DOFs, on the other hand, are still expressed in the primitive (bead) variables with all N copies because we did not make any approximation on them. The Liouvillian $\mathcal{L}^{[M]}$ has the same expression in Eqs. (54)–(56) but with following substitutions: $U_0^{[N]}(\mathcal{Q}) \to U_0^{[M]}(\mathcal{Q}_M)$, $U_e^{[N]}(\mathcal{Q}, \mathbf{q}, \mathbf{p}) \to U_e^{[N]}(\mathcal{Q}_M, \mathbf{q}, \mathbf{p})$, and $\mathcal{V}(R_l(\mathcal{Q})) \to \mathcal{V}(R_l(\mathcal{Q}_M))$, whereas these new potential only contains the Matsubara modes, for example,

$$U_0^{[M]}(\mathcal{Q}_M) = \lim_{N \to \infty} \frac{1}{N} \sum_{l=1}^{N} V_0\left(\sum_{n=-(M-1)/2}^{(M-1)/2} T_{ln} \sqrt{N} \mathcal{Q}_n \right), \qquad (60)$$

and similarly for $U_e^{[M]}(\mathcal{Q}_M, \mathbf{q}, \mathbf{p})$ and $\mathcal{V}(R_l(\mathcal{Q}_M))$ by replacing the sum in Eqs. (48) and (49) from originally over all modes to the sum over only the Matsubara modes. Note that the nuclear coordinate $R_l(\mathcal{Q}_M) = \sum_{n=-(M-1)/2}^{(M-1)/2} T_{ln} \sqrt{N} \mathcal{Q}_n$ is different than the original coordinate $R_l(\mathcal{Q}) = \sum_{n=-(N-1)/2}^{(N-1)/2} T_{ln} \sqrt{N} \mathcal{Q}_n$; the former one only contains a smooth (and imaginary-time differentiable) Matsubara mode, and later one contains all modes.

Furthermore, $H_M(\mathcal{P}_M, \mathcal{Q}_M)$ is expressed as

$$H_M(\mathcal{P}_M, \mathcal{Q}_M) = \sum_{n=-(M-1)/2}^{(M-1)/2} \frac{\mathcal{P}_n^2}{2m} + U_0^{[M]}(\mathcal{Q}_M), \qquad (61)$$

and the Matsubara phase θ_M takes the following form:

$$\theta_M(\mathcal{P}_M, \mathcal{Q}_M) = \sum_{n=-(M-1)/2}^{(M-1)/2} \mathcal{P}_n \tilde{\omega}_n \mathcal{Q}_{-n}, \qquad (62)$$

where $\tilde{\omega}_n = 2n\pi/\beta\hbar$ is the Matsubara frequency [Eq. (51)].

The $\Gamma(\mathcal{Q}_M, \mathbf{q}, \mathbf{p})$ term in Eq. (58) corresponds to the QBD originated from the electronic–nuclear interaction, which is expressed as follows:

$$\Gamma(\mathcal{Q}_M, \mathbf{q}, \mathbf{p}) = \phi \cdot e^{-\frac{g_N}{\hbar}} \mathrm{Tr}_e\left[\prod_{l=1}^{N} \left(\mathbf{C}_l - \frac{1}{2}\mathcal{I} \right) \mathcal{M}(R_l(\mathcal{Q}_M)) \right], \qquad (63)$$

where $\phi = 2^{(\mathcal{K}+1)N}/\hbar^N$, with $\mathcal{G}_N = \sum_{l=1}^{N}\left(\mathbf{q}_l^{\mathrm{T}}\mathbf{q}_l + \mathbf{p}_l^{\mathrm{T}}\mathbf{p}_l\right)$. Furthermore, $\mathbf{C}_l$ is expressed as

$$\mathbf{C}_l = \left(\mathbf{q}_l + i\mathbf{p}_l\right) \times \left(\mathbf{q}_l - i\mathbf{p}_l\right)^{\mathrm{T}}, \tag{64}$$

and $\mathcal{I}$ is the $(\mathcal{K} \times \mathcal{K})$ identity matrix. Note that $\left(\mathbf{C}_l - \frac{1}{2}\mathcal{I}\right)$ can be interpreted as the reduced density matrix associated with the lth bead.[57] In addition, $\mathcal{M}_{ij}(R_l(\mathcal{Q}_M))$ is the matrix element of the electronic Boltzmann operator expressed as follows:

$$\mathcal{M}_{ij}(R_l(\mathcal{Q}_M)) = \langle i|e^{-\beta_N \hat{V}_e(R_l(\mathcal{Q}_M))}|j\rangle, \tag{65}$$

where $\hat{V}_e(R_l(\mathcal{Q}_M)) = \sum_{ij}\mathcal{V}_{ij}(R_l(\mathcal{Q}_M))|i\rangle\langle j|$ is the state-dependent potential operator evaluated at the lth bead position R_l in terms of the Matsubara coordinate, $R_l = \sum_{n=-(M-1)/2}^{(M-1)/2}\sqrt{N}T_{ln}\mathcal{Q}_n$. The expression of Γ was originally derived in the MV-RPMD partition function expression.[57]

Finally, the partition function is expressed as

$$\mathcal{Z}_M = \alpha_N \cdot \alpha_M \int d\mathcal{Q}_M \int d\mathcal{P}_M \int d\mathbf{q} \int d\mathbf{p}$$
$$\times \Gamma(\mathcal{Q}_M, \mathbf{q}, \mathbf{p}) e^{-\beta(H_M(\mathcal{P}_M, \mathcal{Q}_M) - i\theta_M(\mathcal{P}_M, \mathcal{Q}_M))}. \tag{66}$$

Note that under the Matsubara limit $N \to \infty$, $M \to \infty$, and $M \ll N$, one can further Taylor expand the sine and cosine terms in Eqs. (54)–(56) as follows:

$$\lim_{N\to\infty}\lim_{M\ll N}\frac{2N}{\hbar}\sin\left(\frac{\hbar}{2N}\sum_{n=-(M-1)/2}^{(M-1)/2}\frac{\overleftarrow{\partial}}{\partial\mathcal{Q}_n}\frac{\overrightarrow{\partial}}{\partial\mathcal{P}_n}\right)$$
$$= \sum_{n=-(M-1)/2}^{(M-1)/2}\frac{\overleftarrow{\partial}}{\partial\mathcal{Q}_n}\frac{\overrightarrow{\partial}}{\partial\mathcal{P}_n} + \mathcal{O}\left(\frac{M^3\hbar^2}{N^2}\right), \tag{67}$$

$$\lim_{N\to\infty}\lim_{M\ll N}\cos\left(\frac{\hbar}{2N}\sum_{n=-(M-1)/2}^{(M-1)/2}\frac{\overleftarrow{\partial}}{\partial\mathcal{Q}_n}\frac{\overrightarrow{\partial}}{\partial\mathcal{P}_n}\right) = 1 + \mathcal{O}\left(\frac{M^2\hbar^2}{N^2}\right). \tag{68}$$

From the above analysis, it is clear that in the Matsubara space, the "effective" Planck constant inside the cosine term is scaled as

$$\hbar \to \frac{M}{N}\hbar \tag{69}$$

and scaled as $\sqrt{M}\frac{M}{N}\hbar$ for the sine term.[70] Thus, the Planck constant can be made as small as desired by properly choosing N and M. Hence, truncating Eqs. (54)–(56) to the first order of $\frac{\overleftarrow{\partial}}{\partial\mathcal{Q}_n}\frac{\overrightarrow{\partial}}{\partial\mathcal{P}_n}$ in the Matsubara space becomes *exact*.

These effective scalings of the Planck constant are the main advantage of the Matsubara dynamics, compared to the previous approaches (see Appendix D) that rely on the truncation of the Liouvillian based on the argument of a "small" $\hbar$, which may or may not be a good approximation. In addition, note that the arguments in Eqs. (67) and (68) do not work for non-Matsubara modes, as the error term becomes $\mathcal{O}((N-M)^3\hbar^2/N^2)$ for Eq. (67) and $\mathcal{O}((N-M)^2\hbar^2/N^2)$ for Eq. (68), which are no longer small under the $N \to \infty$ limit.

Therefore, under the Matsubara limit, we can exactly express the original Matsubara Liouvillian $\mathcal{L}^{[M]}$ [with the expression of Eqs. (54)–(56) with $\mathcal{Q}_M$] in the following *equivalent* expression:

$$\mathcal{L}^{[M]} = \sum_{n=-(M-1)/2}^{(M-1)/2}\frac{\mathcal{P}_n}{m}\frac{\overrightarrow{\partial}}{\partial\mathcal{Q}_n} - \sum_{n=-(M-1)/2}^{(M-1)/2}$$
$$\times\left(\frac{\partial U_0^{[M]}(\mathcal{Q}_M)}{\partial\mathcal{Q}_n} + \frac{\partial U_e^{[M]}(\mathcal{Q}_M, \mathbf{q}, \mathbf{p})}{\partial\mathcal{Q}_n}\right)\frac{\overrightarrow{\partial}}{\partial\mathcal{P}_n}$$
$$+ \frac{1}{\hbar}\sum_{l=1}^{N}\left(\mathbf{p}_l^{\mathrm{T}}\mathcal{V}(R_l(\mathcal{Q}_M))\overrightarrow{\nabla}_{\mathbf{q}_l} - \mathbf{q}_l^{\mathrm{T}}\mathcal{V}(R_l(\mathcal{Q}_M))\overrightarrow{\nabla}_{\mathbf{p}_l}\right), \tag{70}$$

where $U_e^{[M]}(\mathcal{Q}_M, \mathbf{q}, \mathbf{p})$ and $\mathcal{V}(R_l(\mathcal{Q}_M))$ are defined analogously as those in Eqs. (48) and (49), respectively, where $\mathcal{Q}_M$ are normal modes in the "Matsubara" domain such that $R_l(\mathcal{Q}_M) = \sum_{n=-(M-1)/2}^{(M-1)/2}T_{ln}\sqrt{N}\mathcal{Q}_n$.

In the above Matsubara Liouvillian, we have explicitly dropped the following higher order term [in $\mathcal{L}^{[M]}$, Eq. (53)]:

$$\mathcal{L}_{\mathrm{h}}^{[M]} = \frac{1}{8}\sum_{l=1}^{N}\frac{\hbar}{N}\sum_{n=-(M-1)/2}^{(M-1)/2}\left(\left[\overrightarrow{\nabla}_{\mathbf{q}_l}^{\mathrm{T}}\frac{\partial\mathcal{V}(R_l(\mathcal{Q}_M))}{\partial\mathcal{Q}_n}\overrightarrow{\nabla}_{\mathbf{q}_l}\right.\right.$$
$$\left.\left.+ \overrightarrow{\nabla}_{\mathbf{p}_l}^{\mathrm{T}}\frac{\partial\mathcal{V}(R_l(\mathcal{Q}_M))}{\partial\mathcal{Q}_n}\overrightarrow{\nabla}_{\mathbf{p}_l}\right]\right)\frac{\overrightarrow{\partial}}{\partial\mathcal{P}_n}, \tag{71}$$

where $\frac{\partial\mathcal{V}(R_l(\mathcal{Q}_M))}{\partial\mathcal{Q}_n}$ is a $(\mathcal{K} \times \mathcal{K})$ matrix, with the matrix element $\frac{\partial\mathcal{V}_{ij}(R_l(\mathcal{Q}_M))}{\partial\mathcal{Q}_n}$. This term accounts for the back action from the electronic DOF to the nuclear subsystem.[82] For each lth-bead term of $\mathcal{L}_{\mathrm{h}}^{[M]}$ [Eq. (56)], it is on the order of $\sim \mathcal{O}(\frac{M}{N}\hbar^0)$ [by noting the fact that $[\hat{q}, \hat{p}] = i\hbar$, thus q scales as $\sqrt{\hbar}$, which effectively cancels the $\hbar$ in Eq. (56)]. The overall scaling of the $\mathcal{L}_{\mathrm{h}}^{[M]}$ term is $\mathcal{O}(M\hbar^0)$. Thus, ignoring $\mathcal{L}_{\mathrm{h}}^{[M]}$ in the current formalism should be viewed as an additional approximation on top of the Matsubara approximation. However, one can potentially make this term as small as desired by choosing a different number of beads for the electronic and nuclear DOF.[55,93] The details of these discussions are provided in Appendix A [Eq. (A14)].

The Matsubara correlation function in Eq. (58) contains an imaginary phase factor θ_M [Eq. (62)], which potentially introduces a sign problem for a system that contains multi-dimensional nuclear DOF. In addition, Γ [Eq. (63)] will also potentially introduce a sign problem (because it is a complex quantity) if the system contains many electronic states $\mathcal{K}$ or if the TCF has a large number of beads N. On the other hand, the numerical experience suggests that Γ itself does not impose a severe sign problem for a two-state system[55,57–59] with a finite N (for $N \leq 16$). Hence, the most problematic phase is θ_M.

To eliminate the phase θ_M, one can perform the following transformation[73] on $\mathcal{P}$:

$$\bar{\mathcal{P}}_n = \mathcal{P}_n - im\tilde{\omega}_n\mathcal{Q}_{-n}. \tag{72}$$

Note that the above transformation has no effect on the centroid mode ($\mathcal{Q}_0$), as $\tilde{\omega}_0$ for the centroid is zero [see Eq. (35) when $n = 0$].

Applying the transformation $\mathcal{P}_n \rightarrow \tilde{\mathcal{P}}_n$ on the Liouvillian $\mathcal{L}^{[M]}$ in Eq. (70) (see the supplementary material for detailed derivations) leads to the following *complex* Liouvillian in terms $\{\tilde{\mathcal{P}}_M, \mathcal{Q}_M\}$:

$$\tilde{\mathcal{L}}^{[M]} = \mathcal{L}_{\text{RP}}^{[M]} + i\mathcal{L}_{\text{I}}^{[M]}, \tag{73}$$

where we denote the real part of $\tilde{\mathcal{L}}^{[M]}$ as the following non-adiabatic RPMD Liouvillian:

$$
\mathcal{L}_{\text{RP}}^{[M]} = \sum_{n=-(M-1)/2}^{(M-1)/2} \frac{\tilde{\mathcal{P}}_n}{m} \frac{\overrightarrow{\partial}}{\partial \mathcal{Q}_n} - \left[m\tilde{\omega}_n^2 \mathcal{Q}_n + \frac{\partial U_0^{[M]}(\mathcal{Q}_M)}{\partial \mathcal{Q}_n} \right. \\
\left. + \frac{\partial U_e^{[M]}(\mathcal{Q}_M, \mathbf{q}, \mathbf{p})}{\partial \mathcal{Q}_n} \right] \frac{\overrightarrow{\partial}}{\partial \tilde{\mathcal{P}}_n} + \frac{1}{\hbar} \sum_{l=1}^{N} \left[\mathbf{p}_l^{\text{T}} \mathcal{V}(R_l(\mathcal{Q}_M)) \overrightarrow{\nabla}_{\mathbf{q}_l} \right. \\
\left. - \mathbf{q}_l^{\text{T}} \mathcal{V}(R_l(\mathcal{Q}_M)) \overrightarrow{\nabla}_{\mathbf{p}_l} \right] \tag{74}
$$

and the imaginary part of $\tilde{\mathcal{L}}^{[M]}$ as

$$\mathcal{L}_{\text{I}}^{[M]} = \sum_{n=-(M-1)/2}^{(M-1)/2} \tilde{\omega}_n \left(\tilde{\mathcal{P}}_n \frac{\overrightarrow{\partial}}{\partial \tilde{\mathcal{P}}_{-n}} - \mathcal{Q}_n \frac{\overrightarrow{\partial}}{\partial \mathcal{Q}_{-n}} \right). \tag{75}$$

Note that there is no mapping related derivative in the above imaginary Liouvillian $\mathcal{L}_{\text{I}}^{[M]}$, and its impact on the electronic dynamics should only come from its influence on the nuclear dynamics, which, in turn, couples to the electronic mapping DOF via $\mathcal{L}_{\text{RP}}^{[M]}$. Thus, the influence from $\mathcal{L}_{\text{I}}^{[M]}$ to mapping variables is indirect.

Using the above Liouvillian $\tilde{\mathcal{L}}^{[M]}$, as well as applying the transformation in Eq. (72) to the quantum Boltzmann operator and the phase space integral in Eq. (58), one has the following equivalent expression of the non-adiabatic Matsubara TCF (see the supplementary material for detailed derivations):

$$
C_{AB}^{[M]}(t) = \frac{\alpha_N \cdot \alpha_M}{\mathcal{Z}_M} \left[\prod_{n=-(M-1)/2}^{(M-1)/2} \int_{a_n}^{b_n} d\tilde{\mathcal{P}}_n \right] \int d\mathcal{Q}_M \int d\mathbf{q} \\
\times \int d\mathbf{p} A(\mathcal{Q}_M) e^{-\beta H_M^{\text{RP}}(\tilde{\mathcal{P}}_M, \mathcal{Q}_M)} \Gamma(\mathcal{Q}_M, \mathbf{q}, \mathbf{p}) e^{\tilde{\mathcal{L}}^{[M]} t} B(\mathcal{Q}_M), \tag{76}
$$

where the original integral $\int_{-\infty}^{\infty} d\mathcal{P}_n$ becomes $\int_{a_n}^{b_n} d\tilde{\mathcal{P}}_n$, with the integration limits $a_n = -\infty - im\tilde{\omega}_n \mathcal{Q}_{-n}$ and $b_n = \infty - im\tilde{\omega}_n \mathcal{Q}_{-n}$. Furthermore, $\Gamma(\mathcal{Q}_M, \mathbf{q}, \mathbf{p})$ is defined previously in Eq. (63), and $H_M^{\text{RP}}(\tilde{\mathcal{P}}_M, \mathcal{Q}_M)$ is the ring-polymer Hamiltonian in the Matsubara domain expressed as follows:

$$H_M^{\text{RP}}(\tilde{\mathcal{P}}_M, \mathcal{Q}_M) = \sum_{n=-(M-1)/2}^{(M-1)/2} \left[\frac{\tilde{\mathcal{P}}_n^2}{2m} + \frac{m}{2} \tilde{\omega}_n^2 \mathcal{Q}_n^2 \right] + U_0^{[M]}(\mathcal{Q}_M). \tag{77}$$

Note that $C_{AB}^{[M]}(t)$ in Eq. (76) is exactly equivalent to Eq. (58), with the difference that Eq. (58) has a real Liouvillian and a complex nuclear phase, whereas Eq. (76) has a complex Liouvillian and a shifted nuclear momentum in the complex plane.

D. Exact quantum statistics with Matsubara modes

Equation (76) is perhaps even more difficult to evaluate than Eq. (58) through a trajectory-based approach due to the complex phase space integral and the complex Liouvillian. However, at $t = 0$, one can analytically perform the integration in the complex phase space. To this end, we use the standard contour integration procedure described in Ref. 73 and shift each imaginary $\tilde{\mathcal{P}}_n$ onto the real axis as $\int_{-\infty - im\tilde{\omega}_n \mathcal{Q}_{-n}}^{\infty - im\tilde{\omega}_n \mathcal{Q}_{-n}} d\tilde{\mathcal{P}}_n \exp[-\beta \frac{\tilde{\mathcal{P}}_n^2}{2m}] = \int_{-\infty}^{\infty} d\tilde{\mathcal{P}}_n \exp[-\beta \frac{\tilde{\mathcal{P}}_n^2}{2m}]$. The details are discussed in the supplementary material. This procedure allows us to write $C_{AB}^{[M]}(t)$ [Eq. (76)] at $t = 0$ as

$$
C_{AB}^{[M]}(0) = \frac{\alpha_N \cdot \alpha_M}{\mathcal{Z}_M^{\text{RP}}} \int d\tilde{\mathcal{P}}_M \int d\mathcal{Q}_M \int d\mathbf{q} \int d\mathbf{p} \\
\times A(\mathcal{Q}_M) B(\mathcal{Q}_M) \Gamma(\mathcal{Q}_M, \mathbf{q}, \mathbf{p}) e^{-\beta H_M^{\text{RP}}(\tilde{\mathcal{P}}_M, \mathcal{Q}_M)}, \tag{78}
$$

and similarly for the partition function $\mathcal{Z}_M^{\text{RP}} = \alpha_N \cdot \alpha_M \int d\tilde{\mathcal{P}}_M \int d\mathcal{Q}_M \int d\mathbf{q} \int d\mathbf{p} \Gamma(\mathcal{Q}_M, \mathbf{q}, \mathbf{p}) e^{-\beta H_M^{\text{RP}}(\tilde{\mathcal{P}}_M, \mathcal{Q}_M)}$, where the original complex phase space integral becomes pure real (by shifting the momentum integral from a complex axis to a pure real axis).

Note that at $t = 0$, $e^{\mathcal{L}t} = 1$, the Matsubara approximation [by discarding $L^{[N-M]}$, see Eq. (52)] no longer influences the value of $C_{AB}(t)$, and hence, $C_{AB}^{[M]}(0)$ gives the exact QBD (where the non-Matsubara modes can be analytically integrated out and do not influence QBD, as shown in Appendix B). Thus, the Boltzmann operator ensures that only the Matsubara modes contribute to the exact QBD. This is a well-known result for path-integral in the electronically adiabatic case.[38,69,90–92]

The expression of $C_{AB}^{[M]}(0)$ in Eq. (78) is reminiscent of the mapping variable (MV)-RPMD partition function expression,[57] with the difference that Eq. (78) is expressed in the Matsubara space. On the other hand, one can directly obtain the MV-RPMD formalism from the generalized Kubo-transformed TCF by taking the $t \rightarrow 0$ limit of $C_{AB}^{[N]}(t)$ in Eq. (14) using the standard path-integral technique, resulting in

$$
C_{AB}^{[N]}(0) = \frac{\alpha_N^0}{\mathcal{Z}} \int d\mathbf{R} \int d\tilde{\mathbf{P}} \int d\mathbf{q} \int d\mathbf{p} A(\mathbf{R}_N) B(\mathbf{R}_N) \Gamma(\mathbf{R}, \mathbf{q}, \mathbf{p}) e^{-\beta H_N^{\text{RP}}(\tilde{\mathbf{P}}, \mathbf{R})}, \tag{79}
$$

where $\Gamma(\mathbf{R}, \mathbf{q}, \mathbf{p}) = \phi \cdot e^{-\frac{\mathcal{G}_N}{\hbar}} \text{Tr}_e \left[\prod_{l=1}^{N} (\mathbf{C}_l - \frac{1}{2}\mathcal{I})\mathcal{M}(R_l) \right]$ and $H_N^{\text{RP}}(\tilde{\mathbf{P}}, \mathbf{R})$ is the standard ring-polymer Hamiltonian in the primitive nuclear coordinate $H_N^{\text{RP}}(\tilde{\mathbf{P}}, \mathbf{R}) = \frac{1}{N} \sum_{l=1}^{N} \left[\frac{\tilde{P}_l^2}{2m} + \frac{m}{2\beta_N^2 \hbar^2}(R_l - R_{l-1})^2 + V_0(R_l) \right]$. Note that the $\int d\tilde{\mathbf{P}}$ integral in Eq. (79) was reintroduced from a constant (which can be re-expressed as the nuclear momentum Gaussian integral) through the standard path-integral procedure, which *does not* appear in the Liouvillian of $C_{AB}^{[N]}(t)$ [Eq. (28)]. On the other hand, the $d\tilde{\mathcal{P}}_M$ in $C_{AB}^{[M]}(t)$ [Eq. (76)] is the *actual* nuclear momentum integral that appears in both initial QBD and the Liouvillian, which was introduced through the multi-dimensional Wigner transform in Eq. (13).

Thus, $C_{AB}^{[N]}(0)$ in Eq. (79) and $C_{AB}^{[M]}(0)$ give the same exact quantum statistics,

$$\lim_{N\to\infty} C_{AB}^{[N]}(0) = \lim_{\substack{N\to\infty \\ M\to\infty}} \lim_{M\ll N} C_{AB}^{[M]}(0), \tag{80}$$

such that the same quantum statistics can either be achieved under a large N limit for regular path-integral ring-polymer or under the large M limit for the Matsubara modes. The adiabatic limit of the above relation is a well-known result.[38,69,90–92] Here, we explicitly demonstrate that this is also true for the non-adiabatic scenario. Note that under the adiabatic limit, the convergence of $C_{AB}^{[N]}(0)$ with respect to an increasing N is much faster[38,69] than the convergence of $C_{AB}^{[M]}(0)$ with respect to M (under the $N\to\infty$ as well as $M\ll N$ limit). We have not performed any numerical test to confirm that this is also true for the non-adiabatic scenario, but we conjecture that this is the case.

V. NON-ADIABATIC RING-POLYMER MOLECULAR DYNAMICS

The analytic continuation procedure performed in $C_{AB}^{[M]}(0)$ [Eq. (78)] is not valid when $t > 0$ in general. This is because that when the dynamics is propagated with $\bar{\mathcal{P}}_M$ and $\mathcal{Q}_M$ in the complex plane, one may encounter well-known singularities,[70,94] leading to a diverging $e^{\mathcal{L}_I^{[M]}t}B(\mathcal{Q}_M)$ such that the function of $\bar{\mathcal{P}}_n$ no longer approaches to 0 when $\bar{\mathcal{P}}_n \to \pm\infty$ from the real axis and breaks the contour integral trick (outlined in the supplementary material).

On the other hand, as proposed in the original Matsubara dynamics work,[73] it is possible to follow a path along which each $\bar{\mathcal{P}}_n$ is partially moved toward the real axis and $\mathcal{L}_I^{[M]}$ is partially discarded so the contour integration trick remains valid, and at the end of the path, $\mathcal{L}_I^{[M]}$ has been completely discarded and $\bar{\mathcal{P}}_n$ has reached the real axis.[70] Applying this approximation on the non-adiabatic Matsubara dynamics leads to the following non-adiabatic RPMD approach, which is the *second key result* of this paper as follows:

$$C_{AB}^{[M]}(t) \approx \frac{\alpha_N \cdot \alpha_M}{\mathcal{Z}_M^{\mathrm{RP}}} \int d\bar{\mathcal{P}}_M \int d\mathcal{Q}_M \int d\mathbf{q} \int d\mathbf{p}$$
$$\times A(\mathcal{Q}_M) e^{-\beta H_M^{\mathrm{RP}}(\bar{\mathcal{P}}_M, \mathcal{Q}_M)} \Gamma(\mathcal{Q}_M, \mathbf{q}, \mathbf{p}) e^{\mathcal{L}_{\mathrm{RP}}^{[M]}t} B(\mathcal{Q}_M). \tag{81}$$

In the above NRPMD expression of TCF, the initial distribution is governed by $e^{-\beta H_M^{\mathrm{RP}}(\bar{\mathcal{P}}_M, \mathcal{Q}_M)} \Gamma(\mathcal{Q}_M, \mathbf{q}, \mathbf{p})$, whereas the quantum dynamics is propagated by the Liouvillian $\mathcal{L}_{\mathrm{RP}}^{[M]}$ [Eq. (74)].

If we choose to use ring-polymer normal mode frequency instead of the Matsubara frequency in the above expression (and denote $\bar{\mathcal{P}}_n$ as $\mathcal{P}_n$ for simplicity) in Eq. (81), it then gives the non-adiabatic RPMD expression for TCF as follows:

$$C_{AB}^{\mathrm{NRP}}(t) = \frac{\alpha_N \cdot \alpha_M}{\mathcal{Z}_N^{\mathrm{RP}}} \int d\mathcal{P} \int d\mathcal{Q} \int d\mathbf{q} \int d\mathbf{p}$$
$$\times \Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p}) e^{-\beta H_N^{\mathrm{RP}}(\mathcal{P}, \mathcal{Q})} A(\mathcal{Q}) e^{\mathcal{L}_{\mathrm{RP}}^{[N]}t} B(\mathcal{Q}), \tag{82}$$

where $\mathcal{Z}_N^{\mathrm{RP}}$ is analogously defined as $\mathcal{Z}_M^{\mathrm{RP}}$ with normal modes instead of Matsubara modes, $\Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p}) = \phi \cdot e^{-\frac{g_N}{\hbar}} \mathrm{Tr}_e[\prod_{l=1}^N (\mathbf{C}_l - \frac{1}{2}\mathcal{I})\mathcal{M}(R_l)]$ [see Eq. (63) for detailed expressions], H_N^{RP} is the state-independent

ring-polymer Hamiltonian (in the initial quantum Boltzmann operator) expressed as $H_N^{\mathrm{RP}}(\mathcal{P}, \mathcal{Q}) = \sum_n \left[\frac{\mathcal{P}_n^2}{2m} + \frac{1}{2} m\omega_n^2 \mathcal{Q}_n^2\right] + U_0^{[N]}(\mathcal{Q})$, and the NRPMD Liouvillian is

$$\mathcal{L}_{\mathrm{RP}}^{[N]} = \sum_{n=-(N-1)/2}^{(N-1)/2} \frac{\mathcal{P}_n}{m} \frac{\overrightarrow{\partial}}{\partial \mathcal{Q}_n} - \left[m\omega_n^2 \mathcal{Q}_n + \frac{\partial U_0^{[N]}(\mathcal{Q})}{\partial \mathcal{Q}_n}\right.$$
$$+ \left.\frac{\partial U_e^{[N]}(\mathcal{Q}, \mathbf{q}, \mathbf{p})}{\partial \mathcal{Q}_n}\right] \frac{\overrightarrow{\partial}}{\partial \mathcal{P}_n} + \frac{1}{\hbar} \sum_{l=1}^N \left[\mathbf{p}_l^{\mathrm{T}} \mathcal{V}(R_l(\mathcal{Q})) \overrightarrow{\nabla}_{\mathbf{q}_l}\right.$$
$$- \left.\mathbf{q}_l^{\mathrm{T}} \mathcal{V}(R_l(\mathcal{Q})) \overrightarrow{\nabla}_{\mathbf{p}_l}\right], \tag{83}$$

which corresponds to the following NRPMD Hamiltonian[54] in the primitive nuclear coordinate as follows:

$$H_N^{\mathrm{NRP}}(\mathbf{P}, \mathbf{R}) = \frac{1}{N} \sum_{l=1}^N \left[\frac{P_l^2}{2m} + \frac{m}{2\beta_N^2 \hbar^2}(R_l - R_{l-1})^2 + V_0(R_l)\right.$$
$$+ \left.\frac{1}{2\hbar} \sum_{i,j=1}^{\mathcal{K}} \mathcal{V}_{ij}(R_l)([p_l]_i[p_l]_j + [q_l]_i[q_l]_j - \delta_{ij}\hbar)\right]. \tag{84}$$

Note that the frequency ω_n is the ring-polymer normal mode frequency [Eq. (35)], whereas $\tilde{\omega}_n$ in Eq. (81) is the Matsubara frequency [Eq. (51)].

Dropping the imaginary part of the Liouvillian $i\mathcal{L}_I^{[M]}$, unfortunately, introduces spurious frequency shift to the non-centroid normal modes, leading to the well-known "spurious resonances" problem in RPMD when there are resonances between ring-polymer frequencies and physical frequencies (such as stretching vibrations).[86,95] This problem can be partially resolved by replacing $i\mathcal{L}_I^{[M]}$ with an effective white-noise Fokker–Planck operator,[96] leading to the thermostatting technique for RPMD.[86,95,96] This thermostatting approach has also been recently incorporated into the NRPMD approach.[56]

Note that the NRPMD approach [Eq. (82)] in the current work [which can be viewed as an approximation of the non-adiabatic Matsubara dynamics $C_{AB}^{[M]}$ through Eq. (81)] samples the same initial distribution of MV-RPMD $\Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p}) e^{-\beta H_N^{\mathrm{RP}}(\mathcal{P}, \mathcal{Q})}$ whereas using the NRPMD Liouvillian in Eq. (83) [or NRPMD Hamiltonian[54] in Eq. (84)] to propagate the dynamics. For a finite N, NRPMD does not preserve the QBD[54,55,97] due to the fact that two different effective Hamiltonians are used for the initial sampling [$\tilde{H}_N^{\mathrm{RP}} = H_N^{\mathrm{RP}}(\mathcal{P}, \mathcal{Q}) - \frac{1}{\beta} \ln|\Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p})|$] and for the dynamical propagation [H_N^{NRP} in Eq. (84)], respectively. However, it was conjectured that under the $N\to\infty$ limit, NRPMD will preserve QBD.[54,97] On the other hand, because the MMST Hamiltonian structure is preserved in the dynamics propagation, NRPMD gives the exact electronic Rabi oscillations when the nuclear dynamics is decoupled from the electronic DOF.[54,55,79] This will be discussed further in Sec. VI as well as in Appendix C.

Our analytical work provides a theoretical justification for the recent numerical success of NRPMD,[54,55] which was initially proposed as a model non-adiabatic path-integral dynamics.[54,55] The connections and differences between the current formalism in

Eq. (82) and the original NRPMD method[54] as well as MV-RPMD approach[57] are discussed in Appendix E.

VI. QUANTUM DETAILED BALANCE

We want to discuss the quantum detailed balance in our current formalism. For a system under the thermal equilibrium, the quantum expectation value does not change in time, $\langle \hat{A}(t) \rangle = \langle \hat{A}(0) \rangle$. Similarly, one can prove that

$$C_{AB}^{K}(t) = C_{BA}^{K}(-t) \tag{85}$$

for Kubo-transformed TCF defined in Eq. (5). The above relation is commonly referred to as the condition for satisfying the detailed balance.

The detailed balance condition is also true for the generalized Kubo-transformed correlation function $C_{AB}^{[N]}(t)$ [Eq. (10)]. This relation will also be rigorously satisfied for $C_{AB}^{[N]}(t)$ in Eq. (14) (after performing the Wigner transform and replace quantum propagator with the Liouvillian $\mathcal{L}^{[N]}$) since Eq. (14) is quantum mechanically exact. The key to achieve the detailed balance condition is

$$\mathcal{L}^{[N]}[e^{-\beta H}]_{\tilde{N}} = 0, \tag{86}$$

where $\mathcal{L}^{[N]}$ is the exact Liouvillian in Eq. (24) and $[e^{-\beta H}]_{\tilde{N}}$ is the linked Wigner transformed quantum Boltzmann operator in Eq. (32), which is also exact quantum mechanically.

The Matsubara partition function in Eq. (66) is expressed as

$$\mathcal{Z}_M = \alpha_N \cdot \alpha_M \int d\mathcal{Q}_M \int d\mathcal{P}_M \int d\mathbf{q} \int d\mathbf{p}$$
$$\times \frac{\Gamma}{|\Gamma|} \cdot e^{-\tilde{\beta}\tilde{H}_M(\mathcal{P}_M, \mathcal{Q}_M)} e^{i\beta\theta_M(\mathcal{P}_M, \mathcal{Q}_M)}, \tag{87}$$

where the new effective Hamiltonian $\tilde{H}_M$ is expressed as

$$\tilde{H}_M(\mathcal{P}_M, \mathcal{Q}_M, \mathbf{q}, \mathbf{p}) = H_M(\mathcal{P}_M, \mathcal{Q}_M) - \frac{1}{\beta} \ln |\Gamma(\mathcal{Q}_M, \mathbf{q}, \mathbf{p})|$$
$$= \sum_{n=-(M-1)/2}^{(M-1)/2} \frac{\mathcal{P}_n^2}{2m} + U_0^{[M]}(\mathcal{Q}_M)$$
$$- \frac{1}{\beta} \ln |\Gamma(\mathcal{Q}_M, \mathbf{q}, \mathbf{p})|. \tag{88}$$

One can prove that for the Matsubara phase, $\theta_M(\mathcal{P}_M, \mathcal{Q}_M)$ is a conserved quantity of the non-adiabatic Matsubara Liouvillian $\mathcal{L}^{[M]}$ in Eq. (70) such that

$$\mathcal{L}^{[M]}\theta_M = \sum_{n=-(M-1)/2}^{(M-1)/2} \frac{\mathcal{P}_n}{m} \frac{\partial\theta_M}{\partial\mathcal{Q}_n} - \sum_{n=-(M-1)/2}^{(M-1)/2} \left(\frac{\partial U_0^{[M]}}{\partial\mathcal{Q}_n} + \frac{\partial U_e^{[M]}}{\partial\mathcal{Q}_n} \right) \frac{\partial\theta_M}{\partial\mathcal{P}_n}$$
$$= \left(\frac{\partial U_0^{[M]}}{\partial\mathcal{Q}_n} + \frac{\partial U_e^{[M]}}{\partial\mathcal{Q}_n} \right) \frac{\partial\mathcal{Q}_n}{\partial\tau} = 0, \tag{89}$$

where we have used the fact that in the Matsubara domain, $\frac{\partial\mathcal{Q}_n}{\partial\tau} = -\tilde{\omega}_n\mathcal{Q}_{-n}$ (see proof in the supplementary material), where τ is

the imaginary time, as well as $\frac{\partial U_0^{[M]}}{\partial\tau} = \frac{\partial U_e^{[M]}}{\partial\tau} = 0$, due to the cyclic symmetry. Also note that the mapping part of the Liouvillian ($\vec{\nabla}_{\mathbf{p}_l}$ and $\vec{\nabla}_{\mathbf{q}_l}$ inside $\mathcal{L}^{[M]}$) does not act on $\theta_M(\mathcal{P}_M, \mathcal{Q}_M)$. This results in Eq. (89), which can be viewed as a generalization of the original proof in the adiabatic Matsubara dynamics.[69] We further numerically demonstrate that the Matsubara phase is a conserved quantity of the non-adiabatic Matsubara Liouvillian $\mathcal{L}^{[M]}$ [Eq. (70)]. Figure 2 presents the time evolution of Matsubara phase $\theta_M(\mathcal{P}_M, \mathcal{Q}_M)$ along a single trajectory. Figures 2(a) and 2(b) correspond to model systems I and II, respectively, where the details of the model Hamiltonian [Eq. (E7)] and parameters (Table I) are provided in Appendix E. Here, we choose $M = 3$ and keep increasing the number of ring-polymer beads N. Clearly, the variation in the Matsubara phase θ_M along a given trajectory flattens as an increasing N, indicating that at $N \to \infty$ limit, the Matsubara phase is preserved by $\mathcal{L}^{[M]}$. This numerical behavior of θ_M in the state-dependent systems presented in Fig. 2 is in close resemblance to those previous numerical tests in state-independent systems.[69]

Unfortunately, we do not know whether the non-adiabatic Matsubara Liouvillian $\mathcal{L}^{[M]}$ commutes with the Hamiltonian in Eq. (88), i.e., the validity of the following relation:

$$\mathcal{L}^{[M]}\tilde{H}_M(\mathcal{P}_M, \mathcal{Q}_M, \mathbf{q}, \mathbf{p}) \overset{?}{=} 0, \tag{90}$$
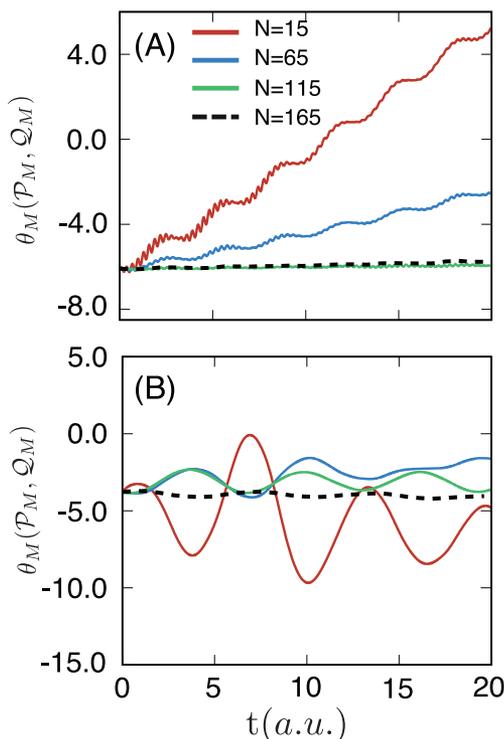
FIG. 2. Time evolution of $\theta_M(\mathcal{P}_M, \mathcal{Q}_M)$ [Eq. (62)] along a single trajectory for model I [panel (a)] and model II [(panel (b)], with $M = 3$ and $N = 15$ (red line), $N = 65$ (blue line), $N = 115$ (green line), and $N = 165$ (black dashed line). Details of the model systems are provided in Appendix E.

as well as for the phase $\mathcal{L}^{[M]}(\Gamma/|\Gamma|) \overset{?}{=} 0$. Thus, at this moment, we are not sure if non-adiabatic Matsubara dynamics preserves the QBD governed by $\mathcal{Z}_M$ for a general non-adiabatic system. As opposed to the original Matsubara approximation, which preserves the QBD for adiabatic systems, the current non-adiabatic Matsubara formalism seems to go against the spirit of the original Matsubara approximation, until one can formally prove Eq. (90).

However, when $V_0(\hat{R})$ is harmonic and when $\mathcal{V}_{ij}(\hat{R})$ is a linear function of R (i.e., an electronic subsystem linearly coupled to a harmonic environment, such as the spin-boson model), only the following terms from the exact quantum Liouvillian in Eqs. (44)–(46) influence the quantum dynamics:

$$\mathcal{L}_n^{[N]} = \sum_{n=-(N-1)/2}^{(N-1)/2} \left(\frac{\mathcal{P}_n}{m} \frac{\overrightarrow{\partial}}{\partial \mathcal{Q}_n} \right) - \left[U_0^{[N]}(\boldsymbol{\mathcal{Q}}) \right.$$
$$\left. + U_e^{[N]}(\boldsymbol{\mathcal{Q}},\mathbf{q},\mathbf{p}) \right] \cdot \left(\sum_{n=-(N-1)/2}^{(N-1)/2} \frac{\overleftarrow{\partial}}{\partial \mathcal{Q}_n} \frac{\overrightarrow{\partial}}{\partial \mathcal{P}_n} \right),$$

$$\mathcal{L}_e^{[N]} = \frac{1}{\hbar} \sum_{l=1}^{N} \left[\mathbf{p}_l^{\mathrm{T}} \mathcal{V}(R_l(\boldsymbol{\mathcal{Q}})) \overrightarrow{\nabla}_{\mathbf{q}_l} - \mathbf{q}_l^{\mathrm{T}} \mathcal{V}(R_l(\boldsymbol{\mathcal{Q}})) \overrightarrow{\nabla}_{\mathbf{p}_l} \right],$$

$$\mathcal{L}_h^{[N]} = \frac{1}{4} \sum_{l=1}^{N} \left[\overrightarrow{\nabla}_{\mathbf{q}_l}^{\mathrm{T}} \mathcal{V}(R_l(\boldsymbol{\mathcal{Q}})) \overrightarrow{\nabla}_{\mathbf{q}_l} + \overrightarrow{\nabla}_{\mathbf{p}_l}^{\mathrm{T}} \mathcal{V}(R_l(\boldsymbol{\mathcal{Q}})) \overrightarrow{\nabla}_{\mathbf{p}_l} \right]$$
$$\times \left(\frac{\hbar}{2N} \sum_{n=-(N-1)/2}^{(N-1)/2} \frac{\overleftarrow{\partial}}{\partial \mathcal{Q}_n} \frac{\overrightarrow{\partial}}{\partial \mathcal{P}_n} \right).$$

In the above Liouvillian, different nuclear normal modes are completely decoupled from each other such that these non-Matsubara modes can be completely integrated out without making any approximation. Thus, under this special limit, the non-Matsubara modes do not contribute to the QBD, and their time evolution is also decoupled from Matsubara modes. Thus, for the special case of the electronic subsystem linearly coupled to the harmonic environment, the non-adiabatic Matsubara dynamics is exact, hence strictly preserving QBD. Furthermore, when electronic and nuclear DOFs are completely decoupled such that the Hamiltonian of the system can be written as $\hat{H} = \frac{\hat{p}^2}{2m} + V_0(\hat{R}) + \sum_{i,j=1}^{\mathcal{K}} \mathcal{V}_{ij}|i\rangle\langle j| = \hat{H}_0 + \hat{V}_e$, the QBD is also preserved by $\mathcal{L}^{[M]}$ (see detailed discussions in Appendix C) because that the following relation

$$\sum_{l=1}^{N} \left[\mathbf{p}_l^{\mathrm{T}} \mathcal{V} \overrightarrow{\nabla}_{\mathbf{q}_l} \Gamma(\mathbf{p},\mathbf{q}) - \mathbf{q}_l^{\mathrm{T}} \mathcal{V} \overrightarrow{\nabla}_{\mathbf{p}_l} \Gamma(\mathbf{p},\mathbf{q}) \right] = 0 \tag{91}$$

is satisfied by both $\mathcal{L}^{[N]}$ and $\mathcal{L}^{[M]}$, where $\Gamma(\mathbf{q},\mathbf{p})$ no longer depends upon $\mathcal{Q}_n$ due to the nuclear position independent electronic potential $\hat{V}_e = \sum_{i,j} \mathcal{V}_{ij}|i\rangle\langle j|$. Note that the quantum–classical Liouville equation (QCLE)[82,98] is also exact for the spin-boson type of problem, strictly preserving the QBD under this special case.[98] However, QCLE does not always preserve QBD under the decoupled limit, especially when the nuclear potential is not harmonic.[98]

For a general case beyond this special limit, we want to explore the conditions that when non-adiabatic Matsubara dynamics preserve the QBD. By requiring Eq. (90), it leads to the following condition:

$$\left[\frac{1}{|\Gamma|} \frac{\partial|\Gamma|}{\partial \mathcal{Q}_n} + \beta \frac{\partial U_e^{[M]}}{\partial \mathcal{Q}_n} \right] \frac{\mathcal{P}_n}{m}$$
$$= -\sum_l \frac{1}{\hbar|\Gamma|} \left[\mathbf{p}_l^{\mathrm{T}} \mathcal{V}(R_l) \overrightarrow{\nabla}_{\mathbf{q}_l} |\Gamma| - \mathbf{q}_l^{\mathrm{T}} \mathcal{V}(R_l) \overrightarrow{\nabla}_{\mathbf{p}_l} |\Gamma| \right], \tag{92}$$

and requiring $\mathcal{L}^{[M]}(\Gamma/|\Gamma|) = 0$ leads to the corresponding condition for the phase. Note that the above relation in Eq. (92) is the sufficient condition for preserving the QBD, whereas the necessary one requires $\sum_n$ for all Matsubara modes in the above equation. Of course, for the electronic–nuclear decoupled case, both $\frac{\partial|\Gamma|}{\partial \mathcal{Q}_n} = 0$ and $\frac{\partial \mathcal{V}}{\partial \mathcal{Q}_n} = 0$, as well as Eq. (91) are satisfied; hence, $\mathcal{L}^{[M]}$ preserves the QBD. Beyond this special case, we do not know if Eq. (92) is always satisfied.

We further investigate the validity of the condition in Eq. (90) numerically. Figure 3 presents the time evolution of $\tilde{H}_M(\boldsymbol{\mathcal{P}}_M,\boldsymbol{\mathcal{Q}}_M,\mathbf{q},\mathbf{p})$ along a single classical trajectory, propagated with $\mathcal{L}^{[M]}$. The model Hamiltonian [Eq. (E7)] and parameters (Table I) are provided in Appendix E. From panel (a) (model I) and panel (b) (model II), one can see that with an increasing number of beads N, while keeping the same number of lowest frequency Matsubara modes ($M = 3$), the variation of $\tilde{H}_M(\boldsymbol{\mathcal{P}}_M,\boldsymbol{\mathcal{Q}}_M,\mathbf{q},\mathbf{p})$ along a given trajectory flattens, indicating that at the $N \to \infty$ limit, $\tilde{H}_M(\boldsymbol{\mathcal{P}}_M,\boldsymbol{\mathcal{Q}}_M,\mathbf{q},\mathbf{p})$ is preserved by $\mathcal{L}^{[M]}$. Thus, it is possible that non-adiabatic Matsubara dynamics actually preserves the QBD based on the numerical evidence. However, we must emphasize that there is no analytical proof yet.

Interestingly, if Eq. (92) is satisfied (i.e., the non-adiabatic Matsubara preserves QBD), then one can show that NRPMD must also preserves QBD. To explicitly demonstrate this, we rewrite the NRPMD time-correlation function in Eq. (81) as follows:

$$C_{AB}^{[M]}(t) = \frac{\alpha_N \cdot \alpha_M}{\mathcal{Z}_M^{\mathrm{RP}}} \int d\bar{\mathcal{P}}_M \int d\boldsymbol{\mathcal{Q}}_M \int d\mathbf{q} \int d\mathbf{p}$$
$$\times A(\boldsymbol{\mathcal{Q}}_M) e^{-\beta \tilde{H}_M^{\mathrm{RP}}(\bar{\mathcal{P}}_M,\boldsymbol{\mathcal{Q}}_M,\mathbf{q},\mathbf{p})} e^{\mathcal{L}_{\mathrm{RP}}^{[M]} t} B(\boldsymbol{\mathcal{Q}}_M), \tag{93}$$

where $\tilde{H}_M^{\mathrm{RP}}(\bar{\mathcal{P}}_M,\boldsymbol{\mathcal{Q}}_M,\mathbf{q},\mathbf{p})$ is the MV-RPMD Hamiltonian (with the Matsubara frequency instead of the ring-polymer frequency) expressed as follows:

$$\tilde{H}_M^{\mathrm{RP}}(\bar{\mathcal{P}}_M,\boldsymbol{\mathcal{Q}}_M,\mathbf{q},\mathbf{p}) = H_M^{\mathrm{RP}}(\bar{\mathcal{P}}_M,\boldsymbol{\mathcal{Q}}_M) - \frac{1}{\beta} \ln|\Gamma(\boldsymbol{\mathcal{Q}}_M,\mathbf{q},\mathbf{p})|$$
$$= \sum_{n=-(M-1)/2}^{(M-1)/2} \left[\frac{\bar{\mathcal{P}}_n^2}{2m} + \frac{m}{2} \tilde{\omega}_n^2 \mathcal{Q}_n^2 \right]$$
$$+ U_0^{[M]}(\boldsymbol{\mathcal{Q}}_M) - \frac{1}{\beta} \ln|\Gamma(\boldsymbol{\mathcal{Q}}_M,\mathbf{q},\mathbf{p})|. \tag{94}$$

The condition for NRPMD to satisfy detailed balance is $\mathcal{L}_{\mathrm{RP}}^{[M]} \tilde{H}_M^{\mathrm{RP}} = 0$, which results in the same condition described in Eq. (92). Hence, if non-adiabatic Matsubara dynamics preserve QBD, then so does NRPMD. In the supplementary material, we provide the numerical results of $\tilde{H}_M^{\mathrm{RP}}$ along a given trajectory, which behave similarly compared to the results of non-adiabatic Matsubara dynamics as shown in Fig. 3.

(A)

(B)
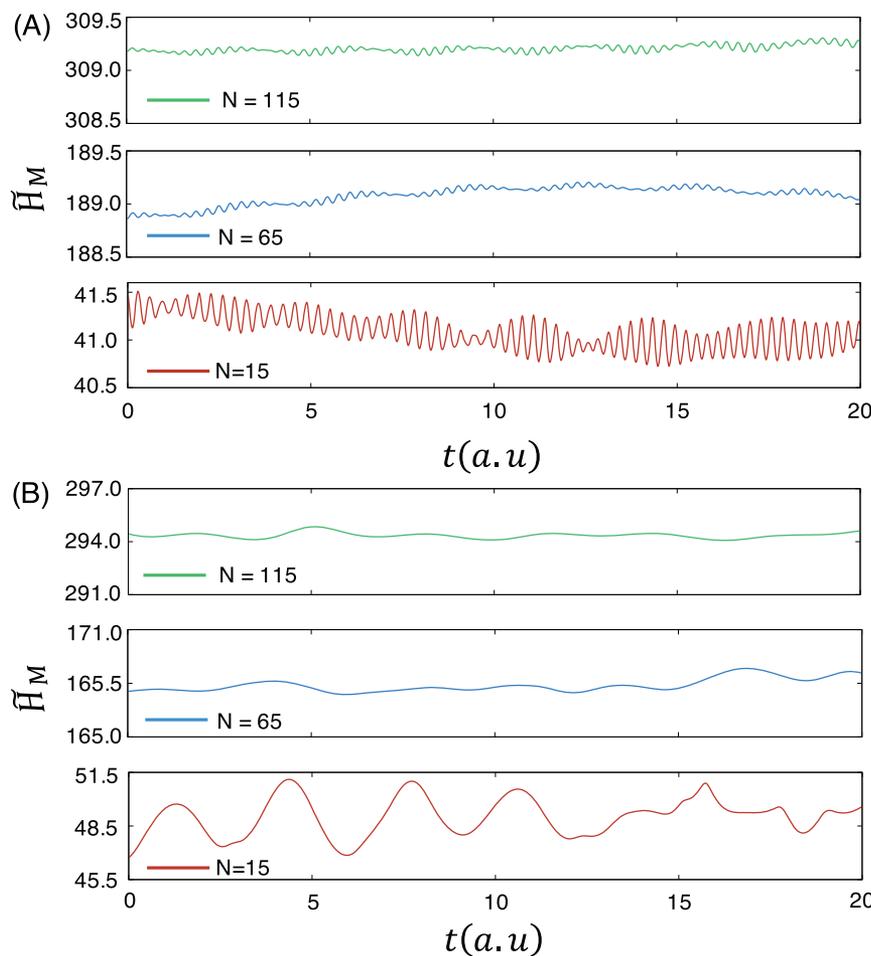
FIG. 3. Time evolution of $\tilde{H}_M$ along a single classical trajectory for model I [panel (a)] and model II [panel (b)], with $M = 3$ and $N = 15$ (red line), $N = 65$ (blue line), and $N = 115$ (green line). Details of the model systems are provided in Appendix E.

VII. TIME-CORRELATION FUNCTIONS WITH ELECTRONIC PROJECTION OPERATORS

Besides the nuclear position auto-correlation function, the electronic projection correlation function is also an important one.[54,55] For example, $\hat{A} = \hat{B} = |i\rangle\langle i|$. When $\hat{A} = |i\rangle\langle i|$, in general, $[e^{-\beta\hat{H}}\hat{A}]_{\tilde{N}} \neq [\hat{A}]_N[e^{-\beta\hat{H}}]_{\tilde{N}}$ based on Eq. (30). Thus, one needs to write down the generalized Kubo-transformed time-correlation function as in Eq. (14). On the other hand, one can follow the same procedure to obtain the normal mode representation of $C_{AB}^{[N]}(t)$ [see Eq. (39)] as

$$C_{AB}^{[N]}(t) = \frac{\alpha_N}{\mathcal{Z}} \int d\mathcal{Q} \int d\mathcal{P} \int d\mathbf{q} \int d\mathbf{p} [e^{-\beta\hat{H}}\hat{A}]_{\tilde{N}} e^{\mathcal{L}^{[N]}t}[\hat{B}]_N, \quad (95)$$

as well as the exact procedure outlined in Sec. IV by making the Matsubara approximation (by discarding the $\mathcal{L}^{[N-M]}$ and integrating out the non-Matsubara modes), reaching to the following expression of $C_{AB}^{[M]}(t)$ [see Eq. (58) for a comparison]:

$$C_{AB}^{[M]}(t) = \frac{\alpha_N . \alpha_M}{\mathcal{Z}_M} \int d\mathcal{Q}_M \int d\mathcal{P}_M \int d\mathbf{q} \int d\mathbf{p}$$
$$\times e^{-\beta(H_M(\mathcal{P}_M,\mathcal{Q}_M) - i\theta_M(\mathcal{P}_M,\mathcal{Q}_M))}$$
$$\times \Gamma_{ii}(\mathcal{Q}_M, \mathbf{q}, \mathbf{p}) e^{\tilde{\mathcal{L}}^{[M]}t}[\hat{B}]_N. \quad (96)$$

In the above equation, Γ_{ii} is Γ in Eq. (63) projected on $|i\rangle\langle i|$ as follows:

$$\Gamma_{ii} = \phi \cdot e^{-\frac{G_N}{\hbar}} \frac{1}{N} \sum_{k=1}^{N} \text{Tr}_e \left[\prod_{l=1}^{k} \left(\mathbf{C}_l - \frac{1}{2}\mathcal{I} \right) \mathcal{M}(R_l(\mathcal{Q}_M)) \right.$$
$$\left. \times |i\rangle\langle i| \prod_{l'=k+1}^{N} \left(\mathbf{C}_{l'} - \frac{1}{2}\mathcal{I} \right) \mathcal{M}(R_{l'}(\mathcal{Q}_M)) \right]$$
$$= \phi \cdot e^{-\frac{G_N}{\hbar}} \text{Tr}_e \left[|i\rangle\langle i| \prod_{l=1}^{N} \left(\mathbf{C}_l - \frac{1}{2}\mathcal{I} \right) \mathcal{M}(R_l(\mathcal{Q}_M)) \right], \quad (97)$$

where the property of trace ensures that each term inside Tr_e are identical; hence, we can replace the bead-averaged expression with the expression after the last equality. The Matsubara Liouvillian $\mathcal{L}^{[M]}$ is the same as expressed in Eq. (70), and $\mathcal{Z}_M$ is the Matsubara partition function expressed in Eq. (66). The Matsubara Liouvillian

$\mathcal{L}^{[M]}$ is the same as expressed in Eq. (70), and $\mathcal{Z}_M$ is the Matsubara partition function expressed in Eq. (66).

Following the same procedure of discarding the imaginary Liouvillian and shifting the momentum integral to the real axis (i.e., the ring-polymer approximation) and replacing the Matsubara frequency with the normal mode frequency, one can arrive at the following RPMD correlation function:

$$C_{AB}^{\text{NRP}}(t) = \frac{\alpha_N \cdot \alpha_M}{\mathcal{Z}_N^{\text{RP}}} \int d\mathcal{P} \int d\mathcal{Q} \int d\mathbf{q} \int d\mathbf{p}$$
$$\times e^{-\beta H_N^{\text{RP}}(\mathcal{P},\mathcal{Q})} \Gamma_{ii}(\mathcal{Q},\mathbf{q},\mathbf{p}) e^{\mathcal{L}_{\text{RP}}^{[M]}t}[\hat{B}]_N. \quad (98)$$

Here, for $\hat{B} = |i\rangle\langle i|$, one can use the following estimator:

$$[\hat{B}]_N = \frac{1}{N}\sum_{k=1}^{N}\int d\boldsymbol{\Delta}_k e^{\frac{i}{\hbar}\mathbf{p}_k\boldsymbol{\Delta}_k}\langle\mathbf{q}_k - \frac{\boldsymbol{\Delta}_k}{2}|i\rangle\langle i|\mathbf{q}_k + \frac{\boldsymbol{\Delta}_k}{2}\rangle$$
$$= \frac{1}{N}\sum_{k=1}^{N}\left[\frac{2^{\mathcal{K}+1}}{\hbar}e^{-\frac{1}{\hbar}(\mathbf{q}_k^2+\mathbf{p}_k^2)}\left([q_k]_i^2 + [p_k]_i^2 - \frac{\hbar}{2}\right)\right], \quad (99)$$

where the detailed proof is provided in the supplementary material. Alternatively, one could also use the mapping relation $|i\rangle\langle i| \rightarrow \hat{a}_i^\dagger \hat{a}_i$ to obtain

$$[\hat{B}]_N = \frac{1}{N}\sum_{k=1}^{N}\int d\boldsymbol{\Delta}_k e^{\frac{i}{\hbar}\mathbf{p}_k\boldsymbol{\Delta}_k}\langle\mathbf{q}_k - \frac{\boldsymbol{\Delta}_k}{2}|\hat{a}_i^\dagger\hat{a}_i|\mathbf{q}_k + \frac{\boldsymbol{\Delta}_k}{2}\rangle$$
$$= \frac{1}{N}\sum_{k=1}^{N}\frac{1}{2\hbar}\left([q_k]_i^2 + [p_k]_i^2 - \hbar\right). \quad (100)$$

The above estimator is used in the original NRPMD approach[54] and has been theoretically justified,[55] as well as derived (based on the property of Wigner transform) and used in MV-RPMD approach for excited state dynamics.[58] In fact, $C_{AB}^{\text{NRP}}(t)$ in Eq. (98) is equivalent to the originally proposed NRPMD population time-correlation function[54,55] when using Eq. (100) for the estimator of the population at time t, with the exception that the expression of Γ_{ii} is obtained using the Wigner representation for the mapping variable in the current theory, whereas in NRPMD, it is obtained by using a simple integral of both mapping positions and momentum.[54] Our derivation explains the success of the original NRPMD approach for simulating the population auto-correlation functions.[54] Numerical examples of the Kubo-transformed population auto-correlation function are provided in Fig. 5 of Appendix E.

As we finishing up introducing the theoretical frameworks in this paper, let us briefly discuss several interesting limits of non-adiabatic Matsubara dynamics and NRPMD. (i) Under the limit that the system only contains electronic subsystems, $C_{AB}^{[M]}(t)$ and $C_{AB}^{\text{NRP}}(t)$ reduce to the same form of $C_{AB}^{[N]}(t)$ (note that there are still N copies of the mapping DOF), which are all quantum mechanically exact. Hence, for the isolated electronic subsystem, both non-adiabatic Matsubara dynamics and NRPMD preserve the exact quantum Rabi oscillations (where an explicit proof can be found in Ref. 79). (ii) Under the single electronic state limit (adiabatic limit), the non-adiabatic Matsubara formalism reduces to the original Matsubara dynamics.[69,70] (iii) For the electronic system linearly couples to the harmonic nuclear bath, both non-adiabatic Matsubara dynamics and NRPMD are exact. (iv) Under the decoupled limit of the electronic and nuclear DOF, non-adiabatic Matsubara dynamics

and NRPMD rigorously preserve QBD and give the exact dynamics for the electronic subsystem but only give an approximate dynamics for the nuclear subsystem (exact when the potential V_0 is purely harmonic[69,70]). (v) Under the $N = 1$ limit, the NRPMD formalism reduced to the Linearized Semi-classical Initial Value Representation (LSC-IVR) approach[16] (with a classical nuclear distribution instead of the Wigner distribution; see more explicit discussions in Appendix D).

VIII. NON-EQUILIBRIUM TIME-CORRELATION FUNCTION

Despite the fact that RPMD was originally developed for equilibrium quantum dynamics simulations, recent theoretical progress has demonstrated that both RPMD and CMD can provide accurate non-equilibrium dynamics upon photo-excitation.[99] This is because that both can be viewed as approximation of the Matsubara dynamics, which is not limited to equilibrium simulations. Thus, we conjecture that NRPMD is also capable of accurately describing the non-equilibrium TCF, and we will explicitly prove this as follows.

For a given photo-induced process, we are often interested in the reduced density matrix dynamics upon the initial excitation of the molecular system. The reduced density matrix element can be expressed as

$$\rho_{ij}(t) = \text{Tr}\left[\hat{\rho}(0)e^{\frac{i}{\hbar}\hat{H}t}|i\rangle\langle j|e^{-\frac{i}{\hbar}\hat{H}t}\right], \quad (101)$$

where the initial density operator $\hat{\rho}(0)$ is expressed as a tensor product of the electronic and nuclear DOF as $\hat{\rho}(0) = |i\rangle\langle i| \otimes \frac{1}{\mathcal{Z}}e^{-\beta\hat{H}_0}$, where $\mathcal{Z} = \text{Tr}[e^{-\beta\hat{H}_0}]$, and $\hat{H}_0$ is the ground state Hamiltonian

$$\hat{H}_0 = \frac{\hat{P}^2}{2m} + U_g(\hat{R}), \quad (102)$$

with the ground state potential $U_g(\hat{R})$ associated with the ground electronic state $|g\rangle$.

The initial density $\hat{\rho}(0)$ is evolved under the influence of the total Hamiltonian $\hat{H}$ [Eq. (1)]. The reduced density matrix element can also be expressed as the following TCF:

$$\rho_{ij}(t) = C_{AB}(t) = \frac{1}{\mathcal{Z}}\text{Tr}\left[e^{-\beta\hat{H}_0}\hat{A}e^{\frac{i}{\hbar}\hat{H}t}\hat{B}e^{-\frac{i}{\hbar}\hat{H}t}\right], \quad (103)$$

where $\hat{A} = |i\rangle\langle i|$ is the initially occupied electronic state and $\hat{B} = |i\rangle\langle j|$. Because $\hat{A}$ and $\hat{H}_0$ commute, $[\hat{A},\hat{H}_0] = 0$, and thus,

$$C_{AB}^{\text{K}}(t) = \frac{1}{\mathcal{Z}\beta}\int_0^\beta d\lambda \text{Tr}[e^{-(\beta-\lambda)\hat{H}_0}\hat{A}e^{-\lambda\hat{H}_0}\hat{B}(t)]$$
$$= \frac{1}{\mathcal{Z}\beta}\int_0^\beta d\lambda \text{Tr}[e^{-(\beta-\lambda)\hat{H}_0}e^{-\lambda\hat{H}_0}\hat{A}\hat{B}(t)]$$
$$= \frac{\int_0^\beta d\lambda}{\beta}\cdot\frac{1}{\mathcal{Z}}\text{Tr}[e^{-\beta\hat{H}_0}\hat{A}\hat{B}(t)] = C_{AB}(t).$$

Hence, one can rewrite the reduced density matrix elements $\rho_{ij}(t)$ in Eq. (103) into the Kubo-transformed time-correlation function $C_{AB}^{\text{K}}(t)$ as follows:

$$\rho_{ij}(t) = \frac{1}{\mathcal{Z}\beta} \int_0^\beta d\lambda \mathrm{Tr}\left[e^{-(\beta-\lambda)\hat{H}_0} \hat{A} e^{-\lambda\hat{H}_0} e^{\frac{i}{\hbar}\hat{H}t} \hat{B} e^{-\frac{i}{\hbar}\hat{H}t} \right]. \quad (104)$$

The above TCF is *not* an equilibrium correlation function. Nevertheless, the Kubo-transformed structure allows us to express it as the discrete version of the time-correlation function as shown in Eq. (5).

Following exactly the same derivation we have outlined in the previous section (Sec. II), we can express $C_{AB}^K(t)$ in Eq. (104) without any approximation as follows:

$$\rho_{ij}(t) = C_{AB}^{[N]}(t) = \frac{\alpha_N}{\mathcal{Z}} \int d\mathbf{R} \int d\mathbf{P} \int d\mathbf{q} \int d\mathbf{p}$$
$$\times [\hat{A}]_N [e^{-\beta\hat{H}_0}]_{\tilde{N}} e^{\mathcal{L}^{[N]}t}[\hat{B}]_N, \quad (105)$$

where the Liouvillian $\mathcal{L}^{[N]}$ has the same expression in Eq. (24) and $[e^{-\beta\hat{H}_0}]_{\tilde{N}}$ has the same expression in Eq. (15) except that $\hat{H}$ is replaced by $\hat{H}_0$. There is no approximation in the above expression. Furthermore, $[\hat{A}]_N = \frac{1}{N}\sum_{k=1}^N [\hat{A}_k]_W$ is the partial Wigner transformed projection operator (along the mapping DOF) with the following expression:

$$[\hat{A}]_N = \frac{1}{N}\sum_{k=1}^N \int d\boldsymbol{\Delta}_k e^{\frac{i}{\hbar}\mathbf{P}_k\boldsymbol{\Delta}_k} \langle \mathbf{q}_k - \frac{\boldsymbol{\Delta}_k}{2}|i\rangle\langle i|\mathbf{q}_k + \frac{\boldsymbol{\Delta}_k}{2}\rangle$$
$$= \frac{1}{N}\sum_{k=1}^N \left[\frac{2^{\mathcal{K}+1}}{\hbar} e^{-\frac{1}{\hbar}(\mathbf{q}_k^2+\mathbf{p}_k^2)} \left([q_k]_i^2 + [p_k]_i^2 - \frac{1}{2} \right) \right], \quad (106)$$

where we have used the overlap relation $\langle \mathbf{q}_k|i\rangle = \sqrt{\frac{2}{\hbar}}\frac{1}{(\pi\hbar)^{\mathcal{K}/4}} q_i e^{\mathbf{q}_k^T \mathbf{q}_k}$ and explicitly performing the standard Gaussian integral (see detailed derivation in the supplementary material).

Similarly, $[\hat{B}]_N = \frac{1}{N}\sum_{k=1}^N [\hat{B}_k]_W$ can be expressed as

$$[\hat{B}]_N = \frac{1}{N}\sum_{k=1}^N \int d\boldsymbol{\Delta}_k e^{\frac{i}{\hbar}\mathbf{P}_k\boldsymbol{\Delta}_k} \langle \mathbf{q}_k - \frac{\boldsymbol{\Delta}_k}{2}|i\rangle\langle j|\mathbf{q}_k + \frac{\boldsymbol{\Delta}_k}{2}\rangle$$
$$= \frac{1}{N}\sum_{k=1}^N \frac{2^{\mathcal{K}+1}}{\hbar}\mathcal{G}\cdot\left\{ ([q_k]_i + i[p_k]_i)([q_k]_j - i[p_k]_j) - \frac{1}{2}\delta_{ij} \right\}, \quad (107)$$

where $\mathcal{G} = e^{-\frac{1}{\hbar}(\mathbf{q}_k^2+\mathbf{p}_k^2)}$. On the other hand, there are other choices for the Wigner transform of operators. For example, the population can be directly Wigner transformed of $\hat{a}_i^\dagger \hat{a}_i$ as shown in Eq. (100), and the Wigner transform of $\hat{a}_i^\dagger \hat{a}_j$ is

$$[\hat{B}]_N = \frac{1}{N}\sum_{k=1}^N \int d\boldsymbol{\Delta}_k e^{\frac{i}{\hbar}\mathbf{P}_k\boldsymbol{\Delta}_k} \langle \mathbf{q}_k - \frac{\boldsymbol{\Delta}_k}{2}|\hat{a}_i^\dagger \hat{a}_j|\mathbf{q}_k + \frac{\boldsymbol{\Delta}_k}{2}\rangle$$
$$= \frac{1}{N}\sum_{k=1}^N \frac{1}{2\hbar}([q_k]_i[q_k]_j + [p_k]_i[p_k]_j - \hbar\delta_{ij}). \quad (108)$$

This estimator has been proposed in the original NRPMD work.[54,55] It has also been derived in the non-equilibrium TCF with MV-RPMD.[58]

Following the Matsubara approximation, we can derive the corresponding expression of the density matrix as follows:

$$\rho_{ij}(t) \approx C_{AB}^{[M]}(t) = \frac{\alpha_N \cdot \alpha_M}{\mathcal{Z}_M} \int d\mathcal{Q}_M \int d\mathcal{P}_M \int d\mathbf{q} \int d\mathbf{p}$$
$$\times e^{-\beta(H_M^0 - i\theta_M)}[\hat{A}]_N e^{\mathcal{L}^{[M]}t}[\hat{B}]_N, \quad (109)$$

where $H_M^0 = \sum_{n=-(M-1)/2}^{(M-1)/2} \frac{\mathcal{P}_n^2}{2m} + \frac{1}{N}\sum_{l=1}^N U_g\left(\sum_{n=-(M-1)/2}^{(M-1)/2} \sqrt{N}T_{ln}\mathcal{Q}_n\right)$, θ_M is expressed in Eq. (62), and the Liouvillian $\mathcal{L}^{[M]}$ is expressed in Eq. (70). This is the non-adiabatic Matsubara dynamics expression for the reduced density matrix elements as the *third key result* of this paper.

Further making the RPMD approximation, we can derive the corresponding NRPMD expression of the reduced density matrix as the *final key result* of this paper,

$$\rho_{ij}(t) \approx C_{AB}^{\mathrm{NRP}}(t) = \frac{\alpha_N \cdot \alpha_M}{\mathcal{Z}_N^{\mathrm{RP}}} \int d\mathcal{P} \int d\mathcal{Q} \int d\mathbf{q} \int d\mathbf{p}$$
$$\times e^{-\beta H_N^0(\mathcal{P},\mathcal{Q})}[\hat{A}]_N e^{\mathcal{L}_{\mathrm{RP}}^{[N]}t}[\hat{B}]_N, \quad (110)$$

where $H_N^0(\mathcal{P},\mathcal{Q}) = \sum_{n=-(N-1)/2}^{(N-1)/2}\left[\frac{\mathcal{P}_n^2}{2m} + \frac{m}{2}\omega_n^2\mathcal{Q}_n^2 \right] + U_g^{[N]}(\mathcal{Q})$, and the Liouvillian $\mathcal{L}_{\mathrm{RP}}^{[N]}$ is expressed in Eq. (83), corresponding to the NRPMD Hamiltonian expressed in Eq. (84).

Thus, we explicitly show that NRPMD is capable to simulate non-equilibrium TCF, explaining the recent numerical success of using NRPMD to simulate the non-equilibrium population dynamics.[56] Similar numerical success in simulating non-equilibrium TCF has also been achieved in MV-RPMD.[58]

IX. CONCLUSION AND FUTURE DIRECTIONS

We present the non-adiabatic Matsubara dynamics, a general framework for computing the time-correlation function of electronically non-adiabatic systems. This new formalism is derived based on the generalized Kubo-transformed time-correlation function using the Wigner representation for both the nuclear DOF and electronic mapping variables.[75–77] By dropping the non-Matsubara nuclear normal modes in the quantum Liouvillian, we derive the non-adiabatic Matsubara dynamics, which can be viewed as a generalization of the original (electronically adiabatic) Matsubara dynamics.[69] The non-adiabatic Matsubara dynamics has two complex phases, one from the nuclear DOF and the other from the electronic DOF. By making a nuclear momentum transformation, one can derive an equivalent expression of non-adiabatic Matsubara dynamics, which has a complex Liouvillian and a complex momentum distribution.

Further making an approximation that drops the imaginary part of the Liouvillian, we arrive at the non-adiabatic ring-polymer molecular dynamics formalism. Thus, NRPMD can be viewed as an approximation of non-adiabatic Matsubara dynamics. Interestingly, the initial distribution of NRPMD coincides with that in the Mapping-Variable (MV)-RPMD,[57] whereas the NRPMD Liouvillian coincides with the Liouvillian used in the originally proposed NRPMD[54] (which has a different initial quantum distribution). Our theoretical derivations explain the numerical success of both of these previous approaches.[54,57] We have further proven that the NRPMD is capable to simulate non-equilibrium TCF, hence justifying such simulations and explaining the recent numerical success.[56] At this moment, we are not sure whether non-adiabatic Matsubara dynamics preserves the quantum Boltzmann distribution (QBD), except for the special limit for electronic states linearly coupled to the harmonic bath, or when the electronic and nuclear DOFs

are completely decoupled. Nevertheless, we derived the condition under which the QBD will be preserved by non-adiabatic Matsubara dynamics. Interestingly, if non-adiabatic Matsubara dynamics preserve the QBD, then NRPMD is also guaranteed to preserve the QBD.

The immediate future direction of the current work is to test the numerical performance of the non-adiabatic Matsubara dynamics for computing equilibrium and non-equilibrium TCFs. The current formalism of $C_{AB}^{[M]}(t)$ makes this a challenging task because the electronic mapping DOFs also have N copies, which are required to take the $N \to \infty$ limit. However, one does not have to use the same number of copies of the mapping DOF and nuclear DOF, and this can be accomplished through the mixed time-slicing technique,[93] which has been successfully implemented in a recent work of NRPMD.[55] By using a finite number of the mapping resolution [Eqs. (7) and (8)], we expect to make the non-adiabatic Matsubara dynamics practical for system with a few nuclear DOF and a few electronic states. Another direction is using the non-adiabatic Matsubara dynamics framework to theoretically derive other existing state-dependent path-integral approaches, such as the non-adiabatic CMD.[100] A third direction is to theoretically explore whether non-adiabatic Matsubara dynamics rigorously preserves quantum Boltzmann distribution (QBD). If so, then non-adiabatic Matsubara dynamics will be a trajectory-based approach that can correctly describe electronic Rabi oscillations and preserve the QBD, a method that is currently lacking.[101] We hope that our current work provides a framework for accurate non-adiabatic quantum dynamics approaches by interfacing the recent development in the field of mapping dynamics[102-109] with the developments of nuclear quantum dynamics.[40,69-73]

SUPPLEMENTARY MATERIAL

See the supplementary material for the details of the derivation of $C_{AB}^{[N]}$; Wigner transform of the MMST Hamiltonian; derivation of the exact non-adiabatic Liouvillian; derivation of Eq. (30); derivation of Eq. (76); derivation of $\mathcal{L}_{RP}^{[M]}$ and $\mathcal{L}_{I}^{[M]}$; analytic continuation at $t = 0$; proof of Eq. (89); derivation of $C_{AB}^{[N]}(0)$ using the path-integral approach; derivation of the estimators for the state-dependent operator; and additional numerical result.

ACKNOWLEDGMENTS

APPENDIX A: DERIVATION OF THE Liouvillian

We provide the derivation of the exact Liouvillian $\mathcal{L}^{[N]}$ [Eq. (24)], the detailed expressions of the non-Matsubara

Liouvillian $\mathcal{L}^{[N-M]}$ [Eq. (52)], as well as the condition when $\mathcal{L}_h^{[M]}$ can be safely ignored.

We start by differentiating a time-dependent Wigner transformed of a general operator $\hat{A}$ as follows:

$$\frac{d}{dt}[\hat{A}(t)]_W = \frac{i}{\hbar}[\hat{H}, \hat{A}(t)]_W = \mathcal{L}^{[1]} \cdot [\hat{A}(t)]_W, \quad (A1)$$

where $[\hat{A}(t)]_W = \int dD e^{\frac{i}{\hbar}PD}\langle R - \frac{D}{2}|\hat{A}(t)|R + \frac{D}{2}\rangle$ is the Wigner transform of the operator $\hat{A}(t) = e^{\frac{i}{\hbar}\hat{H}t}\hat{A}e^{-\frac{i}{\hbar}\hat{H}t}$, $\hat{H} = \frac{\hat{P}^2}{2m} + \hat{V}(\hat{R})$, with the nuclear position operator $\hat{R}$ and corresponding momentum operator $\hat{P}$ and $\hat{V}(\hat{R})$ is any general form of the potential energy operator. The corresponding Liouvillian is

$$\mathcal{L}^{[1]} = \frac{2}{\hbar}[\hat{H}]_W \cdot \sin\left(\frac{\hat{\Lambda}\hbar}{2}\right), \quad (A2)$$

where the details of the derivation are provided in the supplementary material.

Next, we derive the exact Liouvillian of the non-adiabatic Hamiltonian in the generalized Kubo-transformed TCF. Because $[\hat{B}(t)]_N$ [Eq. (17)] is a simple bead-averaged Wigner transform, the Liouvillian $\mathcal{L}^{[N]}$ in Eq. (18) has the following expression:

$$\mathcal{L}^{[N]} = \sum_{l=1}^{N} \frac{2}{\hbar}[\hat{H}_l]_W \cdot \sin\left(\frac{\hbar}{2}\hat{\Lambda}_l\right), \quad (A3)$$

where $\hat{\Lambda}_l$ is defined in Eq. (20) and $[\hat{H}_l]_W$ is the Wigner transform of the MMST mapping Hamiltonian [Eq. (1)] associated with the lth bead, with the expression in Eq. (22). Because $\mathcal{L}^{[N]}$ contains N mathematically identical terms (labeled as $l \in [1, N]$), one only needs to derive the expression of one term and sum them up. Below, we explicitly derive one of this term denoting as $\mathcal{L}^{[1]}$, and we drop the label l for simplicity. With the operator $\hat{\Lambda} = \hat{\Lambda}^e + \hat{\Lambda}^n$ defined in Eq. (20), one can rewrite Eq. (A3) as

$$\begin{aligned}\mathcal{L}^{[1]} &= \frac{2}{\hbar}[\hat{H}]_W \cdot \sin\left(\frac{\hbar}{2}\hat{\Lambda}^n + \frac{\hbar}{2}\hat{\Lambda}^e\right)\\ &= \frac{2}{\hbar}[\hat{H}]_W \cdot \left[\sin\left(\frac{\hbar}{2}\hat{\Lambda}^n\right)\cos\left(\frac{\hbar}{2}\hat{\Lambda}^e\right) + \cos\left(\frac{\hbar}{2}\hat{\Lambda}^n\right)\sin\left(\frac{\hbar}{2}\hat{\Lambda}^e\right)\right].\end{aligned} \quad (A4)$$

Explicitly expanding the terms related to the mapping derivatives as $\cos\left(\frac{\hbar}{2}\hat{\Lambda}^e\right) = 1 - \frac{1}{8}\hbar^2[\hat{\Lambda}^e]^2 + \mathcal{O}([\hat{\Lambda}^e]^4)$, $\sin\left(\frac{\hbar}{2}\hat{\Lambda}^e\right) = \frac{\hbar}{2}\hat{\Lambda}^e + \mathcal{O}([\hat{\Lambda}^e]^3)$, and note that the $V_e(R, \mathbf{q}, \mathbf{p})$ term inside $[\hat{H}]_W$ contains up to the second order of $\mathbf{p}$ and $\mathbf{q}$ [see Eq. (23)] such that $V_e[\hat{\Lambda}^e]^n = 0$ for $n \geq 3$, one can rewrite Eq. (A4) exactly as follows:

$$\begin{aligned}\mathcal{L}^{[1]} &= \frac{2}{\hbar}\left[\frac{P^2}{2m} + V_0(R) + \frac{1}{2\hbar}\sum_{i,j=1}^{\mathcal{K}}\mathcal{V}_{ij}(R)(p_ip_j + q_iq_j - \delta_{ij}\hbar)\right]\\ &\quad \times \left[\sin\left(\frac{\hbar}{2}\hat{\Lambda}^n\right)\left(1 - \frac{\hbar^2}{8}[\hat{\Lambda}^e]^2\right) + \cos\left(\frac{\hbar}{2}\hat{\Lambda}^n\right)\frac{\hbar}{2}\hat{\Lambda}^e\right]. \quad (A5)\end{aligned}$$

Each term of Eq. (A5) can be explicitly evaluated (see the supplementary material for details), resulting in the *exact* non-adiabatic Liouvillian as follows:

$$\mathcal{L}^{[1]} = \frac{P}{m}\frac{\overrightarrow{\partial}}{\partial R} - \frac{2}{\hbar}\left[V_0(R) + V_e(R,\mathbf{q},\mathbf{p})\right]\sin\left(\frac{\hbar}{2}\frac{\overleftarrow{\partial}}{\partial R}\frac{\overrightarrow{\partial}}{\partial P}\right)$$

$$+ \left[\mathbf{p}^{\mathrm{T}}\boldsymbol{\mathcal{V}}(R)\overrightarrow{\nabla}_{\mathbf{q}} - \mathbf{q}^{\mathrm{T}}\boldsymbol{\mathcal{V}}(R)\overrightarrow{\nabla}_{\mathbf{p}}\right]\frac{1}{\hbar}\cos\left(\frac{\hbar}{2}\frac{\overleftarrow{\partial}}{\partial R}\frac{\overrightarrow{\partial}}{\partial P}\right)$$

$$+ \frac{1}{4}\left[\overrightarrow{\nabla}_{\mathbf{q}}^{\mathrm{T}}\boldsymbol{\mathcal{V}}(R)\overrightarrow{\nabla}_{\mathbf{q}} + \overrightarrow{\nabla}_{\mathbf{P}_l}^{\mathrm{T}}\boldsymbol{\mathcal{V}}(R)\overrightarrow{\nabla}_{\mathbf{p}}\right]\sin\left(\frac{\hbar}{2}\frac{\overleftarrow{\partial}}{\partial R}\frac{\overrightarrow{\partial}}{\partial P}\right). \quad \text{(A6)}$$

Adding a total of N mathematically identical terms together (each has the same expression of the above Liouvillian $\mathcal{L}^{[1]}$), we have $\mathcal{L}^{[N]}$ expressed in Eq. (24).

Next, we explicitly express the error term of the Liouvillian $\mathcal{L}^{[N-M]}$ when applying the Matsubara approximation. The Matsubara approximation discards $(N - M)$ non-Matsubara modes from Eq. (43), and the non-Matsubara Liouvillian is expressed as follows:

$$\mathcal{L}^{[N-M]} = \mathcal{L}^{[N]} - \mathcal{L}^{[M]} = \mathcal{L}_{\mathrm{n}}^{[N-M]} + \mathcal{L}_{\mathrm{e}}^{[N-M]} + \mathcal{L}_{\mathrm{h}}^{[N-M]}, \quad \text{(A7)}$$

where we have further decomposing the non-Matsubara Liouvillian in three terms. Using the following trigonometric identities

$$\sin(a+b) - \sin(a) = 2\sin\left(\frac{b}{2}\right)\cos\left(a+\frac{b}{2}\right),$$

$$\cos(a+b) - \cos(a) = -2\sin\left(a+\frac{b}{2}\right)\sin\left(\frac{b}{2}\right),$$

we can express the non-Matsubara Liouvillian as follows:

$$\mathcal{L}_{\mathrm{n}}^{[N-M]} = \sum_{n=(M+1)/2}^{(N-1)/2}\left[\frac{\mathcal{P}_{-n}}{m}\frac{\partial}{\partial \mathcal{Q}_{-n}} + \frac{\mathcal{P}_n}{m}\frac{\partial}{\partial \mathcal{Q}_n}\right]$$

$$- \frac{4N}{\hbar}\left[U_0^{[N]}(\boldsymbol{\mathcal{Q}}) + U_e^{[N]}(\boldsymbol{\mathcal{Q}},\mathbf{q},\mathbf{p})\right]\sin\left(\frac{\hat{b}}{2}\right)\cos\left(\hat{a}+\frac{\hat{b}}{2}\right), \quad \text{(A8)}$$

$$\mathcal{L}_{\mathrm{e}}^{[N-M]} = -\frac{2}{\hbar}\sum_{l=1}^{N}\left[\mathbf{p}_l^{\mathrm{T}}\boldsymbol{\mathcal{V}}(R_l(\boldsymbol{\mathcal{Q}}))\overrightarrow{\nabla}_{\mathbf{q}_l} - \mathbf{q}_l^{\mathrm{T}}\boldsymbol{\mathcal{V}}(R_l(\boldsymbol{\mathcal{Q}}))\overrightarrow{\nabla}_{\mathbf{p}_l}\right]$$

$$\times \sin\left(\hat{a}+\frac{\hat{b}}{2}\right)\sin\left(\frac{\hat{b}}{2}\right), \quad \text{(A9)}$$

$$\mathcal{L}_{\mathrm{h}}^{[N-M]} = \frac{1}{2}\sum_{l=1}^{N}\left[\overrightarrow{\nabla}_{\mathbf{q}_l}^{\mathrm{T}}\boldsymbol{\mathcal{V}}(R_l(\boldsymbol{\mathcal{Q}}))\overrightarrow{\nabla}_{\mathbf{q}_l} + \overrightarrow{\nabla}_{\mathbf{P}_l}^{\mathrm{T}}\boldsymbol{\mathcal{V}}(R_l(\boldsymbol{\mathcal{Q}}))\overrightarrow{\nabla}_{\mathbf{p}_l}\right]$$

$$\times \sin\left(\frac{\hat{b}}{2}\right)\cos\left(\hat{a}+\frac{\hat{b}}{2}\right), \quad \text{(A10)}$$

where the operators $\hat{a}$ and $\hat{b}$ are defined as

$$\hat{a} = \frac{\hbar}{2N}\sum_{n=-(M-1)/2}^{(M-1)/2}\frac{\overleftarrow{\partial}}{\partial \mathcal{Q}_n}\frac{\overrightarrow{\partial}}{\partial \mathcal{P}_n}, \quad \text{(A11)}$$

$$\hat{b} = \frac{\hbar}{2N}\sum_{n=(M+1)/2}^{(N-1)/2}\frac{\overleftarrow{\partial}}{\partial \mathcal{Q}_n}\frac{\overrightarrow{\partial}}{\partial \mathcal{P}_n} + \frac{\overleftarrow{\partial}}{\partial \mathcal{Q}_{-n}}\frac{\overrightarrow{\partial}}{\partial \mathcal{P}_{-n}}. \quad \text{(A12)}$$

Finally, we want to discuss under which condition one can safely drop the higher order coupling term $\mathcal{L}_{\mathrm{h}}^{[M]}$ [Eq. (71)] under

the Matsubara approximation. We find that this term can be made as small as desired by choosing a different number of beads for the electronic mapping DOF and nuclear DOF, which is commonly referred to as the mixed time-slicing technique.[55,93] We explicitly assume that the TCF in Eq. (28) can converge by using N_e beads for the mapping variables and N nuclear beads (with M Matsubara modes) under the condition $N_e \ll N$ where N/N_e is an integer. Then, $\mathcal{L}_{\mathrm{h}}^{[M]}$ under this condition can be expressed as[55]

$$\mathcal{L}_{\mathrm{h}}^{[M]} = \frac{1}{4}\sum_{\alpha}^{N_e}\sum_{l'=1}^{N/N_e}\frac{N_e}{N}\left[\overrightarrow{\nabla}_{\mathbf{q}_\alpha}^{\mathrm{T}}\boldsymbol{\mathcal{V}}(R_l)\overrightarrow{\nabla}_{\mathbf{q}_\alpha} + \overrightarrow{\nabla}_{\mathbf{P}_\alpha}^{\mathrm{T}}\boldsymbol{\mathcal{V}}(R_l)\overrightarrow{\nabla}_{\mathbf{P}_\alpha}\right]$$

$$\times \sin\left(\frac{\hbar}{2N}\sum_{n=-(M-1)/2}^{(M-1)/2}\frac{\overleftarrow{\partial}}{\partial \mathcal{Q}_n}\frac{\overrightarrow{\partial}}{\partial \mathcal{P}_n}\right), \quad \text{(A13)}$$

where the nuclear bead index is $l = l' + (\alpha - 1)\cdot\frac{N}{N_e}$ and $\boldsymbol{\mathcal{V}}(R_l) = \boldsymbol{\mathcal{V}}(R_l(\boldsymbol{\mathcal{Q}}_M))$. Note that there is an additional normalization constant N_e/N appearing in front of the electronic–nuclear coupling potential, whereas the $1/N$ term inside the sine function is originated from the nuclear normal mode transformation [Eq. (36)]. Under the Matsubara limit, this higher order coupling term becomes

$$\mathcal{L}_{\mathrm{h}}^{[M]} = \frac{1}{8}\frac{\hbar}{N}\sum_{\alpha}^{N_e}\sum_{l'=1}^{N/N_e}\frac{N_e}{N}\left[\overrightarrow{\nabla}_{\mathbf{q}_\alpha}^{\mathrm{T}}\boldsymbol{\mathcal{V}}(R_l)\overrightarrow{\nabla}_{\mathbf{q}_\alpha} + \overrightarrow{\nabla}_{\mathbf{P}_\alpha}^{\mathrm{T}}\boldsymbol{\mathcal{V}}(R_l)\overrightarrow{\nabla}_{\mathbf{P}_\alpha}\right]$$

$$\times \left(\sum_{n=-(M-1)/2}^{(M-1)/2}\frac{\overleftarrow{\partial}}{\partial \mathcal{Q}_n}\frac{\overrightarrow{\partial}}{\partial \mathcal{P}_n}\right), \quad \text{(A14)}$$

which has a formal scaling of $\mathcal{O}(\frac{MN_e}{N}\hbar^0)$. Of course, when $N_e = N$, the formal scaling reduces back to $\mathcal{O}(M\hbar^0)$. On the other hand, one can still choose the $N_e \ll N$ limit such that $M \cdot N_e \ll N$. Under such a limit, $\mathcal{L}_{\mathrm{h}}^{[M]}$ can be safely ignored. Having this flexibility to avoid evaluating the $\mathcal{L}_{\mathrm{h}}$ term is a big theoretical advantage, compared to the Poisson Bracket Mapping Equation (PBME) method where this term is often required in order to achieve accurate quantum dynamics.[25,82,84] We must admit that we do not know for an arbitrary system if one can always choose $M \cdot N_e \ll N$ to converge the non-adiabatic Matsubara dynamics. This is subject to future investigations.

APPENDIX B: QUANTUM BOLTZMANN DISTRIBUTION IN THE NON-ADIABATIC MATSUBARA DYNAMICS

To obtain the quantum Boltzmann distribution function under the Matsubara limit in Eq. (58), we first write down the total Boltzmann operator in the normal mode representation as

$$[e^{-\beta\hat{H}}]_{\tilde{N}} = \int d\boldsymbol{\mathcal{D}}\int d\boldsymbol{\Delta}\prod_{n=-(N-1)/2}^{(N-1)/2}e^{\frac{i}{\hbar}N\mathcal{P}_n\mathcal{D}_n}\prod_{l=1}^{N}e^{\frac{i}{\hbar}p_l\Delta_l}$$

$$\times \langle\mathbf{q}_{l-1}-\tfrac{1}{2}\Delta_{l-1},\xi_{l-1}^{-}|\hat{\mathcal{P}}e^{-\beta_N\hat{H}}\hat{\mathcal{P}}|\mathbf{q}_l+\frac{\Delta_l}{2},\xi_l^{+}\rangle, \quad \text{(B1)}$$

which is the same as Eq. (41) and $\xi^{\pm}$ is previously defined in Eq. (40). The expression in Eq. (B1) is equivalent to Eq. (104) of the work by Hele and Ananth[79] but in the normal mode representation.

Next, we integrate out the non-Matsubara $\mathcal{P}$ modes. By the construction of the Matsubara dynamics (i.e., discarding the non-Matsubara Liouvillian), there is no functional dependency of non-Matsubara $\mathcal{P}$ modes in operator $\hat{B}$, and thus, we can integrate out the non-Matsubara $\mathcal{P}$ momenta, giving a product of the Dirac delta function in non-Matsubara $\mathcal{D}$ modes of the form

$$
\prod_{n=-(N-1)/2}^{-(M+1)/2} \times \prod_{n=(M+1)/2}^{(N-1)/2} \int_{-\infty}^{\infty} d\mathcal{P}_n e^{\frac{i}{\hbar} N\mathcal{P}_n\mathcal{D}_n}
$$
$$
= (2\pi\hbar)^{(N-M)} \cdot \prod_{n=-(N-1)/2}^{-(M+1)/2} \times \prod_{n=(M+1)/2}^{(N-1)/2} \delta(\mathcal{D}_n),
$$

which helps to further integrate out $\mathcal{D}^{[N-M]}$ modes from Eq. (B1). After this, $[e^{-\beta\hat{H}}]_{\bar{N}}$ [Eq. (B1)] becomes

$$
[e^{-\beta\hat{H}}]_{\bar{N}}(\mathcal{P}_M, \mathcal{Q}, \mathbf{q}, \mathbf{p}) = (2\pi\hbar)^{(N-M)} \int d\mathcal{D}_M \int d\boldsymbol{\Delta}
$$
$$
\times \prod_{n=-(M-1)/2}^{(M-1)/2} e^{iN\mathcal{P}_n\mathcal{D}_n/\hbar} \times \prod_{l=1}^{N} e^{i\mathbf{p}_l\boldsymbol{\Delta}_l/\hbar}
$$
$$
\times \Big\langle \mathbf{q}_{l-1} - \frac{1}{2}\boldsymbol{\Delta}_{l-1}, \eta_{l-1}^-(\mathcal{Q}, \mathcal{D}_M) \Big| \hat{\mathcal{P}} e^{-\beta_N\hat{H}} \hat{\mathcal{P}}
$$
$$
\times \Big| \mathbf{q}_l + \frac{1}{2}\boldsymbol{\Delta}_l, \eta_l^+(\mathcal{Q}, \mathcal{D}_M) \Big\rangle, \quad (B2)
$$

where $\int d\mathcal{D}_M = \prod_{n=-(M-1)/2}^{n=(M-1)/2} d\mathcal{D}_n$ only includes the Matsubara modes, whereas $\mathcal{Q}_n$ contains all modes (together with all $\mathcal{Q}$-dependent terms in the Liouvillian). Furthermore, $\eta_l^\pm$ is now expressed as

$$
\eta_l^\pm = \sum_{n=-(N-1)/2}^{(N-1)/2} \sqrt{N}T_{ln}\mathcal{Q}_n \pm \sum_{n=-(M-1)/2}^{(M-1)/2} \frac{1}{2}\sqrt{N}T_{ln}\mathcal{D}_n, \quad (B3)
$$

where $\mathcal{D}_n$ only contains the Matsubara modes.

We further split the Boltzmann operator in Eq. (B2) through a symmetric Trotter expansion under the $N \to \infty$ limit, noting that $|\eta_l^\pm\rangle\langle\eta_l^\pm|$ commutes with $\hat{\mathcal{P}}$ (as they belong to two different DOFs) and evaluating the nuclear kinetic energy term $\frac{\hat{P}^2}{2m}$ explicitly through the standard path-integral technique (see the supplementary material for details). This leads to

$$
[e^{-\beta\hat{H}}]_{\bar{N}}(\mathcal{P}_M, \mathcal{Q}, \mathbf{q}, \mathbf{p}) = (2\pi\hbar)^{(N-M)} \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} \int d\mathcal{D}_M \int d\boldsymbol{\Delta}
$$
$$
\times \prod_{n=-(M-1)/2}^{(M-1)/2} e^{\frac{i}{\hbar} N\mathcal{P}_n\mathcal{D}_n} \times \prod_{l=1}^{N} e^{\frac{i}{\hbar}\mathbf{p}_l\boldsymbol{\Delta}_l}
$$
$$
\times \exp\left[-\beta_N \frac{m}{2\beta_N^2\hbar^2}(\eta_{l-1}^- - \eta_l^+)^2\right]
$$
$$
\times e^{-\frac{\beta_N}{2}[V_0(\eta_l^-)+V_0(\eta_l^+)]} \Big\langle \mathbf{q}_{l-1} - \frac{1}{2}\boldsymbol{\Delta}_{l-1} \Big|
$$
$$
\times \hat{\mathcal{P}} e^{-\frac{\beta_N}{2}[\hat{V}_e(\eta_l^-)+\hat{V}_e(\eta_l^+)]} \hat{\mathcal{P}} \Big| \mathbf{q}_l + \frac{1}{2}\boldsymbol{\Delta}_l \Big\rangle. \quad (B4)
$$

Applying a well-known trigonometric identities,[69,70] one can explicitly evaluate the $(\eta_{l-1}^- - \eta_l^+)^2$ term as follows:

$$
(\eta_{l-1}^- - \eta_l^+)^2 = 4 \sum_{n=-(M-1)/2}^{(M-1)/2} \left(\sqrt{N}\mathcal{Q}_n \sin\xi_n + \sqrt{N}\frac{\mathcal{D}_{-n}}{2}\cos\xi_n\right)^2
$$
$$
+ (\beta_N\hbar)^2 \sum_{n=(M+1)/2}^{(N-1)/2} \omega_n^2 N(\mathcal{Q}_n^2 + \mathcal{Q}_{-n}^2), \quad (B5)
$$

where $\xi_n = \frac{n\pi}{N}$. Note that the first sum includes all Matsubara modes and the second sum includes all non-Matsubara modes. Using the relation in Eq. (B5), the quantum Boltzmann operator in Eq. (B4) becomes

$$
[e^{-\beta\hat{H}}]_{\bar{N}}(\mathcal{P}_M, \mathcal{Q}, \mathbf{q}, \mathbf{p}) = (2\pi\hbar)^{(N-M)} \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} \int d\mathcal{D}_M \prod_{n=-(M-1)/2}^{(M-1)/2} e^{\frac{i}{\hbar} N\mathcal{P}_n\mathcal{D}_n} \exp\left[-\frac{m\beta_N}{2}\sum_{n=(M+1)/2}^{(N-1)/2}\omega_n^2 N(\mathcal{Q}_n^2 + \mathcal{Q}_{-n}^2)\right]
$$
$$
\times \exp\left[-2\beta_N \frac{m}{(\beta_N\hbar)^2} \sum_{n=-(M-1)/2}^{(M-1)/2}\left(\sqrt{N}\mathcal{Q}_n\sin\xi_n + \sqrt{N}\frac{\mathcal{D}_{-n}}{2}\cos\xi_n\right)^2\right]
$$
$$
\times \exp\left[-\frac{\beta_N}{2}\sum_{l=1}^{N}[\hat{V}_0(\eta_l^-) + \hat{V}_0(\eta_l^+)]\right] \cdot \int d\boldsymbol{\Delta} \prod_{l=1}^{N} e^{\frac{i}{\hbar}\mathbf{p}_l\boldsymbol{\Delta}_l} \Big\langle \mathbf{q}_{l-1} - \frac{1}{2}\boldsymbol{\Delta}_{l-1} \Big| \hat{\mathcal{P}} e^{-\frac{1}{2}\beta_N[\hat{V}_e(\eta_l^-)+\hat{V}_e(\eta_l^+)]} \hat{\mathcal{P}} \Big| \mathbf{q}_l + \frac{1}{2}\boldsymbol{\Delta}_l \Big\rangle. \quad (B6)
$$

Under the limit $N \to \infty$, the Gaussian function that involves $\mathcal{D}_{-n}$ term has the following form:

$$
\exp\left[-\frac{mN^2}{2\beta\hbar^2}\cos^2\xi_n\mathcal{D}_{-n}^2\right] = \sqrt{\frac{2\pi\beta\hbar^2}{mN^2}}[\cos\xi_n]^{-1} \cdot \delta(\mathcal{D}_{-n}).
$$

Using the property $\int f(x+a)\delta(x)dx = f(a)\int\delta(x)dx$ (a steepest-descent argument), we can move all terms related to the potential, including $\exp[-\beta_N\hat{V}_0(\eta_l^\pm)]$ and $\exp[-\beta_N\hat{V}_e(\eta_l^\pm)]$ related terms outside the $d\mathcal{D}_M$ integral [and set $D_{-n} = 0$ for $\eta_l^\pm$ terms in Eq (B3)], resulting in

$$
[e^{-\beta\hat{H}}]_{\bar{N}}(\mathcal{P}_M, \mathcal{Q}, \mathbf{q}, \mathbf{p}) = (2\pi\hbar)^{(N-M)} \left(\frac{m}{2\pi\beta_N\hbar^2}\right)^{N/2} e^{-\beta_N\sum_{l=1}^{N}V_0(R_l)} \exp\left[-\frac{m\beta_N}{2}\sum_{n=(M+1)/2}^{(N-1)/2}\omega_n^2 N(\mathcal{Q}_n^2 + \mathcal{Q}_{-n}^2)\right]
$$
$$
\times \Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p}) \times \prod_{n=-(M-1)/2}^{(M-1)/2} \int d\mathcal{D}_n e^{\frac{i}{\hbar} N\mathcal{P}_n\mathcal{D}_n} \exp\left[-N\frac{2m}{\beta_N\hbar^2}\left(\mathcal{Q}_{-n}\sin(\xi_{-n}) + \frac{1}{2}\mathcal{D}_n\cos(\xi_{-n})\right)^2\right], \quad (B7)
$$

where we explicitly write down each integral for the Matsubara $\mathcal{D}_n$ mode, $R_l = \sum_{n=-(N-1)/2}^{(N-1)/2} \sqrt{N} T_{ln} \mathcal{Q}_n$, and we have defined the following mapping integral as

$$\Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p}) \equiv \int d\Delta \prod_{l=1}^{N} e^{\frac{i}{\hbar}\mathbf{p}_l \Delta_l} \langle \mathbf{q}_{l-1} - \frac{1}{2}\Delta_{l-1} | \hat{\mathcal{P}} e^{-\beta_N \hat{V}_e(R_l)} \hat{\mathcal{P}} | \mathbf{q}_l + \frac{1}{2}\Delta_l \rangle. \tag{B8}$$

We further explicitly integrate out $\int d\mathcal{D}_n$ in the last line of Eq. (B7) (by denoting $\xi_n = n\pi/N$) as follows:

$$\begin{aligned}
I_n &= \int d\mathcal{D}_n \exp\left[\frac{i}{\hbar} N \mathcal{P}_n \mathcal{D}_n - N\frac{2m}{\beta_N \hbar^2}\left(-\mathcal{Q}_{-n}\sin\xi_n + \frac{1}{2}\mathcal{D}_n\cos\xi_n \right)^2 \right] \\
&= \exp\left[-\frac{2mN}{\beta_N \hbar^2}\mathcal{Q}_{-n}^2\sin^2\xi_n \right]\exp\left[-N\frac{\beta_N}{2m\cos^2\xi_n}\mathcal{P}_n^2 \right] \\
&\quad \times \int d\mathcal{D}_n \exp\left[-N\frac{m}{\beta_N\hbar^2}\frac{\cos^2\xi_n}{2}\left(\mathcal{D}_n - i\frac{\beta_N\hbar}{m\cos^2\xi_n}\mathcal{P}_n \right)^2 \right] \\
&\quad \times \exp\left[N\frac{2m}{\beta_N\hbar^2}\sin\xi_n\cdot\cos\xi_n\cdot\mathcal{Q}_{-n}\mathcal{D}_n \right]. \tag{B9}
\end{aligned}$$

Note that the Gaussian term inside the above $\int d\mathcal{D}_n$ integral is

$$\begin{aligned}
&\exp\left[-N\frac{m}{\beta_N\hbar^2}\frac{\cos^2\xi_n}{2}\left(\mathcal{D}_n - i\frac{\beta_N\hbar}{m\cos^2\xi_n}\mathcal{P}_n \right)^2 \right] \\
&\sim \delta\left(\mathcal{D}_n - i\frac{\beta_N\hbar}{m\cos^2\xi_n}\mathcal{P}_n \right), \tag{B10}
\end{aligned}$$

which again allows the $d\mathcal{D}_n$ integral to be evaluated through the steepest-descent fashion, resulting in

$$\begin{aligned}
\mathcal{I}_n &= \mathcal{C}_n\cdot\exp\left[-N\frac{\beta_N}{2m\cos^2\xi_n}\mathcal{P}_n^2 + iN\frac{2\tan\xi_n}{\hbar}\mathcal{Q}_{-n}\mathcal{P}_n \right] \\
&\quad \times \exp\left[-\frac{2mN}{\beta_N\hbar^2}\mathcal{Q}_{-n}^2\sin^2\xi_n \right], \tag{B11}
\end{aligned}$$

where $\mathcal{C}_n = \sqrt{\pi}/\sqrt{N\frac{m}{\beta_N\hbar^2}\frac{\cos^2\xi_n}{2}}$.

Because the $d\mathcal{D}_n$ integral is in the Matsubara domain, we can further simplify the expression by taking the Matsubara limit ($N \to \infty$ and $n \in M \ll N$), resulting in $\cos^2\xi_n \to 1$, $\sin^2\xi_n \sim \mathcal{O}((\frac{n}{N})^2) \to 0$, and $\tan\xi_n \to \xi_n = n\pi/N$. Thus, the final expression of the thermal Boltzmann operator in Eq. (B7) is expressed as

$$\begin{aligned}
[e^{-\beta\hat{H}}]_{\bar{N}}(\mathcal{P}_M, \mathcal{Q}, \mathbf{q}, \mathbf{p}) &= \left(\frac{2\pi m}{\beta_N} \right)^{(N-M)/2} e^{-\beta_N \sum_{l=1}^{N} V_0(R_l)} \\
&\quad \times \exp\left[-\frac{m\beta_N}{2}\sum_{n=(M+1)/2}^{(N-1)/2}\omega_n^2 N(\mathcal{Q}_n^2 + \mathcal{Q}_{-n}^2) \right] \\
&\quad \times \Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p})\cdot\exp\left[-\beta\frac{\mathcal{P}_n^2}{2m} \right] \\
&\quad \cdot \exp\left[2i\left(\frac{n\pi}{\hbar} \right)\mathcal{Q}_{-n}\mathcal{P}_n \right]. \tag{B12}
\end{aligned}$$

In addition, one can explicitly evaluate the electronic mapping integral in Eq. (B8). Recall that $\hat{\mathcal{P}} = \sum_i |i\rangle\langle i|$ is the projection operator

in SEO mapping subspace, and the overlap with electronic states is expressed as

$$\langle \mathbf{q}|i\rangle = \sqrt{\frac{2}{\hbar}}\frac{1}{(\pi\hbar)^{\mathcal{K}/4}}[\mathbf{q}]_i e^{-\mathbf{q}^{\mathrm{T}}\mathbf{q}/2\hbar}. \tag{B13}$$

Using Eq. (B13), one can re-express Γ as follows:

$$\begin{aligned}
\Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p}) &= \frac{2^N}{\hbar^N}\frac{1}{(\pi\hbar)^{N\mathcal{K}/2}}\prod_{l=1}^{N}\int d\Delta_l (\mathbf{q}_{l-1} - \Delta_{l-1}/2)^{\mathrm{T}} \\
&\quad \times \mathcal{M}(R_l(\mathcal{Q})).(\mathbf{q}_l + \Delta_l/2)e^{-\frac{1}{\hbar}\left(\frac{1}{4}\Delta_l^{\mathrm{T}}\Delta_l + \mathbf{q}_l^{\mathrm{T}}\mathbf{q}_l - i\mathbf{p}_l^{\mathrm{T}}\Delta_l \right)}. \tag{B14}
\end{aligned}$$

Rearranging the pre-factors of Eq. (B14) and grouping terms associated with Δ_l (using the cyclic property of trace), we have

$$\begin{aligned}
\Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p}) &= \frac{2^N}{\hbar^N}\frac{1}{(\pi\hbar)^{N\mathcal{K}/2}}e^{-\sum_{l=1}^{N}(\mathbf{q}_l^{\mathrm{T}}\mathbf{q}_l + \mathbf{p}_l^{\mathrm{T}}\mathbf{p}_l)}\prod_{l=1}^{N}\int d\Delta_l \\
&\quad \times \mathrm{Tr}_e\left[(\mathbf{q}_l + \Delta_l/2)\cdot(\mathbf{q}_l - \Delta_l/2)^{\mathrm{T}}\cdot\mathcal{M}(R_l(\mathcal{Q})) \right] \\
&\quad \times e^{-\frac{1}{\hbar}\sum_l \left(\frac{1}{2}\Delta_l - i\mathbf{p}_l \right)^2}. \tag{B15}
\end{aligned}$$

Analytically performing the integration over Δ_l (which is a standard Gaussian integral) leads to the final form of $\Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p})$ as follows:

$$\Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p}) = \phi\cdot e^{-\frac{G_N}{\hbar}}\mathrm{Tr}_e\left[\prod_{l=1}^{N}\left(\mathbf{C}_l - \frac{1}{2}\mathcal{I} \right)\mathcal{M}(R_l(\mathcal{Q})) \right], \tag{B16}$$

which has the same expression in Eq. (63), except that Eq. (B16) depends on all normal modes $\mathcal{Q}$.

Using the above results, we have the following thermal-Boltzmann operator:

$$\begin{aligned}
&[e^{-\beta\hat{H}}]_{\bar{N}}(\mathcal{P}_M, \mathcal{Q}, \mathbf{q}, \mathbf{p}) \\
&= \left(\frac{2\pi m}{\beta_N} \right)^{(N-M)/2}\Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p})\cdot\prod_{n=-(M-1)/2}^{(M-1)/2}e^{-\beta\frac{\mathcal{P}_n^2}{2m}}\cdot e^{i\beta\tilde{\omega}_n\mathcal{P}_n\mathcal{Q}_{-n}} \\
&\quad \times \exp\left[-\beta_N\sum_{l=1}^{N}V_0\left(\sum_{n=-(N-1)/2}^{(N-1)/2}\sqrt{N}T_{ln}\mathcal{Q}_n \right) \right] \\
&\quad \times \exp\left[-\frac{m\beta_N}{2}\sum_{n=(M+1)/2}^{(N-1)/2}\omega_n^2 N(\mathcal{Q}_n^2 + \mathcal{Q}_{-n}^2) \right]. \tag{B17}
\end{aligned}$$

Substituting Eq. (B17) into Eq. (57), we get

$$\begin{aligned}
C_{AB}^{[M]}(t) &= \lim_{N\to\infty}\frac{\alpha_N}{\mathcal{Z}_N}\int d\mathcal{Q}\int d\mathcal{P}_M\int d\mathbf{q}\int d\mathbf{p} \\
&\quad \times A(\mathcal{Q})[e^{-\beta\hat{H}}]_{\bar{N}}(\mathcal{P}_M, \mathcal{Q}, \mathbf{q}, \mathbf{p})e^{\mathcal{L}^{[M]}t}B(\mathcal{Q}). \tag{B18}
\end{aligned}$$

Under the Matsubara limit $M \to \infty$, and $M \ll N$, one recognize that the Gaussian part of the non-Matsubara normal modes in $[e^{-\beta\hat{H}}]_{\bar{N}}(\mathcal{P}_M, \mathcal{Q}, \mathbf{q}, \mathbf{p})$ are nascent Dirac delta functions [by noting the expression of ω_n in Eq. (35)] as follows:

$$\lim_{\substack{M\to\infty \\ M\ll N}}\exp\left(-\frac{2mN^2\sin^2(n\pi/N)\mathcal{Q}_n^2}{\beta\hbar^2} \right) \sim \delta(\mathcal{Q}_n). \tag{B19}$$

Thus, we can further integrate out the non-Matsubara $\mathcal{Q}$ modes from Eq. (B17) (based on a steepest descent argument), leading to the following effective changes inside the nuclear coordinate integral:

$$\exp\left[-\beta_N \sum_{l=1}^{N} V_0\left(\sum_{n=-(N-1)/2}^{(N-1)/2} T_{ln}\mathcal{Q}_n\right)\right] \to \exp[-\beta U_0^{[M]}(\mathcal{Q}_M)], \quad (B20)$$

where $U_0^{[M]}(\mathcal{Q}_M)$ is defined in Eq. (60), as well as

$$\text{Tr}_e\left[\prod_{l=1}^{N}\left(\mathcal{C}_l - \frac{1}{2}\mathcal{I}\right)\mathcal{M}(\mathcal{Q})\right] \to \text{Tr}_e\left[\prod_{l=1}^{N}\left(\mathcal{C}_l - \frac{1}{2}\mathcal{I}\right)\mathcal{M}(\mathcal{Q}_M)\right] \quad (B21)$$

for the Γ related term. Note that the Liouvillian $\mathcal{L}^{[M]}$ only depends on Matsubara modes $\mathcal{Q}_M$. Because these quantities only depend on the Matsubara mode $\mathcal{Q}_M$, we can move them outside the integral of the non-Matsubara modes,

$$C_{AB}^{[M]}(t) = \lim_{N\to\infty} \frac{\alpha_N}{\mathcal{Z}_N} \int d\mathcal{Q}_M \int d\mathcal{P}_M \int d\mathbf{q} \int d\mathbf{p}$$
$$\times A(\mathcal{Q}_M)[e^{-\beta\hat{H}}]_{\tilde{N}}(\mathcal{Q}_M, \mathcal{P}_M, \mathbf{q}, \mathbf{p}) e^{\mathcal{L}^{[M]}t} B(\mathcal{Q}_M)$$
$$\times \prod_{n=(M+1)/2}^{(N-1)/2} \int d\mathcal{Q}_n d\mathcal{Q}_{-n} e^{-\beta\sum_{n=(M+1)/2}^{(N-1)/2} \frac{m}{2}\omega_n^2(\mathcal{Q}_n^2+\mathcal{Q}_{-n}^2)}, \quad (B22)$$

where Gaussian integral in the last line of the above equation can be analytically performed, resulting in the constant α_M in Eq. (59). The final results of $C_{AB}^{[M]}(t)$ is expressed in Eq. (58).

APPENDIX C: DETAILED BALANCE FOR SYSTEM WITH DECOUPLED ELECTRONIC AND NUCLEAR DOF

For the system that has a decoupled electronic–nuclear interaction,

$$\hat{H} = \frac{\hat{P}^2}{2m} + V_0(\hat{R}) + \sum_{i,j=1}^{\mathcal{K}} \mathcal{V}_{ij}|i\rangle\langle j| = \hat{H}_0 + \hat{V}_e, \quad (C1)$$

where $\mathcal{V}_{ij}$ is a constant, leading to $\partial\mathcal{V}_{ij}/\partial R = 0$. This case also includes two limits: (1) electronically adiabatic system ($\hat{V}_e = 0$) or (2) there is only electronic subsystem ($\hat{T} + \hat{V}_0 = 0$).

For the electronic–nuclear decoupling case, the exact thermal Boltzmann operator is

$$[e^{-\beta\hat{H}}]_{\tilde{N}} = \Gamma(\mathbf{q}, \mathbf{p}) \int d\mathbf{D} \prod_{l=1}^{N} e^{\frac{i}{\hbar}P_l D_l}\langle R_{l-1} - \frac{1}{2}D_{l-1}|e^{-\beta_N\hat{H}_0}|R_l + \frac{1}{2}D_l\rangle, \quad (C2)$$

where the electronic part $\Gamma(\mathbf{q}, \mathbf{p})$ becomes

$$\Gamma(\mathbf{q}, \mathbf{p}) = \phi \cdot e^{-\frac{g_N}{\hbar}} \text{Tr}_e\left[\prod_{l=1}^{N}\left(\mathbf{C}_l - \frac{1}{2}\mathcal{I}\right)\mathcal{M}\right], \quad (C3)$$

where $\mathcal{M}_{ij} = \langle i|e^{-\beta_N\hat{V}_e}|j\rangle$.

The exact Liouvillian in Eq. (24) becomes

$$\mathcal{L}^{[N]} = \sum_{l=1}^{N}\left\{\frac{P_l}{m}\frac{\overrightarrow{\partial}}{\partial R_l} - V_0(R_l)\frac{2}{\hbar}\sin\left(\frac{\hbar}{2}\frac{\overleftarrow{\partial}}{\partial R_l}\frac{\overrightarrow{\partial}}{\partial P_l}\right)\right.$$
$$\left. + \frac{1}{\hbar}[\mathbf{p}_l^{\text{T}}\mathcal{V}\overrightarrow{\nabla}_{\mathbf{q}_l} - \mathbf{q}_l^{\text{T}}\mathcal{V}\overrightarrow{\nabla}_{\mathbf{p}_l}]\right\}, \quad (C4)$$

where the nuclear Liouvillian (the first term) and the electronic Liouvillian (the second term) are completely decoupled. The detailed balance condition $\mathcal{L}^{[N]}[e^{-\beta\hat{H}}]_{\tilde{N}} = 0$ leads to

$$\sum_{l=1}^{N}[\mathbf{p}_l^{\text{T}}\mathcal{V}\overrightarrow{\nabla}_{\mathbf{q}_l}\Gamma - \mathbf{q}_l^{\text{T}}\mathcal{V}\overrightarrow{\nabla}_{\mathbf{p}_l}\Gamma] = 0 \quad (C5)$$

for the electronic subsystem and $\mathcal{L}^{[N]}\{\int d\mathbf{D} \prod_{l=1}^{N} e^{\frac{i}{\hbar}P_l D_l}\langle R_{l-1} - \frac{1}{2}D_{l-1}|e^{-\beta_N\hat{H}_0}|R_l + \frac{1}{2}D_l\rangle\} = 0$ for the nuclear DOF.

Under the same decoupling limit, the non-adiabatic Matsubara Liouvillian becomes

$$\mathcal{L}^{[M]} = \sum_{n=-(M-1)/2}^{(M-1)/2} \frac{\mathcal{P}_n}{m}\frac{\overrightarrow{\partial}}{\partial\mathcal{Q}_n} - \frac{\partial U_0^{[M]}(\mathcal{Q}_M)}{\partial\mathcal{Q}_n}\frac{\overrightarrow{\partial}}{\partial\mathcal{P}_n}$$
$$+ \frac{1}{\hbar}\sum_{l=1}^{N}\left(\mathbf{p}_l^{\text{T}}\mathcal{V}\overrightarrow{\nabla}_{\mathbf{q}_l} - \mathbf{q}_l^{\text{T}}\mathcal{V}\overrightarrow{\nabla}_{\mathbf{p}_l}\right).$$

Hence, under this limit, the non-adiabatic Matsubara Liouvillian becomes the separable addition of the Matsubara Liouvillian for the nuclear DOF (first line) and the exact mapping Liouvillian for the isolated electronic DOF (second line). Comparing with the exact Liouvillian in Eq. (C4), one can see that the electronic part of the Liouvillian is also exact in $\mathcal{L}^{[M]}$ for this special case. The effective Hamiltonian $\tilde{H}_M$ in the initial distribution becomes

$$\tilde{H}_M = H_M(\mathcal{P}_M, \mathcal{Q}_M) - \frac{1}{\beta}\ln|\Gamma(\mathbf{q}, \mathbf{p})|,$$
$$= \sum_{n=-(M-1)/2}^{(M-1)/2} \frac{\mathcal{P}_n^2}{2m} + U_0^{[M]}(\mathcal{Q}_M) - \frac{1}{\beta}\ln|\Gamma(\mathbf{q}, \mathbf{p})|. \quad (C6)$$

We can explicitly show that under such a decoupling limit, non-adiabatic Matsubara dynamics preserves the QBD as follows:

$$\mathcal{L}^{[M]}\tilde{H}_M(\mathcal{P}_M, \mathcal{Q}_M, \mathbf{q}, \mathbf{p})$$
$$= \mathcal{L}^{[M]}H_M(\mathcal{P}_M, \mathcal{Q}_M) - \sum_{l=1}^{N}\frac{1}{\beta\hbar|\Gamma(\mathbf{q}, \mathbf{p})|}$$
$$\times\left[\mathbf{p}_l^{\text{T}}\mathcal{V}\overrightarrow{\nabla}_{\mathbf{q}_l}|\Gamma(\mathbf{q}, \mathbf{p})| - \mathbf{q}_l^{\text{T}}\mathcal{V}\overrightarrow{\nabla}_{\mathbf{p}_l}|\Gamma(\mathbf{q}, \mathbf{p})|\right] = 0, \quad (C7)$$

where we have used Eq. (C5), as well as $\mathcal{L}^{[M]}H_M(\mathcal{P}_M, \mathcal{Q}_M) = 0$, which can be easily verified (see Ref. 72 for details) by acting $\mathcal{L}^{[M]}$ on $H_M(\mathcal{P}_M, \mathcal{Q}_M)$. Hence, we proved that under the decoupling limit, non-adiabatic Matsubara dynamics preserves the QBD.

APPENDIX D: CONNECTIONS TO LINEARIZED PATH-INTEGRAL APPROACHES

We would like to connect the current formalism of $C_{AB}^{[N]}(t)$ with the previously developed linearized path-integral approaches. Most of these approaches are based on the Wigner representation for the mapping and the nuclear DOF, which can be formally viewed

as various approximate forms of the $N = 1$ case of $C_{AB}^{[N]}(t)$. Since they are extensively used to compute density matrix dynamics, we will mainly focus our discussion on the non-equilibrium correlation function [Eq. (103)]. On the other hand, the following discussions on Liouvillians are also valid for the thermal-equilibrium time-correlation function [Eq. (14)].

We begin by writing down the non-equilibrium TCF in Eq. (105) with $N = 1$ as follows:

$$C_{AB}^{[1]}(t) = \frac{\alpha_1}{\mathcal{Z}} \int d\mathbf{R} \int d\mathbf{P} \int d\mathbf{q} \int d\mathbf{p} [\hat{A}]_W [e^{-\beta \hat{H}_0}]_W e^{\mathcal{L}^{[1]}t} [\hat{B}]_W, \quad \text{(D1)}$$

where $\alpha_1 = 1/(2\pi\hbar)^{\mathcal{K}+1}$, $[\hat{A}]_W = \int d\Delta e^{\frac{i}{\hbar}\mathbf{P}\Delta} \langle \mathbf{q} - \frac{\Delta}{2}|i\rangle\langle i|\mathbf{q} + \frac{\Delta}{2}\rangle$, and $[e^{-\beta \hat{H}_0}]_W = \int dD e^{\frac{i}{\hbar}PD} \langle R - \frac{D}{2}|e^{-\beta_N \hat{H}_0}|R + \frac{D}{2}\rangle$, and the Liouvillian $\mathcal{L}^{[1]}$ is expressed in Eq. (A6). The expressions of $C_{AB}^{[1]}(t)$ and the Liouvillian $\mathcal{L}^{[1]}$ are, in principle, exact, giving rise to the exact quantum dynamics. Note that the mapping variables q_i, p_i are in the order of $\mathcal{O}(\sqrt{\hbar})$ [because $[p_i, q_i] = i\hbar$, hence there is an $1/\hbar$ term in the MMST Hamiltonian in Eq. (4)].

One can make approximations to $\mathcal{L}^{[1]}$ by truncating all terms up to $\mathcal{O}(\hbar)$ as follows:

$$\frac{2}{\hbar} \sin\left(\frac{\hbar}{2} \frac{\overleftarrow{\partial}}{\partial R} \frac{\overrightarrow{\partial}}{\partial P} \right) \approx \frac{\overleftarrow{\partial}}{\partial R} \frac{\overrightarrow{\partial}}{\partial P} + \mathcal{O}(\hbar^2), \quad \text{(D2)}$$

$$\frac{1}{\hbar} \cos\left(\frac{\hbar}{2} \frac{\overleftarrow{\partial}}{\partial R} \frac{\overrightarrow{\partial}}{\partial P} \right) \approx \frac{1}{\hbar} + \mathcal{O}(\hbar), \quad \text{(D3)}$$

and dropping the third line in $\mathcal{L}^{[1]}$ [Eq. (A6)], which corresponds to a term that is in the order of $\mathcal{O}(\hbar^0)$, the Liouvillian $\mathcal{L}^{[1]}$ is reduced to the following form:

$$\mathcal{L}_{\text{LSC}}^{[1]} = \frac{P}{m} \frac{\overrightarrow{\partial}}{\partial R} - \frac{2}{\hbar}[V_0(R) + V_e(R, \mathbf{q}, \mathbf{p})] \frac{\overleftarrow{\partial}}{\partial R} \frac{\overrightarrow{\partial}}{\partial P}$$
$$+ \frac{1}{\hbar}[\mathbf{p}^{\mathrm{T}} \mathcal{V}(R) \overrightarrow{\nabla}_\mathbf{q} - \mathbf{q}^{\mathrm{T}} \mathcal{V}(R) \overrightarrow{\nabla}_\mathbf{p}] + \mathcal{O}(\hbar^0), \quad \text{(D4)}$$

which is the Liouvillian used in the Linearized Semi-classical Initial Value Representation (LSC-IVR)[16] approach. Note that the error for the first line in $\mathcal{L}_{\text{LSC}}$ is $\mathcal{O}(\hbar^2)$ and the error for the second line in $\mathcal{L}_{\text{LSC}}$ is $\mathcal{O}(\hbar)$. However, the dropped term (the third line) in $\mathcal{L}^{[1]}$ corresponds to a term of $\mathcal{O}(\hbar^0)$. This ultimately determines the accuracy of $\mathcal{L}_{\text{LSC}}^{[1]}$ to be up to $\mathcal{O}(\hbar^0)$.

On the other hand, if one chooses to truncate $\mathcal{L}^{[1]}$ up to the linear order of the nuclear operator $\hat{\Lambda}^n = \frac{\overleftarrow{\partial}}{\partial P} \frac{\overrightarrow{\partial}}{\partial R} - \frac{\overleftarrow{\partial}}{\partial R} \frac{\overrightarrow{\partial}}{\partial P}$, which is commonly referred to as the mixed quantum–classical (MQC) Liouville approximation,[98] then $\mathcal{L}^{[1]}$ reduces to the following expression:

$$\mathcal{L}_{\text{MQC}}^{[1]} = \frac{P}{m} \frac{\overrightarrow{\partial}}{\partial R} - \frac{2}{\hbar}[V_0(R) + V_e(R, \mathbf{q}, \mathbf{p})] \frac{\overleftarrow{\partial}}{\partial R} \frac{\overrightarrow{\partial}}{\partial P}$$
$$+ \frac{1}{\hbar}[\mathbf{p}^{\mathrm{T}} \mathcal{V}(R) \overrightarrow{\nabla}_\mathbf{q} - \mathbf{q}^{\mathrm{T}} \mathcal{V}(R) \overrightarrow{\nabla}_\mathbf{p}]$$
$$+ \frac{\hbar}{8}[\overrightarrow{\nabla}_\mathbf{q}^{\mathrm{T}} \mathcal{V}(R) \overrightarrow{\nabla}_\mathbf{q} + \overrightarrow{\nabla}_\mathbf{p}^{\mathrm{T}} \mathcal{V}(R) \overrightarrow{\nabla}_\mathbf{p}] \frac{\overleftarrow{\partial}}{\partial R} \frac{\overrightarrow{\partial}}{\partial P} + \mathcal{O}((\hat{\Lambda}^n)^2), \quad \text{(D5)}$$

which was first derived in the Poisson Bracket Mapping Equation (PBME) approach.[25,82] Note that the last term scales as $\mathcal{O}(\hbar^0)$, leading to the accuracy of $\mathcal{L}_{\text{MQC}}^{[1]}$ up to $\mathcal{O}(\hbar)$. However, the last term was not straightforward to evaluate.[82] Hence, in the common PBME approach, this term is often dropped, and $\mathcal{L}_{\text{LSC}}^{[1]}$ is used in the PBME calculation. Later, it was shown[82,84] that this term can be approximately expressed as

$$\frac{\hbar}{8}[\overrightarrow{\nabla}_\mathbf{q}^{\mathrm{T}} \mathcal{V}(R) \overrightarrow{\nabla}_\mathbf{q} + \overrightarrow{\nabla}_{\mathbf{p}_l}^{\mathrm{T}} \mathcal{V}(R) \overrightarrow{\nabla}_\mathbf{p}] \frac{\overleftarrow{\partial}}{\partial R} \frac{\overrightarrow{\partial}}{\partial P}$$
$$= \sum_{ij} \frac{\mathcal{K}}{2(\mathcal{K}+4)\hbar} \left(q_j q_j + p_i p_j - \frac{\hbar}{2}\delta_{ij} \right) \frac{\partial \mathcal{V}_{ij}(R)}{\partial R} \frac{\overrightarrow{\partial}}{\partial P}. \quad \text{(D6)}$$

Explicitly including this term and using $\mathcal{L}_{\text{MQC}}^{[1]}$ for QCLE (which is referred to as the non-Hamiltonian PBME[84]) indeed improve the accuracy of the population dynamics in spin-boson problems.[84] Note that under the Matsubara limit, this term can be made as small as needed based on the mixed-time slicing argument [see Eq. (A14) in Appendix A].

Of course, the form of the Liouvillian is not the only factor that influences the results of $C_{AB}^{[1]}(t)$. For the population dynamics, how to approximate $[\hat{A}]_W$ and $[\hat{B}]_W$ will also significantly influence the accuracy of these approximated methods.[109] For example, when computing $\rho_{jj}(t) = \text{Tr}[\hat{\rho}(0)e^{\frac{i}{\hbar}\hat{H}t}|j\rangle\langle j|e^{-\frac{i}{\hbar}\hat{H}t}]$, the standard LSC-IVR approach[16,18] corresponds to

$$C_{AB}^{\text{LSC}}(t) = \frac{\alpha_1}{\mathcal{Z}} \int d\mathbf{R} \int d\mathbf{P} \int d\mathbf{q} \int d\mathbf{p} [|i\rangle\langle i|]_W [e^{-\beta \hat{H}_0}]_W e^{\mathcal{L}_{\text{LSC}}^{[1]} \cdot t} [|j\rangle\langle j|]_W, \quad \text{(D7)}$$

and the standard PBME approach[25,82] corresponds to

$$C_{AB}^{\text{PBME}}(t) = \frac{\alpha_1}{\mathcal{Z}} \int d\mathbf{R} \int d\mathbf{P} \int d\mathbf{q} \int d\mathbf{p} [|i\rangle\langle i|]_W [e^{-\beta \hat{H}_0}]_W e^{\mathcal{L}_{\text{LSC}}^{[1]} \cdot t} [\hat{a}_j^\dagger \hat{a}_j]_W, \quad \text{(D8)}$$

where $|j\rangle\langle j|$ is the electronic projection operator and $\hat{a}_j^\dagger \hat{a}_j$ is the corresponding operator in the mapping representation. Their Wigner transforms are

$$[|j\rangle\langle j|]_W = \frac{2^{\mathcal{K}+1}}{\hbar} e^{-\frac{1}{\hbar}\sum_i(q_i^2 + p_i^2)} \left(q_j^2 + p_j^2 - \frac{\hbar}{2} \right), \quad \text{(D9)}$$

$$[\hat{a}_j^\dagger \hat{a}_j]_W = \frac{1}{2\hbar}(q_j^2 + p_j^2 - \hbar). \quad \text{(D10)}$$

The numerical comparisons between these two approaches have been extensively discussed in the recent work,[109–111] and recent development on choosing the identity operator[109,111,112] has also shown to significantly improve the population dynamics, even just using a less accurate Liouvillian $\mathcal{L}_{\text{LSC}}^{[1]}$. Along the same direction, one can use the mapping action variable's Wigner transform[113] to construct $[\hat{A}]_W$ and $[\hat{B}]_W$ and engineer various shapes of Window functions for these estimators.[107,108,114] This idea has also lead to a significant improvement of the population dynamics.[33]

Finally, if one takes $N = 1$ for the nuclear DOF and $N = 2$ for the electronic mapping DOF, as well as making the truncation in Eqs. (D2) and (D3) and dropping the last term in Eq. (A6), the exact Liouvillian $\mathcal{L}^{[N]}$ [Eq. (24)] reduces to the partially linearized Liouvillian as follows:

$$\mathcal{L}_{\text{PL}} = \frac{P}{m}\frac{\overrightarrow{\partial}}{\partial R} - \frac{2}{\hbar}\left[V_0(R) + \sum_{l=1}^{2}V_{\text{e}}(R,\mathbf{q}_l,\mathbf{p}_l)\right]\frac{\overleftarrow{\partial}}{\partial R}\frac{\overrightarrow{\partial}}{\partial P}$$
$$+ \sum_{l=1}^{2}\frac{1}{\hbar}[\mathbf{p}_l^{\text{T}}\mathcal{V}(R)\overrightarrow{\nabla}_{\mathbf{q}_l} - \mathbf{q}_l^{\text{T}}\mathcal{V}(R)\overrightarrow{\nabla}_{\mathbf{p}_l}], \quad \text{(D11)}$$

which is reminiscent of the Liouvillian used in the Forward–Backward trajectory solution (FBTS) for the QCLE[26,27] and is also closely related to the equation of motion in the Partial Linearized Density Matrix (PLDM) path-integral approach.[22,115,116] In addition, the recently proposed two-oscillator mapping of PBME[117] also adapts the same Liouvillian $\mathcal{L}_{\text{PL}}$, even though the two copies of the mapping variables are introduced through the mapping relation of the electronic states. However, we have to be cautious to draw any further connections between the correlation function $C_{AB}^{[N]}(t)$ in Eq. (105) and those in FBTS and PLDM, as the latter two approaches use the coherent state representation for the mapping DOFs instead of the Wigner representation used in this work, and hence should be viewed as the hybrid Husimi (mapping)–Wigner (nuclear) representation for non-adiabatic path-integral dynamics.

APPENDIX E: NUMERICAL TESTS OF THE NON-ADIABATIC RPMD

Finally, we provide discussions of the current approach with the previous state-dependent RPMD approaches, as well as preliminary numerical tests of the non-adiabatic RPMD correlation function in Eq. (82).

The originally proposed NRPMD does not sample the MV-RPMD initial distribution $\Gamma \cdot e^{-\beta H_N^{\text{RP}}}$ described in Eq. (82). Instead, it uses a simple position and momentum mapping variable resolution in the initial QBD,[54] resulting in the following TCF:

$$C_{AB}^{\text{NRP}'}(t) = \frac{1}{\mathcal{Z}_N^{\text{RP}}}\int d\mathcal{P}\int d\mathcal{Q}\int d\mathbf{q}\int d\mathbf{p}$$
$$\times \Gamma'(\mathcal{Q},\mathbf{q},\mathbf{p})e^{-\beta H_N^{\text{RP}}(\mathcal{P},\mathcal{Q})}A(\mathcal{Q})\cdot e^{\mathcal{L}_{\text{RP}}^{[N]}t}B(\mathcal{Q}), \quad \text{(E1)}$$

where $\Gamma'(\mathcal{Q},\mathbf{q},\mathbf{p})$ is expressed as[54]

$$\Gamma'(\mathcal{Q},\mathbf{q},\mathbf{p}) = \phi' e^{-\frac{\mathcal{G}_N}{\hbar}}\prod_{l=1}^{N}[\mathbf{p}_{l-1}^{\text{T}}\mathcal{M}(R_l)\mathbf{q}_l]\cdot[\mathbf{q}_l^{\text{T}}\mathcal{M}(R_l)\mathbf{p}_l]$$
$$= \phi' e^{-\frac{\mathcal{G}_N}{\hbar}}\text{Tr}_{\text{e}}\prod_{l=1}^{N}[\mathcal{M}(R_l)\mathbf{q}_l\mathbf{q}_l^{\text{T}}\mathcal{M}(R_l)\mathbf{p}_l\mathbf{p}_l^{\text{T}}], \quad \text{(E2)}$$

where $\phi' = \left(\frac{4}{\pi^K}\right)^N$, $\mathcal{G}_N = \sum_{l=1}^{N}(\mathbf{q}_l^{\text{T}}\mathbf{q}_l + \mathbf{p}_l^{\text{T}}\mathbf{p}_l)$, and $\mathcal{M}_{ij}(R_l) = \langle i|e^{-\frac{1}{2}\beta_N\hat{V}_{\text{e}}(R_l)}|j\rangle$. Thus, the only difference between the original NRPMD[54] and the NRPMD formalism in this work is the expression of the initial Boltzmann operator. Note that Γ' is pure real, as opposed to the complex Γ in Eq. (82).

The MV-RPMD approach, on the other hand, samples the initial distribution with $\tilde{H}_N^{\text{RP}} = H_N^{\text{RP}}(\mathcal{P},\mathcal{Q}) - \frac{1}{\beta}\ln|\mathfrak{R}[\Gamma(\mathcal{Q},\mathbf{q},\mathbf{p})]|$ and uses the same Hamiltonian to propagate dynamics, resulting in the following TCF:

$$C_{AB}^{\text{MV}}(t) = \frac{1}{\mathcal{Z}_N^{\text{RP}}}\int d\mathcal{P}\int d\mathcal{Q}\int d\mathbf{q}\int d\mathbf{p}$$
$$\times |\mathfrak{R}[\Gamma(\mathcal{Q},\mathbf{q},\mathbf{p})]|e^{-\beta\tilde{H}_N^{\text{RP}}(\mathcal{P},\mathcal{Q})}A(\mathcal{Q})\cdot e^{\mathcal{L}_{\text{MV}}^{[N]}t}B(\mathcal{Q}), \quad \text{(E3)}$$

where the MV-RPMD Liouvillian is expressed as

$$\mathcal{L}_{\text{MV}}^{[N]} = \sum_n\frac{\mathcal{P}_n}{m}\frac{\overrightarrow{\partial}}{\partial\mathcal{Q}_n} - \left[m\omega_n^2\mathcal{Q}_n + \frac{\partial U_0^{[N]}(\mathcal{Q})}{\partial\mathcal{Q}_n}\right.$$
$$\left.-\frac{1}{\beta|\mathfrak{R}[\Gamma]|}\frac{\partial|\mathfrak{R}[\Gamma]|}{\partial\mathcal{Q}_n}\right]\frac{\overrightarrow{\partial}}{\partial\mathcal{P}_n} + \frac{1}{\beta|\mathfrak{R}[\Gamma]|}$$
$$\times\sum_{l=1}^{N}\left[-\left(\frac{\partial|\mathfrak{R}[\Gamma]|}{\partial\mathbf{p}_l}\right)^{\text{T}}\cdot\overrightarrow{\nabla}_{\mathbf{q}_l} + \left(\frac{\partial|\mathfrak{R}[\Gamma]|}{\partial\mathbf{q}_l}\right)^{\text{T}}\cdot\overrightarrow{\nabla}_{\mathbf{p}_l}\right], \quad \text{(E4)}$$

which directly corresponds to the MV-RPMD Hamiltonian[57] $\tilde{H}_N^{\text{RP}} = H_N^{\text{RP}}(\mathcal{P},\mathcal{Q}) - \frac{1}{\beta}\ln|\mathfrak{R}[\Gamma(\mathcal{Q},\mathbf{q},\mathbf{p})]|$. To the best of our knowledge, there is no rigorous theoretical justification of the Liouvillian $\mathcal{L}_{\text{MV}}^{[N]}$. Because of using $\mathcal{L}_{\text{MV}}^{[N]}$, MV-RPMD is not capable to provide the correct electronic Rabi oscillations when the electronic and nuclear DOFs are decoupled.[57,101] In contrast, non-adiabatic Matsubara dynamics and NRPMD are exact under the electron–nuclear decoupled limit when the nuclear potential is harmonic.[79] On the other hand, MV-RPMD does preserve the QBD at any given N because it uses the same Hamiltonian for initial sampling and for dynamics propagation.[57]

Note that in the MV-RPMD approach,[57] to facilitate the calculation with real trajectories, it was proposed to use $\mathfrak{R}[\Gamma]$ (only taking the real part of Γ) in both the initial Boltzmann distribution as well as in the above Liouvillian. This argument is based on the fact that the partition function $\mathcal{Z}_N^{\text{RP}}$ is real, and the operator estimators do not contain any imaginary part; hence, the real and the imaginary part of the estimators are completely separated, and the ensemble average of the imaginary part should go to zero. This is true if both $\hat{A}$ and $\hat{B}$ are not related to electronic states (mapping variables). On the other hand, there is no rigorous justification why this should also be applied to the Liouvillian. For general operators, one should recognize that Γ is indeed complex, and a more rigorous trajectory approach in MV-RPMD should be replacing $\Gamma \to |\Gamma|$ in the distribution and the Liouvillian and then performing the ensemble average by weighting each trajectory with phase $\Gamma/|\Gamma|$.

To numerically compute TCF with the current NRPMD approach, we rewrite Eq. (82) as follows:

$$C_{AB}^{\text{NRP}}(t) = \frac{\alpha_N \cdot \alpha_M}{\mathcal{Z}_N^{\text{RP}}}\int d\mathcal{P}\int d\mathcal{Q}\int d\mathbf{q}\int d\mathbf{p}$$
$$\times \frac{\Gamma(\mathcal{Q},\mathbf{q},\mathbf{p})}{|\Gamma(\mathcal{Q},\mathbf{q},\mathbf{p})|}\cdot|\Gamma(\mathcal{Q},\mathbf{q},\mathbf{p})|\cdot e^{-\beta H_N^{\text{RP}}(\mathcal{P},\mathcal{Q})}A(\mathcal{Q})$$
$$\times e^{\mathcal{L}_{\text{RP}}^{[N]}t}B(\mathcal{Q}), \quad \text{(E5)}$$

where the initial distribution $|\Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p})| \cdot e^{-\beta H_N^{RP}(\mathcal{P}, \mathcal{Q})}$ is sampled by Monte Carlo (based on a simple metropolis algorithm), the dynamics is propagated by $e^{\mathcal{L}_{RP}^{[N]}}$ through a simple numerical integrator,[55] and each trajectory is weighted by a complex phase $\frac{\Gamma}{|\Gamma|}$. However, we can further take advantage of the pure real estimators for A and B, as well as the Liouvillian $\mathcal{L}_{RP}^{[N]}$, to rewrite Eq. (82) as

$$
\begin{aligned}
C_{AB}^{NRP}(t) = \frac{\alpha_N \cdot \alpha_M}{\mathcal{Z}_N^{RP}} \int d\mathcal{P} \int d\mathcal{Q} \int d\mathbf{q} \int d\mathbf{p} \\
\times \, \mathrm{sgn}(\mathfrak{R}[\Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p})]) \cdot |\mathfrak{R}[\Gamma(\mathcal{Q}, \mathbf{q}, \mathbf{p})]| \\
\times \, e^{-\beta H_N^{RP}(\mathcal{P}, \mathcal{Q})} A(\mathcal{Q}) e^{\mathcal{L}_{RP}^{[N]} t} B(\mathcal{Q}),
\end{aligned} \tag{E6}
$$

where $\mathrm{sgn}(\mathfrak{R}[\Gamma])$ is the sign (plus or minus) of the real part of Γ. The above expression is based on the fact that $C_{AB}^{[N]}(t)$ is pure real and the $\mathrm{Im}[\Gamma]$ part is completely separated from the $\mathfrak{R}[\Gamma]$ and does not contribute to the value of the $C_{AB}^{[N]}(t)$. (Note that the ensemble average of $\mathrm{Im}[\Gamma]$ is 0, but $\mathrm{Im}[\Gamma]$ for the individual trajectory is not).

To assess the numerical performance of the current NRPMD formalism, we adapt a commonly used model system that contains one nuclear coordinate and two electronic states,[54,57]

$$
\hat{H} = \frac{\hat{P}^2}{2M} + \frac{1}{2} M \omega^2 \hat{R}^2 + \begin{bmatrix} \varepsilon + c\hat{R} & \Delta \\ \Delta & -\varepsilon - c\hat{R} \end{bmatrix}, \tag{E7}
$$

where Δ is the electronic coupling, c is the vibronic coupling, and 2ε is the energy bias between the two diabatic states. We choose a reduced unit system such that $M = \hbar = 1$ and $\omega = \beta = c = 1$. We choose $N = 8$ beads for models I and V and $N = 6$ beads for

TABLE I. Parameters (in a.u.) for model systems I–VI.

	I	II	III	IV	V	VI
ε	0	0	1.5	0	0	2
Δ	10	0.10	0.10	1	4	1

models II–IV and for model VI. A total of 10^6 trajectories are used for tight numerical convergence, even though only 10^4 trajectories are sufficient to provide the basic trend.

Table I presents the parameters for all of the model systems used in this paper. In particular, models I and V are in the adiabatic regime, where $\Delta \gg \beta^{-1}$; models II and III are in the non-adiabatic regime, where $\Delta \ll \beta^{-1}$; and models IV and VI are in the intermediate regime, where $\Delta \sim \beta^{-1}$. Models III and VI are asymmetric cases with finite diabatic energy bias 2ε, and the rest of the model systems are symmetric cases with $\epsilon = 0$.

Figure 4 presents the nuclear position auto-correlation function computed from NRPMD (black), MV-RPMD (blue dashed), and the numerical exact method (red) for models I–IV. Model I in Fig. 4(a) is in the adiabatic regime. In this case, NRPMD goes back to the standard RPMD and agrees with the exact result due to the near Harmonic adiabatic potential. Model II in Fig. 4(b) is in the non-adiabatic regime. This is the most challenging case and the most relevant regime for non-adiabatic electron transfer[46] and proton-coupled electron transfer reactions.[47] In this regime, mean-field RPMD starts to break down even at a very short time, as shown in the previous work.[57] NRPMD, on the other hand, performs reasonably well compared to numerically exact discrete value representation (DVR)[118] calculations at a longer time. Model III corresponds
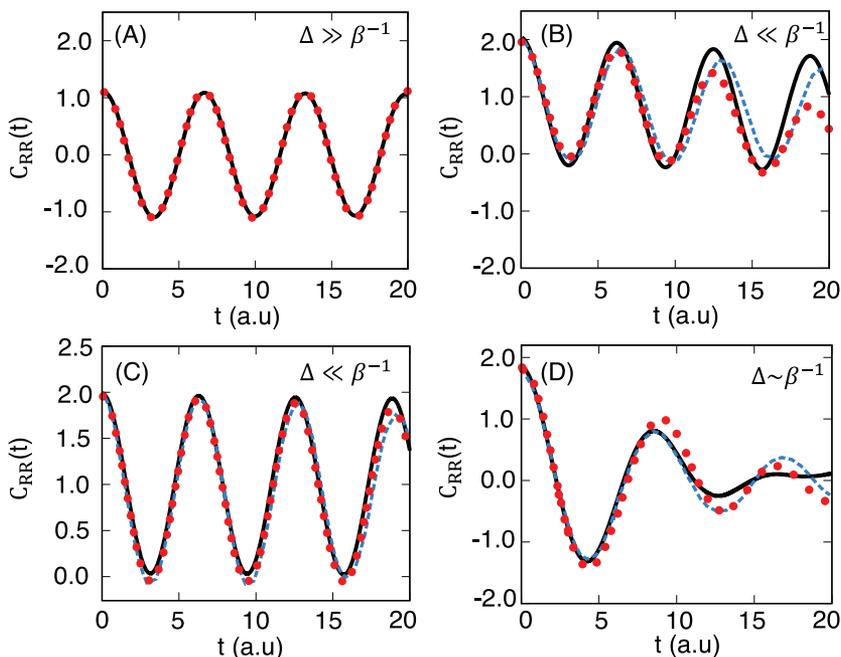
FIG. 4. The Kubo-transformed nuclear position auto-correlation function for models I–IV obtained from NRPMD (black solid), MV-RPMD (blue dashed), and numerical exact results (red dots). Results for (a) model I (symmetric, adiabatic), (b) model II (symmetric, non-adiabatic), (c) model III (asymmetric, non-adiabatic), and (d) model IV (symmetric, intermediate).

FIG. 5. The Kubo-transformed population correlation function for models IV–VI obtained from NRPMD (black solid) with numerical exact results (red dots). Results for (a) model V (symmetric, adiabatic), (b) model VI (asymmetric, intermediate), and (c) model IV (symmetric, intermediate).

We find that the numerical results obtained with the current NRPMD formalism (for the current model systems) are not significantly different than those obtained from the original NRPMD[54] due to the same Liouvillian used in both formalisms. On the other hand, the correlation function obtained from MV-RPMD[57] starts to oscillate with a different frequency [see Fig. 4(b)] compared to the quantum result at a longer time, especially for models II and III, even though it uses the same initial QBD for NRPMD. This might happen because of the inter-bead couplings for mapping DOF in the Liouvillian [Eq. (E4)], which starts to contaminate the physical frequency of the system. The same behavior has also been found for population related quantities,[57] and MV-RPMD is not capable to capture the electronic Rabi oscillations presented in Fig. 5. On the other hand, MV-RPMD does preserve QBD for any arbitrary number of beads N, whereas for a finite number of N, there is no rigorous proof that NRPMD preserve QBD[54,55,97] at a single trajectory level.

DATA AVAILABILITY

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

REFERENCES

[1]H.-D. Meyer, U. Manthe, and L. S. Cederbaum, Chem. Phys. Lett. **165**, 73 (1990).
[2]M. Beck, A. Jackle, G. Worth, and H. Meyer, Phys. Rep. **324**, 1 (2000).
[3]H. Wang and M. Thoss, J. Chem. Phys. **119**, 1289 (2003).
[4]P. Eisenbrandt, M. Ruckenbauer, S. Römer, and I. Burghardt, J. Chem. Phys. **149**, 174101 (2018).
[5]G. W. Richings and S. Habershon, J. Chem. Phys. **148**, 134116 (2018).
[6]D. V. Makhov, W. J. Glover, T. J. Martinez, and D. V. Shalashilin, J. Chem. Phys. **141**, 054110 (2014).
[7]B. F. E. Curchod and T. J. Martínez, Chem. Rev. **118**, 3305 (2018).
[8]P. L. Walters and N. Makri, J. Chem. Phys. **144**, 044108 (2016).
[9]P. L. Walters and N. Makri, J. Phys. Chem. Lett. **6**, 4959 (2015).
[10]S. M. Greene and V. S. Batista, J. Chem. Theory Comput. **13**, 4034 (2017).
[11]J. Ren, Z. Shuai, and G. K.-L. Chan, J. Chem. Theory Comput. **14**, 5027 (2018).
[12]J. C. Tully, J. Chem. Phys. **93**, 1061 (1990).
[13]J. E. Subotnik, A. Jain, B. Landry, A. Petit, W. Ouyang, and N. Bellonzi, Annu. Rev. Phys. Chem. **67**, 387 (2016).
[14]L. Wang, A. Akimov, and O. V. Prezhdo, J. Phys. Chem. Lett. **7**, 2100 (2016).
[15]R. Crespo-Otero and M. Barbatti, Chem. Rev. **118**, 7026 (2018).
[16]W. H. Miller, J. Phys. Chem. A **105**, 2942 (2001).
[17]W. H. Miller, J. Phys. Chem. A **113**, 1405 (2009).
[18]X. Sun, H. Wang, and W. H. Miller, J. Chem. Phys. **109**, 4190 (1998).
[19]Q. Shi and E. Geva, J. Phys. Chem. A **108**, 6109 (2004).
[20]S. Bonella and D. F. Coker, J. Chem. Phys. **122**, 194102 (2005).
[21]N. Makri, Phys. Chem. Chem. Phys. **13**, 14442 (2011).
[22]P. Huo and D. F. Coker, J. Chem. Phys. **135**, 201101 (2011).
[23]M. Lee, P. Huo, and D. F. Coker, Annu. Rev. Phys. Chem. **67**, 639 (2016).
[24]D. M. Kernan, G. Ciccotti, and R. Kapral, J. Phys. Chem. B **112**, 424 (2008).
[25]H. Kim, A. Nassimi, and R. Kapral, J. Chem. Phys. **129**, 084102 (2008).
[26]C.-Y. Hsieh and R. Kapral, J. Chem. Phys. **137**, 22A507 (2012).
[27]C.-Y. Hsieh and R. Kapral, J. Chem. Phys. **138**, 134110 (2013).
[28]R. Kapral, J. Phys.: Condens. Matter **27**, 073201 (2015).
[29]P. V. Parandekar and J. C. Tully, J. Chem. Theory Comput. **2**, 229 (2006).
[30]J. R. Schmidt, P. V. Parandekar, and J. C. Tully, J. Chem. Phys. **129**, 044104 (2008).
[31]S. Habershon and D. E. Manolopoulos, J. Chem. Phys. **131**, 244518 (2009).
[32]U. Müller and G. Stock, J. Chem. Phys. **111**, 77 (1999).

to the asymmetric non-adiabatic regime [Fig. 4(c)] with diabatic energy bias 2ϵ, and model IV is in the intermediate regime. In both regimes, NRPMD behaves reasonably well.

Figure 5 presents the electronic population correlation function $C_{11}^K(t)$ [where $\hat{A} = \hat{B} = |1\rangle\langle 1|$ in $C_{AB}^K(t)$] computed from the NRPMD approach (black) and the numerically exact approach (red dots) from DVR.[118] For the NRPMD simulations, we use Eq. (98) and the expression of $[\hat{B}]_N$ in Eq. (100). Again, NRPMD agrees very well with exact results in both the adiabatic regime for model V presented in Fig. 5(a) and for the intermediate regimes for models VI and IV presented in Figs. 5(b) and 5(c).

[33] W. H. Miller and S. J. Cotton, Faraday Discuss. **195**, 9 (2016).

[34] A. Kelly, N. Brackbill, and T. E. Markland, J. Chem. Phys. **142**, 094110 (2015).

[35] A. Kelly, A. Montoya-Castillo, L. Wang, and T. E. Markland, J. Chem. Phys. **144**, 184105 (2016).

[36] E. Mulvihill, A. Schubert, X. Sun, B. D. Dunietz, and E. Geva, J. Chem. Phys. **150**, 034101 (2019).

[37] B. J. Berne and D. Thirumalai, Annu. Rev. Phys. Chem. **37**, 401 (1986).

[38] D. M. Ceperley, Rev. Mod. Phys. **67**, 279 (1995).

[39] D. Chandler and P. G. Wolynes, J. Chem. Phys. **74**, 4078 (1981).

[40] J. Cao and G. A. Voth, J. Chem. Phys. **100**, 5106 (1994).

[41] S. Jang and G. A. Voth, J. Chem. Phys. **111**, 2371 (1999).

[42] Q. Shi and E. Geva, J. Chem. Phys. **118**, 7562 (2003).

[43] S. Habershon, D. E. Manolopoulos, T. E. Markland, and T. F. Miller, Annu. Rev. Phys. Chem. **64**, 124105 (2013).

[44] I. R. Craig and D. E. Manolopoulos, J. Chem. Phys. **121**, 3368 (2004).

[45] A. R. Menzeleev, N. Ananth, and T. F. Miller, J. Chem. Phys. **132**, 034106 (2010).

[46] A. R. Menzeleev, N. Ananth, and T. F. Miller, J. Chem. Phys. **135**, 074106 (2011).

[47] J. S. Kretchmer and T. F. Miller, J. Chem. Phys. **138**, 134109 (2013).

[48] J. S. Kretchmer and T. F. Miller, Inorg. Chem. **55**, 1022 (2016).

[49] R. L. Kenion and N. Ananth, Phys. Chem. Chem. Phys. **18**, 26117 (2016).

[50] R. F. N. Boekelheide and T. F. Miller, Proc. Natl. Acad. Sci. U. S. A. **108**, 16159 (2011).

[51] L. Wang, S. D. Fried, S. G. Boxer, and T. E. Markland, Proc. Natl. Acad. Sci. U. S. A. **111**, 18454 (2014).

[52] O. Marsalek and T. E. Markland, J. Phys. Chem. Lett. **8**, 1545 (2017).

[53] T. E. Markland and M. Ceriotti, Nat. Rev. Chem. **2**, 0109 (2018).

[54] J. O. Richardson and M. Thoss, J. Chem. Phys. **139**, 031102 (2013).

[55] J. O. Richardson, P. Meyer, M.-O. Pleinert, and M. Thoss, Chem. Phys. **482**, 124 (2017).

[56] S. N. Chowdhury and P. Huo, J. Chem. Phys. **150**, 244102 (2019).

[57] N. Ananth, J. Chem. Phys. **139**, 124102 (2013).

[58] J. R. Duke and N. Ananth, J. Phys. Chem. Lett. **6**, 4219 (2015).

[59] S. Pierre, J. R. Duke, T. J. H. Hele, and N. Ananth, J. Chem. Phys. **147**, 234103 (2017).

[60] T. Yoshikawa and T. Takayanagi, Chem. Phys. Lett. **564**, 1 (2013).

[61] A. R. Menzeleev, F. Bell, and T. F. Miller, J. Chem. Phys. **140**, 064103 (2014).

[62] J. S. Kretchmer, N. Boekelheide, J. J. Warren, J. R. Winkler, H. B. Gray, and T. F. Miller, Proc. Natl. Acad. Sci. U. S. A. **115**, 6129 (2018).

[63] S. N. Chowdhury and P. Huo, J. Chem. Phys. **147**, 214109 (2017).

[64] P. Shushkov, R. Li, and J. C. Tully, J. Chem. Phys. **137**, 22A549 (2012).

[65] F. A. Shakib and P. Huo, J. Phys. Chem. Lett. **8**, 3073 (2017).

[66] X. Tao, P. Shushkov, and T. F. Miller, J. Chem. Phys. **148**, 102327 (2018).

[67] X. Tao, P. Shushkov, and T. F. Miller, J. Phys. Chem. A **123**, 3013 (2019).

[68] R. Kaur and R. Welsch, J. Chem. Phys. **150**, 114105 (2019).

[69] T. J. H. Hele, M. J. Willatt, A. Muolo, and S. C. Althorpe, J. Chem. Phys. **142**, 134103 (2015).

[70] M. J. Willatt, "Matsubara dynamics and its practical implementations," Ph.D. thesis (University of Cambridge, 2017).

[71] K. A. Jung, P. E. Videla, and V. S. Batista, J. Chem. Phys. **151**, 034108 (2019).

[72] K. A. Jung, P. E. Videla, and V. S. Batista, J. Chem. Phys. **153**, 124112 (2020).

[73] T. J. H. Hele, M. J. Willatt, A. Muolo, and S. C. Althorpe, J. Chem. Phys. **142**, 191101 (2015).

[74] S. Karsten, S. D. Ivanov, S. I. Bokarev, and O. Kühn, J. Chem. Phys. **149**, 194103 (2018).

[75] H. D. Meyer and W. H. Miller, J. Chem. Phys. **70**, 3214 (1979).

[76] G. Stock and M. Thoss, Phys. Rev. Lett. **78**, 578 (1997).

[77] G. Stock and M. Thoss, Phys. Rev. A **59**, 64 (1999).

[78] N. Ananth and T. F. Miller, J. Chem. Phys. **133**, 234103 (2010).

[79] T. J. H. Hele and N. Ananth, Faraday Discuss. **195**, 269 (2016).

[80] M. Hillery, R. F. O'Connell, M. O. Scully, and E. P. Wigner, Phys. Rep. **106**, 121 (1984).

[81] J. E. Moyal, Math. Proc. Cambridge Philos. Soc. **45**, 99–124 (1949).

[82] A. N. S. Bonella and R. Kapral, J. Chem. Phys. **133**, 134115 (2010).

[83] P. Ehrenfest, Z. Phys. **45**, 455 (1927).

[84] H. W. Kim and Y. M. Rhee, J. Chem. Phys. **140**, 184106 (2014).

[85] H. J. Groenewold, Physica **12**, 405 (1946).

[86] M. Ceriotti, M. Parrinello, T. E. Markland, and D. E. Manolopoulos, J. Chem. Phys. **133**, 124104 (2010).

[87] G. Trenins and S. C. Althorpe, J. Chem. Phys. **149**, 014102 (2018).

[88] G. Trenins, M. J. Willatt, and S. C. Althorpe, J. Chem. Phys. **151**, 054109 (2019).

[89] M. J. Willatt, M. Ceriotti, and S. C. Althorpe, J. Chem. Phys. **148**, 102336 (2018).

[90] C. Chakravarty, Int. Rev. Phys. Chem. **16**, 421 (1997).

[91] C. Chakravarty, M. C. Gordillo, and D. M. Ceperley, J. Chem. Phys. **109**, 2123 (1998).

[92] D. L. Freeman and J. D. Doll, J. Chem. Phys. **80**, 5709 (1984).

[93] R. P. Steele, J. Zwickl, P. Shushkov, and J. C. Tully, J. Chem. Phys. **134**, 074112 (2011).

[94] C. M. Bender, D. C. Brody, and D. W. Hook, J. Phys. A: Math. Theor. **41**, 352003 (2008).

[95] M. Rossi, M. Ceriotti, and D. E. Manolopoulos, J. Chem. Phys. **140**, 234116 (2014).

[96] T. J. H. Hele, Mol. Phys. **115**, 1435 (2017).

[97] M. A. C. Saller, J. E. Runeson, and J. O. Richardson, *Quantum Chemistry and Dynamics of Excited States: Methods and Applications* (John Wiley & Sons Ltd., 2020), p. 629.

[98] R. Kapral, Annu. Rev. Phys. Chem. **57**, 129 (2006).

[99] R. Welsch, K. Song, Q. Shi, S. C. Althorpe, and T. F. Miller, J. Chem. Phys. **145**, 204118 (2016).

[100] J.-L. Liao and G. A. Voth, J. Phys. Chem. B **106**, 8449 (2002).

[101] S. C. Althorpe, N. Ananth, G. Angulo, R. D. Astumian, V. Beniwal, J. Blumberger, P. G. Bolhuis, B. Ensing, D. R. Glowacki, S. Habershon, S. Hammes-Schiffer, T. J. H. Hele, N. Makri, D. E. Manolopoulos, L. K. McKemmish, T. F. Miller, W. H. Miller, A. J. Mulholland, T. Nekipelova, E. Pollak, J. O. Richardson, M. Richter, P. R. Chowdhury, D. Shalashilin, and R. Szabla, Faraday Discuss. **195**, 311 (2016).

[102] J. E. Runeson and J. O. Richardson, J. Chem. Phys. **151**, 044119 (2019).

[103] J. E. Runeson and J. O. Richardson, J. Chem. Phys. **152**, 084110 (2020).

[104] J. R. Mannouch and J. O. Richardson, J. Chem. Phys. **153**, 194109 (2020).

[105] J. R. Mannouch and J. O. Richardson, J. Chem. Phys. **153**, 194110 (2020).

[106] J. Liu, J. Chem. Phys. **145**, 204105 (2016).

[107] S. J. Cotton and W. H. Miller, J. Chem. Phys. **150**, 104101 (2019).

[108] S. J. Cotton and W. H. Miller, J. Chem. Phys. **139**, 234112 (2013).

[109] M. A. C. Saller, A. Kelly, and J. O. Richardson, J. Chem. Phys. **150**, 071101 (2019).

[110] E. Mulvihill, X. Gao, Y. Liu, A. Schubert, B. D. Dunietz, and E. Geva, J. Chem. Phys. **151**, 074103 (2019).

[111] X. Gao, M. A. C. Saller, Y. Liu, A. Kelly, J. O. Richardson, and E. Geva, J. Chem. Theory Comput. **16**, 2883–2895 (2020).

[112] M. A. C. Saller, A. Kelly, and J. O. Richardson, Faraday Discuss. **221**, 150–167 (2020).

[113] W. H. Miller and S. J. Cotton, J. Chem. Phys. **145**, 081102 (2016).

[114] S. J. Cotton and W. H. Miller, J. Chem. Phys. **145**, 144108 (2016).

[115] P. Huo and D. F. Coker, Mol. Phys. **110**, 1035 (2012).

[116] P. Huo and D. F. Coker, J. Chem. Phys. **137**, 22A535 (2012).

[117] H. W. Kim and Y. M. Rhee, J. Chem. Phys. **153**, 214103 (2020).

[118] D. T. Colbert and W. H. Miller, J. Chem. Phys. **96**, 1982 (1992).