

Deriving the exact nonadiabatic quantum propagator in the mapping variable representation

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We derive an exact quantum propagator for nonadiabatic dynamics in multi-state systems using the mapping variable representation, where classical-like Cartesian variables are used to represent both continuous nuclear degrees of freedom and discrete electronic states. The resulting Liouvillian is a Moyal series that, when suitably approximated, can allow for the use of classical dynamics to efficiently model large systems. We demonstrate that different truncations of the exact Liouvillian lead to existing approximate semiclassical and mixed quantum-classical methods and we derive an associated error term for each method. Furthermore, by combining the imaginary-time path-integral representation of the Boltzmann operator with the exact Liouvillian, we obtain an analytic expression for thermal quantum real-time correlation functions. These results provide a rigorous theoretical foundation for the development of accurate and efficient classical-like dynamics to compute observables such as electron transfer reaction rates in complex quantized systems.

1 Introduction

The accurate calculation of nonadiabatic dynamics has been a longstanding problem in chemical physics since the 1930s^{1,2}, being fundamental to charge and energy transfer in biological and chemical systems^{3,4}. Many approximate methods have been developed using classical, or classical-like dynamics to describe nonadiabatic quantum processes with the electronic degrees of freedom treated as discrete states, including Marcus theory^{3,5,6}, surface hopping^{7–10}, semiclassical¹¹ and mixed quantum-classical^{12–14} methods.

A particularly successful approach involves the use of mapping variables, where discrete electronic degrees of freedom are mapped onto continuous positions and momenta of fictitious harmonic oscillators. Originally proposed by Meyer and Miller^{15,16}, this mapping was shown to be exact by Stock and Thoss^{17,18} and has been developed using various semiclassical^{19–21}, quasiclassical²², (partially) linearized^{23–30}, and path integral^{31–34} techniques.

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Here, we derive from first principles the exact nonadiabatic quantum propagator in the mapping variable representation and relate this to the conventional adiabatic (single surface) Liouvillian, the Moyal series^{35,36}. We show that careful approximation of the exact propagator leads to a number of existing methods, and we provide the associated error term in each case. Furthermore, using the generalized Kubo transform^{37–39}, previously employed to obtain approximate quantum dynamics methods in single-surface systems^{40–42}, we obtain an analytic expression for the nonadiabatic quantum Boltzmann distribution and the exact propagator in the path-integral representation.

The article is structured as follows: in section 2, we provide an overview of background theory, in section 3 we derive the exact propagator and make approximations that lead to various existing methods. Thermal correlation functions are discussed in section 4, in section 5 we obtain an exact path-integral propagator using the Generalized Kubo transform, and we present our conclusions in section 6.

2 Background theory

The background theory for mapping variables and Wigner transforms are reviewed here to provide context for the main body of the article; for a detailed review of mapping variables and other nonadiabatic techniques, see Ref 18.

2.1 Mapping variables

For simplicity we consider a system with one Cartesian dimension position R with conjugate momentum P , mass m and \mathcal{K} diabatic electronic states with overall Hamiltonian*

$$\hat{H} = \frac{\hat{p}^2}{2m} + V_0(\hat{R}) + \sum_{n,m=1}^{\mathcal{K}} |\phi_n\rangle V_e(\hat{R})_{nm} \langle\phi_m| \quad (1)$$

$$\equiv \frac{\hat{p}^2}{2m} + \sum_{n,m=1}^{\mathcal{K}} |\phi_n\rangle [V_e(\hat{R})_{nm} + \delta_{nm} V_0(\hat{R})] \langle\phi_m|, \quad (2)$$

where $V_0(\hat{R})$ is any state-independent part of the potential and $V_e(\hat{R})_{nm}$ is a matrix element of the nonadiabatic potential matrix $\mathbf{V}_e(\hat{R})$. The equivalence of Eq. (1) and Eq. (2) follows from application of the identity

$$\hat{\mathbf{1}} = \int dR \sum_{n=1}^{\mathcal{K}} |R, \phi_n\rangle \langle R, \phi_n|, \quad (3)$$

and we assume throughout that $\mathbf{V}_e(\hat{R})$ is real and symmetric; extension to a complex hermitian Hamiltonian (and multidimensional systems) is straightforward.

The Hamiltonian can equivalently be written in the singly excited oscillator (SEO) basis $\{|n\rangle\}$, $n = 1, \dots, \mathcal{K}$, where $|n\rangle$ corresponds to one quantum of excitation in the n th oscillator and zero quanta in the remaining $\mathcal{K} - 1$ oscillators^{15–18}.

* We also assume a sufficiently high temperature that exchange effects may be neglected.

This is achieved by mapping

$$|\phi_n\rangle\langle\phi_m| \mapsto \hat{a}_n^\dagger \hat{a}_m, \quad (4)$$

where \hat{a}_n^\dagger creates one quantum of excitation in the n th oscillator and \hat{a}_m destroys one quantum in the m th oscillator. An operator \hat{O} in the diabatic representation can then be expressed as

$$\hat{O} = \sum_{n,m=1}^{\mathcal{K}} \hat{a}_n^\dagger O(\hat{R}, \hat{P})_{nm} \hat{a}_m \quad (5)$$

where $O(\hat{R}, \hat{P})_{nm}$ is a scalar [matrix element of $\mathbf{O}(\hat{R}, \hat{P})$] in the space of electronic states, but an operator in the space of nuclear co-ordinates and momenta.

Writing the creation and annihilation operators in the position and momentum representation[†],

$$\hat{a}_m = \frac{1}{\sqrt{2\hbar}}(\hat{q}_m + i\hat{p}_m), \quad \hat{a}_n^\dagger = \frac{1}{\sqrt{2\hbar}}(\hat{q}_m - i\hat{p}_m), \quad (6)$$

we find

$$\hat{O} = \frac{1}{2\hbar} \sum_{n,m=1}^{\mathcal{K}} O_{nm}(\hat{R}, \hat{P})(\hat{q}_n \hat{q}_m + \hat{p}_n \hat{p}_m - \delta_{nm} \hbar). \quad (7)$$

The only operators in the mapping variable representation which correspond to a physically observable quantity are those of the functional form in Eq. (7), whose application upon a SEO will stay in the subspace of SEOs¹⁷.

The SEO eigenstates in the position representation are

$$\langle \mathbf{q} | n \rangle = \sqrt{\frac{2}{\hbar}} \frac{1}{(\pi \hbar)^{\mathcal{K}/4}} q_n e^{-\mathbf{q} \cdot \mathbf{q} / 2\hbar} \quad (8)$$

and the corresponding identity to Eq. (3)

$$\hat{\mathbf{I}} = \int dR \sum_{n=1}^{\mathcal{K}} |R, n\rangle \langle R, n|. \quad (9)$$

The identity expressed in electronic position-space variables,

$$\hat{\mathbf{I}}' = \int dR \int d\mathbf{q} |R, \mathbf{q}\rangle \langle R, \mathbf{q}|, \quad (10)$$

is overcomplete, since it includes all possible excitations of any of the \mathcal{K} oscillators, rather than just SEO states. However, using the SEO projection operator, $\hat{\mathcal{S}} = \sum_{n=1}^{\mathcal{K}} |n\rangle \langle n|$, we can constrain the position-space identity in Eq. (10) to the subspace of SEOs³²,

$$\hat{\mathbf{I}} = \int dR \int d\mathbf{q} \hat{\mathcal{S}} |R, \mathbf{q}\rangle \langle R, \mathbf{q}| \quad (11)$$

$$= \int dR \int d\mathbf{q} |R, \mathbf{q}\rangle \langle R, \mathbf{q}| \hat{\mathcal{S}}. \quad (12)$$

[†] Following others, we set the (arbitrary) mass and frequency of the harmonic oscillators to unity in atomic units but retain \hbar necessary to construct semiclassical approximations to the propagator.

2.2 Wigner transformed operators

Here we present standard results for Wigner distributions^{35,43,44} adapted to the mapping variable representation introduced in the previous section.

The Wigner transform⁴³ of an operator in the mapping variable representation is

$$[\hat{O}]_W(R, P, \mathbf{q}, \mathbf{p}) = \int dD \int d\Delta e^{iPD/\hbar} e^{i\mathbf{p}\cdot\Delta/\hbar} \times \langle R - D/2, \mathbf{q} - \Delta/2 | \hat{O} | R + D/2, \mathbf{q} + \Delta/2 \rangle. \quad (13)$$

Inserting Eq. (7) into Eq. (13) and evaluating the integrals over Δ gives

$$[\hat{O}]_W(R, P, \mathbf{q}, \mathbf{p}) = \frac{1}{2\hbar} \int dD e^{iPD/\hbar} \text{Tr}[(\mathbf{C} - \hbar\mathbf{1}) \langle R - D/2 | \mathbf{O}(\hat{R}, \hat{P}) | R - D/2 \rangle], \quad (14)$$

where $\mathbf{1}$ is the $\mathcal{K} \times \mathcal{K}$ identity matrix,

$$\mathbf{C} = (\mathbf{q} + i\mathbf{p}) \otimes (\mathbf{q} - i\mathbf{p})^T, \quad (15)$$

and \hat{O} is written in the matrix representation

$$\langle R - D/2 | \mathbf{O}(\hat{R}, \hat{P}) | R + D/2 \rangle_{nm} \equiv \langle R - D/2 | O(\hat{R}, \hat{P})_{nm} | R + D/2 \rangle. \quad (16)$$

If the projection operator \hat{S} is inserted alongside the operator \hat{O} (denoted with a subscript S), the Wigner transform is³²

$$[\hat{O}_S]_W(R, P, \mathbf{q}, \mathbf{p}) \equiv [\hat{S}\hat{O}\hat{S}]_W(R, P, \mathbf{q}, \mathbf{p}) \quad (17)$$

$$= \int dD \int d\Delta \sum_{n,m=1}^{\mathcal{K}} e^{iPD/\hbar} e^{i\mathbf{p}\cdot\Delta/\hbar} \times \langle \mathbf{q} - \Delta/2 | n \rangle \langle R - D/2 | O(\hat{R}, \hat{P})_{nm} | R + D/2 \rangle \langle m | \mathbf{q} + \Delta/2 \rangle \quad (18)$$

$$= \frac{2^{\mathcal{K}+1}}{\hbar} e^{-G/\hbar} \int dD e^{iPD/\hbar} \text{Tr} \left[(\mathbf{C} - \frac{\hbar}{2}\mathbf{1}) \langle R - D/2 | \hat{\mathbf{O}}(\hat{R}, \hat{P}) | R + D/2 \rangle \right], \quad (19)$$

where

$$G = \mathbf{q} \cdot \mathbf{q} + \mathbf{p} \cdot \mathbf{p}, \quad (20)$$

and we have noted that $|n\rangle$ does not depend on R to obtain Eq. (18).

In some circumstances \hat{O} can be written as a nuclear-only part \hat{O}_n and an electronic part \hat{O}_e [such as the Hamiltonian in Eq. (1)] and the operator in the mapping variable representation becomes

$$[\hat{O}]_W(R, P, \mathbf{q}, \mathbf{p}) = [\hat{O}_n]_W + \frac{1}{2\hbar} \text{Tr}[(\mathbf{C} - \hbar\mathbf{1}) [\mathbf{O}_e(\hat{R}, \hat{P})]_W] \quad (21)$$

where the nuclear-only Wigner transform is

$$[\hat{O}_n]_W = \int dD e^{iPD/\hbar} \langle R - D/2 | O_n(\hat{R}, \hat{P}) | R + D/2 \rangle \quad (22)$$

and the integral over D in Eq. (14) has been taken inside the trace of electronic variables

$$([\mathbf{O}_e(\hat{R}, \hat{P})]_W)_{nm} = \int dD e^{iPD/\hbar} \langle R - D/2 | O(\hat{R}, \hat{P})_{nm} | R + D/2 \rangle. \quad (23)$$

Although the nuclear-only part in Eq. (22) is solely a function of R and P , for generality in what follows the electronic part of the operator in Eq. (23) may be parametrically dependent upon the nuclear position and momenta as well as a function of \mathbf{q} and \mathbf{p} .

The trace of the product of two operators is simply the integral of the product of their Wigner transforms⁴⁴

$$\text{Tr}[\hat{O}_1 \hat{O}_2] = \frac{1}{(2\pi\hbar)^{\mathcal{X}+1}} \int dR \int dP \int d\mathbf{q} \int d\mathbf{p} [\hat{O}_1]_W [\hat{O}_2]_W, \quad (24)$$

though in the mapping variable representation this must be combined with SEO identities (\hat{S}) in order to confine the mapping variables to the correct Hilbert space. If there is no trace we can adapt the standard relation for the Wigner transform of a product^{36,44}

$$[\hat{O}_1 \hat{O}_2]_W = [\hat{O}_1]_W e^{-i\mathbf{\Lambda}\hbar/2} [\hat{O}_2]_W \quad (25)$$

to the mapping variable representation, where the $\mathbf{\Lambda}$ -operator is the negative of the Poisson bracket operator

$$\mathbf{\Lambda} = \begin{pmatrix} \Lambda_n \\ \Lambda_e \end{pmatrix}, \quad (26)$$

with the nuclear derivative (scalar in one dimension)

$$\Lambda_n = \overleftarrow{\partial}_P \overrightarrow{\partial}_R - \overleftarrow{\partial}_R \overrightarrow{\partial}_P, \quad (27)$$

and the electronic derivative

$$\Lambda_e = \overleftarrow{\nabla}_{\mathbf{p}} \cdot \overrightarrow{\nabla}_{\mathbf{q}} - \overleftarrow{\nabla}_{\mathbf{q}} \cdot \overrightarrow{\nabla}_{\mathbf{p}}. \quad (28)$$

We use the shorthand $\partial_P = \frac{\partial}{\partial P}$ and likewise for ∂_R ,

$$\nabla_{\mathbf{p}} = \begin{pmatrix} \partial_{p_1} \\ \partial_{p_2} \\ \vdots \\ \partial_{p_{\mathcal{X}}} \end{pmatrix} \quad (29)$$

and likewise for $\nabla_{\mathbf{q}}$, and the arrows represent the direction in which the derivative acts^{40,44}.

3 Correlation functions

Consider a general correlation function

$$c_{AB}(t) = \text{Tr}[\hat{A} e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar}] \quad (30)$$

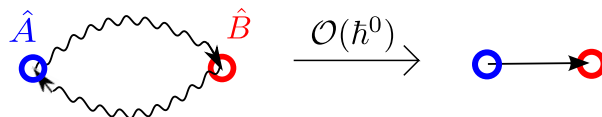


Fig. 1 Schematic path-integral diagram for the correlation function $c_{AB}(t)$ in Eq. (30), showing the effect of truncating the real-time evolution at $O(\hbar^0)$. Wavy lines represent quantum real-time evolution and straight lines classical time-evolution. Blue and red circles represent \hat{A} and \hat{B} respectively, which are assumed to be local.

whose path-integral form is illustrated in Fig. 1. Out of the theoretically infinite possibilities for inserting SEO identities^{25,31,32}, we choose the simplest form to construct a Wigner-transformed time-evolved operator: we insert Eq. (11) to the right of \hat{A} and Eq. (12) to the left, followed by Wigner transforming to give

$$c_{AB}(t) = \frac{1}{(2\pi\hbar)^{\mathcal{K}+1}} \int dR \int dP \int d\mathbf{q} \int d\mathbf{p} [\hat{A}_S]_{\text{W}}(R, P, \mathbf{q}, \mathbf{p}) [\hat{B}(t)]_{\text{W}}(R, P, \mathbf{q}, \mathbf{p}), \quad (31)$$

where we use the shorthand $\hat{B}(t) = e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar}$. The Wigner-transformed operators $[\hat{A}_S]_{\text{W}}(R, P, \mathbf{q}, \mathbf{p})$ and $[\hat{B}(t)]_{\text{W}}(R, P, \mathbf{q}, \mathbf{p})$ can be evaluated in accordance with Eq. (19) and Eq. (14) respectively,

$$[\hat{A}_S]_{\text{W}} = \frac{2^{\mathcal{K}+1}}{\hbar} e^{-G/\hbar} \int dD e^{iPD/\hbar} \text{Tr} \left[\left(\mathbf{C} - \frac{\hbar}{2} \mathbf{1} \right) \langle R - D/2 | \hat{A} | R + D/2 \rangle \right], \quad (32)$$

$$[\hat{B}(t)]_{\text{W}} = \frac{1}{2\hbar} \int dD e^{iPD/\hbar} \text{Tr} \left[\left(\mathbf{C} - \hbar \mathbf{1} \right) \langle R - D/2 | \hat{B}(t) | R + D/2 \rangle \right], \quad (33)$$

where we use the matrix representation of the operators defined in Eq. (16) and omit functional dependence of the operators on $(R, P, \mathbf{q}, \mathbf{p})$ (and will continue to do so). The functional form of Eq. (32) is slightly more complex than Eq. (33) due to the presence of SEO identities.

3.1 Derivation of the exact propagator

We now use the Liouvillian formalism^{45,46} to derive an exact propagator in the mapping variable representation. Differentiating Eq. (31) gives

$$\frac{d}{dt} c_{AB}(t) = \frac{1}{(2\pi\hbar)^{\mathcal{K}+1}} \int dR \int dP \int d\mathbf{q} \int d\mathbf{p} [\hat{A}_S]_{\text{W}} \left[\frac{i}{\hbar} [\hat{H}, \hat{B}(t)] \right]_{\text{W}}, \quad (34)$$

and using Eq. (25) to expand the Wigner transform of the product of operators in the commutator, we obtain

$$\left[\frac{i}{\hbar} [\hat{H}, \hat{B}(t)] \right]_{\text{W}} = \frac{2}{\hbar} [\hat{H}]_{\text{W}} \sin(\mathbf{\Lambda}\hbar/2) [\hat{B}(t)]_{\text{W}}, \quad (35)$$

whose functional form is similar to the Moyal series representation of the adiabatic propagator^{44,47}. Using Eq. (35), we can now define a Liouvillian[‡]

$$\mathcal{L} = \frac{2}{\hbar} [\hat{H}]_{\text{W}} \sin(\mathbf{\Lambda}\hbar/2), \quad (36)$$

[‡] Following the convention of Zwanzig⁴⁵, we do not define the Liouvillian with a prefactor of i .

and represent the correlation function in Eq. (31) as,

$$c_{AB}(t) = \frac{1}{(2\pi\hbar)^{\mathcal{K}+1}} \int dR \int dP \int d\mathbf{q} \int d\mathbf{p} [\hat{A}_S]_{\mathbf{W}} e^{\mathcal{L}t} [\hat{B}(0)]_{\mathbf{W}}. \quad (37)$$

To find \mathcal{L} in terms of $\{R, P, \mathbf{q}, \mathbf{p}\}$, we first evaluate the Wigner transform of the mapping variable Hamiltonian¹⁷ in Eq. (1) using Eq. (21),

$$[\hat{H}]_{\mathbf{W}} = \frac{P^2}{2m} + V_0(R) + V_e(R, \mathbf{q}, \mathbf{p}), \quad (38)$$

where the nonadiabatic potential has been abbreviated as $V_e(R, \mathbf{q}, \mathbf{p}) = \text{Tr}[(\mathbf{C} - \hbar\mathbf{1})\mathbf{V}_e(R)]/2\hbar$, with $\mathbf{V}_e(R)$ the nonadiabatic potential matrix in Eq. (1). We then separate the sine function in Eq. (36) into nuclear and electronic parts,

$$\sin(\mathbf{\Lambda}\hbar/2) = \sin(\Lambda_n\hbar/2) \cos(\mathbf{\Lambda}_e\hbar/2) + \sin(\mathbf{\Lambda}_e\hbar/2) \cos(\Lambda_n\hbar/2). \quad (39)$$

Since the mapping variable Hamiltonian only contains terms up to second order in \mathbf{p} and \mathbf{q} , we can without approximation truncate the trigonometric series in $\mathbf{\Lambda}_e$ to give

$$\frac{2}{\hbar} [\hat{H}]_{\mathbf{W}} \sin(\mathbf{\Lambda}\hbar/2) = [\hat{H}]_{\mathbf{W}} \left[\frac{2}{\hbar} \sin(\Lambda_n\hbar/2) \left(1 - \frac{\hbar^2}{8} \mathbf{\Lambda}_e^2 \right) + \cos(\Lambda_n\hbar/2) \mathbf{\Lambda}_e \right]. \quad (40)$$

Using the definition of \mathcal{L} in Eq. (36) and evaluating the derivatives in Eq. (40) we obtain the exact quantum Liouvillian in the mapping variable representation,

$$\begin{aligned} \mathcal{L} = & \frac{P}{m} \frac{\partial}{\partial R} - \frac{2}{\hbar} [V_0(R) + V_e(R, \mathbf{q}, \mathbf{p})] \sin\left(\frac{\hbar}{2} \overleftrightarrow{\partial_R \partial_P}\right) \\ & + \frac{1}{\hbar} [\mathbf{p}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{q}} - \mathbf{q}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{p}}] \cos\left(\frac{\hbar}{2} \overleftrightarrow{\partial_R \partial_P}\right) \\ & + \frac{1}{4} [\overrightarrow{\nabla}_{\mathbf{q}}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{q}} + \overrightarrow{\nabla}_{\mathbf{p}}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{p}}] \sin\left(\frac{\hbar}{2} \overleftrightarrow{\partial_R \partial_P}\right), \end{aligned} \quad (41)$$

one of the central results of the paper. Similar to Ref. 25, we can define

$$\mathcal{L} = \mathcal{L}_n + \mathcal{L}_R + \mathcal{L}_h, \quad (42)$$

where

$$\mathcal{L}_n = \frac{P}{m} \frac{\partial}{\partial R} - \frac{2}{\hbar} [V_0(R) + V_e(R, \mathbf{q}, \mathbf{p})] \sin\left(\frac{\hbar}{2} \overleftrightarrow{\partial_R \partial_P}\right) \quad (43)$$

corresponds to nuclear evolution on an Ehrenfest-like surface⁴⁸,

$$\mathcal{L}_R = \frac{1}{\hbar} [\mathbf{p}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{q}} - \mathbf{q}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{p}}] \cos\left(\frac{\hbar}{2} \overleftrightarrow{\partial_R \partial_P}\right) \quad (44)$$

corresponds to Rabi oscillations of the electronic degrees of freedom (d.o.f.) with higher-order coupling terms to nuclear motion, and

$$\mathcal{L}_h = \frac{1}{4} [\overrightarrow{\nabla}_{\mathbf{q}}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{q}} + \overrightarrow{\nabla}_{\mathbf{p}}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{p}}] \sin\left(\frac{\hbar}{2} \overleftrightarrow{\partial_R \partial_P}\right) \quad (45)$$

corresponds to coupled higher-order derivatives of nuclear and electronic motion. Finally, we note that exact quantum evolution is invariant to moving the state independent potential (or any part thereof) into the nonadiabatic matrix, as shown in Appendix A, though this will not necessarily hold when approximations are made to the propagator¹⁸.

In the following sections we analyse various analytic limits of the exact quantum propagator in Eq. (41).

3.2 Single surface propagation

For system on a single electronic surface with $V_e(R, \mathbf{q}, \mathbf{p}) = 0$, Eq. (41) reduces to

$$\mathcal{L}_n = \frac{P}{m} \frac{\partial}{\partial R} - V_0(R) \sin\left(\frac{\hbar}{2} \overleftrightarrow{\partial_R \partial P}\right), \quad (46)$$

which is the conventional single-surface Moyal series Liouvillian^{35–37,44}.

3.3 Electronic-only propagation

If there are no nuclear dimensions, or no coupling between nuclear and electronic d.o.f. where the observables are in electronic space, the correlation function in Eq. (31) becomes

$$c_{AB}(t) = \frac{1}{(2\pi\hbar)^{\mathcal{K}}} \int d\mathbf{q} \int d\mathbf{p} [\hat{A}_S]_{\mathbf{w}(\mathbf{q}, \mathbf{p})} [\hat{B}(t)]_{\mathbf{w}(\mathbf{q}, \mathbf{p})}, \quad (47)$$

and the parts of the Liouvillian with nuclear dependence vanish, $\mathcal{L}_{\text{nuc}} = 0$, $\mathcal{L}_h = 0$, and

$$\mathcal{L}_R = \frac{1}{\hbar} \left(\mathbf{p}^T \mathbf{V}_e \overrightarrow{\nabla}_{\mathbf{q}} - \mathbf{q}^T \mathbf{V}_e \overrightarrow{\nabla}_{\mathbf{p}} \right). \quad (48)$$

Since Eq. (48) only contains single derivatives (i.e. deterministic motion) in \mathbf{p} and \mathbf{q} , classical trajectories in the mapping variables will exactly reproduce the quantum correlation function in Eq. (47). To prove this, we first observe from Eq. (7) that

$$\begin{aligned} \mathcal{L}_R [\hat{B}(t)]_{\mathbf{w}(\mathbf{q}, \mathbf{p})} &= \frac{1}{2\hbar} [\mathcal{L}_R(\mathbf{q} - i\mathbf{p})^T] \mathbf{B}(t)(\mathbf{q} + i\mathbf{p}) + (\mathbf{q} - i\mathbf{p})^T \mathbf{B}(t) [\mathcal{L}_R(\mathbf{q} + i\mathbf{p})] \\ &= \frac{i}{\hbar} \frac{1}{2\hbar} [\mathbf{V}_e, (\mathbf{q} - i\mathbf{p})^T \mathbf{B}(t)(\mathbf{q} + i\mathbf{p})], \end{aligned} \quad (49)$$

and integrating Eq. (49) over t gives

$$[\hat{B}(t)]_{\mathbf{w}(\mathbf{q}, \mathbf{p})} = \frac{1}{2\hbar} \text{Tr}[(\mathbf{C} - \hbar \mathbf{1}) e^{+i\mathbf{V}_e t/\hbar} \mathbf{B} e^{-i\mathbf{V}_e t/\hbar}]. \quad (50)$$

Inserting Eq. (50) into Eq. (47) yields

$$\begin{aligned} c_{AB}(t) &= \frac{1}{(\pi\hbar)^{\mathcal{K}}} \frac{1}{\hbar^2} \int d\mathbf{q} \int d\mathbf{p} e^{-G/\hbar} \\ &\quad \times \text{Tr}[(\mathbf{C} - \frac{\hbar}{2} \mathbf{1}) \mathbf{A}] \text{Tr}[(\mathbf{C} - \hbar \mathbf{1}) e^{+i\mathbf{V}_e t/\hbar} \mathbf{B} e^{-i\mathbf{V}_e t/\hbar}], \end{aligned} \quad (51)$$

and integrating out the electronic d.o.f. (noting that only even powers of q_n or p_n survive), we find

$$c_{AB}(t) = \text{Tr}[\mathbf{A}e^{+i\mathbf{V}_e t/\hbar}\mathbf{B}e^{-i\mathbf{V}_e t/\hbar}], \quad (52)$$

which is the conventional correlation function in the matrix representation of quantum mechanics, where $e^{\pm i\mathbf{V}_e t/\hbar}$ corresponds to the Rabi oscillations.

This analysis shows that

$$\mathbf{q}(t) + i\mathbf{p}(t) = e^{-i\mathbf{V}_e t/\hbar}[\mathbf{q}(0) + i\mathbf{p}(0)], \quad (53)$$

which suggests that q_n and p_n can be considered the real and imaginary part respectively of the amplitude of n th electronic state, as suggested by the original action-angle interpretation of mapping variables^{15,16}. We caution against taking this analogy too far, since the sum of the square magnitude of amplitudes is unity, whereas the corresponding quantity in mapping variables, $[\mathbf{q} \cdot \mathbf{q} + \mathbf{p} \cdot \mathbf{p}]$ in Eq. (19) has a Gaussian distribution.

3.4 Approximate evolution

Truncating the exact Liouvillian [\mathcal{L} in Eq. (41)] to different orders in \hbar we find different semiclassical and mixed quantum-classical methods emerge.

Although these methods have been very successful at investigating nonadiabatic systems,^{19,23–30,49} and provide ways to systematically improve the dynamics⁵⁰, truncation to finite powers in \hbar does not generally mean that the error in the overall correlation function scales as $O(\hbar)$.⁴⁷ In addition, the dynamics does not normally conserve the quantum Boltzmann distribution, which can lead to spurious effects in numerical simulations⁵¹. Nevertheless, for a single electronic surface, semiclassical methods have recently been developed whereby classical trajectories conserve the quantum Boltzmann distribution⁴².

We firstly truncate the exact Liouvillian [Eq. (41)] to $O(\hbar^0)$ giving

$$\begin{aligned} \mathcal{L}_0 = & \frac{P}{m} \frac{\partial}{\partial R} - [V_0(R) + V_e(R, \mathbf{q}, \mathbf{p})] \overleftrightarrow{\partial_R \partial P} \\ & + \frac{1}{\hbar} \left[\mathbf{p}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{q}} - \mathbf{q}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{p}} \right], \end{aligned} \quad (54)$$

which is the linearized semiclassical propagator in the mapping variable representation¹¹, corresponding to classical evolution under the mapping variable Hamiltonian in Eq. (38). Inserting Eq. (54) into Eq. (37), we obtain the mapping variable LSC-IVR correlation function¹⁹,

$$c_{AB}(t)_{\text{LSC}} = \frac{1}{(2\pi\hbar)^{\mathcal{K}+1}} \int dR \int dP \int d\mathbf{q} \int d\mathbf{p} [\hat{A}_S]_{\text{W}} [\hat{B}(0)]_{\text{W}}(R_t, P_t, \mathbf{q}_t, \mathbf{p}_t), \quad (55)$$

where $(R_t, P_t, \mathbf{q}_t, \mathbf{p}_t)$ are obtained by solving for the classical trajectories generated by $[\hat{H}]_{\text{W}}$ with initial conditions $(R, P, \mathbf{q}, \mathbf{p})$ at time zero. Obtaining classical-like dynamics by truncating the Liouvillian at \hbar^0 is no surprise^{40,47}, however,

deriving the semiclassical Liouvillian by approximating the quantum Liouvillian allows for the explicit evaluation of the error in the evolution:

$$\begin{aligned} \mathcal{L} - \mathcal{L}_0 = & -\frac{2}{i\hbar} [V_0(R) + V_e(R, \mathbf{q}, \mathbf{p})] \sum_{j=3, \text{ odd}}^{\infty} \left(\frac{i\hbar \overleftarrow{\partial}_R \overrightarrow{\partial}_P}{2} \right)^j \\ & + \frac{1}{\hbar} \left[\mathbf{p}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{q}} - \mathbf{q}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{p}} \right] \sum_{j=2, \text{ even}}^{\infty} \left(\frac{i\hbar \overleftarrow{\partial}_R \overrightarrow{\partial}_P}{2} \right)^j \\ & + \frac{1}{4} \left[\overrightarrow{\nabla}_{\mathbf{q}}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{q}} + \overrightarrow{\nabla}_{\mathbf{p}}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{p}} \right] \sin \left(\frac{\hbar \overleftarrow{\partial}_R \overrightarrow{\partial}_P}{2} \right), \end{aligned} \quad (56)$$

from which we see that all error terms are third order and higher derivatives, and (by construction) scale as $O(\hbar)$ or greater. However, the appealing property of single-surface LSC-IVR being exact in the harmonic limit⁴⁰ does not extend to non-adiabatic systems unless there is no R dependence in \mathbf{V}_e . For instance, the error in evolution for the commonly-used spin-boson model of a two-state system bilinearly coupled to a harmonic bath^{25,32} will correspond to the third line of Eq. (56).

Instead of truncating the entire propagator w.r.t. some order of \hbar , one could selectively linearize in the derivatives of nuclear co-ordinates and momenta, but keep all terms in electronic d.o.f., giving

$$\begin{aligned} \mathcal{L}'_0 = & \frac{P}{m} \frac{\partial}{\partial R} - [V_0(R) + V_e(R, \mathbf{q}, \mathbf{p})] \overleftarrow{\partial}_R \overrightarrow{\partial}_P \\ & + \frac{1}{\hbar} \left[\mathbf{p}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{q}} - \mathbf{q}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{p}} \right] \\ & + \frac{\hbar}{8} \left[\overrightarrow{\nabla}_{\mathbf{q}}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{q}} + \overrightarrow{\nabla}_{\mathbf{p}}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{p}} \right] \overleftarrow{\partial}_R \overrightarrow{\partial}_P \end{aligned} \quad (57)$$

which is the mixed quantum-classical Liouville approach in mapping variables²⁵, with an error term

$$\begin{aligned} \mathcal{L} - \mathcal{L}'_0 = & -\frac{2}{i\hbar} [V_0(R) + V_e(R, \mathbf{q}, \mathbf{p})] \sum_{j=3, \text{ odd}}^{\infty} \left(\frac{i\hbar \overleftarrow{\partial}_R \overrightarrow{\partial}_P}{2} \right)^j \\ & + \frac{1}{\hbar} \left[\mathbf{p}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{q}} - \mathbf{q}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{p}} \right] \sum_{j=2, \text{ even}}^{\infty} \left(\frac{i\hbar \overleftarrow{\partial}_R \overrightarrow{\partial}_P}{2} \right)^j \\ & + \frac{1}{4i} \left[\overrightarrow{\nabla}_{\mathbf{q}}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{q}} + \overrightarrow{\nabla}_{\mathbf{p}}^T \mathbf{V}_e(R) \overrightarrow{\nabla}_{\mathbf{p}} \right] \sum_{j=3, \text{ odd}}^{\infty} \left(\frac{i\hbar \overleftarrow{\partial}_R \overrightarrow{\partial}_P}{2} \right)^j. \end{aligned} \quad (58)$$

This will be exact for a spin-boson system, though the third order derivative in Eq. (57) is not amenable to conventional classical trajectories²⁵. Nevertheless, there exist some methods to capture higher-order terms in the Moyal series⁵⁰ including different evolution of forward and backward trajectories in electronic d.o.f.^{27,28} and related partially linearized density matrix (PLDM) approaches.^{23,24,49,52}

4 Thermal correlation functions

Here we consider and address the difficulties of multiple operators at zero time in mapping variable correlation functions^{20,21}. For a symmetrized thermal corre-

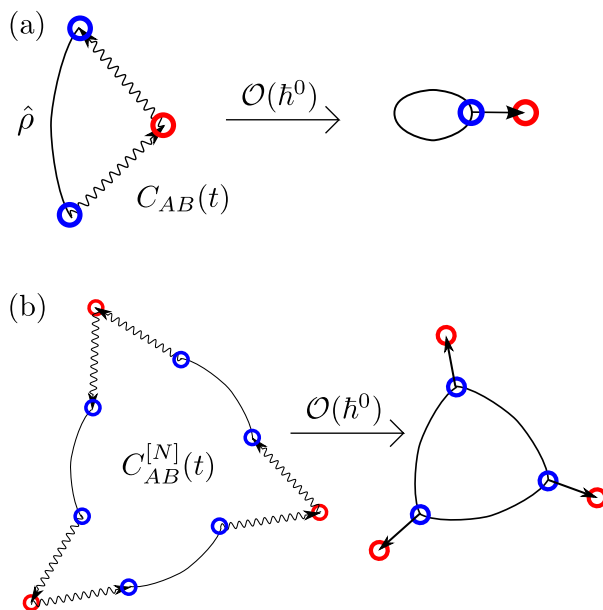


Fig. 2 Schematic path-integral diagrams for the correlation functions (a) $C_{AB}(t)$ and (b) $C_{AB}^{[N]}(t)$ in Eq. (59) and Eq. (66) respectively, showing the effect of truncating the real-time evolution at $\mathcal{O}(\hbar^0)$. Wavy lines represent quantum real-time evolution, curved lines imaginary time evolution (or any nonlocal density operator) and straight lines classical time-evolution. Blue and red circles represent \hat{A} and \hat{B} respectively, which are assumed to be local.

lation function [illustrated in Fig. 2(a)]

$$C_{AB}(t) = \text{Tr} \left[\frac{1}{2} (\hat{A}' \hat{\rho} + \hat{\rho} \hat{A}') e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} \right], \quad (59)$$

where $\hat{\rho}$ is an arbitrary density matrix (often $e^{-\beta\hat{H}}$), the Wigner transform of the two operators at zero time is³⁶

$$\left[\frac{1}{2} (\hat{A}' \hat{\rho} + \hat{\rho} \hat{A}') \right]_{\text{W}} = [\hat{A}']_{\text{W}} \cos(\mathbf{\Lambda}\hbar/2) [\hat{\rho}]_{\text{W}}. \quad (60)$$

If \hat{A}' is only first order in positions and momenta (such as $\hat{A}' = \hat{R}$), or \hat{A}' and $\hat{\rho}$ act in different d.o.f. (such as $\hat{\rho}$ being a nuclear Boltzmann distribution and \hat{A} selecting a specific electronic state) then only the first term in the cosine expansion will survive and $[\frac{1}{2} (\hat{A}' \hat{\rho} + \hat{\rho} \hat{A}')]_{\text{W}} = [\hat{A}']_{\text{W}} [\hat{\rho}]_{\text{W}}$.

Here, we evaluate Eq. (60) for general \hat{A}' , written as its nuclear-only part $[\hat{A}'_{\text{n}}]_{\text{W}}$ and electronic part $[\hat{A}'_{\text{e}}]_{\text{W}}$ as in Eq. (21),

$$[\hat{A}']_{\text{W}} = [\hat{A}'_{\text{n}}]_{\text{W}} + \frac{1}{2\hbar} \text{Tr} \left[(\mathbf{C} - \hbar\mathbf{I}) [\hat{A}'_{\text{e}}]_{\text{W}} \right]. \quad (61)$$

Since any physical operator in the mapping variable representation only contains terms up to second order in \mathbf{p} and \mathbf{q} [c.f. Eq. (7)], we expand the cosine function

in Eq. (60) and without approximation truncate the trigonometric series in $\mathbf{\Lambda}_e$ to give

$$[\hat{A}']_W \cos(\mathbf{\Lambda}\hbar/2) = [\hat{A}']_W \left[\left(1 - \frac{\hbar^2}{8} \mathbf{\Lambda}_e^2 \right) \cos(\Lambda_n \hbar/2) - \frac{\hbar}{2} \mathbf{\Lambda}_e \sin(\Lambda_n \hbar/2) \right], \quad (62)$$

and by inserting Eq. (61) into Eq. (62) we obtain

$$\begin{aligned} [\hat{A}']_W \cos(\mathbf{\Lambda}\hbar/2) &= \left\{ [\hat{A}'_n]_W + \frac{1}{2\hbar} \text{Tr} \left[(\mathbf{C} - \hbar \mathbf{1}) [\hat{\mathbf{A}}'_e]_W \right] \right\} \cos(\Lambda_n \hbar/2) \\ &\quad - \frac{\hbar}{8} \left(\vec{\nabla}_p^T [\hat{\mathbf{A}}'_e]_W \vec{\nabla}_p + \vec{\nabla}_q^T [\hat{\mathbf{A}}'_e]_W \vec{\nabla}_q \right) \cos(\Lambda_n \hbar/2) \\ &\quad - \frac{1}{2} \left(\mathbf{p}^T [\hat{\mathbf{A}}'_e]_W \vec{\nabla}_q - \mathbf{q}^T [\hat{\mathbf{A}}'_e]_W \vec{\nabla}_p \right) \sin(\Lambda_n \hbar/2), \quad (63) \end{aligned}$$

which is the cosine analogue³⁶ of the sine Moyal series in Eq. (41). The first line corresponds to the classical (\hbar^0) term and higher nuclear derivatives, the second to a diffusion-like term in the electronic co-ordinates (with higher-order terms in nuclear d.o.f.) and the third line to mixed nuclear-electronic terms. The complicated form of Eq. (63) explains the previously noted difficulties of evaluating two operators at zero time in the mapping variable representation²⁰ and provides a mathematical framework to solve this problem. For example, the thermal population of the α th state, where $\hat{A}' = \hat{S}_\alpha = \frac{1}{2\hbar}(p_\alpha^2 + q_\alpha^2 - \hbar)$, can be found using Eq. (63) as

$$\left[\frac{1}{2} (\hat{S}_\alpha \hat{\rho} + \hat{\rho} \hat{S}_\alpha) \right]_W = \frac{1}{4\hbar^2} (p_\alpha^2 + q_\alpha^2 - \hbar) \text{Tr} [(\mathbf{C} - \hbar \mathbf{1}) [\hat{\rho}]_W] - \frac{1}{4} ([\hat{\rho}]_W)_{\alpha\alpha} \quad (64)$$

where the $([\hat{\rho}]_W)_{\alpha\alpha}/4$ term arises from the higher derivatives on the second line of Eq. (63).

5 Generalized Kubo transformed correlation functions

For a thermal correlation function to be computable by standard path-integral techniques, both the distribution and dynamics need to be obtained in terms of classical-like variables. To achieve this, we construct the Generalized Kubo correlation function^{37–39,53} in mapping variables from which the quantum Boltzmann distribution and exact Liouvillian can be obtained analytically.

Consider the conventional Kubo-transformed correlation function⁵⁴,

$$C_{AB}^{\text{Kubo}}(t) = \frac{1}{\beta} \int_0^\beta d\lambda \text{Tr} \left[e^{-(\beta-\lambda)\hat{A}} e^{-\lambda\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} \right] \quad (65)$$

which is even and real like classical correlation functions, and can be related to the symmetric-split correlation function in Eq. (59) by a simple Fourier transform relationship⁵⁵. To rewrite Eq. (65) in a form where the Boltzmann operator is amenable to algebraic evaluation, we discretize the integral over λ and insert position, SEO and $e^{i\hat{H}t/\hbar} e^{-i\hat{H}t/\hbar}$ identities to give the Generalized Kubo transform

illustrated in Fig. 2(b),[§]

$$\begin{aligned}
 C_{AB}^{[N]}(t) = & \int d\mathbf{R} \int d\mathbf{D} \int d\mathbf{q} \int d\mathbf{\Delta} \sum_{\mathbf{n}, \mathbf{m}=1}^{\mathcal{K}} \\
 & \times \prod_{i=0}^{N-1} \langle \mathbf{q}_{i-1} - \mathbf{\Delta}_{i-1}/2, R_{i-1} - D_{i-1}/2 | n_i \rangle \langle n_i | \frac{1}{2} (\hat{A} e^{-\beta_N \hat{H}} + e^{-\beta_N \hat{H}} \hat{A}) | m_i \rangle \\
 & \times \langle m_i | \mathbf{q}_i + \mathbf{\Delta}_i/2, R_i + D_i/2 \rangle \\
 & \times \langle \mathbf{q}_i + \mathbf{\Delta}_i/2, R_i + D_i/2 | e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} | \mathbf{q}_i - \mathbf{\Delta}_i/2, R_i - D_i/2 \rangle,
 \end{aligned} \tag{66}$$

where the operators have become

$$\hat{A} = \frac{1}{N} \sum_{k=0}^{N-1} \hat{A}_k, \tag{67}$$

with \hat{A}_k acting on the k th imaginary-time bead (and likewise for \hat{B})⁴⁰. In Eq. (66), the operator \hat{A} has been symmetrized around the quantum Boltzmann operator, and we use the shorthand

$$\sum_{\mathbf{n}, \mathbf{m}=1}^{\mathcal{K}} \equiv \sum_{n_0=1}^{\mathcal{K}} \dots \sum_{n_{N-1}=1}^{\mathcal{K}} \times \sum_{m_0=1}^{\mathcal{K}} \dots \sum_{m_{N-1}=1}^{\mathcal{K}}. \tag{68}$$

One can show by substituting Eq. (67) into Eq. (66) and integrating out identities that the Generalized Kubo correlation function is equivalent to the conventional Kubo correlation function⁵⁴ in the $N \rightarrow \infty$ limit,⁴⁰

$$\lim_{N \rightarrow \infty} C_{AB}^{[N]}(t) = C_{AB}^{\text{Kubo}}(t). \tag{69}$$

However, we use the Generalized Kubo transform to allow explicit evaluation of the quantum Boltzmann operator.

We now Wigner-transform Eq. (66) giving

$$\begin{aligned}
 C_{AB}^{[N]}(t) = & \frac{1}{(2\pi\hbar)^{(\mathcal{K}+1)N}} \int d\mathbf{R} \int d\mathbf{P} \int d\mathbf{q} \int d\mathbf{p} \\
 & \times [e^{-\beta\hat{H}} \hat{A}]_{\bar{N}}(\mathbf{R}, \mathbf{P}, \mathbf{q}, \mathbf{p}) [\hat{B}(t)]_N(\mathbf{R}, \mathbf{P}, \mathbf{q}, \mathbf{p})
 \end{aligned} \tag{70}$$

where the \bar{N} subscript in $[e_S^{-\beta\hat{H}} \hat{A}]_{\bar{N}}$ denotes that the Wigner transform links together the i th and $(i+1)$ th bead whereas the subscript N in $[\hat{B}(t)]_N$ means the individual bra-kets only concern a single bead.[¶] The integrals over \mathbf{R}, \mathbf{P} and \mathbf{D} are N dimensional whereas those over \mathbf{q}, \mathbf{p} and $\mathbf{\Delta}$ are $N \times \mathcal{K}$ dimensional. In Appendix C we show (dropping the $(\mathbf{R}, \mathbf{P}, \mathbf{q}, \mathbf{p})$ dependence for clarity)

$$[e_S^{-\beta\hat{H}} \hat{A}]_{\bar{N}} = [\hat{A}]_N \cos(\mathbf{\Lambda}_N \hbar/2) [e_S^{-\beta\hat{H}}]_{\bar{N}}, \tag{71}$$

[§] In Eq. (66) \hat{A} is placed in the imaginary time-evolution bra-ket; it could equivalently be placed within the real-time evolution³⁷; here it is kept with the Boltzmann distribution for computational convenience.

[¶] Of course, one could equivalently define the Generalized Kubo transform with $[e_S^{-\beta\hat{H}} \hat{A}]_N$ and $[\hat{B}(t)]_{\bar{N}}$, but the former method is more algebraically convenient for determining time-evolution.

with $[\hat{A}]_N$ and $\mathbf{\Lambda}_N$ the multi-bead generalizations of $[\hat{A}]_W$ and $\mathbf{\Lambda}$, defined in Eq. (101) and Eq. (103) respectively. The quantum Boltzmann distribution in the path-integral representation is evaluated explicitly (in Appendix C) as

$$\begin{aligned}
 [e_S^{-\beta\hat{H}}]_{\bar{N}} &= \frac{2^{(\mathcal{X}+1)N}}{\hbar^N} \left(\frac{m}{2\pi\beta_N\hbar^2} \right)^{N/2} e^{-G_N/\hbar} \int d\mathbf{D} \\
 &\times e^{i\sum_{i=0}^{N-1} P_i D_i/\hbar} e^{-m\sum_{i=0}^{N-1} [(R_{i-1}-R_i)-(D_{i-1}+D_i)/2]^2/\beta_N\hbar^2} \\
 &\times e^{-\beta_N\sum_{i=0}^{N-1} [V_0(R_{i-1}-D_{i-1}/2)+V_0(R_i+D_i/2)]/2} \\
 &\times \text{Tr} \left[\prod_{i=0}^{N-1} \mathbf{M}(R_{i-1}-D_{i-1}/2)\mathbf{M}(R_i+D_i/2) \left(\mathbf{C}_i - \frac{\hbar}{2}\mathbf{1} \right) \right] \quad (72)
 \end{aligned}$$

where G_N and \mathbf{C}_i are the multi-bead generalizations of G and \mathbf{C} [defined in Eq. (108) and Eq. (109)] and $\mathbf{M}(R) = e^{-\beta_N V_e(R)/2}$. The Wigner-transformed real-time evolution is given as

$$\begin{aligned}
 [\hat{B}(t)]_N &= \int d\mathbf{D} \int d\mathbf{\Delta} \prod_{i=0}^{N-1} e^{iP_i D_i/\hbar} e^{i\mathbf{p}_i \cdot \mathbf{\Delta}_i/\hbar} \\
 &\times \langle \mathbf{q}_i - \mathbf{\Delta}_i/2, R_i - D_i/2 | e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar} | \mathbf{q}_i + \mathbf{\Delta}_i/2, R_i + D_i/2 \rangle. \quad (73)
 \end{aligned}$$

5.1 Generalized Kubo propagator

In order to determine the Generalized Kubo propagator, we differentiate $C_{AB}^{[N]}(t)$ in Eq. (34) with respect to t ,

$$\frac{d}{dt} C_{AB}^{[N]}(t) = \frac{1}{(2\pi\hbar)^{(\mathcal{X}+1)N}} \int d\mathbf{R} \int d\mathbf{P} \int d\mathbf{q} \int d\mathbf{p} [e_S^{-\beta\hat{H}} \hat{A}]_{\bar{N}} \left[\frac{i}{\hbar} [\hat{H}, \hat{B}(t)] \right]_N \quad (74)$$

where

$$\begin{aligned}
 &\left[\frac{i}{\hbar} [\hat{H}, \hat{B}(t)] \right]_N \\
 &= \int d\mathbf{D} \int d\mathbf{\Delta} \left[\prod_{i=0}^{N-1} e^{iP_i D_i/\hbar} e^{i\mathbf{p}_i \cdot \mathbf{\Delta}_i/\hbar} \right] \\
 &\times \sum_{j=0}^{N-1} \frac{i}{\hbar} \langle \mathbf{q}_j - \mathbf{\Delta}_j/2, R_j - D_j/2 | [\hat{H}, \hat{B}(t)] | \mathbf{q}_j + \mathbf{\Delta}_j/2, R_j + D_j/2 \rangle \\
 &\times \prod_{i=0, i \neq j}^{N-1} \langle \mathbf{q}_i - \mathbf{\Delta}_i/2, R_i - D_i/2 | \hat{B}(t) | \mathbf{q}_i + \mathbf{\Delta}_i/2, R_i + D_i/2 \rangle. \quad (75)
 \end{aligned}$$

Because the commutator is in a bra-ket containing variables of a single (j th) bead, the Moyal series can be determined as for the one-bead case and then summed over all beads, giving

$$\mathcal{L}^{[N]} = [\hat{H}_N]_W \sin(\mathbf{\Lambda}_N \hbar/2) \quad (76)$$

where

$$[\hat{H}_N]_{\mathbf{w}} = \sum_{i=0}^{N-1} [\hat{H}_i]_{\mathbf{w}}, \quad (77)$$

and \mathbf{A}_N is the multi-bead form of the derivative operator defined in Eq. (103). This allows the generalized Kubo correlation function to be formally expressed in mapping variables as

$$C_{AB}^{[N]}(t) = \frac{1}{(2\pi\hbar)^{(N+1)N}} \int d\mathbf{R} \int d\mathbf{P} \int d\mathbf{q} \int d\mathbf{p} \times \left\{ [\hat{A}]_N \cos(\mathbf{A}_N \hbar/2) [e_S^{-\beta \hat{H}}]_N \right\} e^{\mathcal{L}^{[N]}t} [\hat{B}(0)]_N, \quad (78)$$

and calculating the full Liouvillian explicitly, analogous to Eq. (43)–Eq. (45), gives

$$\begin{aligned} \mathcal{L}^{[N]} = \sum_{i=0}^{N-1} \left\{ \frac{P_i}{m} \partial_{R_i} - \frac{2}{\hbar} [V_0(R_i) + V_e(R_i, \mathbf{q}_i, \mathbf{p}_i)] \sin\left(\frac{\hbar}{2} \overleftarrow{\partial}_{R_i} \overrightarrow{\partial}_{P_i}\right) \right. \\ + \frac{1}{\hbar} \left[\mathbf{p}_i \mathbf{V}_e(R_i) \overrightarrow{\nabla}_{\mathbf{q}_i} - \mathbf{q}_i \mathbf{V}_e(R_i) \overrightarrow{\nabla}_{\mathbf{p}_i} \right] \cos\left(\frac{\hbar}{2} \overleftarrow{\partial}_{R_i} \overrightarrow{\partial}_{P_i}\right) \\ \left. + \frac{1}{4} \left[\overrightarrow{\nabla}_{\mathbf{q}_i} \mathbf{V}_e(R_i) \overrightarrow{\nabla}_{\mathbf{q}_i} + \overrightarrow{\nabla}_{\mathbf{p}_i} \mathbf{V}_e(R_i) \overrightarrow{\nabla}_{\mathbf{p}_i} \right] \sin\left(\frac{\hbar}{2} \overleftarrow{\partial}_{R_i} \overrightarrow{\partial}_{P_i}\right) \right\}. \quad (79) \end{aligned}$$

The distribution in Eq. (72) and this Liouvillian is the second major result of this paper.

The generalized Kubo Liouvillian $\mathcal{L}^{[N]}$ corresponds to the motion of N individual and independent replicas of the system, connected at zero time through the quantum Boltzmann operator. Consequently, it shares many properties with the simpler Liouvillian \mathcal{L} in Eq. (41) since there are no cross terms in $\mathcal{L}^{[N]}$ between different beads. Providing no approximation is made to the evolution, the results in Appendices A and B hold and the correlation function is invariant to placing the state-independent potential in the diabatic matrix. For a single surface it reduces to the conventional Moyal series [summed over beads as in Eq. (43) of Ref. 40], and truncation of Eq. (79) to $O(\hbar^0)$ gives LSC-IVR in the multi-bead representation, as detailed in Appendix D.

6 Conclusions

In this article we have derived the exact nonadiabatic quantum Liouvillian in the mapping variable representation and shown how its approximation leads to pre-existing approximate methods, briefly discussing the evaluation of multiple operators at zero time. Using the Generalized Kubo transform we have then obtained an analytic expression for the thermal distribution and its associated Liouvillian.

Future research includes determining computationally tractable but accurate approximations to the exact nonadiabatic propagator that, for instance, reproduce the correct Rabi oscillations and preserve the quantum Boltzmann distribution. These could be quasiclassical or linearized models^{22–30}, nonadiabatic

generalizations of Matsubara dynamics^{40–42,56} and may lead to methods similar to nonadiabatic CMD⁵⁷ and RPMD^{32,58–60}.

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A The exact propagator is invariant to including $V_0(R)$ in $V_e(R)$

To prove that the exact evolution is invariant to placing $V_0(R)$ (or any constant w.r.t. \mathbf{p} and \mathbf{q}) inside the electronic evolution $V_e(R, \mathbf{q}, \mathbf{p})$, we return to the correlation function in Eq. (34), noting

$$\begin{aligned} \frac{d}{dt} c_{AB}(t) &= \frac{1}{(2\pi\hbar)^{\mathcal{K}+1}} \int dR \int dP \int d\mathbf{q} \int d\mathbf{p} [\hat{A}_S]_{\mathbf{w}} \mathcal{L}[\hat{B}(t)]_{\mathbf{w}} \\ &= \frac{1}{(2\pi\hbar)^{\mathcal{K}+1}} \int dR \int dP \int d\mathbf{q} \int d\mathbf{p} [\hat{B}(t)]_{\mathbf{w}} \mathcal{L}^\dagger[\hat{A}_S]_{\mathbf{w}} \end{aligned} \quad (80)$$

where \mathcal{L}^\dagger is the adjoint of \mathcal{L} . In Appendix B we prove that, despite \mathcal{L} containing derivatives up to infinite order, $\mathcal{L} = -\mathcal{L}^\dagger$ as for the classical Liouvillian. By using Eq. (25) in reverse,

$$-\mathcal{L}[\hat{A}_S]_{\mathbf{w}} = -\frac{i}{\hbar} \left[\hat{H}, \sum_{n,m=1}^{\mathcal{K}} |n\rangle\langle n|\hat{A}|m\rangle\langle m| \right]. \quad (81)$$

We then define a Hamiltonian with part of the state-independent potential moved inside the nonadiabatic matrix,

$$\hat{H}_\alpha = \frac{\hat{P}^2}{2m} + V_0(\hat{R}) - \alpha(\hat{R}) + \sum_{n,m=1}^{\mathcal{K}} |n\rangle[V_{nm}(\hat{R}) + \delta_{nm}\alpha(\hat{R})]\langle m|, \quad (82)$$

from which we observe

$$\begin{aligned} -\frac{i}{\hbar} \left[\hat{H}_\alpha, \sum_{n,m=1}^{\mathcal{K}} |n\rangle\langle n|\hat{A}|m\rangle\langle m| \right] &= -\frac{i}{\hbar} \sum_{n,m=1}^{\mathcal{K}} |n\rangle\langle n|[\hat{H}, \hat{A}]|m\rangle\langle m| \\ &= -\frac{i}{\hbar} \left[\hat{H}, \sum_{n,m=1}^{\mathcal{K}} |n\rangle\langle n|\hat{A}|m\rangle\langle m| \right], \end{aligned} \quad (83)$$

and therefore infer

$$\mathcal{L}_\alpha[\hat{A}_S]_{\mathbf{w}} = \mathcal{L}[\hat{A}_S]_{\mathbf{w}} \quad (84)$$

as required. The above proof will not hold if the Moyal expansions in the propagator are truncated, nor if SEO eigenstates are absent from $[\hat{A}_S]_{\mathbf{w}}(R, P, \mathbf{q}, \mathbf{p})$.

B Adjoint of Moyal Series Liouvillian

Here we prove that

$$\begin{aligned}\frac{d}{dt}c_{AB}(t) &= \frac{1}{(2\pi\hbar)^{\mathcal{K}+1}} \int dR \int dP \int d\mathbf{q} \int d\mathbf{p} [\hat{A}_S]_{\mathbf{W}} \mathcal{L}[\hat{B}(t)]_{\mathbf{W}} \\ &= - \frac{1}{(2\pi\hbar)^{\mathcal{K}+1}} \int dR \int dP \int d\mathbf{q} \int d\mathbf{p} [\hat{B}(t)]_{\mathbf{W}} \mathcal{L}[\hat{A}_S]_{\mathbf{W}}.\end{aligned}\quad (85)$$

We observe that the Liouvillian \mathcal{L} defined in Eq. (36) can be rewritten as

$$\mathcal{L} = \frac{i}{\hbar} [\hat{H}]_{\mathbf{W}} \left(e^{-i\Lambda\hbar/2} - e^{i\Lambda\hbar/2} \right), \quad (86)$$

making it sufficient to prove

$$\int dr \int d\zeta A(Be^{-i\hbar\Lambda/2}C) = \int dr \int d\zeta C(Be^{i\hbar\Lambda/2}A), \quad (87)$$

where r and ζ are general position and momentum co-ordinates of which A, B and C are general analytic functions, and we use one dimension for simplicity, a multidimensional generalization being straightforward. With these phase space variables

$$\Lambda = \overleftarrow{\partial}_{\zeta} \overrightarrow{\partial}_r - \overleftarrow{\partial}_r \overrightarrow{\partial}_{\zeta} \quad (88)$$

and we use the shorthand $\partial_{\zeta} = \overrightarrow{\partial}_{\zeta}$, likewise for ∂_r . The arrows denote the direction in which the derivative acts but when not specified, all derivatives act to the right.

From Eq. (88) it immediately follows for integer j that

$$A\Lambda^j B = (-1)^j B\Lambda^j A. \quad (89)$$

and from the definition of the exponential

$$e^{-i\hbar\Lambda/2} = \sum_{j=0}^{\infty} \left(\frac{-i\hbar}{2} \right)^j \frac{1}{j!} \Lambda^j, \quad (90)$$

so if we can show Eq. (87) holds for each j th term of the exponential individually then it will hold for the sum of those terms.

To prove this by induction, for the $j = 0$ term we have the trivial result that $A(B\Lambda^0 C) = C(B\Lambda^0 A)$ by the commutativity of multiplication of scalar functions. We then assume that the j th term of Eq. (87) holds, i.e.

$$\int dr \int d\zeta A(B\Lambda^j C) = (-1)^j \int dr \int d\zeta C(B\Lambda^j A), \quad (91)$$

and consider (to within multiplicative constants) the $(j + 1)$ th term

$$\int dr \int d\zeta AB\Lambda^{j+1}C = \int dr \int d\zeta A[(B\Lambda^j)\overleftarrow{\partial}_\zeta\overrightarrow{\partial}_r C] - A[(B\Lambda^j)\overleftarrow{\partial}_r\overrightarrow{\partial}_\zeta C] \quad (92)$$

$$= \int dr \int d\zeta A[\partial_\zeta(B\Lambda^j)](\partial_r C) - A[\partial_r(B\Lambda^j)](\partial_\zeta C) \quad (93)$$

$$= \int dr \int d\zeta -[\partial_r A \partial_\zeta(B\Lambda^j)]C + [\partial_\zeta A \partial_r(B\Lambda^j)]C \quad (94)$$

$$= \int dr \int d\zeta -(\partial_r A)\partial_\zeta(B\Lambda^j)C - A[\partial_r \partial_\zeta(B\Lambda^j)]C \\ + (\partial_\zeta A)[\partial_r(B\Lambda^j)]C + A[\partial_\zeta \partial_r(B\Lambda^j)]C \quad (95)$$

$$= \int dr \int d\zeta -(\partial_r A)(\partial_\zeta B)\Lambda^j C + (\partial_\zeta A)(\partial_r B)\Lambda^j C, \quad (96)$$

where we assume the surface terms vanish when integrating by parts⁴⁴ and derivatives only act within their brackets; for instance, ∂_ζ in Eq. (92) does not act on A . We now define $A' = \partial_r A$, $B' = \partial_\zeta B$ and use Eq. (91) (since A and B are arbitrary functions) to show

$$\int dr \int d\zeta AB\Lambda^{j+1}C = (-1)^j \int dr \int d\zeta -C(\partial_\zeta B)\Lambda^j(\partial_r A) + C(\partial_r B)\Lambda^j(\partial_\zeta A) \\ = (-1)^{j+1} \int dr \int d\zeta C(B\Lambda^{j+1}A) \quad (97)$$

Combining Eq. (90) and Eq. (97) gives Eq. (87) and therefore Eq. (85), as required. We note that this proof is in the framework of the Wigner transforms but can also be obtained by using the properties of a quantum mechanical trace and then the formula for the Wigner transform of a product.

C Quantum Boltzmann distribution

We define the projected Boltzmann operator

$$e_S^{-\beta_N \hat{H}} = \hat{S} e^{-\beta_N \hat{H}} \hat{S} \quad (98)$$

such that

$$[e_S^{-\beta \hat{H}} \hat{A}]_{\bar{N}} \\ = \int d\mathbf{D} \int d\mathbf{\Delta} \prod_{i=0}^{N-1} e^{iP_i D_i / \hbar} e^{i\mathbf{p}_i \cdot \mathbf{\Delta}_i / \hbar} \\ \times \langle \mathbf{q}_{i-1} - \mathbf{\Delta}_{i-1}/2, R_{i-1} - D_{i-1}/2 | \frac{1}{2} (\hat{A} e_S^{-\beta_N \hat{H}} + e_S^{-\beta_N \hat{H}} \hat{A}) | \mathbf{q}_i + \mathbf{\Delta}_i/2, R_i + D_i/2 \rangle. \quad (99)$$

Using Eq. (25), and placing cross terms between adjacent beads in the Boltzmann operator and not in \hat{A} gives

$$[e_S^{-\beta \hat{H}} \hat{A}]_{\bar{N}} = [\hat{A}]_N \left[\sum_{i=0}^{N-1} \cos(\mathbf{\Lambda}_i \hbar / 2) \right] [e_S^{-\beta \hat{H}}]_{\bar{N}} \quad (100)$$

where

$$[\hat{A}]_N = \int d\mathbf{D} \int d\Delta \prod_{i=0}^{N-1} e^{iP_i D_i / \hbar} e^{i\mathbf{p}_i \cdot \Delta_i / \hbar} \times \langle \mathbf{q}_i - \Delta_i / 2, R_i - D_i / 2 | \hat{A} | \mathbf{q}_i + \Delta_i / 2, R_i + D_i / 2 \rangle. \quad (101)$$

For a linear operator as defined in Eq. (67), we can reduce Eq. (101) to

$$[\hat{A}]_N = \frac{1}{N} \sum_{k=0}^{N-1} [\hat{A}_k]_W, \quad (102)$$

a sum over individual Wigner-transformed \hat{A}_k . Since there are no cross terms between beads in $[\hat{A}]_N$, the summation over derivatives in Eq. (100) can be taken inside the cosine function to obtain Eq. (71) with a generalized $\mathbf{\Lambda}$ operator

$$\mathbf{\Lambda}_N = \sum_{i=0}^{N-1} \mathbf{\Lambda}_i \quad (103)$$

where $\mathbf{\Lambda}_i$ is Eq. (26) acting on the i th path-integral bead.

We then evaluate the quantum Boltzmann distribution in terms of SEO eigenstates

$$\begin{aligned} [e_S^{-\beta \hat{H}}]_{\bar{N}} &= \int d\mathbf{D} \int d\Delta \sum_{\mathbf{n}, \mathbf{m}=1}^{\mathcal{K}} \prod_{i=0}^{N-1} e^{iP_i D_i / \hbar} e^{i\mathbf{p}_i \cdot \Delta_i / \hbar} \langle \mathbf{q}_{i-1} - \Delta_{i-1} / 2 | n_i \rangle \\ &\quad \times \langle R_{i-1} - D_{i-1} / 2, n_i | e^{-\beta_N \hat{H}} | R_i + D_i / 2, m_i \rangle \langle m_i | \mathbf{q}_i + \Delta_i / 2 \rangle \quad (104) \\ &= \left(\frac{2}{\hbar} \right)^N \frac{1}{(\pi \hbar)^{\mathcal{K}N/2}} \int d\mathbf{D} \int d\Delta \left\{ \prod_{i=0}^{N-1} e^{iP_i D_i / \hbar} e^{i\mathbf{p}_i \cdot \Delta_i / \hbar} e^{-(\mathbf{q}_i \cdot \mathbf{q}_i + \Delta_i \cdot \Delta_i / 4) / \hbar} \right\} \\ &\quad \times \text{Tr} \left[\prod_{i=0}^{N-1} \mathbf{K}_i(\mathbf{q}_i + \Delta_i / 2) \otimes (\mathbf{q}_i - \Delta_i / 2)^T \right] \quad (105) \end{aligned}$$

where we use vector notation for convenience and define the nuclear Boltzmann matrix as

$$(\mathbf{K}_i)_{nm} = \langle R_{i-1} - D_{i-1} / 2, n_i | e^{-\beta_N \hat{H}} | R_i + D_i / 2, m_i \rangle. \quad (106)$$

We evaluate the integrals over mapping variables in Eq. (105) in a similar method to Eq. (32) and Ref. 32,

$$[e_S^{-\beta \hat{H}}]_{\bar{N}} = \frac{2^{(\mathcal{K}+1)N}}{\hbar^N} e^{-G_N / \hbar} \int d\mathbf{D} e^{i \sum_{i=0}^{N-1} P_i D_i / \hbar} \text{Tr} \left[\prod_{i=0}^{N-1} \mathbf{K}_i \left(\mathbf{C}_i - \frac{\hbar}{2} \mathbf{1} \right) \right] \quad (107)$$

where

$$G_N = \sum_{i=0}^{N-1} \mathbf{q}_i \cdot \mathbf{q}_i + \mathbf{p}_i \cdot \mathbf{p}_i, \quad (108)$$

$$\mathbf{C}_i = (\mathbf{q}_i + i\mathbf{p}_i) \otimes (\mathbf{q}_i - i\mathbf{p}_i)^T. \quad (109)$$

Evaluation of the \mathbf{K}_i matrices is more complicated than for a conventional ring polymer expression due to the presence of the ‘stretch’ variables \mathbf{D} . We choose to symmetrically split the quantum Boltzmann distribution (although similar results are obtained with an asymmetric splitting),

$$\lim_{N \rightarrow \infty} e^{-\beta_N \hat{H}} = e^{-\beta_N \hat{V}/2} e^{-\beta_N \hat{T}} e^{-\beta_N \hat{V}/2} \quad (110)$$

and since the nuclear kinetic energy operator is, by construction, diagonal in the diabatic basis,

$$\begin{aligned} \mathbf{K}_i = & \sqrt{\frac{m}{2\pi\beta_N\hbar^2}} \mathbf{M}(R_{i-1} - D_{i-1}/2) e^{-m[(R_{i-1}-R_i)-(D_{i-1}+D_i)/2]^2/\beta_N\hbar^2} \\ & \times e^{-\beta_N[V_0(R_{i-1}-D_{i-1}/2)+V_0(R_i+D_i/2)]/2} \mathbf{M}(R_i + D_i/2) \end{aligned} \quad (111)$$

where $\mathbf{M}(R) = e^{-\beta_N V_e(R)/2}$ is an exponential matrix. Combining Eq. (107) and Eq. (111) gives Eq. (72). For a general potential, the stretch \mathbf{D} cannot be integrated out from Eq. (72) without approximation due to its presence in the exponential potential matrices \mathbf{M} , such that Eq. (72) is qualitatively different from the nonadiabatic ring-polymer potential³². We also observe that there are no spring terms in electronic degrees of freedom.

D Truncation of $\mathcal{L}^{[N]}$ to $O(\hbar^0)$

Evaluating the \hbar^0 approximation to Eq. (79) yields

$$\begin{aligned} \mathcal{L}_0^{[N]} = & \sum_{i=0}^{N-1} \left\{ \frac{P_i}{m} \partial_{R_i} - [V_0(R_i) + V_e(R_i, \mathbf{q}_i, \mathbf{p}_i)] \frac{\hbar \overleftrightarrow{\partial}_{R_i}}{2} \partial_{P_i} \right. \\ & \left. + \frac{1}{\hbar} \left[\mathbf{p}_i^T \mathbf{V}_e(R_i) \overleftrightarrow{\nabla}_{\mathbf{q}_i} - \mathbf{q}_i^T \mathbf{V}_e(R_i) \overleftrightarrow{\nabla}_{\mathbf{p}_i} \right] \right\}, \end{aligned} \quad (112)$$

which, for linear observables, is identical to the LSC-IVR Kubo-transformed correlation function as discussed above, and can be seen by considering individual terms in the sum over \hat{B}_i .⁴⁰

The evolution of the electronic positions and momenta in Eq. (112) is identical to that used by Richardson and Thoss³¹, and does not in general conserve the quantum Boltzmann distribution.

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