Statistical mechanics of quantum-classical systems

Steve Nielsen and Raymond Kapral
Chemical Physics Theory Group, Department of Chemistry, University of Toronto, Toronto, ON M5S 3H6, Canada

Giovanni Ciccotti
INFM and Dipartimento di Fisica, Università "La Sapienza," Piazzale Aldo Moro, 2, 00185 Roma, Italy

The statistical mechanics of systems whose evolution is governed by mixed quantum-classical dynamics is investigated. The algebraic properties of the quantum-classical time evolution of operators and of the density matrix are examined and compared to those of full quantum mechanics. The equilibrium density matrix that appears in this formulation is stationary under the dynamics and a method for its calculation is presented. The response of a quantum-classical system to an external force which is applied from the distant past when the system is in equilibrium is determined. The structure of the resulting equilibrium time correlation function is examined and the quantum-classical limits of equivalent quantum time correlation functions are derived. The results provide a framework for the computation of equilibrium time correlation functions for mixed quantum-classical systems. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1400129]

I. INTRODUCTION

Often situations arise where it is appropriate to study composite dynamical systems with interacting quantum mechanical and classical degrees of freedom. In condensed matter physics such situations occur when one is interested in the dynamics of a light quantum particle or set of quantum degrees of freedom interacting with more massive particles.[1–3] Specific examples include proton transfer,[4] solvation dynamics of an excess electron,[5] and nonradiative relaxation processes of molecules in a liquid-state environment.[6] In these circumstances it is not feasible to attempt a full quantum solution of the Schrödinger equation for the entire system. Consequently one is led to consider the dynamics of a quantum subsystem coupled to a bath where the environmental degrees of freedom are treated classically. Such mixed quantum-classical systems arise in other contexts as well.[7]

Different formulations of the dynamics of such mixed quantum-classical systems have appeared in the literature. In these reduced descriptions of the quantum dynamics the environmental degrees of freedom are accounted for by the inclusion of dissipative and decoherence terms in the equations of motion,[8–10] through multistate Fokker–Planck dynamics[11] or representations by quantum stochastic processes.[12] Other approaches utilize a more detailed treatment of the classical environment. These include simple adiabatic dynamics where the classical system evolves on a potential energy surface determined from a single adiabatic eigenstate, or Ehrenfest mean field models where the classical evolution is governed by a mean force determined from the instantaneous value of the quantum wave function.[13,14] These descriptions produce a definite classical evolution but do not always give physically correct results. If we relax the continuity of the trajectory of the classical variables,[15] we are led to consider surface-hopping algorithms.[16–19] Evolution equations for the quantum-classical density matrix where the evolution operator is expressed in terms of a quantum-classical bracket have also been studied[20–26] and their solutions have been formulated in terms of surface-hopping trajectories.[26–28]

In this paper we develop the statistical mechanics of mixed quantum-classical systems. We take as a starting point the evolution equation for the mixed quantum-classical density matrix.[21,23–26,29] This equation may be derived by partial Wigner transforming the quantum Liouville equation over the bath degrees of freedom corresponding to massive particles and expanding the resulting evolution operator to linear order in the mass ratio $(m/M)^{1/2}$, where m and M are the characteristic masses of the quantum subsystem and bath particles, respectively.[26] The resulting evolution equation can be recast as an integral equation in which classical trajectory segments are interspersed with environment-induced quantum transitions and corresponding bath momentum changes.[27]

The canonical equilibrium density matrix for quantum-classical systems is constructed to be stationary under the quantum-classical evolution. Its form is derived and compared with its full quantum analog. A linear response derivation is carried out to determine the response function and the forms of the equilibrium time correlation functions appearing in quantum-classical systems. Mixed quantum-classical dynamics and the associated correlation functions present differences from their full quantum analogs: Identities among quantum correlation functions hold only approximately in the quantum-classical limit and properties such as time translation invariance are also only approximately valid.

The paper is organized as follows: Section II presents the formal structure of mixed quantum-classical dynamics and contrasts it with that of full quantum mechanics. In Sec. III we discuss the canonical equilibrium density matrix and in Sec. IV a linear response derivation of the response function

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is carried out and a general discussion of the properties of mixed quantum-classical correlation functions is given. Concluding remarks are made in Sec. V and Appendixes A–C contain additional details.

II. QUANTUM-CLASSICAL DYNAMICS

Consider a quantum system which may be partitioned into two interacting subsystems, a quantum subsystem with particles of mass m, and a quantum bath with particles of mass M, $(M \gg m)$. In order to describe the distinctive features of quantum-classical dynamics, we begin with a brief overview of the algebraic structure of quantum and classical dynamics in the Wigner representation of the quantum bath.

A. Quantum and classical dynamics

The von Neumann evolution equation for the quantum mechanical density matrix $\hat{\rho}$ is

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}(t)], \tag{1}$$

where $\hat{H}$ is the Hamiltonian of the system. Its formal solution is

$$\hat{\rho}(t) = e^{-i\hat{L}t} \hat{\rho}(0) = e^{-i\hat{H}t/\hbar} \hat{\rho}(0) e^{i\hat{H}t/\hbar}, \tag{2}$$

with $i\hat{L} = (i/\hbar)[\hat{H}, \ ]$ the quantum Liouville operator.

An alternative form of the evolution equation may be obtained by taking the partial Wigner transform over the bath degrees of freedom. This partial Wigner transform of the density matrix is defined by

$$\hat{\rho}_W(R, P) = (2\pi\hbar)^{-3N} \int dz \, e^{iP \cdot z/\hbar} \left\langle R - \frac{z}{2} \middle| \hat{\rho} \middle| R + \frac{z}{2} \right\rangle, \tag{3}$$

while the corresponding transform of an operator $\hat{A}$ is given by

$$\hat{A}_W(R, P) = \int dz \, e^{-iP \cdot z/\hbar} \left\langle R + \frac{z}{2} \middle| \hat{A} \middle| R - \frac{z}{2} \right\rangle. \tag{4}$$

Both the density matrix and quantum operators retain their abstract operator character in the quantum subsystem degrees of freedom but are now functions in the (R, P) phase space of the quantum bath. To proceed we use the fact that the Wigner transform of a product of operators is given by[30]

$$(\hat{A}\hat{B})_W(R, P) = \hat{A}_W(R, P) e^{\hbar \Lambda/2i} \hat{B}_W(R, P), \tag{5}$$

where the left and right acting differential operator Λ is the negative of the Poisson bracket operator,

$$\Lambda = \overleftarrow{\nabla}_P \cdot \overrightarrow{\nabla}_R - \overleftarrow{\nabla}_R \cdot \overrightarrow{\nabla}_P, \tag{6}$$

and the arrows indicate the directions in which the gradient operators act. Using this result and taking the partial Wigner transform of Eq. (1) we find

$$\frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} = -\frac{i}{\hbar} (\hat{H}_W e^{\hbar \Lambda/2i} \hat{\rho}_W(t) - \hat{\rho}_W(t) e^{\hbar \Lambda/2i} \hat{H}_W)$$

$$= -\frac{i}{\hbar} (\vec{H}_\Lambda \hat{\rho}_W(t) - \hat{\rho}_W(t) \tilde{H}_\Lambda)$$

$$\equiv -i\hat{L}_W \hat{\rho}_W(t)$$

$$\equiv -(H_W, \hat{\rho}_W(t))_Q. \tag{7}$$

In these equations we have defined the right $(\vec{H}_\Lambda)$ and left $(\tilde{H}_\Lambda)$ acting operators,

$$\vec{H}_\Lambda = \hat{H}_W(R, P) e^{\hbar \Lambda/2i},$$

$$\tilde{H}_\Lambda = e^{\hbar \Lambda/2i} \hat{H}_W(R, P) \tag{8}$$

where the partially Wigner transformed Hamiltonian $\hat{H}_W$ is

$$\hat{H}_W(R, P) = \frac{P^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}_W(\hat{q}, R). \tag{9}$$

Here $\hat{p}$ and $\hat{q}$ are the momentum and position operators, respectively, of the quantum subsystem and $\hat{V}_W(\hat{q}, R)$ is the partially Wigner transformed total potential energy operator, which is the sum of the quantum subsystem, quantum bath, and subsystem-bath potential energies.

The second equality in Eq. (7) defines the quantum Liouville operator $i\hat{L}_W$ in the partial Wigner representation and the associated Lie bracket $(H_W, \ )_Q$. More generally the Lie bracket of two partially Wigner transformed operators is defined as

$$(\hat{A}_W, \hat{B}_W)_Q = \frac{i}{\hbar} (\vec{A}_\Lambda \hat{B}_W - \hat{B}_W \tilde{A}_\Lambda)$$

$$= \frac{i}{\hbar} (\hat{A}_W e^{\hbar \Lambda/2i} \hat{B}_W - \hat{B}_W e^{\hbar \Lambda/2i} \hat{A}_W). \tag{10}$$

Here the $\vec{A}_\Lambda$ and $\tilde{A}_\Lambda$ operators are defined as in Eq. (8) with the replacement $\hat{H}_W \rightarrow \hat{A}_W$.

The formal solution of Eq. (7) is

$$\hat{\rho}_W(R, P, t) = e^{-i\vec{H}_\Lambda t/\hbar} \hat{\rho}_W(R, P, 0) e^{i\tilde{H}_\Lambda t/\hbar}$$

$$= e^{-i\hat{L}_W t} \hat{\rho}_W(R, P, 0). \tag{11}$$

A similar set of equations may be written for the evolution of any quantum operator $\hat{A}$. In the Wigner representation these equations and their solutions, respectively, take the form

$$\frac{d\hat{A}_W(t)}{dt} = i\hat{L}_W \hat{A}_W(t) = (\hat{H}_W, \hat{A}_W(t))_Q \tag{12}$$

and

$$\hat{A}_W(t) = e^{i\hat{L}_W t} \hat{A}_W = e^{i\vec{H}_\Lambda t/\hbar} \hat{A}_W e^{-i\tilde{H}_\Lambda t/\hbar}. \tag{13}$$

[We shall drop the dependence of quantities like $\hat{A}_W(R, P)$ on the bath phase space coordinates when confusion is unlikely to arise.]

The Wigner transform of a product of operators satisfies the associative product rule,

$$(\hat{A}\hat{B}\hat{C})_W = ((\hat{A}_W e^{\hbar\Lambda/2i}\hat{B}_W)e^{\hbar\Lambda/2i}\hat{C}_W)$$

$$= (\hat{A}_W e^{\hbar\Lambda/2i}(\hat{B}_W e^{\hbar\Lambda/2i}\hat{C}_W)), \tag{14}$$

with an obvious generalization to products of n operators. Consider a quantum operator $\hat{C} = \hat{A}\hat{B}$ which is the product of two operators. Since the time evolution of $\hat{C}$ may be written as $\hat{C}(t) = \hat{A}(t)\hat{B}(t)$, its partial Wigner transform is

$$\hat{C}_W(t) = \hat{A}_W(t)e^{\hbar\Lambda/2i}\hat{B}_W(t). \tag{15}$$

We may also obtain this result by considering the action of the Liouville operator on the operator product in the partial Wigner representation:

$$i\hat{L}_W\hat{C}_W = \frac{i}{\hbar}(\hat{H}_W e^{\hbar\Lambda/2i}(\hat{A}_W e^{\hbar\Lambda/2i}\hat{B}_W))$$

$$- \frac{i}{\hbar}((\hat{A}_W e^{\hbar\Lambda/2i}\hat{B}_W)e^{\hbar\Lambda/2i}\hat{H}_W)$$

$$= (i\hat{L}_W\hat{A}_W)e^{\hbar\Lambda/2i}\hat{B}_W + \hat{A}_W e^{\hbar\Lambda/2i}(i\hat{L}_W\hat{B}_W). \tag{16}$$

In writing the last line of this equation we have used the associative property in Eq. (14). From this result we may immediately compute the repeated action of $i\hat{L}_W$ on $\hat{C}_W$ and, using the definition of the exponential evolution operator as a power series, find Eq. (15) by identification of the two power series expansions. We shall make use of this lengthier route to Eq. (15) in the sequel where the analogous demonstration for mixed quantum-classical systems is not so straightforward.

The quantum mechanical Lie bracket, either in its original form as $(i/\hbar)[\hat{A},\hat{B}]$ or in its partially Wigner transformed form $(\hat{A}_W,\hat{B}_W)_Q$, satisfies the Jacobi identity,

$$(\hat{A}_W,(\hat{B}_W,\hat{C}_W)_Q)_Q + (\hat{C}_W,(\hat{A}_W,\hat{B}_W)_Q)_Q$$

$$+ (\hat{B}_W,(\hat{C}_W,\hat{A}_W)_Q)_Q = 0. \tag{17}$$

We may remark on several limiting situations of this general formulation of quantum dynamics. If the quantum bath is absent and the system comprises only quantum subsystem degrees of freedom, we simply have the usual quantum dynamical description in terms of the von Neumann equation (1). If one considers the quantum bath dynamics alone without a quantum subsystem, one has the ordinary Wigner representation of quantum mechanics and all partially Wigner transformed operators become simple phase space functions: $\hat{A}_W(R,P) \to A_W(R,P)$. The classical limit of the quantum bath dynamics, which consists in keeping only terms of order $\hbar^0$ in the evolution operator, is obtained by the following truncation of the power series expression of the exponential operator: $\exp(\hbar\Lambda/2i) = 1 + \hbar\Lambda/2i$. In this limit the bracket $(H_W,)_Q$ reduces to the Poisson bracket $\{H_W, \}$ and the Wigner representation of the quantum Liouville equation becomes the classical Liouville equation, $\partial\rho_C/\partial t = -\{H_W,\rho_C\} = -iL_C\rho_C(t)$, whose solution may be written as

$$\rho_C(R,P,t) = e^{-iL_C t}\rho_C(R,P,0)$$

$$= e^{-1/2 H_W \Lambda t}\rho_C(R,P,0)e^{1/2\Lambda H_W t}. \tag{18}$$

The Poisson bracket is a Lie bracket and satisfies the Jacobi identity. Of course, products of classical phase space functions satisfy the associative property. Consequently, both quantum and classical dynamics have a Lie algebraic structure and products of quantum operators or classical phase space functions satisfy an associative product rule.

B. Quantum-classical dynamics

The formulation of quantum dynamics in the partial Wigner representation allows the limit of a mixed quantum-classical system to be taken easily. In such quantum-classical dynamics, the full quantum dynamics of the subsystem is taken into account while the bath, in isolation, evolves according to the classical equations of motion. This limit is taken by replacing $\vec{H}_\Lambda$ and $\tilde{H}_\Lambda$ by their expansions to first order in $\hbar$:

$$\vec{H}_\Lambda \to \vec{\mathcal{H}}_\Lambda = \hat{H}_W\left(1 + \frac{\hbar\Lambda}{2i}\right),$$

$$\tilde{H}_\Lambda \to \tilde{\mathcal{H}}_\Lambda = \left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{H}_W. \tag{19}$$

The full system evolution, which includes the interaction between the quantum subsystem and classical bath, is then given by the mixed quantum-classical Liouville equation:[20–26]

$$\frac{\partial\hat{\rho}_W(R,P,t)}{\partial t} = -\frac{i}{\hbar}[\hat{H}_W,\hat{\rho}_W(t)] + \frac{1}{2}(\{\hat{H}_W,\hat{\rho}_W(t)\}$$

$$- \{\hat{\rho}_W(t),\hat{H}_W\})$$

$$\equiv -(\hat{H}_W,\hat{\rho}_W(t)) \equiv -i\hat{\mathcal{L}}\hat{\rho}_W(t). \tag{20}$$

The last equalities in Eq. (20) define the mixed quantum-classical Liouville operator $\hat{\mathcal{L}}$, and the bracket which takes the form[23,24]

$$(\hat{A}_W,\hat{B}_W) = \frac{i}{\hbar}(\vec{\mathcal{A}}_\Lambda\hat{B}_W - \hat{B}_W\tilde{\mathcal{A}}_\Lambda)$$

$$= \frac{i}{\hbar}\left(\hat{A}_W\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{B}_W - \hat{B}_W\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{A}_W\right)$$

$$= \frac{i}{\hbar}[\hat{A}_W,\hat{B}_W] - \frac{1}{2}(\{\hat{A}_W,\hat{B}_W\} - \{\hat{B}_W,\hat{A}_W\}), \tag{21}$$

where $\vec{\mathcal{A}}_\Lambda$ is defined as $\vec{\mathcal{H}}_\Lambda$ in Eq. (19) with $\hat{H}_W \to \hat{A}_W$. The bracket reduces to the quantum Lie bracket $(i\hbar)^{-1}[\hat{A}_W,\hat{B}_W]$ when the classical bath is absent and to the classical Lie bracket (Poisson bracket) $\{A_W,B_W\}$ when the quantum subsystem is absent.

Using this notation, the evolution equations for $\hat{\rho}_W(t)$ and an operator $\hat{A}_W$ are given, respectively, by

$$\frac{\partial\hat{\rho}_W(t)}{\partial t} = -(\hat{H}_W,\hat{\rho}_W(t)) \tag{22}$$

and

$$\frac{d\hat{A}_W(t)}{dt} = (\hat{H}_W, \hat{A}_W(t)), \tag{23}$$

in apparent complete analogy with pure quantum and classical dynamics. However, a number of important differences exist which we now examine.

Consider the product of three operators in the mixed quantum-classical limit. From Eq. (14) we have

$$(\hat{A}\hat{B}\hat{C})_W \rightarrow \left(\left(\hat{A}_W \left(1 + \frac{\hbar \Lambda}{2i} \right) \hat{B}_W \right) \left(1 + \frac{\hbar \Lambda}{2i} \right) \hat{C}_W \right)$$

$$= \left(\hat{A}_W \left(1 + \frac{\hbar \Lambda}{2i} \right) \left(\hat{B}_W \left(1 + \frac{\hbar \Lambda}{2i} \right) \hat{C}_W \right) \right)$$

$$- \frac{\hbar^2}{4} (((\hat{A}_W \Lambda \hat{B}_W) \Lambda \hat{C}_W)$$

$$- (\hat{A}_W \Lambda (\hat{B}_W \Lambda \hat{C}_W))), \tag{24}$$

where the last term is $\mathcal{O}(\hbar^2)$. Thus, the associative product rule is no longer exact but is valid only to terms $\mathcal{O}(\hbar^2)$. This has important implications for the dynamics. In particular, in this limit, consider the action of the mixed quantum-classical Liouville operator on the product of two operators, $\hat{C}_W = \hat{A}_W(1 + \hbar \Lambda/2i)\hat{B}_W$:

$$i\hat{\mathcal{L}}\hat{C}_W = \frac{i}{\hbar} \left(\vec{\mathcal{H}}_\Lambda \left(\hat{A}_W \left(1 + \frac{\hbar \Lambda}{2i} \right) \hat{B}_W \right) \right)$$

$$- \frac{i}{\hbar} \left(\left(\hat{A}_W \left(1 + \frac{\hbar \Lambda}{2i} \right) \hat{B}_W \right) \vec{\mathcal{H}}_\Lambda \right)$$

$$= (i\hat{\mathcal{L}}\hat{A}_W) \left(1 + \frac{\hbar \Lambda}{2i} \right) \hat{B}_W$$

$$+ \hat{A}_W \left(1 + \frac{\hbar \Lambda}{2i} \right) (i\hat{\mathcal{L}}\hat{B}_W) + \mathcal{O}(\hbar). \tag{25}$$

Thus, while Eq. (16) is exact, the corresponding quantum-classical equation is valid only to terms $\mathcal{O}(\hbar)$. From this result it follows that

$$\hat{C}_W(t) = e^{i\hat{\mathcal{L}}t}\hat{C}_W = (e^{i\hat{\mathcal{L}}t}\hat{A}_W) \left(1 + \frac{\hbar \Lambda}{2i} \right)(e^{i\hat{\mathcal{L}}t}\hat{B}_W) + \mathcal{O}(\hbar)$$

$$= \hat{A}_W(t) \left(1 + \frac{\hbar \Lambda}{2i} \right) \hat{B}_W(t) + \mathcal{O}(\hbar). \tag{26}$$

Consequently, the evolution of a composite operator in quantum-classical dynamics cannot be determined exactly in terms of the quantum-classical evolution of its constituent operators, but only to terms $\mathcal{O}(\hbar)$, in contrast both to quantum and classical dynamics. This result has implications for the computation of time correlation functions discussed in Sec. V.

The Jacobi identity involving the quantum-classical bracket is valid only to terms $\mathcal{O}(\hbar)$:

$$(\hat{A}_W, (\hat{B}_W, \hat{C}_W)) + (\hat{C}_W, (\hat{A}_W, \hat{B}_W)) + (\hat{B}_W, (\hat{C}_W, \hat{A}_W))$$

$$= \mathcal{O}(\hbar); \tag{27}$$

thus, the quantum-classical bracket is not strictly a Lie bracket. As a consequence, Poisson's theorem, which states that the Poisson bracket (or the quantum Lie bracket) of any two constants of the motion is also a constant of the motion, fails. More generally, from this result we conclude that products or powers of the constants of the motion are constants of the motion only to $\mathcal{O}(\hbar)$.

The formal solutions of the equations of motion that parallel those of full quantum mechanics also require some discussion. For example, the formal solution of Eq. (23) can be written as

$$\hat{A}_W(t) = e^{i\hat{\mathcal{L}}t}\hat{A}_W = \mathcal{S}(e^{i\vec{\mathcal{H}}_\Lambda t/\hbar}\hat{A}_W e^{-i\vec{\mathcal{H}}_\Lambda t/\hbar}). \tag{28}$$

Here the operator $\mathcal{S}$ specifies the rule that must be used to evaluate the exponential operators in the second equality in Eq. (28). Appendix A gives the details of the rules that must be followed in order for the formal solution involving the exponentials of the left $\vec{\mathcal{H}}_\Lambda$ and right $\vec{\mathcal{H}}_\Lambda$ operators to be equivalent to that obtained using the quantum-classical Liouville operator.

Given this compact formulation of mixed quantum-classical dynamics that exploits the formal similarity with full quantum mechanics, we turn to a description of the statistical mechanics of such systems. In the next section we consider the determination of the equilibrium density matrix for a mixed quantum-classical system and then turn in the following section to a more general study of the properties of equilibrium time correlation functions.

III. EQUILIBRIUM DENSITY MATRIX

The quantum mechanical equilibrium canonical density matrix has the familiar form

$$\hat{\rho}_e^Q = Z^{-1}e^{-\beta\hat{H}}, \tag{29}$$

where Z is the partition function, $Z = \text{Tr} \exp(-\beta\hat{H})$. Its partial Wigner transform is given by

$$\hat{\rho}_{We}^Q(R,P) = \int dz \, e^{iP \cdot z/\hbar} \left\langle R - \frac{z}{2} \middle| \hat{\rho}_e^Q \middle| R + \frac{z}{2} \right\rangle. \tag{30}$$

We denote the corresponding canonical equilibrium density matrix in the quantum-classical limit by $\hat{\rho}_{We}(R,P)$ which is defined to be the approximation to $\hat{\rho}_{We}^Q(R,P)$ that is stationary under quantum-classical dynamics:

$$i\hat{\mathcal{L}}\hat{\rho}_{We} = \frac{i}{\hbar}(\vec{\mathcal{H}}_\Lambda \hat{\rho}_{We} - \hat{\rho}_{We}\vec{\mathcal{H}}_\Lambda) = 0. \tag{31}$$

The solution of Eq. (31) can be found in the following way: we first write $\hat{\rho}_{We}$ as a power series in $\hbar$ [or in the mass ratio $(m/M)^{1/2}$ if scaled variables are used]

$$\hat{\rho}_{We} = \sum_{n=0}^{\infty} \hbar^n \hat{\rho}_{We}^{(n)}. \tag{32}$$

Substituting this expression in Eq. (31) and grouping by powers of $\hbar$, we obtain the following recursion relations: for $n = 0$:

$$i[\hat{H}_W, \hat{\rho}_{We}^{(0)}] = 0 \tag{33}$$

and for $n \geq 0$,

$$i[\hat{H}_W, \hat{\rho}_{We}^{(n+1)}] = \tfrac{1}{2}\{\hat{H}_W, \hat{\rho}_{We}^{(n)}\} - \tfrac{1}{2}\{\hat{\rho}_{We}^{(n)}, \hat{H}_W\}. \tag{34}$$

An analogous set of recursion relations may be written for the partial Wigner transform of the full quantum mechanical canonical equilibrium density matrix. These recursion relations are given in Appendix B where it is shown that $\hat{\rho}_{We}^Q(R,P)$ and $\hat{\rho}_{We}(R,P)$ are identical to $\mathcal{O}(\hbar)$. We shall exploit this feature below where the solutions of the mixed quantum-classical recursion relations are presented.

It is convenient to analyze the structure of the recursion relations and obtain their solutions in an adiabatic basis. The adiabatic states are defined to be the eigenstates of the quantum subsystem with fixed classical coordinates,

$$\hat{h}_W(R)|\alpha;R\rangle = E_\alpha(R)|\alpha;R\rangle, \tag{35}$$

where

$$\hat{h}_W(R) = \frac{\hat{P}^2}{2m} + \hat{V}_W(\hat{q},R). \tag{36}$$

Taking matrix elements of Eqs. (33) and (34), respectively, we find,

$$iE_{\alpha\alpha'}\rho_{We}^{(0)\alpha\alpha'} = 0, \tag{37}$$

$$iE_{\alpha\alpha'}\rho_{We}^{(n+1)\alpha\alpha'} = -iL_{\alpha\alpha'}\rho_{We}^{(n)\alpha\alpha'} + \sum_{\nu\nu'} J_{\alpha\alpha',\nu\nu'}\rho_{We}^{(n)\nu\nu'}. \tag{38}$$

This set of equations is equivalent to $\sum_{\nu\nu'} i\mathcal{L}_{\alpha\alpha',\nu\nu'}\rho_{We}^{\nu\nu'} = 0$ with $\rho_{We}^{\nu\nu'}$ written as a power series in $\hbar$. In these equations, using the definitions in Ref. 26, we have the classical Liouville operator,

$$iL_{\alpha\alpha'} = \frac{P}{M} \cdot \frac{\partial}{\partial R} + \frac{1}{2}(F_W^\alpha + F_W^{\alpha'}) \cdot \frac{\partial}{\partial P}, \tag{39}$$

where $F_W^\alpha = -\langle\alpha;R|\partial\hat{V}_W(\hat{q},R)/\partial R|\alpha;R\rangle$ is the Hellmann–Feynman force for state α, the energy difference $E_{\alpha\alpha'}(R) = E_\alpha(R) - E_{\alpha'}(R)$, and the term responsible for nonadiabatic transitions,

$$J_{\alpha\alpha',\nu\nu'} = -\frac{P}{M} \cdot d_{\alpha\nu}\left(1 + \frac{1}{2}S_{\alpha\nu} \cdot \frac{\partial}{\partial P}\right)\delta_{\alpha'\nu'}$$

$$- \frac{P}{M} \cdot d_{\alpha'\nu'}^*\left(1 + \frac{1}{2}S_{\alpha'\nu'}^* \cdot \frac{\partial}{\partial P}\right)\delta_{\alpha\nu}. \tag{40}$$

In this equation the nonadiabatic coupling matrix element is

$$d_{\alpha\alpha'} = \langle\alpha;R|\frac{\partial}{\partial R}|\alpha';R\rangle, \tag{41}$$

while the quantity $S_{\alpha\nu}$ is defined as

$$S_{\alpha\nu} = (F_W^{\alpha\nu} - F_W^\alpha\delta_{\alpha\nu})\left(\frac{P}{M} \cdot d_{\alpha\nu}\right)^{-1}$$

$$= E_{\alpha\nu}d_{\alpha\nu}\left(\frac{P}{M} \cdot d_{\alpha\nu}\right)^{-1}, \tag{42}$$

and specifies the momentum transfer to and from the classical subsystem arising from quantum transitions.

Equation (37) provides no information about the diagonal elements $\rho_{We}^{(0)\alpha\alpha} \equiv \rho_{We}^{(0)\alpha}$ but requires that the off-diagonal elements $\rho_{We}^{(0)\alpha\alpha'}$ be zero. Similarly, Eq. (38) for $n=0$ provides no information about the diagonal elements $\rho_{We}^{(1)\alpha\alpha} \equiv \rho_{We}^{(1)\alpha}$ but relates the off-diagonal elements $\rho_{We}^{(1)\alpha\alpha'}$ to the diagonal elements $\rho_{We}^{(0)\alpha}$. For $n \geq 1$ Eq. (38) determines the diagonal elements $\rho_{We}^{(n)\alpha}$ in terms of the off-diagonal elements of the same order, and the off-diagonal elements $\rho_{We}^{(n+1)\alpha\alpha'}$ in terms of the diagonal and off-diagonal elements of $\rho_{We}^{(n)\alpha\alpha'}$. Thus, provided we know the diagonal elements $\rho_{We}^{(0)\alpha}$ there is sufficient information to determine the complete solution of $\rho_{We}^{\alpha\alpha'}$.

The method used to solve Eq. (38) for the diagonal elements $\rho_{We}^{(n)\alpha}$ requires some discussion. Writing this equation explicitly for the diagonal elements we have

$$iL_\alpha\rho_{We}^{(n)\alpha} = \sum_{\nu>\nu'} 2\Re(J_{\alpha\alpha,\nu\nu'}\rho_{We}^{(n)\nu\nu'}), \tag{43}$$

where we have used $\rho_{We}^{\alpha\alpha'} = \rho_{We}^{\alpha'\alpha*}$ and $J_{\alpha\alpha,\nu\nu'} = J_{\alpha\alpha,\nu'\nu}^*$ and the fact that $J_{\alpha\alpha,\nu\nu} = 0$ when a real adiabatic basis is chosen. The left-hand side of Eq. (43) consists of a linear self-adjoint differential operator iL_α acting on the diagonal elements of the density matrix, $iL_\alpha\rho_{We}^{(n)\alpha} = \{H_W^\alpha, \rho_W^{(n)\alpha}\}$ and, due to the Poisson bracket form of this operator, one can determine $\rho_W^{(n)\alpha}$ only up to a constant of the motion under the adiabatic Hamiltonian H_W^α. To insure that a solution can be found we must invoke the theorem of the Fredholm alternative which requires that the right-hand side of Eq. (43) be orthogonal to the null-space of iL_α.[31] This null-space consists of the constants of the motion under the adiabatic Hamiltonian H_W^α—at least any function $F(H_W^\alpha(R,P))$ of this Hamiltonian. Hence we must verify that the following condition is satisfied:

$$\int dR\,dP \sum_{\nu>\nu'} 2\Re(J_{\alpha\alpha,\nu\nu'}\rho_{We}^{(n)\nu\nu'})F(H_W^\alpha) = 0. \tag{44}$$

We show in Appendix C that $\Re(J_{\alpha\alpha,\nu\nu'}\rho_{We}^{(n)\nu\nu'})$ is a no dd function of P. This, along with the fact that $F(H_W^\alpha)$ is an even function of P since it is a function of the Hamiltonian, guarantees the validity of Eq. (44).

Thus, we may write the formal solution of Eq. (43) as

$$\rho_{We}^{(n)\alpha} = (iL_\alpha)^{-1} \sum_{\nu>\nu'} 2\Re(J_{\alpha\alpha,\nu\nu'}\rho_{We}^{(n)\nu\nu'}), \tag{45}$$

and the formal solution of Eq. (38) for $\alpha \neq \alpha'$ as

$$\rho_{We}^{(n+1)\alpha\alpha'} = \frac{i}{E_{\alpha\alpha'}}\left(iL_{\alpha\alpha'}\rho_{We}^{(n)\alpha\alpha'} - \sum_{\nu\nu'} J_{\alpha\alpha',\nu\nu'}\rho_{We}^{(n)\nu\nu'}\right). \tag{46}$$

Using the formal results outlined above, we may construct the form of the mixed quantum-classical canonical equilibrium density matrix. In Appendix B we show that

$$\rho_{We}^{(0)\alpha} = Z_0^{-1}e^{-\beta H_W^\alpha}, \quad Z_0 = \sum_\alpha \int dR\,dP\,e^{-\beta H_W^\alpha}, \tag{47}$$

and that $\rho_{We}^{(1)\alpha} = 0$. Then, taking $n=0$ in Eq. (46) we obtain, after some algebra,

$$\rho_{We}^{(1)\alpha\alpha'} = -i\frac{P}{M} \cdot d_{\alpha\alpha'}\rho_{We}^{(0)\alpha}\left(\frac{\beta}{2}(1+e^{-\beta E_{\alpha'\alpha}})\right.$$

$$\left. + \frac{1-e^{-\beta E_{\alpha'\alpha}}}{E_{\alpha\alpha'}}\right)(1-\delta_{\alpha\alpha'}). \tag{48}$$

We may then use these results in the recursion relations to obtain all higher order terms in the expansion. The higher order terms are more difficult to evaluate and, as we shall show in the following section, the explicit solutions to $\mathcal{O}(\hbar)$ will suffice since all results we can obtain are reliable only to this order.

IV. TIME CORRELATION FUNCTIONS

To derive expressions for transport properties in terms of equilibrium time correlation functions, one may consider the response of a system to an external force using linear response theory or monitor the equilibrium fluctuations in a system. In this section we examine linear response theory for mixed quantum-classical systems.

A. Response function

Standard descriptions of linear response theory[32] assume that a system which is in thermal equilibrium in the distant past is subjected to a time dependent external force. The response of the system to this external force is determined by computing the average value of some property at time t using the density matrix determined to linear order in the force. We adopt a similar point of view here except that we suppose the system follows quantum-classical dynamics instead of full quantum mechanics.

The mixed quantum-classical system is subjected to a time dependent external force $F(t)$ which couples to the observable $\hat{A}_W^\dagger$ († is the adjoint) and is applied from the distant past. The partially Wigner transformed Hamiltonian of the system in the presence of the external force is

$$\hat{\mathbf{H}}_W(t) = \hat{H}_W - \hat{A}_W^\dagger F(t). \tag{49}$$

The evolution equation for the density matrix is obtained from Eq. (22) by replacing $\vec{\mathcal{H}}_\Lambda$ and $\bar{\mathcal{H}}_\Lambda$ by $\vec{\mathbf{H}}_\Lambda(t)$ and $\bar{\mathbf{H}}_\Lambda(t)$, respectively, to yield

$$\frac{\partial\hat{\rho}_W(t)}{\partial t} = (i\hbar)^{-1}(\vec{\mathbf{H}}_\Lambda(t)\hat{\rho}_W(t) - \hat{\rho}_W(t)\bar{\mathbf{H}}_\Lambda(t))$$

$$= -(i\hat{\mathcal{L}} - i\hat{\mathcal{L}}_A F(t))\hat{\rho}_W(t), \tag{50}$$

where $\vec{\mathbf{H}}_\Lambda(t) = \vec{\mathcal{H}}_\Lambda - \vec{\mathcal{A}}_\Lambda F(t)$ and $i\hat{\mathcal{L}}_A$ has a form analogous to $i\hat{\mathcal{L}}$ with $\hat{A}_W^\dagger$ replacing $\hat{H}_W$, $i\hat{\mathcal{L}}_A = (\hat{A}_W^\dagger,)$. The formal solution of this equation is found by integrating from t_0 to t,

$$\hat{\rho}_W(t) = e^{-i\hat{\mathcal{L}}(t-t_0)}\hat{\rho}_W(t_0)$$

$$+ \int_{t_0}^t dt'\, e^{-i\hat{\mathcal{L}}(t-t')}i\hat{\mathcal{L}}_A\hat{\rho}_W(t')F(t'). \tag{51}$$

Choosing $\hat{\rho}_W(t_0)$ to be the equilibrium density matrix, $\hat{\rho}_{We}$, defined to be invariant under quantum-classical dynamics, $i\hat{\mathcal{L}}\hat{\rho}_{We} = 0$, the first term on the right-hand side of Eq. (51) coincides with $\hat{\rho}_{We}$ and is independent of t_0. We can

now assume that the system with Hamiltonian $\hat{H}_W$ is in thermal equilibrium from $t = -\infty$ up to t_0. With this boundary condition, to first order in the external force Eq. (51) yields

$$\hat{\rho}_W(t) = \hat{\rho}_{We} + \int_{-\infty}^t dt'\, e^{-i\hat{\mathcal{L}}(t-t')}i\hat{\mathcal{L}}_A\hat{\rho}_{We}F(t'). \tag{52}$$

The nonequilibrium average value of any operator $\hat{B}_W$ over the density matrix $\hat{\rho}_W(t)$, $\overline{B(t)} = \text{Tr}'\int dR\, dP\, \hat{B}_W\hat{\rho}_W(t)$ may be computed to determine the response of the system to the external force. Using Eq. (52) we may write this as

$$\Delta\overline{B_W}(t) = \int_{-\infty}^t dt'\, \text{Tr}'\int dR\, dP\, \hat{B}_W e^{-i\hat{\mathcal{L}}(t-t')}i\hat{\mathcal{L}}_A\hat{\rho}_{We}F(t')$$

$$= -\int_{-\infty}^t dt'\langle(\hat{A}_W^\dagger, \hat{B}_W(t-t'))\rangle F(t')$$

$$\equiv \int_{-\infty}^t dt'\, \phi_{BA}(t-t')F(t'), \tag{53}$$

where $\Delta\overline{B_W}(t) = \overline{B_W}(t) - \langle\hat{B}_W\rangle$. In this equation we made use of integration by parts and cyclic permutations under the trace to move the evolution operator onto $\hat{B}_W$ and $i\hat{\mathcal{L}}_A$ onto $\hat{B}_W(t-t')$. Then using the definition of $i\hat{\mathcal{L}}_A$ as the quantum-classical bracket and the definition of the average $\langle\hat{f}_W\rangle = \text{Tr}'\int dR\, dP\, \hat{f}_W\hat{\rho}_{We}$ for any operator $\hat{f}_W$, we arrive at the form in the second line. The prime on the trace denotes the fact that the trace is over the quantum subsystem states. The last line defines the response function ϕ_{BA} which is given by

$$\phi_{BA}(t) = -\langle(\hat{A}_W^\dagger, \hat{B}_W(t))\rangle. \tag{54}$$

The response function in Eq. (54) was derived by considering a system following quantum-classical dynamics, in equilibrium in the past, subject to a time dependent external force. This quantum-classical response function should now be compared with the reduction of the response function for a fully quantum mechanical system to its quantum-classical form.

The quantum expression for the response function is[32]

$$\phi_{BA}^Q(t) = -\frac{i}{\hbar}\text{Tr}[\hat{A}^\dagger, \hat{\rho}_e^Q]\hat{B}(t) = \frac{i}{\hbar}\text{Tr}[\hat{A}^\dagger, \hat{B}(t)]\hat{\rho}_e^Q, \tag{55}$$

which, taking the partial Wigner transform of the second equality in Eq. (55), may be written as

$$\phi_{BA}^Q(t) = -\text{Tr}'\int dR\, dP\, \frac{i}{\hbar}(\hat{A}_W^\dagger e^{\hbar\Lambda/2i}\hat{B}_W(t)$$

$$- \hat{B}_W(t)e^{\hbar\Lambda/2i}\hat{A}_W^\dagger)\hat{\rho}_{We}^Q$$

$$= -\text{Tr}'\int dR\, dP\, \frac{i}{\hbar}(\vec{A}_\Lambda\hat{B}_W(t) - \hat{B}_W(t)\bar{A}_\Lambda)\hat{\rho}_{We}^Q$$

$$= -\langle(\hat{A}_W^\dagger, \hat{B}_W(t))_Q\rangle. \tag{56}$$

To obtain the first equality we have used the fact that the partial Wigner transform of $\text{Tr}\,\hat{A}\hat{B} = \text{Tr}'\int dR\, dP\, \hat{A}_W\hat{B}_W$.

We wish to take the mixed quantum-classical limit of this expression but this cannot be done by a simple expan-

sion in $\hbar$. Mixed quantum-classical dynamics is defined by the evolution equation (20) where the evolution operator is obtained by an expansion to first order in $\hbar$ (or the mass ratio); however, the time-evolved density matrix contains all orders in $\hbar$ since it involves the exponential of the evolution operator. The same arguments apply to operators at time t and the equilibrium density matrix.

As an ansatz one may replace the time dependent operator $\hat{B}_W(t)$ and the quantum equilibrium density matrix $\hat{\rho}_{We}^Q$ by their quantum-classical forms. In addition, we may replace the quantum Lie bracket $(\,,\,)_Q$ by its quantum classical analog, $(\,,\,)_Q \to (\,,\,)$ which is equivalent to replacing the exponential operator $\exp(\hbar\Lambda/2i)$ by its expansion to linear order in $\hbar$, $\exp(\hbar\Lambda/2i) \to 1 + \hbar\Lambda/2i$. After these replacements the response function takes the form

$$\phi_{BA}(t) = -\mathrm{Tr}' \int dR\, dP\, \frac{i}{\hbar} (\hat{A}_W^\dagger(1 + \hbar\Lambda/2i)\hat{B}_W(t)$$
$$- \hat{B}_W(t)(1 + \hbar\Lambda/2i)\hat{A}_W^\dagger)\hat{\rho}_{We}$$
$$= \langle (\hat{A}_W^\dagger, \hat{B}_W(t)) \rangle, \qquad (57)$$

which is exactly the result in Eq. (54) obtained by performing a linear response derivation directly on the mixed quantum-classical equations of motion. This entitles one to use the above intuitive correspondence rule to convert a quantum mechanical correlation function to its mixed quantum-classical analog.

In the linear response approach to dynamical phenomena there are various useful equivalent ways to represent the response function. Moreover, since the response function is essentially an equilibrium correlation function, its computation is generally simplified by using the symmetry properties of the equilibrium system. As we shall see in the next sections the situation is much less favorable in the quantum-classical case since many of the rigorous equivalences established in quantum or classical response theory are only approximately true in the quantum-classical limit. The first and most important equivalence is obtained through the Kubo identity; therefore, we begin our discussion with this case.

B. Kubo transformed correlation functions

In quantum mechanics, correlation functions often appear in Kubo transformed form. Making use of the quantum mechanical identity,

$$\frac{i}{\hbar}[\hat{A}^\dagger, \hat{\rho}_e^Q] = \int_0^\beta d\lambda\, \hat{\rho}_e^Q \dot{\hat{A}}^\dagger(-i\hbar\lambda), \qquad (58)$$

in the first equality of Eq. (55) we may write the response function as

$$\phi_{BA}^Q(t) = -\int_0^\beta d\lambda\, \mathrm{Tr}\, \dot{\hat{A}}^\dagger(-i\hbar\lambda)\hat{B}(t)\hat{\rho}_e^Q$$
$$= -\int_0^\beta d\lambda\, \mathrm{Tr}' \int dR\, dP\, (\dot{\hat{A}}^\dagger{}_W(-i\hbar\lambda)$$
$$\times e^{\hbar\Lambda/2i}\hat{B}_W(t))\hat{\rho}_{We}^Q, \qquad (59)$$

where we have again written the second line in partially Wigner transformed form. Using the correspondence rule to take the quantum-classical limit of this expression, we obtain

$$\phi_{BA}(t) = -\int_0^\beta d\lambda\, \mathrm{Tr}' \int dR\, dP(\dot{\hat{A}}_W^\dagger(-i\hbar\lambda)$$
$$\times (1 + \hbar\Lambda/2i)\hat{B}_W(t))\hat{\rho}_{We}. \qquad (60)$$

We shall show now that Eqs. (57) and (60) are not equal and agree only to $\mathcal{O}(\hbar)$. The quantum mechanical identity [Eq. (58)] used to obtain the Kubo transformed correlation function uses the explicit form for the thermal density matrix of $\hat{\rho}_e^Q = Z^{-1}e^{-\beta\hat{H}}$. In the quantum-classical case the structure of $\hat{\rho}_{We}$ is complicated (see Sec. III) and we do not have a closed form expression for it. Consequently, it is necessary to obtain an expression for $\hat{\rho}_{We}$ that is analogous to $\hat{\rho}_e^Q$ so that manipulations parallel to those in the quantum derivation may be performed. We shall see that this is possible only to terms $\mathcal{O}(\hbar^2)$.

The unnormalized equilibrium quantum density matrix, $\hat{\Omega}_e^Q$, satisfies the Bloch equation,

$$\frac{\partial \hat{\Omega}_e^Q}{\partial\beta} = -\hat{H}\hat{\Omega}_e^Q = -\hat{\Omega}_e^Q\hat{H}. \qquad (61)$$

Taking its partial Wigner transform we may write it in the form

$$\frac{\partial \hat{\Omega}_{We}^Q}{\partial\beta} = -\vec{H}_\Lambda \hat{\Omega}_{We}^Q = -\hat{\Omega}_{We}^Q \vec{H}_\Lambda, \qquad (62)$$

with the boundary condition $\hat{\Omega}_{We}^Q(\beta=0) = 1$.

The normalized formal solution (taking into account the boundary condition) is

$$\hat{\rho}_{We}^Q = Z^{-1}(e^{-\beta\vec{H}_\Lambda}1) = Z^{-1}(1\, e^{-\beta\vec{H}_\Lambda}). \qquad (63)$$

By the usual rule the quantum-classical limit should be obtained by the replacement $H_\Lambda \to \mathcal{H}_\Lambda$. However, by direct calculation one may show that $(\exp(-\beta\vec{\mathcal{H}}_\Lambda)1)$ and $(1\exp(-\beta\vec{\mathcal{H}}_\Lambda))$ agree only to first order in $\hbar$.[33] Moreover, to first order in $\hbar$ they also agree with $\hat{\rho}_{We}$ whose explicit form to this order is given in Eqs. (47) and (48). Thus, to this order these expressions may be used interchangeably.

The Kubo identity (58) in the partial Wigner representation is

$$(\hat{\rho}_{We}^Q, \hat{A}_W^\dagger)_Q = \int_0^\beta d\lambda\, \hat{\rho}_{We}^Q e^{\hbar\Lambda/2i}\dot{\hat{A}}_W^\dagger(-i\hbar\lambda), \qquad (64)$$

and its quantum-classical analog, which holds only approximately, is

$$(\hat{\rho}_{We}, \hat{A}_W^\dagger) = \int_0^\beta d\lambda\, \hat{\rho}_{We}\left(1 + \frac{\hbar\Lambda}{2i}\right)\dot{\hat{A}}_W^\dagger(-i\hbar\lambda) + \mathcal{O}(\hbar)$$
$$\equiv \mathcal{K} + \mathcal{O}(\hbar). \qquad (65)$$

This result is derived as follows: performing the integral over λ we obtain

$$i\hbar \mathcal{K} = -\hat{\rho}_{We}\left(1 + \frac{\hbar\Lambda}{2i}\right)\mathcal{S}(e^{\beta\vec{\mathcal{H}}_\Lambda}\hat{A}_W^\dagger e^{-\beta\vec{\mathcal{H}}_\Lambda})$$

$$+ \hat{\rho}_{We}\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{A}_W^\dagger$$

$$= -Z^{-1}(1e^{-\beta\vec{\mathcal{H}}_\Lambda})\left(1 + \frac{\hbar\Lambda}{2i}\right)\mathcal{S}(e^{\beta\vec{H}_\Lambda}\hat{A}_W^\dagger e^{-\beta\vec{\mathcal{H}}_\Lambda})$$

$$+ \hat{\rho}_{We}\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{A}_W^\dagger + \mathcal{O}(\hbar^2), \tag{66}$$

where we have used one of the "equivalent" expressions for $\hat{\rho}_{We}$, and we remind the reader that the interpretation of $\mathcal{S}(\ )$ is given in Appendix A. Next, expanding the exponential operator and using the quantum-classical associative product rule [valid to terms $\mathcal{O}(\hbar^2)$] we may show that

$$(1e^{-\beta\vec{\mathcal{H}}_\Lambda})\left(1 + \frac{\hbar\Lambda}{2i}\right) = e^{-\beta\vec{\mathcal{H}}_\Lambda} + \mathcal{O}(\hbar^2), \tag{67}$$

$$\left(1 + \frac{\hbar\Lambda}{2i}\right)(e^{-\beta\vec{\mathcal{H}}_\Lambda}1) = e^{-\beta\vec{\mathcal{H}}_\Lambda} + \mathcal{O}(\hbar^2), \tag{68}$$

and use these results to manipulate Eq. (66). We have

$$i\hbar \mathcal{K} = -Z^{-1}e^{-\beta\vec{\mathcal{H}}_\Lambda}\mathcal{S}(e^{\beta\vec{\mathcal{H}}_\Lambda}\hat{A}_W^\dagger e^{-\beta\vec{\mathcal{H}}_\Lambda})$$

$$+ \hat{\rho}_{We}\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{A}_W^\dagger + \mathcal{O}(\hbar^2). \tag{69}$$

To further simplify the right-hand side of this equation we use the relation

$$e^{-\beta\vec{\mathcal{H}}_\Lambda}\mathcal{S}(e^{\beta\vec{\mathcal{H}}_\Lambda}\hat{A}_W^\dagger e^{-\beta\vec{\mathcal{H}}_\Lambda}) = \hat{A}_W^\dagger e^{-\beta\vec{\mathcal{H}}_\Lambda} + \mathcal{O}(\hbar^2), \tag{70}$$

which may be proved by direct expansion of the exponential operators. Then using Eq. (68) we have

$$i\hbar \mathcal{K} = -Z^{-1}\hat{A}_W^\dagger\left(1 + \frac{\hbar\Lambda}{2i}\right)(e^{-\beta\vec{\mathcal{H}}_\Lambda}1) + \hat{\rho}_{We}\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{A}_W^\dagger$$

$$+ \mathcal{O}(\hbar^2)$$

$$= -\hat{A}_W^\dagger\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{\rho}_{We} + \hat{\rho}_{We}\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{A}_W^\dagger + \mathcal{O}(\hbar^2)$$

$$= i\hbar(\hat{\rho}_{We}, \hat{A}_W^\dagger) + \mathcal{O}(\hbar^2). \tag{71}$$

Starting with Eq. (54) and using Eq. (65) gives

$$\phi_{BA}(t) = -\text{Tr}'\int dR\,dP(\hat{A}_W^\dagger, \hat{B}_W(t))\hat{\rho}_{We}$$

$$= -\text{Tr}'\int dR\,dP(\hat{\rho}_{We}, \hat{A}_W^\dagger)\hat{B}_W(t)$$

$$= -\int_0^\beta d\lambda\,\text{Tr}'\int dR\,dP\left(\dot{\hat{A}}_W^\dagger(-i\hbar\lambda)\right.$$

$$\left.\times\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{B}_W(t)\right)\hat{\rho}_{We} + \mathcal{O}(\hbar). \tag{72}$$

The last equality has been obtained by substituting Eq. (65) and then using cyclic permutation of the trace and integration by parts.

Following Kubo, we may define a new correlation function, also in the mixed quantum-classical limit, by

$$\langle\hat{A}_W; \hat{B}_W(t)\rangle = \frac{1}{\beta}\int_0^\beta d\lambda\,\text{Tr}'\int dR\,dP\left(\hat{A}_W^\dagger(-i\hbar\lambda)\right.$$

$$\left.\times\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{B}_W(t)\right)\hat{\rho}_{We}. \tag{73}$$

Using this notation, the response function may be written simply as

$$\phi_{BA}(t) = -\beta\langle\dot{\hat{A}}_W; \hat{B}_W(t)\rangle + \mathcal{O}(\hbar). \tag{74}$$

Equation (74) may be useful in practical calculations. However, since the equivalence between the two forms of the response function [Eqs. (57) and (74)] cannot be established to all orders in $\hbar$, the magnitude of their numerical difference must be evaluated in specific applications in order to determine the applicability of Eq. (74).

C. Time translation invariance

For both quantum and classical systems in equilibrium the time evolution of an observable generates a stationary random process. In particular, ensemble averages of observables are independent of time and time correlation functions do not depend on the time origin but only on time differences. For quantum-classical dynamics the ensemble average of an observable is independent of time,

$$\text{Tr}'\int dR\,dP\,\hat{A}_W(t)\hat{\rho}_{We} = \text{Tr}'\int dR\,dP(e^{i\mathcal{L}t}\hat{A}_W)\hat{\rho}_{We}$$

$$= \text{Tr}'\int dR\,dP\hat{A}_W(e^{-i\mathcal{L}t}\hat{\rho}_{We})$$

$$= \text{Tr}'\int dR\,dP\hat{A}_W\hat{\rho}_{We}, \tag{75}$$

where we have used the stationarity of $\hat{\rho}_{We}$, while for the time correlation function in Eq. (57) we only have

$$\langle(\hat{A}_W, \hat{B}_W(t))\rangle = \langle(\hat{A}_W(\tau), \hat{B}_W(t+\tau))\rangle + \mathcal{O}(\hbar). \tag{76}$$

Indeed, for the exact equality to hold one needs

$$\hat{A}_W^\dagger(\tau)\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{B}_W(t+\tau) = \left(\hat{A}_W^\dagger\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{B}_W(t)\right)(\tau). \tag{77}$$

A special case of this is, for any operators $\hat{C}_W$ and $\hat{D}_W$, $\hat{C}_W(t)[1 + (\hbar\Lambda/2i)]\hat{D}_W(t) = (\hat{C}_W[1 + (\hbar\Lambda/2i)]\hat{D}_W)(t)$. A necessary and sufficient condition for this to be true is

$$i\hat{\mathcal{L}}\left(\hat{C}_W\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{D}_W\right)$$

$$= (i\hat{\mathcal{L}}\hat{C}_W)\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{D}_W + \hat{C}_W\left(1 + \frac{\hbar\Lambda}{2i}\right)(i\hat{\mathcal{L}}\hat{D}_W). \tag{78}$$

However, we have shown in Eq. (25) that this is true only to $\mathcal{O}(\hbar)$. Thus, time translation invariance is valid only approximately in quantum-classical dynamics.

V. CONCLUSION

The results obtained in this paper provide the basis for the computation of equilibrium time correlation functions in many-body quantum-classical systems. The numerical computation of time correlation functions entails both the simulation of the evolution of dynamical variables or operators that enter in the correlation function of interest and sampling over a convenient weight function $(\exp(-\beta \hat{H}_W))$ which is part of the quantum-classical canonical equilibrium density matrix. Algorithms have been developed for the simulation of quantum-classical evolution and their further development is a topic of continuing research. Sampling methods for the calculation of quantum-classical time correlations require additional considerations. Typically, in simulations of classical equilibrium time correlation functions the ensemble average is replaced by a time average and the information needed to sample from the equilibrium distribution is obtained from a long molecular dynamics trajectory. The validity of such a procedure hinges on the assumed ergodicity and stationarity of the system and replaces direct sampling from the equilibrium distribution using Monte Carlo methods by a time average. This ensemble average method has been used occasionally but since it is not necessary and is algorithmically more complex, requiring both Monte Carlo and molecular dynamics programs, its practical importance has been minor. For quantum-classical systems neither the assumption of ergodicity nor stationarity can be made and sampling from the equilibrium distribution or another suitable weight function must be carried out to evaluate the correlation functions.

The analysis presented in this paper gives all of the information needed to compute equilibrium time correlations in the quantum-classical limit in a consistent fashion and, thus, provides a useful way to treat a large class of many-body systems where the environmental degrees of freedom have a classical character.

ACKNOWLEDGMENTS

APPENDIX A

The meaning of the formal solution in the second equality in Eq. (28) will be established here by comparing the two forms in this equation

$$\hat{A}_W(t) = \mathcal{S}(e^{i\vec{\mathcal{H}}_\Lambda t/\hbar} \hat{A}_W e^{-i\vec{\mathcal{H}}_\Lambda t/\hbar}), \tag{A1}$$

and

$$\hat{A}_W(t) = e^{i\hat{\mathcal{L}}t} \hat{A}_W. \tag{A2}$$

The first few terms (thought of as a power series expansion in $it/\hbar$) are, from Eq. (A2),

$$
\begin{aligned}
e^{i\hat{\mathcal{L}}t}\hat{A}_W = &\hat{A}_W + \frac{it}{\hbar}(\vec{\mathcal{H}}_\Lambda \hat{A}_W - \hat{A}_W \vec{\mathcal{H}}_\Lambda) - \frac{t^2}{2\hbar^2}(\vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda \hat{A}_W \\
&- \vec{\mathcal{H}}_\Lambda(\hat{A}_W \vec{\mathcal{H}}_\Lambda) - (\vec{\mathcal{H}}_\Lambda \hat{A}_W)\vec{\mathcal{H}}_\Lambda + \hat{A}_W \vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda) \\
&- \frac{it^3}{6\hbar^3}(\vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda \hat{A}_W - \vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda(\hat{A}_W \vec{\mathcal{H}}_\Lambda) \\
&- \vec{\mathcal{H}}_\Lambda((\vec{\mathcal{H}}_\Lambda \hat{A}_W)\vec{\mathcal{H}}_\Lambda) + \vec{\mathcal{H}}_\Lambda(\hat{A}_W \vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda) \\
&- (\vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda \hat{A}_W)\vec{\mathcal{H}}_\Lambda + (\vec{\mathcal{H}}_\Lambda(\hat{A}_W \vec{\mathcal{H}}_\Lambda))\vec{\mathcal{H}}_\Lambda \\
&+ (\vec{\mathcal{H}}_\Lambda \hat{A}_W)\vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda - \hat{A}_W \vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda) + \cdots, \tag{A3}
\end{aligned}
$$

and, from Eq. (A1),

$$
\begin{aligned}
\mathcal{S}e^{i\vec{\mathcal{H}}_\Lambda t/\hbar} &\hat{A}_W e^{-i\vec{\mathcal{H}}_\Lambda t/\hbar} \\
= &\hat{A}_W + \frac{it}{\hbar}\mathcal{S}(\vec{\mathcal{H}}_\Lambda \hat{A}_W - \hat{A}_W \vec{\mathcal{H}}_\Lambda) - \frac{t^2}{2\hbar^2}\mathcal{S}(\vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda \hat{A}_W \\
&- 2\vec{\mathcal{H}}_\Lambda \hat{A}_W \vec{\mathcal{H}}_\Lambda + \hat{A}_W \vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda) - \frac{it^3}{6\hbar^3}\mathcal{S}(\vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda \hat{A}_W \\
&- 3\vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda \hat{A}_W \vec{\mathcal{H}}_\Lambda + 3\vec{\mathcal{H}}_\Lambda \hat{A}_W \vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda \\
&- \hat{A}_W \vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda) + \cdots. \tag{A4}
\end{aligned}
$$

For these expressions to agree we must make assignments like

$$
\begin{aligned}
\mathcal{S}(\vec{\mathcal{H}}_\Lambda &\hat{A}_W \vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda) \\
\equiv &\tfrac{1}{3}((\vec{\mathcal{H}}_\Lambda \hat{A}_W)\vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda + (\vec{\mathcal{H}}_\Lambda(\hat{A}_W \vec{\mathcal{H}}_\Lambda))\vec{\mathcal{H}}_\Lambda \\
&+ \vec{\mathcal{H}}_\Lambda(\hat{A}_W \vec{\mathcal{H}}_\Lambda \vec{\mathcal{H}}_\Lambda)). \tag{A5}
\end{aligned}
$$

In general the term $\mathcal{S}((\vec{\mathcal{H}}_\Lambda)^j \hat{A}_W (\vec{\mathcal{H}}_\Lambda)^k)$ is composed of $(j+k)!/j!k!$ separate terms each with a prefactor of $j!k!/(j+k)!$. Each of these separate terms corresponds to a unique association of terms indicating the order in which the $\mathcal{H}_\Lambda$ operators act.

APPENDIX B

This appendix concerns the relationship between the quantum $\hat{\rho}_{We}^Q(R,P)$ and quantum-classical $\hat{\rho}_{We}(R,P)$ equilibrium density matrices in the canonical ensemble. We begin by deriving the recursion relations for the quantum mechanical equilibrium density matrix.

The thermal density matrix $\hat{\rho}_{We}^Q$ is stationary under the quantum dynamics in Eq. (7),

$$
\begin{aligned}
0 = &(\hat{H}_W, \hat{\rho}_{We}^Q)_Q \\
= &\frac{i}{\hbar}(\hat{H}_W e^{\hbar\Lambda/2i}\hat{\rho}_{We}^Q - \hat{\rho}_{We}^Q e^{\hbar\Lambda/2i}\hat{H}_W). \tag{B1}
\end{aligned}
$$

If we substitute the expansion,

$$\hat{\rho}_{We}^{Q} = \sum_{n=0}^{\infty} \hat{\rho}_{We}^{Q(n)} \hbar^n, \tag{B2}$$

into Eq. (B1) and group by powers of $\hbar$ we obtain (using the fact that the P dependence of H is of the form $P^2/2M$)

$$0 = (i\hbar)^{-1}[\hat{H}_W, \hat{\rho}_{We}^{Q(0)}], \tag{B3}$$

$$0 = \hbar^0(i[\hat{H}_W, \hat{\rho}_{We}^{Q(1)}] - \tfrac{1}{2}\hat{\rho}_{We}^{Q(0)}\Lambda\hat{H}_W + \tfrac{1}{2}\hat{H}_W\Lambda\hat{\rho}_{We}^{Q(0)}), \tag{B4}$$

$$0 = \hbar^1\left(-i[\hat{H}_W, \hat{\rho}_{We}^{Q(2)}] + \frac{1}{2}\hat{\rho}_{We}^{Q(1)}\Lambda\hat{H}_W - \frac{1}{2}\hat{H}_W\Lambda\hat{\rho}_{We}^{Q(1)} \right.$$
$$\left. + \frac{1}{8i}\hat{\rho}_{We}^{Q(0)}\Lambda^2\hat{H}_W - \frac{1}{8i}\hat{H}_W\Lambda^2\hat{\rho}_{We}^{Q(0)}\right), \tag{B5}$$

$$0 = \hbar^2\left(-i[\hat{H}_W, \hat{\rho}_{We}^{Q(3)}] + \frac{1}{2}\hat{\rho}_{We}^{Q(2)}\Lambda\hat{H}_W - \frac{1}{2}\hat{H}_W\Lambda\hat{\rho}_{We}^{Q(2)} \right.$$
$$+ \frac{1}{8i}\hat{\rho}_{We}^{Q(1)}\Lambda^2\hat{H}_W - \frac{1}{8i}\hat{H}_W\Lambda^2\hat{\rho}_{We}^{Q(1)} - \frac{1}{48}\hat{\rho}_{We}^{Q(0)}\Lambda^3\hat{H}_W$$
$$\left. + \frac{1}{48}\hat{H}_W\Lambda^3\hat{\rho}_{We}^{Q(0)}\right), \tag{B6}$$

and so on. These results should be compared with the mixed quantum-classical recursion relations given in Eqs. (33) and (34).

Notice that the first two recursion relations are identical in the quantum-classical and fully quantum mechanical systems [see Eqs. (33) and (34) for $n=0$, (B3), and (B4)]. Hence, we can calculate the first two terms for the quantum mechanical system (in the partially Wigner transformed representation) and the results will also be valid for the quantum-classical system.

In quantum mechanics we have for the unnormalized canonical equilibrium density matrix, $\hat{\Omega}_{We}^{Q}$

$$\hat{\Omega}_{We}^{Q} = (e^{-\beta\hat{H}})_W$$
$$= 1 - \beta\hat{H}_W + \frac{\beta^2}{2}\hat{H}_W e^{\hbar\Lambda/2i}\hat{H}_W - \cdots. \tag{B7}$$

This power series in β must be converted into a power series with respect to $\hbar$. Extracting the first two terms in this new power series gives

$$\hat{\Omega}_{We}^{Q} = e^{-\beta\hat{H}_W} + \frac{\hbar}{2i}\frac{\partial\hat{H}_W}{\partial P}\sum_{n=0}^{\infty}\frac{(-\beta)^{n+2}}{(n+2)!}$$
$$\times \sum_{j=0}^{n}(n-2j)\hat{H}_W^{n-j}\frac{\partial\hat{H}_W}{\partial R}\hat{H}_W^{j} + \mathcal{O}(\hbar^2), \tag{B8}$$

after isolating the zeroth and first order terms and proving by induction to first order in $\hbar$ that

$$(\hat{H}^{n+2})_W^{(1st)} = \frac{\hbar}{2i}\frac{\partial\hat{H}_W}{\partial P}\sum_{j=0}^{n}(n-2j)\hat{H}_W^{n-j}\frac{\partial\hat{H}_W}{\partial R}\hat{H}_W^{j}. \tag{B9}$$

The operators $\hat{H}_W$ and $\partial\hat{H}_W/\partial R$ do not commute and so the order must be preserved as shown.

It is possible to show that in the adiabatic basis representation (properly normalized) these are the results quoted in Eqs. (47) and (48). We have established the equivalence between the second term on the right-hand side of Eq. (B8) and Eq. (48) by a direct calculation which shows that the matrix representation of this term in Eq. (B8) is the same as the Taylor expansion of Eq. (48) in powers of β.

APPENDIX C

Here we establish that $\Re(J_{\alpha\alpha,\nu\nu'}\rho_{We}^{(n)\nu\nu'})$ is a no dd function of P. Using the definitions in Sec. III, this is equivalent to the condition that $\Re((-(P/M)\cdot d_{\alpha\alpha'}^* - \frac{1}{2}E_{\alpha\alpha'}d_{\alpha\alpha'}^*(\partial/\partial P))\rho_{We}^{(n)\alpha\alpha'})$ be an odd function of P or, choosing to work with a real adiabatic basis so that $d_{\alpha\alpha'}$ is real, this simplifies to the conditions that $P\Re(\rho_{We}^{(n)\alpha\alpha'})$ and $\partial/\partial P\Re(\rho_{We}^{(n)\alpha\alpha'})$ be odd functions of P. The effect of multiplication by P or differentiation with respect to P is to change the parity of the factor $\Re(\rho_{We}^{(n)\alpha\alpha'})$, if indeed this factor has a definite parity; thus, we must show that $\Re(\rho_{We}^{(n)\alpha\alpha'})$ is an even function of P. For technical reasons it will also be useful to show that $\Im(\rho_{We}^{(n)\alpha\alpha'})$ is an odd function of P.

We use an inductive proof. The statements are true for $n=1$. From Eq. (48) we see that $\rho_{We}^{(1)\alpha\alpha} = 0$ and that $\rho_{We}^{(1)\alpha\alpha'}$ is pure imaginary and odd in P for $\alpha \neq \alpha'$. Assuming

$$\Re(\rho_{We}^{(n)\alpha\alpha'}) \quad \text{even function of } P \forall \alpha, \alpha', n, \tag{C1}$$

$$\Im(\rho_{We}^{(n)\alpha\alpha'}) \quad \text{odd function of } P \forall \alpha, \alpha', n, \tag{C2}$$

we show that these conditions are true for $n+1$. From Eq. (46) we have

$$\Re(\rho_{We}^{(n+1)\alpha\alpha'}) = \frac{1}{E_{\alpha\alpha'}}\left\{-\frac{P}{M}\cdot\frac{\partial}{\partial R}\Im(\rho_{We}^{(n)\alpha\alpha'}) \right.$$
$$-\frac{1}{2}(F^\alpha + F^{\alpha'})\frac{\partial}{\partial P}\Im(\rho_{We}^{(n)\alpha\alpha'})$$
$$-\sum_{\alpha''}\left(d_{\alpha\alpha''}\left(\frac{1}{2}E_{\alpha\alpha''}\frac{\partial}{\partial P} + \frac{P}{M}\right)\Im(\rho_{We}^{(n)\alpha''\alpha'}) \right.$$
$$\left.+ d_{\alpha'\alpha''}\left(\frac{1}{2}E_{\alpha'\alpha''}\frac{\partial}{\partial P} + \frac{P}{M}\right)\Im(\rho_{We}^{(n)\alpha\alpha''})\right)\right\}. \tag{C3}$$

Each of the terms on the right-hand side is even with respect to P so $\Re(\rho_{We}^{(n+1)\alpha\alpha'})$ is even in P. The analysis of $\Im(\rho_{We}^{(n+1)\alpha\alpha'})$ is similar and will be omitted. Thus, the statement is true for $n+1$ completing the inductive proof.

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