Quantum Statistical Dynamics with Trajectories

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Summary. In this chapter we review the key issues in the construction of a mixed quantum–classical statistical mechanics. Two approaches are outlined: First, the construction of a formally consistent quantum–classical scheme which entails modified dynamical equations, and a modified equilibrium distribution that is the stationary state of the quantum–classical dynamics. Second, an approach which starts from the exact quantum correlation functions and introduces approximations for both the dynamics and (possibly separately) the equilibrium distribution. The first scheme is internally consistent, but inconsistencies arise in the properties of the quantum–classical correlation functions including the fact that time translation invariance and the Kubo identity are only valid to $\mathcal{O}(\hbar)$. The second scheme does not address the consistency issues explicitly, but has to provide suitable criteria for approximations for both the dynamics and the equilibrium distribution. Two approaches to the practical implementation of this second scheme are presented (1) a mixed quantum–classical propagation, closely related to the first scheme and (2) a linearized path integral approach.

1 Introduction

Consider quantum systems which can be partitioned into two subsystems, one of which behaves almost classically while the other requires a full quantum description. It is reasonable to assume that the overall quantum behavior of the total system will be simplified due to the presence of this almost classical component. This fact has motivated the development of mixed quantum–classical methods, an idea which has attracted considerable interest for a number of years. In spite of the simplicity of this idea, the formulation of a mixed quantum–classical dynamics is not a simple problem, and many conceptual difficulties arise making this a very active area of research.

A great deal of effort in this area has been devoted to the development of approximate quantum–classical dynamical schemes while much less effort has been invested in exploring statistical mechanical issues. In the physical sciences one is interested in the calculation of time-dependent expectation values and (equilibrium) correlation functions. In order to compute these quantities one needs not only mechanics but also statistical mechanics.

One can imagine investigating statistical mechanical issues from two perspectives (1) construct a fictitious world in which one formulates statistical mechanics based on an underlying quantum–classical dynamics or (2) begin with the full quantum statistical mechanical description of the real world and make approximations to the quantum dynamics that lead to a representation in terms of trajectories. There are advantages and disadvantages to both schemes. As we shall see it is difficult to construct a consistent mixed quantum–classical formulation, however, if scheme (1) could be carried out one would have a consistent statistical mechanical formulation in the fictitious quantum–classical world. The essential issue then would be to determine the extent to which this fictitious world is a faithful model of the corresponding real one defined above. In scheme (2) the starting point is the correct statistical mechanical description of the quantum world but approximations are used to reduce the dynamics to trajectories. These approximations introduce inconsistencies in the formulation. In particular the full quantum equilibrium distribution is not stationary under the approximate quantum evolution.

In this chapter we will address some of these issues and illustrate the ideas by considering specific examples of methods which construct approximate trajectory descriptions of quantum evolution. In Sect. 2 we describe the formulation of a statistical mechanics based on quantum–classical equations of motion and point out some difficulties that arise in carrying out this program. In Sect. 3 we consider formulations based on approximations to the dynamics in the full quantum statistical mechanical expressions for time correlation functions. The ideas are illustrated by considering two examples that approximate the dynamics in terms of trajectories. Finally we conclude with some observations and perspectives for future research.

2 Quantum–Classical Worlds

We begin by formulating the quantum laws underlying dynamics and statistical mechanics. Let $\hat{B}$ be an observable of the system, then the Heisenberg equation describing its motion is

$$\frac{\mathrm{d}\hat{B}(t)}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{B}(t)] \; . \tag{1}$$

The Liouville–von Neuman equation of motion for the density matrix $\hat{\rho}$ is given instead by

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{\mathrm{i}}{\hbar}[\hat{H}, \hat{\rho}(t)] \; , \tag{2}$$

and the equation for the average value of an observable can be written in either of the following two equivalent forms obtained using cyclic permutation of the trace:

$$\overline{B(t)} = \mathrm{Tr}\hat{B}\hat{\rho}(t) = \mathrm{Tr}\hat{B}(t)\hat{\rho}(0) \; . \tag{3}$$

As described in the Sect. 1 we partition our system into two subsystems: the first subsystem contains n degrees of freedom representing particles with mass m and coordinate operators $\hat{q}$; the second subsystem comprises N degrees of freedom describing particles of mass M and coordinate operators $\hat{Q}$. The hamiltonian operator may be written as

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}(\hat{q}, \hat{Q}) \equiv \frac{\hat{P}^2}{2M} + \hat{h}(\hat{Q}) \; , \tag{4}$$

where $\hat{p}$ and $\hat{P}$ are momentum operators, $\hat{V}(\hat{q}, \hat{Q})$ is the total potential energy, and $\hat{h}$ is the hamiltonian of the first subsystem in the field of the second subsystem with fixed coordinates. We employ a condensed notation such that $\hat{q} = (\hat{q}_1, \hat{q}_2, \ldots, \hat{q}_n)$ and $\hat{Q} = (\hat{Q}_1, \hat{Q}_2, \ldots, \hat{Q}_N)$, with an analogous notation for $\hat{p}$ and $\hat{P}$.

Let us now consider the partial Wigner transformation [1] of the density matrix with respect to the subset of Q coordinates [2],

$$\hat{\rho}_{\mathrm{W}}(R, P) = (2\pi\hbar)^{-N} \int \mathrm{d}Z \mathrm{e}^{\mathrm{i}P\cdot Z/\hbar} \langle R - \frac{Z}{2} | \hat{\rho} | R + \frac{Z}{2} \rangle \; . \tag{5}$$

In this representation the quantum Liouville equation is

$$\begin{aligned} \frac{\partial \hat{\rho}_{\mathrm{W}}(R, P, t)}{\partial t} &= -\frac{\mathrm{i}}{\hbar} \Big((\hat{H}\hat{\rho})_{\mathrm{W}} - (\hat{\rho}\hat{H})_{\mathrm{W}} \Big) \\ &= -\frac{\mathrm{i}}{\hbar} \Big(\hat{H}_{\mathrm{W}} \mathrm{e}^{\hbar\Lambda/2\mathrm{i}} \hat{\rho}_{\mathrm{W}}(t) - \hat{\rho}_{\mathrm{W}}(t) \mathrm{e}^{\hbar\Lambda/2\mathrm{i}} \hat{H}_{\mathrm{W}} \Big) \; , \end{aligned} \tag{6}$$

where the partially Wigner transformed hamiltonian is

$$\hat{H}_{\mathrm{W}}(R, P) = \frac{P^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}_{\mathrm{W}}(\hat{q}, R) \; , \tag{7}$$

and Λ is the negative of the Poisson bracket operator, $\Lambda = \overleftarrow{\nabla}_P \cdot \overrightarrow{\nabla}_R - \overleftarrow{\nabla}_R \cdot \overrightarrow{\nabla}_P$, where the direction of an arrow indicates the direction in which the operator acts. To obtain this equation we used the definition of the partial Wigner transform of an observable

$$\hat{A}_{\mathrm{W}}(R, P) = \int \mathrm{d}Z \mathrm{e}^{-\mathrm{i}P\cdot Z/\hbar} \langle R + \frac{Z}{2} | \hat{A} | R - \frac{Z}{2} \rangle \; , \tag{8}$$

and the fact that the partial Wigner transform of a product of operators is [3]

$$(\hat{A}\hat{B})_{\mathrm{W}}(R, P) = \hat{A}_{\mathrm{W}}(R, P) \mathrm{e}^{\hbar\Lambda/2\mathrm{i}} \hat{B}_{\mathrm{W}}(R, P) \; . \tag{9}$$

Suppose now that the subsystem comprising the particles with masses M is taken to represent an environment or bath and assume that $M \gg m$. In this limit it can be shown that $\mathrm{e}^{\hbar\Lambda/2\mathrm{i}}$ can be replaced by $(1 + \hbar\Lambda/2\mathrm{i})$

and the full von Neuman equation reduces to the quantum–classical Liouville equation [2, 4–10]

$$\begin{aligned}\frac{\partial\hat{\rho}_{\mathrm{W}}(R,P,t)}{\partial t} &= -\frac{\mathrm{i}}{\hbar}[\hat{H}_{\mathrm{W}},\hat{\rho}_{\mathrm{W}}(t)] + \frac{1}{2}\left(\left\{\hat{H}_{\mathrm{W}},\hat{\rho}_{\mathrm{W}}(t)\right\} - \left\{\hat{\rho}_{\mathrm{W}}(t),\hat{H}_{\mathrm{W}}\right\}\right)\\ &\equiv -\mathrm{i}\hat{\mathcal{L}}\hat{\rho}_{\mathrm{W}}(t) \equiv -(\hat{H}_{\mathrm{W}},\hat{\rho}_{\mathrm{W}}(t))\ . \end{aligned} \tag{10}$$

Here [,] is a commutator, while { , } indicates a Poisson parenthesis on the R and P variables. The second line of this equation defines the quantum–classical Liouville operator $\hat{\mathcal{L}}$ and the quantum–classical bracket. The quantum–classical equation of motion for a dynamical variable $\hat{B}_{\mathrm{W}}$ can be written in a similar form as

$$\frac{\mathrm{d}\hat{B}_{\mathrm{W}}(t)}{\mathrm{d}t} = \mathrm{i}\hat{\mathcal{L}}\hat{B}_{\mathrm{W}}(t) \equiv (\hat{H}_{\mathrm{W}},\hat{B}_{\mathrm{W}}(t))\ . \tag{11}$$

Equation (10) is the quantum–classical Liouville equation describing the coupled evolution of our two subsystems. It can be shown that as a result of the coupling a purely newtonian description of bath dynamics is no longer possible [11]. However, it is possible to express the solution of this equation in terms of an ensemble of surface hopping trajectories [2].

Even though this evolution is well defined, quantum–classical dynamics does not possess a Lie algebraic structure like quantum or classical mechanics since the Jacobi identity is violated by the quantum–classical bracket [12, 13]

$$(\hat{A}_{\mathrm{W}},(\hat{B}_{\mathrm{W}},\hat{C}_{\mathrm{W}})) + (\hat{C}_{\mathrm{W}},(\hat{A}_{\mathrm{W}},\hat{B}_{\mathrm{W}})) + (\hat{B}_{\mathrm{W}},(\hat{C}_{\mathrm{W}},\hat{A}_{\mathrm{W}})) \neq 0\ . \tag{12}$$

This leads to pathologies in the general formulation of quantum–classical dynamics and statistical mechanics [12, 13].

A fundamental ingredient of statistical mechanics is the equilibrium density which is the stationary solution of the Liouville equation. The well known form of the quantum canonical equilibrium density is $\hat{\rho}_e = Z_Q^{-1}\exp(-\beta\hat{H})$ which, expressed in terms of the partial Wigner transform, can be written as

$$\hat{\rho}_{\mathrm{We}}(R,P) = (2\pi\hbar)^{-N}\int \mathrm{d}Z\mathrm{e}^{\mathrm{i}P\cdot Z/\hbar}\langle R-\frac{Z}{2}|\hat{\rho}_{\mathrm{e}}|R+\frac{Z}{2}\rangle\ . \tag{13}$$

This quantity is not stationary under quantum–classical dynamics. So the equilibrium density of the quantum–classical approach has to be determined by solving the equation

$$\mathrm{i}\hat{\mathcal{L}}\hat{\rho}_{\mathrm{We}} = 0. \tag{14}$$

An explicit solution for this equation has not been found although a recursive one, obtained by developing the density matrix in a power series in $\hbar$ or the mass ratio, $\mu = m/M$, in the partial Wigner representation, can be written down. While it is difficult to find the full solution to any order in $\hbar$, it is not difficult to find the solution analytically to $\mathcal{O}(\hbar)$. To this order the result agrees with that of the partial Wigner transform of the exact canonical quantum equilibrium density. This expression for the equilibrium density matrix to $\mathcal{O}(\hbar)$ can be useful for testing the validity of approximate calculations of time correlation functions.

To complete the presentation of this approach we now define the quantum–classical forms of equilibrium time correlation functions and their associated transport coefficients. The issue we address is the construction of a nonequilibrium statistical mechanics in a world obeying quantum–classical dynamics. To carry out this program we begin by constructing a linear response theory for quantum–classical dynamics [12]. The formalism parallels that for quantum (or classical) systems. We suppose the quantum–classical system with hamiltonian $\hat{H}_{\rm W}$ is subjected to a time dependent external force that couples to the observable $\hat{A}_{\rm W}$, so that the total hamiltonian is

$$\hat{\mathbf{H}}_{\rm W}(t) = \hat{H}_{\rm W} - \hat{A}_{\rm W}F(t) \ . \tag{15}$$

The evolution equation for the density matrix takes the form

$$\frac{\partial \hat{\rho}_{\rm W}(t)}{\partial t} = -({\rm i}\hat{\mathcal{L}} - {\rm i}\hat{\mathcal{L}}_A F(t))\hat{\rho}_{\rm W}(t) \ , \tag{16}$$

where ${\rm i}\hat{\mathcal{L}}_A$ has a form analogous to ${\rm i}\hat{\mathcal{L}}$ with $\hat{A}_{\rm W}$ replacing $\hat{H}_{\rm W}$, ${\rm i}\hat{\mathcal{L}}_A = (\hat{A}_{\rm W},)$. The formal solution of this equation is found by integrating from t_0 to t,

$$\hat{\rho}_{\rm W}(t) = {\rm e}^{-{\rm i}\hat{\mathcal{L}}(t-t_0)}\hat{\rho}_{\rm W}(t_0) + \int_{t_0}^{t} {\rm d}t' \ {\rm e}^{-{\rm i}\hat{\mathcal{L}}(t-t')}{\rm i}\hat{\mathcal{L}}_A\hat{\rho}_{\rm W}(t')F(t') \ . \tag{17}$$

We now choose, as usual, $\hat{\rho}_{\rm W}(t_0)$ to be the equilibrium density matrix, $\hat{\rho}_{\rm We}$. As discussed above $\hat{\rho}_{\rm We}$ is the invariant solution of the quantum–classical dynamics, ${\rm i}\hat{\mathcal{L}}\hat{\rho}_{\rm We} = 0$. In this case the first term on the right-hand side of (17) reduces to $\hat{\rho}_{\rm We}$ and is independent of t_0. We may assume that the system with hamiltonian $\hat{H}_{\rm W}$ is in thermal equilibrium at $t_0 = -\infty$, and with this boundary condition, to first order in the external force, (17) is

$$\hat{\rho}_{\rm W}(t) = \hat{\rho}_{\rm We} + \int_{-\infty}^{t} {\rm d}t' \ {\rm e}^{-{\rm i}\hat{\mathcal{L}}(t-t')}{\rm i}\hat{\mathcal{L}}_A\hat{\rho}_{\rm We}F(t') \ . \tag{18}$$

Then, computing $\overline{B_{\rm W}(t)} = {\rm Tr}' \int {\rm d}R \ {\rm d}P \, \hat{B}_{\rm W}\hat{\rho}_{\rm W}(t)$, where ${\rm Tr}'$ is the partial trace over the quantum degrees of freedom, to obtain the response function, we find

$$\begin{aligned}\overline{B_{\rm W}(t)} &= \int_{-\infty}^{t} {\rm d}t' \ {\rm Tr}' \int {\rm d}R\,{\rm d}P \ \hat{B}_{\rm W}{\rm e}^{-{\rm i}\hat{\mathcal{L}}(t-t')}{\rm i}\hat{\mathcal{L}}_A\hat{\rho}_{\rm We}F(t') \\ &= \int_{-\infty}^{t} {\rm d}t' \ \langle(\hat{B}_{\rm W}(t-t'), \hat{A}_{\rm W})\rangle F(t') \equiv \int_{-\infty}^{t} {\rm d}t' \ \phi_{BA}^{\rm QC}(t-t')F(t') \ .\end{aligned} \tag{19}$$

Thus, the quantum–classical form of the response function is

$$\phi_{BA}^{\mathrm{QC}}(t) = \langle (\hat{B}_{\mathrm{W}}(t), \hat{A}_{\mathrm{W}}) \rangle_{\mathrm{QC}} = \mathrm{Tr}' \int \mathrm{d}R \; \mathrm{d}P \; \hat{B}_{\mathrm{W}}(t) (\hat{A}_{\mathrm{W}}, \hat{\rho}_{\mathrm{We}}) \;, \tag{20}$$

where in writing the second equality in (20), we have used cyclic permutations under the trace and integrations by parts. The derivation of linear response theory in the quantum–classical world is completely analogous to that in quantum mechanics up to (20). However, the simplifications that are easily derived in the full quantum, or classical worlds are not available at the moment for the quantum–classical world. In particular, the calculation of the response function in the quantum–classical approach should be performed using (20) and cannot be started using well-known standard time correlation function expressions (notice that the Kubo transformed form can be shown to differ from the expression given in (20) by terms of $\mathcal{O}(\hbar^2)$ [12]).

At this point we have all the ingredients for the computation of transport properties and expectation values of dynamical variables in a quantum–classical world. The equilibrium time correlation function in (20) entails evolution of $\hat{B}_{\mathrm{W}}(t)$ under quantum–classical dynamics, evaluation of the quantum–classical bracket of $\hat{A}_{\mathrm{W}}$ and $\hat{\rho}_{\mathrm{We}}$, and an integration over the classical phase space coordinates and trace over the quantum states.

While this statistical mechanical formulation is complete, it is worth remarking that some aspects of the quantum mechanical calculation do not carry over to the quantum–classical world. These concern time translation invariance and alternate forms for the time correlation function expressions for transport coefficients. The first issue we examine is time translation invariance of the equilibrium time correlation functions [11]. A quantum mechanical response function can be written in the two equivalent forms

$$\phi_{BA}(t) = \langle \frac{\mathrm{i}}{\hbar} [\hat{B}(t), \hat{A}] \rangle = \langle \frac{\mathrm{i}}{\hbar} [\hat{B}(t+\tau), \hat{A}(\tau)] \rangle \;, \tag{21}$$

as is easily seen using stationarity of the canonical equilibrium density matrix and cyclic permutations under the trace. This property is not exactly satisfied by the correlation function in quantum–classical response function (20). To see this we may write (20) more explicitly as

$$\begin{aligned} \phi_{BA}^{\mathrm{QC}}(t) &= \langle (\hat{B}_{\mathrm{W}}(t), \hat{A}_{\mathrm{W}}) \rangle_{\mathrm{QC}} \qquad (22) \\ &= \frac{\mathrm{i}}{\hbar} \Big(\langle \hat{B}_{\mathrm{W}}(t) \, (1 + \hbar \Lambda / 2\mathrm{i}) \, \hat{A}_{\mathrm{W}} \rangle_{\mathrm{QC}} - \langle \hat{A}_{\mathrm{W}} \, (1 + \hbar \Lambda / 2\mathrm{i}) \, \hat{B}_{\mathrm{W}}(t) \rangle_{\mathrm{QC}} \Big), \end{aligned}$$

Using cyclic permutations under the trace, integration by parts and the fact that $\hat{\rho}_{\mathrm{We}}$ is invariant under quantum–classical dynamics, one may show that

$$\langle \hat{B}_{\mathrm{W}}(t) \, (1 + \hbar \Lambda / 2\mathrm{i}) \, \hat{A}_{\mathrm{W}} \rangle_{\mathrm{QC}} = \langle \mathrm{e}^{\mathrm{i}\mathcal{L}\tau} (\hat{B}_{\mathrm{W}}(t) \, (1 + \hbar \Lambda / 2\mathrm{i}) \, \hat{A}_{\mathrm{W}}) \rangle_{\mathrm{QC}} \;. \tag{23}$$

However, the evolution of a composite operator in quantum–classical dynamics cannot be written exactly in terms of the quantum–classical evolution of its constituent operators, but only to terms $\mathcal{O}(\hbar)$. To see this, consider the action of the quantum–classical Liouville operator on the composite operator $\hat{C}_{\mathrm{W}} = \hat{B}_{\mathrm{W}}(1 + \hbar\mathit{\Lambda}/2\mathrm{i})\hat{A}_{\mathrm{W}}$. A straightforward calculation shows that

$$\mathrm{i}\hat{\mathcal{L}}\hat{C}_{\mathrm{W}} = (\mathrm{i}\hat{\mathcal{L}}\hat{B}_{\mathrm{W}})\left(1 + \frac{\hbar\mathit{\Lambda}}{2\mathrm{i}}\right)\hat{A}_{\mathrm{W}} + \hat{B}_{\mathrm{W}}\left(1 + \frac{\hbar\mathit{\Lambda}}{2\mathrm{i}}\right)(\mathrm{i}\hat{\mathcal{L}}\hat{A}_{\mathrm{W}}) + \mathcal{O}(\hbar)\ . \tag{24}$$

It follows that

$$\begin{aligned}\hat{C}_{\mathrm{W}}(\tau) = \mathrm{e}^{\mathrm{i}\hat{\mathcal{L}}\tau}\hat{C}_{\mathrm{W}} &= \left(\mathrm{e}^{\mathrm{i}\hat{\mathcal{L}}\tau}\hat{B}_{\mathrm{W}}\right)\left(1 + \frac{\hbar\mathit{\Lambda}}{2\mathrm{i}}\right)\left(\mathrm{e}^{\mathrm{i}\hat{\mathcal{L}}\tau}\hat{A}_{\mathrm{W}}\right) + \mathcal{O}(\hbar) \\ &= \hat{B}_{\mathrm{W}}(\tau)\left(1 + \frac{\hbar\mathit{\Lambda}}{2\mathrm{i}}\right)\hat{A}^{\dagger}_{\mathrm{W}}(\tau) + \mathcal{O}(\hbar)\ .\end{aligned} \tag{25}$$

Therefore, the quantum–classical correlation function satisfies standard time translation invariance only to $\mathcal{O}(\hbar)$,

$$\phi^{\mathrm{QC}}_{BA}(t) = \langle(\hat{B}_{\mathrm{W}}(t), \hat{A}_{\mathrm{W}})\rangle_{\mathrm{QC}} = \langle(\hat{B}_{\mathrm{W}}(t+\tau), \hat{A}_{\mathrm{W}}(\tau))\rangle_{\mathrm{QC}} + \mathcal{O}(\hbar)\ , \tag{26}$$

although its most strict form, (23), is surely satisfied.

Next, we consider alternate forms for correlations that are commonly used in computations. The quantum mechanical response functions can be written in an equivalent form using the Kubo identity. The quantum–classical version of the Kubo identity holds only to $\mathcal{O}(\hbar)$ [12],

$$(\hat{A}_{\mathrm{W}}, \hat{\rho}_{\mathrm{We}}) = \int_0^{\beta} \mathrm{d}\lambda\ \hat{\rho}_{\mathrm{We}}(1 + \frac{\hbar\mathit{\Lambda}}{2\mathrm{i}})\dot{\hat{A}}_{\mathrm{W}}(-\mathrm{i}\hbar\lambda) + \mathcal{O}(\hbar)\ . \tag{27}$$

Since the quantum–classical form of the Kubo identity is valid only to $\mathcal{O}(\hbar)$, the various autocorrelation function expressions for transport coefficients, to which we are accustomed, are equivalent only to $\mathcal{O}(\hbar)$. The results of comparisons of computations of both forms of the correlation functions can provide information about the reduction to the quantum–classical limit.

A discussion of the scheme used to simulate quantum–classical dynamics is postponed to next section and we simply remark here that statistical mechanical quantities may be computed within the quantum–classical framework. A limitation is a lack of knowledge of the exact form of the equilibrium density matrix, so we cannot compute exact quantum-classical time correlation functions. Note however that relaxation from given initial density matrices can be computed without any approximation other than that on the dynamics. So, for example, since quantum–classical dynamics is exact for the spin-boson model, it is possible to compute the exact relaxation, given an initial nonequilibrium distribution. Simulations of this model have confirmed the utility of surface-hopping algorithms for its study.

3 Approximations to the Real World

A very different route is to begin with any rigorous expression for the quantum mechanical response, e.g., in terms of quantum time correlation functions – since we know that they are all fundamentally equivalent – and make approximations to either or both the dynamics and equilibrium density. This approach implicitly avoids questions of consistency but they exist. These inconsistencies make these treatments invalid. However, if by a stroke of luck or design the inconsistencies are numerically small, these methods can often be very useful. With these approaches we can in principle independently approximate the equilibrium structure or the propagator so that we have more freedom than with the mixed quantum–classical statistical mechanical approach of the previous section.

The quantum time correlation function of two operators of the system is defined as

$$\begin{aligned} C_{AB}(t;\beta) &\equiv \langle \hat{A}\hat{B}(t)\rangle = \mathrm{Tr}\ \hat{A}\hat{B}(t)\hat{\rho}_{\mathrm{e}} \\ &= \frac{1}{Z_Q}\mathrm{Tr}\ \hat{A}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}t\hat{H}}\hat{B}\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}t\hat{H}}\mathrm{e}^{-\beta\hat{H}}\ . \end{aligned} \tag{28}$$

There are many different ways described in the literature to construct approximations to this correlation function [14–19]. Here we will illustrate how such approximations are implemented using two example approaches that we have explored:

(1) Mixed Wigner representation approach

The first approach [20,21] we consider uses the ingredients of the quantum–classical Liouville dynamics discussed in Sect. 2. We begin by introducing the coordinate representation of the operators so that the correlation function becomes

$$C_{AB}(t;\beta) = \mathrm{Tr}' \int \mathrm{d}Q_1\,\mathrm{d}Q_2\ \langle Q_1|\hat{B}(t)|Q_2\rangle\langle Q_2|\hat{\rho}_{\mathrm{e}}\hat{A}|Q_1\rangle\ . \tag{29}$$

Making use of the change of variables, $Q_1 = R - Z/2$ and $Q_2 = R + Z/2$, this equation may be written in the equivalent form

$$\begin{aligned} C_{AB}(t;\beta) = \mathrm{Tr}' \int \mathrm{d}R\,\mathrm{d}Z\ &\langle R - \frac{Z}{2}|\hat{B}(t)|R + \frac{Z}{2}\rangle \\ &\times\langle R + \frac{Z}{2}|\hat{\rho}_{\mathrm{e}}\hat{A}|R - \frac{Z}{2}\rangle\ . \end{aligned} \tag{30}$$

The next step in the calculation is to replace the coordinate space matrix elements of the operators with their representation in terms of Wigner transformed quantities. The partial Wigner transform of an operator, $\hat{O}$, is defined in (8) while the inverse transform is

$$\langle R + \frac{Z}{2}|\hat{O}|R - \frac{Z}{2}\rangle = \frac{1}{(2\pi\hbar)^N}\int \mathrm{d}P\mathrm{e}^{\frac{\mathrm{i}}{\hbar}P\cdot Z}\hat{O}_{\mathrm{W}}(R,P)\ . \tag{31}$$

For simplicity we write $X \equiv (R, P)$. It is convenient to consider a representation of such operators in basis of eigenfunctions, here we consider an adiabatic basis to make connection with surface-hopping dynamics. The partial Wigner transformed hamiltonian can be written as $\hat{H}_{\mathrm{W}} = P^2/2M + \hat{h}_{\mathrm{W}}(R)$. The last equality defines the hamiltonian $\hat{h}_{\mathrm{W}}(R)$ for the light mass subsystem in the presence of fixed particles of the heavy mass subsystem. The adiabatic basis is determined from the solutions of the eigenvalue problem, $\hat{h}_{\mathrm{W}}(R)|\alpha; R\rangle = E_\alpha(R)|\alpha; R\rangle$. The adiabatic representation of $\hat{O}_{\mathrm{W}}(X)$ is

$$\hat{O}_{\mathrm{W}}(X) = \sum_{\alpha\alpha'} |\alpha; R\rangle O_{\mathrm{W}}^{\alpha\alpha'}(X) \langle\alpha'; R| \, , \tag{32}$$

where $O_{\mathrm{W}}^{\alpha\alpha'}(X) = \langle\alpha; R|\hat{O}_{\mathrm{W}}(X)|\alpha'; R\rangle$.

By inserting (32) into (31) we can express the coordinate representation of the operator $\hat{O}$ as

$$\langle R - \frac{Z}{2}|\hat{O}|R + \frac{Z}{2}\rangle = \frac{1}{(2\pi\hbar)^N} \sum_{\alpha\alpha'} \int \mathrm{d}P \, \mathrm{e}^{\frac{\mathrm{i}}{\hbar} P \cdot Z} |\alpha; R\rangle (O)_{\mathrm{W}}^{\alpha\alpha'}(X) \langle\alpha'; R| \, . \tag{33}$$

Using this result in (30), we obtain

$$C_{AB}(t; \beta) = \sum_{\alpha,\alpha'} \int \mathrm{d}X \, (\hat{B}(t))_{\mathrm{W}}^{\alpha\alpha'}(X) (\hat{\rho}_{\mathrm{e}} \hat{A})_{\mathrm{W}}^{\alpha'\alpha}(X) \, . \tag{34}$$

This equation is still formaly exact but now we approximate the dynamics using the quantum–classical evolution given in (11).

In the adiabatic basis the quantum–classical Liouville operator defined in (10) takes the form

$$\mathrm{i}\mathcal{L}_{\alpha'\alpha,\beta'\beta}(X) = \Big(\mathrm{i}\omega_{\alpha'\alpha}(R) + \mathrm{i}L_{\alpha'\alpha}(X)\Big)\delta_{\alpha'\beta'}\delta_{\alpha\beta} - J_{\alpha'\alpha,\beta'\beta}(X) \, , \tag{35}$$

where $\omega_{\alpha\alpha'}(R) = (E_\alpha(R) - E_{\alpha'}(R))/\hbar$ and

$$\mathrm{i}L_{\alpha'\alpha}(X) = \frac{P}{M} \cdot \frac{\partial}{\partial R} + \frac{1}{2}\Big(F_{\mathrm{W}}^{\alpha'}(R) + F_{\mathrm{W}}^{\alpha}(R)\Big) \cdot \frac{\partial}{\partial P} \, , \tag{36}$$

is the classical Liouville operator involving the mean of the Hellmann–Feynman forces where $F_{\mathrm{W}}^{\alpha} = -\langle\alpha; R|\frac{\partial \hat{V}_{\mathrm{W}}(\hat{q}, R)}{\partial R}|\alpha; R\rangle = -\langle\alpha; R|\frac{\partial \hat{H}_{\mathrm{W}}(R)}{\partial R}|\alpha; R\rangle$. Quantum transitions and bath momentum changes are described by

$$\begin{aligned} J_{\alpha'\alpha,\beta'\beta}(X) = & -\frac{P}{M} \cdot d_{\alpha'\beta'} \left(1 + \frac{1}{2} S_{\alpha'\beta'}(R) \cdot \frac{\partial}{\partial P}\right) \delta_{\alpha\beta} \\ & -\frac{P}{M} \cdot d_{\alpha\beta} \left(1 + \frac{1}{2} S_{\alpha\beta}(R) \cdot \frac{\partial}{\partial P}\right) \delta_{\alpha'\beta'} \, , \end{aligned} \tag{37}$$

where $S_{\alpha\beta} = (E_\alpha - E_\beta) d_{\alpha\beta} (\frac{P}{M} \cdot d_{\alpha\beta})^{-1}$ and $d_{\alpha\beta} = \langle\alpha; R|\nabla_R|\beta; R\rangle$ is the nonadiabatic coupling matrix element.

In this approximation the correlation function is then given by

$$C_{AB}(t;\beta) = \sum_{\alpha,\alpha'} \int \mathrm{d}X \; B_{\mathrm{W}}^{\alpha\alpha'}(X,t)(\hat{\rho}_{\mathrm{e}}\hat{A})_{\mathrm{W}}^{\alpha'\alpha}(X), \tag{38}$$

where

$$B_{\mathrm{W}}^{\alpha\alpha'}(X,t) = (\mathrm{e}^{\mathrm{i}\mathcal{L}t}\hat{B}_{\mathrm{W}}(X))^{\alpha\alpha'} \; . \tag{39}$$

Various ways of simulating nonadiabatic transitions in quantum–classical dynamics have been devised, as well as schemes for computing the evolution operator [2, 9, 20–26]. These schemes typically employ an ensemble of surface hopping trajectories with classical trajectory segments [21, 25, 26]. Approximations must also be introduced to evaluate the equilibrium density matrix. In making these approximations the consistency problem is not necessarily the most serious. In the desire to achieve consistency one could use the quantum–classical equilibrium density matrix, however, there would remain two problems. (1) This quantity is not known in closed form therefore expressions based on approximations for it would leave the consistency unattained. (2) As mentioned, (38) is not an admissible form for the quantum–classical response as given in (20) (although it can be related to $\mathcal{O}(\hbar)$) and therefore would not result in a consistent, interesting, quantum–classical object. Chemical rate coefficients written in terms of Kubo transformed correlation functions have been computed using this strategy [21, 27]. In the case of spin boson type models for reaction rates the fact that one knows the exact Wigner transformed equilibrium bath density can be exploited along with a quadratic approximation near the barrier top to obtain an estimate of the reaction rate that includes quantum equilibrium effects [21]. In more complex systems, like models for proton transfer in the condensed phase, one can exploit the high temperature limit to obtain suitable approximation to the equilibrium density [28]. See Chapter XX in this volume for a discussion of this approach applied to reaction rate problems.

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Although algorithms have been developed that have allowed one to simulate chemical reaction rates and short time relaxation processes, further algorithmic development is needed to simulate quantum–classical dynamics for long times.

(2) Linearized path integral approach

An alternative to the calculation of quantum time correlation functions is offered by the so-called linearized path integral approach [17, 18, 29–33]. In developing this approach it is simplest to work with a basis defined as the tensor product, $|Q\alpha\rangle$, of bath position states $|Q\rangle$ and a quantum subsystem basis $|\alpha\rangle$ which, for convenience, we choose to be independent of bath configuration (see Chap. XX in this volume for a discussion of how this formalism changes when the adiabatic basis is used). The quantum time correlation function in this representation becomes

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$$\langle \hat{A}\hat{B}(t)\rangle = \sum_{\alpha\beta,\alpha'\beta'} \int \mathrm{d}Q_0\ \mathrm{d}Q_N\ \mathrm{d}Q'_0\ \mathrm{d}Q'_N \langle Q_0\alpha|\hat{\rho}_{\mathrm{e}}\hat{A}|Q'_0\alpha'\rangle \tag{40}$$

$$\times\langle Q'_0\alpha'|\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{H}t}|Q'_N\beta'\rangle\langle Q'_N\beta'|\hat{B}|Q_N\beta\rangle\langle Q_N\beta|\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}t}|Q_0\alpha\rangle.$$

Here the hamiltonian is the usual one defined in (4), while the quantum subsystem hamiltonian has matrix elements $h_{\alpha\beta}(\hat{Q}) = \langle\alpha|\hat{h}(\hat{Q})|\beta\rangle$.

A convenient representation to account for the effects of the quantum subsystem transitions on the bath degrees of freedom is offered by the mapping hamiltonian formalism [34, 35, 37–39]. The core of this idea is to replace the quantum subsystem with a system of fictitious harmonic oscillators which can take only a restricted set of excitations representing the states of the basis. Therefore the states of the real system are mapped onto states of the fictitious harmonic oscillator system according to

$$|\alpha\rangle \to |m_\alpha\rangle = |0_1,\ldots,1_\alpha,..0_n\rangle. \tag{41}$$

This prescription maps the Hilbert space spanned by the original n quantum subsystem states into one coinciding with a subspace of n-oscillators of unit mass with at most one quantum of excitation in a single specific oscillator. Under these conditions the hamiltonian of the fictitious system is obtained by requiring that its matrix elements are equal to those of the corresponding physical states $\langle m_\alpha|\hat{h}_m(\hat{Q})|m_\beta\rangle = \langle\alpha|\hat{h}(\hat{Q})|\beta\rangle$. So that

$$\hat{h}_m(\hat{Q}) = \frac{1}{2}\sum_\lambda h_{\lambda,\lambda}(\hat{Q})(\hat{q}_\lambda^2 + \hat{p}_\lambda^2 - \hbar) + \frac{1}{2}\sum_{\lambda,\lambda'} h_{\lambda,\lambda'}(\hat{Q})(\hat{q}_{\lambda'}\hat{q}_\lambda + \hat{p}_{\lambda'}\hat{p}_\lambda) \tag{42}$$

where $\hat{q}_\lambda$ and $\hat{p}_\lambda$ are the λth mapping oscillator's position and momentum operators reconstructed from the creation and annhilation operators of the occupation number representation. Then the total hamiltonian of the system becomes $\hat{H}_m = \hat{P}^2/2M + \hat{h}_m(\hat{Q})$ and the propagator matrix elements of the real system are given by the mapping propagator matrix elements

$$\langle Q_N\beta|\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}t}|Q_0\alpha\rangle = \langle Q_N m_\beta|\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}_m t}|Q_0 m_\alpha\rangle. \tag{43}$$

To proceed, we now apply standard discrete path integral techniques to express the right-hand side of (43) as a functional integral over bath subsystem paths of an integrand containing the quantum subsystem transition amplitude evaluated along each path. This result parallels that of Pechukas [40] thus

$$\langle Q_N m_\beta|\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}_m t}|Q_0 m_\alpha\rangle = \int \prod_{k=1}^{N-1} \mathrm{d}Q_k \frac{\mathrm{d}P_k}{2\pi\hbar}\frac{\mathrm{d}P_N}{2\pi\hbar}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}S} \tag{44}$$

$$\times\langle m_\beta|\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\epsilon\hat{h}_m(Q_N)}\ldots\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\epsilon\hat{h}_m(Q_1)}|m_\alpha\rangle,$$

where

$$S = \epsilon \sum_{k=1}^{N} \left[P_k \frac{(Q_k - Q_{k-1})}{\epsilon} - \frac{P_k^2}{2M} \right] \tag{45}$$

and $\epsilon = t/N$ is the time slice.

The transition amplitude $\langle m_\beta | \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\epsilon \hat{h}_m(Q_N)} \cdots \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\epsilon \hat{h}_m(Q_1)} | m_\alpha \rangle$ contains a discrete time ordered propagator that evolves the initial mapping subsystem state according to the time dependent mapping hamiltonian where the time-dependence arises because of the changing configuration of the bath along the path $(Q_1, \ldots, Q_N)$. For any given specification of the bath subsystem path, the quadratic nature of the mapping hamiltonian in the mapping subsystem variables in (42) allows us to obtain an exact expression for the mapping transition amplitude. A particularly convenient expression for the transition amplitude can be obtained using semiclassical methods which are exact for quadratic hamiltonians with time-dependent coefficients (see [41] for details of the manipulations). The result is

$$\begin{aligned} &\langle m_\beta | \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\epsilon \hat{h}_m(Q_N)} \cdots \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\epsilon \hat{h}_m(Q_1)} | m_\alpha \rangle \\ &\quad \sim \int \mathrm{d}q_0 \, \mathrm{d}p_0 \, (q_{\beta t} + \mathrm{i} p_{\beta t})(q_{\alpha 0} - \mathrm{i} p_{\alpha 0}) \times \exp\left\{ -\frac{1}{2} \sum\nolimits_\lambda (q_{\lambda 0}^2 + p_{\lambda 0}^2) \right\} \end{aligned} \tag{46}$$

Here $(q_t, p_t) = (q_{1t}, \ldots, q_{nt}, p_{1t}, \ldots, p_{nt})$ is the mapping phase space point that evolves *classically* from the initial sampled point (q_0, p_0) to time t according to the given realization of the discrete time-dependent hamiltonian $(\hat{h}_m(Q_N), \ldots, \hat{h}_m(Q_1))$.

This expression for the transition amplitude can now be conveniently rewritten by introducing a polar representation of the complex polynomials appearing in the above result, thus

$$\begin{aligned} \langle m_\beta | \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\epsilon \hat{h}_m(Q_N)} \cdots \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\epsilon \hat{h}_m(Q_1)} | m_\alpha \rangle = \int \mathrm{d}q_0 \, \mathrm{d}p_0 \, r_{t,\beta}(\{Q_k\}) \mathrm{e}^{-\mathrm{i}\Theta_{t\beta}(\{Q_k\})} \\ \times r_{0\alpha} \mathrm{e}^{\mathrm{i}\Theta_{0,\alpha}} G_0 . \end{aligned} \tag{47}$$

Here $G_0 = \exp\left\{ -\frac{1}{2} \sum_\lambda (q_{0,\lambda}^2 + p_{0,\lambda}^2) \right\}$, $r_{t,\beta}(\{Q_k\}) = \sqrt{q_{t,\beta}^2(\{Q_k\}) + p_{t,\beta}^2(\{Q_k\})}$, and

$$\begin{aligned} \Theta_{t,\beta}(\{Q_k\}) &= \tan^{-1}\left(\frac{p_{0,\beta}}{q_{0,\beta}} \right) + \int_0^t \mathrm{d}\tau \, h_{\beta,\beta}(Q_\tau) \\ &\quad + \int_0^t \mathrm{d}\tau \sum_{\lambda \neq \beta} \left[h_{\beta,\lambda}(Q_\tau) \frac{(p_{\tau\beta} p_{\tau\lambda} + q_{\tau\beta} q_{\tau\lambda})}{(p_{\tau\beta}^2 + q_{\tau\beta}^2)} \right] \\ &= \tan^{-1}\left(\frac{p_{0,\beta}}{q_{0,\beta}} \right) + \int_0^t \theta_\beta(Q_\tau) \mathrm{d}\tau . \end{aligned} \tag{48}$$

Equation (48) defines the function $\theta_\beta(Q)$.

Substituting (47) and its analogue for the backward propagator (primed quantities) into the expression for the correlation function we finally obtain

$$\begin{aligned}\langle \hat{A}\hat{B}(t)\rangle = \sum_{\alpha\beta,\alpha'\beta'} \int \mathrm{d}Q_0\, \mathrm{d}Q'_0 \int \prod_{k=1}^{N} \mathrm{d}Q_k \frac{\mathrm{d}P_k}{2\pi\hbar} \int \prod_{k=1}^{N} \mathrm{d}Q'_k \frac{\mathrm{d}P'_k}{2\pi\hbar} \int \mathrm{d}q_0\, \mathrm{d}p_0\, \mathrm{d}q'_0\, \mathrm{d}p'_0 \\ \times \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(S-S')} r'_{0\alpha'} \mathrm{e}^{-\mathrm{i}\Theta'_{0,\alpha'}} G'_0 r_{0\alpha} \mathrm{e}^{\mathrm{i}\Theta_{0,\alpha}} G_0 \langle Q_0\alpha|\hat{\rho}_{\mathrm{e}}\hat{A}|Q'_0\alpha'\rangle \\ \times \langle Q'_N\beta'|B|Q_N\beta\rangle r_{t,\beta}(\{Q_k\}) \mathrm{e}^{-\mathrm{i}\Theta_{t\beta}(\{Q_k\})} r'_{t,\beta'}(\{Q'_k\}) \mathrm{e}^{\mathrm{i}\Theta'_{t\beta'}(\{Q'_k\})}.\end{aligned} \tag{49}$$

Here we employ a shorthand notation labeling the mapping oscillator states with their state index, e.g., $m_\alpha \equiv \alpha$.

All manipulations performed so far are exact, and the nuclear evolution is still described at the full quantum level. To proceed to a computable expression [17,41], we now change bath subsystem variables to mean, $\bar{R}_k = (Q_k + Q'_k)/2$, and difference, $Z_k = Q_k - Q'_k$, coordinates (with similar transformation for the bath momenta, $\bar{P}_k = (P_k + P'_k)/2$ and $Y_k = P_k - P'_k$ say) and Taylor series expand the phase in (49). Truncating this expansion to linear order we obtain the following approximate expression for the correlation function

$$\begin{aligned}\langle \hat{A}\hat{B}(t)\rangle = \sum_{\alpha\beta,\alpha'\beta'} \int \mathrm{d}q_0\, \mathrm{d}p_0\, \mathrm{d}q'_0\, \mathrm{d}p'_0\, r'_{0\alpha'} \mathrm{e}^{-\mathrm{i}\Theta'_{0,\alpha'}} G'_0 r_{0\alpha} \mathrm{e}^{\mathrm{i}\Theta_{0,\alpha}} G_0 \\ \times \int \mathrm{d}\bar{R}_0\, \mathrm{d}Z_0 \int \prod_{k=1}^{N} \mathrm{d}\bar{R}_k \frac{\mathrm{d}\bar{P}_k}{2\pi\hbar} \int \prod_{k=1}^{N} \mathrm{d}Z_k \frac{\mathrm{d}Y_k}{2\pi\hbar} \\ \times \langle \bar{R}_0 + \frac{Z_0}{2}\alpha|\hat{\rho}_{\mathrm{e}}\hat{A}|\bar{R}_0 - \frac{Z_0}{2}\alpha'\rangle \mathrm{e}^{-\mathrm{i}\bar{P}_1 Z_0} \\ \times \langle \bar{R}_N - \frac{Z_N}{2}\beta'|B|\bar{R}_N + \frac{Z_N}{2}\beta\rangle \mathrm{e}^{\mathrm{i}\bar{P}_N Z_N} \\ \times \mathrm{e}^{-\mathrm{i}\epsilon[\nabla\theta_\beta(\bar{R}_N)+\nabla\theta'_{\beta'}(\bar{R}_N)]/2\}Z_N} \\ \times r_{t,\beta}(\{\bar{R}_k\}) r'_{t,\beta'}(\{\bar{R}_k\}) \mathrm{e}^{-\mathrm{i}\epsilon\sum_{k=1}^{N}[\theta_\beta(\bar{R}_k)-\theta'_{\beta'}(\bar{R}_k)]} \\ \times \mathrm{e}^{-\mathrm{i}\epsilon\sum_{k=1}^{N-1}\{(\bar{P}_{k+1}-\bar{P}_k)/\epsilon+[\nabla\theta_\beta(\bar{R}_k)+\nabla\theta'_{\beta'}(\bar{R}_k)]/2\}Z_k} \\ \times \mathrm{e}^{-\mathrm{i}\epsilon\sum_{k=1}^{N}\{\bar{P}_k/M-(\bar{R}_k-\bar{R}_{k-1})/\epsilon\}Y_k}\end{aligned} \tag{50}$$

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The integrals over the end-point difference coordinates Z_0 and Z_N in this linearized approximate form can be performed defining the Wigner transformed operators

$$(\hat{\rho}_{\mathrm{e}}\hat{A})^{\alpha,\alpha'}_{\mathrm{W}}(\bar{R}_0,\bar{P}_1) = \int \mathrm{d}Z_0 \langle \bar{R}_0 + \frac{Z_0}{2}\alpha|\hat{\rho}_{\mathrm{e}}\hat{A}|\bar{R}_0 - \frac{Z_0}{2}\alpha'\rangle \mathrm{e}^{-\mathrm{i}\bar{P}_1 Z_0} \tag{51}$$

and in the limit of $\epsilon \to 0$

$$(\hat{B})_{\mathrm{W}}^{\beta',\beta}(\bar{R}_N,\bar{P}_N) = \int \mathrm{d}Z_N \langle \bar{R}_N + \frac{Z_N}{2}\beta'|\hat{B}|\bar{R}_N - \frac{Z_N}{2}\beta\rangle \mathrm{e}^{-\mathrm{i}\bar{P}_N Z_N}. \tag{52}$$

All integrals over the difference coordinates, Z_k, and difference momenta, Y_k for $0 < k < N$ can also be performed as they are integral representations of delta functions, so the linearized approximation for the time correlation function can finally be expressed as

$$\begin{aligned}\langle \hat{A}\hat{B}(t)\rangle = \sum_{\alpha\beta,\alpha'\beta'} &\int \mathrm{d}\bar{R}_0\, \mathrm{d}q_0\, \mathrm{d}p_0\, \mathrm{d}q_0'\, \mathrm{d}p_0'\, r_{0\alpha'}' \mathrm{e}^{-\mathrm{i}\Theta_{0,\alpha'}'} G_0' r_{0\alpha} \mathrm{e}^{\mathrm{i}\Theta_{0,\alpha}} G_0 \\ &\times \int \prod_{k=1}^{N} \mathrm{d}\bar{R}_k \frac{\mathrm{d}\bar{P}_k}{2\pi\hbar} (\hat{\rho}_{\mathrm{e}}\hat{A})_{\mathrm{W}}^{\alpha,\alpha'}(\bar{R}_0,\bar{P}_1)(\hat{B})_{\mathrm{W}}^{\beta',\beta}(\bar{R}_N,\bar{P}_N) \\ &\times r_{t,\beta}(\{\bar{R}_k\}) r_{t,\beta'}'(\{\bar{R}_k\}) \mathrm{e}^{-\mathrm{i}\epsilon\sum_{k=1}^{N}(\theta_\beta(\bar{R}_k)-\theta_{\beta'}'(\bar{R}_k))} \\ &\times \prod_{k=1}^{N-1} \delta\left(\frac{\bar{P}_{k+1}-\bar{P}_k}{\epsilon} - F_k^{\beta,\beta'}\right) \prod_{k=1}^{N} \delta\left(\frac{\bar{P}_k}{M} - \frac{\bar{R}_k - \bar{R}_{k-1}}{\epsilon}\right),\end{aligned} \tag{53}$$

where

$$\begin{aligned}F_k^{\beta,\beta'} &= -\frac{1}{2}\left\{\nabla_{\bar{R}_k} h_{\beta,\beta}(\bar{R}_k) + \nabla_{\bar{R}_k} h_{\beta',\beta'}(\bar{R}_k)\right\} \\ &\quad -\frac{1}{2}\sum_{\lambda\neq\beta} \nabla_{\bar{R}_k} h_{\beta,\lambda}(\bar{R}_k) \left\{\frac{(p_{\beta k}p_{\lambda k} + q_{\beta k}q_{\lambda k})}{(p_{\beta k}^2 + q_{\beta k}^2)}\right\} \\ &\quad -\frac{1}{2}\sum_{\lambda\neq\beta'} \nabla_{\bar{R}_k} h_{\beta',\lambda}(\bar{R}_k) \left\{\frac{(p_{\beta' k}'p_{\lambda k}' + q_{\beta' k}'q_{\lambda k}')}{p_{\beta' k}'^2 + q_{\beta' k}'^2)}\right\}.\end{aligned} \tag{54}$$

The product of δ-functions in (53) amounts to a time-stepping prescription in which the mean path evolves classically. As the motion of the mapping variables is already classical, the calculation of the time correlation function has been reduced to a two step procedure (1) sampling a set of initial conditions for the bath variables from a probability distribution related to the partial Wigner transform of the thermal density times the operator $\hat{A}$, i.e., the factor $(\hat{\rho}_{\mathrm{e}}\hat{A})_{\mathrm{W}}^{\alpha,\alpha'}(\bar{R}_0,\bar{P}_1)$ in (53), and a Gaussian distribution, $G_0'G_0$ as defined under (47), for the mapping subsystem variables; (2) integration of a set of coupled classical equations of motion for the mapping and bath variables. The first of these tasks can be accomplished only approximately using recently developed local harmonic approximate methods for sampling the Wigner density for complex systems [17,18]. The second task of evolving the classical dynamics is straightforward. However, we note that depending on the specific term of the correlation function which is being evaluated, the forces in (54) are determined by different time-dependent linear combinations of pairs of diagonal, and off-diagonal elements of the quantum subsystem hamiltonian. The diagonal terms are identified by the *final* states in the propagators appearing in the original expression for the correlation function, while the off-diagonal terms are responsible for the feedback between bath motion and changes in the quantum subsystem state occupations. The latter are affected by the bath propagation through the parametric dependence of the classical counterpart of (42), but the coupling mechanism is not deducible from a single hamiltonian. In spite of this unusual characteristic, all propagations required in this approximate evaluation of the correlation function are classical and local in time and maintain the usual properties of classical, or quantum, mechanics e.g., time reversibility).

To highlight the basic similarities between the two approximate approaches we have outlined here for computing time correlation functions in mixed quantum–classical systems, (53) can be put into the form of (38) by making the following identification

$$\begin{aligned}
B_{\mathrm{W}}^{\alpha\alpha'}(X,t) = \sum_{\beta\beta'} \int & \mathrm{d}q_0\,\mathrm{d}p_0\,\mathrm{d}q_0'\,\mathrm{d}p_0'\, r_{0\alpha'}'\mathrm{e}^{-\mathrm{i}\Theta_{0,\alpha'}'} G_0' r_{0\alpha}\mathrm{e}^{\mathrm{i}\Theta_{0,\alpha}} G_0 \\
& \times \int \mathrm{d}\bar{R}_1 \prod_{k=2}^{N} \mathrm{d}\bar{R}_k \frac{\mathrm{d}\bar{P}_k}{2\pi\hbar} (\hat{B})_{\mathrm{W}}^{\beta',\beta}(X_t(X)) \\
& \times r_{t,\beta}(\{\bar{R}_k\}) r_{t,\beta'}'(\{\bar{R}_k\}) \mathrm{e}^{-\mathrm{i}\epsilon\sum_{k=1}^{N}(\theta_\beta(\bar{R}_k)-\theta_{\beta'}'(\bar{R}_k))} \\
& \times \prod_{k=1}^{N-1} \delta\left(\frac{\bar{P}_{k+1}-\bar{P}_k}{\epsilon} - F_k^{\beta,\beta'}\right) \prod_{k=1}^{N} \delta\left(\frac{\bar{P}_k}{M} - \frac{\bar{R}_k-\bar{R}_{k-1}}{\epsilon}\right), \quad (55)
\end{aligned}$$

where now the initial phase space point is $X = (\bar{R}_0, \bar{P}_1)$, and the terminal point, $X_t = (\bar{R}_N, \bar{P}_N)$, is an implicit function of X determined by sequentially evaluating the δ-function integrals and classically time stepping the propagation of the bath. Comparing this result with the expressions at the end of the previous section it is clear that the basic features of these two approaches are similar but that the underlying dynamics is very different. These differences stem in part from the different representations employed but also result from different approximations made in the derivations. It is beyond the scope of this chapter to present a detailed comparison of these two approaches. As mentioned earlier and outlined below, they both yield good results for model condensed phase systems so exploring the connections between these different ideas may prove fruitful in developing algorithms for implementing mixed quantum–classical methods for computing time correlation functions.

The central approximation of the linearized path integral approach to nonadiabatic dynamics outlined here is that the Taylor expansion of the phase of the integrand in the path integral expression for the correlation function can be truncated at low order. One could imagine computing higher order corrections with significant additional computational effort beyond the linearized approach. This lowest order approximation, however, has proved particularly reliable in various model test calculations [41]. With the spin-boson model, for example, calculations of the time dependent expectation value of the spin population difference, starting from a nonequilibrium initial condition in which the coupling between an excited spin and an independent, thermal equilibrium harmonic oscillator bath is turned on at $t = 0$, gave results that were in excellent agreement with exact calculations [42] over a wide range of friction and temperature. Small deviations between exact results and those of the linearized approximate approach are observed at low temperature and high friction. Under these conditions the assumption that the only important contributions to the correlation function (or time-dependent expectation value) come from pairs of forward and backward paths that remain "close" to one another (keeping only terms to linear order in the path difference) is violated since at low temperatures the initial bath density has larger off-diagonal elements so forward and backward bath paths which differ significantly can begin to make contributions and these are ignored in the linearized scheme. The linearized path integral approach, however, is found to converge very quickly with trajectory ensemble size for these nonadiabatic problems, requiring fewer than 1,000 trajectories to converge these spin-boson calculations. This feature makes these methods promising for realistic model condensed applications in future studies.

In general the appeal of these methods is that they require Monte Carlo sampling and trajectories, features that scale favorably with the dimensions of the system, especially when compared with basis set methods. Unfortunately a quantitative assessment of this favorable conjecture is far from evident.

4 Conclusion

We have seen that it is possible to develop a consistent approach to equilibrium and nonequilibrium quantum–classical statistical mechanics. However, due to the different algebraic structures of the exact quantum bracket in the Wigner representation and its quantum–classical counterpart described here, the formulation contains one unpleasant feature: the nonassociative property of the product. This feature leads to a violation of the Jacobi identity so that in contrast to both quantum and classical mechanics, the quantum–classical approach does not have a Lie algebraic structure. This in turn leads to the fact that the Onsager reciprocal relation and the Kubo identity are valid only to order $\mathcal{O}(\hbar)$. It is conceivable that this approach can be improved by developing a quantum–classical bracket that satisfies the Lie algebraic structure. This is a challenge worthy of future research. Even if such a program could be carried out one would be left with the task of testing the fidelity of this quantum–classical world as a model of the real quantum world in the limit discussed in this chapter.

In the other approach considered here we saw that one could start with the full quantum statistical mechanical structure of the time correlation function and develop approximations to both the quantum evolution and equilibrium density. This type of approach readily leads to promising results as demonstrated in applications to models. The major drawback of such an approach is that the consistency between the quantum equilibrium structure and the approximate dynamics is lost, although one has gained the possibility to consider independently approximations to the evolution and the equilibrium structure. Examples of the utility of being able to make independent approximations to the evolution and equilibrium structure in which the consistency problem does not seem to matter much include applications reported in various references [21, 27, 28, 33, 41]. These local successes, however, not at all justify a general statement and we do not yet know the physical conditions that need to be satisfied to guarantee that the inconsistency problem will not be crucial. In the context of the approaches described in Sect. 3 one can also attempt to consistently approximate the equilibrium structure and dynamics although it is unclear at the present time how such consistency could be achieved.

In contrasting the two approaches we should not lose sight of the fact that the ultimate aim is to compare theoretical predictions with rigorous results for the real problem. We have seen that approximations enter both schemes in various ways. As we noted earlier we must ascertain the validity of quantum–classical worlds as models of the real world. In fact, since a consistent quantum–classical world has not yet been constructed we have the residual task of testing the validity of predictions of this model. This would be instrumental not only in realizing its limitations and give ways to improve the approach but also in establishing a preliminary test of the correspondence between the quantum–classical and the real worlds. Simulations on model systems indicate that violations of the Lie algebraic structure and its consequences may be minor for many applications [27], and thus scheme (1) may have practical utility. In the approach that begins with exact quantum equilibrium time correlation function, the freedom to approximate both the equilibrium density and the dynamics, separately or together, provides one with additional possibilities. Some of these approximations could indeed be unfaithful to the real world and highly inconsistent, while others may provide results much closer to the real quantum world. Of course there is nothing unique about the approaches we have discussed here, and other fresh ideas can come from many alternative formulations of quantum mechanics and/or ways to go to the semiclassical limit of quantum mechanics and, moreover, there is no indication that these alternative approaches will be less successful [43, 44]. So the way ahead is open and, at this point, it is unclear which alternative will prevail. Thus, it is worth pursuing these programs of research in all directions.

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References

1. E. Wigner: Phys. Rev. **40**, 749 (1932)
2. R. Kapral and G. Ciccotti: J. Chem. Phys. **110**, 8919 (1999)
3. K. Imre, E. Özizmir, M. Rosenbaum and P. F. Zwiefel: J. Math. Phys. **5**, 1097 (1967); M. Hillery, R. F. O'Connell, M. O. Scully and E. P. Wigner: Phys. Repts. **106**, 121 (1984)
4. I. V. Aleksandrov: Z. Naturforsch. **36a**, 902 (1981)
5. V. I. Gerasimenko: Theor. Math. Phys. **50**, 77 (1982); D. Ya. Petrina, V. I. Gerasimenko and V. Z. Enolskii: Sov. Phys. Dokl. **35**, 925 (1990)
6. W. Boucher and J. Traschen: Phys. Rev. D **37**, 3522 (1988)
7. W. Y. Zhang and R. Balescu: J. Plasma Phys. **40**, 199 (1988); R. Balescu and W. Y. Zhang: J. Plasma Phys. **40**, 215 (1988)
8. O. V. Prezhdo and V. V. Kisil: Phys. Rev. A **56**, 162 (1997)
9. C. C. Martens and J.-Y. Fang: J. Chem. Phys. **106**, 4918 (1996); A. Donoso and C. C. Martens: J. Phys. Chem. **102**, 4291 (1998); D. Kohen and C. C. Martens: J. Chem. Phys. **111**, 4343 (1999); **112**, 7345 (2000)
10. I. Horenko, C. Salzmann, B. Schmidt and C. Schütte: J. Chem. Phys. **117**, 11075 (2002)
11. R. Kapral and G. Ciccotti: *A Statistical Mechanical Theory of Quantum Dynamics in Classical Environments*, in *Bridging Time Scales: Molecular Simulations for the Next Decade*, 2001, eds. P. Nielaba, M. Mareschal and G. Ciccotti, (Springer, Berlin Heidelberg New York, 2003), p. 445
12. S. Nielsen, R. Kapral and G. Ciccotti: J. Chem. Phys. **115**, 5805 (2001)
13. J. Caro and L. L. Salcedo: Phys. Rev. A **60**, 842 (1999)
14. E. Rabani and D. Reichman: J. Chem. Phys. **120**, 1458 (2004)
15. S. A. Egorov, E. Rabani and B. J. Berne: J. Phys. Chem. B **103**, 10978 (1999)
16. A. A. Golosov, D. R. Reichman and E. Rabani: J. Chem. Phys. **118**, 457 (2003)
17. J. A. Poulsen, G. Nyman, and P. J. Rossky: J. Chem. Phys. **119**, 12179 (2003); J. Phys. Chem A **108**, 8743 (2004); Proc. Natl Acad. Sci. **102**, 6709 (2005)
18. Q. Shi and E. Geva: J. Chem. Phys. **118**, 8173 (2003); J. Chem. Phys. **120**, 10647 (2004); Q. Shi and E. Geva: J. Phys. Chem. A **107**, 9059 (2003); J. Phys. Chem. A **107**, 9070 (2003)
19. Q. Shi and E. Geva: J. Phys. Chem. A **108**, 6109 (2004); J. Chem. Phys. **121**, 3393 (2004)
20. A. Sergi and R. Kapral: J. Chem. Phys. **121** 7565 (2004)
21. H. Kim and R. Kapral: J. Chem. Phys. 214105 (2005); J. Chem. Phys. (in press)
22. D. Mac Kernan, G. Ciccotti and R. Kapral: J. Chem. Phys. **106** (2002)
23. C. Wan and J. Schofield: J. Chem. Phys. **113**, 7047 (2000)
24. M. Santer, U. Manthe, G. Stock: J. Chem. Phys. **114**, 2001 (2001)
25. D. Mac Kernan, G. Ciccotti and R. Kapral: J. Phys. Condens. Matter **14**, 9069 (2002)

AQ: Please update in press reference.

26. A. Sergi, D. Mac Kernan, G. Ciccotti and R. Kapral: Theor. Chem. Acc. **110**, 49 (2003)
27. A. Sergi and R. Kapral: J. Chem. Phys. **118**, 8566 (2003)
28. G. Hanna and R. Kapral: J. Chem. Phys. **122**, 244505 (2005)
29. R. Hernandez and G. Voth: Chem. Phys. Letts. **223**, 243 (1998)
30. W. H. Miller: J. Phys. Chem. A **105**, 2942 (2001); H. Wang, X. Sun and W. H. Miller: J. Chem. Phys. **108**, 9726 (1998); X. Sun, H. Wang and W. H. Miller: J. Chem. Phys. **109**, 7064 (1998); M. Thoss, H. Wang and W. H. Miller: J. Chem. Phys. **114**, 47 (2001)
31. S. Zhang and E. Pollak: J. Chem. Phys. **118**, 4357 (2003)
32. M. F. Herman and D. F. Coker: J. Chem. Phys. **111**, 1801 (1999)
33. S. Causo, G. Ciccotti, D. Montemayor, S. Bonella, and D. F. Coker: J. Phys. Chem. B **109**, 6855 (2005)
34. W. H. Miller and C. W. McCurdy: J. Chem. Phys. **69**, 5163 (1978)
35. C. W. McCurdy, H. D. Meyer and W. H. Miller: J. Chem. Phys. **70**, 3177 (1979)
36. X. Sun and W. H. Miller: J. Chem. Phys. **106**, 6346 (1997)
37. G. Stock and M. Thoss: Phys. Rev. Lett. **78**, 578 (1997)
38. G. Stock and M. Thoss: Phys. Rev. A **59**, 64 (1999)
39. S. Bonella and D. F. Coker: J. Chem. Phys. **118**, 4370 (2003); J. Chem. Phys. **114**, 7778 (2001); Chem. Phys. **268**, 323–334 (2001)
40. P. Pechukas: Phys. Rev. **181**, 166, 174 (1969)
41. S. Bonella and D. F. Coker: J. Chem. Phys. **122**, 194102 (2005); Proc. Natl Acad. Sci. **102**, 6715 (2005); Comp. Phys. Commun. **169**, 267 (2005)
42. N. Makri and K. Thompson: Chem. Phys. Lett. **291**, 101 (1998); K. Thompson and N. Makri: J. Chem. Phys. **110**, 1343 (1999); N. Makri: J. Phys. Chem. B **103**, 2823 (1999)
43. I. Burghardt: J. Chem. Phys. **122**, 094103 (2005)
44. O. V.Prezhdo: Theor. Chem. Acc. **114**, (2005)

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