

16 A Statistical Mechanical Theory of Quantum Dynamics in Classical Environments

Raymond Kapral¹ and Giovanni Ciccotti²

¹ Chemical Physics Theory Group, Department of Chemistry,
University of Toronto, Toronto, ON M5S 3H6, Canada

² INFN and Dipartimento di Fisica, Università “La Sapienza”,
Piazzale Aldo Moro, 2, 00185 Roma, Italy

16.1 Introduction

Since it is difficult to simulate the quantum dynamics of large, complex many-body systems, one is led to construct a statistical mechanical description of matter based on a mixture of quantum and classical dynamics. Many physically interesting systems may be partitioned into subsystems where certain degrees of freedom must necessarily be treated quantum mechanically, while others behave classically to a high degree of accuracy. Examples of systems with these characteristics are familiar and include proton and electron transfer processes and systems with electronic degrees of freedom coupled to heavy nuclei. In these cases it is useful to construct a quantum-classical dynamics that not only accounts for the quantum and classical dynamics of the two isolated subsystems but also describes their interaction. [1,2,3] The most widely used approaches are based on surface-hopping schemes where the coupling between the two subsystems induces quantum transitions. [4,5,6,7]

The primary interest is in the computation of quantities such as expectation values of dynamical variables or transport coefficients usually determined from integrals of time correlation functions. Consequently it is not sufficient to simply focus on the development of quantum-classical dynamics; instead one must formulate the statistical mechanics of such systems in order to provide a route to the computation of these observables. In this chapter we develop a scheme for carrying out quantum-classical evolution of many-body systems and, having established the nature of this dynamics, formulate a statistical mechanics for such systems and devise schemes for the computation of expectation values in this quantum-classical world.

We begin the presentation with a brief overview of quantum statistical mechanics in Sect. 16.2 where the response function and autocorrelation function expressions for transport properties are given. This section also introduces the partial Wigner representation and formulates quantum statistical mechanics in this form. The passage to quantum-classical dynamics is considered in Sect. 16.3 and the forms of the quantum-classical Liouville equation for the density matrix and dynamical variables are presented. Since quantum-classical dynamics has some unusual features, its nature is discussed

in Sect. 16.4. The evolution equation for the density matrix is expressed in an adiabatic basis and the evolution of the density matrix is determined in terms of an ensemble of surface-hopping trajectories. Section 16.5 carries out an analogous analysis for the evolution of a dynamical variable. The quantum-classical form of the canonical equilibrium density matrix is the topic of Sect. 16.6. A knowledge of this quantity is necessary for the computation of equilibrium statistical mechanical properties. Nonequilibrium statistical mechanics in the quantum-classical world is formulated in Sect. 16.7. This section gives the expressions for quantum-classical transport properties and time correlation functions. Properties of the correlation functions are discussed and comparisons with full quantum mechanics are made. Section 16.8 gives an example of the calculation of the expectation value of an observable for a many-body system: the spin-boson model. The conclusions of the chapter are given in Sect. 16.9.

16.2 Quantum Dynamics and Statistical Mechanics

The time evolution of the quantum mechanical density matrix $\hat{\rho}$ is given by the von Neumann equation,

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar} [\hat{H}, \hat{\rho}(t)], \quad (16.1)$$

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

$$\hat{\rho}(t) = e^{-i\hat{L}t} \hat{\rho}(0) = e^{-i\hat{H}t/\hbar} \hat{\rho}(0) e^{i\hat{H}t/\hbar}, \quad (16.2)$$

with $i\hat{L} = (i/\hbar)[\hat{H}, \]$ the quantum Liouville operator. In the Heisenberg picture of quantum mechanics, the time evolution of a dynamical variable \hat{B} is given by

$$\frac{d\hat{B}(t)}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{B}(t)], \quad (16.3)$$

whose formal solution is

$$\hat{B}(t) = e^{i\hat{L}t} \hat{B} = e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar}. \quad (16.4)$$

Usually, one is not simply interested in the time evolution of such quantities but rather in statistical mechanical quantities like the average values of observables, dynamical properties or transport coefficients defined in terms of time integrals of correlation functions. The average value of a dynamical variable is given by

$$\overline{B(t)} = \text{Tr} \hat{B} \hat{\rho}(t) = \text{Tr} \hat{B}(t) \hat{\rho}(0), \quad (16.5)$$

where we have used the fact that the time dependence can be transferred from the density matrix to the operator using cyclic permutations under the

trace. Thus, as is well known, one may either evolve a given initial density matrix backward in time and compute the average of \hat{B} using the time evolved density matrix to find $\overline{B(t)}$ or evolve the operator forward in time and average over the initial value of the density matrix.

In quantum mechanical systems in thermal equilibrium, we are often interested in the calculation of transport properties such as diffusion coefficients or rate constants. The microscopic forms for such transport coefficients can be obtained by applying linear response theory to a system in equilibrium subjected to an external force or by monitoring the decay of fluctuations about the equilibrium state. In linear response theory, it is assumed that a time dependent external force $F(t)$ couples to an operator \hat{A}^\dagger . Then the system hamiltonian takes the form

$$\hat{H}(t) = \hat{H} - \hat{A}^\dagger F(t) , \tag{16.6}$$

and the evolution equation for the density matrix reads

$$\begin{aligned} \frac{\partial \hat{\rho}(t)}{\partial t} &= (i\hbar)^{-1} [\hat{H}(t), \hat{\rho}(t)] , \\ &= -(i\hat{L} - i\hat{L}_A F(t)) \hat{\rho}(t) , \end{aligned} \tag{16.7}$$

where $i\hat{L}_A \equiv (i/\hbar)[\hat{A}^\dagger, \]$. The adjoint of \hat{A} is denoted by \hat{A}^\dagger .

Assuming the system was in thermal equilibrium in the distant past, the solution of this equation to linear order in the external force is [8]

$$\hat{\rho}(t) = \hat{\rho}_e^Q + \int_{-\infty}^t dt' e^{-i\hat{L}(t-t')} i\hat{L}_A \hat{\rho}_e^Q F(t') . \tag{16.8}$$

Here $\hat{\rho}_e^Q = Z_Q^{-1} \exp(-\beta\hat{H})$ is the canonical equilibrium density matrix and $Z_Q = \text{Tr} \exp(-\beta\hat{H})$ is the partition function. The response of the system to the external force may be determined by computing the average value of an operator \hat{B} using the density matrix at time t ,

$$\begin{aligned} \overline{B(t)} &= \text{Tr} \hat{B} \hat{\rho}(t) = \int_{-\infty}^t dt' \text{Tr} \hat{B} e^{-i\hat{L}(t-t')} i\hat{L}_A \hat{\rho}_e^Q F(t') \\ &= \frac{i}{\hbar} \int_{-\infty}^t dt' \text{Tr} \hat{B}(t-t') [\hat{A}^\dagger, \hat{\rho}_e^Q] F(t') \\ &= \frac{i}{\hbar} \int_{-\infty}^t dt' \text{Tr} [\hat{B}(t-t'), \hat{A}^\dagger] \hat{\rho}_e^Q F(t') \equiv \int_{-\infty}^t dt' \phi_{BA}(t-t') F(t') . \end{aligned} \tag{16.9}$$

For simplicity, the operator \hat{B} was assumed to have zero average value in equilibrium. The last line in (16.9) defines the response function

$$\phi_{BA}(t) = \langle \frac{i}{\hbar} [\hat{B}(t), \hat{A}^\dagger] \rangle_Q , \tag{16.10}$$

where the angle brackets denote a quantum canonical equilibrium average, $\langle \dots \rangle_Q = \text{Tr} \dots \hat{\rho}_e^Q$.

The response function may be written in a equivalent form by using the quantum mechanical operator identity, [8]

$$\frac{i}{\hbar} [\hat{A}^\dagger, \hat{\rho}_e^Q] = \int_0^\beta d\lambda \hat{\rho}_e^Q \dot{\hat{A}}^\dagger(-i\hbar\lambda), \quad (16.11)$$

in the second line of (16.9) to obtain

$$\phi_{BA}(t) = \int_0^\beta d\lambda \text{Tr} \dot{\hat{A}}^\dagger(-i\hbar\lambda) \hat{B}(t) \hat{\rho}_e^Q. \quad (16.12)$$

If we choose $\hat{B} = \hat{A} \equiv \hat{f}_A$, the flux corresponding to the operator \hat{A} , the response has the form of a macroscopic law and the response function is proportional to the flux autocorrelation function

$$\phi_{AA}(t) = \langle \frac{i}{\hbar} [\hat{f}_A(t), \hat{A}^\dagger] \rangle_Q = \int_0^\beta d\lambda \text{Tr} \dot{\hat{f}}_A^\dagger(-i\hbar\lambda) \hat{f}_A(t) \hat{\rho}_e^Q \equiv \beta \langle \dot{\hat{f}}_A^\dagger; \hat{f}_A(t) \rangle_Q. \quad (16.13)$$

The last equality defines the Kubo transformed correlation function. A simple transport property λ_A in quantum mechanics is proportional to the time integral of the flux autocorrelation function,

$$\lambda_A \propto \int_0^\infty dt \langle \frac{i}{\hbar} [\hat{f}_A(t), \hat{A}^\dagger] \rangle_Q \propto \int_0^\infty dt \langle \dot{\hat{f}}_A; \hat{f}_A(t) \rangle_Q. \quad (16.14)$$

The quantum mechanical correlation functions satisfy time translation symmetry,

$$\langle \dot{\hat{f}}_A; \hat{f}_A(t) \rangle_Q = \langle \dot{\hat{f}}_A(\tau); \hat{f}_A(t + \tau) \rangle_Q, \quad (16.15)$$

as can be verified by using the explicit form of the canonical equilibrium density matrix and cyclic permutations under the trace.

16.2.1 Mixed Representation of Quantum Statistical Mechanics

To obtain an alternative description of the quantum statistical mechanics of the system, we partition it into two subsystems: the first subsystem contains n particles with masses m and coordinate operators \hat{q} ; the second subsystem comprises N particles with masses M and coordinate operators \hat{Q} .

The hamiltonian operator may be written as

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}(\hat{q}, \hat{Q}), \quad (16.16)$$

where \hat{p} and \hat{P} are momentum operators and $\hat{V}(\hat{q}, \hat{Q})$ is the total potential energy. We employ a condensed notation such that $\hat{q} = (\hat{q}_1, \hat{q}_2, \dots, \hat{q}_{3n})$ and $\hat{Q} = (\hat{Q}_1, \hat{Q}_2, \dots, \hat{Q}_{3N})$, with an analogous notation for \hat{p} and \hat{P} .

The alternative description we wish to consider is based on a partial Wigner transformation [9] of the density matrix with respect to the subset of Q coordinates, [10]

$$\hat{\rho}_W(R, P) = (2\pi\hbar)^{-3N} \int dz e^{iP \cdot z/\hbar} \langle R - \frac{z}{2} | \hat{\rho} | R + \frac{z}{2} \rangle . \quad (16.17)$$

In this representation the quantum Liouville equation is,

$$\begin{aligned} \frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} &= -\frac{i}{\hbar} \left((\hat{H}\hat{\rho})_W - (\hat{\rho}\hat{H})_W \right) \\ &= -\frac{i}{\hbar} \left(\hat{H}_W e^{\hbar\Lambda/2i} \hat{\rho}_W(t) - \hat{\rho}_W(t) e^{\hbar\Lambda/2i} \hat{H}_W \right) , \end{aligned} \quad (16.18)$$

where the partially Wigner transformed Hamiltonian is

$$\hat{H}_W(R, P) = \frac{P^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}_W(\hat{q}, R) , \quad (16.19)$$

and Λ is the negative of the Poisson bracket operator,

$$\Lambda = \overleftarrow{\nabla}_P \cdot \overrightarrow{\nabla}_R - \overleftarrow{\nabla}_R \cdot \overrightarrow{\nabla}_P . \quad (16.20)$$

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,

$$\hat{A}_W(R, P) = \int dz e^{-iP \cdot z/\hbar} \langle R + \frac{z}{2} | \hat{A} | R - \frac{z}{2} \rangle , \quad (16.21)$$

and the fact that the partial Wigner transform of a product of operators is [11]

$$(\hat{A}\hat{B})_W(R, P) = \hat{A}_W(R, P) e^{\hbar\Lambda/2i} \hat{B}_W(R, P) . \quad (16.22)$$

We may rewrite the quantum Liouville equation in a more compact form [12]

$$\begin{aligned} \frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} &= -\frac{i}{\hbar} \left(\overrightarrow{H}_\Lambda \hat{\rho}_W(t) - \hat{\rho}_W(t) \overleftarrow{H}_\Lambda \right) , \\ &\equiv -i \hat{L}_W \hat{\rho}_W(t) \equiv -(H_W, \hat{\rho}_W(t))_Q . \end{aligned} \quad (16.23)$$

by defining the quantum Liouville operator and quantum Lie bracket. In these equations we have defined the right ($\overrightarrow{H}_\Lambda$) and left ($\overleftarrow{H}_\Lambda$) acting operators,

$$\overrightarrow{H}_\Lambda = \hat{H}_W(R, P) e^{\hbar\Lambda/2i} , \quad \overleftarrow{H}_\Lambda = e^{\hbar\Lambda/2i} \hat{H}_W(R, P) . \quad (16.24)$$

The second equality in (16.23) defines the quantum Liouville operator $i\hat{L}_W$ in the partial Wigner representation while the third defines the associated Lie bracket $(H_W, \cdot)_Q$. More generally the Lie bracket of two partially Wigner transformed operators is defined as

$$\begin{aligned} (\hat{A}_W, \hat{B}_W)_Q &= \frac{i}{\hbar} \left(\vec{A}_\Lambda \hat{B}_W - \hat{B}_W \overleftarrow{A}_\Lambda \right) \\ &= \frac{i}{\hbar} \left(\hat{A}_W e^{\hbar\Lambda/2i} \hat{B}_W - \hat{B}_W e^{\hbar\Lambda/2i} \hat{A}_W \right). \end{aligned} \quad (16.25)$$

Here the \vec{A}_Λ and $\overleftarrow{A}_\Lambda$ operators are defined as in (16.24) with the replacement $\vec{H}_W \rightarrow \hat{A}_W$.

The formal solution of (16.23) is

$$\begin{aligned} \hat{\rho}_W(R, P, t) &= e^{-i\vec{H}_\Lambda t/\hbar} \hat{\rho}_W(R, P, 0) e^{i\overleftarrow{H}_\Lambda t/\hbar}, \\ &= e^{-i\hat{L}_W t} \hat{\rho}_W(R, P, 0). \end{aligned} \quad (16.26)$$

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,

$$\frac{d\hat{A}_W(R, P, t)}{dt} = i\hat{L}_W \hat{A}_W(R, P, t) = (H_W(R, P), \hat{A}_W(R, P, t))_Q, \quad (16.27)$$

and

$$\hat{A}_W(R, P, t) = e^{i\hat{L}_W t} \hat{A}_W(R, P) = e^{i\vec{H}_\Lambda t/\hbar} \hat{A}_W(R, P) e^{-i\overleftarrow{H}_\Lambda t/\hbar}. \quad (16.28)$$

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. However, we stress that the time dependence of the observables cannot be expressed as, e.g., $\hat{A}_W(R(t), P(t))$

We now consider some important properties of products of partially Wigner transformed operators. The Wigner transform of a product of operators satisfies the associative product rule,

$$\begin{aligned} (\hat{A}\hat{B}\hat{C})_W &= \left((\hat{A}_W e^{\hbar\Lambda/2i} \hat{B}_W) e^{\hbar\Lambda/2i} \hat{C}_W \right) \\ &= \left(\hat{A}_W e^{\hbar\Lambda/2i} \left(\hat{B}_W e^{\hbar\Lambda/2i} \hat{C}_W \right) \right), \end{aligned} \quad (16.29)$$

which may be generalized to products of n operators.

Next, 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

$$\hat{C}_W(t) = \hat{A}_W(t) e^{\hbar\Lambda/2i} \hat{B}_W(t). \quad (16.30)$$

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,

$$(\hat{A}_W, (\hat{B}_W, \hat{C}_W)_Q)_Q + (\hat{C}_W, (\hat{A}_W, \hat{B}_W)_Q)_Q + (\hat{B}_W, (\hat{C}_W, \hat{A}_W)_Q)_Q = 0, \tag{16.31}$$

so that it has the Lie algebraic structure of any true dynamics, quantum or classical.

This general formulation of quantum dynamics reduces to standard descriptions in certain limiting cases. If the Q subsystem is absent, the system comprises only q degrees of freedom and we recover the usual quantum dynamical description in terms of the von Neumann equation (16.1). If one considers the Q dynamics alone without any q subsystem, one has the ordinary Wigner representation of quantum mechanics and all partially Wigner transformed operators become simple phase space functions: $\hat{A}_W(R, P) \rightarrow A_W(R, P)$. The classical limit of the quantum Q dynamics, which consists in keeping only terms of order \hbar^0 in the evolution operator, is obtained by truncating the power series expansion of the exponential operator: $\exp(\hbar\Lambda/2i) = 1 + \hbar\Lambda/2i$. In this limit the bracket $(H_W, \cdot)_Q$ reduces to the Poisson bracket $\{H_W, \cdot\}$, 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,

$$\rho_C(R, P, t) = e^{-iL_C t} \rho_C(R, P, 0) = \rho_C(R(-t), P(-t), 0). \tag{16.32}$$

Having given this brief overview of quantum statistical mechanics, we turn to the central problem of this chapter: the construction of the analogs of these results for quantum-classical systems.

16.3 Quantum-Classical World

As discussed above, we consider a quantum mechanical system partitioned into two subsystems. Now, however, the second subsystem, comprising N particles with masses M and coordinate operators \hat{Q} , is taken to represent an environment or bath with $M \gg m$. We wish to study the limit where the bath degrees of freedom may be treated classically but the quantum character of the first subsystem (hereafter referred to as the quantum subsystem) cannot be neglected. The approximation to the full quantum dynamics we want to consider is depicted schematically in Fig. 16.1.

The passage to quantum-classical dynamics is made by first scaling distances in terms of the wavelength appropriate for the mass m particles, $\lambda_m = (\hbar^2/m\epsilon_0)^{1/2}$, where ϵ_0 is a suitable energy unit, scaling the momenta of the light and heavy particles by $p_m = (m\lambda_m/t_0) = (m\epsilon_0)^{1/2}$

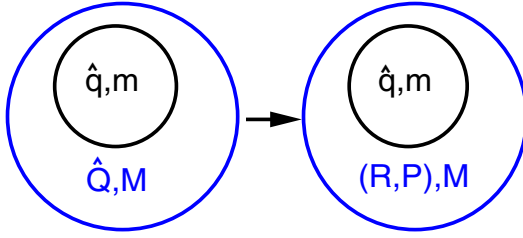


Fig. 16.1. Schematic representation of a quantum system partitioned into two subsystems and its approximation as a quantum subsystem in a classical bath.

and $P_M = (M\epsilon_0)^{1/2}$, respectively, and time by $t_0 = \hbar/\epsilon_0$. [10] The evolution operator in the quantum Liouville equation may then be expanded in $\mu = (m/M)^{1/2}$ and retaining terms to first order in this quantity we find (in the original unscaled variables), [10]

$$\begin{aligned} \frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} &= -\frac{i}{\hbar} [\hat{H}_W, \hat{\rho}_W(t)] + \frac{1}{2} \left(\left\{ \hat{H}_W, \hat{\rho}_W(t) \right\} - \left\{ \hat{\rho}_W(t), \hat{H}_W \right\} \right) \\ &= -\frac{i}{\hbar} \left(\overrightarrow{\mathcal{H}}_\Lambda \hat{\rho}_W(t) - \hat{\rho}_W(t) \overleftarrow{\mathcal{H}}_\Lambda \right) \\ &\equiv -i \hat{\mathcal{L}} \hat{\rho}_W(t) \equiv -(\hat{H}_W, \hat{\rho}_W(t)) , \end{aligned} \tag{16.33}$$

where we have defined the right and left acting operators, respectively, as

$$\overrightarrow{\mathcal{H}}_\Lambda = \hat{H}_W \left(1 + \frac{\hbar\Lambda}{2i} \right) , \quad \overleftarrow{\mathcal{H}}_\Lambda = \left(1 + \frac{\hbar\Lambda}{2i} \right) \hat{H}_W , \tag{16.34}$$

the quantum-classical Liouville operator $\hat{\mathcal{L}}$ and the quantum-classical bracket as

$$(\hat{A}_W, \hat{B}_W) = \frac{i}{\hbar} \left(\overrightarrow{\mathcal{A}}_\Lambda \hat{B}_W - \hat{B}_W \overleftarrow{\mathcal{A}}_\Lambda \right) , \tag{16.35}$$

where $\overrightarrow{\mathcal{A}}_\Lambda$ is defined as $\overrightarrow{\mathcal{H}}_\Lambda$ in (16.34) with $\hat{H}_W \rightarrow \hat{A}_W$. Equation (16.33) is the quantum-classical Liouville equation [10,13,14,15,16,17,18,19,20] whose solution will be discussed later in this chapter. The quantum-classical Liouville equation describes the coupled evolution of these two subsystems. We shall see that as a result of this coupling a purely Newtonian description of the bath dynamics is no longer possible. The quantum-classical equation of motion for a dynamical variable \hat{B}_W can be written in a similar form as

$$\frac{d\hat{B}_W(t)}{dt} = (\hat{H}_W, \hat{B}_W(t)) . \tag{16.36}$$

The formal solutions of (16.33) and (16.36) are [12]

$$\hat{\rho}_W(t) = e^{-i\hat{\mathcal{L}}t} \hat{\rho}_W(0) = \mathcal{S} \left(e^{-i\vec{\mathcal{H}}_{\Lambda}t} \hat{\rho}_W(0) e^{i\overleftarrow{\mathcal{H}}_{\Lambda}t} \right), \quad (16.37)$$

and

$$\hat{B}_W(t) = e^{i\hat{\mathcal{L}}t} \hat{B}_W = \mathcal{S} \left(e^{i\vec{\mathcal{H}}_{\Lambda}t/\hbar} \hat{B}_W e^{-i\overleftarrow{\mathcal{H}}_{\Lambda}t/\hbar} \right), \quad (16.38)$$

where the operator \mathcal{S} is needed to prescribe how the left and right acting operators are to be evaluated to yield the evolution determined by the quantum-classical Liouville operator. The presence of the \mathcal{S} operator signals the existence of differences in the formal structures of quantum-classical and quantum dynamics. Quantum-classical dynamics does not possess a Lie algebraic structure like quantum mechanics since the properties in (16.29), (16.30) and (16.31) are violated to some order in \hbar . In particular, the Jacobi identity [18,12]

$$(\hat{A}_W, (\hat{B}_W, \hat{C}_W)) + (\hat{C}_W, (\hat{A}_W, \hat{B}_W)) + (\hat{B}_W, (\hat{C}_W, \hat{A}_W)) = \mathcal{O}(\hbar), \quad (16.39)$$

is valid only to terms $\mathcal{O}(\hbar)$.

16.4 Nature of Quantum-Classical Dynamics

In order to gain insight into the nature of quantum-classical dynamics, in this section we show how the evolution of the density matrix can be expressed in terms of an ensemble of trajectories. Equation (16.33) is independent of the basis used to represent the quantum subsystem, and any convenient basis may be chosen to study the evolution. Here, however, we use an adiabatic basis since it provides a fruitful way to analyze the dynamics and carry out simulations. As we shall see below, we are forced to adopt an Eulerian description of the density matrix evolution since the evolution operator cannot be reduced to a streaming operator acting on the “classical” (R, P) coordinates. At each coordinate point R of the classical bath we define the Hamiltonian

$$\hat{h}_W(R) = \frac{\hat{p}^2}{2m} + \hat{V}_W(\hat{q}, R), \quad (16.40)$$

whose eigenvalue problem

$$\hat{h}_W(R)|\alpha; R\rangle = E_\alpha(R)|\alpha; R\rangle, \quad (16.41)$$

yields the adiabatic states and energies. In this adiabatic basis the density matrix has matrix elements $\rho_W^{\alpha\alpha'}(R, P, t) = \langle \alpha; R | \hat{\rho}_W(R, P, t) | \alpha'; R \rangle$. The density matrix may be written as a vector function with components ρ_W^s by associating an index $s = \alpha\mathcal{N} + \alpha'$ with the pair $(\alpha\alpha')$, where $0 \leq \alpha, \alpha' < \mathcal{N}$ for an \mathcal{N} -state quantum subsystem.

Using this notation and introducing a subscript to label different values of s , e.g. $s_k = \alpha_k \mathcal{N} + \alpha'_k$, the quantum-classical Liouville equation has the form [21,22,23]

$$\frac{\partial \rho_W^{s_j}(R, P, t)}{\partial t} = \sum_{s_k} -i \mathcal{L}_{s_j s_k} \rho_W^{s_k}(R, P, t). \quad (16.42)$$

After some algebra, the matrix elements of the quantum-classical Liouville operator are found to be [10,21]

$$\begin{aligned} -i \mathcal{L}_{s_j s_k} &= -(i\omega_{s_j} + iL_{s_j})\delta_{s_j s_k} + J_{s_j s_k} \\ &\equiv -i \mathcal{L}_{s_j s_k}^0 + J_{s_j s_k}. \end{aligned} \quad (16.43)$$

The diagonal term $i \mathcal{L}_{s_j s_k}^0 = i \mathcal{L}_{s_j}^0 \delta_{s_j s_k} = (i\omega_{s_j} + iL_{s_j})\delta_{s_j s_k}$ contains the frequency $\omega_{s_j}(R) = (E_{\alpha_j}(R) - E_{\alpha'_j}(R))/\hbar$ and the classical Liouville operator L_{s_j}

$$iL_{s_j} = \frac{P}{M} \cdot \frac{\partial}{\partial R} + \frac{1}{2} \left(F_W^{\alpha_j} + F_W^{\alpha'_j} \right) \cdot \frac{\partial}{\partial P}, \quad (16.44)$$

where $F_W^{\alpha_j} = -\langle \alpha_j; R | \frac{\partial \hat{V}_W(\hat{r}; R)}{\partial R} | \alpha_j; R \rangle = -\partial E_{\alpha_j}(R)/\partial R$ is the Hellmann-Feynman force that governs the motion on the adiabatic surface corresponding to the state $|\alpha_j; R\rangle$ of the \hat{q} subsystem. The term $J_{s_j s_k}$ is responsible for non-adiabatic transitions and has the form [10]

$$\begin{aligned} J_{s_j s_k} &= -\frac{P}{M} \cdot d_{\alpha_j \alpha_k} \left(1 + \frac{1}{2} S_{\alpha_j \alpha_k} \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha'_j \alpha'_k} \\ &\quad - \frac{P}{M} \cdot d_{\alpha'_j \alpha'_k}^* \left(1 + \frac{1}{2} S_{\alpha'_j \alpha'_k}^* \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha_j \alpha_k}, \end{aligned} \quad (16.45)$$

where $S_{\alpha_j \alpha_k} = (E_{\alpha_j} - E_{\alpha_k})d_{\alpha_j \alpha_k} (\frac{P}{M} \cdot d_{\alpha_j \alpha_k})^{-1}$ and $d_{\alpha_j \alpha_k} = \langle \alpha_j; R | \frac{\partial}{\partial R} | \alpha_k; R \rangle$ is the non-adiabatic coupling matrix element which determines the non-adiabaticity of the system. Henceforth, we choose a real-valued adiabatic basis so that $d_{\alpha\alpha} = 0$ and $J_{s_j s_k}$ is off-diagonal. Moreover, when the first term on the right hand side of (16.45) is non-zero, the second term is zero, and vice versa. Specifically, the first term is non-zero for values of s_j and s_k such that $s_j - s_k = \pm \ell \mathcal{N}$, while the second term is non-zero only if $s_j - s_k = \pm \ell$, where $1 \leq \ell < \mathcal{N}$. These two conditions restrict the sequences of transitions that can occur. [23]

We can solve the equation for the density matrix formally to give

$$\rho_W^{s_j}(R, P, t) = \sum_{s_k} (e^{-i\mathcal{L}t})_{s_j, s_k} \rho_0^{s_k}(R, P), \quad (16.46)$$

where $\rho_0^{s_k}(R, P) \equiv \rho_W^{s_k}(R, P, 0)$. Using the form of the Liouville operator $i \mathcal{L}_{s_j, s_k}$ in (16.43), we may use the Dyson identity to write the evolution

operator as

$$(e^{-i\mathcal{L}t})_{s_j, s_k} = e^{-i\mathcal{L}_{s_j}^0 t} \delta_{s_j, s_k} + \sum_{s_l} \int_0^t dt' e^{-i\mathcal{L}_{s_j}^0 (t-t')} J_{s_j s_l} (e^{-i\mathcal{L}t'})_{s_l, s_k} . \tag{16.47}$$

Equation (16.47) may be substituted into (16.46) and iterated to yield

$$\begin{aligned} \rho_W^{s_0}(R, P, t) = & e^{-i\mathcal{L}_{s_0}^0 t} \rho_0^{s_0}(R, P) + \sum_{n=1}^{\infty} \sum_{s_1 \dots s_n} \int_0^{t_0} dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n \\ & \times \prod_{k=1}^n \left[e^{-i\mathcal{L}_{s_{k-1}}^0 (t_{k-1} - t_k)} J_{s_{k-1} s_k} \right] e^{-i\mathcal{L}_{s_n}^0 t_n} \rho_0^{s_n}(R, P) , \end{aligned} \tag{16.48}$$

where $t_0 \equiv t$. In this representation of the dynamics, the evolution operator $\exp(-i\mathcal{L}_{s_j}^0 t)$ determines the evolution between the quantum transitions governed by $J_{s_j s_k}$. For a diagonal contribution with $s_j \sim (\alpha_j \alpha_j)$, $\exp(-i\mathcal{L}_{s_j}^0 t) = \exp(-iL_{\alpha_j} t)$ is the ordinary classical evolution operator governed by the potential $E_{\alpha_j}(R)$,

$$e^{-iL_{s_j} t} f_{s_j}(R, P) = f_{s_j}(R_{0, s_j}^t, P_{0, s_j}^t) , \tag{16.49}$$

where $f_{s_j}(R, P)$ is a function of the phase space point (R, P) . Here $(R_{0, s_j}^t, P_{0, s_j}^t)$ is the result of backward evolution to time zero of the phase point (R, P) at time t . For an off-diagonal contribution with $s_j \sim (\alpha_j \alpha'_j)$, the phase factor comes into play and in Ref. [10] we have shown that

$$\begin{aligned} e^{-(i\omega_{s_j} + iL_{s_j})t} f_{s_j}(R, P) = & e^{-i \int_0^t d\tau \omega_{s_j}(R_{0, s_j}^\tau, P_{0, s_j}^\tau)} e^{-iL_{s_j} t} f_{s_j}(R, P) \\ \equiv & W_{s_j}(t, 0) f_{s_j}(R_{0, s_j}^t, P_{0, s_j}^t) . \end{aligned} \tag{16.50}$$

In this case the classical evolution is determined by the mean potential $(E_{\alpha_j}(R) - E_{\alpha'_j}(R))/2$ of the two coherently coupled adiabatic states.

Figure 16.2 shows one of the trajectory segments contributing to the second order term in the density matrix. In this figure we are interested in the value of the $(\alpha\alpha)$ component of the density matrix at phase point (R, P) at time t . The phase point (R, P) is evolved backward in time on the E_α potential energy surface until time t'' where a quantum transition to adiabatic state β occurs. At this time the operator $J_{\alpha\alpha, \alpha\beta}$ acts, for example, to change the state of the second index of the density matrix, $(\alpha\alpha) \rightarrow (\alpha\beta)$; a corresponding continuous change occurs in the bath momentum determined by the momentum derivative in the J operator. States α and β are now coherently coupled. The phase point evolves backward in time on the mean of the E_α and E_β potential energy surfaces between time t'' where the quantum transition occurred and time t' where another quantum transition takes place.

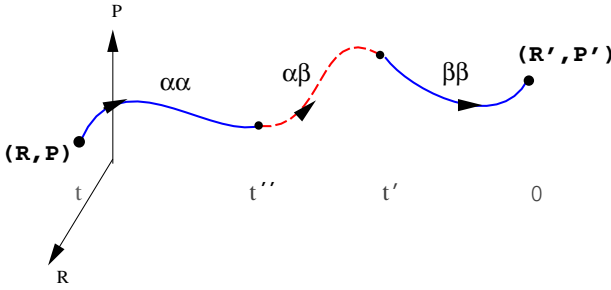


Fig. 16.2. Schematic picture of a trajectory that enters into the computation of the density matrix.

During this time interval the phase factor (using an obvious generalization of the definition in (16.50))

$$W_{\alpha\beta}(t', t'') = e^{-i \int_{t''}^{t'} d\tau \omega_{\alpha\beta}(R_{t''}^{\tau, \alpha\beta})} , \tag{16.51}$$

accumulates its value reflecting the coherent evolution of the off-diagonal element of the density matrix. At time t' a second quantum transition, e.g., $(\alpha\beta) \rightarrow (\beta\beta)$, occurs. As before the operator $J_{\alpha\beta, \beta\beta}$ determines the nature of this transition and specifies the momentum change in the bath. Due to this second quantum transition the system is once again in a diagonal state $(\beta\beta)$. As a result of this transition back to the diagonal state, no phase factor enters the evolution to time zero on the single adiabatic surface E_β to yield the phase point (R', P') .

The density matrix element at time t can be constructed from an ensemble of such “surface-hopping” trajectories where all possible numbers of quantum transitions to all possible intermediate quantum states at all possible intermediate times are considered. This ensemble of trajectories provides an exact solution of the density matrix in the quantum-classical limit.

In order to illustrate the nature of this ensemble we consider a simple example where a two-level quantum subsystem is coupled to a single classical one-dimensional harmonic oscillator. [21,22] Since the classical phase space is two dimensional, we may easily visualize the classical trajectories that contribute to the density matrix evaluation. The hamiltonian $\hat{h}_W(R)$ can be written in terms of the quantum subsystem hamiltonian (\hat{h}_s) plus the bath (V_b) and coupling (\hat{V}_c) potentials as $\hat{h}_W(R) = \hat{h}_s + V_b(R) + \hat{V}_c(\hat{q}, R)$, with $\hat{h}_s = \hat{p}^2/2m + \hat{V}_s$. The eigenvalue problem for \hat{h}_s is $\hat{h}_s|i\rangle = \tilde{\epsilon}_i|i\rangle$, where the space is spanned by the two eigenstates $|1\rangle$ and $|2\rangle$. We take the matrix elements of the coupling potential in this basis to be $\langle i|\hat{V}_c(\hat{q}, R)|j\rangle = \hbar\gamma(R)(1 - \delta_{ij})$ where we have assumed that $V_{ii} = 0$. In terms of the diabatic or spin up and spin down states, $|\uparrow\rangle = 2^{-1/2}(|1\rangle + |2\rangle)$ and $|\downarrow\rangle = 2^{-1/2}(|1\rangle - |2\rangle)$, respectively, and taking the energy constant at zero, the hamiltonian matrix of $\hat{h}_W(R)$ is

$$\mathbf{h}_W = -\hbar\Omega\hat{\sigma}_x + V_b(R)\mathbf{I} + \hbar\gamma(R)\hat{\sigma}_z, \quad (16.52)$$

where $2\hbar\Omega = \tilde{\epsilon}_2 - \tilde{\epsilon}_1$, \mathbf{I} is the unit matrix and the Pauli matrices are

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (16.53)$$

The solution of the eigenvalue problem for \mathbf{h}_W yields the adiabatic energies and eigenstates. The adiabatic energies are

$$E_{1,2}(R) = V_b(R) \mp \hbar(\Omega^2 + \gamma(R)^2)^{1/2}. \quad (16.54)$$

The adiabatic eigenstates are

$$\begin{aligned} |1; R\rangle &= (2(1 + G^2))^{-1/2} ((1 + G)|\uparrow\rangle + (1 - G)|\downarrow\rangle), \\ |2; R\rangle &= (2(1 + G^2))^{-1/2} ((G - 1)|\uparrow\rangle + (1 + G)|\downarrow\rangle), \end{aligned} \quad (16.55)$$

with $G(R) = (\gamma(R))^{-1}(-\Omega + (\Omega^2 + \gamma(R)^2)^{1/2})$. The non-adiabatic coupling matrix element is $d_{12} = -d_{21} = -(1 + G^2)^{-1}G'$.

An example of the ensemble of trajectories containing up to four non-adiabatic transitions, contributing to the 11-element of the density matrix at phase point (R, P) at a specific time $t = 4.4$ is shown in Fig. 16.3 for this system. [21] In this figure the three solid curves represent deterministic classical evolution on the three potential energy surfaces that enter into the description of the dynamics: the ground state adiabatic surface, $E_1(R)$, (outermost curve

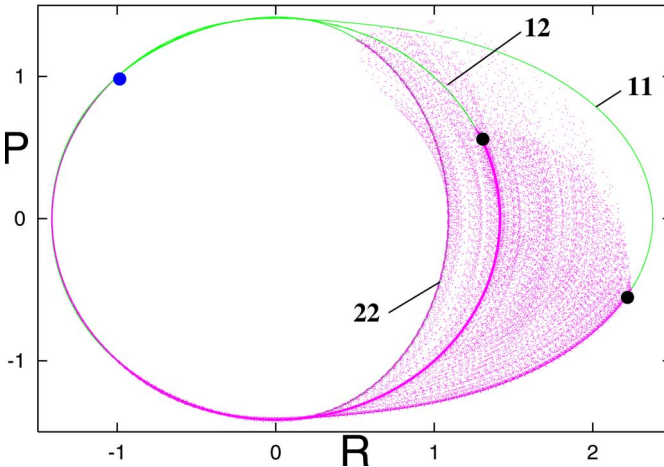


Fig. 16.3. The ensemble of trajectories containing up to four non-adiabatic transitions contributing to the 11-element of the density matrix at phase point $(-1, 1)$ at time t .

labeled 11), the excited state adiabatic surface, $E_2(R)$, (innermost curve labeled 22) and the mean of these two surfaces, $(E_1(R) + E_2(R))/2 = V_b(R)$, which is the same as the bare bath potential energy for this model system with two quantum states (middle curve labeled 12). All members of the ensemble start at phase point $(-1, 1)$ at time t indicated by a heavy dot. As an illustration of how the features of the trajectories can be understood, consider, for example, those trajectories that involve a single non-adiabatic transition between times t and 0. If the non-adiabatic transition $1 \rightarrow 2$ takes place at $t = 0^+$, the system will evolve on the ground adiabatic state (outermost curve) for entire trajectory ending at the heavy dot on the $E_1(R)$ surface. If the non-adiabatic transition takes place at $t = t^+$, the system will evolve on the bath potential (middle curve) for its entire history ending at the heavy dot on the $V_b(R)$ curve. If the transition occurs at any time intermediate between these two limits, ($t = 4.4$ and $t = 0$), the trajectory will end at a point on an arc that lies at the end of the high density region between the 12 and 11 curves and connects the two heavy dots on these curves. For these trajectories it is $\rho_0^{12}(R_{t,12}, P_{t,12})$ (and a similar quantity with $(1 \leftrightarrow 2)$) that determines the $\rho_W^{11}(R, P, t)$. A similar analysis can be carried out for trajectories with a larger number of non-adiabatic transitions.

16.5 Time Evolution of Dynamical Variables

In most statistical mechanical applications one is not interested in the evolution of a particular element of the density matrix at a particular phase point but, rather, in expectations of dynamical variables or time correlation functions. It is therefore often more useful to consider the evolution of a dynamical variable instead of the density matrix. Although the methods used to carry out this evolution are similar to those for the density matrix, it is convenient to show how the quantum-classical evolution equation for a dynamical variable can be analyzed.

The equation of motion for the dynamical variable was given in (16.36) and its formal solution, which was given in (16.38) can be written more explicitly as

$$B_W^{sj}(R, P, t) = \sum_{s_k} (e^{i\mathcal{L}t})_{s_j s_k} B_0^{s_k}(R, P), \tag{16.56}$$

where $B_W^{sj}(R, P, 0) = B_0^{sj}(R, P)$. Using the form of the Liouville operator $i\mathcal{L}_{s_j s_k}$ in (16.43), we may use a variant of the identity in (16.47) to write the evolution operator as

$$(e^{i\mathcal{L}t})_{s_j s_k} = e^{i\mathcal{L}_{s_j}^0 t} \delta_{s_j s_k} - \sum_{s_l} \int_0^t dt' e^{i\mathcal{L}_{s_j}^0 t'} J_{s_j s_l} (e^{i\mathcal{L}(t-t')})_{s_l s_k}. \tag{16.57}$$

Substitution of this expression into (16.36), followed by iteration of the resulting equation and the change of variables $\tau_1 = t_1$ and $\tau_i = t_i + \tau_{i-1}$,

($i > 1$), yields the result,

$$\begin{aligned}
 B_W^{s_0}(R, P, t) &= e^{\mathcal{L}_{s_0}^0 t} B_0^{s_0}(R, P) + \sum_{n=1}^{\infty} (-1)^n \sum_{s_1 \dots s_n} \int_0^t d\tau_1 \int_{\tau_1}^t d\tau_2 \dots \int_{\tau_{n-1}}^t d\tau_n \\
 &\quad \times \prod_{k=1}^n \left[e^{i\mathcal{L}_{s_{k-1}}^0 (\tau_k - \tau_{k-1})} J_{s_{k-1} s_k} \right] e^{i\mathcal{L}_{s_n}^0 (t - \tau_n)} B_0^{s_n}(R, P). \quad (16.58)
 \end{aligned}$$

The forward-evolved classical trajectory segments are defined in a manner that parallels the earlier discussion for the backward-evolved trajectories. We let

$$(\bar{R}_{s_j, t}, \bar{P}_{s_j, t}) = e^{iL_{s_j} t}(R, P), \quad (16.59)$$

be the trajectory that starts at (R, P) at time 0 and ends at $(\bar{R}_{s_j, t}, \bar{P}_{s_j, t})$ at time t . The action of the evolution operator $e^{i\mathcal{L}_{s_j}^0 t}$ on any phase function is

$$\begin{aligned}
 e^{i\mathcal{L}_{s_j}^0 t} f_{s_j}(R, P) &= e^{i \int_0^t d\tau \omega_{s_j}(\bar{R}_{s_j, \tau})} e^{iL_{s_j} t} f_{s_j}(R, P) \\
 &\equiv \mathcal{W}_{s_j}(t, 0) f_{s_j}(\bar{R}_{s_j, t}, \bar{P}_{s_j, t}). \quad (16.60)
 \end{aligned}$$

We may write the form of the dynamical variable at time t more explicitly by using the forms of the phase points evolved under quantum-classical dynamics. In (16.45) we saw that J could be written as the sum of two contributions that determine which of the two indices in s_j changes in a non-adiabatic transition. We use a symbol $\kappa = 0, 1$ to denote these two contributions and label the S and d factors with the same symbol. While the dynamics may be carried out using the explicit expression for J as discussed in the previous section, in many instances it is sufficient to write J in the momentum-jump approximation [10]. To present the evolution results in their simplest form, we utilize this approximation in the remainder of this section.

The momentum-jump approximation to J may be constructed in the following way. The operator J involves differential operators of the form $(1 + \frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial P})$ acting on functions of the classical phase space coordinates. It is possible to write this operator approximately as a ‘‘momentum jump’’ operator whose effect on the momentum is to shift it by some value. In order to carry out this calculation one must account for the fact that $S_{\alpha\beta}$ depends on the momenta. In spite of this dependence, one may introduce a translation operator in a new variable to complete the demonstration. Since $S_{\alpha\beta} = \Delta E_{\alpha\beta} \hat{d}_{\alpha\beta} (\frac{P}{M} \cdot \hat{d}_{\alpha\beta})^{-1}$, with $\Delta E_{\alpha\beta} = E_{\alpha} - E_{\beta}$, we may write

$$\begin{aligned}
 \left(1 + \frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial P} \right) &= 1 + \frac{1}{2} \Delta E_{\alpha\beta} M \frac{1}{(P \cdot \hat{d}_{\alpha\beta})} \frac{\partial}{\partial (P \cdot \hat{d}_{\alpha\beta})} \\
 &= 1 + \Delta E_{\alpha\beta} M \frac{\partial}{\partial (P \cdot \hat{d}_{\alpha\beta})^2} \quad (16.61)
 \end{aligned}$$

If we now consider the action of the operator on any function $f(P)$ of the momentum, we have

$$\begin{aligned} & \left(1 + \Delta E_{\alpha\beta} M \frac{\partial}{\partial(P \cdot \hat{d}_{\alpha\beta})^2} \right) f(P) \approx e^{\Delta E_{\alpha\beta} M \partial / \partial(P \cdot \hat{d}_{\alpha\beta})^2} f(P) \\ &= e^{\Delta E_{\alpha\beta} M \partial / \partial(P \cdot \hat{d}_{\alpha\beta})^2} f\left(\hat{d}_{\alpha\beta}^\perp(P \cdot \hat{d}_{\alpha\beta}^\perp) + \hat{d}_{\alpha\beta} \operatorname{sgn}(P \cdot \hat{d}_{\alpha\beta}) \sqrt{(P \cdot \hat{d}_{\alpha\beta})^2}\right) \\ &= f\left(\hat{d}_{\alpha\beta}^\perp(P \cdot \hat{d}_{\alpha\beta}^\perp) + \hat{d}_{\alpha\beta} \operatorname{sgn}(P \cdot \hat{d}_{\alpha\beta}) \sqrt{(P \cdot \hat{d}_{\alpha\beta})^2 + \Delta E_{\alpha\beta} M}\right). \end{aligned} \quad (16.62)$$

In the second line of this equation we have written the momentum vector as a sum of its components along $\hat{d}_{\alpha\beta}$ and perpendicular to $\hat{d}_{\alpha\beta}^\perp$, and in the last line we have used the fact that the exponential operator is a translation operator in the variable $(P \cdot \hat{d}_{\alpha\beta})^2$. If the energy difference times the mass $\Delta E_{\alpha\beta} M$ is small, we may expand the square root in the argument of f to obtain,

$$\begin{aligned} & f\left(\hat{d}_{\alpha\beta}^\perp(P \cdot \hat{d}_{\alpha\beta}^\perp) + \hat{d}_{\alpha\beta} \operatorname{sgn}(P \cdot \hat{d}_{\alpha\beta}) \sqrt{(P \cdot \hat{d}_{\alpha\beta})^2 + \Delta E_{\alpha\beta} M}\right) \\ & \approx f\left(\hat{d}_{\alpha\beta}^\perp(P \cdot \hat{d}_{\alpha\beta}^\perp) + \hat{d}_{\alpha\beta}(P \cdot \hat{d}_{\alpha\beta}) + \frac{1}{2}(P \cdot \hat{d}_{\alpha\beta})^{-1} \Delta E_{\alpha\beta} M\right) \\ & = f\left(P + \frac{1}{2} S_{\alpha\beta}\right). \end{aligned} \quad (16.63)$$

Collecting these results we may write,

$$\left(1 + \frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial P} \right) f(P) \approx e^{\Delta E_{\alpha\beta} M \partial / \partial(P \cdot \hat{d}_{\alpha\beta})^2} f(P) = f\left(P + \frac{1}{2} S_{\alpha\beta}\right). \quad (16.64)$$

Thus, to lowest order in the small parameter $\Delta E_{\alpha\beta} M$ we may write the operators in J as momentum translation (jump) operators.

This approximation may yield useful results beyond its strict domain of validity. Non-adiabatic transitions are likely to occur when adiabatic potential energy surfaces lie close in energy so that $\Delta E_{\alpha\beta}$ is small. In such circumstances the non-adiabatic coupling matrix element $d_{\alpha\beta}$ is typically large. The momentum jump approximation will be valid in such cases provided $P \cdot d_{\alpha\beta}$ is not too small. If $\Delta E_{\alpha\beta}$ is large, i.e. when the approximation fails, the prefactor of $(1 + \frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial P})$, $P \cdot d_{\alpha\beta} / M$, is typically small and the contributions to the evolution coming from the J factors carry a small weight.

If we then consider the evolution of a phase point using the first-order momentum jump approximation, we can label the evolved phase point with state and κ labels to specify its history. Using this notation, the sequence of bath phase space coordinates at times $\tau_1, \tau_2, \dots, \tau_n$, supposing that one of the

components of J acts at each of these times, is

$$\begin{aligned}
 (\bar{R}_{s_0, \tau_1}, \bar{P}_{s_0, \tau_1}) &= e^{iL_{s_0}(\tau_1)}(R, P) \\
 (\bar{R}_{s_1, \tau_2}^{\tau_1, \kappa_1}, \bar{P}_{s_1, \tau_2}^{\tau_1, \kappa_1}) &= e^{iL_{s_1}(\tau_2 - \tau_1)}(\bar{R}_{s_0, \tau_1}, \bar{P}_{s_0, \tau_1} + \frac{S_1^{\kappa_1}}{2}) \\
 &\dots \\
 (\bar{R}_{s_i, \tau_{i+1}}^{\tau_i, \kappa_i}, \bar{P}_{s_i, \tau_{i+1}}^{\tau_i, \kappa_i}) &= e^{iL_{s_i}(\tau_{i+1} - \tau_i)}(\bar{R}_{s_{i-1}, \tau_i}^{\tau_{i-1}, \kappa_{i-1}}, \bar{P}_{s_{i-1}, \tau_i}^{\tau_{i-1}, \kappa_{i-1}} + \frac{S_i^{\kappa_i}}{2}). \tag{16.65}
 \end{aligned}$$

Here $\{\tau_i, \kappa_i\} = ((\tau_1, \kappa_1), (\tau_2, \kappa_2), \dots, (\tau_i, \kappa_i))$ labels the history of the choice of the two terms in J .

Using this form we may write the solution in terms of surface-hopping trajectories as

$$\begin{aligned}
 B_W^{s_0}(R, P, t) &= \mathcal{W}_{s_0}(t, 0)B_0^{s_0}(\bar{R}_{s_0, t}, \bar{P}_{s_0, t}) \\
 &+ \sum_{n=1}^{\infty} (-1)^n \sum_{s_1 \kappa_1, \dots, s_n \kappa_n} \int_0^t d\tau_1 \int_{\tau_1}^t d\tau_2 \dots \int_{\tau_{n-1}}^t d\tau_n \\
 &\times \prod_{k=1}^n \left[\mathcal{W}_{s_{k-1}}(\tau_k, \tau_{k-1}) \frac{\bar{P}_{s_{k-1}, \tau_k}^{\tau_k, \kappa_k}}{M} \cdot d_{s_{k-1} \rightarrow s_k}^{\kappa_k}(\bar{R}_{s_{k-1}, \tau_k}^{\tau_k, \kappa_k}) \right] \\
 &\times \mathcal{W}_{s_n}(t, \tau_n)B_0^{s_n}(\bar{R}_{s_{n-1}, \tau_n}^{\tau_n, \kappa_n}, \bar{P}_{s_{n-1}, \tau_n}^{\tau_n, \kappa_n}). \tag{16.66}
 \end{aligned}$$

16.5.1 Equations for Canonical Variables

To gain some appreciation for the nature of quantum-classical evolution of a dynamical variable, we consider the equations of motion for the ‘‘classical’’ canonical variables. Letting $B_0^{\alpha\alpha'} = R\delta_{\alpha\alpha'}$ or $B_0^{\alpha\alpha'} = P\delta_{\alpha\alpha'}$, and using (16.36) we find

$$\frac{dR_W^{\alpha\alpha'}(t)}{dt} = \sum_{\beta\beta'} i\mathcal{L}_{\alpha\alpha', \beta\beta'} R_W^{\beta\beta'}(t) = \sum_{\beta\beta'} (e^{i\mathcal{L}t})_{\alpha\alpha', \beta\beta'} \frac{P}{M} \delta_{\beta\beta'} \equiv \frac{P_W^{\alpha\alpha'}(t)}{M} \tag{16.67}$$

$$\frac{dP_W^{\alpha\alpha'}(t)}{dt} = \sum_{\beta\beta'} i\mathcal{L}_{\alpha\alpha', \beta\beta'} P_W^{\beta\beta'}(t) = \sum_{\beta\beta'} (e^{i\mathcal{L}t})_{\alpha\alpha', \beta\beta'} F_W^{\beta} \delta_{\beta\beta'} \equiv F_W^{\alpha\alpha'}(t), \tag{16.68}$$

where we have used the fact that $i\mathcal{L}_{\alpha\alpha', \beta\beta'} R = (P/M)\delta_{\alpha\beta}\delta_{\alpha'\beta'}$ and $i\mathcal{L}_{\alpha\alpha', \beta\beta'} P = F_W^{\beta}\delta_{\alpha\beta}\delta_{\alpha'\beta'}$. While the first equation for the time evolution of the position has the same form as Newton’s equations of motion, the second equation of motion for the momentum does not. The ‘‘force’’ $F_W^{\alpha\alpha'}(t)$ cannot be expressed

simply as function of $R_W^{\alpha\alpha'}(t)$ as may be verified by repeated application of $i\mathcal{L}$ to its initial value. Consequently, to evaluate the canonical variables one must use the techniques described above for a general dynamical variable.

16.6 Quantum-Classical Equilibrium Density

The form of the canonical equilibrium density that appears in the quantum mechanical expressions for transport coefficients is $\hat{\rho}_e^Q = Z_Q^{-1} \exp(-\beta\hat{H})$ and expressed in terms of the partial Wigner transform it can be written as

$$\hat{\rho}_{W_e}^Q(R, P) = (2\pi\hbar)^{-3N} \int dz e^{iP \cdot z/\hbar} \langle R - \frac{z}{2} | \hat{\rho}_e^Q | R + \frac{z}{2} \rangle . \tag{16.69}$$

The equilibrium density is stationary under full quantum dynamics, either in its original or partial Wigner transformed forms. It is not stationary under quantum-classical dynamics and in this section we discuss the quantum-classical analog of this equilibrium density which satisfies, [12]

$$i\hat{\mathcal{L}}\hat{\rho}_{W_e} = \frac{i}{\hbar} (\overrightarrow{\mathcal{H}}_A \hat{\rho}_{W_e} - \hat{\rho}_{W_e} \overleftarrow{\mathcal{H}}_A) = 0 . \tag{16.70}$$

One way to find a solution of this equation is in terms of a power series expansion in \hbar . Letting

$$\hat{\rho}_{W_e} = \sum_{n=0}^{\infty} \hbar^n \hat{\rho}_{W_e}^{(n)} , \tag{16.71}$$

substituting this expression in (16.70) and grouping by powers of \hbar , we obtain the following recursion relations: for $n = 0$,

$$i \left[\hat{H}_W, \hat{\rho}_{W_e}^{(0)} \right] = 0 , \tag{16.72}$$

and for $n \geq 0$,

$$i \left[\hat{H}_W, \hat{\rho}_{W_e}^{(n+1)} \right] = \frac{1}{2} \left\{ \hat{H}_W, \hat{\rho}_{W_e}^{(n)} \right\} - \frac{1}{2} \left\{ \hat{\rho}_{W_e}^{(n)}, \hat{H}_W \right\} . \tag{16.73}$$

If a similar set of recursion relations is written for the partial Wigner transform of the full quantum mechanical canonical equilibrium density matrix, one finds that the two set of recursion relations are identical to $\mathcal{O}(\hbar)$. Since the recursion relations permit us to obtain the terms higher order in \hbar from those with lower orders, we have sufficient information to construct the quantum-classical stationary density that is consistent with the quantum mechanical equilibrium density to order \hbar .

To compute the equilibrium density, it is convenient for our purposes to consider these recursion relations in an adiabatic basis where they take the form,

$$iE_{\alpha\alpha'} \rho_{W_e}^{(0)\alpha\alpha'} = 0 , \tag{16.74}$$

$$iE_{\alpha\alpha'}\rho_{W_e}^{(n+1)\alpha\alpha'} = -iL_{\alpha\alpha'}\rho_{W_e}^{(n)\alpha\alpha'} + \sum_{\nu\nu'} J_{\alpha\alpha',\nu\nu'}\rho_{W_e}^{(n)\nu\nu'} . \quad (16.75)$$

One may prove that these equations can be solved to any order in \hbar to obtain the equilibrium density. While it is difficult to find the full solution to any order in \hbar , it is not difficult to find the solution analytically to order \hbar . It is given by [12]

$$\begin{aligned} \rho_{W_e}^{\alpha\alpha'} &= \rho_{W_e}^{(0)\alpha} \left(\delta_{\alpha\alpha'} - i\frac{P}{M} \cdot d_{\alpha\alpha'} \left(\frac{\beta}{2}(1 + e^{-\beta E_{\alpha'\alpha}}) \right. \right. \\ &\quad \left. \left. + \frac{1}{E_{\alpha\alpha'}}(1 - e^{-\beta E_{\alpha'\alpha}}) \right) (1 - \delta_{\alpha\alpha'}) \right) + \mathcal{O}(\hbar^2) . \end{aligned} \quad (16.76)$$

The utility of this expression for the equilibrium density matrix to $\mathcal{O}(\hbar)$ for the calculation of time correlation functions can be subjected to numerical test.

16.7 Quantum-Classical Time Correlation Functions

We are now in a position to address the problem posed at the beginning of this chapter in Sect. 16.2: the nature of the quantum-classical forms for equilibrium time correlation functions and their associated transport coefficients. The more general 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}_W is subjected to a time dependent external force that couples to the observable \hat{A}_W , so that the total hamiltonian is

$$\hat{\mathbf{H}}_W(t) = \hat{H}_W - \hat{A}_W^\dagger F(t) . \quad (16.77)$$

The evolution equation for the density matrix takes the form

$$\begin{aligned} \frac{\partial \hat{\rho}_W(t)}{\partial t} &= (i\hbar)^{-1} \left(\vec{\mathbf{H}}_\Lambda(t) \hat{\rho}_W(t) - \hat{\rho}_W(t) \overleftarrow{\mathbf{H}}_\Lambda(t) \right) , \\ &= -(i\hat{\mathcal{L}} - i\hat{\mathcal{L}}_A F(t)) \hat{\rho}_W(t) , \end{aligned} \quad (16.78)$$

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

$$\begin{aligned} \hat{\rho}_W(t) &= e^{-i\hat{\mathcal{L}}(t-t_0)} \hat{\rho}_W(t_0) \\ &\quad + \int_{t_0}^t dt' e^{-i\hat{\mathcal{L}}(t-t')} i\hat{\mathcal{L}}_A \hat{\rho}_W(t') F(t') . \end{aligned} \quad (16.79)$$

In parallel with the derivation for quantum mechanical systems outlined in Sect. 16.2, we choose $\hat{\rho}_W(t_0)$ to be the equilibrium density matrix, $\hat{\rho}_{W_e}$. As discussed in Sect. 16.6, $\hat{\rho}_{W_e}$ is defined to be invariant under quantum-classical dynamics, $i\hat{\mathcal{L}}\hat{\rho}_{W_e} = 0$. In this case the first term on the right hand side of (16.79) reduces to $\hat{\rho}_{W_e}$ and is independent of t_0 . We may assume that the system with hamiltonian \hat{H}_W is in thermal equilibrium at $t_0 = -\infty$, and with this boundary condition, to first order in the external force, (16.79) is

$$\hat{\rho}_W(t) = \hat{\rho}_{W_e} + \int_{-\infty}^t dt' e^{-i\hat{\mathcal{L}}(t-t')} i\hat{\mathcal{L}}_A \hat{\rho}_{W_e} F(t'). \quad (16.80)$$

Then, computing $\overline{B_W(t)} = \text{Tr}' \int dRdP \hat{B}_W \hat{\rho}_W(t)$ to obtain the response function, we find

$$\begin{aligned} \overline{B_W(t)} &= \int_{-\infty}^t dt' \text{Tr}' \int dRdP \hat{B}_W e^{-i\hat{\mathcal{L}}(t-t')} i\hat{\mathcal{L}}_A \hat{\rho}_{W_e} F(t') \\ &= \int_{-\infty}^t dt' \langle (\hat{B}_W(t-t'), \hat{A}_W^\dagger) \rangle F(t') \equiv \int_{-\infty}^t dt' \phi_{BA}^{QC}(t-t') F(t'). \end{aligned} \quad (16.81)$$

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

$$\phi_{BA}^{QC}(t) = \langle (\hat{B}_W(t), \hat{A}_W^\dagger) \rangle. \quad (16.82)$$

The derivation of linear response theory in the quantum-classical world is completely analogous to that in quantum mechanics. The response function in (16.82) is structurally similar to that in (16.10) with the quantum-classical bracket replacing the quantum Lie bracket, $(i/\hbar)[\ , \] \rightarrow (\ , \)$, the dynamical variable $\hat{B}_W(t)$ evolves under quantum-classical dynamics instead of full quantum mechanics and the trace over the quantum canonical density matrix is replaced by an average over $\hat{\rho}_{W_e}$. One may regard these replacements as correspondence rule to transform a quantum response function to the quantum-classical response function.

Knowing the response function, we may derive an expression for a transport property by taking $\hat{B}_W = \hat{A}_W = i\mathcal{L}\hat{A}_W \equiv \hat{f}_{AW}$. The quantum-classical analog of the expression for a quantum mechanical transport coefficient in (16.14) is given by

$$\lambda_A \propto \int_0^\infty dt \langle (\hat{f}_{AW}(t), \hat{A}_W^\dagger) \rangle = \int_0^\infty dt \text{Tr}' \int dRdP \hat{f}_{AW}(t) (\hat{A}_W^\dagger, \hat{\rho}_{W_e}). \quad (16.83)$$

In writing the second line of (16.83) we have used cyclic permutations under the trace and integrations by parts. In addition to this direct derivation

via linear response theory, this form can also be obtained by applying the correspondence rule to the first expression on the right hand side of (16.14).

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 (16.83) entails evolution of $\hat{f}_W(t)$ under quantum-classical classical dynamics as discussed in Sect. 16.5, evaluation of the quantum-classical bracket of \hat{A}_W^\dagger and $\hat{\rho}_{We}$, and an integration over the classical phase space coordinates and trace over the quantum states. In this formulation of quantum-classical nonequilibrium statistical mechanics, correlation functions should be computed by ensemble averages of dynamical quantities, as specified by (16.83), rather than by time averages. In addition, we observe that while $\hat{\rho}_{We}$ is not a probability density, $\hat{\rho}_W^{(0)}$ provides a weight function for sampling the phase space points and quantum states for the evaluation of the average.

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. Consider the quantum mechanical response function in (16.10). This function may also be written as

$$\phi_{BA}(t) = \langle \frac{i}{\hbar} [\hat{B}(t), \hat{A}^\dagger] \rangle_Q = \langle \frac{i}{\hbar} [\hat{B}(t + \tau), \hat{A}^\dagger(\tau)] \rangle_Q, \quad (16.84)$$

using the form 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 (16.82). To see this we may write (16.82) more explicitly as

$$\begin{aligned} \phi_{BA}^{QC}(t) &= \langle (\hat{B}_W(t), \hat{A}_W^\dagger) \rangle \\ &= \frac{i}{\hbar} \left(\langle \hat{B}_W(t) (1 + \hbar\Lambda/2i) \hat{A}_W^\dagger \rangle - \langle \hat{A}_W^\dagger (1 + \hbar\Lambda/2i) \hat{B}_W(t) \rangle \right), \end{aligned} \quad (16.85)$$

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

$$\langle \hat{B}_W(t) (1 + \hbar\Lambda/2i) \hat{A}_W^\dagger \rangle = \langle e^{i\mathcal{L}\tau} (\hat{B}_W(t) (1 + \hbar\Lambda/2i) \hat{A}_W^\dagger) \rangle. \quad (16.86)$$

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

$\hat{C}_W = \hat{B}_W(1 + \hbar\Lambda/2i)\hat{A}_W^\dagger$. We have

$$\begin{aligned} i\hat{\mathcal{L}}\hat{C}_W &= \frac{i}{\hbar} \left(\overset{\rightarrow}{\mathcal{H}}_\Lambda \left(\hat{B}_W \left(1 + \frac{\hbar\Lambda}{2i} \right) \hat{A}_W^\dagger \right) \right) \\ &\quad - \frac{i}{\hbar} \left(\left(\hat{B}_W \left(1 + \frac{\hbar\Lambda}{2i} \right) \hat{A}_W^\dagger \right) \overset{\leftarrow}{\mathcal{H}}_\Lambda \right), \\ &= (i\hat{\mathcal{L}}\hat{B}_W) \left(1 + \frac{\hbar\Lambda}{2i} \right) \hat{A}_W^\dagger + \hat{B}_W \left(1 + \frac{\hbar\Lambda}{2i} \right) (i\hat{\mathcal{L}}\hat{A}_W^\dagger) + \mathcal{O}(\hbar). \end{aligned} \tag{16.87}$$

It follows that

$$\begin{aligned} \hat{C}_W(\tau) &= e^{i\hat{\mathcal{L}}\tau}\hat{C}_W = \left(e^{i\hat{\mathcal{L}}\tau}\hat{B}_W \right) \left(1 + \frac{\hbar\Lambda}{2i} \right) \left(e^{i\hat{\mathcal{L}}\tau}\hat{A}_W^\dagger \right) + \mathcal{O}(\hbar) \\ &= \hat{B}_W(\tau) \left(1 + \frac{\hbar\Lambda}{2i} \right) \hat{A}_W^\dagger(\tau) + \mathcal{O}(\hbar). \end{aligned} \tag{16.88}$$

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

$$\phi_{BA}^{QC}(t) = \langle (\hat{B}_W(t), \hat{A}_W^\dagger) \rangle = \langle (\hat{B}_W(t + \tau), \hat{A}_W^\dagger(\tau)) \rangle + \mathcal{O}(\hbar), \tag{16.89}$$

although its most strict form, (16.86), is surely satisfied. Consequently, transport properties should be computed using ensemble averages as in (16.83), rather than through time averages assuming ergodicity.

Next, we consider alternate forms for correlations that are commonly used in computations. We saw that the quantum mechanical response function (16.10) could be written in the equivalent form (16.12) using the Kubo identity (16.11). However, the quantum-classical version of the Kubo identity holds only to $\mathcal{O}(\hbar)$, [12]

$$(\hat{A}_W^\dagger, \hat{\rho}_{We}) = \int_0^\beta d\lambda \hat{\rho}_{We} \left(1 + \frac{\hbar\Lambda}{2i} \right) \hat{A}_W^\dagger(-i\hbar\lambda) + \mathcal{O}(\hbar). \tag{16.90}$$

If we then write the quantum-classical transport coefficient (16.83) as

$$\lambda_A \propto \int_0^\infty dt \text{Tr}' \int dRdP \hat{f}_{AW}(t) (\hat{A}_W^\dagger, \hat{\rho}_{We}), \tag{16.91}$$

and use (16.90), we find another expression for the transport coefficient in Kubo transformed form,

$$\lambda_A \propto \int_0^\infty dt \int_0^\beta d\lambda \text{Tr}' \int dRdP \left(\hat{f}_{AW}^\dagger(-i\hbar\lambda) \left(1 + \frac{\hbar\Lambda}{2i} \right) \hat{f}_{AW}(t) \right) \hat{\rho}_{We} + \mathcal{O}(\hbar), \tag{16.92}$$

Since the quantum-classical form of the Kubo identity is valid only to $\mathcal{O}(\hbar)$, the two forms of the autocorrelation function expressions for the transport coefficient are no longer equivalent. The results of comparisons of computations of both forms of the correlation functions can provide information about the reduction to the quantum-classical limit.

16.8 Simulation Schemes

In this section we give a few technical details concerning the implementation of the development presented above needed to simulate quantum-classical dynamics and evaluate expectation values and time correlation functions.

To simulate quantum-classical evolution one must evaluate the action of the time evolution operator $\exp(i\mathcal{L}t)$ on a dynamical variable. There are many ways to do this. While we have stressed the use of an adiabatic basis, the choice of basis is often determined by the physical application under consideration. One may implement schemes that treat the operator J responsible for non-adiabatic transitions and bath momentum changes either exactly [21,23] or approximately by momentum jump approximations [10,21,22,23]. Finally, a variety of schemes may be devised for the computation of the evolution operator. [10,21,22,19,23,24,25]

To illustrate the application of the formalism and techniques described here to a many-body system, we consider the calculation of the average value of an observable \hat{B}_W at time t for the spin-boson system [23],

$$\overline{B_W(t)} = \sum_{\alpha\alpha'} \int dRdP B_W^{\alpha\alpha'}(t) \rho_W^{\alpha'\alpha}(R, P, 0), \quad (16.93)$$

where $\hat{\rho}_W(R, P, 0)$ is the initial value of the density matrix. We have expressed the expectation value in an adiabatic basis. In order to compute such average values, one must sample initial phase space points and quantum states from a weight determined by $\rho_W^{\alpha'\alpha}(R, P, 0)$ and evolve $B_W^{\alpha\alpha'}(t)$ according to quantum-classical dynamics. We have already shown in (16.66) how to express the time evolution of $B_W^{\alpha\alpha'}(t)$ in terms of a sequence of surface-hopping trajectories. Consequently, a solution for $\overline{B_W(t)}$ in terms of surface-hopping trajectories may be found using a hybrid Monte Carlo-Molecular Dynamics scheme that combines a numerical implementation of (16.66) with sampling according to $\rho_W^{\alpha'\alpha}(R, P, 0)$. [21,22,23]

In order to complete the calculation of the n^{th} order term in (16.66) we must carry out the sums over the discrete s_k indices and perform the multiple time integrals. Not all the sequences $\{s_0, \dots, s_n\}$ contribute since only a subset \mathcal{S} of the sequences is physically permissible. The allowed sequences have $s_k - s_{k+1} = \pm\ell\mathcal{N}$ or $s_k - s_{k+1} = \pm\ell$ for $1 \leq \ell < \mathcal{N}$. One can either count all the elements of \mathcal{S} contributing to (16.66) or estimate the sum through a Monte Carlo sampling of the summand over \mathcal{S} . [23]

The time integrals that must be computed are of the type

$$\mathcal{I} = \int_0^{t_0} dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n f(t_1, t_2, \dots, t_n), \quad (16.94)$$

and simplest Monte Carlo method that can be used for their evaluation involves uniform sampling. Alternatively, sampling based on least-discrepancy sequences or other more sophisticated sampling schemes may be used. [23]

16.8.1 Spin–Boson Model

The spin-boson model is one of the most widely studied model systems because it provides a simple description of many physical phenomena and is amenable to analysis. [26,27,28,29] It has served as testing ground for many simulation methods [30,31] and it is in this spirit which we study it here. The spin-boson model describes a two-level system, with states $\{|\uparrow\rangle, |\downarrow\rangle\}$, bilinearly coupled to a harmonic bath of N oscillators with masses M_j and frequencies ω_j , and has hamiltonian

$$\hat{H} = -\hbar\Omega\hat{\sigma}_x + \sum_{j=1}^N \left(\frac{\hat{P}_j^2}{2M_j} + \frac{1}{2}M_j\omega_j^2\hat{R}_j^2 - c_j\hat{R}_j\hat{\sigma}_z \right). \quad (16.95)$$

The energy gap of the isolated two-state system is $2\hbar\Omega$ and $\hat{\sigma}_x$ and $\hat{\sigma}_z$ are Pauli matrices. The coupling constants c_j and frequencies ω_j in this hamiltonian have been taken from Makri and Thompson [31],

$$c_j = \sqrt{\xi\hbar\omega_0 M_j \omega_j}, \quad \omega_j = -\omega_c \ln \left(1 - j \frac{\omega_0}{\omega_c} \right), \quad (16.96)$$

where $\omega_0 = (\omega_c/N) (1 - \exp(-\omega_{max}/\omega_c))$. The spectral density is characterized by the Kondo parameter ξ and frequency ω_c . The parameter ω_{max} is a cut-off frequency. With this parameter choice we have a model of an infinite bath with Ohmic spectral density in terms of a finite number of oscillators.

Taking the partial Wigner transform[9] over the bath degrees of freedom, the hamiltonian becomes

$$\begin{aligned} \hat{H}_W &= -\hbar\Omega\hat{\sigma}_x + \sum_{j=1}^N \left(\frac{P_j^2}{2M_j} + \frac{1}{2}M_j\omega_j^2 R_j^2 - c_j R_j \hat{\sigma}_z \right), \\ &= \sum_{j=1}^N \frac{P_j^2}{2M_j} - \hbar\Omega\hat{\sigma}_x + V_b(R) + \hbar\gamma(R)\hat{\sigma}_z. \end{aligned} \quad (16.97)$$

which depends on the classical phase space coordinates (R, P) and the spin degrees of freedom. The last three terms in the second line of (16.97) have

the same form (16.52) with

$$V_b(R) = \sum_{j=1}^N \frac{1}{2} M_j \omega_j^2 \hat{R}_j^2, \quad (16.98)$$

and $\gamma(R) = -\sum_{j=1}^N c_j R_j$. The adiabatic energies $E_\alpha(R)$, ($\alpha = 1, 2$) and corresponding eigenvectors have the same forms as (16.54) and (16.55).

The results will be presented in dimensionless variables, $R'_j = (M_j \omega_c / \hbar)^{1/2} R_j$ and $P'_j = (\hbar M_j \omega_c)^{-1/2} P_j$, and we henceforth drop the primes on the variables and assume that these dimensionless variables are used.

We have assumed that the density matrix at $t = 0$ is uncorrelated so that the subsystem is in state $|\uparrow\rangle$ and bath is in thermal equilibrium,

$$\hat{\rho}(0) = \hat{\rho}_s(0) Z_b^{-1} e^{-\beta \hat{H}_b}, \quad \hat{\rho}_s(0) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad (16.99)$$

where Z_b is the bath partition function. The partial Wigner transform of this initial density operator is [9]

$$\hat{\rho}_W(R, P, 0) = \hat{\rho}_s(0) \rho_{bW}(R, P), \quad (16.100)$$

where

$$\rho_{bW}(R, P) = \prod_{i=1}^N \frac{\tanh(\beta \omega_i / 2)}{\pi} \exp \left[-\frac{2 \tanh(\beta \omega_i / 2)}{\omega_i} \left(\frac{P_i^2}{2} + \frac{\omega_i^2 R_i^2}{2} \right) \right]. \quad (16.101)$$

The time evolution of the difference in population between the ground and excited states (expectation value of $\hat{\sigma}_z$)

$$\overline{\hat{\sigma}_z(t)} = \text{Tr}' \int dR dP \hat{\sigma}_z(t) \hat{\rho}_W(R, P, 0) = \sum_{\alpha\alpha'} \int dR dP \sigma_z^{\alpha\alpha'}(t) \rho_W^{\alpha'\alpha}(R, P, 0), \quad (16.102)$$

was computed for this ten-oscillator spin-boson model using the surface-hopping scheme discussed in Sects. 16.4 and 16.5. The calculations were carried out using both the exact form of the J operator as well as its representation in terms of the momentum jump approximation. [23]

The results obtained using the quantum-classical surface-hopping scheme [23] are compared below with the known numerically exact results [31] for this model. Figure 16.4 (left panel) is a plot of $\overline{\hat{\sigma}_z(t)}$ versus time computed using the surface-hopping algorithm including up to four ($n = 4$) non-adiabatic transitions along with the influence functional results for a Kondo parameter of $\xi = 0.007$. One can see that for the time interval shown our results for $n = 4$ are in complete accord with those of Makri and Thompson. [31]

It is instructive to examine the individual adiabatic and non-adiabatic contributions to the surface-hopping solution as a function of time. These

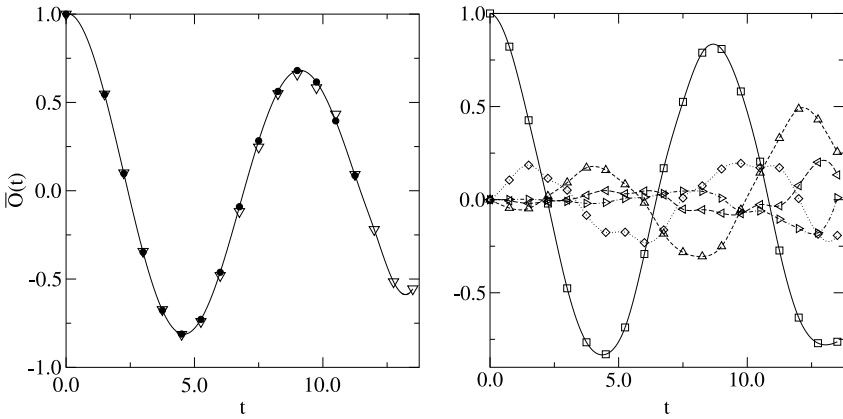


Fig. 16.4. Left panel: $\overline{\sigma_z(t)}$ versus time for $\xi = 0.007$. Influence functional results (filled circle) (see text), surface-hopping results for n up to 4 (down triangle). Right panel: Contributions to $\overline{\sigma_z(t)}$ versus time for $\xi = 0.007$. Individual contributions are: adiabatic dynamics, $n = 0$, (square); non-adiabatic contributions, $n = 1$, (diamond); $n = 2$, (up triangle); $n = 3$, (left triangle); $n = 4$, (right triangle).

results are shown in Fig. 16.4 (right panel). While the coupling to the bath is quite weak and adiabatic dynamics dominates the structure for this value of the Kondo parameter, the dynamics has non-negligible non-adiabatic components. The convergence of the surface-hopping results may also be gauged from an examination of this figure: the third and fourth order contributions are small over the entire time interval studied. Additional details of the simulation method as well as results for stronger coupling may be found in Ref. [23].

16.9 Conclusion

Quantum-classical dynamics leads to viable methods for studying many-body systems where the quantum character of certain degrees of freedom must be taken into account. In this chapter we have presented a formulation of quantum-classical dynamics that accounts for the coupled evolution of quantum and classical subsystems and have given a description of quantum-classical dynamics in terms of an ensemble of “surface-hopping” trajectories. In addition, the nonequilibrium statistical mechanics of such systems was constructed and expressions for expectation values of dynamical variables and transport properties were derived. The statistical mechanical formulation provides formulas for time correlation functions and specifies how they must be evaluated in simulations. Consequently, the results presented here provide one with all the theoretical tools needed to evaluate observables in a quantum-classical world. Further developments of the topics presented here will likely center on extensions of the theory of quantum-classical dynamics,

the construction of efficient simulation schemes for quantum-classical evolution and applications to realistic systems with physical interest.

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