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Quantum-Classical Dynamics in a Classical Bath[†]

Raymond Kapral

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

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A derivation of the equations of motion for a mixed quantum-classical system in a dissipative environment is presented. The classical environment of the quantum subsystem is taken to be composed of two parts: the first part, termed the classical subsystem, comprises those degrees of freedom that are coupled directly to the quantum subsystem, whereas the second part is a large bath that is coupled only to the classical subsystem. Projection operator methods are used to eliminate the bath degrees of freedom yielding a dissipative equation of motion for the coupled quantum and classical subsystems.

1. Introduction

We consider the dynamics of a quantum system embedded in a classical dissipative environment. In many circumstances one is interested in situations where a certain number of degrees of freedom of a system must be treated quantum mechanically, whereas the remainder can be treated classically to a good degree of accuracy. If the classical environment is very large and its dynamics occurs on a rapid time scale, it may often be approximated by dissipative equations of motion.

Such a treatment of the environment is well known for a classical Brownian particle in a fluid and leads to the Langevin or Fokker−Planck equations of motion. The effects of the environment are contained in the friction coefficient and random force. The Fokker−Planck equation for the probability density $\rho(R, P, T)$ of finding the Brownian particle with momentum P and position R at time t is[1]

$$\frac{\partial \rho(R, P, t)}{\partial t} = -\left(\frac{P}{M}\cdot\frac{\partial}{\partial R} + \mathcal{F}(R)\cdot\frac{\partial}{\partial P}\right)\rho(t) + \zeta\frac{\partial}{\partial P}\left(\frac{P}{M} + k_{\mathrm{B}}T\frac{\partial}{\partial P}\right)\rho(t) \quad (1)$$

where ζ is the friction coefficient. The first two terms in this equation describe the streaming and motion in the mean potential with mean force $\mathcal{F}$, whereas the last term accounts for the dynamical effects of the environment on this motion.

Master and Fokker−Planck equations involving frictional dissipation have also been derived for open quantum systems.[2−5] In these approaches, the environmental degrees of freedom are often taken to be a harmonic bath bilinearly coupled to the subsystem of interest, and the equation of motion for the reduced density matrix takes the form[3]

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}(t)] - \frac{\zeta M k_{\mathrm{B}}T}{\hbar^2}[\hat{R}, [\hat{R}, \hat{\rho}(t)]] - \frac{i\zeta}{\hbar}\left[\hat{R}, \frac{1}{2}(\hat{P}\hat{\rho}(t) + \hat{\rho}(t)\hat{P})\right] \quad (2)$$

where $\hat{R}$ and $\hat{P}$ are the position and momentum operators of the degrees of freedom of the quantum subsystem to which the bath couples, and ζ is a friction coefficient related to the Ohmic spectral distribution of the harmonic bath.

These dissipative equations of motion have also been employed to study systems where a subset of nuclear degrees of freedom of the quantum subsystem are singled out as having a more classical character. When the remaining quantum degrees of freedom are treated in a Hilbert space representation and the nuclear degrees of freedom are Wigner transformed, one obtains the multistate quantum Fokker−Planck equation of Tanimura and Mukamel.[5,6]

At the outset, we restrict our considerations to systems that can be modeled as deterministic mixed quantum-classical systems in which a subset of quantum degrees of freedom is identified and the remainder of the degrees of freedom are assumed to have a classical-like character. The motivation for this decomposition arises both from the nature of the systems chosen for study, for example, systems with light and heavy particles and, on the practical side, from our inability to simulate fully quantum systems with many degrees of freedom that arise in condensed phase dynamics. Derivations of such mixed quantum-classical models from the full quantum mechanical equations of motion show that even the "classical" degrees of freedom acquire a quantum character and no longer follow Newton's equations of motion, since both types of degrees of freedom remain coupled.[7−14] Such deterministic mixed quantum-classical models form the basis for most of the surface-hopping schemes currently in use to treat nonadiabatic dynamics.[14−19] The mutual coupling between these subsystems is evident in the algorithms that account for the momentum changes in the classical degrees of freedom that accompany quantum transitions.

In this paper we consider the case where part of the deterministic classical environment may be described as a heat bath. More specifically, we focus on a system composed of a quantum subsystem embedded in a classical environment but imagine that the quantum degrees of freedom communicate directly only with a certain subset of the classical degrees of freedom. These special classical degrees of freedom are coupled to the much larger remainder of degrees of freedom of the environment which, themselves, do not couple directly to the quantum subsystem. The quantum and classical subsystems are fully coupled and, within the context of mixed quantum-classical

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dynamics, the quantum dynamics affects the classical evolution and vice versa.

One may easily imagine situations where such a description applies; for example, one may consider a proton or electron transfer process in a condensed phase. The solvent molecules in the immediate neighborhood of the transferring proton or electron will couple directly to its dynamics, but the distant solvent molecules will act like a dissipative environment. Other applications of this type, where electronic degrees of freedom are coupled to specific nuclear degrees of freedom which are themselves coupled to a dissipative bath, are the domain of descriptions by the multistate quantum Fokker−Planck equation.[5,6]

We carry out a reduction of the deterministic mixed quantum-classical equations of motion to dissipative equations where a portion of the classical environmental dynamics is described by a Fokker−Planck operator with a specific form for the friction tensor that depends on the remaining classical coordinates. In section 2 we specify the system described above in quantitative terms. Section 3 uses projection operator methods to obtain an equation of motion for the relevant degrees of freedom in the quantum subsystem and its directly coupled classical environment. This complicated equation is reduced to an evolution equation for a mixed quantum-classical system in a dissipative bath in section 4. The conclusions of the study are presented in section 5.

2. Mixed Quantum-Classical Dynamics

The starting point of the calculation is the equation of motion for a mixed quantum-classical system,[8−14]

$$\frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} = -\frac{i}{\hbar}[\hat{H}_W, \hat{\rho}_W(t)] + \frac{1}{2}(\{\hat{H}_W, \hat{\rho}_W(t)\} - \{\hat{\rho}_W(t), \hat{H}_W\}) = -i\hat{L}\ \hat{\rho}_W(R, P, t) \quad (3)$$

The last line in eq 3 defines the mixed quantum-classical Liouville operator, $\hat{L}$. This equation is obtained from the quantum mechanical Liouville equation for the entire system, assumed to be composed of a quantum subsystem of particles of mass m and a quantum environment of particles of mass M. A partial Wigner transform[20] over the quantum environmental degrees of freedom is performed while maintaining a Hilbert space description of the quantum subsystem. Finally, the small mass ratio or $\hbar$ limit is taken for the environmental degrees of freedom to obtain eq 3.[13] The partially Wigner transformed density matrix in the mixed quantum-classical limit, $\hat{\rho}_W(R, P, t)$, depends on the classical phase space coordinates of the environment, (R, P), but is still an abstract operator in the quantum subsystem Hilbert space. The partially Wigner-transformed Hamiltonian appearing in this equation is

$$\hat{H}_W(R, P) = \frac{P^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}_W(\hat{q}, R) \quad (4)$$

where $\hat{p}$ and $\hat{q}$ are the quantum subsystem momentum and position operators. The potential energy $\hat{V}_W(\hat{q}, R)$ includes all contributions arising from interactions within the quantum subsystem, its classical environment, and the coupling between them. We note that because coupling between the quantum and classical subsystems is retained in this equation, their evolutions are neither independent nor are they mean-field-like. For example, if this evolution equation is expressed in an adiabatic basis, the coupling terms are responsible both for quantum transitions among the adiabatic states and the momentum changes in the classical degrees of freedom that occur as a result of these transitions. Consequently, within this semiclassical approximation of the environment, they provide a means to study surface-hopping descriptions of nonadiabatic dynamics in a consistent manner.

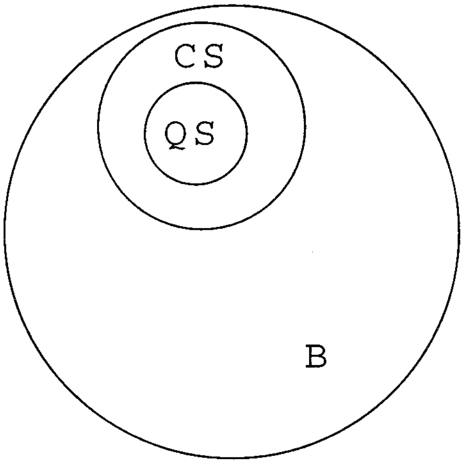

Figure 1. Schematic picture of a quantum subsystem (QS) coupled to a classical environment which is itself partitioned into a classical subsystem (CS) and a bath (B).

We now suppose that the environment is partitioned into two subsystems: a classical subsystem and bath with phase space coordinates (R', P') and (R'', P''), respectively. Thus, $(R, P) = (R', R'', P', P'') = (R', P')\ (R'', P'')$. The classical subsystem is coupled directly to the quantum subsystem; however, we assume the classical bath couples only to the classical subsystem. A schematic representation of such a system is depicted in Figure 1. Because several types of subsystems will figure in the presentation below, we shall consistently use the following terminology: the quantum degrees of freedom will be referred to as the *quantum subsystem*; the classical degrees of freedom that are directly coupled to the quantum subsystem will be called the *classical subsystem*. These two subsystems taken as a single dynamical system will be called the *mixed quantum-classical subsystem*. The remaining classical degrees of freedom form a *bath* for this mixed quantum-classical subsystem. Given these specifications, we may write the partially Wigner-transformed Hamiltonian in the form

$$\begin{aligned}\hat{H}_W\,(R, P) &= \frac{P'^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}'_W(\hat{q}, R') + \frac{P''^2}{2M} + V_B(R'') + V_{CB}(R', R'') \\ &\equiv \hat{H}'_W(R', P') + H''_B(R'', P'') + V_{CB}(R', R'') \\ &\equiv \hat{H}'_W\,(R', P') + H_0(R', R'', P'') \end{aligned} \quad (5)$$

Here we have defined $\hat{H}_W\ (R', P') = P'^2/2M + \hat{p}^2/2m + \hat{V}'_W(\hat{q}, R')$ as the Hamiltonian for the mixed quantum-classical subsystem, while $H_0(R', R'', P'') = H''_B(R'', P'') + V_{CB}(R', R'')$ is the Hamiltonian for the classical bath, $H''_B(R'', P'') = P'^2/2M + V_B(R'')$, in the potential field $V_{CB}(R', R'')$ of the fixed particles in the classical subsystem.

Using the decomposition in eq 5, the mixed quantum-classical Liouville operator for the entire system may be written as

$$i\hat{L} = i\hat{L}\,' + iL_0 \quad (6)$$

Here and in the sequel we use the following notation: if a quantity depends only on (R', P') or (R'', P'') it will have a prime or double prime, respectively. If a quantity depends on both types of classical phase space coordinates, it will lack primes.

3. Projection onto a Mixed Quantum-Classical Subsystem

We now project the bath (R'', P'') variables to obtain an equation of motion for the mixed quantum-classical subsystem. In particular, we seek an evolution equation for

$$\hat{\rho}'_W(t) \equiv \hat{\rho}'_W(R', P', t) = \int dR''dP''\ \hat{\rho}_W(R, P, t) \qquad (7)$$

We follow a procedure analogous to that used in the derivation of equations of motion for a quantum subsystem in a quantum environment,[21] but modified to account for the mixed quantum-classical description of the dynamics. To this end we define the projection operator $\mathcal{P}$ acting on any mixed quantum-classical operator $\hat{f}(R, P)$ as[22]

$$\mathcal{P}\ \hat{f}(R, P) = \frac{1}{2}(\hat{\rho}_{\rm ce}(\int {\rm d}R''{\rm d}P''\ \hat{f}) + (\int {\rm d}R''{\rm d}P''\ \hat{f})\ \hat{\rho}^{\dagger}_{\rm ce}) \qquad (8)$$

This symmetrized form is used because the observables and density matrix are operators in the quantum degrees of freedom.[21,23] The operator $\hat{\rho}_{\rm ce}$ is defined as follows: suppose $\hat{\rho}_{W,{\rm e}}$ is the canonical equilibrium density matrix for the entire system, the mixed quantum-classical subsystem plus the bath. It is stationary under the mixed quantum-classical evolution, $i\hat{\mathcal{L}}\ \hat{\rho}_{W,{\rm e}} = 0$. We let

$$\rho_{\rm ce}(R, P) = \rho_{W,{\rm e}}(R, P)(\rho'_{\rm c})^{-1}(R', P') \qquad (9)$$

where

$$\hat{\rho}'_{\rm c}(R', P') = \int {\rm d}R''\ {\rm d}P''\hat{\rho}_{W,{\rm e}}(R, P) \qquad (10)$$

Its adjoint is $\hat{\rho}^{\dagger}_{\rm ce} = (\hat{\rho}'_{\rm c})^{-1}\hat{\rho}_{W,{\rm e}}$. While $\hat{\rho}_{\rm ce}$ does not have a simple physical interpretation, its classical analogue is a conditional probability density familar in derivations of Langevin or Fokker−Planck equations in Brownian motion theory.[24] In the quantum case its use permits a clear classification of terms in the generalized equation of motion.[21]

Using the fact that

$$\int {\rm d}R''\ {\rm d}P''\ \mathcal{P}\ \hat{\rho}_W\,(R, P, t) = \hat{\rho}'_W(R', P', t) \qquad (11)$$

and standard projection operator algebra[25], we find

$$\begin{aligned}\frac{\partial\hat{\rho}'_W(t)}{\partial t} = &-\int {\rm d}R''\ {\rm d}P''\ i\mathcal{L}\ (\hat{\rho}_{\rm ce}, \rho'_W(t))_s + \\ &\int_0^t {\rm d}t'\int {\rm d}R''{\rm d}P''\ i\hat{\mathcal{L}}\ e^{-i\mathcal{Q}\mathcal{L}\,(t\,-\,t')}\ \mathcal{Q}\ i\hat{\mathcal{L}}\ (\hat{\rho}_{\rm ce}, \hat{\rho}'_W(t'))_{\rm s} - \\ &\int {\rm d}R''{\rm d}P''\ i\mathcal{L}\ e^{-i\mathcal{Q}\hat{\mathcal{L}}\,t}\mathcal{Q}\ \hat{\rho}_W(0) \\ \equiv\ &\mathcal{S}\,(t) + \mathcal{M}\,(t) + \mathcal{I}\,(t)\end{aligned} \qquad (12)$$

where we have defined the symbol $(\hat{A}, \hat{B})_s$ by

$$(\hat{A}, \hat{B})_{\rm s} = \frac{1}{2}(\hat{A}\hat{B} + \hat{B}\hat{A}^{\dagger}) \qquad (13)$$

for any operators $\hat{A}$ and $\hat{B}$. We shall continue to use this notation below in order to write equations in a compact form. In eq 12, $\mathcal{Q} = 1 - \mathcal{P}$ is the complement of $\mathcal{P}$ while the last line of this equation defines the streaming, $\mathcal{S}$, memory, $\mathcal{M}$, and initial condition, $\mathcal{I}$, terms. More explicit forms for the streaming and memory terms can be derived using the definitions of the operators given above.

Using the definition of the operator $i\mathcal{L}$, the streaming term may be evaluated to give

$$\mathcal{S}\,(t) = -i\hat{\mathcal{L}}'\hat{\rho}'_W(t) - \frac{\partial}{\partial P'}\cdot(\hat{\mathcal{F}}_{\rm ce}, \hat{\rho}'_W(t))_{\rm s} \qquad (14)$$

where $\hat{\mathcal{F}}_{\rm ce} = -\langle {}^{\partial V_{\rm CB}}/_{\partial R'}\rangle_{\rm ce}$ and the angle brackets define an average over the bath degrees of freedom using $\hat{\rho}_{\rm ce}$,

$$\langle\cdots\rangle_{\rm ce} = \int {\rm d}R''\ {\rm d}P''\cdots\hat{\rho}_{\rm ce} \qquad (15)$$

The $-i\hat{\mathcal{L}}'_W(t)$ contribution to the streaming term describes the time evolution of the mixed quantum-classical subsystem isolated from the bath. This term has exactly the form of the mixed quantum-classical Liouville equation with the classical environment restricted to the classical subsystem degrees of freedom, (R', P'). The second term yields an additional "force" term to the evolution arising from the classical subsystem-bath coupling potential energy averaged over the bath degrees of freedom with $\hat{\rho}_{\rm ce}$. The form of this force-like quantity is complicated because $\hat{\rho}_{\rm ce}$ depends on both R' and P' and is still an operator in the quantum degrees of freedom.

The computation of the memory term entails the evaluation of $\mathcal{Q}\ i\hat{\mathcal{L}}\ (\hat{\rho}_{\rm ce}, \hat{\rho}'_W(t))_{\rm s}$. Once again, using the definitions of the operators given above, we may write this term more explicitly as

$$\begin{aligned}\mathcal{Q}\ i\hat{\mathcal{L}}\ (\hat{\rho}_{\rm ce}, \hat{\rho}'_W(t))_{\rm s} = &\ \mathcal{Q}\ F_{\rm CB}\cdot\frac{\partial}{\partial P'}(\hat{\rho}_{\rm ce}, \hat{\rho}'_W)_{\rm s} - \\ &\frac{P'}{M}\cdot\frac{\partial}{\partial R'}(\hat{\rho}_{\rm ce}, \hat{\rho}'_W)_{\rm s} + \left(F_{\rm CB}, \frac{\partial}{\partial P'}(\hat{\rho}_{\rm ce}, \hat{\rho}'_W)_{\rm s}\right)_{\rm s} + \\ &\frac{1}{2}(\hat{\rho}_{\rm ce}, \{\hat{V}'_{\rm QC}, \hat{\rho}'_W\}')_{\rm s} - \frac{1}{2}(\hat{\rho}_{\rm ce}, \{\hat{\rho}'_{\rm W}, \hat{V}'_{\rm QC}\}')_{\rm s} + \\ &\frac{1}{2}([\hat{H}'_{\rm W}, \hat{\rho}_{\rm ce}]\hat{\rho}'_W + \hat{\rho}'_W[\hat{H}'_{\rm W}, \hat{\rho}^{\dagger}_{\rm ce}]) - (\{H_0, \hat{\rho}_{\rm ce}\}'', \hat{\rho}'_W)_{\rm s}\end{aligned} \qquad (16)$$

Here the force due to the coupling potential is $F_{\rm CB} = -\partial V_{\rm CB}/\partial R'$. The form of this term arises from the operator character and full phase space dependence of $\hat{\rho}_{\rm ce}$. Even thought the bath couples only to the classical subsystem degrees of freedom, and not directly to the quantum operators, the subsystem dynamics is complicated due to the indirect coupling arising from these effects.

Inserting this expression into the memory term in eq 12 and simplifying the action of the first $i\hat{\mathcal{L}}$ operator we find

$$\begin{aligned}\mathcal{M}\,(t) = &\int_0^{\rm t}{\rm d}t'\frac{\partial}{\partial P'}\int {\rm d}R''\ {\rm d}P''\ F_{\rm CB}{\rm e}^{-i\mathcal{Q}\hat{\mathcal{L}}(t-t')} \\ &\left(\mathcal{Q}\ F_{\rm CB}\cdot\frac{\partial}{\partial P'}(\hat{\rho}_{\rm ce}, \hat{\rho}'_W(t'))_{\rm s} - \frac{P'}{M}\cdot\frac{\partial}{\partial R'}(\hat{\rho}_{\rm ce}, \hat{\rho}'_W(t'))_{\rm s} + \right. \\ &\left(F_{\rm CB}, \frac{\partial}{\partial P'}(\hat{\rho}_{\rm ce}, \hat{\rho}'_W(t'))_{\rm s}\right)_{\rm s} + \frac{1}{2}(\hat{\rho}_{\rm ce}, \{\hat{V}'_{\rm QC}, \hat{\rho}'_W(t')\}')_{\rm s} - \\ &\frac{1}{2}\,(\hat{\rho}_{\rm ce}, \{\hat{\rho}'_W(t'), \hat{V}'_{\rm QC}\}')_{\rm s} + \frac{1}{2}\,([\hat{H}'_W, \hat{\rho}_{\rm ce}]\hat{\rho}'_W(t') + \\ &\hat{\rho}'_W(t')[\hat{H}'_W, \hat{\rho}^{\dagger}_{\rm ce}]) - (\{H_0, \hat{\rho}_{\rm ce}\}'', \hat{\rho}'_W(t'))_{\rm s}\end{aligned} \qquad (17)$$

The memory term accounts for dynamical contributions coming from the coupling to the bath. As it stands, this equation is not very useful. Below we shall consider the approximations needed to convert it into a useful form and examine the content of the resulting dissipative dynamics.

4. Dissipative Mixed Quantum-Classical Evolution

The projection operator formalism provided an equation of motion for the mixed quantum-classical subsystem; however, this equation is not closed because it depends on the initial condition of the density matrix of the entire system, $\hat{\rho}_W(0)$. To proceed further, we assume that the characteristic relaxation time of the bath, τ_B, is much shorter than that of the mixed quantum-classical subsystem. If we consider the evolution for times long compared to τ_B, the initial condition term $\mathcal{I}(t)$ will decay to zero and may be neglected because its projected evolution occurs on the bath time scale.

To simplify the streaming and memory terms, we first examine the structure of $\hat{\rho}_{ce}$ in more detail. To this end we write the equilibrium density matrix for the entire system, $\hat{\rho}_{W,e}$ as

$$\hat{\rho}_{W,e} = \hat{\rho}_{W,e}(R', P')\rho_0(R, P) + \hat{\chi}_{W,e} \tag{18}$$

where $\hat{\rho}_{W,e}(R', P')$ is the equilibrium density for the isolated mixed quantum-classical system satisfying

$$i\hat{\mathcal{L}}'\hat{\rho}'_{W,e}(R', P') = 0 \tag{19}$$

and $\rho_0(R,P)$ is the bath equilibrium density conditional upon a fixed configuration of the classical particles in the mixed quantum-classical subsystem satisfying

$$i\mathcal{L}_0\rho_0(R, P) = 0 \tag{20}$$

The bath conditional density is given by

$$\rho_0(R, P) = Z_0(R')^{-1}\mathrm{e}^{-\beta H_0} \tag{21}$$

where

$$Z_0(R') = \int \mathrm{d}R''\, \mathrm{d}P''\, \mathrm{e}^{-\beta H_0} \tag{22}$$

Because the equilibrium density satisfies $i\hat{\mathcal{L}}\hat{\rho}_{W,e} = 0$, we may solve for the correction $\hat{\chi}_{W,e}$ in the form

$$\hat{\chi}_{W,e} = (i\hat{\mathcal{L}})^{-1}F_{CB}\left(\left(\frac{\partial}{\partial P'} + \beta\frac{P'}{M}\right)\hat{\rho}'_{W,e}\right)\rho_0 \tag{23}$$

To lowest order in either $\hbar$ or, if an adiabatic basis is used, to lowest order in the nonadiabatic coupling, $\hat{\rho}'_{W,e} = Z^{-1}\exp(-\beta H'_W)$,[26] and in this approximation $\hat{\chi}_{W,e} = 0$ because of the action of $(\partial/\partial P' + \beta P'/M)$ on $\hat{\rho}'_{W,e}$. Consequently, we may replace $\hat{\rho}_{W,e}$ by the first term in eq 18 to a good approximation.

In this approximation we have $\hat{\rho}_{ce} = \rho_0$, which is no longer an operator in the quantum degrees of freedom. As a result we have simply $(\hat{\rho}_{ce}, \hat{\rho}'_W(t))_s = \rho_0\hat{\rho}'_W(t)$. The streaming term may now be written as

$$\mathcal{S}(t) = -i\hat{\mathcal{L}}'\hat{\rho}'_W - \mathcal{F}\cdot\frac{\partial}{\partial P'}\hat{\rho}'_W \tag{24}$$

with the mean force $\mathcal{F}$ defined by $\mathcal{F} = -\langle\partial V_{CB}/\partial R'\rangle_0$. Using the fact that

$$\frac{\partial\rho_0(R, P)}{\partial R'} = \beta(F_{CB} - \mathcal{F})\rho_0(R, P) = \beta\delta F_{CB}\rho_0(R, P) \tag{25}$$

where we have defined $\delta F_{CB}(R'', R') = F_{CB}(R'', R') - \mathcal{F}(R')$, we may write the memory term in the simpler form

$$\mathcal{M}(t) = \int_0^t \mathrm{d}t'\, \frac{\partial}{\partial P'}\langle\delta F_{CB}\mathrm{e}^{-i\mathcal{Q}_0\hat{\mathcal{L}}(t-t')}\delta F_{CB}\rangle_0\left(\frac{\partial}{\partial P'} + \beta\frac{P'}{M}\right)\hat{\rho}'_W(t') \tag{26}$$

where $\mathcal{Q}_0 = 1 - \mathcal{P}_0$ with $\mathcal{P}_0\hat{f} = \rho_0 \int \mathrm{d}R''\, \mathrm{d}P''\, \hat{f}$. The angle brackets $\langle\cdots\rangle_0$ denote an equilibrium average over ρ_0:

$$\langle\cdots\rangle_0 = \int \mathrm{d}R''\, \mathrm{d}P''\cdots\rho_0 \tag{27}$$

The evolution operator is $i\hat{\mathcal{L}} = i\hat{\mathcal{L}}' + i\mathcal{L}_0$. In accord with our assumption that bath dynamical variables decay rapidly, we may approximately write the force autocorrelation function in this expression in terms of the fixed particle force autocorrelation function, so that

$$\mathcal{M}(t) = \int_0^t \mathrm{d}t'\, \frac{\partial}{\partial P'}\cdot\mathcal{K}(t - t')\mathrm{e}^{-i\hat{\mathcal{L}}'(t-t')}\cdot\left(\frac{\partial}{\partial P'} + \beta\frac{P'}{M}\right)\hat{\rho}'_W(t') \tag{28}$$

where

$$\mathcal{K}(t) = \langle\delta F_{CB}\mathrm{e}^{-i\mathcal{L}_0 t}\delta F_{CB}\rangle_0 \tag{29}$$

Because this correlation will decay on the bath time scale, for times long compared to the bath relaxation time we may replace the correlation function by its delta function limit and write it in terms of the fixed particle friction tensor $\zeta(R')$ as

$$\mathcal{K}(t) \approx 2\delta(t)\int_0^\infty \mathrm{d}t\, \mathcal{K}(t) \equiv 2\beta^{-1}\zeta(R')\delta(t) \tag{30}$$

Thus, the memory kernel takes the form

$$\mathcal{M}(t) = \zeta(R') : \frac{\partial}{\partial P'}\left(\frac{P'}{M} + k_B T\frac{\partial}{\partial P'}\right)\hat{\rho}'_W(t) \tag{31}$$

Putting these results together we obtain a dissipative equation for the mixed quantum-classical evolution

$$\frac{\partial\hat{\rho}'_W(t)}{\partial t} = -i\hat{\mathcal{L}}'\hat{\rho}'_W - \mathcal{F}\cdot\frac{\partial}{\partial P'}\hat{\rho}'_W + \zeta(R') : \frac{\partial}{\partial P'}\left(\frac{P'}{M} + k_B T\frac{\partial}{\partial P'}\right)\hat{\rho}'_W(t) \tag{32}$$

The effects of the dynamics of the bath degrees of freedom on the mixed quantum-classical subsystem take the form of a Fokker–Planck-like operator that depends on the fixed particle friction tensor. Because of the dependence of the friction tensor on the configuration space coordinates of the classical subsystem, this expression is difficult to deal with, although forms for the R' dependence of $\zeta(R')$ are known when the interactions are computed in hydrodynamics.[27] If the configuration dependence of the friction tensor is neglected we have

$$\frac{\partial\hat{\rho}'_W(t)}{\partial t} = -i\hat{\mathcal{L}}'\hat{\rho}'_W - \mathcal{F}\cdot\frac{\partial}{\partial P'}\hat{\rho}'_W - i\hat{\mathcal{L}}'_{FP}\hat{\rho}'_W(t) \tag{33}$$

where $\mathcal{L}'_{FP}$ is the usual Fokker–Planck operator

$$-i\mathcal{L}'_{FP} = \zeta\frac{\partial}{\partial P'}\cdot\left(\frac{P'}{M} + k_B T\frac{\partial}{\partial P'}\right) \tag{34}$$

This equation is equivalent to the multistate quantum Fokker–Planck equation[2] in the semiclassical limit.

5. Conclusion

Dissipative equations of motion for open quantum systems have been derived by many authors and continue to be a topic of active investigation.[2]

Equations 32 and 33 are the main results of this paper. Several features of their derivation and structure merit additional comment. Given the semiclassical description of the environment that is adopted from the outset of the calculation, no further restrictions on the form of the bath or its interactions with the classical subsystem are made. In particular, the bath need not be a collection of harmonic oscillators bilinearly coupled to the system of interest. Projection operator methods must be applied with care when extracting subsystem dynamics from the dynamics of the full quantum system. The choice of projection operator determines whether initial condition effects on the evolution can be neglected after a transient time; it also determines the balance between the contributions of the streaming and memory terms in the weak coupling limit of the final subsystem evolution equation.[21] Similar considerations enter in the present projection operator formalism because the operator character of the relevant dynamical quantities survives in the semiclassical limit. In addition to these considerations, the present projection operators have been constructed to yield the correct structure of the multiparticle Brownian motion of the classical subsystem.

The result of this analysis is eq 32, which retains the full semiclassical structure of the quantum and classical subsystem dynamics, including their mutual coupling, but accounts for the interaction of bath with the classical subsystem through a multiparticle Fokker–Planck operator with a space-dependent friction coefficient that depends on the coordinates of the classical subsystem. An explicit expression is given for this quantity in terms of a fixed-particle bath force autocorrelation function analogous to that appearing in the Brownian motion theory for many particles. Multiparticle Brownian motion theory involves a number of subtle features; for example, it is only in the fixed-particle limit that the friction kernel takes a simple form and the Langevin and Fokker–Planck descriptions exhibit differences in general.[24] The fixed particle space-dependent friction kernel appearing in eq 32 may be computed from the purely classical evolution of the fixed-particle forces on the classical subsystem particles; thus, while the calculation is difficult, it is within the scope of current molecular dynamics simulation methods.

In the limit where there is a single relevant degree of freedom in the classical subsystem, or all configuration space dependence of the friction is suppressed, the friction tensor reduces to a constant scalar. The resulting equation is identical in form (when expressed in a quantum subsystem basis) to the semiclassical limit of the multistate quantum Fokker–Planck equation of Tanimura and Mukamel.[6]

The multiparticle Fokker–Planck description of the effects of the bath on the dynamics of a mixed quantum-classical system could prove useful in some circumstances. As noted earlier, one practical reason for adopting a description in terms of mixed quantum-classical dynamics, or variants that incorporate additional dispersion in the nuclear degrees of freedom, is that simulations of the dynamics of realistic many-body systems become feasible.[14–18,28–32] However, for very large systems one may still wish to single out some of the classcial degrees of freedom for a less detailed treatment. As an example, one may consider the dynamics of a proton or electron transfer in a large biomolecule in a solvent. Some aspects of the solvent dynamics can be captured by a friction tensor that depends on the configuration of the biopolymer. Such space-dependent frictional effects are familiar in polymer dynamics and arise from Oseen interactions among the polymer units.[33]

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References and Notes

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