ELSEVIER

Chemical Physics 268 (2001) 79–89

Chemical Physics

www.elsevier.nl/locate/chemphys

Subsystem dynamics in mixed quantum–classical systems

Mohamad Toutounji, Raymond Kapral *

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

Received 24 November 2000

Abstract

Starting with the mixed quantum–classical Liouville equation, projection operator methods are used to derive an equation of motion for a quantum subsystem dissipatively interacting with a classical bath. The resulting generalized master equation is reduced to the Lindblad equation after making a Markovian approximation in the weak coupling limit. The bath subsystem dynamics is studied from a similar perspective. For situations where the classical subsystem consists of few degrees of freedom, or one is interested in the nature of the modifications of its dynamics as a result of coupling to a large, rapidly relaxing quantum bath, a classical analog of the Lindblad equation is derived and discussed. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Dissipation and decoherence are ubiquitous phenomena and play important roles in the chemistry, physics, and biology of open quantum systems. Often a large system can be described adequately as a subsystem, consisting of one or few degrees of freedom, dissipatively interacting with its environment (thermal bath) comprising a large number of degrees of freedom. Examples include electron transfer in solution and in large biological molecules, vibrational relaxation of molecules in solution, impurity centers in solids and excitons in semiconductors coupled to acoustic or optical phonon modes, ultrafast optical spectra of chromophores in crystalline or glassy hosts and proton transfer and diffusion in liquids and solids.

The description of the dynamics of a subsystem interacting with a bath entails defining a reduced density operator in the Hilbert space of the subsystem. In principle, the reduced density operator can be obtained by evolving the complete density operator under the quantum Liouville equation and then tracing over the bath degrees of freedom. Since it is often impossible to follow the full dynamics of the subsystem plus bath, the development of microscopic quantum theories of subsystem dynamics, which include dissipative effects arising from interactions with the bath, has been a long-standing topic of research in chemistry and physics [1,2].

Over the past few decades methods have been developed to obtain equations of motion for subsystems interacting with an environment. A considerable amount of early research was devoted to the derivation of quantum master or Langevin equations, focusing mainly on subsystems weakly coupled to their environment [3–11]. Generalized master equations have been derived by Nakajima [12], and Zwanzig [13] using projection operator

---

* Corresponding author. Tel.: +1-416-978-6106; fax: +1-416-978-5325.

E-mail address: rkapral@gatto.chem.utoronto.ca (R. Kapral).

0301-0104/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0301-0104(01)00290-7

techniques. The choice of starting equation and projection operator are important in such derivations and these issues have been considered [14–18].

While classical dissipative systems can be modelled by the well-known Fokker–Planck or Langevin equations, the description of quantum dissipative dynamics remains a challenging problem [1,2,19–30]. Quantum master equations for strong subsystem–bath coupling have been constructed [2,29,31–33]; however, most approximate relaxation theories are derived under weak coupling conditions. The early theories of Block and Wangsness [34] and Fano [35], later extended by Redfield [36–43] grew out of applications of second order time-dependent perturbation theory to derive a set of relaxation equations. Redfield theory is widely used in chemical applications, especially for electron transfer, ultrafast optical spectroscopy and nuclear magnetic resonance spectroscopy. A number of other general models have been constructed [44–46]. Approaches that are based on the equation of motion that arises in the axiomatic semigroup theory of Lindblad [47], Gorini et al. [48] and other workers [2,28,29,49–52] are commonly employed.

These theories may be written in the general form

$$\frac{\partial \hat{\rho}_Q(t)}{\partial t} = -\frac{\mathrm{i}}{\hbar}[\hat{h}_\mathrm{s}, \hat{\rho}_Q(t)] + L_\mathrm{d}\hat{\rho}_Q(t), \tag{1}$$

where L_d is a damping operator and $\hat{h}_\mathrm{s}$ and $\hat{\rho}_Q(t)$ denote the Hamiltonian and the reduced density operator of the subsystem, respectively. An equation of motion of the Lindblad form where the damping operator is $L_\mathrm{d}\hat{\rho}_Q(t) = -\gamma[\hat{A}, [\hat{A}, \hat{\rho}_Q(t)]]$, generates a completely positive dynamics and is frequently used in applications. Here $\hat{A}$ is a Hermitian operator involved in the coupling of the subsystem to the bath.

In this paper we consider mixed quantum–classical systems where a subset of the degrees of freedom of the system is treated quantum mechanically and the remainder classically. The mixed quantum–classical Liouville equation for the entire system [53–61] [1] incorporates a detailed description of subsystem–bath interactions and is amenable to solution using surface-hopping schemes [62,63]. Starting with this full system evolution equation we project out the classical bath degrees of freedom to derive an equation of motion for the quantum subsystem. We then consider a weak coupling limit and reduce the non-Markovian subsystem evolution equation to Lindblad form. One of the advantages of this formulation is that for systems which can be accurately described by mixed quantum–classical dynamics the coefficients appearing in the Lindblad equation take the form of easily computed classical bath autocorrelation functions.

In the weak coupling limit the impact of the classical subsystem on the quantum subsystem dynamics is of interest and the effect of the quantum subsystem on the classical bath is neglected. If one considers the coupling between a large quantum subsystem and a few degree of freedom classical subsystem, or must account for the details of the coupling between the two subsystems, one may no longer ignore the perturbations on the classical subsystem. This is the case for most surface-hopping schemes for quantum rate processes in classical environments. To investigate this problem we reverse the roles of the quantum subsystem and classical bath and project out the quantum mechanical degrees of freedom and derive an equation of motion for a classical subsystem interacting with a quantum bath.

The outline of the paper is as follows: An exact reduced equation of motion for the quantum subsystem is derived in Section 2. The Lindblad equation is obtained after invoking a Markovian approximation in the weak coupling limit. The derivation of the classical subsystem reduced equation of motion is given in Section 3 and the conclusions of the study are presented in Section 4.

2. Quantum subsystem dynamics

We consider a quantum mechanical many-body system that is partitioned into a quantum subsystem and a quantum bath or environment. The time evolution of the density matrix $\hat{\rho}(t)$ of the entire

---

[1] In Ref. [57] the Poisson bracket terms in the evolution equation are not anti-symmetric.

system (subsystem plus bath) is governed by the quantum Liouville equation

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

where the Hamiltonian operator is given by

$$\hat{H} = \frac{\hat{P}^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}(\hat{q},\hat{Q}). \tag{3}$$

The quantum subsystem position and momentum operators are denoted by $\hat{q}$ and $\hat{p}$, respectively, while the analogous quantum bath operators are denoted by $\hat{Q}$ and $\hat{P}$. The total potential energy operator may be written as $\hat{V}(\hat{q},\hat{Q}) = \hat{V}_\mathrm{s}(\hat{q}) + \hat{V}_\mathrm{B}(\hat{Q}) + \hat{V}_\mathrm{c}(\hat{q},\hat{Q})$, where the subscripts s, B and c refer to the quantum subsystem, bath and coupling, respectively. We suppress vector notation to avoid cluttering the equations but system is understood to have many degrees of freedom.

Mixed quantum–classical descriptions of the dynamics are appropriate in many-body systems where the focus is on certain degrees of freedom whose quantum character cannot be neglected, while evolution of the remaining degrees of freedom, in the absence of interactions with the quantum subsystem, can be treated classically [53–61,64]. Such descriptions underlie the constructions of surface-hopping algorithms [62,63,65–76].

The evolution equation for a mixed quantum–classical system (quantum subsystem coupled to a classical bath) analyzed in this paper has been obtained in a number of earlier investigations [53–61]. One way to obtain this equation of motion is to first perform a partial Wigner transform [77] with respect to the bath coordinates, Q, retaining the quantum mechanical nature of the subsystem coordinates, and then expand the resulting equation to linear order in the mass ratio $(m/M)^{1/2}$ (or $\hbar$). The hats signify quantum mechanical operators while purely classical quantities lack hats. The resulting mixed quantum–classical Liouville equation is

$$\begin{aligned}\frac{\partial\hat{\rho}_\mathrm{W}(R,P,t)}{\partial t} &= -\frac{\mathrm{i}}{\hbar}[\hat{H}_\mathrm{W},\hat{\rho}_\mathrm{W}(t)] + \frac{1}{2}(\{\hat{H}_\mathrm{W},\hat{\rho}_\mathrm{W}(t)\} \\ &\quad - \{\hat{\rho}_\mathrm{W}(t),\hat{H}_\mathrm{W}\}) = -\mathrm{i}\mathscr{L}\hat{\rho}_\mathrm{W}(t).\end{aligned} \tag{4}$$

Here { , } is the Poisson bracket, $\hat{\rho}_\mathrm{W}(R,P,t)$ is the partially Wigner transformed density matrix in the mixed quantum–classical limit and R and P denote the set of classical bath phase space coordinates. The partial Wigner transform of the Hamiltonian is

$$\hat{H}_\mathrm{W}(R,P) = \frac{P^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}_\mathrm{W}(\hat{q},R), \tag{5}$$

with $\hat{V}_\mathrm{W}(\hat{q},R)$ the partially Wigner transformed total potential energy operator, which is the sum of the quantum subsystem, bath and subsystem–bath potential energies. Eq. (4) will form the starting point for our derivation of a quantum mechanical master equation in the limit of weak subsystem–bath interactions.

2.1. Projected dynamics

Suppose that one wishes to monitor the evolution of the quantum subsystem only and not the bath, or that one is constrained to do so, say, by the resolution limits of the measuring apparatus. For this purpose one may define a reduced density matrix $\hat{\rho}_Q(t)$ as

$$\hat{\rho}_Q(t) = \int \mathrm{d}R\,\mathrm{d}P\,\hat{\rho}_\mathrm{W}(R,P,t). \tag{6}$$

To derive an equation of motion for $\hat{\rho}_Q(t)$ we introduce an operator that projects onto the quantum part of the full density operator $\hat{\rho}_\mathrm{W}(R,P,t)$. In analogy with studies of fully quantum systems [16–18] we define a time-independent tetradic projection operator $\mathscr{P}$ such that

$$\begin{aligned}\mathscr{P}\hat{f}(R,P) = \frac{1}{2}\bigg(&\hat{\rho}_\mathrm{b}(R,P)\bigg(\int \mathrm{d}R\,\mathrm{d}P\hat{f}(R,P)\bigg) \\ &+ \bigg(\int \mathrm{d}R\,\mathrm{d}P\hat{f}(R,P)\bigg)\hat{\rho}_\mathrm{b}^\dagger(R,P)\bigg),\end{aligned} \tag{7}$$

where $\hat{\rho}_\mathrm{b}(R,P)$ is an equilibrium distribution function determined in the following way: when the entire mixed quantum–classical system is at equilibrium it is characterized by the equilibrium density matrix, $\hat{\rho}_\mathrm{W,e}$, which is obtained from the canonical equilibrium density matrix of the full quantum system by taking the mixed quantum–classical limit. It is stationary under mixed quantum–classical dynamics, $\mathrm{i}\hat{\mathscr{L}}\hat{\rho}_{\mathrm{W,e}} = 0$ [78]. Given $\hat{\rho}_{\mathrm{W,e}}$ defined in this way, we also define

$$\begin{aligned}\hat{\rho}_{\mathrm{b}}(R,P) &= \hat{\rho}_{\mathrm{W,e}}(R,P)\hat{\rho}_{\mathrm{s}}^{-1},\\ \hat{\rho}_{\mathrm{b}}^{\dagger}(R,P) &= \hat{\rho}_{\mathrm{s}}^{-1}\hat{\rho}_{\mathrm{W,e}}(R,P),\end{aligned} \tag{8}$$

where

$$\hat{\rho}_{\mathrm{s}} = \int \mathrm{d}R\,\mathrm{d}P\,\hat{\rho}_{\mathrm{W,e}}(R,P). \tag{9}$$

Here $\hat{\rho}_{\mathrm{s}}$ is the equilibrium density matrix for the quantum subsystem in equilibrium with the classical bath and $\hat{\rho}_{\mathrm{s}}^{-1}$ is its inverse. Coupling between the quantum subsystem and the large, rapidly relaxing classical bath is responsible for the relaxation to equilibrium of the quantum subsystem. In isolation it need not relax to equilibrium since it may comprise only a few degrees of freedom. From its definition, its form is obtained from the complete mixed quantum–classical equilibrium density matrix by integrating out the bath phase space coordinates. Given this definition of $\hat{\rho}_{\mathrm{s}}$, $\hat{\rho}_{\mathrm{b}}$ is the analog of a conditional bath equilibrium density. The densities are normalized so that

$$\int \mathrm{d}R\,\mathrm{d}P\,\hat{\rho}_{\mathrm{b}}(R,P) = 1. \tag{10}$$

The density $\hat{\rho}_{\mathrm{b}}$ is still an operator in the quantum degrees of freedom since both subsystems remain coupled even in thermal equilibrium. Later, we shall see that in the weak coupling limit $\hat{\rho}_{\mathrm{b}}$ may be replaced by the canonical equilibrium density for the isolated bath.

The complement of $\mathscr{P}$ is $\mathscr{Q} = \mathbb{1} - \mathscr{P}$, where $\mathbb{1}$ is a unit tetradic operator. The $\mathscr{P}$ and $\mathscr{Q}$ operators satisfy the projection operator properties: $\mathscr{P}^2 = \mathscr{P}$ and $\mathscr{Q}^2 = \mathscr{Q}$ (idempotency) and $\mathscr{P}\mathscr{Q} = \mathscr{Q}\mathscr{P} = \mathbf{0}$ (orthogonality). Using $\mathscr{P}$ and $\mathscr{Q}$, $\hat{\rho}_{\mathrm{W}}$ can be written as

$$\hat{\rho}_{\mathrm{W}} = \frac{1}{2}\left(\hat{\rho}_{\mathrm{b}}\hat{\rho}_{Q} + \hat{\rho}_{Q}\hat{\rho}_{\mathrm{b}}^{\dagger}\right) + \mathscr{Q}\hat{\rho}_{\mathrm{W}}. \tag{11}$$

We shall drop the (R,P) arguments when confusion is unlikely to arise.

Making use of the usual projection operator algebra [13] applied to Eq. (4) one obtains

$$\begin{aligned}\frac{\partial\rho_{Q}(t)}{\partial t} = &-\int \mathrm{d}R\,\mathrm{d}P\,\mathrm{i}\hat{\mathscr{L}}\frac{1}{2}\left(\hat{\rho}_{\mathrm{b}}\hat{\rho}_{Q}(t) + \hat{\rho}_{Q}(t)\hat{\rho}_{\mathrm{b}}^{\dagger}\right)\\ &+\int_0^t \mathrm{d}t' \int \mathrm{d}R\,\mathrm{d}P\,\mathrm{i}\hat{\mathscr{L}}\,\mathrm{e}^{-\mathrm{i}\mathscr{Q}\hat{\mathscr{L}}(t-t')}\\ &\times \mathscr{Q}\mathrm{i}\hat{\mathscr{L}}\frac{1}{2}\left(\hat{\rho}_{\mathrm{b}}\hat{\rho}_{Q}(t') + \hat{\rho}_{Q}(t')\hat{\rho}_{\mathrm{b}}^{\dagger}\right)\\ &-\int \mathrm{d}R\,\mathrm{d}P\,\mathrm{i}\hat{\mathscr{L}}\,\mathrm{e}^{-\mathrm{i}\mathscr{Q}\hat{\mathscr{L}}t}\mathscr{Q}\hat{\rho}_{\mathrm{W}}(0).\end{aligned} \tag{12}$$

This non-Markovian evolution equation describes the dynamics of an open quantum system in contact with a classical deterministic bath. The use of the symmetrized form of the projection operator defined in Eq. (7) in this derivation has a number of desirable features: the first term on the right-hand side of Eq. (12) (streaming term) is hermitian and is thus consistent with the time derivative of the hermitian reduced density matrix [16]. Furthermore, as argued by Romero-Rochin and coworkers [17,18] for fully quantum systems, it leads to a consistent partition into streaming and dissipative contributions (second term on right-hand side) where each term is zero at equilibrium.

In Eq. (12) $\hat{\rho}_{\mathrm{W}}(0)$ is the initial value of the mixed quantum–classical density matrix. Often product initial conditions are assumed, which take the form $\hat{\rho}_{\mathrm{W}}(0) = \hat{\rho}_{Q}(0)\rho_{\mathrm{B,e}}$ for our system, with $\rho_{\mathrm{B,e}}$ the canonical equilibrium density matrix for the bath in isolation from the quantum subsystem. For such initial conditions, with the projection operator defined in terms of $\rho_{\mathrm{B,e}}$ instead of $\hat{\rho}_{\mathrm{b}}$ and its adjoint, the last term on the right-hand side of Eq. (12) vanishes. However, such product initial conditions are difficult to achieve physically. The use of product initial condition terms and the implications for their use on the evolution of quantum subsystem dynamics has been considered in the literature. For example, it has been shown that product initial conditions lead to completely positive reduced dynamics, whereas correlated initial conditions need not do so [2,17,18,24,79]. In the present calculation, in parallel with analogous treatments for fully quantum systems [17,18], we make no assumption on the form of the initial condition. We assume that the isolated bath relaxes to equilibrium on some characteristic fast time scale τ_{B} and, with the choice of the projection operator (7), for times greater than τ_{B} the initial condition term will decay to zero [17,18]. We henceforth consider the time evolution of $\hat{\rho}_Q(t)$ for $t > \tau_{\mathrm{B}}$ where the initial condition term has decayed to zero.

The partially Wigner transformed Hamiltonian can be written as the sum of quantum subsystem, bath and interaction terms as

$$\begin{aligned}\hat{H}_{\mathrm{W}}(R,P) &= \frac{\hat{p}^2}{2m} + \hat{V}_{\mathrm{s}} + \frac{P^2}{2M} + V_{\mathrm{B}}(R) + \hat{V}_{\mathrm{c}}(\hat{q},R) \\ &= \hat{h}_{\mathrm{s}} + H_{\mathrm{B}}(R,P) + \hat{V}_{\mathrm{c}}(\hat{q},R).\end{aligned} \tag{13}$$

Using this decomposition of the Hamiltonian we can partition the Liouvillian $\hat{\mathscr{L}}$ in the form

$$\hat{\mathscr{L}} = \hat{\mathscr{L}}_{\mathrm{s}} + \mathscr{L}_{\mathrm{B}} + \hat{\mathscr{L}}', \tag{14}$$

with

$$\begin{aligned}&\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}} = \frac{\mathrm{i}}{\hbar}[\hat{h}_{\mathrm{s}},\ ], \quad \mathrm{i}\mathscr{L}_{\mathrm{B}} = -\{H_{\mathrm{B}},\ \}, \\ &\mathrm{i}\hat{\mathscr{L}}' = \frac{\mathrm{i}}{\hbar}[\hat{V}_{\mathrm{c}},\ ] - \frac{1}{2}\Big(\{\hat{V}_{\mathrm{c}},\ \} - \{\ ,\hat{V}_{\mathrm{c}}\}\Big),\end{aligned} \tag{15}$$

where $\hat{\mathscr{L}}_{\mathrm{s}}$, $\mathscr{L}_{\mathrm{B}}$, and $\hat{\mathscr{L}}'$ are subsystem, bath, and subsystem–bath interaction Liouvillians, respectively. Since $\mathscr{P}$ and $\hat{\mathscr{L}}_{\mathrm{s}}$ commute and $\mathscr{P}\mathrm{i}\mathscr{L}_{\mathrm{B}} = \mathrm{i}\mathscr{L}_{\mathrm{B}}\mathscr{P} = 0$, then Eq. (12) becomes

$$\begin{aligned}\frac{\partial\hat{\rho}_Q(t)}{\partial t} = &-\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}}\hat{\rho}_Q(t) - \int \mathrm{d}R\,\mathrm{d}P\,\mathrm{i}\hat{\mathscr{L}}' \\ &\times \frac{1}{2}\Big(\hat{\rho}_{\mathrm{b}}\hat{\rho}_Q(t) + \hat{\rho}_Q(t)\hat{\rho}_{\mathrm{b}}^{\dagger}\Big) \\ &+ \int_0^t \mathrm{d}t' \int \mathrm{d}R\,\mathrm{d}P\,\mathrm{i}\hat{\mathscr{L}}'\,\mathrm{e}^{-\mathrm{i}\mathscr{Q}\hat{\mathscr{L}}(t-t')} \\ &\times \bigg(\mathscr{Q}\mathrm{i}\hat{\mathscr{L}}'\frac{1}{2}\Big(\hat{\rho}_{\mathrm{b}}\hat{\rho}_Q(t') + \hat{\rho}_Q(t')\hat{\rho}_{\mathrm{b}}^{\dagger}\Big) \\ &- \frac{1}{2}\bigg((\mathrm{i}\hat{\mathscr{L}}'\hat{\rho}_{\mathrm{W,e}}) - \hat{\rho}_{\mathrm{b}}\Big(\int \mathrm{d}R\,\mathrm{d}P\,\mathrm{i}\hat{\mathscr{L}}'\hat{\rho}_{\mathrm{W,e}}\Big)\bigg) \\ &\times \hat{\rho}_{\mathrm{s}}^{-1}\hat{\rho}_Q(t') - \frac{1}{2}\hat{\rho}_Q(t')\hat{\rho}_{\mathrm{s}}^{-1}\bigg((\mathrm{i}\hat{\mathscr{L}}'\hat{\rho}_{\mathrm{W,e}}) \\ &- \Big(\int \mathrm{d}R\,\mathrm{d}P\,\mathrm{i}\hat{\mathscr{L}}'\hat{\rho}_{\mathrm{W,e}}\Big)\hat{\rho}_{\mathrm{b}}^{\dagger}\bigg)\bigg).\end{aligned} \tag{16}$$

In order to obtain the result in this form we used the fact that

$$(\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}} + \mathrm{i}\mathscr{L}_{\mathrm{B}})\hat{\rho}_{\mathrm{W,e}} = -\mathrm{i}\hat{\mathscr{L}}'\hat{\rho}_{\mathrm{W,e}} \tag{17}$$

and, using $\hat{\rho}_{\mathrm{W,e}} = \hat{\rho}_{\mathrm{b}}\hat{\rho}_{\mathrm{s}} = \hat{\rho}_{\mathrm{s}}\hat{\rho}_{\mathrm{b}}^{\dagger}$, that

$$\begin{aligned}&\hat{\rho}_{\mathrm{b}}\hat{\rho}_{\mathrm{s}}(\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}}\hat{\rho}_{\mathrm{s}}^{-1}) = -\hat{\rho}_{\mathrm{b}}(\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}}\hat{\rho}_{\mathrm{s}})\hat{\rho}_{\mathrm{s}}^{-1}, \\ &(\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}}\hat{\rho}_{\mathrm{s}}^{-1})\hat{\rho}_{\mathrm{s}}\hat{\rho}_{\mathrm{b}}^{\dagger} = -\hat{\rho}_{\mathrm{s}}^{-1}(\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}}\hat{\rho}_{\mathrm{s}})\hat{\rho}_{\mathrm{b}}^{\dagger}.\end{aligned} \tag{18}$$

The first two terms in Eq. (16) describe the reversible (streaming) motion of the quantum subsystem: the first term just specifies the quantum evolution of the isolated subsystem, while the second term accounts for the change in the reversible evolution due to the coupling to the classical bath. The memory term accounts for all relaxation effects in the quantum subsystem that arise from interactions with the bath. We shall analyze these terms in detail in the next section in the weak coupling limit where further insight into their structure will be obtained.

2.2. Weak coupling limit

Consider the dynamics generated by $\hat{\mathscr{L}} = \hat{\mathscr{L}}_{\mathrm{s}} + \mathscr{L}_{\mathrm{B}} + \lambda\hat{\mathscr{L}}'$, where λ is a dimensionless parameter measuring the strength of the subsystem–bath interaction. We wish to determine the evolution in the weak coupling limit.

We may expand the equilibrium density $\hat{\rho}_{\mathrm{W,e}}$ and the density operators $\hat{\rho}_{\mathrm{b}}$ and $\hat{\rho}_{\mathrm{s}}$ appearing in the generalized master equation in powers of this ordering parameter as

$$\hat{\rho}_{\mathrm{W,e}} = \hat{\rho}_{\mathrm{W,e}}^{(0)} + \lambda\hat{\rho}_{\mathrm{W,e}}^{(1)} + \cdots, \tag{19}$$

$$\hat{\rho}_{\mathrm{b}} = \hat{\rho}_{\mathrm{b}}^{(0)} + \lambda\hat{\rho}_{\mathrm{b}}^{(1)} + \cdots = \rho_{\mathrm{B,e}} + \lambda\hat{\rho}_{\mathrm{b}}^{(1)} + \cdots \tag{20}$$

and

$$\hat{\rho}_{\mathrm{s}} = \hat{\rho}_{\mathrm{s}}^{(0)} + \lambda\hat{\rho}_{\mathrm{s}}^{(1)} + \cdots = \hat{\rho}_{Q,\mathrm{e}} + \lambda\hat{\rho}_{\mathrm{s}}^{(1)} + \cdots, \tag{21}$$

respectively. In the $\lambda \to 0$ limit $\hat{\rho}_{\mathrm{b}} \to \rho_{\mathrm{B,e}}$, $\hat{\rho}_{\mathrm{s}} \to \hat{\rho}_{Q,\mathrm{e}}$ and $\hat{\rho}_{\mathrm{W,e}} \to \rho_{\mathrm{B,e}}\hat{\rho}_{Q,\mathrm{e}}$, where, in the canonical ensemble,

$$\rho_{\mathrm{B,e}} = Z_{\mathrm{B}}^{-1}\,\mathrm{e}^{-\beta H_{\mathrm{B}}}, \quad \hat{\rho}_{Q,\mathrm{e}} = Z_Q^{-1}\,\mathrm{e}^{-\beta\hat{h}_{\mathrm{s}}}, \tag{22}$$

with Z_{B} and Z_Q the classical bath and isolated subsystem partition functions, respectively. Also, in this limit the projection operator reduces to $\mathscr{P} \to \mathscr{P}_0$ where

$$\mathscr{P}_0\cdot = \rho_{\mathrm{B,e}}\int \mathrm{d}R\,\mathrm{d}P\,\cdot\,. \tag{23}$$

Expanding the streaming term and memory kernel in Eq. (16) to second order in λ yields

$$\begin{aligned}\frac{\partial\hat{\rho}_Q(t)}{\partial t} &= -\mathrm{i}(\hat{\mathscr{L}}_{\mathrm{s}} + \lambda\langle\hat{\mathscr{L}}'\rangle_{\mathrm{B}})\hat{\rho}_Q(t) - \lambda^2\int \mathrm{d}R\,\mathrm{d}P\,\mathrm{i}\hat{\mathscr{L}}' \\ &\quad\times\frac{1}{2}\left(\hat{\rho}_{\mathrm{b}}^{(1)}\hat{\rho}_Q(t) + \hat{\rho}_Q(t)\hat{\rho}_{\mathrm{b}}^{(1)\dagger}\right) \\ &\quad+\frac{\lambda^2}{2}\int_0^t \mathrm{d}t'\int \mathrm{d}R\,\mathrm{d}P\,\mathrm{i}\hat{\mathscr{L}}'\,\mathrm{e}^{-\mathrm{i}(\hat{\mathscr{L}}_{\mathrm{s}}+\mathscr{L}_{\mathrm{B}})(t-t')} \\ &\quad\times\left(\mathscr{Q}_0\mathrm{i}\hat{\mathscr{L}}'\rho_{\mathrm{b}}\hat{\rho}_Q(t') - \frac{1}{2}\left((\mathrm{i}\hat{\mathscr{L}}'\rho_{\mathrm{B,e}}\hat{\rho}_{Q,\mathrm{e}})\right.\right. \\ &\quad\left. - \rho_{\mathrm{B,e}}\left(\int \mathrm{d}R\,\mathrm{d}P\,\mathrm{i}\hat{\mathscr{L}}'\rho_{\mathrm{B,e}}\hat{\rho}_{Q,\mathrm{e}}\right)\right)\hat{\rho}_{Q,\mathrm{e}}^{-1}\hat{\rho}_Q(t') \\ &\quad-\frac{1}{2}\hat{\rho}_Q(t')\hat{\rho}_{Q,\mathrm{e}}^{-1}\left((\mathrm{i}\hat{\mathscr{L}}'\rho_{\mathrm{B,e}}\hat{\rho}_{Q,\mathrm{e}})\right. \\ &\quad\left.\left. - \rho_{\mathrm{B,e}}\left(\int \mathrm{d}R\,\mathrm{d}P\,\mathrm{i}\hat{\mathscr{L}}'\rho_{\mathrm{B,e}}\hat{\rho}_{Q,\mathrm{e}}\right)\right)\right). \end{aligned} \tag{24}$$

The angle brackets are defined as $\langle\cdot\rangle_{\mathrm{B}} = \int \mathrm{d}R\,\mathrm{d}P\cdots\rho_{\mathrm{B,e}}$.

We may write the interaction potential energy operator as the sum of products of $\hat{A}$ and $B(R)$, subsystem operators and bath functions, respectively, as

$$\hat{V}_{\mathrm{c}}(\hat{q},R) = \hat{A}\cdot B(R). \tag{25}$$

Using this form we may write Eq. (24) as

$$\begin{aligned}\frac{\partial\hat{\rho}_Q(t)}{\partial t} &= -\frac{\mathrm{i}}{\hbar}[\hat{h}_{\mathrm{s}} + \lambda\hat{A}\cdot\langle B\rangle_{\mathrm{B}}, \hat{\rho}_Q(t)] \\ &\quad-\frac{\lambda^2}{2}\int \mathrm{d}R\,\mathrm{d}P\,\frac{\mathrm{i}}{\hbar}B\cdot\left[\hat{A}, \left(\hat{\rho}_{\mathrm{b}}^{(1)}\hat{\rho}_Q(t)\right.\right. \\ &\quad\left.\left.+\hat{\rho}_Q(t)\hat{\rho}_{\mathrm{b}}^{(1)\dagger}\right)\right] + \frac{\lambda^2}{2}\int_0^t \mathrm{d}t'\left(\left(\frac{\mathrm{i}}{\hbar}\right)^2\right. \\ &\quad\times\langle\delta B(t-t')\delta B\rangle_{\mathrm{B}} : \left([\hat{A}, \mathrm{e}^{-\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}}(t-t')}[\hat{A}, \hat{\rho}_Q(t')]]\right. \\ &\quad\left.+[\hat{A}, \mathrm{e}^{-\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}}(t-t')}(\hat{C}^\dagger\hat{\rho}_Q(t') - \hat{\rho}_Q(t')\hat{C})]\right) \\ &\quad+\left(\frac{\mathrm{i}}{\hbar}\right)\langle\{\delta B(t-t'), \delta B\}\rangle_{\mathrm{B}} : \left(\left[\hat{A}, \mathrm{e}^{-\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}}(t-t')}\right.\right. \\ &\quad\left.\times\frac{1}{2}(\hat{A}\hat{\rho}_Q(t') + \hat{\rho}_Q(t')\hat{A})\right] \\ &\quad\left.\left.-\left[\hat{A}, \mathrm{e}^{-\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}}(t-t')}\frac{1}{2}(\hat{C}^\dagger\hat{\rho}_Q(t') + \hat{\rho}_Q(t')\hat{C})\right]\right)\right) \\ &\equiv -\mathrm{i}(\hat{\mathscr{L}}_{\mathrm{s}} + \lambda\langle\hat{\mathscr{L}}'\rangle_{\mathrm{B}})\hat{\rho}_Q(t) + \frac{\lambda^2}{2}(\mathscr{S}(t) + \mathscr{M}(t)). \end{aligned} \tag{26}$$

In this equation the ":" refers to second rank tensor contraction, which for the dyadic forms appearing in Eq. (26) and subsequent equations is defined by $ab : cd = \sum_{ij} a_i b_j c_j d_i$ for any vectors a, b, c and d with components labeled by indices i and j. The last line of Eq. (26) defines the $\mathcal{O}(\lambda^2)$ contributions to the streaming and memory terms. We have defined $\delta B = B - \langle B\rangle_{\mathrm{B}}$ and $\hat{C} = \hat{\rho}_{Q,\mathrm{e}}^{-1}\hat{A}\hat{\rho}_{Q,\mathrm{e}}$. The bath correlation functions are given by

$$\begin{aligned}\langle\delta B\delta B(t-t')\rangle_{\mathrm{B}} &= \int \mathrm{d}R\,\mathrm{d}P\,\delta B\,\mathrm{e}^{\mathrm{i}\mathscr{L}_{\mathrm{B}}(t-t')}\,\delta B\rho_{\mathrm{B,e}} \\ &= \int \mathrm{d}R\,\mathrm{d}P\,\delta B\,\delta B(t-t')\rho_{\mathrm{B,e}} \end{aligned} \tag{27}$$

and $\langle\{\delta B(t-t'), \delta B\}\rangle_{\mathrm{B}}$ is defined similarly.

This Born approximation introduces a separation of time scales; the relaxation time of the bath, τ_{B}, which is assumed to be fast, and a slower time scale, τ_{R}, corresponding to the relaxation time of the system induced by the weak interaction with the bath. The latter scale is of the order $\tau_{\mathrm{R}} \sim \lambda^{-2} \gg \tau_{\mathrm{B}}$. For τ_{B} to be short (fast bath relaxation), one needs to consider temperatures in such a way that τ_{R} is greater than the thermal time $\beta\hbar$. Therefore, the weak interaction approximation works best at high temperatures and noticeable deviations take place in the low temperature limit. In light of the above, the Born approximation restricts the application of the resulting generalized master equation to weakly damped systems with relaxation times, τ_{R}, that are large compared to the relevant time scales of the reversible motion [2,15,17,18,29,80].

If, as assumed, bath correlations decay much more rapidly than the time scale that characterizes the quantum subsystem dynamics, one may approximate the bath correlation functions in the memory integral by

$$\begin{aligned}\langle\delta B(t-t')\delta B\rangle_{\mathrm{B}} &\approx 2\left(\int_0^\infty \mathrm{d}t\langle\delta B(t)\delta B\rangle_{\mathrm{B}}\right) \\ &\quad\times\delta(t-t') \equiv 2\gamma_{\mathrm{B}}\delta(t-t'), \\ \langle\{\delta B(t-t'), \delta B\}\rangle_{\mathrm{B}} &\approx 2\left(\int_0^\infty \mathrm{d}t\langle\{\delta B(t), \delta B\}\rangle_{\mathrm{B}}\right) \\ &\quad\times\delta(t-t') \equiv 2\gamma'_{\mathrm{B}}\delta(t-t'). \end{aligned} \tag{28}$$

This Markovian approximation may be obtained by taking the half-sided Fourier transform of Eq. (26) and taking the limit of a rapid bath relaxation time compared to the other characteristic times in the system in the evaluation of the memory kernel. The autocorrelation function in the second line of Eq. (28) may be rewritten as $\langle\{\delta B(t), \delta B\}\rangle_{\mathrm{B}} = \beta\langle\delta B(t)\delta\dot{B}\rangle_{\mathrm{B}}$. Thus, this correlation function has the form of a cross correlation between a dynamical variable B and its flux. It will vanish at $t = 0$ and its time integral will generally be much small than the autocorrelation function of B in the first equation in Eq. (28).

We may use these results to compute the memory term, $\mathscr{M}(t)$. Invoking this Markovian approximation by using Eq. (28) in the memory function in Eq. (26), one finds

$$\begin{aligned}\mathscr{M}(t) = \frac{1}{2}\Bigg(\left(\frac{\mathrm{i}}{\hbar}\right)^2 \gamma_{\mathrm{B}} : \Big(\Big[\hat{A}, [\hat{A}, \hat{\rho}_Q(t)]\Big] \\ + \Big[\hat{A}, \Big(\hat{C}^\dagger \hat{\rho}_Q(t) - \hat{\rho}_Q(t)\hat{C}\Big)\Big]\Big) \\ - \left(\frac{\mathrm{i}}{\hbar}\right)\gamma'_{\mathrm{B}} : \Big(\Big[\hat{A}, \frac{1}{2}(\hat{A}\hat{\rho}_Q(t) + \hat{\rho}_Q(t)\hat{A})\Big] \\ - \Big[\hat{A}, \frac{1}{2}(\hat{C}^\dagger \hat{\rho}_Q(t) + \hat{\rho}_Q(t)\hat{C})\Big]\Big)\Bigg). \qquad (29)\end{aligned}$$

In order to compute the $\mathscr{O}(\lambda^2)$ contribution to the streaming term we must first evaluate $\hat{\rho}_{\mathrm{b}}^{(1)}$. Given the definition $\hat{\rho}_{\mathrm{b}} = \hat{\rho}_{\mathrm{W,e}}\hat{\rho}_{\mathrm{s}}^{-1}$ and the expansion in Eq. (20) we may write to $\mathscr{O}(\lambda^2)$,

$$\begin{aligned}\hat{\rho}_{\mathrm{b}} = \hat{\rho}_{\mathrm{W,e}}^{(0)}\hat{\rho}_{Q,\mathrm{e}}^{-1} + \lambda\Big(\hat{\rho}_{\mathrm{W,e}}^{(1)}\hat{\rho}_{Q,\mathrm{e}}^{-1} \\ - \hat{\rho}_{\mathrm{W,e}}^{(0)}\hat{\rho}_{Q,\mathrm{e}}^{-1}\hat{\rho}_{\mathrm{s}}^{(1)}\hat{\rho}_{Q,\mathrm{e}}^{-1}\Big) + \cdots, \qquad (30)\end{aligned}$$

with $\hat{\rho}_{\mathrm{s}}^{(1)} = \int \mathrm{d}R\,\mathrm{d}P\,\hat{\rho}_{\mathrm{W,e}}^{(1)}$. The calculation of $\hat{\rho}_{\mathrm{W,e}}^{(1)}$ can be accomplished by substituting the expansion in Eq. (19), into $\mathrm{i}\hat{\mathscr{L}}\hat{\rho}_{\mathrm{W,e}} = 0$ and collecting terms in λ. From this it follows that $\hat{\rho}_{\mathrm{W,e}}^{(0)} = \rho_{\mathrm{B,e}}\hat{\rho}_{Q,\mathrm{e}}$, as noted earlier, and

$$\begin{aligned}\hat{\rho}_{\mathrm{W,e}}^{(1)} &= -(\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}} + \mathrm{i}\mathscr{L}_{\mathrm{B}})^{-1}\mathrm{i}\hat{\mathscr{L}}'\hat{\rho}_{\mathrm{W,e}}^{(0)} \\ &= -\int_0^\infty \mathrm{d}t'\,\mathrm{e}^{-(\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}} + \mathrm{i}\mathscr{L}_{\mathrm{B}})t'}\mathrm{i}\hat{\mathscr{L}}'\hat{\rho}_{\mathrm{W,e}}^{(0)}. \qquad (31)\end{aligned}$$

Using the explicit form of the coupling operator $\mathrm{i}\hat{\mathscr{L}}'$ we may write this result as

$$\begin{aligned}\hat{\rho}_{\mathrm{W,e}}^{(1)} = -\int_0^\infty \mathrm{d}t'\,\mathrm{e}^{-\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}}t'}\Big(\frac{\mathrm{i}}{\hbar}[\hat{A}, \hat{\rho}_{Q,\mathrm{e}}] \cdot B(-t')\rho_{\mathrm{B,e}} \\ - \frac{1}{2}(\hat{A}\hat{\rho}_{Q,\mathrm{e}} + \hat{\rho}_{Q,\mathrm{e}}\hat{A}) \cdot \{B(-t'), \rho_{\mathrm{B,e}}\}\Big). \qquad (32)\end{aligned}$$

With this result and Eq. (30) we find

$$\begin{aligned}\hat{\rho}_{\mathrm{b}}^{(1)} = -\int_0^\infty \mathrm{d}t'\,\mathrm{e}^{-\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}}t'}\Big(\frac{\mathrm{i}}{\hbar}[\hat{A}, \hat{\rho}_{Q,\mathrm{e}}]\hat{\rho}_{Q,\mathrm{e}}^{-1} \cdot \delta B(-t')\rho_{\mathrm{B,e}} \\ - \frac{1}{2}(\hat{A}\hat{\rho}_{Q,\mathrm{e}} + \hat{\rho}_{Q,\mathrm{e}}\hat{A})\hat{\rho}_{Q,\mathrm{e}}^{-1} \cdot \{B(-t'), \rho_{\mathrm{B,e}}\}\Big), \qquad (33)\end{aligned}$$

with a similar expression for $\hat{\rho}_{\mathrm{B}}^{(1)\dagger}$,

$$\begin{aligned}\hat{\rho}_{\mathrm{b}}^{(1)\dagger} = -\int_0^\infty \mathrm{d}t'\,\mathrm{e}^{-\mathrm{i}\hat{\mathscr{L}}_{\mathrm{s}}t'}\Big(\frac{\mathrm{i}}{\hbar}\hat{\rho}_{Q,\mathrm{e}}^{-1}[\hat{A}, \hat{\rho}_{Q,\mathrm{e}}] \cdot \delta B(-t')\rho_{\mathrm{B,e}} \\ - \frac{1}{2}\hat{\rho}_{Q,\mathrm{e}}^{-1}(\hat{A}\hat{\rho}_{Q,\mathrm{e}} + \hat{\rho}_{Q,\mathrm{e}}\hat{A}) \cdot \{B(-t'), \rho_{\mathrm{B,e}}\}\Big). \qquad (34)\end{aligned}$$

Substituting these results into the expression for $\mathscr{S}(t)$ and envoking rapid decay of bath correlations (Eq. (28)) we have

$$\begin{aligned}\mathscr{S}(t) = \frac{1}{2}\Bigg(\left(\frac{\mathrm{i}}{\hbar}\right)^2 \gamma_{\mathrm{B}} : \Big(\Big[\hat{A}, [\hat{A}, \hat{\rho}_Q(t')]\Big] \\ - \Big[\hat{A}, \Big(\hat{C}^\dagger \hat{\rho}_Q(t) - \hat{\rho}_Q(t)\hat{C}\Big)\Big]\Big) \\ - \left(\frac{\mathrm{i}}{\hbar}\right)\gamma'_{\mathrm{B}} : \Big(\Big[\hat{A}, \frac{1}{2}(\hat{A}\hat{\rho}_Q(t') + \hat{\rho}_Q(t)\hat{A})\Big] \\ + \Big[\hat{A}, \frac{1}{2}(\hat{C}^\dagger \hat{\rho}_Q(t) + \hat{\rho}_Q(t)\hat{C})\Big]\Big)\Bigg). \qquad (35)\end{aligned}$$

Collecting these results, Eq. (26) becomes

$$\begin{aligned}\frac{\partial\hat{\rho}_Q(t)}{\partial t} = -\frac{\mathrm{i}}{\hbar}[\hat{h}_{\mathrm{s}} + \hat{A} \cdot \langle B\rangle_{\mathrm{B}}, \hat{\rho}_Q(t)] \\ + \left(\frac{\mathrm{i}}{\hbar}\right)^2 \gamma_{\mathrm{B}} : \Big[\hat{A}, [\hat{A}, \hat{\rho}_Q(t)]\Big] \\ - \frac{\mathrm{i}}{\hbar}\gamma'_{\mathrm{B}} : \Big[\hat{A}, \frac{1}{2}\Big(\hat{A}\hat{\rho}_Q(t) + \hat{\rho}_Q(t)\hat{A}\Big)\Big], \qquad (36)\end{aligned}$$

where we have set the ordering parameter λ to unity. Eq. (36) is compatible with the form of Lindblad equation [2,29,47,81]. The first term represents the reversible motion of the subsystem, whereas the second and the third terms represent the Markovian dynamics induced by the weak subsystem–bath interaction.

3. The bath master equation

The mixed quantum–classical evolution equation accounts for the mutual interactions between the quantum subsystem and classical bath. Consequently, not only is the quantum subsystem dynamics affected by interaction with the bath, as manifested by the dissipative contributions in the Lindblad equation derived above, but the dynamics of the bath will also be changed by interaction with the quantum subsystem. This interaction enters in surface-hopping schemes for non-adiabatic dynamics [62,63,65–75] and will be especially important when the classical "bath" has few degrees of freedom or when a few degrees of freedom are directly coupled to the quantum subsystem.

The coupling between the quantum and classical subsystems has the effect of destroying a Newtonian representation of the bath dynamics. In order to examine the nature of this breakdown we consider an extreme case where a small classical system is coupled to a large, rapidly relaxing quantum bath. The analysis of this case is carried out by projecting the full mixed quantum–classical density matrix on to the subspace of the classical degrees of freedom.

We seek an equation for

$$\rho_{\mathrm{B}}(R,P,t) = \mathrm{Tr}'\,\hat{\rho}_{\mathrm{W}}(R,P,t), \tag{37}$$

where Tr$'$ denotes a trace over the quantum subsystem degrees of freedom. Using the projection operator $\mathscr{P}\hat{f} = \hat{\rho}_q \mathrm{Tr}'\hat{f}$, where $\hat{\rho}_q = \hat{\rho}_{\mathrm{W,e}} \times (\mathrm{Tr}'\hat{\rho}_{\mathrm{W,e}})^{-1}$, the mixed quantum–classical Liouville equation may be reduced to

$$\begin{aligned}\frac{\partial \rho_{\mathrm{B}}(t)}{\partial t} = {} & -\mathrm{Tr}'\,\mathrm{i}\hat{\mathscr{L}}\hat{\rho}_q\rho_{\mathrm{B}}(R,P,t) \\ & + \int_0^t \mathrm{d}t'\,\mathrm{Tr}'\,\mathrm{i}\hat{\mathscr{L}}\,\mathrm{e}^{-\mathrm{i}\hat{\mathscr{Q}}\hat{\mathscr{L}}(t-t')}\,\hat{\mathscr{Q}}\mathrm{i}\hat{\mathscr{L}}\hat{\rho}_q\rho_{\mathrm{B}}(R,P,t') \\ & - \mathrm{Tr}'\,\mathrm{i}\hat{\mathscr{L}}\mathrm{e}^{-\mathrm{i}\hat{\mathscr{Q}}\hat{\mathscr{L}}t}\,\hat{\mathscr{Q}}\hat{\rho}_{\mathrm{W}}(0).\end{aligned} \tag{38}$$

Simplifying the expressions in Eq. (38) using the definition of the Liouville operator yields

$$\begin{aligned}\frac{\partial \rho_{\mathrm{B}}(t)}{\partial t} = {} & \{\langle\hat{H}_{\mathrm{W}}\rangle_q, \rho_{\mathrm{B}}(t)\} - \frac{\mathrm{i}}{\hbar}\int_0^t \mathrm{d}t'\,\mathrm{Tr}'\Big\{\hat{H}_{\mathrm{W}}, \mathrm{e}^{-\mathrm{i}\hat{\mathscr{Q}}\hat{\mathscr{L}}(t-t')} \\ & \times [\hat{H}_{\mathrm{W}}, \hat{\rho}_q]\rho_{\mathrm{B}}(t')\Big\} \\ & + \frac{1}{2}\int_0^t \mathrm{d}t'\,\mathrm{Tr}'\Big\{\hat{H}_{\mathrm{W}}, \mathrm{e}^{-\mathrm{i}\hat{\mathscr{Q}}\hat{\mathscr{L}}(t-t')} \\ & \times\Big(\{\delta\hat{H}_{\mathrm{W}}, \rho_{\mathrm{B}}(t')\}\hat{\rho}_q + \hat{\rho}_q\{\delta\hat{H}_{\mathrm{W}}, \rho_{\mathrm{B}}(t')\}\Big)\Big\} \\ & - \mathrm{Tr}'\,\mathrm{i}\hat{\mathscr{L}}\,\mathrm{e}^{-\mathrm{i}\hat{\mathscr{Q}}\hat{\mathscr{L}}t}\,\hat{\mathscr{Q}}\hat{\rho}_{\mathrm{W}}(0),\end{aligned} \tag{39}$$

where $\langle\hat{H}_{\mathrm{W}}\rangle_q = \mathrm{Tr}'\,\hat{H}_{\mathrm{W}}\hat{\rho}_q$. Using the forms of $\hat{H}_{\mathrm{W}}$ and $\hat{V}_{\mathrm{c}}(\hat{q},R)$ one can write Eq. (39) more explicitly as

$$\begin{aligned}\frac{\partial \rho_{\mathrm{B}}(t)}{\partial t} = {} & \{H_{\mathrm{B}} + \langle\hat{A}\rangle_q\cdot B, \rho_{\mathrm{B}}(t)\} \\ & - \frac{\mathrm{i}}{\hbar}\int_0^t \mathrm{d}t'\,\mathrm{Tr}'\Big\{H_{\mathrm{B}} + \hat{A}\cdot B, \mathrm{e}^{-\mathrm{i}\hat{\mathscr{Q}}\hat{\mathscr{L}}(t-t')} \\ & \times\Big([\hat{A}, \hat{\rho}_q]\cdot B\rho_{\mathrm{B}}(t')\Big)\Big\} \\ & + \frac{1}{2}\int_0^t \mathrm{d}t'\,\mathrm{Tr}'\Big\{H_{\mathrm{B}} + \hat{A}\cdot B, \mathrm{e}^{-\mathrm{i}\hat{\mathscr{Q}}\hat{\mathscr{L}}(t-t')} \\ & \times\Big(\{B, \rho_{\mathrm{B}}(t')\}\cdot[\delta\hat{A}, \hat{\rho}_q]_+\Big)\Big\} \\ & - \mathrm{Tr}'\,\mathrm{i}\hat{\mathscr{L}}\,\mathrm{e}^{-\mathrm{i}\hat{\mathscr{Q}}\hat{\mathscr{L}}t}\,\hat{\mathscr{Q}}\hat{\rho}_{\mathrm{W}}(0),\end{aligned} \tag{40}$$

where the anticommutator $[\hat{A}_1, \hat{A}_2]_+ = \hat{A}_1\hat{A}_2 + \hat{A}_2\hat{A}_1$, for any operators $\hat{A}_1$ and $\hat{A}_2$.

We may take the Markovian limit of this equation by introducing a weak coupling approximation that is the analog of that used in the quantum subsystem case. We suppose that the quantum subsystem relaxation time τ_Q is much more rapid that the characteristic relaxation time of the classical subsystem. Then for times greater than τ_Q we may drop the initial condition term. The equilibrium density operator $\hat{\rho}_q$ that enters in the definition of the projection operator may be replaced by the canonical equilibrium density for the quantum subsystem $\hat{\rho}_{Q,\mathrm{e}} = \mathrm{e}^{-\beta\hat{h}_{\mathrm{s}}}/\mathrm{Tr}'(\mathrm{e}^{-\beta\hat{h}_{\mathrm{s}}})$. In this weak coupling limit we have

$$
\begin{aligned}
\frac{\partial \rho_{\mathrm{B}}(t)}{\partial t} = {} & \{H_{\mathrm{B}} + \langle \hat{A} \rangle_Q \cdot B, \rho_{\mathrm{B}}(t)\} - \frac{\mathrm{i}}{\hbar} \int_0^t \mathrm{d}t' \\
& \times \langle [\hat{A}, \hat{A}(t-t')] \rangle_Q : \left\{ B, \mathrm{e}^{-\mathrm{i}\mathscr{L}_{\mathrm{B}}(t-t')} \times B \rho_{\mathrm{B}}(t') \right\} \\
& + \frac{1}{2} \int_0^t \mathrm{d}t' \langle [\delta\hat{A}, \delta\hat{A}(t-t')]_+ \rangle_Q : \left\{ B, \mathrm{e}^{-\mathrm{i}\mathscr{L}_{\mathrm{B}}(t-t')} \right. \\
& \left. \times \{B, \rho_{\mathrm{B}}(t')\} \right\}, \qquad (41)
\end{aligned}
$$

where $\langle \hat{f} \rangle_Q = \mathrm{Tr}' \hat{f} \hat{\rho}_{Q,\mathrm{e}}$.

Given the rapid relaxation of the quantum bath, we may approximate the quantum bath equilibrium correlation functions by their delta function forms as

$$
\begin{aligned}
& -\frac{\mathrm{i}}{\hbar} \langle [\hat{A}, \hat{A}(t-t')] \rangle_Q \approx 2\nu'_Q \delta(t-t'), \\
& \frac{1}{2} \langle [\delta\hat{A}, \delta\hat{A}(t-t')]_+ \rangle_Q \approx 2\nu_Q \delta(t-t').
\end{aligned} \qquad (42)
$$

Eq. (41) reduces to

$$
\begin{aligned}
\frac{\partial \rho_{\mathrm{B}}(t)}{\partial t} = {} & \{H_{\mathrm{B}} + \langle \hat{A} \rangle_Q \cdot B, \rho_{\mathrm{B}}(t)\} + \nu'_Q \\
& : \{B, B\rho_{\mathrm{B}}(t')\} + \nu_Q : \{B, \{B, \rho_{\mathrm{B}}(t')\}\}. \qquad (43)
\end{aligned}
$$

This is the classical analog of the Lindblad equation appropriate for the description of a classical system coupled to a large quantum mechanical dissipative bath whose relaxation time is much faster than that of the classical subsystem. The first term on the right-hand side just specifies the usual classical Newtonian evolution of the bath degrees of freedom in the presence of an additional potential contribution arising from the coupling to the quantum bath, averaged over a quantum equilibrium distribution. The third term has the form of a double Poisson bracket, analogous to the double commutator in the Lindblad equation. This term provides a dissipative contribution to the classical dynamics and prevents a description of the dynamics in terms of simple Newtonian trajectories. Since the coupling function $B(R)$ depends only on the classical coordinates, this dissipative term has the form of a diffusion operator in momentum space.

One may solve this equation using the techniques developed for the study of surface-hopping dynamics [62,63] and represent the solution in terms of an ensemble of stochastic trajectory segments to simulate the momentum space diffusion.

4. Conclusion

Lindblad-type equations are widely used to investigate the dynamics open quantum systems and have been derived using a variety of approaches. It is well known that equations of this type result from a weak coupling limit of the exact subsystem evolution equations and this restricts their domain of applicability [2]. So it is not surprising that our reduction of the Liouville equation for a mixed quantum–classical system to an equation of motion for the quantum subsystem alone has this form. However, we have established the conditions under which the reduction applies for this mixed quantum–classical case. In addition, the phenomenological coefficients that appear in the Lindblad equation have precise definitions in terms of easily-computed purely classical bath correlation functions.

For a classical subsystem coupled to a large, rapidly relaxing quantum bath, a similar reduction of the mixed quantum–classical Liouville equation yielded a classical evolution equation, analogous to the Lindblad equation, that provides insight into the nature of the modification of the bath dynamics as a result of coupling to a quantum system. The bath evolution loses its Newtonian character and can be represented in terms of stochastic classical trajectory segments with diffusion in momentum space arising from the dissipative double Poisson bracket term in the evolution equation.

The main motivations for considering mixed quantum–classical dynamics are that this approximation to the full quantum dynamics is expected to be appropriate in many instances and the full dynamics can be simulated using surface-hopping and other techniques. Thus, although the approximate subsystem equations have limited applicability, the results in this paper provide one with the tools to assess the utility of such equations for realistic many-body systems.

Acknowledgements

This work was supported in part by a grant from the Natural Sciences and Engineering Research Council of Canada. Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the ACS, for partial support of this research.

References

[1] E.B. Davis, Quantum Theory of Open Systems, Academic Press, London, 1976.
[2] U. Weiss, Quantum Dissipative Systems, World Scientific, Singapore, 1999.
[3] P.G. Bergmann, J.L. Lebowitz, Phys. Rev. 99 (1955) 578.
[4] L. Van Hove, Physica 23 (1957) 441.
[5] E.W. Montroll, Lectures in Theoretical Physics 3 (1960) 221.
[6] I. Prigogine, P. Resibois, Physica 27 (1961) 541.
[7] P.N. Argyres, P.L. Kelley, Phys. Rev. A 134 (1964) 98.
[8] R. Bausch, Z. Phys. 193 (1966) 246.
[9] G. Emch, G.L. Swell, J. Math. Phys. 9 (1968) 946.
[10] J.M. Blatt, Prog. Theor. Phys. 22 (1969) 499.
[11] H. Haken, Rev. Mod. Phys. 47 (1975) 67.
[12] S. Nakajima, Prog. Theor. Phys. 20 (1958) 948.
[13] R. Zwanzig, Lectures in Theoretical Physics 3 (1960) 106.
[14] B. Robertson, W.C. Mitchell, J. Math. Phys. 12 (1971) 563.
[15] W. Peier, Physica 57 (1972) 565.
[16] K. Kassner, Phys. Rev. A 36 (1987) 5381.
[17] V. Romero-Rochin, I. Oppenheim, Physica A 155 (1989) 52.
[18] V. Romero-Rochin, A. Orsky, I. Oppenheim, Physica A 156 (1989) 244.
[19] H. Dekker, Phys. Rep. 80 (1980) 1.
[20] C.W. Gardiner, M.J. Collett, Phys. Rev. A 31 (1985) 3761.
[21] W.H. Zurek, Phys. Today, 44 (10) (1991) 36 and references therein.
[22] W.H. Zurek, Phys. Rev. D 24 (1981) 1516.
[23] W.H. Zurek, Phys. Rev. D 26 (1982) 1862.
[24] P. Pechukas, Phys. Rev. Lett. 73 (1994) 1060.
[25] H.P. Breuer, F. Petruccione, Phys. Rev. Lett. 74 (1995) 3788.
[26] O.W. Ford, R.F. O'Connell, Phys. Rev. Lett. 77 (1996) 798.
[27] W.B. Davis, M.R. Wasielewski, R. Kosloff, M.A. Ratner, J. Phys. Chem. A 102 (1998) 9360.
[28] R. Kosloff, M.A. Ratner, W.B. Davis, J. Chem. Phys. 106 (1997) 7036.
[29] R. Karrlein, H. Grabert, Phys. Rev. E 55 (1997) 153.
[30] A.O. Caldeira, A.J. Leggett, Physica A 121 (1983) 587.
[31] D.E. Makarov, N. Makri, Chem. Phys. Lett. 221 (1994) 482.
[32] D.E. Makarov, N. Makri, J. Chem. Phys. 102 (1995) 4600.
[33] B.L. Hu, J. Paz, Y. Zhang, Phys. Rev. D 45 (1992) 2843.
[34] R.K. Wangsness, F. Block, Phys. Rev. 89 (1953) 728.
[35] U. Fano, Rev. Mod. Phys. 29 (1957) 74.
[36] A. Redfield, in: J. Waugh (Ed.), Advances in Magnetic Resonance, vol. 1, Academic Press, New York, 1965.
[37] K. Blum, Density Matrix Theory and Applications, Plenum Press, New York, 1981.
[38] R. Silbey, R.A. Harris, J. Chem. Phys. 80 (1985) 2615.
[39] R. Silbey, R.A. Harris, J. Phys. Chem. 93 (1989) 7062.
[40] W.T. Pollard, R.A. Friesner, J. Chem. Phys. 100 (1994) 5054.
[41] B.B. Laird, J.L. Skinner, J. Chem. Phys. 94 (1991) 4391.
[42] B.B. Laird, J.L. Skinner, J. Chem. Phys. 94 (1991) 4405.
[43] K. Lindenberg, B.J. West, The Nonequilibrium Statistical Mechanics of Open and Closed Systems, VCH, New York, 1990.
[44] S. Mukamel, Principles of Nonlinear Optical Spectroscopy, Oxford University Press, Oxford, 1995.
[45] K. Allinger, B. Carmeli, D. Chandler, J. Chem. Phys. 84 (1993) 435.
[46] D.W. Oxtoby, Annu. Rev. Phys. Chem. 32 (1981) 77.
[47] G. Lindblad, Commun. Math. Phys. 48 (1976) 119.
[48] V. Gorini, A. Kossakowski, E.C.G. Sudarshan, J. Math. Phys. 17 (1976) 821.
[49] R. Aliki, K. Lendi, Quantum Dynamical Semigroups and Applications, Lecture Notes in Physics, vol. 286, Springer, Berlin, 1987 and references therein.
[50] A. Tameshtit, J.E. Sipe, Phys. Rev. Lett 77 (1996) 2600.
[51] M.R. Gallis, Phys. Rev. A 48 (1993) 1028.
[52] B.V. Bondarev, Phys. Lett. A 153 (1991) 326.
[53] I.V. Aleksandrov, Z. Naturforsch. 36a (1981) 902.
[54] W. Boucher, J. Traschen, Phys. Rev. D 37 (1988) 3522.
[55] W.Y. Zhang, R. Balescu, J. Plasma Phys. 40 (1988) 199.
[56] R. Balescu, W.Y. Zhang, J. Plasma Phys. 40 (1988) 215.
[57] A. Anderson, Phys. Rev. Lett. 74 (1995) 621.
[58] O.V. Prezhdo, V.V. Kisil, Phys. Rev. A 56 (1997) 162.
[59] C.C. Martens, J.-Y. Fang, J. Chem. Phys. 106 (1996) 4918.
[60] A. Donoso, C.C. Martens, J. Phys. Chem. 102 (1998) 4291.
[61] R. Kapral, G. Ciccotti, J. Chem. Phys. 110 (1999) 8919.
[62] S. Nielsen, R. Kapral, G. Ciccotti, J. Chem. Phys. 112 (2000) 6543.
[63] S. Nielsen, R. Kapral, G. Ciccotti, J. Stat. Phys. 101 (2000) 225.
[64] P. Pechukas, Phys. Rev. 181 (1969) 166–174.
[65] J.C. Tully, J. Chem. Phys. 93 (1990) 1061.
[66] J.C. Tully, Int. J. Quant. Chem. 25 (1991) 299.
[67] D.S. Sholl, J.C. Tully, J. Chem. Phys. 109 (1998) 7702.
[68] S. Hammes-Schiffer, J.C. Tully, J. Chem. Phys. 101 (1994) 4657.
[69] L. Xiao, D.F. Coker, J. Chem. Phys. 100 (1994) 8646.
[70] D.F. Coker, L. Xiao, J. Chem. Phys. 102 (1995) 496.
[71] H.S. Mei, D.F. Coker, J. Chem. Phys. 104 (1996) 4755.
[72] F. Webster, P.J. Rossky, P.A. Friesner, Comp. Phys. Commun. 63 (1991) 494.

[73] F. Webster, E.T. Wang, P.J. Rossky, P.A. Friesner, J. Chem. Phys. 100 (1994) 483.
[74] M. ben-Nun, T.J. Martinez, J. Chem. Phys. 108 (1998) 7244.
[75] M. ben-Nun, T.J. Martinez, J. Chem. Phys. 112 (2000) 6113.
[76] C. Wan, J. Schofield, J. Chem. Phys. 113 (2000) 7047.
[77] E. Wigner, Phys. Rev. 40 (1932) 479.
[78] S. Nielsen, R. Kapral, G. Ciccotti, Statistical mechanics of mixed quantum–classical systems, in preparation.
[79] A. Suarez, R. Silbey, I. Oppenheim, J. Chem. Phys. 97 (1992) 5101.
[80] T. Dittrich, P. Hanggi, G.-L. Ingold, B. Kramer, G. Schon, W. Zwerger, Wiley, Berlin, 1997.
[81] S. Gao, Phys. Rev. Lett. 79 (1997) 3101.