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# Quantum Dynamics in Almost Classical Environments

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**Abstract.** In this chapter we discuss approaches to solving quantum dynamics in the condensed phase based on the quantum-classical Liouville method. Several representations of the quantum-classical Liouville equation (QCLE) of motion have been investigated and subsequently simulated. We discuss the benefits and limitations of these approaches. By making further approximations to the QCLE, we show that standard approaches to this problem, i.e., mean-field and surface-hopping methods, can be derived. The computation of transport coefficients, such as chemical rate constants, represent an important class of problems where the QCL method is applicable. We present a general quantum-classical expression for a time-dependent transport coefficient which incorporates the full system's initial quantum equilibrium structure. As an example of the formalism, the computation of a reaction rate coefficient for a simple reactive model is presented. These results are compared to illuminate the similarities and differences between various approaches discussed in this chapter.

## 1 Introduction

The elucidation of real-time quantum molecular dynamics remains a challenging and fascinating problem of importance in physics, chemistry and biology. Current experimental techniques are beginning to allow one to probe dynamical events in previously unexplored regimes; for example, sub-femtosecond to picosecond time scales in condensed media. In order to describe such dynamics from both theoretical and numerical points of view, one is faced with a task that becomes exponentially more difficult with the number of degrees of freedom. For small systems, with roughly ten to one hundred particles, full quantum simulations can be carried out but at a large computational cost. In order to describe larger, more complicated systems we are forced to make approximations to full quantum mechanics in order to obtain dynamical in-

formation. Indeed, in some instances a full quantum mechanical treatment is probably unnecessary. This is the case if one is interested in a small subset of system degrees of freedom whose quantum mechanical character is important, while the remainder of the system (environment) may be approximated by classical mechanics [1–3]. For example, a decomposition of this type is appropriate for a subsystem composed of light particles, like electrons or protons, interacting with a solvent of heavy molecules.

In this paper we restrict our consideration of such systems to descriptions based on quantum-classical Liouville dynamics [3]. We begin with a discussion of this equation and its properties. The quantum-classical Liouville equation describes the dynamics of a quantum subsystem coupled to an almost classical environment. The term “almost” used here and in the title refers to the fact that while the environment evolves by the classical equations of motion in the absence of coupling to the quantum subsystem, in the presence of coupling a description in terms of single classical trajectories is no longer possible. After this introduction, we outline a number of ways one may construct numerical solutions to this equation by projecting it onto different bases. In certain limits, making approximations, quantum-classical Liouville dynamics may be reduced to some commonly-used mixed quantum-classical approaches, in particular, mean field and surface hopping schemes, as well as the Wigner-Liouville approach. Quantum time correlation functions, which are related to transport properties, are then discussed. As an example, the computation of quantum chemical reaction rates is described in the penultimate section. Some perspectives on the work are given in conclusions.

## 2 Quantum-Classical Liouville Dynamics

The time evolution of a quantum mechanical system is governed by the quantum Liouville-von Neumann equation,

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

where  $\hat{\rho}(t)$  is the density matrix,  $\hat{H}$  is the total Hamiltonian, and the square brackets denote the commutator. Quantum-classical Liouville dynamics is an approximation to this equation that is appropriate for situations where the full quantum system may be partitioned into a quantum subsystem, and a classical environment. This partition is motivated by the observation that for many condensed phase processes the quantum mechanical character of only a few degrees of freedom need be taken into account to accurately describe the system’s overall dynamics. To this end, we let  $\hat{q} = \{\hat{q}_i\}$ ,  $i = 1, \dots, n$  be a set of coordinate operators for the  $n$  subsystem degrees of freedom with mass  $m$ , while the remaining  $N$  environmental degrees of freedom with mass  $M$  have coordinate operators  $\hat{Q} = \{\hat{Q}_i\}$ ,  $i = 1, \dots, N$ . The total Hamiltonian can then be written as

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

where we have written the momentum operators for the subsystem and environment as  $\hat{p}$  and  $\hat{P}$ , respectively. In keeping with this partition scheme, the potential energy operator,  $\hat{V}(\hat{q}, \hat{Q})$  can be decomposed into subsystem, environment, and coupling terms:  $\hat{V}(\hat{q}, \hat{Q}) = \hat{V}_s(\hat{q}) + \hat{V}_e(\hat{Q}) + \hat{V}_c(\hat{q}, \hat{Q})$ .

By performing a partial Wigner transform with respect to the coordinates of the environment, we obtain a classical-like phase space representation of those degrees of freedom. The subsystem coordinate operators are left untransformed, thus, retaining the operator character of the density matrix and Hamiltonian in the subsystem Hilbert space [4]. In order to take the partial Wigner transform of Eq. (1) explicitly, we express the Liouville-von Neumann equation in the  $\{Q\}$  representation,

$$\frac{\partial \langle Q | \hat{\rho}(t) | Q' \rangle}{\partial t} = -\frac{i}{\hbar} \int dQ'' \left( \langle Q | \hat{H} | Q'' \rangle \langle Q'' | \hat{\rho}(t) | Q' \rangle - \langle Q | \hat{\rho}(t) | Q'' \rangle \langle Q'' | \hat{H} | Q' \rangle \right). \tag{3}$$

Using the definition of the Wigner transform [5] of the density matrix,

$$\hat{\rho}_W(R, P) = (2\pi\hbar)^{-3N} \int dZ e^{iP \cdot Z / \hbar} \langle R - \frac{Z}{2} | \hat{\rho} | R + \frac{Z}{2} \rangle, \tag{4}$$

and the formula for the partial Wigner transform of a product of two operators [6]

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

Eq. (3) becomes

$$\begin{aligned} \frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} = & -\frac{i}{\hbar} \left( \hat{H}_W(R, P) e^{\hbar\Lambda/2i} \hat{\rho}_W(R, P, t) \right. \\ & \left. - \hat{\rho}_W(R, P, t) e^{\hbar\Lambda/2i} \hat{H}_W(R, P) \right). \end{aligned} \tag{6}$$

The operator  $\Lambda = \overleftarrow{\nabla}_P \cdot \overrightarrow{\nabla}_R - \overleftarrow{\nabla}_R \cdot \overrightarrow{\nabla}_P$  is the negative of the Poisson bracket operator, and the subscript  $W$  indicates the partial Wigner transform. The partial Wigner transform of the total Hamiltonian is written as,

$$\hat{H}_W(R, P) = \frac{P^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}_W(\hat{q}, R). \tag{7}$$

The quantum-classical Liouville equation can be derived by formally expanding the operator on the right side of Eq. (6) to  $\mathcal{O}(\hbar^0)$ . One may justify [4] such an expansion for systems where the masses of particles in the environment are much greater than those of the subsystem,  $M \gg m$ . In this case the small parameter in the theory is  $\mu = (m/M)^{1/2}$ . This factor emerges in the equation of motion quite naturally through a scaling of the variables motivated

by the classical theory of Brownian motion. Through such an analysis [4], one obtains the quantum-classical Liouville (QCL) equation [3, 4, 7–15]

$$\begin{aligned} \frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} &= -\frac{i}{\hbar} \left[ \hat{H}_W(R, P), \hat{\rho}_W(R, P, t) \right] \\ &\quad + \frac{1}{2} (\{ \hat{H}_W(R, P), \hat{\rho}_W(R, P, t) \} - \{ \hat{\rho}_W(R, P, t), \hat{H}_W(R, P) \}) \\ &= -i \hat{\mathcal{L}} \hat{\rho}_W(R, P, t). \end{aligned} \quad (8)$$

The last line defines the mixed quantum-classical Liouville (super)operator  $\hat{\mathcal{L}}$ .

The QCL superoperator has many desirable features required to produce physical dynamics; it conserves total mass, energy, momentum and phase space volumes [4, 16, 17]. However, it does not provide a fully consistent treatment of mixed quantum-classical dynamics. The quantum-classical bracket defined by the right side of Eq. (8) does not possess a Lie algebraic structure since it fails to satisfy the Jacobi identity [16, 18]. A detailed discussion of the consequences of this lack of a Lie algebraic structure can be found in Ref. [16]. There have been attempts to construct quantum-classical brackets that possess a Lie algebraic structure [19, 20] although these constructions have been shown to have difficulties [21, 22]. In addition to these attempts, there have been more recent formulations of quantum-classical dynamics based on different premises that have a Lie algebraic structure [23]. In spite of these limitations the quantum-classical Liouville description is one of the most accurate, computationally tractable methods for the study of the quantum dynamics of large complex systems. In particular, we observe that it equivalent to the full quantum dynamics described by Eq. (1) for arbitrary quantum subsystems bilinearly coupled to harmonic baths. In addition, as we shall see, approximations to QCL dynamics yield mean field and surface-hopping schemes.

In the next section we describe how the QCL equation may be expressed in any basis that spans the subsystem Hilbert space. Here we observe that the subsystem may also be Wigner transformed to obtain a phase-space-like representation of the subsystem variables as well as those of the environment. Taking the Wigner transform of Eq. (8) over the subsystem, we obtain the quantum-classical Wigner-Liouville equation [24],

$$\begin{aligned} \left[ \frac{\partial}{\partial t} + i\mathcal{L}_\ell^{(0)} + i\mathcal{L}_h^{(0)} \right] \rho_W(p, P, r, R, t) \\ = \frac{2}{\hbar(\pi\hbar)^n} \int ds \left[ \int d\tilde{r} V(r - \tilde{r}, R) \sin\left(\frac{2s\tilde{r}}{\hbar}\right) \right] \rho_W(p - s, P, r, R, t) \\ + \int ds \Delta F(R, s) \frac{\partial}{\partial P} \rho_W(p - s, P, r, R, t), \end{aligned} \quad (9)$$

where the force  $\Delta F(R, s)$  is defined as

$$\Delta F(R, s) = \frac{1}{(\pi\hbar)^n} \frac{\partial}{\partial R} \left[ \int d\tilde{r} \cos(2s\tilde{r}/\hbar) V(r - \tilde{r}, R) \right]. \quad (10)$$

The classical free streaming Liouville operators are  $i\mathcal{L}_\ell^{(0)} = \frac{p}{m} \frac{\partial}{\partial r}$  and  $i\mathcal{L}_h^{(0)} = \frac{P}{M} \frac{\partial}{\partial R}$  for the light ( $\ell$ ) subsystem particles and ( $h$ ) heavy environmental particles, respectively. The quantum-classical Wigner-Liouville equation (9) can be written in a more compact form,

$$\left[ \frac{\partial}{\partial t} + i\mathcal{L}_\ell + i\mathcal{L}_h \right] \rho_W(p, P, r, R, t) = \int ds K(s, P, r, R) \rho_W(p - s, P, r, R, t) \tag{11}$$

where  $i\mathcal{L}_\ell = \frac{p}{m} \frac{\partial}{\partial r} + F_s(r) \frac{\partial}{\partial p}$  is the full classical Liouville operator for the subsystem and  $i\mathcal{L}_h = \frac{P}{M} \frac{\partial}{\partial R} + F_e(R) \frac{\partial}{\partial P}$  is the full classical Liouville operator for the environment. Here  $F_s(r) = -\partial V_s(r)/\partial r$  and  $F_e(R) = -\partial V_e(R)/\partial R$ . The kernel  $K(s, P, r, R)$  is the sum of two contributions,  $K = K_\ell + K_h$  with

$$K_h(s, P, r, R) = \frac{1}{(\pi\hbar)^n} \left\{ \frac{\partial}{\partial R} \int d\tilde{r} \cos(2s\tilde{r}/\hbar) V_c(r - \tilde{r}, R) \right\} \frac{\partial}{\partial P},$$

$$K_\ell(s, P, r, R) = -\frac{\partial V_s(r)}{\partial r} \frac{d\delta(s)}{ds} + \frac{2}{\hbar(\pi\hbar)^n} \int d\tilde{r} [V_s(r - \tilde{r}) + V_c(r - \tilde{r}, R)] \sin\left(\frac{2s\tilde{r}}{\hbar}\right). \tag{12}$$

This equation gives the dynamics of the quantum-classical system in terms of phase space variables  $(R, P)$  for the bath and the Wigner transform variables  $(r, p)$  for the quantum subsystem. This equation cannot be simulated easily but can be used when a representation in a discrete basis is not appropriate. It is easy to recover a classical description of the entire system by expanding the potential energy terms in a Taylor series to linear order in  $\tilde{r}$ . Such classical approximations, in conjunction with quantum equilibrium sampling, are often used to estimate quantum correlation functions and expectation values. Classical evolution in this full Wigner representation is exact for harmonic systems since the Taylor expansion truncates.

### 3 Representations and Solutions

In many cases, in order to compute the dynamics of condensed phase systems, one invokes a basis representation for the quantum degrees of freedom in the system. Typically, one computes the dynamics of these systems in order to obtain quantities of interest, such as an average value,  $\overline{A(t)} = \text{Tr} [\hat{A}\hat{\rho}(t)]$ , or a correlation function, as will be discussed below. Since such averages are basis independent one may project Eq. (8) onto any convenient basis. This is in principle a nice feature, and one that is often exploited to aid in calculations. However, it is important to note that the basis onto which one chooses to project the QCLE has important implications on how one goes about solving the resulting equations of motion. Ultimately the time-dependent average value of an observable is expressed as a trace over quantum subsystem

states and a phase space average over classical-like coordinates; this feature is intimately linked to constructing a solution using statistical mechanics. Trajectory-based simulation methods for computing phase-space averages are often sought once the system Hamiltonian is known in a given basis. However, other schemes have been proposed that do not rely on computing ensembles of trajectories [25, 26].

In this section we present the major basis representations that have been used in the literature to solve the QCLE. For each representation - subsystem, adiabatic, force, and mapping, respectively - we present the QCLE in the particular representation, and briefly describe the schemes used to solve the equation of motion in that particular basis. We discuss the strengths and shortcomings of each representation.

### 3.1 The subsystem basis

When partitioning a system into a subsystem and its environment, the Hamiltonian one obtains, Eq. (2), is composed of subsystem, environment, and coupling parts. Thus, representing the QCLE in the subsystem basis is a natural starting point.

Let us consider a simple partitioning of the total Hamiltonian into two parts; one containing terms corresponding to the isolated quantum subsystem only,  $\hat{h}_s$ , and a remainder that contains all the bath and coupling terms. The subsystem basis is then defined by the following eigenvalue problem,  $\hat{h}_s|\alpha\rangle = \epsilon_\alpha|\alpha\rangle$ , where  $\hat{h}_s = \hat{p}^2/2m + \hat{V}_s(\hat{q})$ . These basis states, and the associated energy eigenvalues, are independent of the coordinates of the environment. The quantum-classical Liouville superoperator when written in the subsystem basis is given by,

$$\begin{aligned}
 -i\mathcal{L}_{\alpha\alpha',\beta\beta'}^s &= -i(\omega_{\alpha\alpha'}^s + L_{\alpha\alpha'}^s)\delta_{\alpha\beta}\delta_{\alpha'\beta'} + \frac{i}{\hbar}(\delta_{\alpha\beta}V_c^{\beta'\alpha'} - V_c^{\alpha\beta}\delta_{\alpha'\beta'}) \\
 &+ \frac{1}{2}\left(\delta_{\alpha'\beta'}\frac{\partial V_c^{\alpha\beta}}{\partial R} + \delta_{\alpha\beta}\frac{\partial V_c^{\beta'\alpha'}}{\partial R}\right) \cdot \frac{\partial}{\partial P},
 \end{aligned} \tag{13}$$

where we have used the following notation for subsystem quantities:  $\omega_{\alpha\alpha'}^s = (\epsilon_\alpha - \epsilon_{\alpha'})/\hbar$ ,  $V_c^{\alpha\alpha'} = \langle\alpha|\hat{V}_c|\alpha'\rangle$ ,  $iL_{\alpha\alpha'}^s = \frac{P}{M} \cdot \frac{\partial}{\partial R} + F_b(R) \cdot \frac{\partial}{\partial P}$ , and  $F_e(R) = -\partial V_e/\partial R$  is the force exerted by the environment. Also, this equation of motion has been derived from the linearized influence functional in a path integral representation expressed in this basis [15]. Thus, in this basis, QCL dynamics is equivalent to the linearized path integral formulation.

Donoso and Martens [13, 27] have developed a method for simulating the dynamics prescribed in this representation in the spirit of classical molecular dynamics. The algorithm is based on writing each element of the density matrix in the subsystem basis as a weighted sum over an ensemble of classical trajectories,

$$\rho_s^{\alpha\alpha'}(X, t) = \sum_{k=1}^{N_{\alpha\alpha'}} a_k^{\alpha\alpha'}(t) \delta(X - X_k^{\alpha\alpha'}(t)). \quad (14)$$

The ensemble contains  $N_{\alpha\alpha'}$  classical trajectories of the type

$$X_k^{\alpha\alpha'}(t) = (R_k^{\alpha\alpha'}(t), P_k^{\alpha\alpha'}(t)),$$

with weight  $a_k^{\alpha\alpha'}(t)$ . Population transfer and phase oscillations in the subsystem occur via the time variation of the weights attributed to the ensemble. However, in this construction the density is not a smooth function of the phase space coordinates [13], so a smoothing process is implemented to obtain appropriately scaled gaussian wavepackets. A short time approximation of the propagator is then performed and the resulting equations of motion for the weights are numerically integrated, whilst the ensemble undergoes Hamiltonian dynamics. The results from simulations using this algorithm (called the semiclassical Liouville method) are generally in excellent agreement with exact quantum mechanical solutions for model problems. The method has also been applied to the computation of vibrational dephasing rates of the  $I_2$  molecule in a low temperature Kr matrix and the results are in good agreement with experiment [28].

### 3.2 The adiabatic basis

In contrast to the subsystem representation, the adiabatic basis depends on the environmental coordinates. As such, one obtains a physically intuitive description in terms of classical trajectories along Born-Oppenheimer surfaces. A variety of systems have been studied using QCL dynamics in this basis. These include: the reaction rate and the kinetic isotope effect of proton transfer in a polar condensed phase solvent and a cluster [29–33], vibrational energy relaxation of a hydrogen bonded complex in a polar liquid [34], photodissociation of  $F_2$  [35], dynamical analysis of vibrational frequency shifts in a Xe fluid [36], and the spin-boson model [37, 38], which is of particular importance as exact quantum results are available for comparison.

The adiabatic basis is defined by the eigenvalue problem,

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

where

$$\hat{h}_W(R) = \hat{H}_W(R, P) - P^2/2M$$

is the Hamiltonian for the subsystem in a static environment, and the adiabatic energies,  $E_\alpha(R)$ , depend parametrically on the coordinates of the environment,  $R$ . In this representation, the time evolution of an element of the density matrix,

$$\langle \alpha; R | \hat{\rho}_W(R, P, t) | \alpha'; R \rangle = \rho_W^{\alpha\alpha'}(R, P, t),$$

is given by

$$\frac{\partial \rho_W^{\alpha\alpha'}(R, P, t)}{\partial t} = -i \sum_{\beta\beta'} \mathcal{L}_{\alpha\alpha', \beta\beta'} \rho_W^{\beta\beta'}(R, P, t), \quad (15)$$

where the evolution operator is now [4]

$$\begin{aligned} i\mathcal{L}_{\alpha\alpha', \beta\beta'} &= i\mathcal{L}_{\alpha\alpha'}^{(0)} \delta_{\alpha\beta} \delta_{\alpha'\beta'} - \mathcal{J}_{\alpha\alpha', \beta\beta'} \\ &= (i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'}) \delta_{\alpha\beta} \delta_{\alpha'\beta'} - \mathcal{J}_{\alpha\alpha', \beta\beta'}. \end{aligned} \quad (16)$$

The structure of  $\mathcal{L}$  given above, consists of two distinct components; (i) classical propagation on mean surfaces accompanied by quantum mechanical phase oscillations with frequency  $\omega_{\alpha\alpha'} = (E_\alpha - E_{\alpha'})/\hbar$ , and (ii) nonadiabatic transitions accompanied by changes in the momentum of the environment in order to conserve energy. The classical Liouville operator

$$iL_{\alpha\alpha'} = \frac{P}{M} \cdot \frac{\partial}{\partial R} + \frac{1}{2} (F_W^\alpha + F_W^{\alpha'}) \cdot \frac{\partial}{\partial P}, \quad (17)$$

propagates the environmental coordinates via Hellmann-Feynman forces,

$$F_W^\alpha = -\langle \alpha; R | \frac{\partial \hat{V}_W(\hat{q}, R)}{\partial R} | \alpha; R \rangle.$$

The operator,  $\mathcal{J}$ , responsible for nonadiabatic transitions may be written as follows,

$$\begin{aligned} \mathcal{J}_{\alpha\alpha', \beta\beta'} &= -\frac{P}{M} \cdot d_{\alpha\beta} \left( 1 + \frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha'\beta'} \\ &\quad - \frac{P}{M} \cdot d_{\alpha'\beta'}^* \left( 1 + \frac{1}{2} S_{\alpha'\beta'}^* \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha\beta}. \end{aligned} \quad (18)$$

where the quantity  $S_{\alpha\beta}$  is defined as

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

where  $F_W^{\alpha\beta}$  are the off-diagonal matrix elements of the force and  $d_{\alpha\beta}$  is the nonadiabatic coupling matrix element,  $d_{\alpha\beta} = \langle \alpha; R | \frac{\partial}{\partial R} | \beta; R \rangle$ . The presence of the nonadiabatic coupling matrix elements in this operator accounts for nonadiabatic transitions, which change the quantum state of the subsystem from a diagonal to an off-diagonal state or vice versa. The environment momentum derivative accounts for the energy transfer involved in the subsystem state change.

Shi and Geva [15] have also derived the QCLE in the adiabatic basis starting from the full path integral expression for the quantum mechanical problem. In this representation the derivation starts with the partial Wigner transform of the environmental degrees of freedom in contrast to what is done

in the subsystem basis. The final form of the equation is then obtained by expressing the adiabatic matrix elements of the partially Wigner transformed density,  $\hat{\rho}_W^{\alpha\alpha'}(R, P; t + \epsilon)$  in terms of  $\hat{\rho}_W^{\alpha\alpha'}(R, P; t)$ , and linearizing the resulting system propagators. It is interesting to note that the choice of basis has consequences on the order of operations between the linearization and partial Wigner transform in the derivation of these equations. In the subsystem basis, the partial Wigner transform is a consequence of the linearization of the forward-backward action, however in the adiabatic case, the partial Wigner transform is applied to the equation of motion, and the propagators are subsequently linearized in order to obtain the QCLE.

It is easy to see how a trajectory picture of the dynamics emerges by applying the Dyson identity to the formal solution of Eq. (15). The iterative solution of the Dyson equation results in a series of trajectory segments. These segments consist of evolution along the surface  $(\alpha\alpha')$ , which may be adiabatic  $(\alpha = \alpha')$  or the arithmetic mean of two adiabatic surfaces,  $(\alpha \neq \alpha')$ , governed by the propagator,  $e^{-i(\omega_{\alpha\alpha'} + L_{\alpha\alpha'})t}$ . Each subsequent term in the series includes this type of propagation interrupted by the nonadiabatic coupling operator,  $\mathcal{J}$ , an incremental number of times. Since, the operator  $\mathcal{J}$  accounts for nonadiabatic transitions, these contributions represent trajectory segments that evolve along some surface, undergo a transition to a new surface, followed by subsequent evolution on this surface and so on.

The presence of the momentum derivatives in  $\mathcal{J}$  makes the action of this operator difficult to simulate, because it acts on all functions to its right. This will generate a branching tree of trajectories. This difficulty is avoided by making the momentum-jump approximation. To see how this approximation is obtained, the following change of variables is made:

$$1 + \frac{1}{2}S_{\alpha\beta} \cdot \frac{\partial}{\partial P} = 1 + \Delta E_{\alpha\beta}M \frac{\partial}{\partial(P \cdot \hat{d}_{\alpha\beta})^2}. \tag{19}$$

For small  $\Delta E_{\alpha\beta}M$  this expression corresponds to the linear expansion of the exponential translation operator  $e^{\frac{\Delta E_{\alpha\beta}M \cdot \frac{\partial}{\partial(P \cdot \hat{d}_{\alpha\beta})^2}}$ , whose action on a function  $f(P)$  is a translation of the environment momentum by  $\Delta E_{\alpha\beta}M$  along the component of the momentum that is parallel to the nonadiabatic coupling matrix element:

$$\begin{aligned} & e^{\frac{\Delta E_{\alpha\beta}M \cdot \frac{\partial}{\partial(P \cdot \hat{d}_{\alpha\beta})^2}} f(P) \\ &= e^{\Delta E_{\alpha\beta}M \cdot \frac{\partial}{\partial(P \cdot \hat{d}_{\alpha\beta})^2}} f \left( (P \cdot \hat{d}_{\alpha\beta}^\perp) \hat{d}_{\alpha\beta}^\perp + \text{sgn}(P \cdot \hat{d}_{\alpha\beta}) \sqrt{(P \cdot \hat{d}_{\alpha\beta})^2} \hat{d}_{\alpha\beta} \right) \\ &= f \left( (P \cdot \hat{d}_{\alpha\beta}) \hat{d}_{\alpha\beta}^\perp + \text{sgn}(P \cdot \hat{d}_{\alpha\beta}) \sqrt{(P \cdot \hat{d}_{\alpha\beta})^2 + \Delta E_{\alpha\beta}M} \hat{d}_{\alpha\beta} \right). \end{aligned} \tag{20}$$

The approximations surrounding the definition of the  $\mathcal{J}$  operator comprise the momentum-jump approximation. This translation or shift of the momentum corresponds precisely to the amount of energy transferred during a transition

and thus satisfies energy conservation. In situations where there is insufficient kinetic energy available from the environment for the subsystem to make the transition,  $\Delta E_{\alpha\beta}M/(P \cdot \hat{d}_{\alpha\beta})^2 > 1$ , the transition is simply not allowed, and the evolution continues evolving on the surface it is on.

Several algorithms exist to simulate this evolution equation [14, 38–41]. The computation of observables in this approach is accomplished by Monte Carlo sampling configurations from the initial quantum equilibrium distribution followed by propagation of the observable by some algorithm [38, 40]. The sequential short time propagation algorithm [40] is one such algorithm where the propagator is divided into  $N$  propagators that act for a short time interval:

$$(e^{i\hat{L}t})_{\alpha\alpha',\alpha_N\alpha'_N} = \sum_{(\alpha_1\alpha'_1)\dots(\alpha_{N-1}\alpha'_{N-1})} \prod_{j=1}^N (e^{i\hat{L}\Delta t_j})_{\alpha_{j-1}\alpha'_{j-1},\alpha_j\alpha'_j}. \quad (21)$$

The short-time propagators can be solved through application of the Dyson identity truncated to first order. The subsequent dynamics of the quantity of interest are obtained by propagating the classical variables along a surface that corresponds to the quantum state  $(\alpha\alpha')$  followed by Monte Carlo sampling of the nonadiabatic transition events:

$$(e^{i\hat{L}\Delta t_j})_{\alpha_{j-1}\alpha'_{j-1},\alpha_j\alpha'_j} \approx \mathcal{W}_{\alpha_{j-1}\alpha'_{j-1}}(t_{j-1}, t_j) e^{iL_{\alpha_{j-1}\alpha'_{j-1}}\Delta t_j} \times \left( \delta_{\alpha_{j-1}\alpha_j} \delta_{\alpha'_{j-1}\alpha'_j} + \Delta t \mathcal{J}_{\alpha_{j-1}\alpha'_{j-1},\alpha_j\alpha'_j} \right). \quad (22)$$

Simulations using this algorithm [40] and the Trotter-based scheme [38] are able to reproduce the exact quantum results for the spin-boson model, verifying its utility.

### 3.3 The force basis

When the quantum-classical Liouville equation is expressed in the adiabatic basis, the most difficult terms to simulate come from the off-diagonal force matrix elements, which give rise to the nonadiabatic coupling matrix elements. As described above, contributions coming from this term were computed using the momentum-jump approximation in the context of a surface-hopping scheme.

One way to simplify this term in the evolution equation is to make use of a basis that diagonalizes the force contribution [42]; i.e., we represent the quantum-classical Liouville equation in a basis  $|i; R\rangle$  such that

$$-\langle i; R | \frac{\partial \hat{V}(R)}{\partial R} | j; R \rangle = F_F^i(R) \delta_{ij}, \quad (23)$$

where the subscript  $F$  is used to denote the force basis. Taking the matrix elements of Eq. (8) in this basis, we obtain

$$\begin{aligned} \frac{\partial \rho_F^{ij}(X, t)}{\partial t} = & -\frac{i}{\hbar} \sum_k \left( \mathcal{H}_F^{ik} \rho_F^{kj}(t) - \rho_F^{ik}(t) \mathcal{H}_F^{kj} \right) \\ & - \left( \frac{P}{M} \cdot \frac{\partial}{\partial R} + \frac{1}{2} (F_F^i + F_F^j) \cdot \frac{\partial}{\partial P} \right) \rho_F^{ij}, \end{aligned} \quad (24)$$

where  $\mathcal{H}_F^{ij} = H_F^{ij} + i\hbar \frac{P}{M} \cdot d_{ij}^F$ . Here  $d_{ij}^F$  is the nonadiabatic coupling element in the force basis. It can be related to the usual nonadiabatic coupling matrix element in the adiabatic basis by inserting complete sets of adiabatic states:

$$d_{ij}^F = \sum_{\alpha\beta} \langle i; R | \alpha; R \rangle d_{\alpha\beta} \langle \beta; R | j; R \rangle. \quad (25)$$

Evolution governed by the last term in Eq. (24) is simple and can be solved in characteristics. The first term is responsible for coupling among the elements of the density matrix and its inclusion makes the computation of the dynamics a difficult task.

The quantum-classical Liouville equation in the force basis has been solved for low-dimensional systems using the multithreads algorithm [42,43]. Assuming that the density matrix is localized within a small volume of the classical phase space, it is written as linear combination of matrices located at  $L$  discrete phase space points as

$$\hat{\rho}_W(R, P, t) = \sum_{k=1}^L \hat{\rho}^{(k)}(t) \delta(R - R_k(t)) \delta(P - P_k(t)). \quad (26)$$

The evolution equations for the quantities entering the right side of this equation are obtained by substitution into the quantum-classical Liouville equation. For a variety of one- and two-dimensional systems for which exact results are known, excellent agreement was found.

### 3.4 The mapping basis

The quantum-classical Liouville equation was expressed in the subsystem basis in Sec. 3.1. Based on this representation, it is possible to recast the equations of motion in a form where the discrete quantum degrees of freedom are described by continuous position and momentum variables [44–49]. In the mapping basis the eigenfunctions of the  $n$ -state subsystem can be replaced with eigenfunctions of  $n$  fictitious harmonic oscillators with occupation numbers limited to 0 or 1:  $|\lambda\rangle \rightarrow |m_\lambda\rangle = |0_1, \dots, 1_\lambda, \dots, 0_n\rangle$ . This mapping basis representation then makes use of the fact that the matrix element of an operator  $\hat{B}_W(X)$  in the subsystem basis,  $B_W^{\lambda\lambda'}(X)$ , can be written in mapping form as  $B_W^{\lambda\lambda'}(X) = \langle \lambda | \hat{B}_W(X) | \lambda' \rangle = \langle m_\lambda | \hat{B}_m(X) | m_{\lambda'} \rangle$ , where

$$\hat{B}_m(X) = \sum_{\lambda\lambda'} B_W^{\lambda\lambda'}(X) \hat{a}_\lambda^\dagger \hat{a}_{\lambda'}. \quad (27)$$

The mapping annihilation and creation operators are given by

$$\hat{a}_\lambda = \sqrt{\frac{1}{2\hbar}}(\hat{q}_\lambda + i\hat{p}_\lambda), \quad \hat{a}_\lambda^\dagger = \sqrt{\frac{1}{2\hbar}}(\hat{q}_\lambda - i\hat{p}_\lambda). \quad (28)$$

The mapping basis has been exploited in quantum-classical calculations based on a linearization of the path integral formulation of quantum correlation functions in the LAND-map method [50–52].

Given this correspondence between the matrix elements of a partially Wigner transformed operator in the subsystem and mapping bases, we can express the quantum-classical Liouville equation in the continuous mapping coordinates [53]. The first step in this calculation is to introduce an  $n$ -dimensional coordinate space representation of the mapping basis,

$$\langle m_\lambda | \hat{B}_m(X) | m_{\lambda'} \rangle = \int dqdq' \langle m_\lambda | q \rangle \langle q | \hat{B}_m(X, t) | q' \rangle \langle q' | m_{\lambda'} \rangle, \quad (29)$$

and then write the coordinate space matrix elements in terms of Wigner transforms in the mapping space to obtain

$$\langle r - \frac{z}{2} | \hat{B}_m(X, t) | r + \frac{z}{2} \rangle = \frac{1}{(2\pi\hbar)^n} \int dp e^{-ipz/\hbar} B_m(x, X, t). \quad (30)$$

Carrying out the this change of representation on the quantum-classical Liouville equation and using the product rule formula for the Wigner transform of a product of operators, we obtain

$$\begin{aligned} \frac{d}{dt} \rho_m(x, X, t) = & -\frac{2}{\hbar} H_m \sin\left(\frac{\hbar A_m}{2}\right) \rho_m(t) \\ & + \frac{\partial H_m}{\partial R} \cos\left(\frac{\hbar A_m}{2}\right) \cdot \frac{\partial B_m(t)}{\partial P} - \frac{P}{M} \cdot \frac{\partial \rho_m(t)}{\partial R}, \end{aligned} \quad (31)$$

where the negative of the Poisson bracket operator on the mapping phase space coordinates is defined as  $A_m = \overleftarrow{\nabla}_p \cdot \overrightarrow{\nabla}_r - \overleftarrow{\nabla}_r \cdot \overrightarrow{\nabla}_p$ . The Hamiltonian in the mapping basis is

$$H_m(x, X) = \frac{P^2}{2M} + V_e(R) + \frac{1}{2\hbar} \sum_{\lambda\lambda'} h_{\lambda\lambda'}(R) (r_\lambda r_{\lambda'} + p_\lambda p_{\lambda'} - \hbar \delta_{\lambda\lambda'}),$$

where  $h_{\lambda\lambda'}(R) = \langle \lambda | \hat{p}^2/2m + V_s(\hat{q}) + V_c(\hat{q}, R) | \lambda' \rangle$ . Explicitly computing the exponential Poisson bracket operators, we find the quantum-classical Liouville equation in the mapping basis,

$$\begin{aligned} \frac{d}{dt} B_m(x, X, t) = & -\{H_m, B_m(t)\}_{x, X} \\ & + \frac{\hbar}{8} \sum_{\lambda\lambda'} \frac{\partial h_{\lambda\lambda'}}{\partial R} \left( \frac{\partial}{\partial r_{\lambda'}} \frac{\partial}{\partial r_\lambda} + \frac{\partial}{\partial p_{\lambda'}} \frac{\partial}{\partial p_\lambda} \right) \cdot \frac{\partial}{\partial P} B_m(t) \\ & \equiv i\mathcal{L}_m B_m(t), \end{aligned} \quad (32)$$

where  $\{A_m, B_m(t)\}_{x,X}$  denotes a Poisson bracket in the full mapping-bath phase space of the system.

The first term in the evolution operator has the form of a Poisson bracket and evolution under this part of the operator can be expressed in terms of characteristics. The corresponding set of ordinary differential equations is

$$\begin{aligned} \frac{dr_\lambda(t)}{dt} &= \frac{1}{\hbar} \sum_{\lambda'} h_{\lambda\lambda'}(R(t)) p_{\lambda'}(t), \\ \frac{dp_\lambda(t)}{dt} &= -\frac{1}{\hbar} \sum_{\lambda'} h_{\lambda\lambda'}(R(t)) r_{\lambda'}(t), \\ \frac{dR(t)}{dt} &= \frac{P(t)}{M}, \quad \frac{dP(t)}{dt} = -\frac{\partial H_m}{\partial R(t)}. \end{aligned} \tag{33}$$

The last term involves derivatives with respect to both mapping and environmental variables. Its contribution is difficult to compute. Calculations on the spin-boson model have shown that even if the last term is neglected, excellent agreement with the exact results for a wide range of system parameters is obtained [53].

## 4 Approximations to the QCL equation

The QCL approach discussed thus far in this chapter provides a good approximation to the quantum dynamics of condensed phase systems. Most often other approximate quantum-classical methods, such as mean field and surface-hopping schemes, have been commonly employed to treat the same class of problems as the QCLE. These methods are attractive due to their computational simplicity; however, many important quantum features, such as quantum coherence and correlations, are not properly handled in these approaches. In this section we discuss these methods and show that starting from the QCLE, an approximate theory in its own right, further approximations lead to these other approaches.

### 4.1 Mean field theory

Mean field theories of mixed quantum-classical systems are based on approximations that neglect correlations in Ehrenfest's equations of motion for the evolution of the position and momentum operators of the heavy-mass nuclear degrees of freedom. The approximate evolution equations take the form of Newton's equations of motion where the forces that the nuclear degrees of freedom experience involve mean forces determined from the time-evolving wave function of the system.

We now show how the mean field equations can be derived as an approximation to the quantum-classical Liouville equation (8) [9]. The Hamiltonian

can be written again as the sum of environmental, subsystem and interaction contributions,

$$\hat{H}_W = \frac{P^2}{2M} + V_e(R) + \frac{\hat{p}^2}{2m} + \hat{V}_s(\hat{q}) + \hat{V}_c(\hat{q}, R) = H_e(X) + \hat{H}_s(\hat{q}) + \hat{V}_c(\hat{q}, R).$$

In order to study the effects of neglecting correlations in this description of the dynamics, we define the reduced density matrices for the environment and subsystem, respectively, as

$$\rho_e(X, t) = \text{Tr}' \hat{\rho}_W(X, t), \quad \hat{\rho}_s(t) = \int dX \hat{\rho}_W(X, t), \tag{34}$$

which are normalized so that  $\int dX \rho_e(X, t) = 1$  and  $\text{Tr}' \hat{\rho}_s(t) = 1$ . We also define the correlation density operator  $\hat{\rho}_{cor}(X, t)$  by  $\hat{\rho}_W(X, t) \equiv \hat{\rho}_s(t) \rho_e(X, t) + \hat{\rho}_{cor}(X, t)$ . Given that the density operator satisfies the normalization  $\text{Tr}' \int dX \rho_W(X, t) = 1$ , we have  $\text{Tr}' \int dX \rho_{cor}(X, t) = 0$ .

If we substitute the above expression for  $\hat{\rho}_W(X, t)$  into the quantum-classical Liouville equation we find

$$\hat{\rho}_s(t) \frac{\partial \rho_e(X, t)}{\partial t} + \rho_e(X, t) \frac{\partial \hat{\rho}_s(t)}{\partial t} + \frac{\partial \hat{\rho}_{cor}(X, t)}{\partial t} = -i \hat{\mathcal{L}} \hat{\rho}_s(t) \rho_e(X, t) - i \hat{\mathcal{L}} \hat{\rho}_{cor}(X, t). \tag{35}$$

To obtain the mean field equations, we make the assumption that all terms in this equation containing  $\hat{\rho}_{cor}(X, t)$  can be neglected. Then, integration over  $X$  and use of the normalization conditions yields

$$\frac{\partial \hat{\rho}_s(t)}{\partial t} = -\frac{i}{\hbar} \left[ \hat{H}_s + \int dX \hat{V}_c \rho_e(X, t), \hat{\rho}_s(t) \right], \tag{36}$$

while the trace over the quantum degrees of freedom gives

$$\frac{\partial \rho_e(X, t)}{\partial t} = \left\{ H_e + \text{Tr}' \hat{V}_c \hat{\rho}_s(t), \rho_e(X, t) \right\} = \left\{ H_{\text{eff}}, \rho_e(X, t) \right\}, \tag{37}$$

where  $H_{\text{eff}} = P^2/2M + V_{\text{eff}}(R)$  and the effective potential is defined as  $V_{\text{eff}}(R) = V_e(R) + \text{Tr}' \hat{V}_c \hat{\rho}_s(t)$ . This equation can be solved in terms of characteristics. The density function takes the form  $\rho_e(X, t) = \delta(X - X(t))$ , where  $X(t) = (R(t), P(t))$  satisfy Newtonian equations of motion,

$$\dot{R}(t) = \frac{P(t)}{M}, \quad \dot{P}(t) = -\frac{\partial V_{\text{eff}}(R(t))}{\partial R(t)}. \tag{38}$$

Using  $\rho_e(X, t) = \delta(X - X(t))$ , we may write

$$\int dX \hat{V}_c(R) \rho_e(X, t) = \hat{V}_c(R(t)). \tag{39}$$

As a result, Eq. (36) is equivalent to the pair of Schrödinger equations,

$$i\hbar \frac{\partial |\psi(R(t), t)\rangle}{\partial t} = \left( \hat{H}_s + \hat{V}_c(R(t)) \right) |\psi(R(t), t)\rangle, \quad (40)$$

and its adjoint. Equations (38) and (40) are the standard mean field equations of motion for a mixed quantum-classical system.

Thus, we see that in order to obtain the mean field equations of motion, the density matrix of the entire system is assumed to factor into a product of subsystem and environmental contributions with neglect of correlations. The quantum dynamics then evolves as a pure state wave function depending on the coordinates evolving in the mean field generated by the quantum density. As we have seen in the previous sections, these approximations are not valid and no simple representation of the quantum-classical dynamics is possible in terms of single effective trajectories. Consequently, in contrast to claims made in the literature [54], quantum-classical Liouville dynamics is not equivalent to mean field dynamics.

## 4.2 Surface-hopping dynamics

Surface-hopping methods provide a more accurate description of nonadiabatic dynamics since they do not force the system to evolve on the mean field determined by a superposition of quantum states. Instead, using a representation in adiabatic eigenstates, in surface-hopping dynamics the classical degrees of freedom evolve on single adiabatic surfaces with hops between these surfaces determined by probabilistic rules [55]. Consequently, the dynamics of the system is correctly described when the evolution takes the system in regions where coupling between quantum states is small or zero. The precise form of the surface-hopping method depends on the nature of the rule used to specify quantum transitions. The fewest switches algorithm of Tully [2, 56] is one of the most popular such schemes.

A connection between surface-hopping schemes and the dynamics prescribed by the QCLE may be established by considering the conditions under which it is reasonable to express the dynamics given by the QCLE in terms of evolution along single adiabatic surfaces or, equivalently, the evolution of diagonal matrix elements in the adiabatic representation. As we have seen, since coherence is described by the off-diagonal elements of the density matrix, the problem reduces to the examination of the conditions under which decoherence leads to rapid decay of the off-diagonal elements. Here we describe the quantum-classical master equation which results in surface-hopping-like trajectories. The full details are given in Ref. [57].

Starting from the QCLE expressed in the adiabatic basis, it is not difficult to derive a generalized master equation for the diagonal elements of the density matrix by formally solving the QCLE (15) in the adiabatic basis for the off-diagonal elements and substituting the resulting solution into the equation for the diagonal elements. The result is the non-Markovian equation,

$$\frac{\partial}{\partial t} \rho_d^\alpha(X, t) = -iL_\alpha \rho_d^\alpha(X, t) + \int_0^t dt' \sum_\beta \mathcal{M}_{\alpha\beta}(t') \rho_d^\beta(X, t - t'), \quad (41)$$

where the memory kernel operator  $\mathcal{M}_{\alpha\beta}(t)$  is given by,

$$\mathcal{M}_{\alpha\beta}(t) = \sum_{\nu\nu', \mu\mu'} \mathcal{J}_{\alpha, \mu\mu'}^{d, o} \left( e^{-i\mathcal{L}^\circ(X)(t)} \right)_{\mu\mu', \nu\nu'} \mathcal{J}_{\nu\nu', \beta}^{o, d}, \quad (42)$$

and acts on all of the classical degrees of freedom that appear in functions to its right.

By considering the action of the operators given in Eq. (42) on functions to its right, the memory kernel operator may be reduced to a memory function.

$$M_{\alpha\beta}^{\alpha\beta}(X, t) = 2\text{Re} [\mathcal{W}_{\alpha\beta}(t, 0)] D_{\alpha\beta}(X) D_{\alpha\beta}(\bar{X}_{\alpha\beta, t}), \quad (43)$$

where  $\mathcal{W}_{\alpha\beta}(t, 0) = e^{-i \int_0^t d\tau \omega_{\alpha\beta}[R(\tau)]}$  is a phase factor,  $D_{\alpha\beta} = (P/M) \cdot d_{\alpha\beta}(R)$ , and the subscripts and superscripts on the memory function label the indices on the first and second  $D$  function respectively. The bar on the phase space variable  $X$  indicates the action of a momentum shift by the  $\mathcal{J}$  operator, and the subscript notation indicates that  $X$  has been evolved along the surface  $(\alpha\beta)$  for a time  $t$ . In this form, the memory function accounts for all coherent evolution segments in the dynamics.

Decoherence arising from interaction of the subsystem with an environment is incorporated into the evolution expression by averaging over an initial distribution of the environmental phase space coordinates. The resulting expression prescribes the evolution of the diagonal elements of the subsystem density matrix and contains the environmental average of the time dependent memory kernel. The environmental average provides a mechanism for decoherence and leads to decay of the memory kernel. In the absence of an environmental average, the memory kernel is a purely oscillatory function and does not decay. However, the environmentally averaged memory kernel does decay and, depending on the system under investigation, if there is a sufficient separation of time scales between the decay of the memory function and other relevant system relaxation times, a Markovian approximation on the memory term may be used. The resulting equation,

$$\begin{aligned} \frac{\partial}{\partial t} \rho_s^\alpha(X_0, t) = & - \int dX_e iL_\alpha e^{-i\hat{Q}_e L_\alpha t} \hat{Q}_e \rho_d^\alpha(X, 0) - \langle iL_\alpha \rangle_e \rho_s^\alpha(X_0, t) \quad (44) \\ & - \int_0^t dt' \langle iL_\alpha e^{-i\hat{Q}_e L_\alpha t'} i\hat{Q}_e L_\alpha \rangle_e \rho_s^\alpha(X_0, t - t') \\ & + \sum_\beta m_{\alpha\beta}(X_0) \hat{j}_{\alpha \rightarrow \beta} \rho_s^\beta(X_0, t) - m_{\alpha\alpha}(X_0) \rho_s^\alpha(X_0, t), \end{aligned}$$

gives the evolution of the subsystem density matrix  $\rho_s^\alpha(X_0, t) \equiv \int dX_e \rho^\alpha(X, t)$ , where  $X_0$  is the set of phase space variables of the subsystem. This expression

is still non-Markovian in character as a result of the projection of the evolution equation onto the subsystem. The final master equation is obtained by lifting the equation back into the full phase space to recover a fully Markovian master equation description:

$$\frac{d}{dt}\rho_d^\alpha(X, t) = -iL_\alpha\rho_d^\alpha(X, t) + \sum_\beta m_{\alpha\beta}(X_0)j_{\alpha\rightarrow\beta}\rho_d^\beta(X, t) - m_{\alpha\alpha}(X_0)\rho_d^\alpha(X, t). \tag{45}$$

where

$$m_{\alpha\beta}(X_0) = \int_0^\infty dt' \langle M_{\alpha\beta}^{\alpha\beta}(X, t') \rangle_e, \tag{46}$$

and  $j_{\alpha\rightarrow\beta}$  is a momentum shift operator [57]. Note that the subscripts on the second memory term in Eq. (45) are the same. This term arises from the memory function corresponding to  $\langle M_{\alpha\nu}^{\nu\alpha}(X, t) \rangle_e$ , where the angle brackets indicate that the average over the environment has been performed. Trajectories accounted for by this term jump to the mean surface and then return to their original surface. Thus, the net effect is no jump, but a phase factor is introduced.

The master equation evolves the classical degrees of freedom on single adiabatic surfaces with instantaneous hops between them. Each single (fictitious) trajectory represents an ensemble of trajectories corresponding to different environment initial conditions. This choice of different environment coordinates for a given initial subsystem coordinate will result in different trajectories on the mean surface; the average over this collection of classical evolution segments results in decoherence. Consequently, this master equation in full phase space provides a description in terms of fictitious trajectories, each of which accounts for decoherence. When the approximations that lead to the master equation are valid, this provides a useful simulation tool since no oscillatory phase factors appear in the trajectory evolution.

The surface-hopping trajectories obtained in the adiabatic representation of the QCLE contain nonadiabatic transitions between potential surfaces including both single adiabatic potential surfaces and the mean of two adiabatic surfaces. This picture is qualitatively different from surface-hopping schemes [2, 56] which make the ansatz that classical coordinates follow some trajectory,  $R(t)$ , while the quantum subsystem wavefunction, expanded in the adiabatic basis, is evolved according to the time dependent Schrödinger equation. The potential surfaces that the classical trajectories evolve along correspond to one of the adiabatic surfaces used in the expansion of the subsystem wavefunction, while the subsystem evolution is carried out coherently and may develop into linear combinations of these states. In such schemes, the environment does not experience the force associated with the true quantum state of the subsystem and decoherence by the environment is not automatically taken into account. Nonetheless, these methods have provided com-

putationally tractable and, under the conditions outlined above, reasonable descriptions of nonadiabatic dynamics.

Coherence is created and destroyed in the QCLE through the action of the momentum-jump operator,  $\hat{\mathcal{J}}$ , and phase information is obtained for off-diagonal evolution segments through the phase term in the propagator (17). The master equation discussed above incorporates this decoherence mechanism in the environmental average of the memory kernel. Decoherence in the quantum subsystem of condensed phase systems is a well established phenomenon [58, 59] and should be accounted for in surface-hopping schemes. We note that various phenomenologically motivated prescriptions have been proposed to incorporate decoherence into the dynamics of the subsystem [56, 60–63].

## 5 Observables and correlation functions

Thus far we have focussed on the dynamics of quantum-classical systems. In practice, we are primarily interested instead in computing observables that can be compared eventually to experimentally obtainable quantities. To this end, consider the general quantum mechanical expression for the expectation value of an observable,

$$\begin{aligned} \overline{A(t)} &= \text{Tr}(\hat{\rho}(t)\hat{A}) = \text{Tr}(\hat{\rho}\hat{A}(t)) & (47) \\ &= \text{Tr}' \int dQ_1 dQ_2 \langle Q_1 | \hat{A}(t) | Q_2 \rangle \langle Q_2 | \hat{\rho}(0) | Q_1 \rangle \\ &= \text{Tr}' \int dR dP \hat{A}_W(R, P, t) \hat{\rho}_W(R, P) = \text{Tr}' \int dX \hat{A}_W(X, t) \hat{\rho}_W(X) \end{aligned} \quad (48)$$

In the above expressions we have introduced the (primed) partial trace over the Hilbert space of the subsystem,  $\text{Tr}' \hat{\rho}_W(R, P) = \rho_e(R, P)$ , and the symbols  $\text{Tr}'$  and  $\text{Tr}_e$  refer to taking the partial trace over the subsystem and environment, respectively.

If we expand Eq. (47) in the coordinate  $\{Q\}$ -representation for the environmental degrees of freedom only we obtain the second line. Taking the Wigner representation for these degrees of freedom and finally, defining the general coordinate  $X = (R, P)$  gives Eq. (48).

For a quantum mechanical system in thermal equilibrium a transport coefficient  $\lambda_{AB}$  may be determined from the time integral of a flux-flux correlation function [64].

$$\lambda_{AB} = \frac{1}{\beta} \int_0^\infty dt \langle \frac{i}{\hbar} [\dot{\hat{B}}(t), \hat{A}] \rangle, \quad (49)$$

where  $\dot{\hat{B}} = (i/\hbar)[\hat{H}, \hat{B}]$  is the flux of  $\hat{B}$ , and  $\beta = (k_B T)^{-1}$ . The equilibrium quantum canonical average is  $\langle \dots \rangle = Z_Q^{-1} \text{Tr} \dots e^{-\beta \hat{H}}$  where  $Z_Q$  is the partition function. The transport coefficient may then be obtained from the plateau value of  $\lambda_{AB}(t)$  [65].

The quantum mechanical forms of the correlation function expressions for transport coefficients are well known and may be derived by invoking linear response theory [64] or the Mori-Zwanzig projection operator formalism [66, 67]. However, we would like to evaluate transport properties for quantum-classical systems. We thus take the quantum mechanical expression for a transport coefficient as a starting point and then consider a limit where the dynamics is approximated by quantum-classical dynamics [68–70]. The advantage of this approach is that the full quantum equilibrium structure can be retained.

In simulations it is convenient to obtain the transport coefficient from the plateau value of  $\lambda_{AB}(t)$ . Writing Eq. (49) in detail, we can express the time-dependent transport coefficient  $\lambda_{AB}(t)$  as,

$$\begin{aligned} \lambda_{AB}(t) &= \frac{1}{\beta} \int_0^t dt' \langle \dot{B}(t); \dot{A} \rangle \\ &= \frac{1}{\beta Z_Q} \int_0^\beta d\lambda \text{Tr} \left( \dot{A} e^{\frac{i}{\hbar} \hat{H}(i\hbar\lambda)} \hat{B}(t) e^{-\frac{i}{\hbar} \hat{H}(i\hbar\lambda) - \beta \hat{H}} \right). \end{aligned} \tag{50}$$

Here we have introduced the notation,  $\langle \cdot; \cdot \rangle$ , to indicate the Kubo transformed-correlation function. Rewriting the expression in the coordinate representation for the full system,  $\{Q\} = \{q\} \{Q\}$  (calligraphic symbols are used to denote variables for the entire system, subsystem plus bath),

$$\begin{aligned} \lambda_{AB}(t) &= \frac{1}{\beta Z_Q} \int_0^\beta d\lambda \int dQ_1 dQ'_1 dQ_2 dQ'_2 \langle Q_1 | \dot{A} | Q'_1 \rangle \langle Q'_1 | e^{\frac{i}{\hbar} \hat{H}(t+i\hbar\lambda)} | Q_2 \rangle \\ &\quad \times \langle Q_2 | \dot{B} | Q'_2 \rangle \langle Q'_2 | e^{-\beta \hat{H} - \frac{i}{\hbar} \hat{H}(t+i\hbar\lambda)} | Q_1 \rangle. \end{aligned} \tag{51}$$

Making a change of variables,  $Q_1 = \mathcal{R}_1 - \mathcal{Z}_1/2$ ,  $Q'_1 = \mathcal{R}_1 + \mathcal{Z}_1/2$ , etc., and then expressing the matrix elements in terms of the Wigner transforms of the operators, we have [69]

$$\begin{aligned} \lambda_{AB}(t) &= \frac{1}{\beta} \int_0^\beta d\lambda \int d\mathcal{X}_1 d\mathcal{X}_2 (\dot{A})_W(\mathcal{X}_1) B_W(\mathcal{X}_2) \frac{1}{(2\pi\hbar)^{2\nu} Z_Q} \\ &\quad \times \int d\mathcal{Z}_1 d\mathcal{Z}_2 e^{-\frac{i}{\hbar} (\mathcal{P}_1 \cdot \mathcal{Z}_1 + \mathcal{P}_2 \cdot \mathcal{Z}_2)} \left\langle \mathcal{R}_1 + \frac{\mathcal{Z}_1}{2} \left| e^{\frac{i}{\hbar} \hat{H}(t+i\hbar\lambda)} \right| \mathcal{R}_2 - \frac{\mathcal{Z}_2}{2} \right\rangle \\ &\quad \times \left\langle \mathcal{R}_2 + \frac{\mathcal{Z}_2}{2} \left| e^{-\beta \hat{H} - \frac{i}{\hbar} \hat{H}(t+i\hbar\lambda)} \right| \mathcal{R}_1 - \frac{\mathcal{Z}_1}{2} \right\rangle. \end{aligned} \tag{52}$$

Here we used the fact that the matrix element of an operator  $\hat{A}$  can be expressed in terms of its Wigner transform  $A_W(\mathcal{X})$  as

$$\left\langle \mathcal{R} - \frac{\mathcal{Z}}{2} \left| \hat{A} \right| \mathcal{R} + \frac{\mathcal{Z}}{2} \right\rangle = \frac{1}{(2\pi\hbar)^\nu} \int d\mathcal{P} e^{-\frac{i}{\hbar} \mathcal{P} \cdot \mathcal{Z}} A_W(\mathcal{X}), \tag{53}$$

where  $\nu$  is the coordinate space dimension.

If we define the spectral density by,

$$W(\mathcal{X}_1, \mathcal{X}_2, t) = \frac{1}{(2\pi\hbar)^{2\nu} Z_Q} \int d\mathcal{Z}_1 d\mathcal{Z}_2 e^{-\frac{i}{\hbar}(P_1 \cdot \mathcal{Z}_1 + P_2 \cdot \mathcal{Z}_2)} \times \left\langle \mathcal{R}_1 + \frac{\mathcal{Z}_1}{2} \left| e^{\frac{i}{\hbar}\hat{H}t} \right| \mathcal{R}_2 - \frac{\mathcal{Z}_2}{2} \right\rangle \left\langle \mathcal{R}_2 + \frac{\mathcal{Z}_2}{2} \left| e^{-\beta\hat{H} - \frac{i}{\hbar}\hat{H}t} \right| \mathcal{R}_1 - \frac{\mathcal{Z}_1}{2} \right\rangle, \quad (54)$$

we can write the transport coefficient as

$$\lambda_{AB}(t) = \int d\mathcal{X}_1 d\mathcal{X}_2 (\dot{A})_W(\mathcal{X}_1) B_W(\mathcal{X}_2) \overline{W}(\mathcal{X}_1, \mathcal{X}_2, t), \quad (55)$$

where

$$\overline{W}(\mathcal{X}_1, \mathcal{X}_2, t) = \frac{1}{\beta} \int_0^\beta d\lambda W(\mathcal{X}_1, \mathcal{X}_2, t + i\hbar\lambda). \quad (56)$$

To take the quantum-classical limit of this general expression for the transport coefficient we partition the system into a subsystem and bath and use the notation  $\mathcal{R} = (r, R)$ ,  $\mathcal{P} = (p, P)$  and  $\mathcal{X} = (r, R, p, P)$  where the lower case symbols refer to the subsystem and the upper case symbols refer to the bath. To make connection with surface-hopping representations of the quantum-classical Liouville equation [4], we first observe that  $A_W(\mathcal{X}_1)$  can be written as

$$A_W(\mathcal{X}_1) = \int dz_1 e^{\frac{i}{\hbar}p_1 \cdot z_1} \langle r_1 - \frac{z_1}{2} | \hat{A}_W(X_1) | r_1 + \frac{z_1}{2} \rangle, \quad (57)$$

where  $\hat{A}_W(X_1)$  is the *partial* Wigner transform of  $\hat{A}$  over the bath degrees of freedom. We may now express the subsystem operators in the adiabatic basis to obtain,

$$A_W(\mathcal{X}_1) = \sum_{\alpha_1 \alpha'_1} \int dz_1 e^{\frac{i}{\hbar}p_1 \cdot z_1} \langle r_1 - \frac{z_1}{2} | \alpha_1; R_1 \rangle A_W^{\alpha_1 \alpha'_1}(X_1) \langle \alpha'_1; R_1 | r_1 + \frac{z_1}{2} \rangle, \quad (58)$$

where  $A_W^{\alpha_1 \alpha'_1}(X_1) = \langle \alpha_1; R_1 | \hat{A}_W(X_1) | \alpha'_1; R_1 \rangle$ . Inserting this expression, and its analog for  $B_W(\mathcal{X}_2)$ , into Eq. (52) we have

$$\lambda_{AB}(t) = - \sum_{\alpha_1, \alpha'_1, \alpha_2, \alpha'_2} \int \prod_{i=1}^2 dX_i A_W^{\alpha_1 \alpha'_1}(X_1) B_W^{\alpha_2 \alpha'_2}(X_2) \times \frac{\partial}{\partial t} \overline{W}^{\alpha'_1 \alpha_1 \alpha'_2 \alpha_2}(X_1, X_2, t), \quad (59)$$

where the matrix elements of  $W$  are given by

$$W^{\alpha'_1 \alpha_1 \alpha'_2 \alpha_2}(X_1, X_2, t) = \int \prod_{i=1}^2 dZ_i e^{-\frac{i}{\hbar}(P_1 \cdot Z_1 + P_2 \cdot Z_2)} \frac{1}{Z_Q} \frac{1}{(2\pi\hbar)^{2\nu_n}} \times \langle \alpha'_1; R_1 | \langle R_1 + \frac{Z_1}{2} | e^{\frac{i}{\hbar}\hat{H}t} | R_2 - \frac{Z_2}{2} \rangle | \alpha_2; R_2 \rangle \times \langle \alpha'_2; R_2 | \langle R_2 + \frac{Z_2}{2} | e^{-\frac{i}{\hbar}\hat{H}t''} | R_1 - \frac{Z_1}{2} \rangle | \alpha_1; R_1 \rangle, \quad (60)$$

with  $t'' = t - i\beta\hbar$ .

The quantum-classical limit of the transport coefficient is obtained by evaluating the evolution equation for the matrix elements of  $\overline{W}$  in the quantum-classical limit. This limit was taken in Ref. [68] and the result is

$$\begin{aligned} \frac{\partial}{\partial t} \overline{W}^{\alpha'_1 \alpha_1 \alpha'_2 \alpha_2}(X_1, X_2, t) = \\ \frac{1}{2} \sum_{\beta'_1 \beta_1 \beta'_2 \beta_2} \left( i\mathcal{L}_{\alpha'_1 \alpha_1, \beta'_1 \beta_1}(X_1) \delta_{\alpha'_2 \beta'_2} \delta_{\alpha_2 \beta_2} - i\mathcal{L}_{\alpha'_2 \alpha_2, \beta'_2 \beta_2}(X_2) \delta_{\alpha'_1 \beta'_1} \delta_{\alpha_1 \beta_1} \right) \\ \times \overline{W}^{\beta'_1 \beta_1 \beta'_2 \beta_2}(X_1, X_2, t). \end{aligned} \quad (61)$$

We use the first equality in Eq. (61), insert this into Eq. (59), and move the evolution operator  $i\mathcal{L}(X_1)$  onto the  $A_W(X_1)$  dynamical variable. Next, we use the second equality in Eq. (61) and formally solve the equation to obtain  $\overline{W}(X_1, X_2, t) = e^{-i\mathcal{L}(X_2)t} \overline{W}(X_1, X_2, 0)$ . Finally we substitute this form for  $\overline{W}(X_1, X_2, t)$  into Eq. (59) and move the evolution operator to the dynamical variable  $B_W(X_2)$ . In the adiabatic basis, the action of the propagator  $e^{-i\mathcal{L}(X_2)t}$  on  $\hat{B}_W(X_2)$  is

$$B_W^{\alpha_2 \alpha'_2}(X_2, t) = \sum_{\beta_2 \beta'_2} \left( e^{-i\mathcal{L}(X_2)t} \right)_{\alpha_2 \alpha'_2, \beta_2 \beta'_2} B_W^{\beta_2 \beta'_2}(X_2). \quad (62)$$

The result of these operations is

$$\begin{aligned} \lambda_{AB}(t) = \sum_{\alpha_1, \alpha'_1, \alpha_2, \alpha'_2} \int \prod_{i=1}^2 dX_i (i\mathcal{L}(X_1) A_W(X_1))^{\alpha_1 \alpha'_1} \\ \times B_W^{\alpha_2 \alpha'_2}(X_2, t) \overline{W}^{\alpha'_1 \alpha_1 \alpha'_2 \alpha_2}(X_1, X_2, 0). \end{aligned} \quad (63)$$

This equation can serve as the basis for the computation of transport properties for quantum-classical systems. Note that full quantum effects are described by the initial value of  $\overline{W}$ .

## 6 Example reaction rate calculation

The rate coefficient of a reactive process is a transport coefficient of interest in chemical physics. It has been shown from linear response theory that this coefficient can be obtained from the reactive flux correlation function of the system of interest. This quantity has been computed extensively in the literature for systems such as proton and electron transfer in solvents as well as clusters [29, 32, 33, 56, 71–76], where the use of the QCL formalism has allowed one to consider quantum phenomena such as the kinetic isotope effect in proton transfer [31]. Here, we will consider the problem of formulating an expression for a reactive rate coefficient in the framework of the QCL theory. Results from a model calculation will be presented including a comparison to the approximate methods described in Sec. 4.

### 6.1 Simulation results

Consider a simple reactive process  $A \rightleftharpoons B$ . The quantum mechanical expression for the time dependent forward rate coefficient for such a process is given by,

$$k_{AB}(t) = -\frac{1}{n_A^{eq}} \int_0^t dt' \langle \delta \hat{N}_B(t'); \delta \hat{N}_A \rangle, \quad (64)$$

where the  $\delta \hat{N}_i$  are the species operators representing the deviations of each species from their equilibrium number densities, and the angled brackets denote the Kubo transformed correlation function as defined in Eq. (50). This expression was derived previously by following the projection operator methods of Mori and Zwanzig in the linear response regime [77]. Following the discussion of the previous section, the quantum classical limit of this expression, (63) can be obtained and is given by [70]

$$k_{AB}(t) = \frac{1}{n_A^{eq}} \sum_{\alpha} \sum_{\alpha' \geq \alpha} (2 - \delta_{\alpha'\alpha}) \times \int dX \text{Re} \left[ N_B^{\alpha\alpha'}(X, t) W_A^{\alpha'\alpha}(X, \frac{i\hbar\beta}{2}) \right]. \quad (65)$$

Here, the integration over  $X_1$  was performed in Eq. (63) to define  $W_A^{\alpha\alpha'}(X, \frac{i\hbar\beta}{2})$  which is the integrated value of the combination of the spectral density function with the time independent operator. This spectral density function contains the quantum equilibrium structure of the system.  $N_B^{\alpha\alpha'}(X, t)$  is the time evolved matrix element of the number operator for the product state B. Thus, to calculate the rate, one samples initial configurations from the quantum equilibrium distribution, and then computes the evolution of the number operator for product state B. The QCL evolution of the species operator is accomplished using one of the algorithms discussed in Sec. 3.2. Alternative approaches to the dynamics may also be used such as the further approximations to the QCLE discussed in Sec. 4.

The sampling of initial configurations from the spectral density function remains a challenging task as the structure of this function is complicated. By factoring this quantity into a subsystem and conditional environment distribution,  $W_A^{\alpha'\alpha}(X, \frac{i\hbar\beta}{2}) = \rho_A^{\alpha'\alpha}(X_0) \rho_e^c(X_e; R_0)$ , the problem simplifies. In particular, if the environment consists of harmonic oscillators, as is the case here, the exact form of the spectral density is known for the environment. For the subsystem, one can appeal to the fact that typically the barrier region, where the largest contribution to the dynamics in this problem take place, is approximately harmonic. Doing so, one is able to obtain an approximate analytic form of this function given by [78],

$$\begin{aligned} \rho_A^{\alpha'\alpha}(X_0) &= \frac{ia}{Z_Q\pi^2} \int dZ_0 e^{-\frac{i}{\hbar}(P_0 \cdot Z_0)} \sum_{\alpha_1\alpha_2} A_{\alpha_1\alpha_2}^{\alpha'\alpha} B_{\alpha_1\alpha_2}(0) \\ &\times \left[ \delta_{\alpha_1\alpha_2} e^{-a(4R_0^2 + Z_0^2)u'_1} 2aM_0Z_0\tilde{u}_1^2 \right. \\ &\quad \left. - d_{\alpha_1\alpha_2}(0) e^{-2a\left[(R_0 + \frac{Z_0}{2})^2 u'_1 + (R_0 - \frac{Z_0}{2})^2 u'_2\right]} \sqrt{\tilde{u}_1\tilde{u}_2} \right], \end{aligned} \tag{66}$$

where  $u'_i = u_i \coth u_i$ ,  $\tilde{u}_i = u_i \operatorname{csch} u_i$ ,  $u_i = \beta\hbar\omega_i/2$ ,  $\omega_i$  is the barrier region frequency for the state  $\alpha_i$  which may be real or imaginary, and  $a = M_0/(2\beta\hbar^2)$ . By numerically integrating over  $Z_0$  we obtain the quantum mechanical equilibrium structure for the subsystem,  $\hat{\rho}_0(X_0)$ . Sampling from this distribution is performed from the harmonic part and subsequently reweighted by the remaining term. With this quantity, in conjunction with that for the environment and Eq. (65), the quantum mechanical rate-coefficient can be computed via computer simulation.

We consider the same reaction model used in previous studies as a simple model for a proton transfer reaction. [31, 57, 79] The subsystem consists of a two-level quantum system bilinearly coupled to a quartic oscillator and the bath consists of  $\nu - 1 = 300$  harmonic oscillators bilinearly coupled to the non-linear oscillator but not directly to the two-level quantum system. In the subsystem representation, the partially Wigner transformed Hamiltonian for this system is,

$$\begin{aligned} \mathbf{H}_W &= \begin{pmatrix} V_q(R_0) + \hbar\Omega & \hbar\gamma_0 R_0 \\ \hbar\gamma_0 R_0 & V_q(R_0) - \hbar\Omega \end{pmatrix} \\ &+ \left( \frac{P_0^2}{2M_0} + \sum_{j=1}^{\nu-1} \frac{P_j^2}{2M_j} + \frac{M_j\omega_j^2}{2} \left( R_j - \frac{c_j}{M_j\omega_j^2} R_0 \right)^2 \right) \mathbf{I}. \end{aligned} \tag{67}$$

The solution of the eigenvalue problem,  $\hat{h}_W(R)|\alpha; R_0\rangle = E_\alpha(R)|\alpha; R_0\rangle$ , yields the adiabatic eigenstates,  $|\alpha; R_0\rangle$ , and eigenvalues

$$E_\alpha(R) = V_q(R_0) + V_e(R_e; R_0) \mp \hbar\sqrt{\Omega^2 + (\gamma_0 R_0)^2},$$

where  $2\Omega$  is the adiabatic energy gap. The parameters of this model characterize a harmonic environment with ohmic spectral density, [80] the details of which can be found elsewhere. [31, 68, 79] The reaction coordinate  $R_0$  undergoes dynamics characteristic of a well defined barrier crossing process and product species operator  $N_B^{\alpha\alpha'}(R_0) = \theta(R_0)\delta_{\alpha\alpha'}$  is initially diagonal in the adiabatic basis. Here  $\theta(R_0)$  is the Heaviside function.

The plot in Fig. 1 shows the reaction rate computed via adiabatic versus nonadiabatic dynamics. The rate constant, given by the plateau value of the correlation function, is lower when nonadiabatic dynamics is considered. This reduction is due to enhanced barrier crossing as a result of motion on either the excited state or mean surfaces. This is seen more clearly in Fig. 2. When the

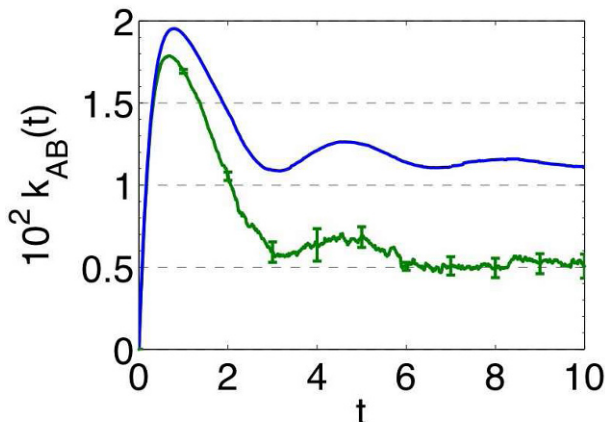


Fig. 1: Nonadiabatic vs adiabatic reaction rate for  $\beta = 1.0$ . The blue (upper) curve is the adiabatic result while the green (lower) curve is the nonadiabatic rate.

system is propagating on either the mean or excited state surface it is confined close to the barrier region such that it crosses the barrier more frequently. On the other hand, once the system jumps down to the ground state, it stabilizes in one of the wells such that recrossings are less frequent. The increase of recrossings due to dynamics on these surfaces leads to decay of the correlation function.

In Fig. 2 one can see the qualitative differences between the dynamics on the various surfaces. Although both excited state and mean surface evolution segments oscillate around the barrier, the mean surface segments are able to explore a wider region due to the broader structure of the mean free energy surface for this model. In contrast, the excited surface trajectories are narrowly confined to the barrier region where the probability of a transition is high. Thus, excited state trajectory segments are short lived. The evolution of trajectories along the mean surface is an important result in QCL dynamics as it entails the proper treatment of coherence that is lacking in surface-hopping approaches.

By inserting the form of the spectral density function discussed above into the rate coefficient expression, the second line of Eq. (65) may be replaced by

$$\int dX \operatorname{Re} \left[ N_B^{\alpha\alpha'}(X, t) W_A^{\alpha'\alpha}(X, \frac{i\hbar\beta}{2}) \right] = \int dX_0 \operatorname{Re} \left[ \langle N_B^{\alpha\alpha'} \rangle_e(X_0, t) \rho_A^{\alpha'\alpha}(X_0, \frac{i\hbar\beta}{2}) \right], \quad (68)$$

where the angle brackets indicate an average over the conditional equilibrium distribution,  $\rho_e^c(X_e; R_0)$ . In this form, the computation of the rate constant

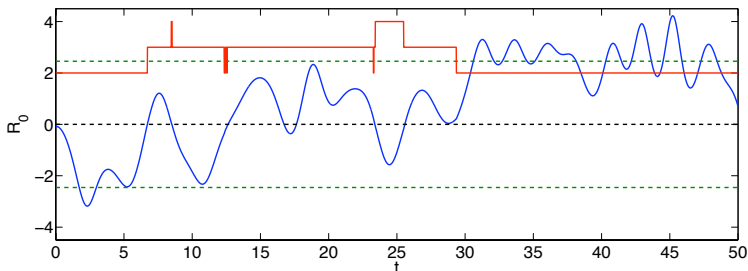


Fig. 2: A segment taken from the time series of a nonadiabatic trajectory. The blue curve is the times series for  $R_0$ , the red curve indicates the surface on which the trajectory is evolving, where a value of 2 on the  $R_0$  axis corresponds to the ground state (1,1), 3 corresponds to the mean surface (1,2) or (2,1), and 4 corresponds to the excited state (2,2). During the evolution on the mean surface and excited state surface the trajectory is confined to the barrier region where it may cross the barrier. In contrast, when the trajectory is on the ground state surface the system stabilizes in one well or the other.

involves the bath averaged observable discussed in Sec. 4.2, allowing us to apply the master equation formalism discussed above.

In Fig. 3, the simulation results for the same model problem are presented using the QCLE, the master equation, Tully's surface-hopping approach, the mean field approach, and adiabatic dynamics. The algorithmic details of each approach can be found elsewhere [2, 40, 79].

From the figure we see that the surface-hopping result using Tully's algorithm is almost identical to the adiabatic rate for the parameters given here. By comparison to both the QCLE simulation and the master equation simulation, one can conclude that for this set of parameters this overestimates the reaction rate. The primary reason for the discrepancy is the manner in which coherence and decoherence is treated in the theory. Although the master equation also restricts motion to single adiabatic surfaces, the probability of hopping is obtained from a calculation that accounts for decoherence in a different manner. The prediction of the rate obtained by the mean-field approach, shown in the figure, underestimates the rate. This can be attributed to the neglect of correlations in the equations of motion as discussed in Sec. 4.1.

We remark that the simulation scheme for master equation dynamics has a number of attractive features when compared to quantum-classical Liouville dynamics. The solution of the master equation consists of two numerically simple parts. The first is the computation of the memory function which involves adiabatic evolution along mean surfaces. Once the transition rates are known as a function of the subsystem coordinates, the sequential short-time propagation algorithm may be used to evolve the observable or density. Since the dynamics is restricted to single adiabatic surfaces, no phase factors

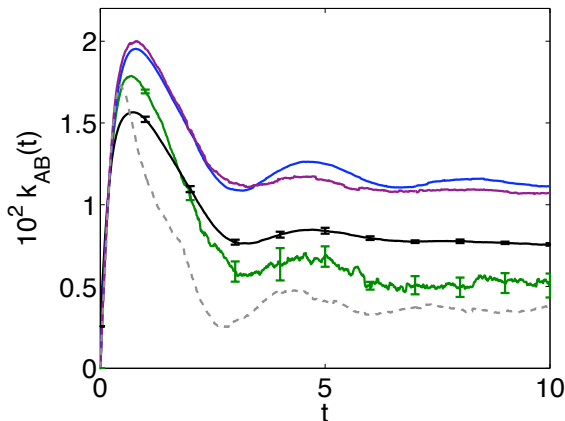


Fig. 3: Forward rate coefficient  $k_{AB}(t)$  as a function of time for  $\beta = 1.0$ . The upper (blue) curve is the adiabatic rate, the purple curve is the result obtained by Tully's surface-hopping algorithm, the middle (black) curve is the quantum master equation result, the green curve is the QCL result, and the lowest dashed line (grey) is the result using mean-field dynamics.

enter this part of the calculation increasing the stability of the algorithm. For complicated reaction coordinates which are arbitrary functions of the environmental coordinates the calculation of the transition rates will be more difficult and time consuming. Of course, the validity of this scheme rests on the accuracy of the Markovian approximation to the memory kernel, which must be determined for the system under consideration.

## 7 Conclusions

We have presented some of the most recent developments in the computation and modeling of quantum phenomena in condensed phased systems in terms of the quantum-classical Liouville equation. In this approach we consider situations where the dynamics of the environment can be treated as if it were almost classical. This description introduces certain non-classical features into the dynamics, such as classical evolution on the mean of two adiabatic surfaces. Decoherence is naturally incorporated into the description of the dynamics. Although the theory involves several levels of approximation, QCL dynamics performs extremely well when compared to exact quantum calculations for some important benchmark tests such as the spin-boson system. Consequently, QCL dynamics is an accurate theory to explore the dynamics of many quantum condensed phase systems.

In practice, one's ability to model any realistic system via the QCLE depends on the appropriate choice of representation of the quantum system.

Each representation brings with it a unique set of challenges and limitations in the development of efficient algorithms for computing the dynamics as well as sampling initial configurations. For these reasons it is interesting to consider some of the earlier more approximate schemes such as the mean field and surface-hopping approaches. We have shown here that there are conditions under which the approximations underlying these methods are reasonable and thus one can take advantage of the computational simplicity involved in these schemes to obtain a computationally cheap solution to the problem. One, however, must keep in mind that the QCLE is already an approximate approach, and that these schemes involve further, often severe, approximations to the QCLE. An important outcome of this analysis is that the QCLE emerges as an analytic tool that one can use as a theoretical basis to evaluate alternative approaches to the problem of quantum dynamics in almost classical environments.

As quantum-classical dynamics is a rapidly emerging field of increasing importance, there are many areas in which further study is needed. For example, as was discussed in Sec. 4.2, the QCLE provides a useful framework to investigate the mechanism of decoherence in various scenarios. This fact allows one to assess the validity of a Markovian approximation to the generalized master equation. Another important area involves alternate representations of the QCLE. For example the mapping basis discussed in Sec. 3.4 is one such example where the use of harmonic oscillator states leads to dynamics in terms of classical trajectories involving new forces. The computational simplicity that this affords is obviously appealing. Although the structure of the higher order correlation terms in the equation of motion are not easily computed, in certain cases it has been shown to be negligible. Further research into this area will prove useful and may yield more stable algorithms allowing for the study of far more difficult systems. For example, an important problem of interest that still lacks a satisfactory solution is the simulation of quantum systems in the condensed phase interacting with a field. Through the use of appropriate choices of representations leading to improved algorithms, this type of problem may soon be solvable.

## Acknowledgements

This work was supported in part by a grant from the Natural Sciences and Engineering Research Council of Canada. One of the authors (AK) acknowledges the support from the Walter C. Sumner foundation.

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