# Transport Coefficients of Quantum-Classical Systems

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### 1 Introduction

Quantum mechanics provides us with the most fundamental description of natural phenomena. In many instances classical mechanics constitutes an adequate approximation and it is widely used in simulations of both static and dynamic properties of many-body systems. Often, however, quantum effects cannot be neglected and one is faced with the task of devising methods to simulate the behavior of the quantum system.

The computation of the equilibrium properties of quantum systems is a challenging problem. The simulation of dynamical properties, such as transport coefficients, presents additional problems since the solution of the quantum equations of motion for many-body systems is even more difficult. This fact has prompted the development of approximate methods for dealing with such problems.

The topic of this chapter is the description of a quantum-classical approach to compute transport coefficients. Transport coefficients are most often expressed in terms of time correlation functions whose evaluation involves two aspects: sampling initial conditions from suitable equilibrium distributions and evolution of dynamical variables or operators representing observables of the system. The schemes we describe for the computation of transport properties pertain to quantum many-body systems that can usefully be partitioned into two subsystems, a quantum subsystem S and its environment  $\mathcal{E}$ . We shall be interested in the limiting situation where the dynamics of the environmental degrees of freedom, in isolation from the quantum subsystem S, obey classical mechanics.

We show how the quantum-classical evolution equations of motion can be obtained as an approximation to the full quantum evolution and point out some of the difficulties that arise because of the lack of a Lie algebraic structure. The computation of transport properties is discussed from two different perspectives. Transport coefficient formulas may be derived by starting from an approximate quantum-classical description of the system. Alternatively, the exact quantum transport coefficients may be taken as the starting point of the computation with quantum-classical approximations made only to the dynamics while retaining the full quantum equilibrium structure. The utility of quantum-classical Liouville methods is illustrated by considering the computation of the rate constants of quantum chemical reactions in the condensed phase.

### 2 Wigner Formulation of Quantum Statistical Mechanics

We begin our discussion with a survey of the quantum dynamics and linear response theory expressions for quantum transport coefficients. Since we wish to make a link to a partial classical description, the use of Wigner transforms

provides a means to introduce a phase space description of the quantum system. Consequently, our formulation of quantum mechanics will be carried out in this Wigner transform framework.

#### 2.1 Dynamics

The von Neumann equation, or quantum mechanical Liouville equation,

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

where  $\hat{H}$  is the Hamiltonian of the system and  $\hat{L}$  is the quantum Liouville operator, specifies the time evolution of the density matrix  $\hat{\rho}$ . The formal solution of (1) is

$$\hat{\rho}(t) = e^{-i\hat{L}t}\hat{\rho}(0) = e^{-i\hat{H}t/\hbar}\hat{\rho}(0)e^{i\hat{H}t/\hbar} .$$
(2)

We may take the Wigner transform of the quantum Liouville equation to obtain an alternate formulation of the equation of motion. The Wigner transforms of the density matrix and an operator  $\hat{A}$  are defined, respectively, by [1]

$$\rho_W(\mathcal{X}) = (2\pi\hbar)^{-\mathcal{N}} \int d\mathcal{Z} e^{i\mathcal{P}\cdot\mathcal{Z}/\hbar} \left\langle \mathcal{R} - \frac{\mathcal{Z}}{2} |\hat{\rho}| \mathcal{R} + \frac{\mathcal{Z}}{2} \right\rangle , \qquad (3)$$

and

$$A_W(\mathcal{X}) = \int d\mathcal{Z} e^{i\mathcal{P}\cdot\mathcal{Z}/\hbar} \left\langle \mathcal{R} - \frac{\mathcal{Z}}{2} |\hat{A}| \mathcal{R} + \frac{\mathcal{Z}}{2} \right\rangle$$
$$= \int d\mathcal{Z} e^{-i\mathcal{P}\cdot\mathcal{Z}/\hbar} \left\langle \mathcal{R} + \frac{\mathcal{Z}}{2} |\hat{A}| \mathcal{R} - \frac{\mathcal{Z}}{2} \right\rangle , \qquad (4)$$

where  $\mathcal{N}$  is the coordinate space dimension of the system and we use calligraphic symbols to denote phase space variables for the entire system,  $\mathcal{X} = (\mathcal{R}, \mathcal{P})$ . (Later in this chapter we shall make a distinction between phase space variables for the entire system and those for the  $\mathcal{S}$  and  $\mathcal{E}$  subsystems. We let  $\mathcal{X} = (x, X)$  where x = (r, p) and X = (R, P) for the  $\mathcal{S}$  and  $\mathcal{E}$  subsystems, respectively.) Taking the Wigner transform of (1) we find

$$\frac{\partial}{\partial t}\rho_W(\mathcal{X},t) = -\frac{i}{\hbar} \left[ (\hat{H}\hat{\rho}(t))_W(\mathcal{X}) - (\hat{\rho}(t)\hat{H})_W(\mathcal{X}) \right] .$$
(5)

To proceed, we must evaluate the Wigner transform of a product of operators. This calculation is given in several reviews [2] but we sketch it here for completeness. Letting  $Q = \mathcal{R} + \mathcal{Z}/2$  and  $Q' = \mathcal{R} - \mathcal{Z}/2$ , we may invert the relation (4) to obtain

$$\langle \mathcal{Q} | \hat{A} | \mathcal{Q}' \rangle = (2\pi\hbar)^{-\mathcal{N}} \int d\mathcal{P} \; e^{i\mathcal{P} \cdot (\mathcal{Q} - \mathcal{Q}')/\hbar} A_W((\mathcal{Q} + \mathcal{Q}')/2, \mathcal{P}) \;. \tag{6}$$

If we introduce the Fourier transform of  $A_W(\mathcal{Q}, \mathcal{P})$ ,

$$A_W(\mathcal{Q}, \mathcal{P}) = \int d\sigma \ d\tau \ e^{i(\sigma \mathcal{Q} + \tau \mathcal{P})/\hbar} \alpha(\sigma, \tau) , \qquad (7)$$

into (6) we find,

$$\langle \mathcal{Q} | \hat{A} | \mathcal{Q}' \rangle = \int d\sigma \; e^{i\sigma(\mathcal{Q} + \mathcal{Q}')/(2\hbar)} \alpha(\sigma, \mathcal{Q}' - \mathcal{Q}) \;. \tag{8}$$

Writing the Wigner transform of a product of operators as

$$(\hat{A}\hat{B})_W(\mathcal{R},\mathcal{P}) = \int d\mathcal{Z}d\mathcal{R}' \ e^{i\mathcal{P}\mathcal{Z}/\hbar} \left\langle \mathcal{R} - \frac{\mathcal{Z}}{2} |\hat{A}|\mathcal{R}' \right\rangle \left\langle \mathcal{R}' |\hat{B}|\mathcal{R} + \frac{\mathcal{Z}}{2} \right\rangle , \quad (9)$$

and inserting (8) and its analog for the the operator  $\hat{B}$  with Fourier coefficients  $\beta$  we find

$$(\hat{A}\hat{B})_{W}(\mathcal{R},\mathcal{P}) = \int d\mathcal{Z}d\mathcal{R}' d\sigma d\sigma' \ e^{i\mathcal{P}\mathcal{Z}/\hbar} e^{i\sigma(\mathcal{R}+\mathcal{R}'-\mathcal{Z}/2)/(2\hbar)} e^{i\sigma'(\mathcal{R}'+\mathcal{R}+\mathcal{Z}/2)/(2\hbar)} \\ \times \alpha(\sigma,\mathcal{R}'-\mathcal{R}+\mathcal{Z}/2)\beta(\sigma',\mathcal{R}-\mathcal{R}'+\mathcal{Z}/2) \\ = \int d\tau d\tau' d\sigma d\sigma' \ \alpha(\sigma,\tau) \\ \times e^{i(\sigma\mathcal{R}+\tau\mathcal{P})/\hbar} e^{i(\sigma'\tau-\sigma\tau')/(2\hbar)} e^{i(\sigma'\mathcal{R}+\tau'\mathcal{P})/\hbar} \beta(\sigma',\tau') .$$
(10)

In the second line we made the change of variables  $\tau = \mathcal{R} - \mathcal{R}' + \mathcal{Z}/2$  and  $\tau' = \mathcal{R}' - \mathcal{R} + \mathcal{Z}/2$ . Finally, we note that

$$e^{i(\sigma\mathcal{R}+\tau\mathcal{P})/\hbar}e^{i(\sigma'\tau-\sigma\tau')/(2\hbar)}e^{i(\sigma'\mathcal{R}+\tau'\mathcal{P})/\hbar}$$

$$=e^{i(\sigma\mathcal{R}+\tau\mathcal{P})/\hbar}(1+i(\sigma'\tau-\sigma\tau')/2\hbar+\dots)e^{i(\sigma'\mathcal{R}+\tau'\mathcal{P})/\hbar}$$

$$=e^{i(\sigma\mathcal{R}+\tau\mathcal{P})/\hbar}(1+\hbar\Lambda/2i+\dots)e^{i(\sigma'\mathcal{R}+\tau'\mathcal{P})/\hbar}$$

$$=e^{i(\sigma\mathcal{R}+\tau\mathcal{P})/\hbar}e^{\hbar\Lambda/2i}e^{i(\sigma'\mathcal{R}+\tau'\mathcal{P})/\hbar}$$

$$=e^{i(\sigma'\mathcal{R}+\tau'\mathcal{P})/\hbar}e^{-\hbar\Lambda/2i}e^{i(\sigma\mathcal{R}+\tau\mathcal{P})/\hbar}, \qquad (11)$$

where  $\Lambda$  is the negative of the Poisson bracket operator,  $\Lambda = \overleftarrow{\nabla}_{\mathcal{P}} \cdot \overrightarrow{\nabla}_{\mathcal{R}} - \overleftarrow{\nabla}_{\mathcal{R}} \cdot \overrightarrow{\nabla}_{\mathcal{P}}$ , where the direction of an arrow indicates the direction in which the operator acts. Inserting this result into (10) and using the definition in (7) we find the result  $(\hat{A}\hat{B})_W = A_W(\mathcal{X})e^{\frac{\hbar\Lambda}{2i}}B_W(\mathcal{X}) = B_W(\mathcal{X})e^{-\frac{\hbar\Lambda}{2i}}A_W(\mathcal{X})$  for the Wigner transform of a product of operators. The second equality follows from the equality in the last two lines of (11). Using these results, the Wigner transform of the quantum Liouville equation can be written as,

$$\frac{\partial}{\partial t}\rho_W(\mathcal{X},t) = -\frac{i}{\hbar} \Big( H_W(\mathcal{X}) e^{\frac{\hbar\Lambda}{2i}} \rho_W(\mathcal{X},t) - \rho_W(\mathcal{X},t) e^{\frac{\hbar\Lambda}{2i}} H_W(\mathcal{X}) \Big) \\
= -\frac{i}{\hbar} \Big( H_W(\mathcal{X}) \Big( e^{\frac{\hbar\Lambda}{2i}} - e^{\frac{-\hbar\Lambda}{2i}} \Big) \rho_W(\mathcal{X},t) \Big) \\
= -\frac{2}{\hbar} H_W(\mathcal{X}) \sin\left(\frac{\hbar\Lambda}{2}\right) \rho_W(\mathcal{X},t) \equiv -iL_W(\mathcal{X}) \rho_W(\mathcal{X},t). (12)$$

Here, the Wigner transformed Hamiltonian is  $H_W(\mathcal{X}) = \mathcal{P}^2/2M + V_W(\mathcal{R})$ . The last line of this equation defines  $iL_W$ , the Wigner form of quantum Liouville operator,  $iL_W = \frac{2}{\hbar}H_W(\mathcal{X})\sin\left(\frac{\hbar \Lambda}{2}\right)$ .

A similar calculation may be carried out for the time evolution of an observable. Starting with the Heisenberg equation of motion for a dynamical variable  $\hat{B}$ ,

$$\frac{d\hat{B}(t)}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{B}(t)] , \qquad (13)$$

and taking the Wigner transform, we obtain,

$$\frac{d}{dt}B_W(\mathcal{X},t) = iL_W(\mathcal{X})B_W(\mathcal{X},t) .$$
(14)

The classical limit of these equations of motion is easily taken by retaining only the term independent of  $\hbar$  in the Liouville operator  $iL_W = \frac{2}{\hbar}H_W(\mathcal{X})\sin\left(\frac{\hbar\Lambda}{2}\right) = H_W(\mathcal{X})\Lambda + O(\hbar)$ . Using this result we find the classical Liouville equation for the density matrix,

$$\frac{\partial}{\partial t}\rho(\mathcal{X},t) = -H(\mathcal{X})\Lambda\rho(\mathcal{X},t) = \{H(\mathcal{X}),\rho(\mathcal{X},t)\}$$
$$\equiv -iL_{cl}(\mathcal{X})\rho(\mathcal{X},t) , \qquad (15)$$

with a similar evolution equation for a dynamical variable,

$$\frac{d}{dt}B(\mathcal{X},t) = iL_{cl}(\mathcal{X})B(\mathcal{X},t) , \qquad (16)$$

where we have dropped the subscript W on the density matrix and Wigner transformed operators in this classical limit.

#### 2.2 Response Theory and Time Correlation Functions

Equilibrium time correlation function expressions for transport properties can be derived using linear response theory [3]. Linear response theory can be carried out directly on the Wigner transformed equations of motion to obtain the transport properties as correlation functions involving Wigner transformed quantities. Alternatively, we may carry out the linear response analysis in terms of abstract operators and insert the Wigner representation of operators in the final form for the correlation function. We use the latter route here.

In linear response theory, it is assumed that a time dependent external force F(t) couples to an observable  $\hat{A}$  (self-adjoint operator) and the response of the system to linear order in the external force is computed. More specifically, the Hamiltonian in the presence of the external force is  $\hat{H}(t) = \hat{H} - \hat{A}F(t)$ , and the evolution equation for the density matrix is

$$\frac{\partial\hat{\rho}(t)}{\partial t} = (i\hbar)^{-1}[\hat{H}(t),\hat{\rho}(t)] = -(i\hat{L} - i\hat{L}_A F(t))\hat{\rho}(t) , \qquad (17)$$

where  $i\hat{L}_A \equiv (i/\hbar)[\hat{A}, ]$ .

Given that the system was in thermal equilibrium in the distant past, the solution of this equation to linear order in the external force is [3]

$$\hat{\rho}(t) = \hat{\rho}_e^Q + \int_{-\infty}^t dt' \ e^{-i\hat{L}(t-t')}i\hat{L}_A \hat{\rho}_e^Q F(t') \ . \tag{18}$$

The canonical equilibrium density matrix is  $\hat{\rho}_e^Q = Z_Q^{-1} \exp(-\beta \hat{H})$  and  $Z_Q = \text{Tr} \exp(-\beta \hat{H})$  is the partition function. The response of the system to the external force in a property B is given by the average value of the operator  $\hat{B}$  using the density matrix at time t (assuming, without loss of generality, that  $\hat{B}$  has an average value of zero in equilibrium),

$$\overline{B(t)} = \operatorname{Tr}\hat{B}\hat{\rho}(t) = \frac{i}{\hbar} \int_{-\infty}^{t} dt' \operatorname{Tr}\hat{B}(t-t')[\hat{A}, \hat{\rho}_{e}^{Q}]F(t')$$
$$= \frac{i}{\hbar} \int_{-\infty}^{t} dt' \operatorname{Tr}[\hat{B}(t-t'), \hat{A}]\hat{\rho}_{e}^{Q}F(t') \equiv \int_{-\infty}^{t} dt' \,\phi_{BA}(t-t')F(t') \quad (19)$$

with the response function defined by

$$\phi_{BA}(t) = \left\langle \frac{i}{\hbar} [\hat{B}(t), \hat{A}] \right\rangle_Q , \qquad (20)$$

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

The response function may be written in an equivalent form by using the quantum mechanical operator identity, [3]

$$\frac{i}{\hbar}[\hat{A},\hat{\rho}_{e}^{Q}] = \int_{0}^{\beta} d\lambda \; \hat{\rho}_{e}^{Q} \dot{\hat{A}}(-i\hbar\lambda) \;, \tag{21}$$

in the second line of (19) to obtain

$$\phi_{BA}(t) = \int_0^\beta d\lambda \operatorname{Tr} \dot{\hat{A}} (-i\hbar\lambda) \hat{B}(t) \hat{\rho}_e^Q .$$
<sup>(22)</sup>

Transport properties are typically expressed as time integrals of flux-flux correlation functions. Letting  $\hat{B} = \dot{\hat{A}} \equiv \hat{j}^A$  be the flux corresponding to the operator  $\hat{A}$ , the quantum expression for a transport coefficient takes the general form,

$$\lambda_A \propto \int_0^\infty dt \; \langle \hat{j}^A; \hat{j}^A(t) \rangle_Q \;, \tag{23}$$

where

$$\beta \langle \hat{j}^A; \hat{j}^A(t) \rangle_Q \equiv \left\langle \frac{i}{\hbar} [\hat{j}^A(t), \hat{A}] \right\rangle_Q = \int_0^\beta d\lambda \, \text{Tr} \hat{j}^A(-i\hbar\lambda) \hat{j}^A(t) \hat{\rho}_e^Q \,, \qquad (24)$$

defines the Kubo transformed correlation function.

We may now insert the definitions of the operators in terms of their Wigner transforms, as discussed in the previous subsection, to obtain equivalent representations of the transport coefficient expressions. Noting that  $\operatorname{Tr} \hat{A} \hat{B} = \int d\mathcal{X} A_W(\mathcal{X}) B_W(\mathcal{X})$  and the rule for the Wigner transform of a product of operators, we can write

$$\left\langle \frac{i}{\hbar} [\hat{j}^{A}(t), \hat{A}] \right\rangle_{Q} = \frac{i}{\hbar} \int d\mathcal{X} \left( j_{W}^{A}(t) e^{\frac{\hbar\Lambda}{2i}} A_{W} - A_{W} e^{\frac{\hbar\Lambda}{2i}} j_{W}^{A}(t) \right) \rho_{We}^{Q}$$
$$= \frac{2}{\hbar} \int d\mathcal{X} \left( j_{W}^{A}(t) \sin\left(\hbar\Lambda/2\right) A_{W} \right) \rho_{We}^{Q} .$$
(25)

Using these results and carrying out this program, we find that a transport coefficient can be written in the following equivalent forms,

$$\lambda_A \propto \frac{1}{\beta} \int_0^\infty dt \, \int d\mathcal{X} \, \frac{2}{\hbar} \Big( j_W^A(t) \sin(\hbar \Lambda/2) A_W \Big) \rho_{We}^Q \,,$$
$$= \frac{1}{\beta} \int_0^\infty dt \, \int_0^\beta d\lambda \, \int d\mathcal{X} \, \left( j_W^A(-i\hbar\lambda) e^{\hbar\Lambda/2i} j_W^A(t) \right) \rho_{We}^Q \,. \tag{26}$$

We see that the correlation functions have a rather complex form when expressed in terms of Wigner transformed variables, involving exponential operators of the Poisson bracket operator.

The classical limits of the correlation function expressions are easily obtained by taking the  $\hbar \rightarrow 0$  limit of these equations. We find,

$$\lambda_A \propto \frac{1}{\beta} \int_0^\infty dt \, \int d\mathcal{X} \left( j^A(t) \Lambda A \right) \rho_e = \int_0^\infty dt \, \int d\mathcal{X} \, j^A j^A(t) \rho_e \,, \quad (27)$$

where  $\rho_e$  is the classical canonical equilibrium density matrix.

### **3** Partial Wigner Representation of Quantum Mechanics

As discussed in the Introduction, our interest is in quantum-classical systems where the environmental degrees of freedom can be treated classically. The above formulation of quantum dynamics and quantum statistical mechanics in the Wigner representation suggests that we consider another formulation of quantum mechanics based on a *partial* Wigner representation where only the degrees of freedom in the  $\mathcal{E}$  subsystem are Wigner transformed [4]. We now sketch how this program can be carried out.

In order to distinguish between the subsystem S and environment  $\mathcal{E}$  variables we 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. Again, calligraphic symbols are used to denote variables for the entire system,  $S \bigoplus \mathcal{E}$ . The Hamiltonian is the sum of the kinetic energy operators of the subsystem and bath and the potential energy of the entire

system,  $\hat{H} = \hat{P}^2/2M + \hat{p}^2/2m + \hat{V}(\hat{q}, \hat{Q})$ . We suppose that the coordinate space dimension of  $\mathcal{S}$  is n and that of  $\mathcal{E}$  is N with  $\mathcal{N} = n + N$ .

The partial Wigner transformation [4] of the density matrix with respect to the subset of Q coordinates is

$$\hat{\rho}_W(R,P) = (2\pi\hbar)^{-N} \int dz e^{iP \cdot z/\hbar} \left\langle R - \frac{z}{2} |\hat{\rho}| R + \frac{z}{2} \right\rangle .$$
(28)

In this representation the quantum Liouville equation is,

$$\frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} = -\frac{i}{\hbar} \left( (\hat{H}\hat{\rho})_W - (\hat{\rho}\hat{H})_W \right)$$
$$= -\frac{i}{\hbar} \left( \hat{H}_W e^{\hbar A/2i} \hat{\rho}_W(t) - \hat{\rho}_W(t) e^{\hbar A/2i} \hat{H}_W \right) , \qquad (29)$$

where the partially Wigner transformed Hamiltonian is

$$\hat{H}_W(R,P) = \frac{P^2}{2M} + \frac{\hat{p}^2}{2m} + \hat{V}_W(\hat{q},R) , \qquad (30)$$

and  $\Lambda$  is again the negative of the Poisson bracket operator, but now operating only on the Wigner variables of  $\mathcal{E}$ . Note also that the partially Wigner transformed density matrix and operators are still operators in the Hilbert space of  $\mathcal{S}$  and not just phase space functions when full Wigner transforms are taken. We may rewrite the quantum Liouville equation in a more compact form [5,6]

$$\frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} = -i\hat{L}_W \hat{\rho}_W(t) \equiv -(\hat{H}_W, \hat{\rho}_W(t))_Q .$$
(31)

by defining the quantum Liouville operator and quantum bracket in this partial Wigner representation. As might be expected, the Heisenberg equation of motion for a partially transformed operator takes the form,

$$\frac{d\hat{A}_W(R, P, t)}{dt} = i\hat{L}_W\hat{A}_W(t) \equiv (\hat{H}_W, \hat{A}_W(t))_Q.$$
(32)

The partial Wigner transform of a product of operators satisfies the associative product rule,

$$(\hat{A}\hat{B}\hat{C})_W = \left( \left( \hat{A}_W e^{\hbar\Lambda/2i} \hat{B}_W \right) e^{\hbar\Lambda/2i} \hat{C}_W \right) = \left( \hat{A}_W e^{\hbar\Lambda/2i} \left( \hat{B}_W e^{\hbar\Lambda/2i} \hat{C}_W \right) \right) .$$
(33)

The time evolution of a quantum operator  $\hat{C} = \hat{A}\hat{B}$ , which is the product of two operators, can be written in the partial Wigner representation as

$$\hat{C}_W(t) = \hat{A}_W(t) e^{\hbar \Lambda/2i} \hat{B}_W(t) .$$
(34)

.

Quantum mechanics in the partial Wigner representation is exact and the partially Wigner transformed quantum bracket satisfies the Jacobi identity,

. .

$$(\hat{A}_W, (\hat{B}_W, \hat{C}_W)_Q)_Q + (\hat{C}_W, (\hat{A}_W, \hat{B}_W)_Q)_Q + (\hat{B}_W, (\hat{C}_W, \hat{A}_W)_Q)_Q = 0,$$
(35)

consistent with the Lie algebraic structure of quantum dynamics.

### 4 Quantum-Classical Dynamics

We saw that it was a simple matter to take the classical limit of the quantum Liouville equation in Wigner transformed form by retaining only those terms in the Liouville operator that were independent of  $\hbar$ ; i.e., taking the  $\hbar \rightarrow 0$  limit of the Liouville operator. We cannot follow so simple a procedure to construct a quantum-classical equation of motion since  $\hbar$  appears in the evolution operator arising from the S degrees of freedom and in the exponential operator involving the Poisson bracket operator coming from the partial Wigner transform over the  $\mathcal{E}$  subsystem degrees of freedom. We now describe how to construct approximate evolution equations.

#### 4.1 Dynamics

While one can imagine various routes to obtain the quantum-classical equations of motion, one way to disentangle these different contributions is to suppose that the particles comprising  $\mathcal{E}$  have mass M while those of  $\mathcal{S}$ have mass m, with  $m \ll M$ . In this circumstance we can scale variables so that distances are measured on the scale characteristic of the light particles,  $\lambda_m = (\hbar^2/m\epsilon_0)^{1/2}$ , with  $\epsilon_0$  some characteristic energy of the system, and velocities of both light and heavy particles are scaled to be comparable using momentum units  $p_m = (m\lambda_m/t_0) = (m\epsilon_0)^{1/2}$  and  $P_M = (M\epsilon_0)^{1/2}$ , respectively. Here  $t_0 = \hbar/\epsilon_0$  is the chosen time unit. This scaling is reminiscent of that used to derive Langevin equations from the Liouville equation in the theory of Brownian motion [7].

Let energy be measured in units of  $\epsilon_0$  and time in units of  $t_0 = \hbar/\epsilon_0$ . In scaled units  $\hat{q}' = \hat{q}/\lambda_m$ ,  $R' = R/\lambda_m$ ,  $\hat{p}' = \hat{p}/p_m$ ,  $P' = P/P_M$  and  $t' = t/t_0$ , we have,

$$\frac{\partial \hat{\rho}'_W(R', P', t)}{\partial t'} = -i \Big( \hat{H}'_W e^{\mu \Lambda'/2i} \hat{\rho}'_W(t') - \hat{\rho}'_W(t') e^{\mu \Lambda'/2i} \hat{H}'_W \Big) \\\approx -i \Big( \hat{H}'_W(1 + \frac{\mu \Lambda'}{2i}) \hat{\rho}'_W(t') - \hat{\rho}'_W(t')(1 + \frac{\mu \Lambda'}{2i}) \hat{H}'_W \Big) . (36)$$

To obtain the second approximate equality we expanded the right hand side to first order in the small parameter  $\mu = (m/M)^{1/2}$ . Returning to unscaled units we have the quantum-classical Liouville equation,

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$$\frac{\partial \hat{\rho}_W(R, P, t)}{\partial t} = -\frac{i}{\hbar} [\hat{H}_W, \hat{\rho}_W(t)] + \frac{1}{2} \Big( \{\hat{H}_W, \hat{\rho}_W(t)\} - \{\hat{\rho}_W(t), \hat{H}_W\} \Big) = -(\hat{H}_W, \hat{\rho}_W(t)) = -i\hat{\mathcal{L}}\hat{\rho}_W(t) , \qquad (37)$$

that gives the time evolution of the quantum-classical density matrix  $\hat{\rho}_W(R, P, t)$  [4, 8–15]. The last two equalities in (37) define the quantumclassical bracket and quantum-classical Liouville operator [4, 5]. In (37), the coupling between the quantum subsystem and bath appears in both terms in the quantum-classical Liouville operator. The quantum character manifests itself in the Poisson bracket terms since the quantum operators do not commute and their order must be respected.

Using a similar procedure we may derive the equation of motion for an observable,  $\hat{A}_W(R, P, t)$  [4]

$$\frac{d\hat{A}_W(R,P,t)}{dt} = (\hat{H}_W, \hat{A}_W(t)) = i\hat{\mathcal{L}}\hat{A}_W(t) , \qquad (38)$$

which is the quantum-classical analog of the Heisenberg equation of motion. This equation manifestly conserves energy.

In contrast to quantum mechanical and classical brackets, the quantumclassical bracket does not satisfy the Jacobi identity since [5]

$$(\hat{A}_W, (\hat{B}_W, \hat{C}_W)) + (\hat{C}_W, (\hat{A}_W, \hat{B}_W)) + (\hat{B}_W, (\hat{C}_W, \hat{A}_W)) \neq 0.$$
 (39)

Consequently, quantum-classical dynamics does not possess a Lie algebraic structure and this leads to pathologies in the general formulation of quantum-classical dynamics and statistical mechanics as we shall see below [5,6].

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

$$i\hat{\mathcal{L}}\hat{C}_W = (i\hat{\mathcal{L}}\hat{B}_W)\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{A}_W + \hat{B}_W\left(1 + \frac{\hbar\Lambda}{2i}\right)(i\hat{\mathcal{L}}\hat{A}_W) + \mathcal{O}(\hbar) .$$
(40)

It follows that

$$\hat{C}_{W}(t) = e^{i\hat{\mathcal{L}}t}\hat{C}_{W} = (1 + i\hat{\mathcal{L}}t + (i\hat{\mathcal{L}})^{2}\frac{t}{2!} + \dots)\left(\hat{B}_{W}\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{A}_{W} + \mathcal{O}(\hbar^{2})\right)$$

$$= \hat{B}_{W}\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{A}_{W} + \mathcal{O}(\hbar^{2})$$

$$+ t\left((i\hat{\mathcal{L}}\hat{B}_{W})\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{A}_{W} + \hat{B}_{W}\left(1 + \frac{\hbar\Lambda}{2i}\right)(i\hat{\mathcal{L}}\hat{A}_{W}) + \mathcal{O}(\hbar)\right)$$

$$+ \frac{t^{2}}{2!}\left(((i\hat{\mathcal{L}})^{2}\hat{B}_{W})\left(1 + \frac{\hbar\Lambda}{2i}\right)\hat{A}_{W} + 2(i\hat{\mathcal{L}}\hat{B}_{W})\left(1 + \frac{\hbar\Lambda}{2i}\right)(i\hat{\mathcal{L}}\hat{A}_{W})$$

$$+ \hat{B}_{W}\left(1 + \frac{\hbar\Lambda}{2i}\right)((i\hat{\mathcal{L}})^{2}\hat{A}_{W}) + \mathcal{O}(\hbar)\right) + \dots . \tag{41}$$

Resumming the series of operators we find,

$$\hat{C}_W(t) = \left(e^{i\hat{\mathcal{L}}t}\hat{B}_W\right) \left(1 + \frac{\hbar\Lambda}{2i}\right) \left(e^{i\hat{\mathcal{L}}t}\hat{A}_W\right) + \mathcal{O}(\hbar)$$
$$= \hat{B}_W(t) \left(1 + \frac{\hbar\Lambda}{2i}\right) \hat{A}_W(t) + \mathcal{O}(\hbar) .$$
(42)

While these features lead to some pathologies in the formulation of quantumclassical dynamics and statistical mechanics, the violations are in terms of higher order in  $\hbar$  for the bath (or, better, the mass ratio  $\mu$ ), so that for systems where quantum-classical dynamics is likely to be applicable the numerical consequences are often small. We remark that almost all quantum-classical schemes suffer from these problems, although these deficiencies are often not highlighted.

The quantum-classical Liouville equation may be expressed in any convenient basis. In particular, the adiabatic basis vectors,  $|\alpha; R\rangle$ , are given by the solutions of  $\hat{h}_W |\alpha; R\rangle = E_{\alpha}(R) |\alpha; R\rangle$ , where  $\hat{h}_W = \frac{\hat{p}^2}{2m} + \hat{V}_W(\hat{q}, R)$ . We take an Eulerian view of the dynamics so that the adiabatic basis vectors are parameterized by the time-independent values of the bath coordinates R. In this basis, the Liouville operator has matrix elements [4],

$$i\mathcal{L}_{\alpha\alpha',\beta\beta'} = (i\omega_{\alpha\alpha'} + iL_{\alpha\alpha'})\delta_{\alpha\beta}\delta_{\alpha'\beta'} - J_{\alpha\alpha',\beta\beta'}$$
  
$$\equiv i\mathcal{L}^{0}_{\alpha\alpha'}\delta_{\alpha\beta}\delta_{\alpha'\beta'} - J_{\alpha\alpha',\beta\beta'}, \qquad (43)$$

where  $\omega_{\alpha\alpha'}(R) = (E_{\alpha}(R) - E_{\alpha'}(R))/\hbar$  is a frequency determined by the difference in energies of adiabatic states and  $iL_{\alpha\alpha'}$  is the Liouville operator for classical evolution under the mean of the Hellmann-Feynman forces for adiabatic states  $\alpha$  and  $\alpha'$ ,

$$iL_{\alpha\alpha'} = \frac{P}{M} \cdot \frac{\partial}{\partial R} + \frac{1}{2} \left( F_W^{\alpha} + F_W^{\alpha'} \right) \cdot \frac{\partial}{\partial P} , \qquad (44)$$

where  $F_W^{\alpha} = -\langle \alpha; R | \frac{\partial \hat{V}_W(\hat{q}, R)}{\partial R} | \alpha; R \rangle$  is the Hellmann-Feynman force for state  $\alpha$ . The operator  $J_{\alpha\alpha',\beta\beta'}$  accounts for non-adiabatic transitions and corresponding changes of the bath momentum. It is given by

$$J_{\alpha\alpha',\beta\beta'} = -\frac{P}{M} \cdot d_{\alpha\beta} \left( 1 + \frac{1}{2} S_{\alpha\beta} \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha'\beta'} -\frac{P}{M} \cdot d^*_{\alpha'\beta'} \left( 1 + \frac{1}{2} S^*_{\alpha'\beta'} \cdot \frac{\partial}{\partial P} \right) \delta_{\alpha\beta} , \qquad (45)$$

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

### 4.2 Transport Properties

We may easily carry out a linear response theory derivation of transport properties based on the quantum-classical Liouville equation that parallels the derivation for quantum systems outlined above. We suppose the quantumclassical system with Hamiltonian  $\hat{H}_W$  is subjected to a time dependent external force that couples to the observable  $\hat{A}_W$ , so that the total Hamiltonian is

$$\hat{\mathcal{H}}_W(t) = \hat{H}_W - \hat{A}_W F(t) . \tag{46}$$

The evolution equation for the density matrix takes the form

$$\frac{\partial \hat{\rho}_W(t)}{\partial t} = -(i\hat{\mathcal{L}} - i\hat{\mathcal{L}}_A F(t))\hat{\rho}_W(t) , \qquad (47)$$

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

$$\hat{\rho}_W(t) = e^{-i\hat{\mathcal{L}}(t-t_0)}\hat{\rho}_W(t_0) + \int_{t_0}^t dt' \ e^{-i\hat{\mathcal{L}}(t-t')}i\hat{\mathcal{L}}_A\hat{\rho}_W(t')F(t') \ .$$
(48)

The next step in the calculation is to choose  $\hat{\rho}_W(t_0)$  to be the equilibrium density matrix,  $\hat{\rho}_{We}$ . One of the differences between quantum and quantumclassical response theories appears at this stage. In quantum mechanics, the quantum canonical equilibrium density is  $\hat{\rho}_e^Q = Z_Q^{-1} \exp(-\beta \hat{H})$  which, when expressed in terms of the partial Wigner transform, can be written as

$$\hat{\rho}_{We}^{Q}(R,P) = (2\pi\hbar)^{-N} \int dZ e^{iP \cdot Z/\hbar} \left\langle R - \frac{Z}{2} | \hat{\rho}_{e}^{Q} | R + \frac{Z}{2} \right\rangle .$$
(49)

The density matrix  $\hat{\rho}_{We}^Q(R, P)$  is not stationary under quantum-classical dynamics. Instead, the equilibrium density of a quantum-classical system has to be determined by solving the equation  $i\hat{\mathcal{L}}\hat{\rho}_{We} = 0$ . An explicit solution of this equation has not been found although a recursive solution, obtained by expressing the density matrix  $\hat{\rho}_{We}$  in a power series in  $\hbar$  or the mass ratio  $\mu$ , can be determined. While it is difficult to find the full solution to all orders in  $\hbar$ , the solution is known analytically to  $\mathcal{O}(\hbar)$ . When expressed in the adiabatic basis, the result is [5]

$$\rho_{We}^{\alpha\alpha'} = \rho_{We}^{(0)\alpha} \Big( \delta_{\alpha\alpha'} - i\hbar \frac{P}{M} \cdot d_{\alpha\alpha'} \Big( \frac{\beta}{2} (1 + e^{-\beta E_{\alpha'\alpha}}) \\ + \frac{1}{E_{\alpha\alpha'}} (1 - e^{-\beta E_{\alpha'\alpha}}) \Big) (1 - \delta_{\alpha\alpha'}) \Big) + \mathcal{O}(\hbar^2) .$$
(50)

If the partial Wigner transform of the exact canonical quantum equilibrium density in (49) is expressed in the adiabatic basis and is expanded to linear order in  $\hbar$ , we obtain the same result as in (50), indicating that the quantum-classical expression is exact to this order.

Using the quantum-classical form for  $\hat{\rho}_{We}$ , which, by construction, is invariant under quantum-classical dynamics, the first term on the right hand side of (48) reduces to  $\hat{\rho}_{We}$  and is independent of  $t_0$ . We may assume that

the system with Hamiltonian  $\hat{H}_W$  is in thermal equilibrium at  $t_0 = -\infty$ , and with this boundary condition, to first order in the external force, (48) is

$$\hat{\rho}_W(t) = \hat{\rho}_{We} + \int_{-\infty}^t dt' \ e^{-i\hat{\mathcal{L}}(t-t')} i\hat{\mathcal{L}}_A \hat{\rho}_{We} F(t') \ . \tag{51}$$

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

$$\overline{B_W(t)} = \int_{-\infty}^t dt' \operatorname{Tr}' \int dR dP \ \hat{B}_W e^{-i\hat{\mathcal{L}}(t-t')} i\hat{\mathcal{L}}_A \hat{\rho}_{We} F(t')$$
$$= \int_{-\infty}^t dt' \left\langle (\hat{B}_W(t-t'), \hat{A}_W) \right\rangle F(t') \equiv \int_{-\infty}^t dt' \ \phi_{BA}^{QC}(t-t') F(t') \ .$$
(52)

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

$$\phi_{BA}^{QC}(t) = \langle (\hat{B}_W(t), \hat{A}_W) \rangle = \text{Tr}' \int dR dP \ \hat{B}_W(t) (\hat{A}_W, \hat{\rho}_{We}) . \tag{53}$$

where, in writing the second equality in (53), we have used cyclic permutations under the trace and integrations by parts.

Given the response function, an expression for a transport coefficient can be obtained by taking  $\hat{B}_W = \hat{A}_W = i\mathcal{L}\hat{A}_W \equiv \hat{j}_W^A$ . The quantum-classical analog of the expression for a quantum mechanical transport coefficient in (23) is given by

$$\lambda_A \propto \int_0^\infty dt \, \langle (\hat{j}_W^A(t), \hat{A}_W) \rangle = \int_0^\infty dt \, \text{Tr}' \int dR dP \, \hat{j}_W^A(t) (\hat{A}_W, \hat{\rho}_{We}) \,. \tag{54}$$

This correlation function expression involves both quantum-classical dynamical evolution of observables and quantum-classical expressions for the equilibrium density.

## 5 Quantum-Classical Approximations for Quantum Correlation Functions

Rather than carrying out a linear response derivation to obtain correlation function expressions for transport coefficients based on the quantum-classical equations of motion, in this section we show how transport coefficients can be obtained by a different route. We take as a starting point the quantum mechanical expression for a transport coefficient and consider a limit where the *dynamics* is approximated by quantum-classical dynamics [17, 18]. The advantage of this approach is that the full quantum equilibrium structure can be retained while still performing the evolution of observables using quantumclassical dynamics, which is computationally more tractable than full quantum evolution.

The quantum mechanical expression for a transport property was given in (23) and its generalization to a time-dependent transport coefficient, defined as the finite time integral of a general flux-flux correlation function involving the fluxes of operators  $\hat{A}$  and  $\hat{B}$ , is

$$\lambda_{AB}(t) = \int_0^t dt' \langle \hat{j}_A; \hat{j}_B(t') \rangle_Q = \langle \dot{\hat{A}}; \hat{B}(t) \rangle = \frac{1}{\beta} \left\langle \frac{i}{\hbar} [\hat{B}(t), \hat{A}] \right\rangle_Q .$$
(55)

It is convenient in simulations to determine the transport coefficient from the plateau value of  $\lambda_{AB}(t)$  [3]. Considering the second equality in (55) in detail, we can write the transport coefficient  $\lambda_{AB}(t)$  as,

$$\lambda_{AB}(t) = \frac{1}{\beta Z_Q} \int_0^\beta d\lambda \operatorname{Tr} \left( \dot{\hat{A}} \left( -i\hbar\lambda \right) \hat{B}(t) e^{-\beta \hat{H}} \right) \\ = \frac{1}{\beta Z_Q} \int_0^\beta d\lambda \operatorname{Tr} \left( \dot{\hat{A}} e^{\frac{i}{\hbar} \hat{H}(t+i\hbar\lambda)} \hat{B} e^{-\frac{i}{\hbar} \hat{H}(t+i\hbar\lambda)} e^{-\beta \hat{H}} \right) \\ = \frac{1}{\beta Z_Q} \int_0^\beta d\lambda \int \prod_{i=1}^4 d\mathcal{Q}_i \langle \mathcal{Q}_1 | \dot{\hat{A}} | \mathcal{Q}_2 \rangle \langle \mathcal{Q}_2 | e^{\frac{i}{\hbar} \hat{H}(t+i\hbar\lambda)} | \mathcal{Q}_3 \rangle \langle \mathcal{Q}_3 | \hat{B} | \mathcal{Q}_4 \rangle \\ \times \langle \mathcal{Q}_4 | e^{-\frac{i}{\hbar} \hat{H}(t+i\hbar\lambda)} e^{-\beta \hat{H}} | \mathcal{Q}_1 \rangle ,$$
(56)

where the last line follows from introducing a coordinate representation  $\{Q\} = \{q\}\{Q\}$  of the operators (recall that calligraphic symbols are used to denote variables for the entire system, subsystem plus bath). Making a change of variables,  $Q_1 = \mathcal{R}_1 - \mathcal{Z}_1/2$ ,  $Q_2 = \mathcal{R}_1 + \mathcal{Z}_1/2$ , etc., and then expressing the matrix elements in terms of the Wigner transforms of the operators using (6), we have [18]

$$\lambda_{AB}(t) = \frac{1}{\beta} \int_{0}^{\beta} d\lambda \int d\mathcal{X}_{1} d\mathcal{X}_{2}(\dot{A})_{W}(\mathcal{X}_{1}) B_{W}(\mathcal{X}_{2}) \frac{1}{\left(2\pi\hbar\right)^{2\mathcal{N}} Z_{Q}} \\ \times \int d\mathcal{Z}_{1} d\mathcal{Z}_{2} e^{-\frac{i}{\hbar}(\mathcal{P}_{1}\cdot\mathcal{Z}_{1}+\mathcal{P}_{2}\cdot\mathcal{Z}_{2})} \left\langle \mathcal{R}_{1} + \frac{\mathcal{Z}_{1}}{2} \left| e^{\frac{i}{\hbar}\hat{H}(t+i\hbar\lambda)} \right| \mathcal{R}_{2} - \frac{\mathcal{Z}_{2}}{2} \right\rangle \\ \times \left\langle \mathcal{R}_{2} + \frac{\mathcal{Z}_{2}}{2} \left| e^{-\beta\hat{H} - \frac{i}{\hbar}\hat{H}(t+i\hbar\lambda)} \right| \mathcal{R}_{1} - \frac{\mathcal{Z}_{1}}{2} \right\rangle.$$
(57)

We define the spectral density by [19, 20],

$$W(\mathcal{X}_{1},\mathcal{X}_{2},t) = \frac{1}{(2\pi\hbar)^{2\mathcal{N}} Z_{Q}} \int d\mathcal{Z}_{1} d\mathcal{Z}_{2} e^{-\frac{i}{\hbar}(\mathcal{P}_{1}\cdot\mathcal{Z}_{1}+\mathcal{P}_{2}\cdot\mathcal{Z}_{2})} \\ \times \left\langle \mathcal{R}_{1} + \frac{\mathcal{Z}_{1}}{2} \left| e^{\frac{i}{\hbar}\hat{H}t} \right| \mathcal{R}_{2} - \frac{\mathcal{Z}_{2}}{2} \right\rangle \left\langle \mathcal{R}_{2} + \frac{\mathcal{Z}_{2}}{2} \left| e^{-\beta\hat{H} - \frac{i}{\hbar}\hat{H}t} \right| \mathcal{R}_{1} - \frac{\mathcal{Z}_{1}}{2} \right\rangle, (58)$$

which, for real t, satisfies the property

$$W(\mathcal{X}_1, \mathcal{X}_2, t)^* = W(\mathcal{X}_2, \mathcal{X}_1, -t) .$$
(59)

Letting

$$\overline{W}(\mathcal{X}_1, \mathcal{X}_2, t) = \frac{1}{\beta} \int_0^\beta d\lambda W(\mathcal{X}_1, \mathcal{X}_2, t + i\hbar\lambda) , \qquad (60)$$

which satisfies the same symmetry property as (59), we can write the transport coefficient as

$$\lambda_{AB}(t) = \int d\mathcal{X}_1 d\mathcal{X}_2(\dot{A})_W(\mathcal{X}_1) B_W(\mathcal{X}_2) \overline{W}(\mathcal{X}_1, \mathcal{X}_2, t)$$
  
$$= \int d\mathcal{X}_1 d\mathcal{X}_2(iL_W(\mathcal{X}_1) A_W(\mathcal{X}_1)) B_W(\mathcal{X}_2) \overline{W}(\mathcal{X}_1, \mathcal{X}_2, t)$$
  
$$= -\int d\mathcal{X}_1 d\mathcal{X}_2 A_W(\mathcal{X}_1) B_W(\mathcal{X}_2)(iL_W(\mathcal{X}_1) \overline{W}(\mathcal{X}_1, \mathcal{X}_2, t)). \quad (61)$$

From (61), the time evolution of  $\overline{W}(\mathcal{X}_1, \mathcal{X}_2, t)$  may be defined by<sup>3</sup>

$$\frac{\partial}{\partial t}\overline{W}(\mathcal{X}_1, \mathcal{X}_2, t) = iL_W(\mathcal{X}_1)\overline{W}(\mathcal{X}_1, \mathcal{X}_2, t) .$$
(62)

Using these results, the transport coefficient expression can be written as

$$\lambda_{AB}(t) = -\int d\mathcal{X}_1 d\mathcal{X}_2 A_W(\mathcal{X}_1) B_W(\mathcal{X}_2) \left(\frac{\partial}{\partial t} \overline{W}(\mathcal{X}_1, \mathcal{X}_2, t)\right).$$
(63)

This transport coefficient expression is exact. The full quantum equilibrium structure is contained in the initial value  $\overline{W}(\mathcal{X}_1, \mathcal{X}_2, 0)$ , which is proportional to the integral over  $\lambda$  of

$$W(\mathcal{X}_1, \mathcal{X}_2, i\hbar\lambda) = \frac{1}{(2\pi\hbar)^{2\mathcal{N}} Z_Q} \int d\mathcal{Z}_1 d\mathcal{Z}_2 e^{-\frac{i}{\hbar}(\mathcal{P}_1 \cdot \mathcal{Z}_1 + \mathcal{P}_2 \cdot \mathcal{Z}_2)} \\ \times \left\langle \mathcal{R}_1 + \frac{\mathcal{Z}_1}{2} \left| e^{-\hat{H}\lambda} \right| \mathcal{R}_2 - \frac{\mathcal{Z}_2}{2} \right\rangle \left\langle \mathcal{R}_2 + \frac{\mathcal{Z}_2}{2} \left| e^{-(\beta - \lambda)\hat{H}} \right| \mathcal{R}_1 - \frac{\mathcal{Z}_1}{2} \right\rangle.$$
(64)

Its time evolution is given by full quantum mechanics in the Wigner representation. In order to obtain a computationally tractable form, we consider a limit where the time evolution of  $\overline{W}(\mathcal{X}_1, \mathcal{X}_2, t)$  is approximated by quantumclassical dynamics.

For future reference, we remark that the evolution equation can be written in other forms using the symmetry relation (59). Taking complex conjugates of both sides of (62) and using the fact that  $(iL_W)^* = iL_W$  gives

<sup>&</sup>lt;sup>3</sup> We may also obtain this equation of motion directly by differentiating the definition of W in (58)

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$$\frac{\partial}{\partial t}\overline{W}(\mathcal{X}_2, \mathcal{X}_1, -t) = iL_W(\mathcal{X}_1)\overline{W}(\mathcal{X}_2, \mathcal{X}_1, -t) .$$
(65)

If we then exchange variables  $\mathcal{X}_1 \leftrightarrow \mathcal{X}_2$  and  $t \leftrightarrow -t$  we get [18]

$$\frac{\partial}{\partial t}\overline{W}(\mathcal{X}_1, \mathcal{X}_2, t) = -iL_W(\mathcal{X}_2)\overline{W}(\mathcal{X}_1, \mathcal{X}_2, t) .$$
(66)

We shall make use of these various equivalent forms of the evolution to write the reaction rate coefficient expression in a form that is most convenient for simulation.

#### 5.1 Quantum-Classical Evolution Equation for W

The Wigner form of the quantum evolution operator  $iL_W(\mathcal{X}_1)$  in (62) for the equation of motion for  $\overline{W}(\mathcal{X}_1, \mathcal{X}_2, t)$  can be rewritten in a form that is convenient for the passage to the quantum-classical limit. Recalling that the system may be partitioned into  $\mathcal{S}$  and  $\mathcal{E}$  subspaces, the Poisson bracket operator  $\Lambda$  can be written as the sum of Poisson bracket operators acting in each of these subspaces as  $\Lambda(\mathcal{X}_1) = \Lambda(x_1) + \Lambda(X_1)$ . Thus, we may write

$$iL_W(\mathcal{X}_1) = \frac{2}{\hbar} H_W(\mathcal{X}_1) \sin(\hbar \Lambda(\mathcal{X}_1)/2)$$
  
$$= \frac{2}{\hbar} H_W(\mathcal{X}_1) \sin(\hbar \Lambda(x_1)/2 + \hbar \Lambda(X_1)/2)$$
  
$$= \frac{2}{\hbar} H_W(\mathcal{X}_1) \Big( \sin(\hbar \Lambda(x_1)/2) \cos(\hbar \Lambda(X_1)/2) + \cos(\hbar \Lambda(x_1)/2) \sin(\hbar \Lambda(X_1)/2) \Big).$$
(67)

If we introduce scaled coordinates as defined in Sect. 4.1 and expand the evolution operator to first order in the mass ratio  $\mu$ , the resulting expression for the quantum-classical evolution operator in unscaled coordinates is<sup>4</sup>

$$i\mathcal{L}(\mathcal{X}_1) = \frac{2}{\hbar} H_W(\mathcal{X}_1) \sin(\hbar \Lambda(x_1)/2) + H_W(\mathcal{X}_1) \cos(\hbar \Lambda(x_1)/2) \Lambda(X_1) .$$
(68)

With this approximate expression for  $iL_W$ , (62) becomes the quantumclassical evolution equation for the spectral density function,

$$\frac{\partial}{\partial t}\overline{W}(\mathcal{X}_1, \mathcal{X}_2, t) = i\mathcal{L}(\mathcal{X}_1)\overline{W}(\mathcal{X}_1, \mathcal{X}_2, t) .$$
(69)

A similar analysis can be carried out on (66) to obtain a quantum-classical evolution equation involving the operator in  $\mathcal{X}_2$  phase space coordinates.

<sup>&</sup>lt;sup>4</sup>  $i\mathcal{L}(\mathcal{X})$  is the Wigner transform of  $i\hat{\mathcal{L}}(X)$  defined earlier in (37) over the  $\mathcal{S}$  subsystem degrees of freedom.

#### 5.2 Adiabatic Basis

Since Wigner transformed quantum mechanics is difficult to compute, we express the  $\mathcal{S}$  subsystem degrees of freedom in an adiabatic basis rather than in a Wigner representation. To this end, we first observe that  $A_W(\mathcal{X}_1)$  can be written as

$$A_W(\mathcal{X}_1) = \int dz_1 \ e^{\frac{i}{\hbar} p_1 \cdot z_1} \left\langle r_1 - \frac{z_1}{2} |\hat{A}_W(X_1)| r_1 + \frac{z_1}{2} \right\rangle, \tag{70}$$

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

$$A_{W}(\mathcal{X}_{1}) = \sum_{\alpha_{1}\alpha_{1}'} \int dz_{1} \ e^{\frac{i}{\hbar}p_{1} \cdot z_{1}} \left\langle r_{1} - \frac{z_{1}}{2} | \alpha_{1}; R_{1} \right\rangle A_{W}^{\alpha_{1}\alpha_{1}'}(X_{1}) \left\langle \alpha_{1}'; R_{1} | r_{1} + \frac{z_{1}}{2} \right\rangle,$$
(71)

where  $A_W^{\alpha_1 \alpha'_1}(X_1) = \langle \alpha_1; R_1 | \hat{A}_W(X_1) | \alpha'_1; R_1 \rangle$ . Starting with (63) and inserting the expression (71) for  $A_W(\mathcal{X}_1)$  and its analog for  $B_W(\mathcal{X}_2)$ , the time-dependent transport coefficient expression becomes

$$\lambda_{AB}(t) = -\sum_{\alpha_1, \alpha_1', \alpha_2, \alpha_2'} \int \prod_{i=1}^2 dX_i \ A_W^{\alpha_1 \alpha_1'}(X_1) B_W^{\alpha_2 \alpha_2'}(X_2) \\ \times \frac{\partial}{\partial t} \overline{W}^{\alpha_1' \alpha_1 \alpha_2' \alpha_2}(X_1, X_2, t),$$
(72)

where

$$W^{\alpha_{1}'\alpha_{1}\alpha_{2}'\alpha_{2}}(X_{1}, X_{2}, t) = \int \prod_{i=1}^{2} dx_{i} dz_{i} \ e^{\frac{i}{\hbar}(p_{1} \cdot z_{1} + p_{2} \cdot z_{2})} \left\langle r_{1} - \frac{z_{1}}{2} | \alpha_{1}; R_{1} \right\rangle$$
$$\times \left\langle \alpha_{1}'; R_{1} | r_{1} + \frac{z_{1}}{2} \right\rangle \left\langle r_{2} - \frac{z_{2}}{2} | \alpha_{2}; R_{2} \right\rangle \left\langle \alpha_{2}'; R_{2} | r_{2} + \frac{z_{2}}{2} \right\rangle W(\mathcal{X}_{1}, \mathcal{X}_{2}, t) , (73)$$

Performing integrals over subsystem  $\mathcal{S}$  coordinates, this expression may also be written in the more explicit form,

$$W^{\alpha_{1}'\alpha_{1}\alpha_{2}'\alpha_{2}}(X_{1}, X_{2}, t) = \int \prod_{i=1}^{2} dZ_{i} e^{-\frac{i}{\hbar}(P_{1} \cdot Z_{1} + P_{2} \cdot Z_{2})} \frac{1}{Z_{Q}} \frac{1}{(2\pi\hbar)^{2N}} \\ \times \left\langle \alpha_{1}'; R_{1} \middle| \left\langle R_{1} + \frac{Z_{1}}{2} \middle| e^{\frac{i}{\hbar}\hat{H}t} \middle| R_{2} - \frac{Z_{2}}{2} \right\rangle \middle| \alpha_{2}; R_{2} \right\rangle \\ \times \left\langle \alpha_{2}'; R_{2} \middle| \left\langle R_{2} + \frac{Z_{2}}{2} \middle| e^{-\frac{i}{\hbar}\hat{H}t - \beta\hat{H}} \middle| R_{1} - \frac{Z_{1}}{2} \right\rangle \middle| \alpha_{1}; R_{1} \right\rangle .$$
(74)

Equation (73) shows how  $W(\mathcal{X}_1, \mathcal{X}_2, t)$  may be related to its matrix elements  $W^{\alpha'_1 \alpha_1 \alpha'_2 \alpha_2}(X_1, X_2, t)$  in the adiabatic basis. Similarly,

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$$W(\mathcal{X}_{1}, \mathcal{X}_{2}, t) = \sum_{\alpha_{1}'\alpha_{1}\alpha_{2}'\alpha_{2}} \int \prod_{i=1}^{2} dz_{i} \ e^{-\frac{i}{\hbar}(p_{1}\cdot z_{1}+p_{2}\cdot z_{2})} \frac{1}{(2\pi\hbar)^{2n}} \left\langle r_{1} + \frac{z_{1}}{2} |\alpha_{1}'; R_{1} \right\rangle$$
$$\times \left\langle \alpha_{1}; R_{1} | r_{1} - \frac{z_{1}}{2} \right\rangle \left\langle r_{2} + \frac{z_{2}}{2} | \alpha_{2}'; R_{2} \right\rangle \left\langle \alpha_{2}; R_{2} | r_{2} - \frac{z_{2}}{2} \right\rangle W^{\alpha_{1}'\alpha_{1}\alpha_{2}'\alpha_{2}}(X_{1}, X_{2}, t) .$$
(75)

relates W to its matrix elements  $W^{\alpha'_1\alpha_1\alpha'_2\alpha_2}$ .

The quantum-classical evolution equation for  $W^{\alpha'_1\alpha_1\alpha'_2\alpha_2}(X_1, X_2, t)$  may now be obtained from (69) by taking matrix elements of this equation using the definitions given above. We obtain [17, 18],

$$\frac{\partial}{\partial t}\overline{W}^{\alpha_1'\alpha_1\alpha_2'\alpha_2}(X_1, X_2, t) = \sum_{\beta_1'\beta_1} i\mathcal{L}_{\alpha_1'\alpha_1, \beta_1'\beta_1}(X_1)\overline{W}^{\beta_1'\beta_1\alpha_2'\alpha_2}(X_1, X_2, t) . (76)$$

The quantum-classical evolution operator  $i\mathcal{L}_{\alpha'\alpha,\beta'\beta}$  appearing in this equation is the same as that already defined in (43). We shall also have occasion to use (66) expressed in terms of matrix elements in the analysis presented below. Using (66), an equivalent form of the evolution equation is,

$$\frac{\partial}{\partial t}\overline{W}^{\alpha_1'\alpha_1\alpha_2'\alpha_2}(X_1, X_2, t) = -\sum_{\beta_2'\beta_2} i\mathcal{L}_{\alpha_2'\alpha_2, \beta_2'\beta_2}(X_2)\overline{W}^{\alpha_1'\alpha_1\beta_2'\beta_2}(X_1, X_2, t) .$$
(77)

#### 5.3 Transport Coefficient

Using these results, we may now obtain a form for transport coefficients which is convenient for simulation. We use the equality in (76), insert this into (72), and move the evolution operator  $i\mathcal{L}(X_1)$  onto the  $A_W(X_1)$  dynamical variable making use of integration by parts and cyclic permutations under the trace. We find

$$\lambda_{AB}(t) = \sum_{\alpha_1, \alpha'_1, \alpha_2, \alpha'_2} \int \prod_{i=1}^2 dX_i \ (i\mathcal{L}(X_1)A_W(X_1))^{\alpha_1\alpha'_1} \\ \times B_W^{\alpha_2\alpha'_2}(X_2)\overline{W}^{\alpha'_1\alpha_1\alpha'_2\alpha_2}(X_1, X_2, t).$$
(78)

Next, we use the equality in (77) 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 (78) 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

$$B_W^{\alpha_2 \alpha'_2}(X_2, t) = \sum_{\beta_2 \beta'_2} \left( e^{-i\mathcal{L}(X_2)t} \right)_{\alpha_2 \alpha'_2, \beta_2 \beta'_2} B_W^{\beta_2 \beta'_2}(X_2) .$$
(79)

The final expression for a transport coefficient is

$$\lambda_{AB}(t) = \sum_{\alpha_1, \alpha'_1, \alpha_2, \alpha'_2} \int \prod_{i=1}^2 dX_i \ (i\mathcal{L}(X_1)A_W(X_1))^{\alpha_1\alpha'_1} \\ \times B_W^{\alpha_2\alpha'_2}(X_2, t)\overline{W}^{\alpha'_1\alpha_1\alpha'_2\alpha_2}(X_1, X_2, 0).$$
(80)

This equation can serve as the basis for the computation of transport properties for quantum-classical systems. The evolution of dynamical variables is carried out using quantum-classical Liouville dynamics as in the quantumclassical linear response expression (54). However, in contrast to (54), full quantum equilibrium effects are incorporated in the initial value of  $\overline{W}$ , which, from its definition in (60), depends on the quantity,

$$W^{\alpha_{1}'\alpha_{1}\alpha_{2}'\alpha_{2}}(X_{1}, X_{2}, i\hbar\lambda) = \int \prod_{i=1}^{2} dZ_{i} e^{-\frac{i}{\hbar}(P_{1} \cdot Z_{1} + P_{2} \cdot Z_{2})} \frac{1}{Z_{Q}} \frac{1}{(2\pi\hbar)^{2N}} \\ \times \left\langle \alpha_{1}'; R_{1} \middle| \left\langle R_{1} + \frac{Z_{1}}{2} \middle| e^{-\hat{H}\lambda} \middle| R_{2} - \frac{Z_{2}}{2} \right\rangle \middle| \alpha_{2}; R_{2} \right\rangle \\ \times \left\langle \alpha_{2}'; R_{2} \middle| \left\langle R_{2} + \frac{Z_{2}}{2} \middle| e^{\hat{H}(\lambda-\beta)} \middle| R_{1} - \frac{Z_{1}}{2} \right\rangle \middle| \alpha_{1}; R_{1} \right\rangle .$$
(81)

### 6 Simulation Algorithms

Thus far we have focused on the formal development of quantum-classical dynamics and the derivation of expressions for transport coefficients which utilize this dynamics. We now turn to a discussion of how quantum-classical Liouville dynamics can be simulated for arbitrary many-body systems.

Various schemes have been proposed for the solution of the quantumclassical Liouville equation [13,21–24]. Here we describe the sequential shorttime algorithm that represents the solution in an ensemble of surface-hopping trajectories [25,26].

#### 6.1 Momentum-Jump Approximation

Before describing the simulation algorithm, it is useful to discuss an approximation to the operator J, defined in (45), which is responsible for both quantum transitions and associated momentum changes in the bath. This operator is difficult to evaluate because it involves derivatives with respect to bath particle momenta. We make an approximation to the  $(1 + (S_{\alpha\beta}/2) \cdot (\partial/\partial P))$ operator in J so that its action on any function of the momenta yields the function evaluated at a shifted momentum value [4,6,26,27].

Here we show the steps leading to this momentum-jump approximation<sup>5</sup>. Since  $S_{\alpha\beta} = \Delta E_{\alpha\beta} \hat{d}_{\alpha\beta} (\frac{P}{M} \cdot \hat{d}_{\alpha\beta})^{-1}$ , with  $\Delta E_{\alpha\beta} = E_{\alpha} - E_{\beta}$ , we may write

<sup>&</sup>lt;sup>5</sup> We present the derivation in a simple form where the masses of all bath particles are the same. The general case for different bath masses has also been derived [27].

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$$\left(1 + \frac{1}{2}S_{\alpha\beta} \cdot \frac{\partial}{\partial P}\right) = 1 + \frac{1}{2}\Delta E_{\alpha\beta}M\frac{1}{(P \cdot \hat{d}_{\alpha\beta})}\frac{\partial}{\partial(P \cdot \hat{d}_{\alpha\beta})}$$
$$= 1 + \Delta E_{\alpha\beta}M\frac{\partial}{\partial[(P \cdot \hat{d}_{\alpha\beta})^2]}$$
(82)

Consider the action of the operator on any function f(P) of the momentum. We obtain,

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

$$= e^{\Delta E_{\alpha\beta}M\partial/\partial [(P \cdot \hat{d}_{\alpha\beta})^2]} f\left(\hat{d}_{\alpha\beta}^{\perp}(P \cdot \hat{d}_{\alpha\beta}^{\perp}) + \hat{d}_{\alpha\beta}\mathrm{sgn}(P \cdot \hat{d}_{\alpha\beta})\sqrt{(P \cdot \hat{d}_{\alpha\beta})^2}\right)$$

$$= f\left(\hat{d}_{\alpha\beta}^{\perp}(P \cdot \hat{d}_{\alpha\beta}^{\perp}) + \hat{d}_{\alpha\beta}\mathrm{sgn}(P \cdot \hat{d}_{\alpha\beta})\sqrt{(P \cdot \hat{d}_{\alpha\beta})^2 + \Delta E_{\alpha\beta}M}\right)$$

$$= f(P + \Delta P) .$$
(83)

In the first line of this equation we made the main assumption that the first two terms on the left hand side could be approximated by the exponential of the operator. In the second line we wrote the momentum vector as a sum of its components along  $\hat{d}_{\alpha\beta}$  and perpendicular to  $\hat{d}_{\alpha\beta}^{\perp}$ , and in the penultimate line we used the fact that the exponential operator is a translation operator in the variable  $(P \cdot \hat{d}_{\alpha\beta})^2$ . In the last line the momentum jump  $\Delta P$  is given by

$$\Delta P = \hat{d}_{\alpha\beta} \left( \operatorname{sgn}(P \cdot \hat{d}_{\alpha\beta}) \sqrt{(P \cdot \hat{d}_{\alpha\beta})^2 + \Delta E_{\alpha\beta} M - (P \cdot \hat{d}_{\alpha\beta})} \right).$$
(84)

The use of this approximation leads to a representation of the dynamics in terms of energy-conserving trajectories.

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

#### 6.2 Short-Time Sequential Propagation Algorithm

An operator  $\hat{A}_W(R, P, t)$  in quantum-classical dynamics has the formal solution  $\hat{A}_W(t) = \exp(i\hat{\mathcal{L}}t)\hat{A}_W(0)$ . The propagator,  $\exp(i\hat{\mathcal{L}}t)$ , can be decomposed into a composition of propagators in time segments of arbitrary length. The evolution of a dynamical variable over any time interval can then be obtained by the successive application of evolution operators in the small time segments [25].

Suppose we are interested in determining the time evolution over a time interval (0, t). We first divide this interval into N segments such that the  $j^{th}$  segment has length  $\Delta t_j = t_j - t_{j-1} = \Delta t$ . We may then write the propagator in the adiabatic basis as

$$(e^{i\hat{\mathcal{L}}t})_{\alpha_0\alpha'_0,\alpha_N\alpha'_N} = \sum_{(\alpha_1\alpha'_1)\dots(\alpha_{N-1}\alpha'_{N-1})} \prod_{j=1}^N (e^{i\hat{\mathcal{L}}(t_j - t_{j-1})})_{\alpha_{j-1}\alpha'_{j-1},\alpha_j\alpha'_j}, \quad (85)$$

where  $(\alpha_0 \alpha'_0) \equiv (\alpha \alpha')$ . Using this expression for the propagator we have

$$A_{W}^{\alpha\alpha'}(R,P,t) = \sum_{(\alpha_{1}\alpha'_{1})\dots(\alpha_{N}\alpha'_{N})} \left[ \prod_{j=1}^{N} (e^{i\hat{\mathcal{L}}(t_{j}-t_{j-1})})_{\alpha_{j-1}\alpha'_{j-1},\alpha_{j}\alpha'_{j}} \right] A_{W}^{\alpha_{N}\alpha'_{N}}(R,P) .$$
(86)

Given this form of a time-dependent observable, the simulation algorithm exploits the structure of the propagator in the short-time segments.

In any time segment  $(t_j - t_{j-1})$ , using the decomposition of the quantumclassical Liouville operator into diagonal  $i\mathcal{L}^0$  and off-diagonal J parts in (43), the quantum-classical propagator may be written in Dyson form as

$$\left( e^{i\hat{\mathcal{L}}(t_{j}-t_{j-1})} \right)_{\alpha_{j-1}\alpha'_{j-1},\alpha_{j}\alpha'_{j}} = e^{i\mathcal{L}^{0}_{\alpha_{j-1}\alpha'_{j-1}}(t_{j}-t_{j-1})} \delta_{\alpha_{j-1}\alpha_{j}} \delta_{\alpha'_{j-1}\alpha'_{j}} - \sum_{\alpha_{l}\alpha'_{l}} \int_{t_{j-1}}^{t_{j}} d\tau_{1} e^{i\mathcal{L}^{0}_{\alpha_{j}\alpha'_{j}}(\tau_{1}-t_{j-1})} J_{\alpha_{j-1}\alpha'_{j-1},\alpha_{l}\alpha'_{l}} \left( e^{i\hat{\mathcal{L}}(t_{j}-\tau_{1})} \right)_{\alpha_{l}\alpha'_{l},\alpha_{j}\alpha'_{j}} .$$

$$(87)$$

Taking the time interval  $\Delta t$  to be small enough, we can approximate the propagator in an interval by the first order term in the Dyson expression as,

$$(e^{i\hat{\mathcal{L}}(t_j-t_{j-1})})_{\alpha_{j-1}\alpha'_{j-1},\alpha_j\alpha'_j} \approx e^{i\mathcal{L}^0_{\alpha_{j-1}\alpha'_{j-1}}\Delta t} \left(\delta_{\alpha_j\alpha'_j,\alpha_{j-1}\alpha'_{j-1}} - \Delta t J_{\alpha_{j-1}\alpha'_{j-1},\alpha_j\alpha'_j}\right)$$
$$= \mathcal{W}_{\alpha_{j-1}\alpha'_{j-1}}(t_{j-1},t_j)e^{iL_{\alpha_{j-1}\alpha'_{j-1}}\Delta t}$$
$$\times \left(\delta_{\alpha_j\alpha'_j,\alpha_{j-1}\alpha'_{j-1}} - \Delta t J_{\alpha_{j-1}\alpha'_{j-1},\alpha_j\alpha'_j}\right), \quad (88)$$

where the phase factor  $\mathcal{W}_{\alpha_{j-1}\alpha'_{j-1}}(t_{j-1},t_j) = e^{i\omega_{\alpha_{j-1}\alpha'_{j-1}}(t_j-t_{j-1})}$  associated with time segment  $(t_j,t_{j-1})$  arises from the action of  $\exp(i\mathcal{L}^0_{\alpha_{j-1}\alpha'_{j-1}}(t_j-t_{j-1}))$ on any phase space function. More specifically, the action of  $\exp(i\mathcal{L}^0_{\alpha\alpha'}(t_2-t_1)) = \exp(-(i\omega_{\alpha\alpha'}+iL_{\alpha\alpha'})(t_2-t_1))$  on any function  $f_{\alpha\alpha'}(R,P)$  may be computed explicitly in terms of time-reversed trajectories starting at the phase point (R,P) at time  $t_2$  and terminating at another phase point at time  $t_1, (t_1 < t_2)$ . In particular we let

$$\tilde{R}_{t_1,\alpha\alpha'}^{t_2} = e^{-iL_{\alpha\alpha'}(t_2 - t_1)}R , 
\tilde{P}_{t_1,\alpha\alpha'}^{t_2} = e^{-iL_{\alpha\alpha'}(t_2 - t_1)}P ,$$
(89)

be the time-reversed trajectory that starts at (R, P) at time  $t_2$  and ends at  $(\tilde{R}_{t_1,\alpha\alpha'}^{t_2}, \tilde{P}_{t_1,\alpha\alpha'}^{t_2})$  at time  $t_1$ . Using the analog of the Dyson identity in (87) for the propagator

$$e^{-i\mathcal{L}^{0}_{\alpha\alpha'}t} = e^{-(i\omega_{\alpha\alpha'}+iL_{\alpha\alpha'})} = e^{-iL_{\alpha\alpha'}t} - \int_{0}^{t} dt' \ e^{-iL_{\alpha\alpha'}t'}i\omega_{\alpha\alpha'}(R)e^{-i\mathcal{L}^{0}_{\alpha\alpha'}(t-t')} ,$$
(90)

solving the equation by iteration and resumming, we may show that

$$e^{-(i\omega_{\alpha\alpha'}+iL_{\alpha\alpha'})(t_2-t_1)}f_{\alpha\alpha'}(R,P) = e^{-i\int_{t_1}^{t_2} d\tau \omega_{\alpha\alpha'}(\tilde{R}_{\tau,\alpha\alpha'})}f_{\alpha\alpha'}(\tilde{R}^{t_2}_{t_1,\alpha\alpha'},\tilde{P}^{t_2}_{t_1,\alpha\alpha'})$$
$$\equiv \mathcal{W}_{\alpha\alpha'}(t_1,t_2)f_{\alpha\alpha'}(\tilde{R}^{t_2}_{t_1,\alpha\alpha'},\tilde{P}^{t_2}_{t_1,\alpha\alpha'}) .$$
(91)

Now that we know how to evolve the dynamics within a small time segment, we can decide to construct a Monte-Carlo-style stochastic algorithm to account for the quantum transitions that arise from the action of J. At the end of each time segment, the system either may remain in the same pair of adiabatic states or make a transition to a new pair of states. More specifically, for an initial pair of quantum states,  $(\alpha_0 \alpha'_0)$ , the phase point (R, P) is evolved for a time  $\Delta t$  to a new value  $(R_{\Delta t}, P_{\Delta t})$  (here we use a simplified notation for the time-evolved phase points in the interval  $\Delta t$ ) using the classical propagator  $e^{iL_{\alpha_0\alpha'_0}\Delta t}$  and the phase factor  $\mathcal{W}_{\alpha_0\alpha'_0}$  is computed. With probability 1/2, one chooses whether the transition  $\alpha_0 \to \alpha_1$  or  $\alpha'_0 \to \alpha'_1$  occurs. The states  $\alpha_1$ and  $\alpha'_1$  are chosen uniformly from the set of allowed final states; the weight  $w_{\alpha_0\alpha'_0,\alpha_1\alpha'_1}$  associated with the final state is the number of allowed final states. Once  $(\alpha_1\alpha'_0)$  or  $(\alpha_0\alpha'_1)$  is chosen, the nonadiabatic coupling matrix element  $d_{\alpha_0\alpha_1}$  (or  $d_{\alpha'_0\alpha'_1}$ ) is computed at  $R_{\Delta t}$  and the probability,  $\pi$ , of a nonadiabatic transition is given by

$$\pi = \left| \frac{P_{\Delta t}}{M} \cdot d_{\alpha_0 \alpha_1}(R_{\Delta t}) \right| \Delta t \left( 1 + \left| \frac{P_{\Delta t}}{M} \cdot d_{\alpha_0 \alpha_1}(R_{\Delta t}) \right| \Delta t \right)^{-1}.$$
 (92)

If the transition is rejected, then

$$A_W^{\alpha_0 \alpha'_0}(R, P, \Delta t) = \mathcal{W}_{\alpha_0 \alpha'_0}(\Delta t) A_W^{\alpha_0 \alpha'_0}(R_{\Delta t}, P_{\Delta t}) \frac{1}{1 - \pi} .$$
(93)

If the transition is accepted, then, using the momentum jump approximation, we translate the momentum  $P_{\Delta t}$  to  $\tilde{P}_{\Delta t} = P_{\Delta t} + \Delta P$  where  $\Delta P$  is defined in (84). We then write

$$A_W^{\alpha_0 \alpha'_0}(R, P, \Delta t) = \mathcal{W}_{\alpha_0 \alpha'_0}(\Delta t) A_W^{\alpha_1 \alpha'_0}(R_{\Delta t}, \tilde{P}_{\Delta t}) \Delta t \\ \times \frac{P_{\Delta t}}{M} \cdot d_{\alpha_0 \alpha_1}(R_{\Delta t}) \frac{1}{\pi} w_{\alpha_0 \alpha'_0, \alpha_1 \alpha'_1} .$$
(94)

From (84) we see that if  $\Delta E_{\alpha\beta} < 0$  (an upward transition from  $\alpha \to \beta$ ) and  $(\bar{P} \cdot \bar{d}_{\alpha\beta})^2 < |\Delta E_{\alpha\beta}|$  so that there is insufficient kinetic energy from bath

momenta along  $\hat{d}_{\alpha\beta}$  for the quantum transition to occur, the argument of the square root is negative leading to imaginary momentum changes. In this case, the quantum transition does not occur and the trajectory is continued adiabatically. The total energy of the system is conserved along a quantum-classical surface-hopping trajectory when the momentum-jump approximation is used, even if the transition is to a pair of coherently coupled surfaces.

### 7 Chemical Reaction Rates

In this section we illustrate applications of the formalism and simulation method by calculating the rate constants of activated chemical reactions. The calculations are carried out by evaluating time-correlation reactive-flux expressions for the rate. The general transport coefficients we derived earlier can easily be specialized to this case. Quantum reaction rates, such as proton and electron transport processes, very appropriately fall into the category of systems that can be studied using quantum-classical dynamics since the light particle (proton or electron) being transferred must be treated quantum mechanically but dynamics of the environment in which the transfer takes place (condensed phase polar solvent or large biomolecule) can often be treated classically to a good approximation.

### 7.1 Reactive-Flux Correlation Functions

For a quantum mechanical system in thermal equilibrium undergoing a transformation  $A \rightleftharpoons B$ , a rate constant  $k_{AB}$  may be calculated from the timedependent reactive-flux correlation function [28],

$$k_{AB}(t) = \frac{1}{n_A^{eq}} \int_0^t dt' \langle \dot{\hat{N}}_A; \, \dot{\hat{N}}_B \rangle = \frac{1}{\beta n_A^{eq}} \left\langle \frac{i}{\hbar} [\hat{N}_B(t), \hat{N}_A] \right\rangle, \tag{95}$$

where  $\hat{N}_A$  is the *A* species operator,  $n_A^{eq}$  is the equilibrium density of species *A*, and  $\hat{N}_A = (i/\hbar)[\hat{H}, \hat{N}_A]$  is the flux of  $\hat{N}_A$  with Hamiltonian  $\hat{H}$ , with an analogous expression for  $\hat{N}_B$ .<sup>6</sup> We may now directly apply the general formula, (80), derived earlier for the quantum-classical limit of quantum time correlation function, to obtain an expression for the reaction rate in the form,

$$k_{AB}(t) = \frac{1}{n_A^{eq}} \sum_{\alpha\alpha'} \int dX N_{BW}^{\alpha\alpha'}(X,t) W_{A'}^{\alpha'\alpha}\left(X,\frac{i\hbar\beta}{2}\right),\tag{96}$$

<sup>&</sup>lt;sup>6</sup> The time evolution of the reactive flux is given by projected dynamics [28] but in simulations we may replace projected dynamics by ordinary dynamics and insert absorbing states in the reactant and product regions to yield well defined plateau values. Such a procedure will be accurate provided there is a sufficient time scale separation between the relaxation time for reactive events and other microscopic relaxation times in the system.

where we used the high temperature approximation

$$\overline{W}(\mathcal{X}_1, \mathcal{X}_2, 0) = W\left(\mathcal{X}_1, \mathcal{X}_2, \frac{i\hbar\beta}{2}\right) + \mathcal{O}(\beta^2) .$$
(97)

The matrix elements of  $W_{A'}$  in the adiabatic basis are given by

$$W_{A'}^{\alpha'\alpha}\left(X,\frac{i\hbar\beta}{2}\right) = \sum_{\alpha_1\alpha_1'} \int dX' \left(i\mathcal{L}(X')N_{AW}(X')\right)^{\alpha_1\alpha_1'} W^{\alpha_1'\alpha_1\alpha_1'\alpha}\left(X',X,\frac{i\hbar\beta}{2}\right),\tag{98}$$

where

$$W^{\alpha_{1}'\alpha_{1}\alpha_{1}\alpha_{1}'\alpha}\left(X', X, \frac{i\hbar\beta}{2}\right) = \frac{1}{(2\pi\hbar)^{2N}Z_{Q}} \int dZdZ' e^{-\frac{i}{\hbar}(P\cdot Z+P'\cdot Z')} \\ \times \left\langle \alpha'; R \middle| \left\langle R + \frac{Z}{2} \middle| e^{-\frac{\beta}{2}\hat{H}} \middle| R' - \frac{Z'}{2} \right\rangle \middle| \alpha_{1}; R' \right\rangle \\ \times \left\langle \alpha'_{1}; R' \middle| \left\langle R' + \frac{Z'}{2} \middle| e^{-\frac{\beta}{2}\hat{H}} \middle| R - \frac{Z}{2} \right\rangle \middle| \alpha; R \right\rangle.$$
(99)

This rate coefficient expression involves quantum-classical evolution of the matrix element  $N_{BW}^{\alpha\alpha'}(X,t)$  but retains the full quantum equilibrium structure of the system.

#### 7.2 Proton Transfer

As an example, we consider the calculation of the rate constant for a proton transfer reaction  $(AH-B \rightleftharpoons A^--H^+B)$  in a hydrogen-bonded complex (AHB)dissolved in a polar solvent. The model we consider [29] has potential parameters chosen to describe proton transfer in a slightly strongly hydrogen-bonded phenol (A) trimethylamine (B) complex in a methyl chloride liquid-state solvent. At the equilibrium A-B separation,  $R_{AB} = 2.7$  Å, the proton potential energy function in the AHB complex has two minima, the deeper minimum corresponding to the stable covalent state and the shallower minimum corresponding to the metastable ionic state. Additional details of the calculations can be found in [27]. This model has been studied often using different methods [30-35].

Proton transfer dynamics in polar liquids can be monitored by the solvent polarization,  $\Delta E(R)$ , [36,37]

$$\xi(R) = \Delta E(R) = \sum_{i,a} z_a e\left(\frac{1}{|\mathbf{R}_i^a - s|} - \frac{1}{|\mathbf{R}_i^a - s'|}\right),$$
 (100)

where  $z_a e$  is the charge on solvent atom a, and s and s' are two points within the complex, one at the center of mass and the other displaced from the center of mass, which correspond to the minima of the bare hydrogen bonding



Fig. 1. (Left) Time series of the solvent polarization ( $\Delta E$ ) for a ground state adiabatic trajectory. (Right) The rate coefficient,  $k_{AB}(t)$ , as a function of time. The dotted line indicates the plateau value  $k_{AB}$ 

potential. The sums run over all solvent molecules *i* and atoms *a*. The solvent polarization is an example of a reaction coordinate for a quantum rate process that depends solely on the environmental coordinates. In Fig. 1 (left panel) we see that  $\Delta E$  tracks the hops of the proton between the reactant/covalent state ( $\Delta E \approx 0.005 \text{ eC/Å}$ ) and the product/ionic state ( $\Delta E \approx 0.0225 \text{ eC/Å}$ ). The complex spends more time in the ionic configuration than in the covalent configuration since electrostatic interactions with the polar solvent preferentially stabilize the ionic configuration of the complex. In the absence of the polar solvent, the complex is primarily found in the covalent configuration.

Since we consider systems at approximately room temperature and the dynamics of the solvent and complex atoms can be accurately captured using classical mechanics, a high temperature/classical approximation may be made to  $\overline{W}^{\alpha'_1\alpha_1\alpha'_2\alpha_2}(X,X')$  to obtain,

$$\overline{W}^{\alpha_1'\alpha_1\alpha_2'\alpha_2}(X,X') = \frac{e^{-\beta\left(\frac{P^2}{2M} + E_{\alpha_1'}(R)\right)}}{(2\pi\hbar)^N Z_Q} \delta_{\alpha_1'\alpha_2} \delta_{\alpha_2'\alpha_1} \delta(X - X') , \quad (101)$$

where  $Z_Q = (2\pi\hbar)^{-N} \sum_{\alpha} \int dR dP e^{-\beta \left(\frac{P^2}{2M} + E_{\alpha}(R)\right)}$ . Using this approximation for the spectral density function, the rate constant for this proton transfer reaction can easily be written. Taking  $\Delta E(R)$  as the reaction coordinate, the A and B species variables can be defined as  $\hat{N}_A = \theta(\Delta E(R) - \Delta E^{\ddagger})$  and  $\hat{N}_B = \theta(\Delta E^{\ddagger} - \Delta E(R))$ , respectively. The time-dependent rate constant is given by

$$k_{AB}(t) = \frac{-1}{n_A^{eq}} \sum_{\alpha} \int dR dP \ \Delta \dot{E}(R) N_B^{\alpha\alpha}(R, P, t) \delta(\Delta E(R) - \Delta E^{\ddagger}) \rho_{W_e}^{\alpha\alpha} .$$
(102)

The time derivative of the solvent polarization can be written as  $\Delta \dot{E}(R) = \frac{P}{M} \cdot \nabla_R \Delta E(R)$ . The canonical equilibrium distribution is given by  $\rho_{W_e}^{\alpha\alpha} = Z_0^{-1} e^{-\beta H_W^{\alpha}}$ , with  $Z_0 = \sum_{\alpha} \int dR dP \ e^{-\beta H_W^{\alpha}}$ . Equation (102) provides a well-

defined formula involving initial sampling from the barrier top  $\Delta E = \Delta E^{\ddagger}$ and quantum-classical time evolution of  $N_B^{\alpha\alpha}(R, P, t)$ .

In Fig. 1 (right panel), we plot the time-dependent rate coefficient obtained from an average over 16000 trajectories. We see that  $k_{AB}(t)$  falls quickly from its initial transition state theory value in a few tenths of a picosecond to a plateau from which the rate constant can be extracted. The decrease in the rate coefficient from its transition state theory value is due to recrossing by the trajectory of the barrier top before the system reaches a metastable state. The value of  $k_{AB}$  obtained from the plateau is  $k_{AB} = 0.013 \text{ ps}^{-1}$ . The adiabatic rate constant is  $k_{AB}^{ad} = 0.019 \text{ ps}^{-1}$ , indicating that nonadiabatic effects influence the proton transfer rate.

#### 7.3 Quantum Sampling of the Reaction Coordinate

In the previous proton transport example the equilibrium structure of the polarization reaction coordinate, which depends on the positions of all particles in the environment, was treated classically. We now consider a simpler reaction model to examine the effect on the reaction rate of treating equilibrium sampling of the reaction coordinate quantum mechanically [38]. This example further illustrates formalism developed in Sect. 5 where the quantum equilibrium structure embodied in the spectral density function W is combined with quantum-classical dynamics to compute the transport property. The imaginary time propagators in W can, in principle, be computed using quantum path integral methods [39] or other approximations such as linearization methods [40–42]. By treating the initial sampling of the reaction coordinate quantum the time-dependent rate coefficient has an initial value of zero in agreement with the full quantum rate expression [28], and its asymptotic value, which gives the rate constant, differs from that obtained using classical initial sampling.

We consider a system in which only one coordinate,  $R_0$ , is directly coupled to the quantum subsystem and this coordinate serves as the reaction coordinate,  $\xi(R) = R_0$ . The coordinate  $R_0$  is, in turn, coupled to a bath. The A and B species operators may be defined as  $\hat{N}_{AW} = \theta(-R_0)$  and  $\hat{N}_{BW} = \theta(R_0)$ , where  $\theta$  is the Heaviside function and the dividing surface is located at  $\xi^{\ddagger} = R_0^{\ddagger} = 0$ . For this choice of species variable,  $W_{A'}^{\alpha'\alpha}(X, \frac{i\hbar\beta}{2})$ defined in (98), can be simplified by performing the integrations over the X'coordinates to yield,

$$W_{A'}^{\alpha'\alpha}\left(X,\frac{i\hbar\beta}{2}\right) = \frac{1}{\left(2\pi\hbar\right)^{N}Z_{Q}}\frac{i\hbar}{M_{0}}\int dZdZ_{0}'(d\delta(Z_{0}')/dZ_{0}')e^{-\frac{i}{\hbar}P\cdot Z}$$

$$\times \left\langle\alpha';R_{0}\right|\left\langle R+\frac{Z}{2}\left|e^{-\frac{\beta}{2}\hat{H}}\right|-\frac{Z_{0}'}{2}\right\rangle\left\langle\frac{Z_{0}'}{2}\left|e^{-\frac{\beta}{2}\hat{H}}\right|R-\frac{Z}{2}\right\rangle\left|\alpha;R_{0}\right\rangle.$$

$$(103)$$

The adiabatic eigenstates depend only on  $R_0$  since the bath is coupled directly only to this coordinate. In the results sketched below we use an approximate analytical expression for this quantity. The details of this calculation and the approximations employed to obtain the result can be found in [38]. As a result of this analysis we find

$$W_{A'}^{\alpha'\alpha}\left(X,\frac{i\hbar\beta}{2}\right) = \frac{1}{2\pi\hbar Z_Q} \frac{1}{\cos^2 u} \sqrt{\frac{2M_0 u'}{\beta\hbar^2 \pi}} e^{-\frac{2M_0 u'}{\beta\hbar^2}R_0^2} \\ \times \frac{P_0}{M_0} e^{-\frac{\beta P_0^2}{2M_0 u'}} F_{\alpha'\alpha}(R_0)\rho_b(P_b,R_b;R_0), \qquad (104)$$

where  $u' \equiv u \cot u$  and  $\rho_b(P_b, R_b; R_0)$  is proportional to the Wigner transform of the canonical equilibrium density matrix for the bath in the field of the  $R_0$ coordinates,

$$\rho_b(P_b, R_b; R_0) = \frac{1}{(2\pi\hbar)^{N-1}} \int dZ_b e^{-\frac{i}{\hbar}P_b \cdot Z_b} \left\langle R_b + \frac{Z_b}{2} \left| e^{-\beta\hat{H}_{b(n)}} \right| R_b - \frac{Z_b}{2} \right\rangle.$$
(105)

The function  $F_{\alpha'\alpha}(R_0)$  is defined by

$$F_{\alpha'\alpha}(R_0) = e^{-\beta\varepsilon_\alpha(R_0)} \left( \delta_{\alpha'\alpha} + \frac{1}{2} \left( 1 - \frac{\beta P_0^2}{M_0 u'} \right) \frac{i\hbar}{P_0} d_{\alpha'\alpha} O_{\alpha'\alpha} \right), \quad (106)$$

with  $O_{\alpha'\alpha}(R_0) = (1 - e^{-\frac{\beta}{2}\varepsilon_{\alpha'\alpha}(R_0)})^2$  and  $\varepsilon_{\alpha'\alpha} = \varepsilon_{\alpha'} - \varepsilon_{\alpha}$ , where the  $\varepsilon_{\alpha}(R_0)$  are related to the  $E_{\alpha}(R_0)$  introduced earlier by  $\varepsilon_{\alpha}(R_0) = E_{\alpha}(R_0) + \frac{1}{2}M_0\omega^{\ddagger 2}R_0^2$ with  $\omega^{\ddagger}$  is the frequency at the barrier top. Note that in contrast to a classical treatment of the reaction coordinate, initial sampling of  $R_0$  is no longer restricted to the barrier top.

As an application of this formalism, we consider a two-level quantum system coupled to a classical bath as a simple model for a transfer reaction in a condensed phase environment. The Hamiltonian operator of this system, expressed in the diabatic basis  $\{|L\rangle, |R\rangle\}$ , has the matrix form [43]

$$\mathbf{H} = \begin{pmatrix} V_n(R_0) + \hbar \gamma_0 R_0 & -\hbar \Omega \\ -\hbar \Omega & V_n(R_0) - \hbar \gamma_0 R_0 \end{pmatrix} + \left( \frac{P_0^2}{2M_0} + \sum_{j=1}^N \frac{P_j^2}{2M_j} + \sum_{j=1}^N \frac{M_j}{2} \omega_j^2 \left( R_j - \frac{c_j}{M_j \omega_j^2} R_0 \right)^2 \right) \mathbf{I} .$$
(107)

In this model, a two-level system is coupled to a classical nonlinear oscillator with mass  $M_0$  and phase space coordinates  $(R_0, P_0)$ . This coupling is given by  $\hbar \gamma_0 R_0$ . The nonlinear oscillator, which has a quartic potential energy function  $V_n(R_0) = aR_0^4/4 - M_0 \omega^{\ddagger 2} R_0^2/2$ , is then bilinearly coupled



Fig. 2. (*Left*) A schematic illustration of the free energy W along a reaction coordinate  $\xi$  for weak coupling to the reaction coordinate. The dotted line at  $\xi = \xi^{\ddagger}$ indicate the position of the barrier top. (*Right*) Comparison of the time-dependent transmission coefficients  $k_{AB}/k_{AB}^{TST}$  for quantum (QRB) and classical (CRB) sampling of the reaction coordinate. Parameters values:  $\beta = 2$ ,  $\gamma_0 = 0.1$ ,  $\Omega = 0.1$ , and  $\xi = 3$ 

to a bath of N independent harmonic oscillators. The bath harmonic oscillators labelled j = 1, ..., N have masses  $M_j$  and frequencies  $\omega_j$ . The bilinear coupling is characterized by an Ohmic spectral density [44, 45],  $J(\omega) = \pi \sum_{j=1}^{N} (c_j^2/(2M_j\omega_j^2)\delta(\omega - \omega_j))$ , where  $c_j = (\xi\hbar\omega_0M_j)^{1/2}\omega_j$ ,  $\omega_j = -\omega_c \ln(1 - j\omega_0/\omega_c)$  and  $\omega_0 = \frac{\omega_c}{N} (1 - e^{-\omega_{max}/\omega_c})$ , with  $\omega_c$  a cut-off frequency.

Figure 2 (left panel) shows the energy profile for a two-level system weakly coupled to the reaction coordinate. Both the ground and excited state surfaces have two minima separated by a high barrier at  $\xi(R_0) = \xi^{\ddagger}$ . The right panel of this figure compares the time dependent rate coefficients for quantum (QRB) and classical (CRB) treatments of the reaction coordinate for a moderately low temperature ( $\beta = 2$ ). At t = 0, the CRB result for the time-dependent transmission coefficient,  $\kappa(t) = k_{AB}/k_{AB}^{TST}$ , where  $k_{AB}^{TST}$  is determined from a classical treatment of the reaction coordinate [38], is non-zero and equal to unity. The QRB results for the time-dependent transmission coefficient are zero at t = 0, which is expected for quantum rate processes [28]. Quantum effects are pronounced and we see that the QRB formulation yields a larger rate constant than the CRB treatment. This enhancement of the quantum rate has also been observed in other studies [39,46,47].

### 8 Conclusion

The computation of quantum mechanical transport properties for many-body systems remains one of the most challenging problems in condensed matter

physics and chemistry. In this chapter we have shown how mixed quantumclassical methods can be used to tackle these problems. Such a quantumclassical description will be appropriate if the system of interest can usefully be partitioned into two subsystems, one of which whose quantum character must be retained while the dynamics of the other subsystem may be approximated by classical mechanics. We saw that many physical systems fall into this category, notably proton and electron transfer reactions occurring in complex condensed phase and other environments.

Using the quantum-classical formulations presented above, transport coefficients can be calculated by sampling from quantum initial states or, more approximately, from quantum-classical initial states combined with quantumclassical dynamics of observables. Quantum-classical dynamics can be simulated in terms of ensembles of surface-hopping trajectories.

Quantum-classical Liouville dynamics is not a fully consistent dynamical theory and there is scope for further development [48]. For systems where a quantum-classical decomposition of the system is appropriate, the numerical consequences of such inconsistencies are likely to be small, as confirmed by calculations on model systems. For quantum systems bilinearly coupled to harmonic baths the computation of transport properties is exact if quantumclassical Liouville dynamics is used in conjunction with sampling from quantum equilibrium distributions. Thus, although not completely free from difficulties, quantum-classical Liouville dynamics has provided a more systematic and complete underpinning to quantum-classical surface-hopping schemes and is a formalism that can be used to investigate the dynamical properties of quantum systems coupled to large and complex many-body environments. Future developments in this area are likely to yield other algorithms and insight into the quantum dynamics of open systems.

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