

## Quantum-classical Liouville dynamics in the mapping basis

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The quantum-classical Liouville equation describes the dynamics of a quantum subsystem coupled to a classical environment. It has been simulated using various methods, notably, surface-hopping schemes. A representation of this equation in the mapping Hamiltonian basis for the quantum subsystem is derived. The resulting equation of motion, in conjunction with expressions for quantum expectation values in the mapping basis, provides another route to the computation of the nonadiabatic dynamics of observables that does not involve surface-hopping dynamics. The quantum-classical Liouville equation is exact for the spin-boson system. This well-known model is simulated using an approximation to the evolution equation in the mapping basis, and close agreement with exact quantum results is found. © 2008 American Institute of Physics.

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### I. INTRODUCTION

Nonadiabatic quantum-mechanical effects are known to be important for the description of the dynamics of many chemical and biological processes. Photochemical dynamics, proton and electron transfer reactions, and vibrational relaxation processes are just a few examples where quantum effects play significant roles. Due to the difficulty in simulating the full quantum dynamics of large, complex, many-body systems, various mixed quantum-classical and semiclassical schemes have been developed. Here we consider quantum dynamics based on the quantum-classical Liouville equation (see Ref. 1 and references therein),

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

where  $[\hat{A}, \hat{B}]$  is the commutator and  $\{\hat{A}, \hat{B}\}$  is the Poisson bracket for any operators  $\hat{A}$  and  $\hat{B}$ . The density matrix  $\hat{\rho}_W(R,P,t)$  is a function of the environmental phase space variables  $(R,P)$  and is an operator in the degrees of freedom of the quantum subsystem. The Hamiltonian  $\hat{H}_W$  includes terms describing the quantum subsystem, its environment, and the coupling between these parts of the system. This equation has been used to describe nonadiabatic dynamics on coupled electronic states,<sup>2,3</sup> vibrational dephasing,<sup>4</sup> proton transfer reactions,<sup>5-9</sup> and population relaxation in the spin-boson model,<sup>10,11</sup> to name a few examples. The simulation of the dynamics using this equation presents challenges, and a number of different schemes have been devised for this purpose. Often the simulation methods are based on specific representations of the quantum degrees of freedom. For ex-

ample, surface-hopping dynamics that make use of the adiabatic basis have been constructed,<sup>10-12</sup> evolution of the density matrix in the diabatic basis has been carried out using a trajectory-based algorithm,<sup>3</sup> and a representation of the dynamics in the force basis has been simulated using the multithread algorithm.<sup>13,14</sup>

The discrete quantum degrees of freedom of the system can be described by the “classical electron analog” model<sup>15</sup> or the mapping formalism.<sup>16-19</sup> Extending Schwinger’s<sup>20</sup> angular momentum formalism to the  $N$ -level case, the mapping formulation employs a quantum-mechanically exact mapping of discrete electronic states onto continuous variables; thus, the dynamics of both electronic and nuclear degrees of freedom are described by continuous variables.<sup>21</sup> The mapping basis has been used to compute quantum dynamics in the context of semiclassical path integral formulations of the theory<sup>15,17,18,22</sup> and in linearized path integral methods.<sup>23-25</sup> In this paper we show how the quantum-classical Liouville equation can be written in this mapping representation. The resulting evolution equation, just as the basis-free quantum-classical Liouville equation (1) from which it was derived, provides a useful description of the dynamics of a quantum subsystem coupled to its environment. Since the quantum-classical Liouville equation is exact for any quantum system bilinearly coupled to a harmonic bath, so is its representation in the mapping basis presented here. The spin-boson model is of this type, and this standard test model, for which exact quantum results are available, is employed to illustrate features of the simulation of the mapping form of the quantum-classical Liouville equation. In particular, we show that an approximation to the evolution operator allows one to accurately simulate the evolution using a few trajectories with an algorithm that does not involve surface-hopping dynamics. Comparisons with the results of other simulation algorithms are made. A discussion of the applicability of this representation of the theory to general many-body quantum systems is given in Sec. IV.

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## II. QUANTUM-CLASSICAL DYNAMICS IN THE MAPPING BASIS

We consider a quantum-mechanical system that is partitioned into a subsystem and bath. The expectation value of an operator  $\hat{B}(t)$  can be written generally as

$$\overline{B(t)} = \text{Tr} \hat{B}(t) \hat{\rho} = \text{Tr}' \int dX \hat{B}_W(X, t) \hat{\rho}_W(X), \quad (2)$$

where a partial Wigner transform over bath degrees of freedom,

$$\hat{B}_W(X) = \int dZ e^{iPZ/\hbar} \left\langle R - \frac{Z}{2} \left| \hat{B} \right| R + \frac{Z}{2} \right\rangle, \quad (3)$$

has been taken. Here,  $X=(R, P)$  denotes phase space variables of the bath. The initial density matrix is  $\hat{\rho}_W(X)$ . The partially Wigner-transformed Hamiltonian of the system can be written as

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

where the subscripts  $s$ ,  $B$ , and  $c$  denote the subsystem, bath, and coupling, respectively. Letting  $\hat{h}_s = \hat{p}^2/2m + \hat{V}_s(\hat{q})$  be the subsystem Hamiltonian, whose eigenvalue problem is  $\hat{h}_s|\lambda\rangle = \varepsilon_\lambda|\lambda\rangle$ , we can write the expectation value of  $\hat{B}(t)$  in the form

$$\overline{B(t)} = \sum_{\lambda, \lambda'} \int dX B_W^{\lambda\lambda'}(X, t) \rho_W^{\lambda'\lambda}(X) \quad (5)$$

in the subsystem basis.

### A. Average value in mapping basis

Next, we write this expectation value in the mapping basis by noting that any operator  $\hat{B}_W(X)$  can be decomposed as  $\hat{B}_W(X) = \sum_{\lambda\lambda'} B_W^{\lambda\lambda'}(X) |\lambda\rangle\langle\lambda'|$ . The evolution of the  $N$ -state subsystem can be conveniently replaced, using mapping relations, with that of  $N$  fictitious harmonic oscillators with occupation numbers limited to 0 or 1, namely,  $|\lambda\rangle \rightarrow |m_\lambda\rangle = |0_1, \dots, 1_\lambda, \dots, 0_N\rangle$ .<sup>15-19,21-25</sup> The matrix element of an operator may then be written in the mapping form,  $B_W^{\lambda\lambda'}(X) = \langle\lambda|\hat{B}_W(X)|\lambda'\rangle = \langle m_\lambda|\hat{B}_m(X)|m_{\lambda'}\rangle$ , where

$$\hat{B}_m(X) = \sum_{\lambda\lambda'} B_W^{\lambda\lambda'}(X) \hat{a}_\lambda^\dagger \hat{a}_{\lambda'}. \quad (6)$$

The annihilation and creation operators on the mapping states are given by

$$\hat{a}_\lambda = \sqrt{\frac{1}{2\hbar}} (\hat{q}_\lambda + i\hat{p}_\lambda), \quad \hat{a}_\lambda^\dagger = \sqrt{\frac{1}{2\hbar}} (\hat{q}_\lambda - i\hat{p}_\lambda) \quad (7)$$

and satisfy the commutation relation  $[\hat{a}_\lambda, \hat{a}_{\lambda'}^\dagger] = \delta_{\lambda\lambda'}$ . Explicitly, we may write

$$\hat{a}_\lambda^\dagger \hat{a}_{\lambda'} = \frac{1}{2\hbar} [\hat{q}_\lambda \hat{q}_{\lambda'} + \hat{p}_\lambda \hat{p}_{\lambda'} - i(\hat{p}_\lambda \hat{q}_{\lambda'} - \hat{q}_\lambda \hat{p}_{\lambda'})]. \quad (8)$$

The matrix elements of  $\hat{B}_m(X)$  in the mapping basis are identical to those of  $\hat{B}_W(X)$  in the subsystem basis, as is easily confirmed using the action of the annihilation and creation operators on the mapping states:  $\hat{a}_\lambda^\dagger \hat{a}_{\lambda'} |m_{\lambda'}\rangle = |m_\lambda\rangle$ .

In the analysis that follows it is convenient to work in a Wigner representation of the mapping basis. To this end we introduce a coordinate representation of the mapping states and annihilation and creation operators,

$$\begin{aligned} \langle q|m_\lambda\rangle &= \langle q_1, q_2, \dots, q_N | 0_1, \dots, 1_\lambda, \dots, 0_N \rangle \\ &= \phi_0(q_1) \cdots \phi_0(q_{\lambda-1}) \phi_1(q_\lambda) \cdots \phi_0(q_N) \end{aligned} \quad (9)$$

and

$$\langle q|\hat{a}_\lambda|q'\rangle = \frac{1}{\sqrt{2\hbar}} \left( q'_\lambda + \hbar \frac{\partial}{\partial q'_\lambda} \right) \delta(q_\lambda - q'_\lambda) \prod_{\mu \neq \lambda}^N \delta(q_\mu - q'_\mu), \quad (10)$$

with an analogous expression for  $\langle q|\hat{a}_\lambda^\dagger|q'\rangle$ . Here

$$\phi_0(q_\lambda) = (\pi\hbar)^{-1/4} e^{-q_\lambda^2/2\hbar}, \quad (11)$$

$$\phi_1(q_\lambda) = \sqrt{2}(\pi\hbar^3)^{-1/4} q_\lambda e^{-q_\lambda^2/2\hbar}.$$

Equation (5) may be written in the mapping basis using the coordinate representation to obtain

$$\begin{aligned} \overline{B(t)} &= \sum_{\lambda, \lambda'} \int dX \langle m_\lambda | \hat{B}_m(X, t) | m_{\lambda'} \rangle \langle m_{\lambda'} | \hat{\rho}_m(X) | m_\lambda \rangle \\ &= \sum_{\lambda, \lambda'} \int dX \int dq dq' dq'' dq''' \langle m_\lambda | q \rangle \langle q | \hat{B}_m(X, t) | q' \rangle \\ &\quad \times \langle q' | m_{\lambda'} \rangle \langle m_{\lambda'} | q'' \rangle \langle q'' | \hat{\rho}_m(X) | q''' \rangle \langle q''' | m_\lambda \rangle. \end{aligned} \quad (12)$$

Note that the coordinate space dimension of the mapping variables is  $N$ . We may now introduce the Wigner transforms of the coordinate space matrix elements of the mapping variables,

$$\left\langle r - \frac{z}{2} \left| \hat{B}_m(X, t) \right| r + \frac{z}{2} \right\rangle = \frac{1}{(2\pi\hbar)^N} \int dp e^{-ipz/\hbar} B_m(x, X, t), \quad (13)$$

$$\left\langle r' - \frac{z'}{2} \left| \hat{\rho}_m(X) \right| r + \frac{z'}{2} \right\rangle = \int dp' e^{-ip'z'/\hbar} \rho_m(x', X),$$

where  $x=(r, p)$  are the phase space coordinates of the mapping variables. Using these definitions, Eq. (12) can be written as

$$\begin{aligned} \overline{B(t)} &= \int dX dx dx' B_m(x, X, t) f(x, x') \rho_m(x', X) \\ &= \int dX dx B_m(x, X, t) \tilde{\rho}_m(x, X), \end{aligned} \quad (14)$$

where  $\tilde{\rho}_m(x, X) = \int dx' f(x, x') \rho_m(x', X)$  and

$$\begin{aligned}
f(x, x') &= \frac{1}{(2\pi\hbar)^N} \sum_{\lambda\lambda'} \int dz dz' \left\langle m_\lambda \left| r - \frac{z}{2} \right\rangle \right. \\
&\quad \times \left\langle r + \frac{z}{2} \left| m_{\lambda'} \right\rangle \left\langle m_{\lambda'} \left| r' - \frac{z'}{2} \right\rangle \right. \\
&\quad \times \left\langle r' + \frac{z'}{2} \left| m_\lambda \right\rangle e^{-i(p \cdot z + p' \cdot z')/\hbar}. \quad (15)
\end{aligned}$$

The function  $f(x, x')$  can be computed explicitly using Eqs. (9) and (11).

## B. Evolution equation in mapping basis

In quantum-classical dynamics the time evolution of an operator may be described by the quantum-classical Liouville equation<sup>26</sup>

$$\frac{d}{dt} \hat{B}_W(t) = \frac{i}{\hbar} [\hat{H}_W, \hat{B}_W(t)] - \frac{1}{2} (\{\hat{H}_W, \hat{B}_W(t)\} - \{\hat{B}_W(t), \hat{H}_W\}). \quad (16)$$

In order to make use of Eq. (14) we must cast this equation in the mapping basis.

Using the results of Sec. II A, the matrix elements of any operator  $\hat{C}_W$  can be written in the form

$$\langle \lambda | \hat{C}_W | \lambda' \rangle = \int dq dq' \langle m_\lambda | q \rangle \langle q | \hat{C}_m | q' \rangle \langle q' | m_{\lambda'} \rangle. \quad (17)$$

Furthermore, if  $\hat{C}_W = \hat{A}_W \hat{B}_W$  is a composition of operators, we have

$$\langle \lambda | \hat{C}_W | \lambda' \rangle = \langle m_\lambda | \hat{C}_m | m_{\lambda'} \rangle = \langle m_\lambda | \hat{A}_m \hat{B}_m | m_{\lambda'} \rangle. \quad (18)$$

Using Eqs. (17) and (18), we can write the quantum-classical Liouville equation as

$$\begin{aligned}
\frac{d}{dt} \langle q | \hat{B}_m(t) | q' \rangle &= \frac{i}{\hbar} \langle q | [\hat{H}_m, \hat{B}_m(t)] | q' \rangle - \frac{1}{2} (\langle q | \{\hat{H}_m, \hat{B}_m(t)\} | q' \rangle \\
&\quad - \langle q | \{\hat{B}_m(t), \hat{H}_m\} | q' \rangle). \quad (19)
\end{aligned}$$

Taking the Wigner transform over the mapping coordinate space, we obtain

$$\begin{aligned}
\frac{d}{dt} B_m(x, X, t) &= \frac{2}{\hbar} H_m \sin\left(\frac{\hbar \Lambda_m}{2}\right) B_m(t) \\
&\quad - \frac{\partial H_m}{\partial R} \cos\left(\frac{\hbar \Lambda_m}{2}\right) \frac{\partial B_m(t)}{\partial P} + \frac{P}{M} \frac{\partial B_m(t)}{\partial R}, \quad (20)
\end{aligned}$$

where the negative of the Poisson bracket operator on the mapping phase space coordinates is defined as  $\Lambda_m = \overleftarrow{\nabla}_p \cdot \overleftarrow{\nabla}_r - \overleftarrow{\nabla}_r \cdot \overleftarrow{\nabla}_p$ . In writing this equation we have used the fact that the Wigner transform of a product of mapping operators is given by

$$(\hat{A}_m(X) \hat{B}_m(X))_W = A_m(x, X) e^{\hbar \Lambda_m / 2i} B_m(x, X). \quad (21)$$

The Wigner transform of a mapping variable is given by

$$A_m(x, X) = \frac{1}{2\hbar} \sum_{\lambda\lambda'} A^{\lambda\lambda'}(R) (r_\lambda r_{\lambda'} + p_\lambda p_{\lambda'} - \hbar \delta_{\lambda\lambda'}). \quad (22)$$

In particular, the mapping Hamiltonian takes the form

$$\begin{aligned}
H_m(x, X) &= \frac{P^2}{2M} + V_B(R) \\
&\quad + \frac{1}{2\hbar} \sum_{\lambda\lambda'} h_{\lambda\lambda'}(R) (r_\lambda r_{\lambda'} + p_\lambda p_{\lambda'} - \hbar \delta_{\lambda\lambda'}), \quad (23)
\end{aligned}$$

where  $h_{\lambda\lambda'}(R) = \langle \lambda | \hat{p}^2 / 2m + V_s(\hat{q}) + V_c(\hat{q}, R) | \lambda' \rangle$ , and we have used the fact that  $h_{\lambda\lambda'} = h_{\lambda'\lambda}$ . Given this form of the Hamiltonian one may show that

$$H_m \Lambda_m B_m = \frac{1}{\hbar} \sum_{\lambda\lambda'} h_{\lambda\lambda'} \left( p_\lambda \frac{\partial}{\partial r_{\lambda'}} - r_\lambda \frac{\partial}{\partial p_{\lambda'}} \right) B_m, \quad (24)$$

$$H_m \Lambda_m^2 B_m = \frac{1}{\hbar} \sum_{\lambda\lambda'} h_{\lambda\lambda'} \left( \frac{\partial}{\partial r_\lambda} \frac{\partial}{\partial r_{\lambda'}} + \frac{\partial}{\partial p_{\lambda'}} \frac{\partial}{\partial p_\lambda} \right) B_m, \quad (25)$$

and

$$H_m \Lambda_m^n B_m = 0 \quad (\text{when } n \geq 3). \quad (26)$$

Then, using these relations, we can simplify Eq. (20) to derive the quantum-classical Liouville equation in the mapping basis:

$$\begin{aligned}
\frac{d}{dt} B_m(x, X, t) &= \frac{1}{\hbar} \sum_{\lambda\lambda'} h_{\lambda\lambda'} \left( p_\lambda \frac{\partial}{\partial r_{\lambda'}} - r_\lambda \frac{\partial}{\partial p_{\lambda'}} \right) B_m(t) \\
&\quad + \left( \frac{P}{M} \frac{\partial}{\partial R} - \frac{\partial H_m}{\partial R} \frac{\partial}{\partial P} \right) B_m(t) \\
&\quad + \frac{\hbar}{8} \sum_{\lambda\lambda'} \frac{\partial h_{\lambda\lambda'}}{\partial R} \left( \frac{\partial}{\partial r_\lambda} \frac{\partial}{\partial r_{\lambda'}} \right. \\
&\quad \left. + \frac{\partial}{\partial p_{\lambda'}} \frac{\partial}{\partial p_\lambda} \right) \frac{\partial}{\partial P} B_m(t). \quad (27)
\end{aligned}$$

Since the quantum-classical Liouville equation is exact for an arbitrary quantum subsystem bilinearly coupled to a harmonic bath, the mapping version of this equation [Eq. (27)] is also exact for such systems.

The first term in Eq. (27) is the quantum evolution of the subsystem in the mapping phase space, while the second term describes the evolution of the bath where the forces involve the mapping coordinates. The complicated third term represents the higher-order correlations between the subsystem and the bath. The evolution equation can be written more compactly as

$$\begin{aligned}
\frac{d}{dt} B_m(x, X, t) &= -\{H_m, B_m(t)\}_{x, X} + \frac{\hbar}{8} \sum_{\lambda\lambda'} \frac{\partial h_{\lambda\lambda'}}{\partial R} \left( \frac{\partial}{\partial r_\lambda} \frac{\partial}{\partial r_{\lambda'}} \right. \\
&\quad \left. + \frac{\partial}{\partial p_{\lambda'}} \frac{\partial}{\partial p_\lambda} \right) \frac{\partial}{\partial P} B_m(t) \equiv i\mathcal{L}_m B_m(t), \quad (28)
\end{aligned}$$

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

equation defines the quantum-classical Liouville operator in the mapping basis,

$$i\mathcal{L}_m = i\mathcal{L}_m^0 + i\mathcal{L}'_m, \quad (29)$$

where

$$i\mathcal{L}_m^0 = -\{H_m, \}_{x,X}, \quad (30)$$

$$i\mathcal{L}'_m = \frac{\hbar}{8} \sum_{\lambda\lambda'} \frac{\partial h_{\lambda\lambda'}}{\partial R} \left( \frac{\partial}{\partial r_{\lambda'}} \frac{\partial}{\partial r_{\lambda}} + \frac{\partial}{\partial p_{\lambda'}} \frac{\partial}{\partial p_{\lambda}} \right) \frac{\partial}{\partial P}.$$

The  $i\mathcal{L}_m^0$  evolution operator, which gives rise to the Poisson bracket in Eq. (28), generates a classical-like evolution of the coupled dynamics of the quantum mapping and classical bath phase space variables that can be simulated by Newtonian trajectories. The force field that the classical variables feel, which depends on the coupling matrix elements in the subsystem basis, continuously changes as a result of the dependence of these forces on the mapping phase space variables. Consequently, the dynamics prescribed by this term is very different from either mean field or adiabatic dynamics and incorporates nonadiabatic effects. The more complex term  $i\mathcal{L}'_m$  can be viewed as dispersion in the mapping Hamiltonian force (arising from the second derivative character in the mapping variables in this term) that the classical variables feel. Consequently, its effects are expected to be smaller than the direct effects from the mapping Hamiltonian force, although the magnitude of this contribution must be analyzed in specific applications. In Sec. III we apply this equation to the spin-boson model and show that accurate results can be obtained when the last term on the right side of this equation is neglected.

### III. SPIN-BOSON MODEL

The spin-boson model is often used as a test case for quantum simulations of many-body systems and we present the results of simulations of this model using the quantum-classical Liouville equation in the mapping basis. The spin-boson model describes a two-level system bilinearly coupled to a harmonic bath of  $N_B$  oscillators with masses  $M_j$  and frequencies  $\omega_j$ . The system Hamiltonian is given by

$$\mathbf{H}_W = \begin{pmatrix} H_B + \hbar\gamma(R) & -\hbar\Omega \\ -\hbar\Omega & H_B - \hbar\gamma(R) \end{pmatrix}, \quad (31)$$

where  $H_B = \sum_j (P_j^2/2M_j + M_j\omega_j^2 R_j^2/2)$  and  $\gamma(R) = -\sum_j c_j R_j$ . The energy gap of the isolated two-state system is  $2\hbar\Omega$ . By substituting Eq. (31) into Eq. (23), we can obtain

$$H_m = H_B + \frac{1}{2}\gamma(R)(r_1^2 + p_1^2 - r_2^2 - p_2^2) - \Omega(r_1 r_2 + p_1 p_2). \quad (32)$$

Equation (28) is an exact evolution equation for the spin-boson model. Previous simulations of the quantum-classical Liouville equation in the adiabatic basis have been carried out using a Trotter-based scheme and were able to reproduce the exact results for a wide range of system parameters.<sup>11</sup> Consequently, the results presented here can be viewed as a test of the utility of the simulation schemes that use the map-

ping basis to represent quantum-classical Liouville dynamics.

As in previous studies we assume that the initial density matrix is uncorrelated so that the subsystem is in the ground state and the bath is in thermal equilibrium, namely,

$$\rho_W(0) = \rho_s(0)\rho_B(X), \quad \rho_s(0) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad (33)$$

where the Wigner distribution of the bath,  $\rho_B(X)$ , is given by<sup>27,28</sup>

$$\rho_B(X) = \prod_{j=1}^N \frac{\beta\omega_j}{2\pi u_j''} \exp \left[ -\frac{\beta}{u_j''} \left\{ \frac{1}{2M_j} P_j^2 + \frac{1}{2} M_j \omega_j^2 R_j^2 \right\} \right], \quad (34)$$

with  $u_j'' = u_j \coth u_j$  and  $u_j = \beta\hbar\omega_j/2$ . The subsystem initial density matrix in the Wigner-transformed mapping basis is

$$\rho_{sm}(x) = (2\pi\hbar)^{-2} (2\hbar)^{-1} (r_1^2 + p_1^2 - \hbar). \quad (35)$$

Using the results in Eq. (14), the time evolution of the population difference between the ground and excited states, given by the expectation value of the Pauli matrix  $\hat{\sigma}_z$ , can be written as

$$\begin{aligned} \overline{\sigma_z(t)} &= \sum_{\lambda\lambda'} \int dX \sigma_z^{\lambda\lambda'}(t) \rho_s^{\lambda'\lambda}(0) \rho_B(X) \\ &= \int dX dx \sigma_{zm}(x, X, t) \tilde{\rho}_{sm}(x) \rho_B(X), \end{aligned} \quad (36)$$

where  $\tilde{\rho}_{sm}(x)$  has the explicit form

$$\tilde{\rho}_{sm}(x) = \frac{2}{\hbar^3 \pi^2} \left( r_1^2 + p_1^2 - \frac{\hbar}{2} \right) e^{-(r^2 + p^2)/\hbar}. \quad (37)$$

The initial value of the Wigner-transformed mapping representation of  $\hat{\sigma}_z$  is  $\sigma_{zm}(x) = (2\hbar)^{-1} (r_1^2 + p_1^2 - r_2^2 - p_2^2)$ .

To compute  $\sigma_z(t)$  we need to solve for  $\sigma_{zm}(x, X, t)$  using Eq. (28). This equation is difficult to solve because of the structure of the last term of the quantum-classical Liouville operator in the mapping basis. For the spin-boson model one may show by direct calculation for short times that the last term does not contribute until the fifth-order initial derivative of  $\sigma_{zm}(x)$ . This suggests that it may be possible to obtain a useful approximate solution by neglecting the last term in the evolution equation (28) so that

$$\frac{d}{dt} \sigma_{zm}(x, X, t) \approx i\mathcal{L}_m^0 \sigma_{zm}(t). \quad (38)$$

The dynamical variable  $\sigma_{zm}(x, X, t)$  evolves by Newtonian equations of motion and admits a solution in terms of characteristics. The corresponding set of ordinary differential equations is<sup>19</sup>

$$\begin{aligned} \frac{dr_{\lambda}(t)}{dt} &= \frac{1}{\hbar} \sum_{\lambda'} h_{\lambda\lambda'}(R(t)) p_{\lambda'}(t), \\ \frac{dp_{\lambda}(t)}{dt} &= -\frac{1}{\hbar} \sum_{\lambda'} h_{\lambda\lambda'}(R(t)) r_{\lambda'}(t), \\ \frac{dR(t)}{dt} &= \frac{P(t)}{M}, \quad \frac{dP(t)}{dt} = -\frac{\partial H_m}{\partial R(t)}. \end{aligned} \quad (39)$$

Using this result, we obtain the simple form for the expectation value,

$$\begin{aligned} \overline{\sigma_z(t)} &= \left( \frac{1}{\pi^2 \hbar^4} \right) \int dx dX \rho_B(X) e^{-(r^2+p^2)/\hbar} \left( r_1^2 + p_1^2 - \frac{\hbar}{2} \right) \\ &\quad \times (r_1(t)^2 + p_1(t)^2 - r_2(t)^2 - p_2(t)^2). \end{aligned} \quad (40)$$

The linear coupling in the spin-boson model is characterized by an Ohmic spectral density,  $J(\omega) = \pi \sum_j c_j^2 / (2M_j \omega_j) \delta(\omega - \omega_j)$ , where  $c_j = (\xi \hbar \Delta \omega M_j)^{1/2} \omega_j$ ,  $\omega_j = -\omega_c \ln(1 - j \Delta \omega / \omega_c)$ , and  $\Delta \omega = \omega_c (1 - e^{-\omega_{\max}/\omega_c}) / N_B$  with  $\omega_c$  the cut-off frequency and  $\xi$  the Kondo parameter.<sup>29</sup> We used  $N_B = 20$  and  $\omega_{\max} = 4\omega_c$ . Dimensionless units with time scaled by  $\omega_c$  are used in the calculations below. The equations of motion were integrated using the velocity Verlet algorithm with time step  $\Delta t = 0.1$ .

The expectation value  $\overline{\sigma_z(t)}$  in Eq. (40) may be computed by sampling the initial bath and mapping variables from Gaussian distributions, reweighting to account for the form of the initial density matrix, and computing  $\sigma_{zm}(x(t))$ . We have also carried out the calculations using focused initial conditions<sup>23,24</sup> where the state mapping variables are initially taken to be  $r_1=1$ ,  $p_1=1$ ,  $r_2=0$ , and  $p_2=0$  (in dimensionless units) when state 1 is initially occupied. Both sampling methods yield comparable results but focused initial conditions require about a factor of 10 fewer trajectories to obtain converged results for this model.

We tested our method for the parameters for which numerically exact results are available. Approximately  $10^4$  trajectories were used to obtain the results in the figures. Comparable results can be obtained even with ten times fewer trajectories. In Fig. 1 the results are compared for a weak system-bath coupling with  $\xi=0.09$ . The adiabatic energy gap is chosen as  $\Omega=0.4$ . For high temperatures, the time-dependent population difference exhibits incoherent behavior as in Fig. 1(a). Our results, as well as those of other methods such as the linearized approach to nonadiabatic dynamics in the mapping basis (LAND-map) and the linearized semiclassical initial value (LSC-IVR) methods, show excellent agreement with the numerically exact results<sup>30</sup> for the high-temperature, weak-coupling case. The reproduction of the coherent or oscillatory behavior at low temperatures shown in Fig. 1(b) is a more severe test, especially at long times. Our results predict the correct frequency of oscillations, but the magnitude of the oscillations are somewhat smaller at long times.

In Fig. 2, we plot  $\langle \sigma_z(t) \rangle$  for a rather high friction constant,  $\xi=2$ , at a high temperature of  $\beta=0.25$ . One can see

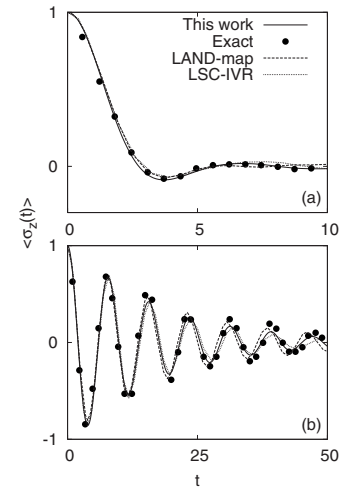


FIG. 1. Electronic population difference  $\langle \sigma_z(t) \rangle$  as a function of  $t$  for two dimensionless parameter sets:  $\Omega=0.4$ ,  $\xi=0.09$ , and  $\beta=0.25$  (a) or 12.5 (b). The solid points are exact results (Ref. 30), the dashed lines are the LAND-map results (Ref. 24), and the dotted lines are the LSC-IVR results (Ref. 22).

that the accuracy of our results does not change for a strong system-bath coupling and is consistently better than other approaches.

As a final test, in Fig. 3 we show  $\langle \sigma_z(t) \rangle$  for two friction constants,  $\xi=0.1$  and 0.5, for a relatively low temperature,  $\beta=3$ . The LAND-map approach predicts the slow incoherent decay instead of oscillation around zero. This discrepancy was attributed to the linearization approximation which underestimates the coherent dynamics. Our results again show reliable accuracy both for weak and strong couplings. Our results are compared with those using the semiclassical influence functional formalism with four time slices. Similar accuracy is obtained.

#### IV. CONCLUSION

The representation of the quantum-classical Liouville equation in the mapping Hamiltonian basis provides the

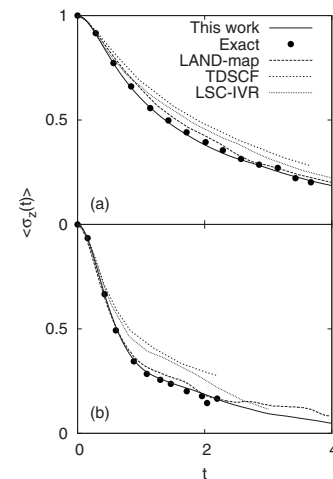


FIG. 2. Electronic population difference  $\langle \sigma_z(t) \rangle$  as a function of  $t$  for two parameter sets:  $\xi=2$ ,  $\beta=0.25$ , and  $\Omega=0.8$  (a) or 1.2 (b). The solid points are exact results (Ref. 31), the dashed lines are the LAND-map results (Ref. 24), the dot-dashed lines are the time dependent self consistent field (TDSCF) results (Ref. 17), and the dotted lines are the LSC-IVR results (Ref. 22).

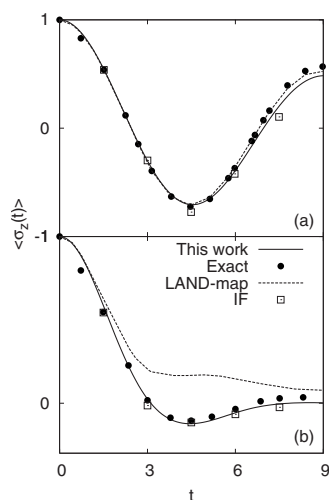


FIG. 3. Electronic population difference  $\langle \sigma_z(t) \rangle$  as a function of  $t$  for two parameter sets:  $\Omega = \frac{1}{3}$ ,  $\beta = 3$ , and  $\xi = 0.1$  (a) or  $0.5$  (b). The solid points are exact results (Ref. 32), the dashed lines are the LAND-map results (Ref. 24), and the open squares are the results obtained using imaginary time path integral semiclassical influence functional formalism with four time slices (Ref. 32).

starting point for the development of a new class of algorithms for the simulation of nonadiabatic dynamics. The simplest such algorithm is constructed by neglecting  $i\mathcal{L}'_m$  in Eq. (29) in the evolution operator. The resulting dynamics is easily solved by characteristics and yields excellent agreement with exact results for the spin-boson model at a small computational cost. The extent to which this approximation is applicable to more general systems requires examination of more complex systems. The work also suggests that it may be possible to construct simulation algorithms that use evolution under  $i\mathcal{L}_m^0$  as a zeroth order scheme about which corrections involving  $i\mathcal{L}'_m$  can be computed. The utility of the mapping formulation of the quantum-classical Liouville equation for the computation of general correlation functions is also another topic that is worth pursuing.

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