

A Centroid Molecular Dynamics Approach for Nonadiabatic Dynamical Processes in Condensed Phases: the Spin-Boson Case[†]

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A centroid molecular dynamics (CMD) approach [*J. Chem. Phys.* **1999** *111*, 2357; *111*, 2371] is developed to study nonadiabatic dynamics in condensed phases, as represented by the spin-boson model. The CMD variables for both electronic and nuclear degrees of freedom are defined on the basis of the concept of a quasi-density operator. The initial distribution of the system investigated is not at thermal equilibrium, and the quasi-density operator is therefore constructed using a mixed centroid and Wigner representation. The CMD approximation is employed for the motion of both electronic and nuclear variables, and a set of nonadiabatic CMD equations are then derived. For the case of the spin-boson model, consisting of two electronic states bilinearly coupled to a harmonic bath, a set of nonadiabatic CMD spin-boson stochastic (generalized Langevin-like) equations can also be obtained by integrating out the bath centroid variables. From the numerical simulations, good agreement is found between the CMD calculations and the exact results.

I. Introduction

Nonadiabatic dynamical processes involving multiple surface crossings in condensed-phase systems provide one of the most active and challenging theoretical topics in physics, chemistry, and biology. A complete quantum mechanical treatment of nonadiabatic dynamics in systems with many degrees of freedom is not yet feasible. By contrast, classical molecular dynamics (MD) simulations are widely available for the adiabatic dynamics of complex molecular systems. A variety of approximations, such as semiclassical¹ and mixed quantum–classical approaches,^{2–8} have thus been developed using MD data as input for studying nonadiabatic dynamics in complex systems.

Approximations often used for the treatment of nonadiabatic dynamics are the mean field method^{2–4} and the surface-hopping method.^{5–9} Both of these approximations are within the class of mixed quantum–classical schemes, namely, electrons are described by quantum wave functions whereas nuclear motion is treated by classical mechanics. In the mean field approach, the classical trajectories are propagated on a mean potential obtained by averaging over the electronic states. Along these lines, the semiclassical time-dependent self-consistent field (SC-TDSCF) approach has been studied.¹⁰ In the surface-hopping method,⁵ a classical trajectory is propagated on a single adiabatic electronic surface and the transition to another adiabatic surface takes place according to some hopping probability. All of these methods can have certain problems related to the ad hoc combination of classical and quantum mechanical theories; that is, they have shortcomings primarily associated with the inconsistent treatment of the electronic and nuclear degrees of freedom.

A consistent description of both electronic and nuclear degrees of freedom using the path integral formalism was given by Pechukas.¹¹ In this method, the classical particles move in a nonlocal force field provided by the quantum system after

employing the semiclassical approximation for the action functional. One then has to run complex-valued trajectories to evaluate the transition matrix element.¹² The theory is self-consistent and exact at the semiclassical level. However, it is not feasible practically and thus its application requires further approximations.¹³

A more practical treatment was devised by Miller and co-workers via a classical electronic analogue model,¹⁴ such that electronic and nuclear degrees of freedom are treated on the same footing. Recently, Stock and Thoss¹⁵ in the same spirit derived a quantum mechanically rigorous mapping Hamiltonian based on Schwinger's theory of angular momentum.¹⁶ The resulting Hamiltonian has a well-defined classical analogue such that both the electronic and the nuclear degrees of freedom can be treated consistently. The classical electronic analogue model can be transformed to the mapping Hamiltonian by transforming the electronic action-angle variables to the corresponding Cartesian-like electronic coordinates and momenta. The general method has been widely used to study nonadiabatic dynamical processes in the recent years.^{15,17–25}

Another strategy to study quantum mechanics in large systems is to implement the path integral centroid formalism. It was first noted by Feynman²⁶ that a path centroid may serve as the most classical-like variable of an equilibrium system. The concept of the path centroid has been widely applied for calculating quantum equilibrium statistics,^{27–30} dynamical properties,³⁰ and quantum-activated rate processes.^{31,32} It provides the basis for a classical-like effective potential on which the centroid molecular dynamics (CMD) method^{30,33–35} was formulated. Applications of CMD^{36,37} have shown that it can capture the main quantum effects for incoherent dynamical processes in condensed phases.

In this paper, we provide some preliminary concepts for the generalization of the CMD approach to treat electronically nonadiabatic dynamics. For this purpose, we employ the spin-boson model, which represents a system of two electronic states bilinearly coupled to an infinite dissipative harmonic bath. This

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popular model has served extensively as a prototype³⁸ to study physical and chemical phenomena in condensed phases or to test a variety of approximation methods, for example, in the study of nonadiabatic dynamics.^{22,39} The spin-boson Hamiltonian can be written as^{40,41}

$$\hat{H} = \epsilon \hat{\sigma}_z + \Delta \hat{\sigma}_x + \sum_{j=1}^M \frac{1}{2} \hat{P}_j^2 + \frac{1}{2} \omega_j^2 \left(\hat{X}_j + \frac{c_j}{\omega_j} \hat{\sigma}_z \right)^2 \quad (1)$$

where the spin operators are $\hat{\sigma}_z = (|1\rangle\langle 1| - |2\rangle\langle 2|)$ and $\hat{\sigma}_x = (|1\rangle\langle 2| + |2\rangle\langle 1|)$, ϵ is an energetic bias, and Δ is the tunneling matrix element between the two states. The operators \hat{X}_j and \hat{P}_j in eq 1 are the position of the j th harmonic solvent mode and its conjugate momentum, respectively, with the frequency ω_j . The constant c_j is the coupling strength between the solvent mode and the system. All essential properties of the bath as it influences the dynamics of the system can be characterized by its spectral density³⁸

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\omega_j} [\delta(\omega - \omega_j) - \delta(\omega + \omega_j)] \quad (2)$$

In this work, we use the spectral density for an Ohmic bath

$$J(\omega) = \frac{\pi}{2} \alpha \hbar \omega e^{-\omega/\omega_c} \quad (3)$$

where ω_c is a cutoff frequency and the dimensionless Kondo parameter, α , is defined in terms of the viscosity, γ , given by

$$\alpha = 2\gamma/(\pi\hbar) \quad (4)$$

It should be noted that several years ago Egger et al.^{42,43} applied the centroid formalism to study nonadiabatic electron transfer using the above spin-boson model. In their studies, the electronic centroid variable related to the spin operator $\hat{\sigma}_z$ was discrete and restricted in the range $[-1, 1]$ without an obvious classical analogue. However, CMD cannot be directly applied to the discrete Hamiltonian in eq 1 by running trajectories consistently for both the electronic and nuclear degrees of freedom. As will be shown in the present paper, this problem can be circumvented by mapping a discrete Hamiltonian into a continuous one as proposed by Stock and Thoss.¹⁵

Consider an N -level system described by the Hamiltonian

$$\hat{\mathcal{H}} = \sum_{n,m} h_{nm}(\hat{\mathbf{X}}, \hat{\mathbf{P}}) |n\rangle \langle m| \quad (5)$$

where $\hat{\mathbf{X}} = \{\hat{X}_j\}$ and $\hat{\mathbf{P}} = \{\hat{P}_j\}$ ($j = 1, \dots, M$) denote the nuclear position coordinates and the conjugate momenta. The Hamiltonian in eq 5 can be mapped into the continuous bosonic representation

$$\hat{H} = \frac{1}{2} \sum_{n,m} h_{nm}(\hat{\mathbf{X}}, \hat{\mathbf{P}}) (\hat{x}_n \hat{x}_m + \hat{p}_n \hat{p}_m - \delta_{n,m}) \quad (6)$$

subject to the completeness relation

$$\sum_{n=1}^N |n\rangle \langle n| = 1 \quad (7)$$

which restricts the dynamics into the $N + M - 1$ -dimensional subspace, and the n th electronic state corresponds to a single quantum excitation (the rest of the modes are in their ground

states). The constraint in eq 7 can be implicitly invoked via sampling a suitable initial distribution of position coordinates and momenta. If the description of the quantum dynamics is exact, the trajectories are always run correctly in the subspace.

Using the mapping approach for the spin-boson problem, we can map the operators $\hat{\sigma}_x$, $\hat{\sigma}_y$, and $\hat{\sigma}_z$, respectively, by

$$\begin{aligned} \hat{\sigma}_x &= \hat{p}_1 \hat{p}_2 + \hat{x}_1 \hat{x}_2, & \hat{\sigma}_y &= \hat{x}_1 \hat{p}_2 - \hat{x}_2 \hat{p}_1, \\ \hat{\sigma}_z &= \frac{1}{2} (\hat{p}_1^2 + \hat{x}_1^2 - \hat{p}_2^2 - \hat{x}_2^2) \end{aligned} \quad (8)$$

where $[\hat{x}_k, \hat{p}_j] = i\delta_{kj}$. With these relationships in hand, the continuous representation for the Hamiltonian in eq 1 can be obtained as well as the constraint condition, which is given by eq 7 when N is set to 2.

The organization of the remaining sections of this paper is as follows: Section II presents the nonadiabatic CMD equations of motion for the spin-boson model. The resulting theory is then tested against exact numerical results in section III, and concluding remarks are given in section IV.

II. Nonadiabatic Centroid Molecular Dynamics Method

The Hamilton in eq 1 can be rewritten in a simple form as

$$\hat{H} = \frac{\hat{\mathbf{P}}^2}{2} + \hat{V}(\hat{\mathbf{X}}) \quad (9)$$

where the coordinates $\hat{\mathbf{X}}$ and their conjugate momenta $\hat{\mathbf{P}}$ are defined in eq 5 and

$$\hat{V}(\hat{\mathbf{X}}) = \epsilon \hat{\sigma}_z + \Delta \hat{\sigma}_x + \sum_{j=1}^M \frac{1}{2} \omega_j^2 \left(\hat{X}_j + \frac{c_j}{\omega_j} \hat{\sigma}_z \right)^2 \quad (10)$$

This Hamiltonian form will be used for the nuclear centroid force calculation discussed later.

It is assumed that the interaction between the system and the bath is switched on at $t = 0$ and the initial population is in the state $|1\rangle$. One then has the initial density operator in the product form

$$\hat{\rho}(0) = \hat{\rho}_s(0) \otimes \frac{e^{-\beta \hat{H}_B}}{\text{Tr}[e^{-\beta \hat{H}_B}]} \quad (11)$$

where \hat{H}_B is the bath Hamiltonian, which can be expressed in terms of the mass-weighted coordinates and momenta as

$$\hat{H}_B = \sum_{j=1}^M \frac{1}{2} \hat{P}_j^2 + \frac{1}{2} \omega_j^2 \hat{X}_j^2 \quad (12)$$

and the initial electronic density operator $\hat{\rho}_s$ is

$$\hat{\rho}_s = \hat{\rho}_s(0) = |1\rangle \langle 1| \quad (13)$$

This nonequilibrium initial condition can be achieved, for instance, by a short pulse optical excitation.^{44,45} It makes the “spin up” sites completely occupied, that is,

$$\langle \hat{\sigma}_z(0) \rangle = 1, \quad \langle \hat{\sigma}_{x,y}(0) \rangle = 0 \quad (14)$$

After time t , the density operator evolves according to

$$\hat{\rho}(t) = e^{-i(\hat{H}/\hbar)t} \hat{\rho}(0) e^{i(\hat{H}/\hbar)t} \quad (15)$$

The survival probability is defined as the portion of $\hat{\rho}(t)$ still remaining on the state $|1\rangle$ and can be written as

$$P_{11}(t) = \text{Tr}[e^{-i(\hat{H}/\hbar)t} \hat{\rho}(0) e^{i(\hat{H}/\hbar)t} \hat{\rho}_s] \quad (16)$$

The preceding equation can also be rewritten in the form of a correlation function as

$$P_{11}(t) = \langle \hat{\rho}_s(0) \hat{\rho}_s(t) \rangle_B \quad (17)$$

where $\langle \dots \rangle_B$ denotes the average over the thermal bath. The survival probability $P_{11}(t)$ can in turn be expressed as

$$P_{11}(t) = \frac{1}{2}[\langle \hat{\sigma}_z(t) \rangle + 1] \quad (18)$$

The averaging over the initial electronic and nuclear states, $\langle \hat{\sigma}_z(t) \rangle$, can be evaluated using the nonadiabatic CMD approach as discussed later.

A. Quasi-Density Operator and Centroid Variables. The discussion of the nonadiabatic CMD approach in this paper is based on recent work from this group, which formulated an exact centroid dynamics theory for the adiabatic case.^{34,35} A centroid variable can be defined using the concept of a quasi-density operator. This quasi-density operator is especially suitable for the study of centroid nuclear dynamics in a thermal ensemble. Nevertheless, to describe a nonadiabatic dynamical process in a nonthermal ensemble, a quasi-density operator can be also defined in a similar way, given by

$$A_c(t) = \text{Tr}[\hat{\delta}_c(t; \mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) \hat{A}] \quad (19)$$

where $\hat{\delta}_c(t; \mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c)$ is the time-evolution of the quasi-density operator $\hat{\delta}_c(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c)$

$$\hat{\delta}_c(t; \mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) = e^{-i(\hat{H}/\hbar)t} \hat{\delta}_c(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) e^{i(\hat{H}/\hbar)t} \quad (20)$$

and

$$\hat{\delta}_c(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) = \frac{\hat{\phi}(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c)}{\text{Tr}[\hat{\phi}(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c)]} \quad (21)$$

In the multidimensional notation, $\hat{\phi}(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c)$ is defined in the present nonadiabatic case as

$$\begin{aligned} \hat{\phi}(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) = & \left(\frac{\hbar}{2\pi} \right)^{M+2} \int \int d\vec{\zeta}_n d\vec{\eta}_n e^{i\vec{\zeta}_n(\hat{\mathbf{X}} - \mathbf{X}_c) + i\vec{\eta}_n(\hat{\mathbf{P}} - \mathbf{P}_c) - \beta\hat{H}_B} \times \\ & \int \int d\vec{\zeta}_e d\vec{\eta}_e e^{i\vec{\zeta}_e(\hat{\mathbf{x}} - \mathbf{x}_c) + i\vec{\eta}_e(\hat{\mathbf{p}} - \mathbf{p}_c)} \hat{\rho}_s \end{aligned} \quad (22)$$

where M and 2 are the numbers of the nuclear and the electronic oscillators, respectively, as given in the Hamiltonian in eq 1. In eq 22, the vector notation means $\vec{\zeta}_n = (\zeta_{n,1}, \dots, \zeta_{n,M})$, $\vec{\eta}_n = (\eta_{n,1}, \dots, \eta_{n,M})$ and $\vec{\zeta}_e = (\zeta_{e,1}, \zeta_{e,2})$, $\vec{\eta}_e = (\eta_{e,1}, \eta_{e,2})$. The above definition of a quasi-density operator is different from that given in ref 34 by noting that the electronic part in eq 22 is defined in the Wigner representation,^{34,46,47} whereas the nuclear part corresponds to the usual centroid representation.³⁴

Obviously, the operator $\hat{\phi}(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c)$ in eq 22 can also be written as a product of $\hat{\phi}_s$ and $\hat{\phi}_B$ for the system and the bath, respectively,

$$\hat{\phi}(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) = \hat{\phi}_s(\mathbf{x}_c, \mathbf{p}_c) \hat{\phi}_B(\mathbf{X}_c, \mathbf{P}_c) \quad (23)$$

where $\mathbf{x}_c = (x_{1,c}, x_{2,c})$, $\mathbf{p}_c = (p_{1,c}, p_{2,c})$ and

$$\hat{\phi}_s(\mathbf{x}_c, \mathbf{p}_c) = \left(\frac{\hbar}{2\pi} \right)^2 \int \int d\vec{\zeta}_e d\vec{\eta}_e e^{i\vec{\zeta}_e(\hat{\mathbf{x}} - \mathbf{x}_c) + i\vec{\eta}_e(\hat{\mathbf{p}} - \mathbf{p}_c)} \hat{\rho}_s;$$

$$\hat{\phi}_B(\mathbf{X}_c, \mathbf{P}_c) = \left(\frac{\hbar}{2\pi} \right)^M \int \int d\vec{\zeta}_n d\vec{\eta}_n e^{i\vec{\zeta}_n(\hat{\mathbf{X}} - \mathbf{X}_c) + i\vec{\eta}_n(\hat{\mathbf{P}} - \mathbf{P}_c) - \beta\hat{H}_B} \quad (24)$$

The relevant distribution functions are given by

$$\rho(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) = \frac{\text{Tr}[\hat{\phi}(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c)]}{Z_s Z_B} = \rho_s(\mathbf{x}_c, \mathbf{p}_c) \rho_B(\mathbf{X}_c, \mathbf{P}_c) \quad (25)$$

and

$$\begin{aligned} \rho_s(\mathbf{x}_c, \mathbf{p}_c) &= \frac{\text{Tr}[\hat{\phi}(\mathbf{x}_c, \mathbf{p}_c)]}{Z_s} \\ \rho_B(\mathbf{X}_c, \mathbf{P}_c) &= \frac{\text{Tr}[\hat{\phi}(\mathbf{X}_c, \mathbf{P}_c)]}{Z_B} \end{aligned} \quad (26)$$

where Z_s and Z_B are the normalization constants.

One thus can write time-dependent centroid spin variables $\sigma_{j,c}(t)$ ($j = x, y, z$), bath positions $X_{j,c}(t)$, and momenta $P_{j,c}(t)$ as

$$\begin{aligned} \sigma_{i,c}(t) &= \text{Tr}[\hat{\delta}_c(t; \mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) \hat{\sigma}_i] \quad (i = x, y, z) \\ P_{j,c}(t) &= \text{Tr}[\hat{\delta}_c(t; \mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) \hat{P}_j] \\ X_{j,c}(t) &= \text{Tr}[\hat{\delta}_c(t; \mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) \hat{X}_j] \quad (j = 1, M) \end{aligned} \quad (27)$$

The initial ($t = 0$) centroid variables can obviously be written as

$$\begin{aligned} \sigma_{i,c} &= \text{Tr}[\hat{\delta}_c(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) \hat{\sigma}_i] \quad (i = x, y, z) \\ P_{j,c} &= \text{Tr}[\hat{\delta}_c(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) \hat{P}_j] \\ X_{j,c} &= \text{Tr}[\hat{\delta}_c(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) \hat{X}_j] \quad (j = 1, M) \end{aligned} \quad (28)$$

Here, the electronic variables are actually expressed in the Wigner representation, while the nuclear variables are the centroid ones, as stated earlier.

Another important variable is the nuclear centroid force F_c , given by

$$\begin{aligned} F_c &= \frac{i}{\hbar} \text{Tr}\{\hat{\delta}_c(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) [\hat{H}, \hat{P}]\} \\ &= -\text{Tr}\left\{ \hat{\delta}_c(\mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) \left(\frac{\partial \hat{V}(\hat{\mathbf{X}})}{\partial \hat{\mathbf{X}}} \right) \right\} \end{aligned} \quad (29)$$

where $F_c = \{F_{c,j} \mid j = 1, \dots, M\}$ and in the case of the spin-boson Hamiltonian

$$F_{c,j} = -\omega_j^2 X_{j,c} - c_j \sigma_{z,c} \quad (30)$$

The time-dependent nuclear centroid force, $F_c(t)$, according to eq 19, is given by

$$F_c(t) = -\text{Tr}\left\{ \hat{\delta}_c(t; \mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) \left(\frac{\partial \hat{V}(\hat{\mathbf{X}})}{\partial \hat{\mathbf{X}}} \right) \right\} \quad (31)$$

of which the functional form is the same as in eq 29.

The average of time-dependent $\sigma_{i,c}(t)$ in eq 18 can be expressed in terms of the centroid variables, given by

$$\langle \sigma_z(t) \rangle = \iiint \frac{d\mathbf{x}_c d\mathbf{p}_c}{(2\pi\hbar)^2} \frac{d\mathbf{X}_c d\mathbf{P}_c}{(2\pi\hbar)^M} \rho_s(\mathbf{x}_c, \mathbf{p}_c) \rho_B(\mathbf{X}_c, \mathbf{P}_c) \sigma_{z,c}(t) \quad (32)$$

where $\sigma_{z,c}(t)$ can be obtained approximately from, for example, solving the nonadiabatic equations [eq 38], given later.

B. Nonadiabatic CMD Spin-Boson Equations of Motion. Employing the definition of the dynamical centroid variable in eq 19 along with eq 20, we can write the time-derivative of a centroid function, $A_c(t)$, as

$$\dot{A}_c(t) = \frac{i}{\hbar} \text{Tr} \{ \hat{\delta}_c(t; \mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) [\hat{H}, \hat{A}] \} \quad (33)$$

With the use of eqs 9 and 27 and the commutation relations

$$[\hat{\sigma}_x, \hat{\sigma}_y] = 2i\hat{\sigma}_z, \quad [\hat{\sigma}_y, \hat{\sigma}_z] = 2i\hat{\sigma}_x, \quad [\hat{\sigma}_z, \hat{\sigma}_x] = 2i\hat{\sigma}_y \quad (34)$$

the equations for the exact nonadiabatic centroid dynamics thus read

$$\begin{aligned} \dot{\sigma}_{x,c} &= -2\epsilon\sigma_{y,c} - 2\sum_{j=1}^M c_j (\hat{X}_j \hat{\sigma}_y)_c \\ \dot{\sigma}_{y,c} &= 2\epsilon\sigma_{x,c} - 2\Delta\sigma_{z,c} + 2\sum_{j=1}^M c_j (\hat{X}_j \hat{\sigma}_x)_c \\ \dot{\sigma}_{z,c} &= 2\Delta\sigma_{y,c} \\ \dot{X}_{j,c} &= P_{j,c} \\ \dot{P}_{j,c} &= -\omega_j^2 X_{j,c} - c_j \sigma_{z,c} \quad (j = 1, \dots, M) \end{aligned} \quad (35)$$

where $(\hat{X}_j \hat{\sigma}_k)_c = \text{Tr}[\hat{\delta}_c(t; \mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) \hat{X}_j \hat{\sigma}_k]$ ($k = x, y$). In the above derivation of the exact centroid dynamical equations, the equality $\hat{\sigma}_z^2 = (|1\rangle\langle 1| + |2\rangle\langle 2|) = 1$ is used.

The exact solution of the above equations is not feasible in practice. One must therefore resort to some kind of approximation, and a CMD-like approximation³⁵ is thus applied in this paper. This approximation assumes the quasi-density operator behaves as

$$\hat{\delta}_c(t; \mathbf{x}_c, \mathbf{p}_c; \mathbf{X}_c, \mathbf{P}_c) \approx \hat{\delta}_c\{\mathbf{x}_c(t), \mathbf{p}_c(t); \mathbf{X}_c(t), \mathbf{P}_c(t)\} \quad (36)$$

such that its functional form at any time t is the same as that at the initial time $t = 0$. Moreover, in the CMD approximation, the time derivative of any CMD variable, $A_c(t)$, defined in eq 33 becomes

$$\dot{A}_c(t) \approx \frac{i}{\hbar} \text{Tr}(\hat{\delta}_c\{\mathbf{x}_c(t), \mathbf{p}_c(t); \mathbf{X}_c(t), \mathbf{P}_c(t)\} [\hat{H}, \hat{A}]) \quad (37)$$

It should be noted that the trace operation in the above equation has nothing to do with the CMD variables.

Applying the CMD-like approximation to the exact centroid dynamical equations in eq 35 and considering eqs 21–25, one may thus obtain the nonadiabatic CMD equations of the motion, given by

$$\begin{aligned} \dot{\sigma}_{x,c} &= -2\epsilon\sigma_{y,c} - 2\sigma_{y,c} \sum_{j=1}^M c_j X_{j,c} \\ \dot{\sigma}_{y,c} &= 2\epsilon\sigma_{x,c} - 2\Delta\sigma_{z,c} + 2\sigma_{x,c} \sum_{j=1}^M c_j X_{j,c} \\ \dot{\sigma}_{z,c} &= 2\Delta\sigma_{y,c} \\ \dot{X}_{j,c} &= P_{j,c} \\ \dot{P}_{j,c} &= -\omega_j^2 X_{j,c} - c_j \sigma_{z,c} \quad (j = 1, \dots, M) \end{aligned} \quad (38)$$

To solve these CMD equations of motion, one needs to specify the initial conditions. The initial distribution functions for the bath modes, $\rho_B(\mathbf{X}_c, \mathbf{P}_c) = [\rho_B(X_{j,c}, P_{j,c})]$ ($j = 1, \dots, M$), are naturally given for eq 32 by

$$\rho_B(X_{j,c}, P_{j,c}) = \hbar\beta\omega_j e^{-\beta/2(P_{j,c}^2 + \omega_j^2 X_{j,c}^2)} \quad (39)$$

which are the exact centroid expressions for harmonic oscillators.

There are various approaches^{19,21,22,24} for treating the initial electronic distributions, all of which are based on the different classical-like approximations. In the Meyer–Miller (MM) method,^{21,22} the initial electronic distribution is derived from the Wigner transform of the coordinate representation of the eigenfunctions for the ground state and the first excited state of a harmonic electronic oscillator. In their quasi-classical approach (QC), Müller and Stock introduced an action-angle initial distribution^{17–19} and found that it can give somewhat more accurate results compared to the MM method.

In this work, the sampling of the action-angle initial conditions¹⁹ is expressed in terms of the electronic CMD positions and momenta as

$$\begin{aligned} p_{1,c} + ix_{1,c} &= \sqrt{3} e^{i\alpha_1} \\ p_{2,c} + ix_{2,c} &= e^{i\alpha_2} \end{aligned} \quad (40)$$

where the phase factors α_1 and α_2 are sampled from the uniform distribution in the $[0, 2\pi)$ interval and the bath coordinates are sampled from eq 39. Using eq 28, we may write the initial conditions for the spin-boson variables as

$$\begin{aligned} \sigma_{x,c} &= p_{1,c} p_{2,c} + x_{1,c} x_{2,c} \\ \sigma_{y,c} &= x_{1,c} p_{2,c} - x_{2,c} p_{1,c} \\ \sigma_{z,c} &= \frac{1}{2}(x_{1,c}^2 + p_{1,c}^2 - x_{2,c}^2 - p_{2,c}^2) \end{aligned} \quad (41)$$

As discussed by Müller and Stock,¹⁹ the so-called zero-point energy (ZPE) flow problem¹⁷ occurs because of the classical approximations used for the quantum nonadiabatic dynamics. This unphysical flow in classical trajectory simulation is caused by the fact that the classical trajectories can enter the phase-space regions violating the uncertainty principle in quantum mechanics. To reduce the ZPE flow, an adjustable parameter γ_e was introduced to modify the initial electronic distribution such that

$$\begin{aligned} p_{1,c} + ix_{1,c} &= \sqrt{2 + \gamma_e} e^{i\alpha_1} \\ p_{2,c} + ix_{2,c} &= \sqrt{\gamma_e} e^{i\alpha_2} \end{aligned} \quad (42)$$

The adjustable parameter γ_e is restricted in the range between

0 and 1. The case of $\gamma_e = 1$ is for no ZPE adjustment, whereas $\gamma_e = 0$ is associated with the full ZPE adjustment. Müller and Stock¹⁹ showed that without the adjustment the electronic dynamics is significantly overestimated while with the full adjustment it is underestimated. Some methods have been suggested^{19,24} to choose this adjustable parameter. To modify the initial electronic condition in this paper, the parameter γ_e is chosen in a way similar to that suggested by Golosov and Reichman²⁴ for the classical mapping approach, that is,

$$\langle \sigma_{i,c}^2 \rangle_c = 1 \quad (i = x, y, z), \quad \langle \sigma_{z,c} \rangle_c = 1, \quad \langle \sigma_{j,c} \rangle_c = 0 \quad (j = x, y) \quad (43)$$

where $\sigma_{i,c}^2$ is defined in eq 28 and $\langle \dots \rangle_c$ is the phase-space averaging over the CMD positions and momenta.

It is interesting to note that the dynamical nonadiabatic CMD equations for the spin-boson system [eq 38] are equivalent in form to the classical mapping equations with the parameter κ set to unity (e.g., see ref 24). As noted by Golosov and Reichman,²⁴ a value of unity for this parameter is important for the accuracy of the mapping equations. Furthermore, in the present CMD approach, the initial bath distribution is rigorously the centroid distribution [eq 39] instead of the Wigner distribution as is often employed in the mapping approach. In the future, we will explore alternative solutions to the exact centroid dynamics equations in eq 35 as well as develop the nonadiabatic CMD approach for general (nonquadratic) diabatic potentials.

C. Stochastic CMD Equations. In the case in which the bath is harmonic, the nonadiabatic CMD equations of motion can be simplified further by noting that the equations of the motion of the bath are linear with respect to the centroid coordinates and momenta, including a time-dependent “parameter”, $\sigma_{z,c}(t)$. On the basis of Zwanzig’s discussion,⁴⁹ these equations can be integrated out. One thus can obtain the trajectories for the CMD bath modes

$$X_{j,c}(t) = \xi_j(t) + \frac{c_j}{\omega_j^2} \sigma_{z,c} \cos \omega_j t - \frac{c_j}{\omega_j^2} \sigma_{z,c}(t) + \int_0^t d\tau \frac{c_j \cos \omega_j(t - \tau)}{\omega_j^2} \dot{\sigma}_{z,c}(\tau) \quad (44)$$

where

$$\xi_j(t) = X_{j,c} \cos(\omega_j t) + \frac{P_{j,c}}{\omega_j} \sin(\omega_j t) \quad (45)$$

Substituting the above equations into eq 38, one therefore obtains the generalized Langevin-like CMD spin-boson stochastic (CMD-SBS) equations

$$\begin{aligned} \dot{\sigma}_{x,c} &= -2\epsilon \sigma_{y,c} - \\ &2\sigma_{y,c} \left[\xi(t) + \gamma(t) \sigma_{z,c} - \sigma_{z,c}(t) \sum_j \frac{c_j^2}{\omega_j^2} + \int_0^t d\tau \gamma(t - \tau) \dot{\sigma}_{z,c}(\tau) \right] \\ \dot{\sigma}_{y,c} &= 2\epsilon \sigma_{x,c} - 2\Delta \sigma_{z,c} + \\ &2\sigma_{x,c} \left[\xi(t) + \gamma(t) \sigma_{z,c} - \sigma_{z,c}(t) \sum_j \frac{c_j^2}{\omega_j^2} + \int_0^t d\tau \gamma(t - \tau) \dot{\sigma}_{z,c}(\tau) \right] \\ \dot{\sigma}_{z,c} &= 2\Delta \sigma_{y,c} \end{aligned} \quad (46)$$

with the friction function

$$\gamma(t) = \sum_j \frac{c_j^2}{\omega_j^2} \cos \omega_j t \quad (47)$$

Another often used Hamiltonian^{50,52} is obtained from eq 1 by subtracting $\sum_j c_j^2/(2\omega_j^2) \sigma_z^2$, which is a constant because $\hat{\sigma}_z^2 = |1\rangle\langle 1| + |2\rangle\langle 2| = 1$. The CMD-SBS equations in this case are therefore the same as in eq 46.

Using the spectral density defined in eq 2, one may note that the friction function is just the cosine Fourier transform of the spectral density

$$\gamma(t) = \frac{2}{\pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega} \cos(\omega t) \quad (48)$$

and the coefficient in the term $(\sum_j c_j^2/\omega_j^2) \sigma_{z,c}(t)$ can also be expressed as

$$\sum_j \frac{c_j^2}{\omega_j^2} = \frac{2}{\pi} \int_0^\infty d\omega \frac{J(\omega)}{\omega} \quad (49)$$

The function $\xi(t)$ in eq 46 is the random force

$$\begin{aligned} \xi(t) &= \sum_j c_j \xi_j(t) \\ &= \sum_j c_j \left[X_{j,c} \cos \omega_j t + \frac{P_{j,c}}{\omega_j} \sin \omega_j t \right] \end{aligned} \quad (50)$$

with zero mean and a correlation function given by

$$\langle \xi(t) \xi(t') \rangle = \frac{1}{\beta} \gamma(t - t') \quad (51)$$

A similar treatment of the harmonic bath in the spin-boson problem was also reported recently.⁵¹ As seen from eq 46, the CMD-SBS equations decompose the factors of the dissipative bath into the friction and the random force, as well as the linear term $(\sum_j c_j^2/\omega_j^2) \sigma_{z,c}(t)$. Without the random force, the CMD-SBS equations are deterministic in the electronic subspace.

III. Numerical Results

The CMD-SBS equations in eq 46 were adapted to run trajectories in the calculations reported in this section. The conventional methods for solving deterministic ordinary differential equations⁵³ are not always applicable for solving stochastic equations because of the noise term.^{54,55} A method, the principle of which is similar to that developed by Hershkovitz,⁵⁵ was used in this paper to construct a Runge–Kutta-like algorithm. The random force was also generated by sampling the initial positions and momenta distribution from eq 39 for each time step in our calculations. The frequencies, ω_j , in eq 50 were uniformly distributed in the interval $(0, 10\omega_c]$, and the parameters c_j were obtained from integration of both sides of eq 2.⁵⁶ The number of the bath modes included must be large enough to model the continuum of the bath. Generally, computing a physical quantity such as reactive flux requires typically 10^4 – 10^6 trajectories.⁵⁵ In our calculations, the Metropolis sampling number was as large as 6×10^5 to obtain convergent results for a fast bath at low temperature.

Four different cases were considered in the calculations: zero energetic bias ($\epsilon = 0$) with two different sets of parameters, a nonzero bias case with a slow bath, and a nonzero bias case with a fast bath. Figures 1 and 2 present the results for the

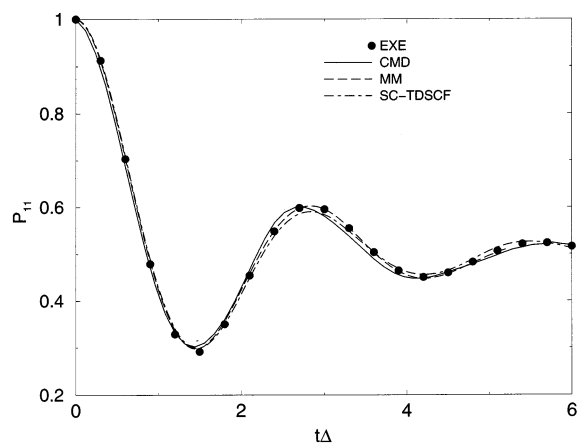


Figure 1. Survival probability, P_{11} , as a function of the reduced time, $t\Delta$, at $\alpha = 0.13$, $\omega_c = 2.5\Delta$, and the reduced bath temperature $\hbar\beta\omega_c = 1.0$. CMD calculations (solid line) are compared with the exact^{24,50} (solid circles), MM^{21,22,24} (long-dashed line), and SC-TDSCF^{24,39} (dot-dashed line) results.

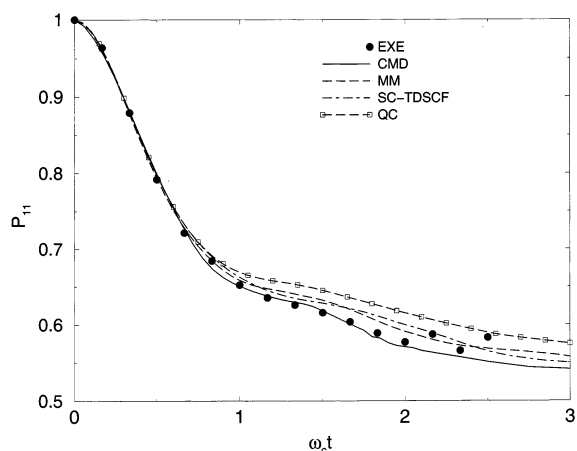


Figure 2. Survival probability, P_{11} , as a function of the reduced time, $\omega_c t$, at $\alpha = 2$, $\Delta = 1.2\omega_c$, and the reduced bath temperature $\hbar\beta\omega_c = 0.25$. CMD results (solid line) are compared with the exact^{24,41} (solid circles), MM^{21,22,24} (long-dashed line), SC-TDSCF^{24,39} (dot-dashed line), and QC^{19,24} (dashed line with open squares) calculations.

unbiased cases. In Figure 1, the Kondo parameter was $\alpha = 0.13$, the cutoff frequency was $\omega_c = 2.5\Delta$ ($\Delta = 1.0$), and the reduced temperature was $\hbar\beta\omega_c = 1.0$. The exact results were taken from ref 24. In Figure 2, the parameters were $\alpha = 2.0$, $\Delta = 1.2\omega_c$ ($\omega_c = 1.0$), and $\hbar\beta\omega_c = 0.25$. The calculations for the biased cases were shown in Figures 3 and 4. A model similar to that used for Figure 3 has been employed to study a photoexcited electron-transfer reaction.⁵² In this model, the nonadiabatic coupling constant was $\Delta = 2500 \text{ cm}^{-1}$, the energetic bias was $\epsilon = 1950 \text{ cm}^{-1}$, the solvent temperature was $T = 300 \text{ K}$, and the reorganization energy was 3900 cm^{-1} . The cutoff frequency, ω_c , in eq 3 was 220 cm^{-1} , and the Kondo parameter α was chosen to yield the total reorganization energy. The intramolecular modes were omitted in our calculations to compare our results with those obtained by Golosov and Reichman in the same model.^{24,57} The inclusion of those intramolecular modes only modulates the results in a quantitative rather than qualitative fashion as pointed out by the latter authors.⁵⁷ For Figure 4, the example discussed by Makri et al.⁴⁰ was adopted in this paper. The Kondo parameter in the Ohmic spectral density of the bath with a cutoff frequency $\omega_c = 7.5\Delta$ is $\alpha = 0.1$. The reduced temperature $\hbar\beta\Delta = 5.0$. All CMD-SBS results are compared

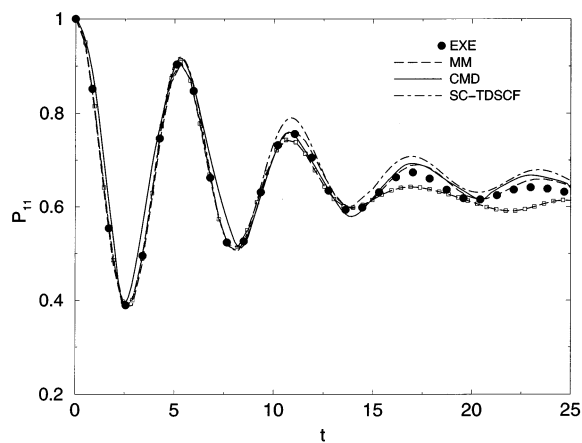


Figure 3. Survival probability, P_{11} , as a function of time (in units of fs) for photoinduced electron transfer in a mixed-valence compound. This is a biased system with a slow bath. The parameters are given in the context, as well as in ref 52. CMD results (solid line) are compared with the exact^{24,52} (solid circles), MM^{21,22,24} (long-dashed line), SC-TDSCF^{24,39} (dot-dashed line), and QC^{19,24} (dashed line with open squares) results.

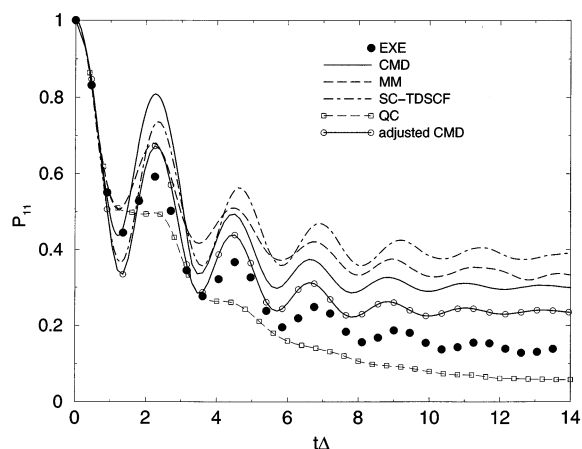


Figure 4. Survival probability, P_{11} , as a function of the reduced time, $t\Delta$, for a biased system at $\alpha = 0.1$, $\epsilon = \Delta$, $\omega_c = 7.5\Delta$, and $\hbar\beta\Delta = 5.0$. CMD results (solid line) are compared with the exact^{24,40} (solid circles), MM^{21,22,24} (long-dashed line), SC-TDSCF^{24,39} (dot-dashed line), and QC^{19,24} (dashed line with open squares) calculations. The solid line with circles is the adjusted CMD results ($\gamma_e = 0.75$).

correspondingly with the numerical exact quantum calculations^{24,40,41,50,52} and other approximations such as the SC-TDSCF,^{24,39} MM,^{21,22,24} QC,^{17–19,24} and short-time (ST)²⁴ approaches.

As seen in Figures 1 and 2, the results from CMD-SBS and other approximations are very similar and all are reasonably close to the numerically exact results. As illustrated in Figure 3, in the case of an energetically biased spin-boson model with a slow bath, the CMD results agree quite well with the exact ones, as well as with the other approximations.

Figure 4 shows that in the case in which the bath is fast, the CMD-SBS results are comparable with SC-TDSCF and MM at short time, whereas they are better at long time. The other classical mapping approaches^{19,24} often implement expressions similar to eq 42 to modulate the electronic initial distribution. The nonadiabatic CMD results can also be improved in the similar way. In our calculations, eq 43 was used and the adjustable parameter γ_e was set to 0.75. The adjusted nonadiabatic CMD results are also shown in Figure 4.

IV. Conclusions

In this paper, a CMD-like approach has been developed for nonadiabatic dynamics in condensed phases. The CMD approach usually provides a classical-like approximation for the study of the finite temperature adiabatic quantum dynamics in a thermal ensemble. However, in the study of the nonadiabatic dynamical processes, the initial distribution of the system is often considered to be nonthermal. To describe the dynamical process in such a nonthermal ensemble, the quasi-density operator has been defined so that the nuclear degrees of freedom are treated as centroids whereas the electronic part is related to a Wigner representation. A set of the CMD-like equations were then obtained in the case of the spin-boson Hamiltonian by applying a CMD-like approximation to the motion of both the electronic and the nuclear dynamical variables. The electronic and the nuclear degrees of freedom were treated consistently by using the mapping Hamiltonian.

The CMD-SBS equations, obtained by integrating out the centroid bath variables, were used for running the trajectories in this work. Numerical results shown in Figures 1–3 illustrate that the agreement between the nonadiabatic CMD and the exact results is quite good for the energetically unbiased spin-boson model and the biased case with a slow bath. This is not too surprising because the characteristic reduced temperature in these cases is at most $u_c = \hbar\beta\omega_c = 1$, which corresponds to the high-temperature limit. For the biased case with a fast bath, CMD encounters the ZPE flow problem as do the other classical mapping approaches. One can then modify the electronic initial distribution with an adjustable parameter, improving the agreement with the exact results. The extension of the present method to systems with general diabatic potentials and the applications of this approach to realistic simulations of nonadiabatic dynamical processes will be the focus of future research.

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