A semiclassical self-consistent-field approach to dissipative dynamics: The spin–boson problem

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A semiclassical time-dependent self-consistent-field approach for the description of dissipative quantum phenomena is proposed. The total density operator is approximated by a semiclassical ansatz, which couples the system degrees of freedom to the bath degrees of freedom in a self-consistent manner, and is thus in the spirit of a classical-path description. The capability of the approach is demonstrated by comparing semiclassical calculations for a spin–boson model with an Ohmic bath to exact path-integral calculations. It is shown that the semiclassical model nicely reproduces the complex dissipative behavior of the spin–boson model for a large range of model parameters. The validity and accuracy of the semiclassical approach is discussed in some detail. It is shown that the method is essentially based on the assumption of complete randomization of nuclear phases. In particular, the assumption of phase randomization allows one to perform the trace over the bath variables through quasiclassical sampling of the nuclear initial conditions without invoking any further approximation. © 1995 American Institute of Physics.

I. INTRODUCTION

Dissipative quantum dynamics has been found to play a key role in many areas of theoretical physics. In the field of chemical physics, condensed phase reactions such as electron and proton transfer processes have been investigated in terms of a dissipative two-level system, often referred to as spin–boson problem. Although there has been significant progress in the development of exact quantum-mechanical propagation techniques, straightforward basis-set methods evidently cannot account for multidimensional condensed phase dynamics, since the computational effort increases exponentially with the number of nonseparable degrees of freedom. Feynman’s path integral formulation appears to be the only exact alternative that would avoid this problem, but one trades the exponential increase of basis functions for a formidable sum over paths, the number of which grows exponentially with propagation time. Even for moderate time regimes and despite considerable advances in the numerical implementation, the evaluation of this sum is rather cumbersome and often only feasible within some approximation. If the problem under consideration allows for a perturbative treatment, “golden rule”-type formulations (for small electronic coupling) and reduced density-matrix theory (for small system–bath coupling) are widely used formulations that have proven to be quite valuable. In the case where the coupling between the individual nuclear degrees of freedom may be assumed to be weak, time-dependent self-consistent-field (TDSCF) methods, which approximate the total density operator by a product of operators depending only on a single nuclear coordinate, have been successfully applied to a variety of problems. The validity of simple TDSCF schemes, however, is not easy to predict, and they have also been shown to fail badly, e.g., in the description of nonadiabatic relaxation processes.

Most path-integral and reduced density-matrix formulations are restricted to harmonic “bath” degrees of freedom. Only very recently, formulations have been developed to generalize the two-level system to a one-dimensional reaction coordinate, or to introduce general basis functions for the evaluation of the path integral. If one is interested in investigating more realistic models for dissipative dynamics (including, e.g., multidimensional anharmonic reaction coordinates and kinetic couplings), it therefore still seems unavoidable that one resorts in one way or another to classical mechanics. For the description of nonadiabatic relaxation processes that involve intersections or avoided crossings of the potential-energy surfaces, one has to invoke mixed quantum-classical schemes, such as surface-hopping and classical-path theories. Both formulations share the idea that the “system” degrees of freedom are described quantum mechanically while the bath degrees of freedom are described classically, but differ in the way the system is coupled to the bath.

In the surface-hopping approach, classical trajectories are propagated on a single adiabatic potential-energy surface until, according to some “hopping criterion,” a transition probability $P_{2 \rightarrow 1}$ to another potential-energy surface is calculated and, depending on the comparison of $P_{2 \rightarrow 1}$ with a random number, the trajectory “hops” to the other adiabatic surface. The many existing variants of the method differ mainly in choice and degree of sophistication of the hopping criteria. They all share the problem that, owing to the hopping processes, the coherence of the total wave function is destroyed after a relatively short time. Classical-path methods, on the other hand, avoid this problem, by propagating the classical degrees of freedom self-consistently in an averaged potential, the value of which is determined by the instantaneous populations of the different quantum states. It is well known from applications in reactive scattering that classical-path methods may lead to unphysical results if the system is asymptotically in a single electronic state. The mean-field approximation, however, seems to be not that critical for the description of bound-state relaxation dynam-
ics. Using the so-called classical electron analog model of Meyer and Miller,\textsuperscript{2,52} it has been shown recently that this simple classical-path approach describes surprisingly accurately the ultrafast electronic and vibrational relaxation dynamics occurring in internal conversion\textsuperscript{48–50} and simple photoisomerization processes.\textsuperscript{51}

In this paper we propose a semiclassical TDSCF approach to describe dissipative quantum phenomena such as the electronic relaxation dynamics of the spin–boson model. Contrary to common quantum-mechanical TDSCF schemes, which assume that the total density operator factorizes in single-mode operators, this ansatz couples the system degrees of freedom to the bath degrees of freedom in a self-consistent manner, and is thus in the spirit of a classical-path description. We apply the ansatz to the spin–boson model, which appears to be an ideal test problem for the approach, as there exists a wealth of approximate theories,\textsuperscript{2,52–57} and numerical reference calculations\textsuperscript{8,10,13} to compare with.

We present computational results for a spin–boson model with an Ohmic bath, which are compared to exact path-integral calculations. It is demonstrated that the semiclassical model is able to reproduce the complex dissipative behavior of the spin–boson model rather accurately and for a large range of model parameters. Examples include the electron transfer dynamics in the low- and high-temperature and adiabatic and nonadiabatic regimes, and the transition from coherent to incoherent relaxation dynamics.

The comprehensive discussion of the paper is devoted to investigate and analyze the validity and accuracy of the semiclassical TDSCF approximation. To this end, we derive a generalized master equation for the electronic population [i.e., for the expectation value of $\sigma_i(t)$], which allows comparison with analytical formulations of the spin–boson model.\textsuperscript{2,52–57} Within the decoupling approximation this equation is shown to be equivalent to the classical limit of a quantum-mechanical expression recently given by Vitali and Grigolini using a polaronic-transformation approach and neglecting the nonclassical reaction force.\textsuperscript{56} Introducing furthermore second-order perturbation theory in the system–bath coupling, we are able to make contact to the so-called “noninteracting-bipolar approximation” (NIBA) of Leggett et al.\textsuperscript{2} The NIBA represents the best-known approximation in the field of quantum dissipation, and has proven to be quite valuable for the qualitative description of many dissipative phenomena. We also compare the semiclassical model to related self-consistent-field formulations such as quantum-mechanical multiconfiguration TDSCF schemes.\textsuperscript{29,30}

We demonstrate that the semiclassical theory can be obtained from the quantum formulation by neglecting quantum-mechanical phase terms, which is equivalent to the assumption of randomization of nuclear phases. The randomization of nuclear phases is found to be the crucial condition for the validity of the semiclassical approach. The condition is shown to be fulfilled, e.g., in the case of a continuous Ohmic bath, and the implications on the applicability of the method is discussed in some detail.

II. A SEMICLASSICAL SELF-CONSISTENT-FIELD ANSATZ

A. Model system

We consider a two-level system $H_S$ which is linearly coupled to a harmonic bath $H_B$ through the system bath coupling $H_{S-B}$, yielding the standard spin–boson Hamiltonian

$$H = H_S + H_B + H_{S-B}$$

(2.1)

where $\sigma_i(i=x,y,z)$ are the Pauli matrices and $I$ represents the unit matrix. As usual, the two-level system is characterized by the electronic coupling $\Delta$, and $m_j, \omega_j$, and $K_j$ denote the mass, the vibrational frequency, and the linear coupling constant of the $j$th oscillator. To be specific, we will refer to the spin and the boson variables as electronic and nuclear degrees of freedom, respectively.

For notational convenience we will henceforth set $\hbar = 1$, and change to dimensionless coordinates and momenta

$$x_j = (m_j \omega_j)^{1/2} X_j,$$

$$p_j = (m_j \omega_j)^{-1/2} P_j,$$

and define analogously $C_j = (m_j \omega_j)^{-1/2} K_j$. Representing furthermore the Pauli matrices in terms of diabatic electronic basis states $|\varphi_1\rangle,|\varphi_2\rangle$, the spin–boson Hamiltonian takes the form

$$H = \sum_{k=1,2} |\varphi_k\rangle \langle \varphi_k | + \{ |\varphi_1\rangle \Delta (|\varphi_2\rangle + \text{h.c.}) \},$$

(2.3)

where $h_0 = 0 \pm \sum_j C_j x_j$, and

$$h_0 = \sum_j \frac{1}{2} \omega_j (p_j^2 + x_j^2).$$

The time-dependent dynamics of the spin–boson problem (2.3) is described by the Liouville–von Neumann equation

$$i \frac{d}{dt} \rho(t) = [H, \rho(t)],$$

(2.4)

where $\rho(t)$ represents the total density operator of system and bath. We assume that at $t = 0$ the electronic system is in the $|\varphi_1\rangle$ electronic state and the bath is in thermal equilibrium

$$\rho(0) = |\varphi_1\rangle \langle \varphi_1 | e^{-\beta_S f \text{Tr} \ e^{-\beta_S h}},$$

(2.5)

where, as usual, $\beta$ denotes the inverse temperature $1/k_BT$. Depending on the physical situation to be described, the bath is initially in the equilibrium geometry of the $|\varphi_1\rangle$ electronic state (i.e., $h_B = h_0$, “tunneling case”), or in the equilibrium geometry of the uncoupled bath Hamiltonian $H_B$ (i.e., $h_B = h_0$, “spectroscopic case”), where the latter case refers to a photoexcitation of the electron from a neutral electronic state (e.g., $|\varphi_0\rangle$) to the $|\varphi_1\rangle$ state.
B. Self-consistent-field ansatz

The main approximation that we are going to make is to assume that for all times the total density operator \( \rho(t) \) can be written as a sum of products of system density operator \( \rho^S(t) \) and bath density operator \( \rho^B(t) \)

\[
\rho(t) = \sum_{\alpha} w_{\alpha} \rho^S_{\alpha}(t) \rho^B_{\alpha}(t),
\]

(2.6a)

\[
\rho^S_{\alpha}(t) = \sum_{k,k'=1,2} \chi^S_{\alpha}(k) |\phi_k\rangle \langle \phi_k'| \chi_k^{S\dagger}(t),
\]

(2.6b)

\[
\rho^B_{\alpha}(t) = |\Phi_\alpha(t)\rangle \langle \Phi_\alpha(t)|.
\]

(2.6c)

Here, the electronic density operator is represented by two complex numbers \( \chi^S(1) \) and \( \chi^S(2) \), the squared moduli of which represent the population probability in the electronic state \( |\phi_1\rangle \) and \( |\phi_2\rangle \), respectively. The nuclear density operator is represented by the multidimensional state vector \( |\Phi\rangle \), which we will assume to be normalized, i.e., \( \langle \Phi | \Phi \rangle = 1 \). The index \( \alpha \) labels the different “configurations” of the TDSCF ansatz (cf. Sec. IV C), \( w_{\alpha} \) being the statistical weight factor, sampled, e.g., from a Boltzmann distribution. To give a concrete example, consider the initial condition (2.5), which requires for the system density operator that \( |\chi^S(0\rangle|^2 = 1 \) and \( |\chi^S(0\rangle|^2 = 0 \), and for the bath density operator that

\[
w_{\alpha} = e^{-\beta \epsilon_\alpha} / \sum \epsilon_\alpha e^{-\beta \epsilon_\alpha},
\]

(2.7a)

\[
\rho^B_{\alpha}(0) = |\alpha\rangle \langle \alpha|,
\]

(2.7b)

where the \( |\alpha\rangle \) are eigenstates of \( h_B \) such that \( h_B|\alpha\rangle = \epsilon_\alpha |\alpha\rangle \).

Note that by virtue of ansatz (2.6) the electronic (system) degrees of freedom are coupled to the nuclear (bath) degrees of freedom in a self-consistent manner. This is in contrast to common TDSCF formulations, which assume that the total density operator factorizes in single-mode density operators,\(^{22-31}\) thus introducing a self-consistent coupling between the individual nuclear degrees of freedom. In other words, the ansatz (2.6) still leaves us with the problem to solve the equations of motion for many nuclear degrees of freedom on a single electronic potential-energy surface.

Let us consider the equations of motion for the system and bath density operator, respectively, that result from the ansatz (2.6). It has been pointed out above that the summation over \( \alpha \) arises from the thermal initial distribution of the bath modes. This is to say that, without any further approximation to Eqs. (2.6), we may solve the Liouville–von Neumann equation for the total density operator \( \rho(t) \) by solving the Schrödinger equation for each individual configuration \( \rho^S_{\alpha}(t) \rho^B_{\alpha}(t) \) and adding up these solutions according to Eq. (2.6a). Therefore, the equations of motion for \( \rho^S_{\alpha}(t) \) and \( \rho^B_{\alpha}(t) \) [and thus for \( \chi^S(1)(t) \) and \( |\Phi_\alpha(t)\rangle \)] can directly be taken from the well-known wave-function TDSCF formalism,\(^{58}\) yielding

\[
\dot{\chi}^{S\dagger}(1)(t) = \langle \Phi_\alpha(t) | h_1 | \Phi_\alpha(t) \rangle \chi^{S\dagger}(1)(t) + \Delta \chi^{S\dagger}(2)(t),
\]

(2.8a)

\[
\dot{\chi}^{S\dagger}(2)(t) = \langle \Phi_\alpha(t) | h_2 | \Phi_\alpha(t) \rangle \chi^{S\dagger}(2)(t) + \Delta \chi^{S\dagger}(1)(t),
\]

(2.8b)

\[
i \Phi_\alpha(x,t) = (|\chi^{S\dagger}(1)(t)|^2 h_1 + |\chi^{S\dagger}(2)(t)|^2 h_2 + \Re \Delta \chi^{S\dagger}(1)(t) \chi^{S\dagger}(2)(t) |\Phi_\alpha(t)\rangle.
\]

(2.9)

It is seen that within the TDSCF approximation the electronic (system) equations of motion reduce to a coupled two-level system with explicitly time-dependent coefficients \( \langle \Phi_\alpha(t) | h (t) | \Phi_\alpha(t) \rangle \). The nuclear (bath) dynamics is described by a single multidimensional wave function \( \Phi_\alpha(x,t) \) propagating in an averaged potential, weighted by the electronic population probabilities \( |\chi^{S\dagger}(k)(t)|^2 (k=1,2) \).

C. Semiclassical approximation

For the sake of notational convenience, we will in the following refer to a single nuclear coordinate \( x \) (instead of \( \sum \chi \)). To motivate an ansatz for the vibrational wave function \( \Phi_\alpha(x,t) \) we rewrite Eq. (2.9) as

\[
\dot{i} \Phi_\alpha(x,t) = \left( \frac{i}{\hbar}(p^2 + x^2) + (\epsilon + Cx)P_\alpha(t) \right) \Phi_\alpha(x,t) + 2\Re \Delta \chi^{S\dagger}(1)(t) \chi^{S\dagger}(2)(t) \Phi_\alpha(x,t),
\]

(2.10)

which is recognized as the time-dependent Schrödinger equation for a driven harmonic oscillator. It is well known that the solution \( \Phi_\alpha(x,t) \) of Eq. (2.10) can be written in terms of Gaussian wave packets as\(^{39,60}\)

\[
\Phi_\alpha(x,t) = \sum_{x_0,p_0} c_\alpha(x_0,p_0) \phi^{(a)}_{x_0,p_0}(x,t),
\]

(2.11)

where the expansion coefficients \( c_\alpha(x_0,p_0) \) are determined by the initial conditions (2.7), and \( x_0 \) and \( p_0 \) denote the initial value for the classical position and momentum, respectively. The Gaussian wave packets

\[
\phi^{(a)}_{x_0,p_0}(x,t) = \pi^{-1/4} \exp \left[ -\frac{1}{2} \left( x - x_0(t) \right)^2 \right]
\]

\[
+ ip_0(t) \left( x - x_0(t) \right) + i \gamma_\alpha(t) \right)
\]

(2.12)

are completely described by the trajectory \( x_0(t) \), the corresponding momentum \( p_\alpha(t) = m \dot{x}_0(t) \), and the action integral \( \gamma_\alpha(t) \).\(^{60}\)
The trajectory \( x_0(t) \) is given by

\[
x_0(t) = x_0 - \omega t + p_0 \sin \omega t - C \int_0^t dt' \sin (\omega t - t') P_\alpha(t')
\]

(2.13)

where \( x_0(0) \) and \( x_0(1) \) denote the unperturbed motion and the motion due to the reaction force \( CP_\alpha(t) \), respectively. The dynamics of the nuclear degrees of freedom thus enter the electronic equations of motion (2.8) through the expression

\[
\langle \Phi_\alpha(t) | h_k | \Phi_\alpha(t) \rangle = \sum_{x_0,p_0} \sum_{x_0',p_0'} c_\alpha^{*}(x_0',p_0') c_\alpha(x_0,p_0)
\]

\[
\times \langle \Phi^{(a)}_{x_0',p_0'}(t) | h_k | \phi^{(a)}_{x_0,p_0}(t) \rangle.
\]

(2.14)

To obtain an expression that is computationally manageable in the case of many nuclear degrees of freedom we have to make an additional approximation to Eqs. (2.6). From a
classical point of view, an obvious approximation to simplify the evaluation of the correlation function (2.14) is to neglect the nondiagonal contributions, i.e.,

$$\langle \Phi_a(t) | h_k | \Phi_a(t) \rangle \approx \sum_{x_0, p_0} |c_a(x_0, p_0)|^2 \times \langle \Phi^{(a)}_{x_0, p_0}(t) | h_k | \Phi^{(a)}_{x_0, p_0}(t) \rangle$$

$$= \sum_{x_0, p_0} |c_a(x_0, p_0)|^2 h_k[x_a(t)], \quad (2.15)$$

where $h_k[x_a(t)]$ denotes the classical Hamiltonian function. Equation (2.15) represents a classical approximation in the sense that the correlation function (2.14) depends no longer on the phases of the Gaussian wave packets $\Phi^{(a)}_{x_0, p_0}(t)$, but are completely determined by the classical trajectory $x_a(t)$. Equation (2.15) amounts to approximate the bath density operator as

$$\rho^B(x, x', t) = \Phi_a(x, t) \Phi_a^*(x', t)$$

$$\approx \sum_{x_0, p_0} |c_a(x_0, p_0)|^2 \Phi^{(a)}_{x_0, p_0}(x, t) \Phi^{(a)}_{x_0, p_0}(x', t).$$

Note that all summation indices $\alpha$ and $x_0, p_0$ refer to initial conditions of the Gaussian wave packets $\Phi^{(a)}_{x_0, p_0}(t)$. Owing to the ansatz (2.6), the system density operator depends only on $\alpha$ but not on $x_0, p_0$. Using the semiclassical approximation for the bath density operator (2.16), we may generalize the ansatz (2.6) such that the system density operator also depends on $\alpha$ and on $x_0, p_0$. This way the sum over $\alpha$ becomes redundant, and we may rewrite Eqs. (2.6) with Eq. (2.16) into a semiclassical TDSCF ansatz for the total density operator

$$\rho(t) = \int dx_0 \int dp_0 \, w(x_0, p_0) \rho^S_{x_0, p_0}(t) \rho^B_{x_0, p_0}(t),$$

$$\rho^S_{x_0, p_0}(t) = \sum_{k, k'} \chi^{(k)}_{x_0, p_0}(t) \chi^{(k')}_{x_0, p_0}(t) \langle \phi_k \phi_{k'} \rangle,$$  

$$\rho^B_{x_0, p_0}(t) = |\psi_{x_0, p_0}(t)|^2.$$  

Formally, Eqs. (2.17) are rather similar to the quantum-mechanical TDSCF ansatz (2.6), because the $\alpha$ summation weighted by $w_\alpha$ has been converted to an integration over $x_0$ and $p_0$, weighted by $w(x_0, p_0)$. Note, however, that the Boltzmann factor $w_\alpha$ refers to the initial vibrational state $|\alpha\rangle$, whereas the function $w(x_0, p_0)$ refers to the classical trajectory $x_0, p_0(t)$ with initial conditions $x_0$ and $p_0$. The function $w(x_0, p_0)$ thus represents the initial distribution of the nuclear degrees of freedom, which may be sampled, e.g., from the thermal Wigner distribution.

$$w(x_0, p_0) = \frac{1}{\pi} \tanh \left( \frac{1}{2} \beta \omega \right) \exp \left[ - \frac{1}{2} \beta \omega \right] (p_0^2 + (x_0 - \delta)^2),$$

where, according to Eq. (2.5), the coordinate shift $\delta$ is $\delta = 0$ for $h_B = h_0$ and $\delta = - C/\omega$ for $h_B = h_1$. The semiclassical TDSCF approximation for the density operator (2.17) is a major result of this work. The TDSCF ansatz (2.17) represents together with the equations of motion (2.8), (2.9) and the initial conditions (2.18) the working equations for the numerical results presented below.

It should be noted that in the present application (i.e., calculation of the electronic population probabilities for the spin–boson problem) the semiclassical TDSCF ansatz (2.17) reduces to a classical-path formulation. The theory developed above can therefore be considered as a derivation of the classical-path formulation, which will turn out to be useful for the discussion of the approximations involved (see Sec. IV). However, the semiclassical TDSCF ansatz (2.17) is only equivalent to a classical-path scheme for diabatic potentials that are at most quadratic in $x$, and for the evaluation of quantities associated with the diagonal matrix elements of the system density operator (e.g., electronic populations, mean values of the bath degrees of freedom). The calculation of electronic coherences, on the other hand, implies the evaluation of expression of the form $\langle \Phi(t) | \Phi(0) \rangle$, where the nuclear phases of the individual wave packets do contribute; the ansatz (2.17) is therefore able to roughly account for pure electronic dephasing effects.

### III. COMPUTATIONAL RESULTS FOR AN OHMIC BATH

We want to demonstrate the capability of the semiclassical TDSCF approach by presenting some computational results for the spin–boson model with an Ohmic bath. Quite recently a number of groups have reported (numerically) exact path-integral calculations, which we will use to check the reliability and accuracy of the TDSCF method.

Within the spin–boson model (2.1) all properties of the bath enter through a single function called the spectral density

$$J(\omega) = \frac{\pi}{2} \sum_j C_j^2 \delta(\omega - \omega_j),$$

which in the case of an Ohmic bath has the form

$$J(\omega) = \frac{\pi}{2} \alpha \omega e^{-\alpha/\omega}. \quad (3.2)$$

The strength of the system–bath coupling is characterized by the dimensionless Kondo parameter $\alpha = 2/\pi \eta$, where $\eta$ is the usual Ohmic viscosity. The special density (3.2) exhibits a wide variety of dissipative phenomena and has been studied extensively by a number of groups. It has a characteristic low-frequency behavior $J(\omega) = \omega_0 \delta$, and is peaked at the cut-off frequency $\omega_c$, which defines the time-scale distribution of the bath dynamics.

The quantity of interest is the time-dependent electronic population
FIG. 1. The electronic population $P(t)$ as a function of the system–bath coupling $\alpha=0.13$ (a), $\alpha=0.25$ (b), and $\alpha=0.64$ (c) and the system parameters $\Delta=1$, $k_B T=2.5\Delta$, $\omega=2.5\Delta$. The TDSCF results (full line) are compared to exact path-integral (dotted line) and NIBA (dashed line) calculations taken from Ref. 8.

$$P(t) = \langle \sigma_z(t) \rangle$$

$$= \int d\mathbf{x}_0 \int d\mathbf{p}_0 \ w(\mathbf{x}_0,\mathbf{p}_0) \left( |x_{n_0, p_0}^{(1)}(t)|^2 - |x_{n_0, p_0}^{(2)}(t)|^2 \right),$$

(3.3)

which is evaluated by solving numerically the electronic equations of motion (2.8), choosing according to Eq. (2.5) the electronic initial conditions as $x_{n_0, p_0}^{(1)}(0) = 1$ and $x_{n_0, p_0}^{(2)}(0) = 0$. The initial conditions for the nuclear variables $x_j(0), p_j(0)$ can either be sampled from the Wigner distribution (2.18), or be obtained via the classical action-angle variables

$$x_j(0) = \sqrt{2n_j + 1} \sin q_j + \delta_j,$$

$$p_j(0) = \sqrt{2n_j + 1} \cos q_j,$$

(3.4)

where the phases $q_j$ are picked randomly from the interval $[0, 2\pi]$, and the quantum numbers $n_j$ are sampled according to the Boltzmann distribution $P(n_j) = \exp(-\beta n_j \omega_j)$. The coordinate shift $\delta_j$ in Eqs. (2.18) and (3.4) reflects the initial mean position of the bath modes $[\delta=0$ for $h_B=h_0$ and $\delta = -C/\omega$ for $h_B=h_1$, cf. Eq. (2.5)], and has been chosen in accordance with the reference calculations we compare to (i.e., for Figs. 1–3 $h_B=h_1$, for Figs. 4–6 $h_B=h_0$). Interestingly, it has been found that both distributions (2.18) and (3.4) give almost identical results. For the calculations reported here we have used action-angle initial conditions (3.4), which in the average seemed to do slightly better.

The bath has been simulated by $N_{\text{mod}}=400$ harmonic modes, the frequencies of which are equally distributed between $\omega_{\text{min}}=0.01 \omega$, and $\omega_{\text{max}}=4 \omega$. This way the times corresponding to the frequency $\omega_{\text{min}}$ and the line spacing $\Delta \omega=(\omega_{\text{max}}-\omega_{\text{min}})/(N_{\text{mod}}-1)$ are safely beyond the observed time evolution of the system. Integration of the spectral density (3.1) over $\omega$ yields the coupling parameters $C_j=[2/\pi \Delta \omega J(\omega_j)]^{1/2}$. To obtain converged results we have run 2500 trajectories, which take about 1 h CPU time on an IBM RS 6000 work station.

To learn about the strong and weak points of the method, we wish to check the model in a large range of model parameters, such as the electronic coupling $\Delta$, the system–bath coupling $\alpha$, and the temperature $T$. As the transition to classical mechanics can be characterized by

$$\hbar \beta \omega \rightarrow 0,$$

(3.5)

the classical method should do well for “small $\hbar$,” high temperatures, and for short times $2\pi/\omega$, where $\omega$ correspond to a typical frequency of the problem.
shows the exact (dotted line) and TDSCF (full line) calculations of the electronic population \( P(t) \) for the parameters \( \omega_0=1, \ k_BT=4\omega_c \). In the case of moderate electronic coupling \( \Delta/\omega_c=0.8 \) (a), the simulations exhibit a monoexponential decay on the golden rule time scale. For stronger electronic coupling \( \Delta/\omega_c=1.2 \) (b), the electronic population is seen to exhibit a rapid initial decay, which is followed by a slower relaxation dynamics. The TDSCF results qualitatively match the reference data, but predict a somewhat slower relaxation, particularly in the case (b) of both strong system–bath and strong electronic coupling. The method therefore seems to do better in the nonadiabatic regime \( (\Delta/\omega_c<1) \) than in the adiabatic regime \( (\Delta/\omega_c\gtrsim1) \), where the mean-approximation may become problematic (cf. Sec. IV).

Another parameter range of the model to check is the behavior at low temperatures. Dealing with an essentially classical model, the medium (Figs. 1 and 2) and high (Fig. 3) temperature cases studied above should certainly be easier to reproduce than the case \( T=0 \). Using an influence–functional approach, Makarov and Makri recently reported exact path-integral calculations for the spin–boson model in the low-temperature regime. As an example of relatively strong system–bath coupling \( \alpha=0.5625 \), Fig. 4 shows the electronic population dynamics for the parameters \( \Delta=1, \ k_BT=0.1\Delta, \ \omega_0=2.5\Delta \). The electronic population is seen to undergo a weakly coherent relaxation, which is somewhat exaggerated by the TDSCF calculation.

As a final test we wish to compare to long-time low-temperature calculations, which have become available by improved path-integral methods only very recently. According to the criteria (3.5), this parameter regime corresponds just to the quantum-mechanical limit. The time evolution of a coherently relaxing system \( (\Delta=1, \ k_BT=0.2\Delta, \ \omega_0=2.5\Delta, \ \alpha=0.09) \) is presented in Fig. 5 for the first 30 time units. Up to about \( t=20 \), we are able to compare to the path-integral data of Makarov and Makri. Although the overall damping

![FIG. 3. Comparison of the electronic populations as obtained by exact quantum Monte Carlo simulations (Ref. 13) (dotted line) and TDSCF calculations (full line) for the case of strong system–bath coupling \( \alpha=2 \) and the parameters \( \omega_0=1, \ k_BT=4\omega_c \). Panel (a) shows the case of medium electronic coupling \( \Delta/\omega_c=0.8 \), panel (b) the case of strong electronic coupling \( \Delta/\omega_c=1.2 \).](image)

Performing extensive quantum Monte Carlo computations, Mak and Chandler have studied in some detail the transition between coherent and incoherent relaxation behavior of the spin–boson model. As a representative example we consider a case where \( \Delta=1, \ k_BT=2.5\Delta, \ \omega_c=2.5\Delta \), and investigate the time evolution of \( P(t) \) as a function of the system–bath coupling measured by the Kondo parameter \( \alpha \). Figure 1 shows the comparison of exact (dotted line), TDSCF (full line), and NIBA (dashed line) calculations, evaluated for \( \alpha=0.13 \) (a), \( \alpha=0.25 \) (b), and \( \alpha=0.64 \) (c), respectively. The computations illustrate nicely the transition from weakly coherent (a) to completely incoherent (c) relaxation dynamics. The TDSCF data are seen to reproduce the exact results almost quantitatively, and are thus a clear improvement to the NIBA data of Ref. 8. As a second example, Fig. 2 shows the transition from coherent to incoherent relaxation in the case of relatively low temperature \( k_BT=0.625\Delta \), where the system–bath coupling has been chosen as \( \alpha=0.32 \) (a), \( \alpha=0.51 \) (b), and \( \alpha=0.64 \) (c), respectively. Again the semiclassical approximation is seen to reproduce the reference results fairly well.

To provide a challenge for the TDSCF approach, we next turn to a case with rather strong system–bath coupling \( (\alpha=2) \), as has been recently studied by Egger and Mak employing exact quantum Monte Carlo methods. Figure 3 shows the exact (dotted line) and TDSCF (full line) calculations of the electronic population \( P(t) \) for the parameters \( \omega_0=1, \ k_BT=4\omega_c \). In the case of moderate electronic coupling \( \Delta/\omega_c=0.8 \) (a), the simulations exhibit a monoexponential decay on the golden rule time scale. For stronger electronic coupling \( \Delta/\omega_c=1.2 \) (b), the electronic population is seen to exhibit a rapid initial decay, which is followed by a slower relaxation dynamics. The TDSCF results qualitatively match the reference data, but predict a somewhat slower relaxation, particularly in the case (b) of both strong system–bath and strong electronic coupling. The method therefore seems to do better in the nonadiabatic regime \( (\Delta/\omega_c<1) \) than in the adiabatic regime \( (\Delta/\omega_c\gtrsim1) \), where the mean-approximation may become problematic (cf. Sec. IV).

Another parameter range of the model to check is the behavior at low temperatures. Dealing with an essentially classical model, the medium (Figs. 1 and 2) and high (Fig. 3) temperature cases studied above should certainly be easier to reproduce than the case \( T=0 \). Using an influence–functional approach, Makarov and Makri recently reported exact path-integral calculations for the spin–boson model in the low-temperature regime. As an example of relatively strong system–bath coupling \( \alpha=0.5625 \), Fig. 4 shows the electronic population dynamics for the parameters \( \Delta=1, \ k_BT=0.1\Delta, \ \omega_0=2.5\Delta, \ \alpha=0.09 \). The electronic population is seen to undergo a weakly coherent relaxation, which is somewhat exaggerated by the TDSCF calculation.

As a final test we wish to compare to long-time low-temperature calculations, which have become available by improved path-integral methods only very recently. According to the criteria (3.5), this parameter regime corresponds just to the quantum-mechanical limit. The time evolution of a coherently relaxing system \( (\Delta=1, \ k_BT=0.2\Delta, \ \omega_0=2.5\Delta, \ \alpha=0.09) \) is presented in Fig. 5 for the first 30 time units. Up to about \( t=20 \), we are able to compare to the path-integral data of Makarov and Makri. Although the overall damping
is slightly exaggerated, the model is seen to nicely reproduce the coherent relaxation dynamics of the spin–boson model in the low-temperature limit.

IV. DISCUSSION

In light of the fact that the simple semiclassical model is capable of describing the complex relaxation dynamics of the spin–boson problem, the obvious question arises how general and how reliably the semiclassical TDSCF ansatz (2.17) is. This is particularly of interest because it has been reported by several workers that TDSCF methods can fail dramatically in curve-crossing problems. The remainder of the paper is therefore devoted to discuss and analyze the validity and applicability of the semiclassical TDSCF approximation. To this end, we will (A) derive a generalized master equation for the electronic population $P(t)$, which allows comparison with analytical formulations of the spin–boson model, (B) discuss the nature of the semiclassical approximation by comparing to exact quantum-mechanical multiconfiguration TDSCF formulations, (C) discuss in some detail the condition of randomization of nuclear phases, which turns out to be the crucial condition for the validity of the semiclassical approach.

A. Generalized master equation description

It is well known that the theoretical description of dissipative dynamics simplifies considerably if one is only interested in the time evolution of the diagonal elements of the electronic density matrix. In the case of the spin–boson model, e.g., one usually considers the time-dependent electronic population [cf. Eq. (3.3)]

$$P(t) = \text{Tr}_{B}\{\rho_{11}(t) - \rho_{22}(t)\},$$

where $\rho_{kk'}^{\pm} = \langle \phi_k^{\pm} | \rho | \phi_{k'}^{\pm} \rangle$ are the electronic matrix elements of the total density operator $\rho(t)$ and $\text{Tr}_B$ denotes the trace over the bath variables. If we restrict ourselves to the calculation of $P(t)$, we may change from the Liouville–von Neumann equation [describing the time evolution of the total density operator $\rho(t)$] to a generalized master equation [describing the time evolution of the population $P(t)$], which will prove to be advantageous for the discussions of the approximations introduced below.

To derive an integrodifferential equation for the diagonal elements $\rho_{kk}$, we insert the formal solution of Eq. (2.4) for the off-diagonal elements $\rho_{kk'}$ into the equation of motion for the diagonal elements $\rho_{kk}$, thus yielding

$$\dot{P}(t) = -(2\Delta)^2 \text{Re} \int_0^t dt' \text{Tr}_B \{e^{-ih_2(t-t')} e^{ih_1(t-t')} \times [\rho_{11}(t') - \rho_{22}(t')]\}. \quad (4.2)$$

Equation (4.2) is still exact. In general, it is an operator equation with respect to the multidimensional boson field, which can only be solved within some approximation.

Intending to solve the integrodifferential Eq. (4.2) in a quantum-mechanical manner, one usually ends up employing an approximation of the decoupling type. Using Eqs. (4.3), we obtain the generalized master equation for the electronic population $P(t)$

$$\dot{P}(t) = -(2\Delta)^2 \text{Re} \int_0^t dt' K(t-t') P(t'). \quad (4.4)$$

To elucidated the basic physics described by Eq. (4.4), it is instructive to consider two simple limiting cases. In the limiting case of vanishing system–bath coupling (i.e., no friction), Eq. (4.4) reduces to the master equation for a two-level system, which has the familiar Rabi solution $P(t) = \cos 2\Delta t$. In the limiting case that the electronic population $P(t)$ does not change much within the time the memory kernel $K(t-t')$ deviates from zero, we may set $P(t') \simeq P(t)$ and the solution of Eq. (4.4) reduces to the standard golden rule expression with rate $k = (2\Delta)^2 \text{Re} \int_0^t K(t) dt$. In general, the generalized master Eq. (4.4) therefore describes the competition between coherent quantum tunneling and localization of the system in a electronic state due to the interaction with the bath.

Let us now introduce the semiclassical formulation of Sec. II into the integrodifferential Eqs. (4.2) and (4.4). Within the TDSCF approximation, it is possible to solve the electronic equations of motion by integrating out the bath degrees of freedom. This is so, because the trajectory $x(t)$ of Eq. (2.13) represents a closed solution for the nuclear dynamics. We may therefore replace the boson operator $h_k$ in Eq. (4.2) by their time-dependent mean values

![Figure 5](https://example.com/fig5.png)

**FIG. 5.** The electronic population $P(t)$ for the parameters $\Delta=1$, $k_B T=0.2 \Delta$, $\omega_0=2.5 \Delta$, $\alpha=0.09$. Compared to the exact path-integral results (Ref. 10) (dotted line), the TDSCF calculation (full line) slightly exaggerates the overall damping of the beating.
\[ e^{-i\hbar(t-t')e^{i\hbar t(t'-t)}} \exp \left[ -i \int_{t'}^t d\tau \frac{\partial}{\partial \Phi_{x_0-p_0}(\tau)} \right] h_2^{\Phi_{x_0-p_0}(\tau)} \]

\[ -h_1 \Phi_{x_0-p_0}(\tau) \]

\[ \exp \left[ 2iC \int_{t'}^t d\tau x_{x_0-p_0}(\tau) \right] , \quad (4.5b) \]

where for clarity the dependency of the trajectory \( x_{x_0-p_0}(t) \) on the nuclear initial conditions has been noted explicitly. Insertion of Eqs. (2.17) and (4.5) into the exact formula (4.2) yields

\[
\hat{P}(t) = -(2\Delta)^2 \Re \int_0^t dt' \int dx_0 \int dp_0 w(x_0, p_0) \times P_{x_0-p_0}(t') \exp \left[ 2iC \int_{t'}^t d\tau x_{x_0-p_0}(\tau) \right] . \quad (4.6)
\]

Equation (4.6) is the desired integrodifferential equation for the electronic population in the semiclassical TDSCF approximation. Here, \( P_{x_0-p_0}(t') \) denotes the electronic population evaluated for a single trajectory \( x_{x_0-p_0}(t) \) with initial conditions \( x_0, p_0 \), whereas \( P(t) \) represents the averaged electronic population defined in Eq. (3.3). Note that the trace over bath variables in Eq. (4.2) has been converted into a classical average over thermally weighted initial states in the semiclassical expression. Furthermore it should be noted that the semiclassical TDSCF ansatz (2.17) has been the only approximation involved in the derivation of the integrodifferential equation (4.6), i.e., the semiclassical evaluation of Eq. (4.2) does not require a decoupling approximation. In order to make contact with other formulations of the spin–boson problem, however, it is nevertheless instructive to consider the limiting cases of the decoupling approximation and system–bath perturbation theory.

Let us first introduce the decoupling approximation (4.3), which assumes that the \( P_{x_0-p_0}(t') \) in Eq. (4.6) are independent of the nuclear initial conditions \( x_0, p_0 \), and enables us to perform the integration over initial conditions in Eq. (4.6) analytically. Note that only the unperturbed solution \( x^{(0)}(t) \) (2.13) is subject of the averaging process. Assuming that initially \( h_B = h_1 \) [cf. Eq. (2.5)], the integration over the Wigner distribution (2.18) yields

\[
\left\langle \exp \left[ 2iC \int_{t'}^t d\tau x^{(0)}_{x_0-p_0}(\tau) \right] \right\rangle _{\text{CI}}
\]

\[ = \int dx_0 \int dp_0 w(x_0, p_0) \exp \left[ 2iC \int_{t'}^t d\tau x^{(0)}_{x_0-p_0}(\tau) \right] \]

\[ = \exp \left[ -2C^2 \omega^3 \coth(\frac{\omega}{2}) (1 - \cos \omega (t-t')) \right. \]

\[ - i \sin \omega t + i \sin \omega t' \], \quad (4.7)

where the subscript CI denotes a classical average. Inserting Eqs. (2.13) and (4.7) in Eq. (4.6) and going back to multimode notation \( (x \rightarrow x_j) \), we finally obtain

\[
\hat{P}(t) = -(2\Delta)^2 \Re \int_0^t dt' K^{(0)}(t-t')K^{(1)}(t,t') P(t'), \quad (4.8)
\]

where

\[
K^{(0)}(t) = \exp \{ i \epsilon t - Q_2(t) \}, \quad (4.9)
\]

\[
K^{(1)}(t,t') = \exp \left[ 2i \sum_j C^2 J_j^2 \int_{t'}^t dt_2 \int_0^t dt_1 \sin \omega_j (t_2-t_1) \times [1 - P(t_1)] \right], \quad (4.10)
\]

and

\[
\epsilon = 2 \sum_j C^2 / \omega^2, \quad (4.11)
\]

\[
Q_2(t) = 2 \sum_j C^2 / \omega^2 \coth(\frac{\omega}{2}) (1 - \cos \omega t). \quad (4.12)
\]

Here \( \epsilon \) is the reorganization energy, and \( Q_2(t) \) is recognized as ubiquitous function from standard spin–boson theory. Equation (4.8) is the master equation for the electronic population \( P(t) \) in the semiclassical TDSCF and decoupling approximations. Within these two approximations, \( K^{(0)}(t-t') \) represents the stationary (“zero-order”) memory kernel, while \( K^{(1)}(t,t') \) is a nonstationary memory function, taking into account the classical reaction force to all orders. Together with the semiclassical TDSCF ansatz (2.17) the integrodifferential Eqs. (4.6) and (4.8) represent the central theoretical results of this paper. Both equations are valid for arbitrary system–bath coupling, and may be therefore expected to describe dissipative quantum dynamics beyond the usually considered low-coupling regime.

Let us compare the master Eq. (4.8) to recent work by Grigolini and co-workers \(^{56,57}\) who have obtained similar results, but used completely different theoretical approaches. Performing a coordinate transformation of the bath modes [sometimes referred to as “(pseud0) polaronic transformation”], and neglecting a nonclassical driving term of the nuclear motion, Vitali and Grigolini \(^{56}\) derived a master equation for the electronic population [Eq. (2.17) in Ref. 56], which is rather similar to our Eq. (4.8). The difference between the two formulations arises, because Vitali and Grigolini performed a quantum-mechanical average over the boson field \( \hat{x} \).
\[ \exp\left(2i\sum_j C_j \int_0^\infty d\tau \hat{x}_j(\tau)\right) \] 
\[ = \left(\exp\left[2i\sum_j C_j \int_0^\infty d\tau \hat{x}_j(\tau)\right] - 2\sum_j C_j \int_0^\infty dt_2 \int_0^{t_2} dt_1 [\hat{x}_j(t_2),\hat{x}_j(t_1)]\right) Q_m \]
\[ \times \exp\{-iQ_1(t-t') + i\epsilon(t-t')\}. \]

Here \( \exp_T \) denotes the time-ordered exponential, the Magnus formula for the harmonic oscillator has been used in Eq. (4.13a), and the function
\[ Q_1(t) = 2\sum_j \frac{C_j^2}{\omega_j} \sin \omega_j t \]
is well-known from standard spin–boson theory. It is seen that the classically averaged result (4.7) is recovered by neglecting the commutator \([\hat{x}_j(t_2),\hat{x}_j(t_1)]\), which gives rise to the additional phase terms in Eq. (4.13). The quantum-mechanical approach of Vitali and Grigolini therefore leads to the identical nonlinear memory function \(K^{(t,t')}(t\rightarrow t')\) as in Eq. (4.10), but replaces the classical expression \(K^{(0)}(t)\) of Eq. (4.9) by the quantum-mechanical kernel
\[ K_{\text{NIBA}}(t) = \exp\{-Q_2(t) + iQ_1(t)\}, \]
which is recognized as the result of the NIBA of Leggett et al. The NIBA represents the best-known approximation in the field of quantum dissipation. It has been derived via a number of different theoretical approaches always requiring at one point or another the decoupling and perturbative approximations.

To investigate the consequences of the classical approximation \(K^{(0)}(t)\) to \(K_{\text{NIBA}}(t)\), let us assume a continuous bath, in which case \(Q_1(t)\) turns out to be a smoothed step function. In the case of an Ohmic bath, for example, \(Q_1(t) = 2a \arctan \omega_0 t\), where \(a\) denotes the Kondo parameter and \(\omega_0\) is the cutoff frequency [cf. Eq. (3.2)]. For \(t>0\), \(Q_1(t)\) may be therefore approximated by a constant, \(Q_1(t) = 2a \arctan \omega_0 t\), which is equivalent to a assumption of randomization of phases (see Sec. IV C). Introducing this condition into Eq. (4.15) and using \(\alpha = \frac{1}{2} \epsilon \omega_0\), the NIBA memory kernel reads
\[ K_{\text{NIBA}}(t) = \exp\left[i \frac{\pi}{2} \epsilon \omega_0 - Q_2(t)\right], \]
which differs from the semiclassical result (4.9) in the way the electronic coupling is affected by the bath. In the quantum-mechanical expression the bath dynamics results in a renormalization of the electronic coupling constant \((\Delta \rightarrow \Delta \sqrt{\cos \pi \alpha})\) in the semiclassical expression (4.9) we obtain a shift of the electronic energy gap by the reorganization energy \(\epsilon_e\). In the assumed case of low system–bath coupling, however, both corrections should be of minor importance.

To conclude this section, it has been shown that the semiclassical ansatz leads to a general master equation for the electronic population which is up to a quantum-mechanical phase factor equivalent to the polaronic transformation approach of Ref. 56 and to the NIBA of Ref. 2. Furthermore it should be stressed that the TDSCF ansatz (2.17) yields the same nonlinear memory function \(K^{(t,t')}(t\rightarrow t')\) as in Ref. 56, indicating that the semiclassical approach takes properly into account the classical reaction field. Employing the Wigner–Weyl formalism, Bonci et al. showed that the total Liouvillian of the spin–boson system can be split up into a semiclassical term \(L_{\text{cl}}\) and a quantum correction \(L_{\text{QGD}}\), where the equations of motion corresponding to \(L_{\text{cl}}\) are identical to our TDSCF Eqs. (2.8) and (2.9). Both theories therefore seem to indicate that the semiclassical TDSCF ansatz (2.17) can be understood as the neglect of the nonclassical reaction field.

B. Relation to quantum TDSCF formulations

Another approach to investigate the nature of the approximation (2.17) is to compare the semiclassical model to quantum-mechanical TDSCF formulations. Let us first consider the most general ansatz for a TDSCF density operator, which in the position representation can be written as
\[ \rho(x,x',t) = \sum_r w_r \sum_{k,k'=1}^2 |\varphi_k(\varphi_{k'}) \sum_{i,i'=1}^n c_{i,i'}^{(k)}(t) \chi_{i,i'}^{(k')} (x_{i,i'}^{(k)} (x_{i,i'}^{(k')})), \]
where \(\varphi_{i,i'}^{(k)}(x_{i,i'}^{(k)})\) denotes the \(i\)th time-dependent expansion function of the coordinate \(x_{i,i'}\) pertaining to the diabatic electronic state \(|\varphi_k\rangle\), \(c_{i,i'}^{(k)}(t)\) represents the corresponding time-dependent expansion coefficients labeled by the vector index \(i = \{i_1, \ldots, i_{N_{\text{mod}}}\}\), and \(w_r\) is a statistical weight factor describing the thermal occupation probability of this configuration. In the parlance of electronic structure theory, we speak of a “single configuration” ansatz if we consider only a single expansion function (i.e., \(n = \{n_1, \ldots, n_{N_{\text{mod}}} = 1\}\), whereas we obtain a “full configuration interaction (CI)” ansatz if we consider the complete expansion (4.17), which in the case of complete basis sets and converged expansion sums of course represents the exact density operator.

Intending to take into account many (say, hundreds) nuclear degrees of freedom, it seems to be clear that one has to drop the exact full CI scheme, which turns out to be rather cumbersome for \(N_{\text{mod}} \geq 10\) vibrational modes. Single-configuration or simple multiconfiguration schemes, on the other hand, have often been found to yield reasonable results only for rather short times (say, for one or two vibrational periods). This approach thus seems to be well suited for the description of ultrafast decay processes (e.g., direct photodissociation) and for the modeling of structureless ab-
which typically last over many vibrational periods of the fast

\[ ^F \]

conversion\textsuperscript{48–50} and simple isomerization processes,\textsuperscript{51} however, approximation\textsuperscript{\( \sim \)}(4.19) therefore avoids the problems associated with nuclear phase factors which often leads to nonsensical results for the electronic dynamics after a rather short time. On the other hand, the simple ansatz (4.18) is of course not able to describe the molecular dynamics in cases where this nuclear phase information is important. Restricting ourselves, however, to cases involving many weakly coupled degrees of freedom, one might expect to a large extent a randomization of the nuclear phases, which would justify the neglect of this phase information. Dissipative electronic relaxation as described by the spin–boson model with an Ohmic bath thus appears to be a perfect candidate for the semiclassical TDSCF approach. By definition, a bath consists of many weakly coupled vibrational modes, therefore randomization of phases appears to be plausible.

The second approximation (ii) of quasiclassical sampling of the density operator also is only appropriate under the assumption of a complete randomization of nuclear phases. As has been shown above, the quasiclassical sampling scheme can be considered as an average over a sum of Gaussian wave packets, where the off-diagonal terms, corresponding to an interference of the individual trajectories, have been neglected (see also the discussion in Ref. 14). To illustrate this point, note that the electronic population (3.3) is evaluated in the same way for a pure initial state (i.e., for \( T=0 \)) as in the case of finite temperature. Regardless of whether the initial state of the system is given as a coherent superposition of basis states (pure initial state) or by an incoherent superposition of basis states (mixed initial state), we thus perform in both cases a completely incoherent summation over trajectories.

To give an example of where the classical method has to break down, consider a spin–boson problem where the overall system–bath coupling \( \alpha \) has been put into a few vibrational degrees of freedom. Unlike the case of many weakly coupled vibrational modes in a quasicontinuous bath, one would expect in the case of a few strongly coupled vibrational modes the nuclear phases to be important. We have chosen a system similar to the model shown in Figs. 4 and 5 (\( \Delta=1, \omega_c=2.5\Delta, T=0 \), and considered four vibrational modes with frequencies \( \omega=0.01, 1.34, 2.67, 4.0 \). The quantum propagation of the density operator \( \rho(t)=|\Psi(t)\rangle\langle\Psi(t)| \) has been performed by expanding \( |\Psi(t)\rangle \) in a direct-product basis constructed from diabatic electronic states and harmonic-oscillator states, and solving the resulting system of coupled first-order differential equations using a Runge–Kutta–Merson scheme with adaptive step size.\textsuperscript{68,69} Figure 6 shows the classical (full lines) and quantum (dotted lines) calculations evaluated for a system–bath coupling of (a) \( \alpha=0.09 \) and (b) \( \alpha=0.5625 \), respectively. While in the exact quantum calculation the coherent electronic oscillation

\[ \rho(x,x',t) = \sum_{x_0,p_0} w(x_0,p_0) \sum_{k,k'} \chi_{x_0,p_0}^{(k)}(t) \phi_k(t) \langle \phi_{k'} | \]

\[ \chi_{x_0,p_0}^{(k)}(t) = \prod_{j=1}^{N_{\text{mod}}} \phi_{x_0,p_0}(x_j,t) \phi_{x_0,p_0}(x_j',t). \]

\[ (4.18) \]

Compared to the exact full CI ansatz (4.17), we have made two major approximations in Eq. (4.18):

(i) We use identical vibrational wave functions for both diabatic electronic states, i.e.,

\[ \phi_{j(1)}(x_j,t) = \phi_{j(2)}(x_j,t) = \phi_j(x_j,t). \]

(ii) The sum over statistical weights \( w_\nu \) and the double sum over expansion functions with variationally determined coefficients in Eq. (4.17) has been replaced by a quasiclassical sampling procedure of nuclear initial conditions.

Approximation (4.19) results in the often discussed problem that, instead of using an extra trajectory for each electronic state, there is a single trajectory propagated in an averaged potential (2.9). It is well known from applications in reactive scattering, that this approximation may lead to unphysical results if the system is asymptotically in a single electronic state but not in a mixture of states.\textsuperscript{47} In the case of bound-state relaxation dynamics including internal conversion\textsuperscript{48–50} and simple isomerization processes\textsuperscript{51} however, approximation (4.19) has not turned out to be a very critical assumption. Note, e.g., that in all spin–boson calculations reported above we have obtained a long-time limit of \( P(t \to \infty) = P_1 - P_2 = 0 \), corresponding to an equal population probability \( P_1 = P_2 = \frac{1}{2} \) in each electronic state. In the case of nonzero bias, e.g., in internal conversion and electron transfer processes, it has been found that the system typically localizes in the lower adiabatic state, but is diabatically still in a mixture of states,\textsuperscript{65} which is nicely reproduced by the classical model.\textsuperscript{48–51}

\[ \text{C. Randomization of nuclear phases} \]

At a first glance, however, approximation (4.19) seems to be unnecessary, because it is only a minor extra effort to calculate two trajectories (one for each electronic state) instead of one. Allowing for two different vibrational wave functions \( \Phi^{(1)} \) and \( \Phi^{(2)} \), the corresponding electronic equations of motion can readily be obtained from Eq. (2.8) by making the replacements \( \langle \Phi(t)|h_2|\Phi(t) \rangle \rightarrow \langle \Phi(t)|h_2|\Phi(t) \rangle \) and \( \Delta \rightarrow \langle \Phi(t)|\Delta|\Phi(t) \rangle \). While within the semiclassical approximation (2.15) the diagonal terms \( \langle \Phi(t)|h_2|\Phi(t) \rangle \) are again independent of the phase of the wave packets, the off-diagonal term \( \Delta \) now explicitly depends on these phases. One of the pitfalls of using a superposition of Gaussian wave packets, however, is that although the sum of classical trajectories (2.13) often gives a rather accurate description of the nuclear dynamics, the corresponding sum of phase-dependent matrix elements does not.\textsuperscript{66,67} Although this shortcoming can be in principle improved by introducing additional semiclassical phase factors the resulting methods are too cumbersome for handling problems with many degrees of freedom.\textsuperscript{66,67}

\[ \text{dotted lines} \]
(\cos \Delta t) is seen to be perturbed only very weakly by the interaction with the four vibrational modes, the classical simulation nevertheless predicts a slow decay of the electronic population in Fig. 6(a). Even more dramatically is the failure of the model for four strongly coupled modes as shown in Fig. 6(b). The quantum population exhibits irregular coherent beatings, whereas the classical population has basically decayed after the first period and fluctuates around zero.

One may note, however, that most quantum TDSCF and path integral calculations have reported only results for one or two electronic or vibrational periods, which are even reproduced here in the worst-case scenario of Fig. 6(b). Furthermore it is interesting to note that the quantum results obtained for four modes [Figs. 6(a) and 6(b)] and four hundred modes (Figs. 5 and 4) show in both cases the same initial time evolution of the electronic population. Within \( t \leq 4 \), corresponding approximately to the period of the level spacing of the four bath modes, the system cannot distinguish whether it is damped by a few or by an infinite number of modes.

As expected, the assumption of a complete randomization of nuclear phases breaks down for a spin–boson problem with a few strongly coupled modes. To study this somewhat vague randomization condition in more detail, let us go back to the perturbative analysis of the spin–boson problem as considered in Sec. IV B. It was shown above that the semiclassical memory kernel (4.9) is (up to a somewhat different renormalization of the electronic coupling) equivalent to the NIBA memory kernel (4.15), if

\[
Q_1(t) = \frac{\pi}{2} \sum_{j} \frac{C_j^2}{\omega_j} \sin(\omega_j t) \rightarrow \text{const.} \quad (4.20)
\]

Note that, as the sum \( Q_1(t) \) of oscillatory functions becomes time independent, all the oscillatory contributions have to cancel each other, which is indistinguishable to the case that the phases of the individual contributions are random.

Figure 7 illustrates this consideration by showing the function \( Q_1(t) \) obtained for the four-mode model of Fig. 6(a) (full line) and for the quasicontinuous model of Fig. 5 (dotted line), respectively. While in the case of an Ohmic bath condition (4.20) is fulfilled after a short initial transient, the four-mode calculation is seen to exhibit an oscillatory rise, which is mainly determined by the lowest frequency of the model. It is instructive to perform a simple numerical experiment and add to each vibrational frequency in \( Q_1(t) \) a randomly chosen phase, i.e., \( \sin(\omega_j t) \rightarrow \sin(\omega_j t + 2\pi \eta_j) \), where \( \eta_j \) are uniform deviates. In the case of four vibrational modes, the resulting function \( Q_1(t) \) depends completely on the phases \( 2\pi \eta_j \), whereas the four-hundred mode calculation for \( Q_1(t) \) is hardly affected by the modification, because in that case the phases of the vibrational modes are already randomized.

It should be emphasized, however, that there are cases of electronically coupled models with few nuclear degrees of freedom that do show electronic relaxation [i.e., \( P(t \rightarrow \infty) \rightarrow 0 \)] and phase randomization. Allowing, e.g., for coordinate-dependent electronic coupling (e.g., \( \Delta \rightarrow \Delta \chi \)), one obtains a conical intersection of the potential-energy surfaces instead of an avoided crossing, which is known to represent a very effective relaxation mechanism. It has been shown for a number of systems including ethylene, pyrazine, benzene, and benzene, that these vibronic coupling models exhibit ultrafast electronic and vibrational relaxation behavior, if at least three strongly coupled vibrational degrees of freedom are involved. Interestingly, it has been found that this relaxation dynamics can be described well by classical-path methods, where it proved advantageous to use dynamical corrections (“Langer-like modifications”) as suggested by Meyer and Miller. The crucial condition for the validity of the classical TDSCF model therefore seems to be a strong enough electronic relaxation dynamics that the

![](image1.png)

**FIG. 6.** Time evolution of the electronic population \( P(t) \) for a four-mode spin–boson model (\( \Delta = 1, \omega_0 = 2.5\Delta, T = 0 \)). The TDSCF (full lines) and exact quantum (dotted lines) calculations are shown for a total system–bath coupling of (a) \( \alpha = 0.09 \) and (b) \( \alpha = 0.5625 \).

![](image2.png)

**FIG. 7.** Time evolution of the function \( Q_1(t) \) obtained for the four-mode model of Fig. 5(a) (full line) and for the quasicontinuous model of Fig. 4 (dotted line).
nuclear phases get randomized rapidly enough not to be important for the overall time evolution of the system.

V. CONCLUSIONS

We have outlined a semiclassical TDSCF approach to describe dissipative quantum phenomena such as the electronic relaxation dynamics of the spin–boson model. We have introduced a semiclassical approximation for the total density operator, which couples the system degrees of freedom to the bath degrees of freedom in a self-consistent manner and is therefore in the spirit of a classical-path formulation. It has been shown that the semiclassical ansatz leads to a general master equation for the electronic population which is up to a quantum-mechanical phase factor equivalent to the polaronic-transformation approach of Vitali and Grigolini\textsuperscript{56} and to the NIBA of Legget \textit{et al.}.\textsuperscript{48} Compared to an exact quantum-mechanical TDSCF representation of the total density operator, the semiclassical ansatz has been shown to be based on two main approximations, namely (i) the use of identical vibrational density operators for both diabatic electronic states and (ii) the assumption of complete randomization of nuclear phases.

The mean-potential approximation \textbf{(4.19)} has been introduced to avoid the problems associated with spurious phase factors, and has proven to represent an appropriate assumption for the description of the dissipative quantum dynamics of the spin–boson model. Unlike the case of reactive-scattering processes, the mean-potential approximation has not turned out to be a very critical assumption for the modeling of bound-state relaxation dynamics.\textsuperscript{48–51} The assumption of complete randomization of nuclear phases, on the other hand, has been found to represent the central approximation of the semiclassical approach. Most important, the randomization assumption makes it possible to perform the trace over the bath variables through quasiclassical sampling of the nuclear initial conditions without invoking any further approximation. The crucial condition for the validity of the semiclassical TDSCF approach therefore is a strong enough electronic relaxation dynamics that the nuclear phases get randomized rapidly enough to be unimportant for the overall time evolution of the system.

To demonstrate the capability of the outlined approach we have compared semiclassical calculations for a spin–boson model with an Ohmic bath to exact path-integral calculations. It has been found that the semiclassical model nicely reproduces the complex dissipative behavior of the spin–boson model for a large range of model parameters, including the transition from coherent to incoherent relaxation dynamics and the electron-transfer dynamics in the nonadiabatic and adiabatic regime.

It is clear, however, that in the case of the spin–boson model the semiclassical approach cannot beat exact path-integral methods, which will soon be able to predict the time evolution of the system for considerably long time regimes.\textsuperscript{10–13} The spin–boson model has mainly been chosen to be able to compare to analytical formulations and exact reference calculations. The benefit of a classical methodology is rather the possibility to easily extend the formulation to a quite general class of problems. In the following, we therefore want to briefly point out some obvious generalizations and extensions of the method.

Owing to the structure of the equations of motions \textbf{(2.8)} and \textbf{(2.9)}, it is first of all clear that the method readily generalizes from the case of a two-state system to a \textit{N}-state system, which also implies the possibility to represent a general reaction coordinate in a quantum-mechanical manner. Further it is straightforward within the semiclassical methodology to evaluate any time-dependent observable of the system (e.g., diabatic and adiabatic electronic population probabilities, electronic autocorrelation function) and the bath (e.g., mean values of the position, momentum, and energy content of a particular vibrational mode).\textsuperscript{49–51} In particular, a general formulation of the nonlinear spectroscopy of electronically coupled systems has been recently developed within a classical-path framework.\textsuperscript{49} Applied to the description of time- and frequency-resolved pump–probe spectroscopy, it has been found that the semiclassical approach provides a promising tool for the modeling and interpretation of modern femtosecond pump–probe experiments.

Finally it should be stressed that the diabatic Hamiltonians \textit{h}_\textit{i} and the electronic coupling \textit{D} are by no means restricted to potential functions up to second order in the coordinate \textit{x}. Recent results for a simple model of nonadiabatic \textit{cis}–\textit{trans} isomerization have shown that the semiclassical model is able to describe the electronic and vibrational relaxation dynamics on strongly anharmonic potential-energy surfaces.\textsuperscript{51} In principle, this opens the possibility of a more realistic description of electron-transfer processes in solution by using a molecular-dynamics (MD) simulation to account for the bath dynamics. The combination of semiclassical methodology and MD simulations would provide an interesting alternative to the more usual indirect approach, where a MD simulation is used to generate a harmonic spectral density, for which in a second step the dynamical problem can be solved with path-integral methods.\textsuperscript{71–73}

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See, for example, the discussion in Ref. 36.


See, for example, Refs. 25 and 26. As usual, we have dropped in Eqs. (2.8) and (2.9) overall phase factors (Refs. 25 and 26), which are unimportant for the calculation of electronic population probabilities.


G. Stock (unpublished).


