Semiclassical Description of Nonadiabatic Quantum Dynamics

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A semiclassical approach is presented that allows us to extend the usual Van Vleck–Gutzwiller formulation to the description of nonadiabatic quantum dynamics on coupled potential-energy surfaces. Based on Schwinger's theory of angular momentum, the formulation employs an exact mapping of the discrete quantum variables onto continuous degrees of freedom. The resulting dynamical problem is evaluated through a semiclassical initial-value representation of the time-dependent propagator. As a first application we have performed semiclassical simulations for a spin-boson model, which reproduce the exact quantum-mechanical results quite accurately. [S0031-9007(96)02196-5]

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In many areas of physics, classical and semiclassical methods represent a valuable approach to describe quantum-dynamical processes. A classical description is well established in cases where both the system under consideration and the observable to be calculated have an obvious classical analog (e.g., the translational-energy distribution after a scattering event). It is less clear, however, how to incorporate discrete quantum-mechanical degrees of freedom (DoF) which do not possess an obvious classical counterpart into a classical theory. As an N-state system coupled to (one or many) continuous DoF describes a large variety of phenomena in chemical and solid state physics as well as in quantum optics [1], a semiclassical modeling of this dynamics is interesting both from a conceptional and a computational point of view.

With this end in mind, numerous quantum-classical hybrid models have been proposed, most notably the "classical-path" approach [2,3] and the "surface-hopping" approach [4,5]. Because of the drastic approximations employed in these models, however, there are well-known shortcomings in both approaches, e.g., classical-path methods do not obey microreversibility and the hopping processes of the surface-hopping methods destroy the coherence of the quantum system [6]. A dynamically consistent formulation of the coupling of quantum and classical DoF can be obtained within the path-integral formalism. Employing a stationary-phase evaluation of the path integral, Pechukas showed that the classical particles move in a nonlocal force field generated by the quantum particles, thus reflecting the nonlocal nature of the quantum system [7]. Pechukas's theory is conceptionally illuminating and is "semiclassically exact" in the sense that it requires only the basic semiclassical Van Vleck–Gutzwiller approximation [8] to the quantum propagator; the calculation of nonlocal forces, however, is in practice more cumbersome than the exact quantum calculation. Employing generalized coherent-states theory [9], the problem of representing both quantum and classical DoF has also been discussed within a phase-space path-integral formulation [10].

In this work, we propose a new semiclassical approach to consistently describe the coupling of quantum and classical DoF, which is semiclassically exact and also promising from a computational point of view. The basic idea is to map the discrete quantum DoF onto continuous DoF and evaluate the resulting dynamical problem by a semiclassical "initial-value representation" [11–14] of the time-dependent propagator. The mapping of discrete DoF onto continuous DoF is based on the representation of spin operators by boson operators. Well-known examples of such a mapping are the Holstein-Primakoff transformation [15], which represents a two-level system by a single nonlinearly coupled boson DoF, and Schwinger's theory of angular momentum [16], which represents an arbitrary spin system by two independent boson DoF.

In order to represent a general N-level system

$$\mathcal{H} = \sum_{n,m} |\psi_n\rangle h_{nm} \langle\psi_m| \tag{1}$$

in terms of N continuous DoF, we need to extend Schwinger's formulation. Representing the N continuous DoF by the harmonic-oscillator creation and annihilation operators $a_n, a_m^\dagger$ with commutation relations $[a_n, a_m^\dagger] = \delta_{n,m}$ and basis states $|n_1, ..., n_N\rangle$, the mapping relations for the operators and basis states read

$$|\psi_n\rangle\langle\psi_m| \mapsto a_n^\dagger a_m \,, \tag{2}$$

$$|\psi_n\rangle \mapsto |0_1 \cdots 1_n \cdots 0_N\rangle \,. \tag{3}$$

According to Eq. (2), the Hamiltonian (1) is written in the "boson representation" as

$$H = \sum_{n,m} a_n^\dagger h_{nm} a_m \,, \tag{4}$$

thus yielding the exact identity for the propagators ($\hbar \equiv 1$)

$$\langle\psi_n|e^{-i\mathcal{H}t}|\psi_m\rangle = \langle 0_1 \cdots 1_n \cdots 0_N|e^{-iHt}|0_1 \cdots 1_m \cdots 0_N\rangle \,. \tag{5}$$

The mapping of the operators (2) preserves the commutation relations, but represents an identity only if it is

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restricted onto the oscillator subspace with a single excitation. Starting with a state in this subspace, however, it is clear from Eq. (4) that the system will always remain in this subspace. In the case of a simple two-level system, the above formalism is equivalent to Schwinger's formulation [16].

In order to go back to our original goal of a consistent semiclassical description of quantum and classical DoF, we consider the generic situation that the matrix elements h_{nm} of the Hamiltonian depend on the continuous DoF $X = \{X_j\}$ with the momenta $P = \{P_j\}$. Identifying the matrix elements with $h_{nm} = [V_0(X) + T(P)]\delta_{n,m} + V_{nm}(X)$, where $V_0(X)$ is a state-independent potential term and $T(P)$ denotes the kinetic energy, we thus obtain

$$\mathcal{H} = [T(P) + V_0(X)]\mathbf{1} + \sum_{n,m} |\psi_n\rangle V_{nm}(X) \langle\psi_m| . \quad (6)$$

Introducing the variables $x_n = (a_n^\dagger + a_n)/\sqrt{2}$, $p_n = i(a_n^\dagger - a_n)/\sqrt{2}$, the corresponding Hamiltonian in the boson representation reads

$$H = h_0(X,P) + \tfrac{1}{2}\sum_{n,m}(x_n x_m + p_n p_m)V_{nm}(X) , \quad (7)$$

where $h_0(X,P) = T(P) + V_0(X) - \frac{1}{2}\sum_n V_{nn}(X)$ and we have assumed that $V_{nm} = V_{nm}^\dagger$. Although the Hamiltonian (7) describes a variety of physical problems [1], we will henceforth refer to the variables x_n, p_n as electronic DoF and to the variables X_j, P_j as nuclear DoF. Equation (6) thus describes a situation ubiquitous in molecular and solid state physics, that is, nuclear motion on nonadiabatically coupled electronic potential-energy surfaces.

As is stated by Eq. (5), the Hamiltonians (6) and (7) are fully equivalent when used as the generator of quantum-mechanical time evolution. Contrary to Eq. (6), however, the quantum-mechanical system described by Eq. (7) has a well-defined classical analog, which will be the focus of the remainder of this work. The transition to classical mechanics is performed by changing from the Heisenberg *operators* $y_k(t)$ ($y_k = x_n, p_n, X_j, P_j$) obeying Heisenberg's equations of motion ($i\dot{y}_k = [y_k, H]$) to the corresponding classical *functions* obeying Hamilton's equations (e.g., $\dot{x}_k = \partial H/\partial p_k$). Furthermore, we need to derive the semiclassical approximation to the time-dependent wave function of the nonadiabatic problem

$$\langle X \,|\, \Psi(t)\rangle = \sum_n \Phi_n(X,t)\,|\psi_n\rangle , \quad (8a)$$

which, as usual, is obtained by expressing the wave function in terms of a coordinate-dependent propagator $K_t(x_1'', \ldots, x_N'', X'' \,|\, x_1', \ldots, x_N', X')$, which then is evaluated within the semiclassical Van Vleck–Gutzwiller approximation [8].

The evaluation of the semiclassical propagator represents a nonlinear boundary-condition problem, i.e., given a trajectory characterized by the position $\mathbf{x}(t) = \mathbf{x}_t$ and momentum $\mathbf{p}(t) = \mathbf{p}_t$, we need to find the roots of the equation $\mathbf{x}_t = \mathbf{x}_t(\mathbf{x}_0, \mathbf{p}_0)$ to calculate the propagator. To circumvent the cumbersome root search, one may rewrite the propagator as an initial-value problem, thereby yielding an initial-value representation of the propagator [11–14]. This way the semiclassical wave function is given as a phase-space integral over the initial conditions $\mathbf{x}_0 = \{x_n(0), X_j(0)\}$, $\mathbf{p}_0 = \{p_n(0), P_j(0)\}$, which is amenable to a Monte Carlo evaluation. In this work, we use a Herman-Kluk-type representation of the propagator [12], which yields for the semiclassical wave function [17]

$$\Phi_n(X,t) = \int d\mathbf{x}_0 \int d\mathbf{p}_0 w_{\mathbf{x}_0\mathbf{p}_0} C_{\mathbf{x}_t\mathbf{p}_t}(t) \chi^{(n)}_{\mathbf{x}_0\mathbf{p}_0}(t) e^{iS(t)} \times \prod_j \phi_{\mathbf{x}_0\mathbf{p}_0}(X_j,t) . \quad (8b)$$

Here $w_{\mathbf{x}_0\mathbf{p}_0}$ denotes the weight function of the integrations, the complex function $C_{\mathbf{x}_t\mathbf{p}_t}(t)$ incorporates the elements of the stability (or monodromy) matrix [12,14], $S(t)$ represents the classical action, and $\phi_{\mathbf{x}_0\mathbf{p}_0}(X_j,t) = \pi^{-1/4}\exp\{-\frac{1}{2}[X_j - X_j(t)]^2 + iP_j(t)[X_j - X_j(t)]\}$ is the Gaussian wave packet (or coherent state) pertaining to the nuclear DoF X_j. Denoting the projection of the electronic wave packet $\phi_{\mathbf{x}_0\mathbf{p}_0}(x_m,t)$ on the corresponding nth harmonic-oscillator eigenfunction by $\langle n \,|\, \phi_m(t)\rangle$, the complex electronic coefficients $\chi^{(n)}_{\mathbf{x}_0\mathbf{p}_0}(t)$ are given as

$$\chi^{(n)}_{\mathbf{x}_0\mathbf{p}_0}(t) = \langle 1 \,|\, \phi_n(t)\rangle \prod_{m\neq n} \langle 0 \,|\, \phi_m(t)\rangle . \quad (8c)$$

Equations (8a)–(8c) describe the time-dependent semiclassical wave function pertaining to the nonadiabatic system (6) and represents the main theoretical result of this Letter. It has been derived by employing (i) a quantum-mechanically exact mapping (2) of the discrete quantum DoF onto continuous DoF and (ii) a semiclassically exact initial-value representation (8b) of the resulting time-dependent propagator, thus treating both quantum and classical DoF on the same dynamical footing.

It is instructive to compare the formulation outlined above with existing semiclassical theories of nonadiabatic dynamics [2,3,18]. The idea of a consistent semiclassical treatment of electronic and nuclear DoF was anticipated in the classical electron analog model of Miller and co-workers, who constructed various classical-path-like Hamiltonian functions which subsequently were "requantized" in order to obtain a semiclassical formulation [3]. While the quantum-mechanical mapping formalism [Eq. (2)] uniquely determines the semiclassical propagator as well as the initial conditions, the quantum-classical analogies employed in Ref. [3] are not unique and involve additional approximations. Furthermore, it is interesting that standard classical-path theories [2] and the semiclassical time-dependent self-consistent-field formulation [18] can be directly derived from Eqs. (8a)–(8c). The latter formulation is obtained by setting $C_{\mathbf{x}_t\mathbf{p}_t}(t) = 1$ and neglecting an electronic phase factor, while the former formulation additionally neglects the action integral and the nuclear Gaussian wave packets [17].

To demonstrate that the semiclassical formulation outlined above is practically useful for the calculation of nonadiabatic processes, we consider a simple but nontrivial application of the theory, that is, the well-known spin-boson problem [1] with a single vibrational mode. The model consists of two coupled electronic states with the matrix elements of $h_0 = \omega/2(X^2 + P^2)$, $V_{11} = \Delta/2 + \kappa X$, $V_{22} = -V_{11}$, and $V_{12} = g$. For the numerical example shown below we choose the bias $\Delta \equiv 1$, the electronic coupling $g = 0.2\Delta$, the vibrational frequency $\omega = 0.1\Delta$, and the vibronic coupling $\kappa = 0.05\Delta$. Although both subproblems of the spin-boson model (i.e., the two-level system and the shifted harmonic oscillator) are solved exactly by the semiclassical formulation given above, the coupled problem (i.e., for $\kappa \neq 0$) is nonseparable and may give rise to highly nonlinear dynamics [19]. To calculate the semiclassical wave function, we have evaluated the phase-space integral in Eq. (8b) via a standard Monte Carlo scheme, solving the equations of motion for the three DoF (x_1, x_2, X) and for the corresponding 6×6 stability matrix for 10^5 trajectories.

Assuming that the system is initially in the electronic state $|\psi_1\rangle$ and in the vibrational ground state of the unshifted harmonic oscillator, Fig. 1 shows the squared modulus of the time-dependent wave function $|\Phi_2(X,t)|^2$ projected on the electronic state $|\psi_2\rangle$. Being zero at time $t = 0$, the wave function exhibits a high-frequency Rabi oscillation due to the electronic coupling which is superimposed by a low-frequency beating due to the vibrational motion. The beating of the intensity is accompanied by a breathing of the width of the wave function. The semiclassical wave function (lower panel) is seen to map the exact quantum-mechanical result (upper panel) in almost every detail. A further quantity of interest in the discussion of nonadiabatic processes is the *total* time-dependent population probability of the electronic state $|\psi_n\rangle$, which is given by

$$P_n(t) = \int dX |\Phi_n(X,t)|^2. \tag{9}$$

Figure 2 compares quantum (dotted line) and semiclassical (full line) calculations of $P_2(t)$, which again are in good agreement. Both the wave function $\Phi_2(X,t)$ and the population probability $P_2(t)$ directly reflect the strong nonadiabatic dynamics of the system, i.e., in the absence of electronic coupling we have $\Phi_2(X,t) \equiv 0$, $P_2(t) \equiv 0$. For larger times ($t > 65$) the vibronic beating of the wave function and the population probability pertains. The accuracy of the semiclassical approximation, however, deteriorates for longer times due to chaotic trajectories which result in a rapidly increasing prefactor $C_{\mathbf{x}_t\mathbf{p}_t}(t)$ in Eq. (8b). These difficulties, however, are not specific to the nonadiabatic Hamiltonian (7), but represent a general problem in the semiclassical evaluation of the time-dependent wave function in the classically chaotic regime [13,14].

In conclusion, we have outlined a semiclassical approach that allows us to extend the Van Vleck–Gutzwiller formulation to the description of nonadiabatic dynamics on coupled potential-energy surfaces. The theory is based on a quantum-mechanically exact mapping of the discrete DoF onto continuous DoF and subsequent evaluation of the resulting dynamical problem through a semiclassical initial-value representation of the time-dependent propagator. We have carried out three-dimensional semiclassical simulations, which reproduce the exact quantum-mechanical results quite accurately.

There are several interesting continuations of this work which include (i) the application of the semiclassical approach to gain a physically more intuitive understanding of nonadiabatic quantum processes, e.g., by studying

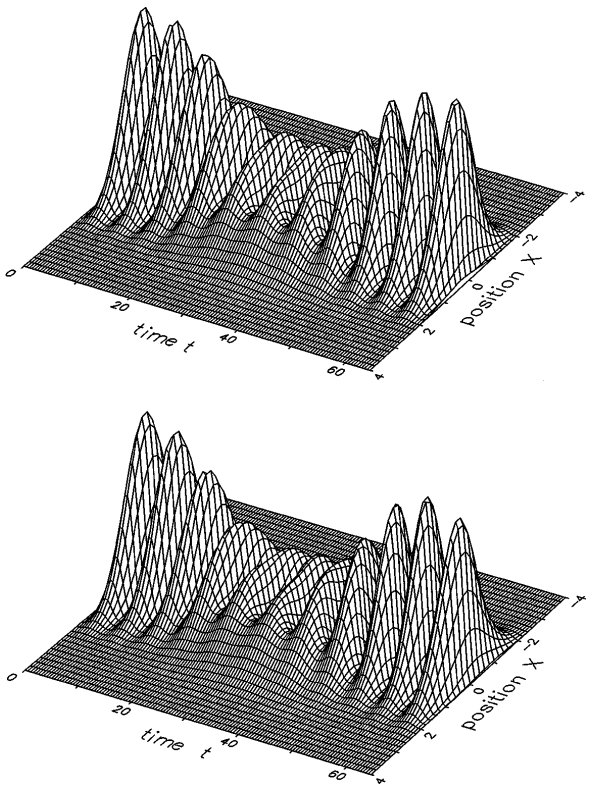

FIG. 1. Squared modulus of the time-dependent wave function projected on the $|\psi_2\rangle$ electronic state. The upper panel shows the exact quantum-mechanical calculation; the lower panel shows the semiclassical approximation.

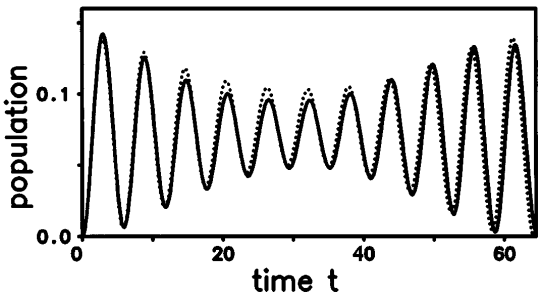

FIG. 2. Quantum-mechanical (dotted line) and semiclassical (full line) calculations of the time-dependent population probability of the $|\psi_2\rangle$ electronic state.

vibronic periodic orbits, (ii) the development of further approximations to the semiclassical wave function to facilitate the computational treatment of complex systems, and (iii) the improvement of the initial-value representation in order to treat chaotic nonadiabatic dynamics, which for multidimensional systems emerges within relatively short times. First results for spin-boson models with up to four vibrational modes appear to be quite encouraging [17].

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