

Forward–backward semiclassical dynamics in the interaction representation

Jiushu Shao and Nancy Makri

School of Chemical Sciences, University of Illinois, 601 South Goodwin Avenue, Urbana, Illinois 61801

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The forward–backward semiclassical dynamics methodology [J. Phys. Chem. **103**, 7753, 9479 (1999)] is reformulated in the interaction representation. The new version of the method allows for a fully quantum mechanical description of a low-dimensional subsystem of interest, along with a semiclassical forward–backward treatment of the solvent coordinates and their coupling to the reference subsystem. Application to the long-time tunneling dynamics in a symmetric double-well system coupled to a harmonic bath shows that the interaction FBSD is capable of capturing quantitatively the tunneling and decoherence effects induced by weakly dissipative environments.
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I. INTRODUCTION

Semiclassical propagation has reemerged in recent years as a promising tool for following the dynamics of polyatomic systems. The time-dependent semiclassical approximation is an asymptotic theory valid in the small \hbar regime. For a system of n degrees of freedom, the Van Vleck propagator^{1,2} can be derived by applying the stationary phase approximation to the path integral. Its coordinate representation takes the form

$$\langle \mathbf{x}_2 | U(t_2, t_1) | \mathbf{x}_1 \rangle_{\text{SC}} = \sum_{\substack{\text{classical paths with} \\ \mathbf{x}(t_1) = \mathbf{x}_1, \mathbf{x}(t_2) = \mathbf{x}_2}} (2\pi i \hbar)^{-(n/2)} \times \left| \det \frac{\partial^2 S}{\partial \mathbf{x}_1 \partial \mathbf{x}_2} \right|^{1/2} e^{iS(\mathbf{x}_1, \mathbf{x}_2)/\hbar} e^{-i\mu\pi/2}, \quad (1)$$

where S is the classical action along a path and μ is the Maslov index which accounts for the phase of topologically distinct orbits. Unlike the path integral expression,³ which includes all paths between the endpoints, only those trajectories satisfying Newton's equations enter the semiclassical propagator. The determinant prefactor amounts to nonclassical contributions from quantum fluctuations from classical trajectories that are included through second order. A number of studies have shown that semiclassical propagation with Eq. (1) is sufficiently accurate for treating nuclear motion, even in strongly chaotic systems.⁴ Specifically, the semiclassical propagator preserves unitarity (within the stationary phase approximation), uncertainty products, and zero point energy, it captures phase interference phenomena semiquantitatively,^{5–12} and allows some tunneling (although it encounters severe difficulties in the so-called “deep tunneling” regime¹³). Miller has shown that when the semiclassical propagator is integrated with respect to one or both endpoints, as in the expressions for the wave function or the survival amplitude, one can change integration variables to obtain an initial value representation where the classical trajectories are specified by their initial (rather than boundary) conditions, and thus semiclassical propagation can be cast in a form convenient for numerical calculations.^{5,14} A similar

task is accomplished by Heller's cellularized form^{15,16} and Herman and Kluk's coherent state representation.^{17,18}

In spite of its appeal, the use of semiclassical theory in numerical calculations has in the past been limited. The major problem encountered in numerical calculations with many degrees of freedom is the need to integrate an oscillatory multidimensional function. As in the case of the real time path integral,^{19–22} various filtering techniques have found some success,^{23,24} but polyatomic systems with strongly anharmonic potentials that support multiple interfering trajectories continue to pose serious difficulties. A second problem is the calculation of the prefactor (i.e., evaluation of the stability matrix and its determinant) that scales as the third power of the number of atoms.

A natural way of smoothing the integrand, and thus overcoming the phase cancellation problem, is the main advantage of the forward–backward semiclassical dynamics (FBSD) methodology introduced recently by Makri and Thompson in the context of influence functionals^{25,26} and extended to semiclassical correlation functions by Miller and co-workers^{27–29} and Makri and co-workers.^{30–33} The basic idea is to combine the two time evolution operators present in ensemble averaged quantities (time correlation functions for reduced density matrices) into a single semiclassical propagator, which now involves trajectories that evolve first forward and subsequently backward in time. As a consequence of this time course, the net forward–backward action is generally small on the scale of \hbar and the integrand is no longer highly oscillatory. These features allow successful application of Monte Carlo techniques.

Shao and Makri have shown that a particular implementation of FBSD can lead to expressions for time correlation functions where the semiclassical prefactor is eliminated, giving rise to a methodology with linear scaling.^{32,33} This prefactor-free formulation is rigorous, in the sense that it involves no *ad hoc* procedures other than the use of the stationary phase approximation. A number of test calculations have shown that the method can successfully describe the dynamics in multidimensional anharmonic systems as long as coherence effects are short-lived. Yet, significant interference is lost in that particular version of FBSD, and the re-

sults have a strong quasiclassical flavor, i.e., are very similar to those obtained with the conventional Wigner method.^{34,35} Particularly bothersome is the inability of the prefactor-free FBSD to describe the tunneling of a particle between two wells in a double-well potential, a situation of importance to many chemical and biological systems.

In the present paper we present a formulation of FBSD in the interaction representation. The latter provides a very useful framework for quantum mechanical calculations. Classical mechanics can also be formulated in the interaction representation.³⁶ Further, using trajectories propagated in the interaction representation gives rise to a superior version of the quasiclassical Wigner scheme.³⁷

In the present paper, the dynamics of a chosen low-dimensional reference system is treated fully quantum mechanically, while the environment is treated by FBSD. This treatment leads to an improved description of quantum interference effects, and the method becomes exact as the coupling between system and environment goes to zero. Thus the interaction form of FBSD provides a useful method in the weak coupling limit where the bare prefactor-free FBSD is least accurate. Naturally, its accuracy is closely linked to one's ability to choose a good reference Hamiltonian, and thus the accuracy of the method degrades when the coupling becomes large.

The theoretical developments are presented in Sec. II. Section III illustrates the method with an application to symmetric tunneling in the presence of a dissipative environment. The interaction-FBSD method is seen to provide essentially quantitative results at weak dissipation, even for very long time propagation. Some concluding remarks are given in Sec. IV.

II. THEORY

A. Prefactor-free FBSD

Throughout this article we focus on correlation function of the type

$$C(t) = \text{Tr}(\rho(0)Ae^{iHt/\hbar}Be^{-iHt/\hbar}). \quad (2)$$

Here $\rho(0)$ is the initial density matrix and H is the Hamiltonian of an n -dimensional system,

$$H = \frac{1}{2}\mathbf{p}^T \cdot \mathbf{m}^{-1} \cdot \mathbf{p} + V(\mathbf{q}), \quad (3)$$

where \mathbf{q} and \mathbf{p} are the position and momentum operators, respectively (the superscript T denotes the transpose of a matrix or a vector), \mathbf{m} is the mass matrix, $V(\mathbf{q})$ the potential energy, and A, B are two scalar operators. In the present paper it is assumed that B depends only on the position vector \mathbf{q} , although it is straightforward to extend the theory to account for a general Hermitian operator. By making use of the identity

$$C(t) = -i \frac{\partial}{\partial \mu} \text{Tr}(\rho(0)Ae^{iHt/\hbar}e^{i\mu B}e^{-iHt/\hbar}) \Big|_{\mu=0}, \quad (4)$$

applying the semiclassical approximation (in the coherent state representation) to the combined product of exponentials and performing some algebra, we have shown that the correlation function can be brought in the following form^{32,33}

$$C(t) = -i(2\pi\hbar)^{-n} \frac{\partial}{\partial n} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \exp\left(\frac{i}{\hbar}S(\mathbf{q}_0, \mathbf{p}_0)\right) \times \langle g(\mathbf{q}_0, \mathbf{p}_0) | \rho_0 A | g(\mathbf{q}_f, \mathbf{p}_f) \rangle \Big|_{\mu=0}. \quad (5)$$

The trajectories in this expression have initial conditions given by the phase space variables $\mathbf{q}_0, \mathbf{p}_0$ and are first integrated forward to the time t . At that time they incur a momentum jump equal to

$$\Delta \mathbf{p}_t = \frac{1}{2}\hbar \mu \nabla B(\mathbf{q}_t) \quad (6)$$

and the action increments by the amount

$$\Delta S_t = \hbar \mu B(\mathbf{q}_t). \quad (7)$$

Subsequently, each trajectory is integrated back to time zero following the classical equations of motion, reaching the point $\mathbf{q}_f, \mathbf{p}_f$, while the total accumulated action is S . Finally, g is a coherent state defined by the wave function

$$\langle \mathbf{q} | g(\mathbf{q}_0, \mathbf{p}_0) \rangle = \left(\frac{2}{\pi}\right)^{n/4} (\det \mathbf{\Gamma})^{1/4} \times \exp\left[-(\mathbf{q} - \mathbf{q}_0)^T \cdot \mathbf{\Gamma} \cdot (\mathbf{q} - \mathbf{q}_0) + \frac{i}{\hbar} \mathbf{p}_0 \cdot (\mathbf{q} - \mathbf{q}_0)\right], \quad (8)$$

where $\mathbf{\Gamma}$ is a positive definite matrix.

It is straightforward to show that the above formalism for the correlation function applied directly to the Heisenberg operator,

$$B_H(t) \equiv e^{iHt/\hbar} B e^{-iHt/\hbar}, \quad (9)$$

i.e., the FBSD expression for $B_H(t)$ is given by the projector

$$B_H(t) = -i(2\pi\hbar)^{-n} \frac{\partial}{\partial \mu} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \times \exp\left(\frac{i}{\hbar}S(\mathbf{q}_0, \mathbf{p}_0)\right) | g(\mathbf{q}_f, \mathbf{p}_f) \rangle \langle g(\mathbf{q}_0, \mathbf{p}_0) | \Big|_{\mu=0} \quad (10)$$

subject to the evolution described above. Note that even at time zero, there is nontrivial forward-backward dynamics because B is involved through Eq. (6). As a consequence of the stationary phase procedure involved in this formulation, even for a harmonic system (or for a general Hamiltonian at $t=0$) Eq. (10) is exact only if B is at most a cubic function of coordinates.

B. FBSD in the interaction representation

We now proceed to rewrite the results of the previous subsection in the interaction representation, for this purpose we divide the Hamiltonian into a suitable reference part H_0 and a term H_{int} comprising the nonseparable part of the environment plus its interaction with the subsystem of interest. As in earlier work, it is important to choose a physically motivated reference, while keeping its form sufficiently simple such that it can be dealt with quantum mechanically by numerical basis set or quadrature techniques.^{38,39}

The propagator associated with the Hamiltonian H can be written as

$$U(t) = \tilde{U}(t)U_0(t), \quad (11)$$

where

$$U_0(t) = e^{-iH_0 t/\hbar} \quad (12)$$

is the propagator generated by H_0 , and $\tilde{U}(t)$ is the propagator in the interaction representation. The latter satisfies the differential equation

$$i\hbar \frac{\partial}{\partial t} \tilde{U}(t) = \tilde{U}(t)H_{\text{int}}(t), \quad (13)$$

where

$$\tilde{H}_{\text{int}}(t) = U_0(t)H_{\text{int}}U_0^{-1}(t) \quad (14)$$

is the coupling term in the interaction representation with the initial condition $\tilde{U}(0) = 1$.

The interaction propagator,

$$\tilde{U}(t) = U(t)U_0^{-1}(t), \quad (15)$$

involves time evolution in two sequential steps: first, the system is propagated in the backward time direction with the reference Hamiltonian; next, the interaction is turned on, and the system is propagated forward with the full potential.^{36,37} In the interaction picture, the Heisenberg operator becomes

$$B_{\text{H}}(t) = U_0^{-1}(t)\tilde{U}^{-1}(t)B\tilde{U}(t)U_0(t) = U_0^{-1}(t)\tilde{B}(t)U_0(t), \quad (16)$$

where

$$\tilde{B}_{\text{H}}(t) \equiv \tilde{U}^{-1}(t)B\tilde{U}(t) \quad (17)$$

is the Heisenberg operator associated with the propagator $\tilde{U}(t)$. We invoke the FBSD formula, Eq. (10), to obtain a semiclassical expression for $\tilde{B}_{\text{H}}(t)$. Here the classical dynamics is generated by the interaction propagator, Eq. (15), as described above. In its FBSD expression for $\tilde{B}_{\text{H}}(t)$, the classical motion goes through five steps. As the first step, trajectories are propagated backwards from time 0 to $-t$ with the reference Hamiltonian. Subsequently, they evolve forward in time, from $-t$ to the time 0, with the full Hamiltonian. At that time each trajectory incurs a jump defined by Eq. (7). The fourth step involves backward propagation to the time $-t$ by the full Hamiltonian. Finally, the reference Hamiltonian moves the trajectories forward once again, to the final time 0.

To complete the prescription for the correlation function, we express the correlation function in the form

$$C(t) = -i(2\pi\hbar)^{-n} \frac{\partial}{\partial \mu} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \exp\left(\frac{i}{\hbar}S(\mathbf{q}_0, \mathbf{p}_0)\right) \times \langle g(\mathbf{q}_0, \mathbf{p}_0) | U_0(t)\rho_0 U_0^{-1}(t) | g(\mathbf{q}_f, \mathbf{p}_f) \rangle_{\mu=0}. \quad (18)$$

The coherent state matrix element now involves the initial density propagated forward and backward under the reference Hamiltonian. Assuming that the latter is amenable to numerical solution by a combination of basis set, quadrature, and analytical methods, it is a simple matter to evaluate this matrix element.

III. APPLICATION TO QUANTUM TUNNELING

One of the most severe problems of FBSD methods is their inability to correctly describe long-time tunneling effects of the type encountered in isomerization reactions. Because the evolution of such processes critically depends on delicate phase relations over many vibrational periods of the reactants, the stationary phase procedure implicit in forward-backward semiclassical methods cannot properly account for through-barrier tunneling. In addition, even the full semiclassical propagator has been shown to fail in the deep tunneling regime.¹⁵ These problems call for a different treatment of the reaction coordinate in such cases, and provide an excellent challenge for FBSD in the interaction representation.

In this section we consider a model that involves tunneling of a particle in a symmetric double-well potential coupled to a weakly dissipative bath of photons. The Hamiltonian is given by the form

$$H = \frac{p_s^2}{2m} + V_0(s) + \sum_{j=1}^n \frac{p_j^2}{2m} + \frac{1}{2}m\omega_j^2 \left(x_j - \frac{c_j s}{m\omega_j^2} \right)^2, \quad (19)$$

where V_0 is a symmetric double well with barrier height equal to about 4 kcal/mol and the mass of the particle is that of a hydrogen atom. The coupling coefficients and frequencies of the bath oscillators are collectively specified by the spectral density function,

$$J(\omega) = \frac{\pi}{2} \sum_{j=1}^n \frac{c_j^2}{m\omega_j} \delta(\omega - \omega_j).$$

We choose a spectral density of the Ohmic form,

$$J(\omega) = \frac{\pi}{2} \hbar \frac{\omega}{s_{\text{min}}^2} \omega e^{-\omega/\omega_c}.$$

Here $\pm s_{\text{min}}$ are the coordinates of the two potential minima, the Kondo parameter α indicates the overall coupling strength between the reaction coordinate and the bath, and ω_c is a cutoff that excludes bath modes of unrealistically high frequencies. We choose $\omega_c = 4\Omega$ where $\hbar\Omega$ is the tunneling splitting of the uncoupled double well.

In the case of a truly dissipative bath, $n \rightarrow \infty$. For the purpose of applying the FBSD methodology, the bath needs to be discretized. Using the discretization procedure described in Ref. 40, we obtained converged results for times up to a 1.5 tunneling periods with a discrete bath corresponding to $n = 30$. Initially the system is in the localized state, i.e.,

$$\tilde{\rho}_0 = |\varphi_0\rangle\langle\varphi_0|,$$

where

$$\varphi_0(s) = \left(\frac{m\omega_{\text{min}}}{\pi\hbar} \right)^{1/4} \exp\left[-\frac{m\omega_{\text{min}}}{2\hbar}(s - s_{\text{min}})^2 \right] \quad (20)$$

is the ground state of the local harmonic approximation at a potential minimum and the oscillators of the bath are in shifted ground states centered at $c_j s_{\text{min}}/m\omega_j^2$. The multidimensional integration is arranged as a sum of two Gaussian forms according to the probability distributions around the two potential energy minima and calculated with the Genz-

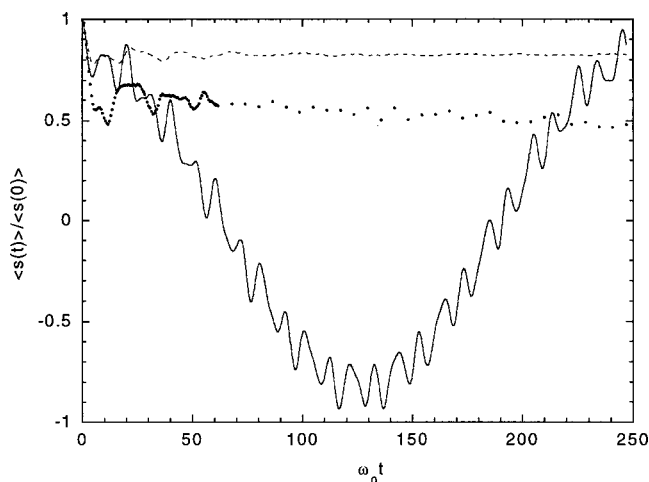


FIG. 1. Scaled average position of a particle in a one-dimensional double-well potential. The solid line shows the results of exact propagation. The dashed and dotted lines show the results of the bare FBSD and the classical Wigner method, respectively.

Monahan algorithm.⁴¹ The reference Hamiltonian is chosen as the one-dimensional adiabatic potential:^{38,39}

$$H_0 = \frac{p_s^2}{2m} + V_0(s). \quad (21)$$

Figure 1 shows the comparison of the results of the bare double-well system treated via exact quantum mechanical propagation, plain FBSD, and the classical Wigner method. Clearly, neither the simple FBSD scheme nor the classical Wigner method can account for quantum tunneling, and both methods break down within a single vibrational period of the potential well.

The plain FBSD and classical Wigner methods are also applied to the dissipative double-well model with $\alpha=0.175$ and the results, together with the exact one based on iterative

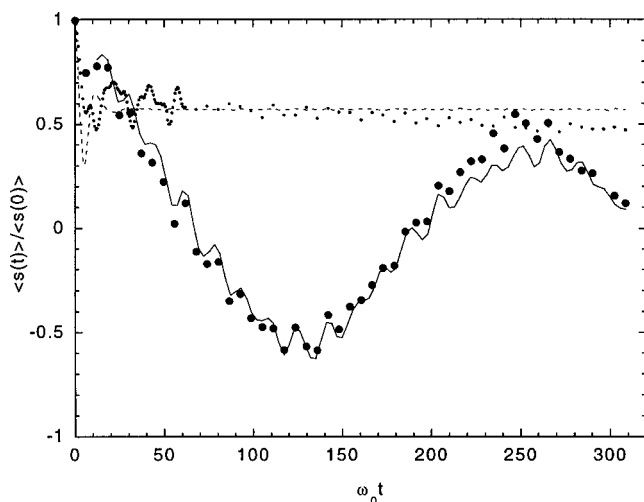


FIG. 2. Scaled average position of a particle in a dissipative double-well potential. The solid line shows the results of numerically exact calculation based on iterative evaluation of the path integral. The dashed and dotted lines show the results of the bare FBSD and the classical Wigner method, respectively. The results of the present interaction-FBSD method with an adiabatic reference are shown as solid circles.

evaluation of the path integral,^{38,42} are displayed in Fig. 2. Again, it is seen that the two semiclassical methods produce reasonable results only at very short times and fail completely to describe the dynamics. By contrast, the interaction representation FBSD provides a correct description of the quenched tunneling oscillations in the dissipative environment for times longer than a tunneling period. It is worth noting that the simulation results shown in Fig. 2 involve very long-time propagation that exceeds 50 vibrational periods in the reactant potential well.

IV. SUMMARY AND DISCUSSION

Use of the interaction representation leads to a quantum-FBSD scheme which combines full quantum mechanical treatment of the subsystem of interest with a forward-backward semiclassical description of its environment. This method is applied to the study of the dissipative tunneling dynamics of a double-well system coupled to a harmonic oscillator bath, a model describing many important chemical processes such as isomerization in solution. While the unmodified FBSD fails to predict tunneling dynamics, the quantum-FBSD formulation based on the interaction representation leads to a correct description of dissipative tunneling dynamics when the coupling between the system and the environment is weak. In the zero coupling limit the interaction FBSD scheme reverts to the full quantum mechanical solution.

Clearly, the success of the interaction-FBSD methodology depends on the suitability of the chosen reference Hamiltonian. If the dynamics generated by the latter provides a reasonable approximation to the evolution of the full Hamiltonian, the forward-backward semiclassical treatment of the environment is able to capture the major effects of coupling, leading to accurate results. However, it appears the scheme is not capable of fully capturing the effects of coupling to the dynamics of the reference system when the corrections to the latter are large.

Since the dynamics of separable reference Hamiltonians tends to be coherent, the interaction FBSD is likely to overestimate coherence effects, while the plain FBSD tends to neglect it. Thus the two methods are in a sense complementary and suitable for different regimes. An interesting question is whether there exists a universal FBSD method that is accurate not only in these two domains, but also in between.

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