

Semiclassical theory of electronically nonadiabatic dynamics: Results of a linearized approximation to the initial value representation

Xiong Sun, Haobin Wang, and William H. Miller

Department of Chemistry, University of California and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

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A linearized approximation to the semiclassical initial value representation (SC-IVR), referred to herein as the LSC-IVR, was used by us in a recent paper [J. Chem. Phys. **108**, 9726 (1998)] to calculate reactive flux correlation functions for a model of a chemical reaction on a single potential energy surface. This paper shows how the LSC-IVR—which is much easier to apply than the full SC-IVR because it linearizes the phase difference between interfering classical trajectories—can be applied to *electronically nonadiabatic* processes, i.e., those involving transitions between different potential-energy surfaces. Applications to several model problems are presented to show its usefulness: These are the nonadiabatic scattering problems used by Tully to test surface-hopping models, and also the spin-boson model of coupled electronic states in a condensed phase environment. Though not as accurate as the full SC-IVR, the LSC-IVR does a reasonably good job for all these applications, even describing correctly Stuckelberg oscillations (interference between nonadiabatic transitions) and the transition between coherent and incoherent behavior in the spin-boson example. © 1998 American Institute of Physics. [S0021-9606(98)02041-8]

I. INTRODUCTION

The semiclassical initial value representation^{1–4} (SC-IVR) is undergoing a rebirth of interest as a way of generalizing classical molecular-dynamics simulations to include quantum interference and tunneling effects. Applications by number of groups are demonstrating the accuracy that the SC-IVR provides for a variety of phenomena: Tunneling and interference in chemical reactions,⁵ photo-dissociation,⁶ vibrational-rotational eigenvalues (including tunneling splitting) of HCl dimer.⁷ It has also been shown how the model of Meyer and Miller⁸ (MM) for treating electronic and nuclear degrees of freedom on a dynamically equivalent footing can be implemented within the SC-IVR,^{9,10} so that it is also possible to describe electronically nonadiabatic processes within this unified dynamical framework.

The evidence is, therefore, mounting that the SC-IVR provides a useful description of quantum effects in essentially all aspects of molecular dynamics, and the crucial question now is how efficiently such calculations can be carried out for systems of interest. An SC-IVR calculation (see Sec. II below) involves a phase space average over the initial conditions of classical trajectories, but it is considerably more difficult than that for ordinary classical mechanics because the integrand is oscillatory (whence arise quantum interference and tunneling effects). The development of efficient algorithms to carry out such calculations is an active area of research.

Much simpler than a full SC-IVR calculation, however, is a linearized approximation to it that we have recently suggested^{11–13} and found to give excellent results for a model of condensed phase unimolecular isomerization (a double well potential coupled to an infinite bath of harmonic

oscillators). The approximation—which involves linearizing the phase difference in the integrand (see Sec. II below)—leads to an extremely simple computational procedure, one that is only slightly more complicated than an ordinary classical calculation. Because of its simplicity, and thus potential for useful applications, it is important to investigate the accuracy of this *linearized* SC-IVR (which we will refer to as the LSC-IVR) for as wide a range of problems as possible; such is the purpose of this paper.

The applications of the LSC-IVR pursued in this paper are to electronically nonadiabatic processes, based on the MM model noted above. Specifically, we apply it to the model problems Tully¹⁴ has used for testing his “fewest switches” version of the surface hopping model for electronically nonadiabatic transitions (which two of us also used earlier⁹ to test the full SC-IVR). We also apply the LSC-IVR to the popular spin-boson problem,¹⁵ a two level system (e.g., two electronic states) coupled to an infinite bath of harmonic oscillators (e.g., a condensed phase environment), looking specifically at the transition between coherent and incoherent tunneling behavior discussed by Mak and Chandler.¹⁶ (Stock and Thoss¹⁰ have earlier successfully treated the two level system coupled to one harmonic mode by the full SC-IVR.) The LSC-IVR provides a reasonably good description of the results in essentially all these cases.

Section II first reviews and summarizes the linearized approximation to the SC-IVR which leads to the LSC-IVR, and the MM approach for treating electronic and nuclear degrees of freedom in a consistent way is summarized in Sec. III. The applications noted in the above paragraph are presented and discussed in Sec. IV, and Sec. V concludes.

II. LINEARIZED SEMICLASSICAL INITIAL VALUE REPRESENTATION (LSC-IVR)

Consider a generic quantum mechanical transition probability from state $|\Psi_1\rangle$ to $|\Psi_2\rangle$ in time t ; the quantum expression for this is

$$P_{2\leftarrow 1}(t) = |S_{2,1}(t)|^2 \quad (2.1a)$$

with

$$\begin{aligned} S_{2,1}(t) &= \langle \Psi_2 | e^{-i\hat{H}t/\hbar} | \Psi_1 \rangle \\ &= \int d\mathbf{q}_1 d\mathbf{q}_0 \Psi_2(\mathbf{q}_1)^* \langle \mathbf{q}_1 | e^{-i\hat{H}t/\hbar} | \mathbf{q}_0 \rangle \Psi_1(\mathbf{q}_0), \end{aligned} \quad (2.1c)$$

where \hat{H} is the (time-independent) Hamiltonian of the system. With the standard semiclassical approximation¹⁷ for the matrix element of the propagator, $e^{-i\hat{H}t/\hbar}$, and the IVR transformation of the integrals,² the SC-IVR expression for the amplitude becomes

$$\begin{aligned} S_{2,1}(t) &= \int d\mathbf{q}_0 d\mathbf{p}_0 \left[\det \left(\frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \right) / (2\pi i \hbar)^F \right]^{1/2} \\ &\quad \times e^{iS_t(\mathbf{q}_0, \mathbf{p}_0)/\hbar} \Psi_2(\mathbf{q}_t)^* \Psi_1(\mathbf{q}_0), \end{aligned} \quad (2.2)$$

where $\mathbf{q}_t(\mathbf{q}_0, \mathbf{p}_0)$ is the coordinate at time t for the classical trajectory with initial condition $(\mathbf{q}_0, \mathbf{p}_0)$, and $S_t(\mathbf{q}_0, \mathbf{p}_0)$ is the action integral along it. (The phase factor $e^{-i\pi\nu_t/2}$, where ν_t is the Maslov index¹⁸—the number of zeros experienced by the determinant of $\partial \mathbf{q}_t / \partial \mathbf{p}_0$ in the time interval $(0, t)$ —is included in Eq. (2.2) as part of the pre-exponential square root.) It is the oscillatory nature of the integrand in Eq. (2.2) that complicates the integration over the phase space of initial conditions.

The linearization approximation that we now make to the SC-IVR of Eq. (2.2) has been described before,^{19,11,12} so we only give a brief synopsis here. One explicitly squares the amplitude in Eq. (2.2) to obtain the transition probability via Eq. (2.1c), and this leads to a double phase space average

$$\begin{aligned} P_{2\leftarrow 1}(t) &= \frac{1}{(2\pi\hbar)^F} \int d\mathbf{q}_0 d\mathbf{p}_0 \int d\mathbf{q}'_0 d\mathbf{p}'_0 \\ &\quad \times \left[\det \left(\frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \cdot \frac{\partial \mathbf{q}'_t}{\partial \mathbf{p}'_0} \right) \right]^{1/2} e^{i[S_t(\mathbf{q}_0, \mathbf{p}_0) - S_t(\mathbf{q}'_0, \mathbf{p}'_0)]/\hbar} \\ &\quad \times \Psi_2(\mathbf{q}_t)^* \Psi_2(\mathbf{q}'_t) \Psi_1(\mathbf{q}_0) \Psi_1(\mathbf{q}'_0)^*, \end{aligned} \quad (2.3)$$

where $\mathbf{q}_t = \mathbf{q}_t(\mathbf{q}_0, \mathbf{p}_0)$ and $\mathbf{q}'_t = \mathbf{q}_t(\mathbf{q}'_0, \mathbf{p}'_0)$. One then makes a sum and difference transformation of the integration variables

$$\mathbf{q}_0 = \bar{\mathbf{q}}_0 + \frac{\Delta \mathbf{q}}{2}, \quad \mathbf{q}'_0 = \bar{\mathbf{q}}_0 - \frac{\Delta \mathbf{q}}{2}, \quad (2.4a)$$

$$\mathbf{p}_0 = \bar{\mathbf{p}}_0 + \frac{\Delta \mathbf{p}}{2}, \quad \mathbf{p}'_0 = \bar{\mathbf{p}}_0 - \frac{\Delta \mathbf{p}}{2}, \quad (2.4b)$$

and expands the phase of the integrand in Eq. (2.3) through second order in $\Delta \mathbf{q}$ and $\Delta \mathbf{p}$

$$\begin{aligned} S_t(\mathbf{q}_0, \mathbf{p}_0) - S_t(\mathbf{q}'_0, \mathbf{p}'_0) &= \frac{\partial S_t(\bar{\mathbf{q}}_0, \bar{\mathbf{p}}_0)}{\partial \bar{\mathbf{q}}_0} \cdot \Delta \mathbf{q} + \frac{\partial S_t(\bar{\mathbf{q}}_0, \bar{\mathbf{p}}_0)}{\partial \bar{\mathbf{p}}_0} \cdot \Delta \mathbf{p} \\ &= (\bar{\mathbf{p}}_t^T \cdot \mathbf{M}_{\mathbf{q}\mathbf{q}} - \bar{\mathbf{p}}_0) \cdot \Delta \mathbf{q} + \bar{\mathbf{p}}_t^T \cdot \mathbf{M}_{\mathbf{q}\mathbf{p}} \cdot \Delta \mathbf{p}, \end{aligned} \quad (2.5)$$

the quadratic terms vanish because the phase difference is an odd function of the difference variables. Consistent with this approximation to the phase, the trajectories \mathbf{q}_t and \mathbf{q}'_t are expanded to first order in $\Delta \mathbf{q}$ and $\Delta \mathbf{p}$, and within this approximation the Jacobian factors are thus independent of $\Delta \mathbf{q}$ and $\Delta \mathbf{p}$, i.e.,

$$\frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \approx \frac{\partial \mathbf{q}'_t}{\partial \mathbf{p}'_0} \approx \frac{\partial \bar{\mathbf{q}}_t}{\partial \bar{\mathbf{p}}_0} = \mathbf{M}_{\mathbf{q}\mathbf{p}}, \quad (2.6a)$$

and similarly

$$\frac{\partial \bar{\mathbf{q}}_t}{\partial \bar{\mathbf{q}}_0} = \mathbf{M}_{\mathbf{q}\mathbf{q}}. \quad (2.6b)$$

(As a matter of interest, note that all of the above approximations following Eq. (2.3) are exact if the system is a set of harmonic oscillators.) The integration over the difference variables $\Delta \mathbf{q}$ and $\Delta \mathbf{p}$ can now be carried out to give the final result of the LSC-IVR

$$P_{2\leftarrow 1}(t) = \frac{1}{(2\pi\hbar)^F} \int d\mathbf{q}_0 d\mathbf{p}_0 \rho_2(\mathbf{q}_t, \mathbf{p}_t)^* \rho_1(\mathbf{q}_0, \mathbf{p}_0), \quad (2.7)$$

where the ‘‘bars’’ have been dropped from \mathbf{q}_0 and \mathbf{p}_0 , and $\rho_n(\mathbf{q}, \mathbf{p})$ is the Wigner distribution function²⁰ of state n , defined as

$$\rho_n(\mathbf{q}, \mathbf{p}) = \int d\Delta \mathbf{q} e^{-i\mathbf{p}^T \cdot \Delta \mathbf{q}/\hbar} \left\langle \mathbf{q} + \frac{\Delta \mathbf{q}}{2} | \Psi_n \right\rangle \left\langle \Psi_n | \mathbf{q} - \frac{\Delta \mathbf{q}}{2} \right\rangle. \quad (2.8)$$

It should be clear that it is much easier to evaluate the LSC-IVR expression than in Eq. (2.7) than the full SC-IVR expression of Eq. (2.2) because the integrand in Eq. (2.7) is essentially free of high-frequency oscillations. [The oscillatory character has been subsumed in the Fourier transforms that define the Wigner distribution functions, Eq. (2.8).]

The same manipulations and approximations can also be carried out for a more general time-correlation function of the form

$$C_{AB}(t) = \text{tr}[\hat{A} e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar}]. \quad (2.9)$$

$P_{2\leftarrow 1}(t)$ above corresponds to Eq. (2.9) with

$$\hat{A} = |\Psi_1\rangle \langle \Psi_1|, \quad (2.10)$$

$$\hat{B} = |\Psi_2\rangle \langle \Psi_2|. \quad (2.11)$$

Writing out the full SC-IVR expression for Eq. (2.9) and making the linearization approximation as above gives

$$C_{AB}(t) = \frac{1}{(2\pi\hbar)^F} \int d\mathbf{q}_0 d\mathbf{p}_0 A_w(\mathbf{q}_0, \mathbf{p}_0) B_w(\mathbf{q}_t, \mathbf{p}_t), \quad (2.12)$$

where $A_w(\mathbf{q}, \mathbf{p})$ and $B_w(\mathbf{q}, \mathbf{p})$ are the Wigner–Weyl transforms of operators \hat{A} and \hat{B} , e.g.,

$$A_w(\mathbf{q}, \mathbf{p}) = \int d\Delta \mathbf{q} \, e^{-i\mathbf{p} \cdot \Delta \mathbf{q} / \hbar} \left\langle \mathbf{q} + \frac{\Delta \mathbf{q}}{2} \left| \hat{A} \right| \mathbf{q} - \frac{\Delta \mathbf{q}}{2} \right\rangle. \quad (2.13)$$

Our previous work on thermal rate constants^{11,12} corresponded to the case of \hat{A} being the Boltzmannized flux operator

$$\hat{A} = e^{-\beta \hat{H}/2} \hat{F} e^{-\beta \hat{H}/2}, \quad (2.14)$$

and \hat{B} being the projection operator onto products

$$\hat{B} = \hat{h}(\mathbf{q}), \quad (2.15)$$

where $h(\mathbf{q})$ is 1(0) for coordinates \mathbf{q} on the product (reactant) side of the dividing surface which separates reactants and products.

It is clear from both Eqs. (2.7) and (2.12) that this LSC-IVR includes quantum effects only via the Wigner functions of the initial and final states; all the real time dynamics is purely classical. This fact manifested itself in our earlier work on thermal rate constants¹² in that quantum effects were well described for *short time*, but the longer time dynamics was that given by classical rather than quantum mechanics. Whether or not this is adequate will depend on the application at hand.

Finally, we note that what we have called the LSC-IVR, i.e., Eq. (2.7) or Eq. (2.12), has appeared in many approximate dynamical theories.^{13,21,23–25} With regard to thermal rate constants, for example, it is very similar to a SC approximation put forth many years ago by one of us.²² Heller²³ has given a particularly illuminating discussion of this type of “Wigner overlap” approximation (and its limitations) and used it for photodissociation. Lee and Scully²⁴ have used it to treat inelastic scattering. More recently, Filinov²⁵ has presented an approach for evaluating time correlation functions that starts with the Wigner transform of the quantum trace expression, the lowest order approximation is Eq. (2.12). Pollack *et al.*¹³ have presented a “quantum transition state theory” that utilizes this expression also. The reason we have emphasized that the result is obtained by linearizing the SC-IVR expression [Eq. (2.2)] is that it suggests immediately how one can improve the LSC-IVR: e.g., by keeping higher order terms in the expansion in $\Delta \mathbf{q}$ and $\Delta \mathbf{p}$, or simply by evaluating the full SC-IVR expression numerically. Indeed, in our own recent work,¹² we saw that the full SC-IVR describes quantum effects in the flux correlation function to significantly longer times than the more approximate LSC-IVR. A more conventional treatment of quantum corrections²⁵ to the time evolution of the Wigner function leads to *additive* corrections of order \hbar^2 , but these cannot describe quantum interference and tunneling behavior (as the full SC-IVR can).

III. THE DYNAMICALLY CONSISTENT TREATMENT OF ELECTRONIC AND NUCLEAR DEGREES OF FREEDOM

Some years ago McCurdy, Meyer, and Miller^{8,26} showed in a series of papers how one could introduce classical degrees of freedom that model a finite number (N , say) of electronic states. In the Cartesian representation for these classical electronic degrees of freedom, the Meyer–Miller (MM) version of this approach gives the following classical Hamiltonian for the electronic $(\mathbf{x}, \mathbf{p}) \equiv \{x_i, p_i\}$, $i = 1 \cdots N$ and nuclear (\mathbf{Q}, \mathbf{P}) degrees of freedom (assumed for simplicity to be Cartesian)

$$H(\mathbf{x}, \mathbf{p}, \mathbf{Q}, \mathbf{P}) = \frac{\mathbf{P}^2}{2\mu} + H_{\text{el}}(\mathbf{x}, \mathbf{p}; \mathbf{Q}) \quad (3.1a)$$

with

$$H_{\text{el}}(\mathbf{x}, \mathbf{p}; \mathbf{Q}) = \sum_{i=1}^N H_{i,i}(\mathbf{Q}) \frac{1}{2} (x_i^2 + p_i^2 - 1) + \sum_{i < j=1}^N H_{i,j}(\mathbf{Q}) (x_i x_j + p_i p_j), \quad (3.1b)$$

where $H_{i,j}(\mathbf{Q})$ is a diabatic electronic Hamiltonian matrix that depends parametrically on nuclear coordinates \mathbf{Q} and is assumed to come from a quantum mechanical electronic structure calculation. (We note that Stock and Thoss¹⁰ have recently shown that this Hamiltonian can also be obtained by extending Schwinger’s angular momentum formalism to the N -level case.) MM used this Hamiltonian to carry out classical trajectory simulations, treating electronic and nuclear degrees of freedom on the same footing; i.e., the initial conditions for the nuclear and electronic degrees of freedom are both sampled by the standard “quasiclassical” prescription (integer values for the initial action variables and random angle variables), histogramming the final action variables to obtain final electronic and nuclear quantum states. The i th electronic state, for example, corresponds to action variable $n_i = \frac{1}{2} (x_i^2 + p_i^2 - 1)$ equal to one, and all other action variables $n_j = 0$ ($j \neq i$). [It is easy to show that with the Hamiltonian of Eq. (3.1) the sum of the electronic action variables is a constant of the motion, i.e., $(d/dt) \sum_{i=1}^N n_i(t) = 0$.] A variety of applications using this model were quite successful.²⁷

More recently, two of us⁹ showed how this classical electronic-nuclear model could be implemented at the SC-IVR level of description, and calculations using the full SC-IVR gave excellent results for Tully’s electronically nonadiabatic model problems. Stock and Thoss¹⁰ also carried out SC-IVR calculations using Eq. (3.1) for the case of a two-level system coupled to one harmonic oscillator, also obtaining excellent agreement with quantum results. (Meyer and Miller,⁸ in fact, also noted that the model could be implemented semiclassically and gave some results of this using “classical S-matrix” theory,²⁸ i.e., the stationary phase limit of the SC-IVR.) All that is needed to apply Eq. (2.2) of the previous section are the initial and final electronic-nuclear wavefunctions, which are of the form

$$\Psi_{i,n}(\mathbf{x}, \mathbf{Q}) = \Phi_i(\mathbf{x}) \chi_n(\mathbf{Q}), \quad (3.2)$$

the nuclear wave function $\chi_n(\mathbf{Q})$ is as before, and the electronic wave function for state i is

$$\Phi_i(\mathbf{x}) = \phi_1(x_i) \prod_{j=1, j \neq i}^N \phi_0(x_j), \quad (3.3a)$$

where $\phi_0(x)$ and $\phi_1(x)$ are the ground and first excited harmonic oscillator wave functions, respectively; thus one has the specific form

$$\Phi_i(\mathbf{x}) = \sqrt{2} \left(\frac{1}{\pi} \right)^{N/4} x_i \exp \left[- \sum_{k=1}^N \frac{1}{2} x_k^2 \right]. \quad (3.3b)$$

The model of the electronic degrees of freedom is thus that of a harmonic oscillator for each electronic state; the i th electronic state corresponds to one vibrational quantum in the i th mode, with all the other modes being in their ground state.

Though the construction of this nuclear-electronic Hamiltonian in Eq. (3.1) was motivated by the desire to have a *classical* model that treated the electronic and nuclear dynamics on an equal footing, it is important to note that the quantum mechanical Hamiltonian operator corresponding to Eq. (3.1) is an *exact* representation of the *quantum* electronic-nuclear dynamical system. This is easy to see because the matrix of the “electronic” Hamiltonian operator \hat{H}_{el} of Eq. (3.1)

$$\begin{aligned} \hat{H}_{\text{el}} = & \sum_{i=1}^N H_{i,i}(\mathbf{Q}) \frac{1}{2} (\hat{x}_i^2 + \hat{p}_i^2 - 1) \\ & + \sum_{i < j=1}^N H_{i,j}(\mathbf{Q}) (\hat{x}_i \hat{x}_j + \hat{p}_i \hat{p}_j), \end{aligned} \quad (3.4)$$

in the basis $\{\Phi_i(\mathbf{x})\}$ of Eq. (3.3) is the original diabatic electronic matrix, i.e.,

$$\langle \Phi_i | \hat{H}_{\text{el}} | \Phi_j \rangle = H_{i,j}(\mathbf{Q}), \quad (3.5)$$

as can be easily verified by using standard harmonic oscillator matrix elements. Furthermore, the total electronic quantum number $\sum_{i=1}^N n_i$ is conserved by \hat{H}_{el} (just as the sum of the action variables is classically), so that the N states $|\Phi_i\rangle$ have no matrix elements with any other oscillator states.

We also note the interesting property that if the dynamics is such that the nuclear trajectory $\mathbf{Q}(t)$ does not depend on the electronic degrees of freedom—e.g., because of high nuclear kinetic energy, weak coupling, etc.—then the SC-IVR treatment of the electronic transition probability will be *exact*. This is because the electronic Hamiltonian in this case, $H_{\text{el}}(\mathbf{x}, \mathbf{p}; \mathbf{Q}(t))$, is a time-dependent quadratic Hamiltonian, for which the semiclassical approximation of Eq. (2.2) is exact. This is a bonus for the SC-IVR, so that to the extent that the nuclear trajectory is not effected much by the electronic degrees of freedom, it will be especially accurate.

The purpose of the present paper is to apply the simplified approximate version of the SC-IVR, i.e., the LSC-IVR result given by Eqs. (2.7) and (2.12), to the MM model of electronically nonadiabatic processes, to see if it is capable of describing them to a useful degree of accuracy. One thus

needs the Wigner functions corresponding to initial and final wave functions of the form in Eqs. (3.2) and (3.3), and it is easy to see that they are given by

$$\rho_{i,n}(\mathbf{x}, \mathbf{p}, \mathbf{Q}, \mathbf{P}) = \rho_i^{\text{el}}(\mathbf{x}, \mathbf{p}) \rho_n(\mathbf{Q}, \mathbf{P}), \quad (3.6)$$

where the electronic factor is especially simple

$$\rho_i^{\text{el}}(\mathbf{x}, \mathbf{p}) = 2^{(N+1)} (x_i^2 + p_i^2 - \frac{1}{2}) \exp \left[- \sum_{k=1}^N (x_k^2 + p_k^2) \right]. \quad (3.7)$$

Finally, it is useful to remind the reader of the connection of the present approach to the “mixed quantum-classical”^{29–32} (or semiclassical time-dependent self-consistent field, SC-TDSCF) model that is popular for treating nonadiabatic molecular dynamics. As has been noted before,⁸ the classical equations of motion generated by the MM Hamiltonian [Eq. (3.1)] are equivalent to the time-dependent Schrödinger equation for the electronic degrees of freedom, the time dependence coming from the classical motion of the nuclear degrees of freedom (whose trajectory is determined by the Ehrenfest average force); these are the same equations of motion as in the mixed quantum-classical/SC-TDSCF model. However, the way the boundary conditions are imposed makes the models different. In the usual implementation of the mixed quantum-classical/SC-TDSCF approach, for example, a given classical trajectory begins in one electronic state but ends up in a mixture of states. The quasiclassical implementation by MM assigns each trajectory to a particular final electronic (and nuclear) state by histogramming the final electronic (and nuclear) action variables; this makes the approach more akin to the surface-hopping model in that a given trajectory is assigned to only one final electronic state. The SC-IVR imposes the initial and final state boundary conditions on the equations of motion through the initial and final wave functions of the electronic and nuclear degrees of freedom (or via the initial and final Wigner functions in the approximate LSC-IVR version), and as noted above, if the Hamiltonian of Eq. (3.1) were implemented fully quantum mechanically, one would have an exact quantum description of the process. The point of view of all of our work, starting with that of McCurdy *et al.*,²⁶ is that the Hamiltonian of Eq. (3.1) allows one to treat the electronic and nuclear degrees of freedom on an equivalent dynamical footing, be it done classically, semiclassically, or fully quantum mechanically.

IV. TEST APPLICATIONS

Here we apply the LSC-IVR, Eqs. (2.7) and (2.12), to several examples to test its accuracy.

A. One-dimensional two-state scattering problems

The first example is the set of three one- (nuclear) dimensional two (electronic)-state scattering problems that Tully¹⁴ used several years ago to test his “fewest switches” version of the surface-hopping model for electronically nonadiabatic dynamics. Two of us also recently used⁹ these model problems to test the full SC-IVR of Sec. II for treating the MM model of Sec. III. We thus refer the reader to Refs.

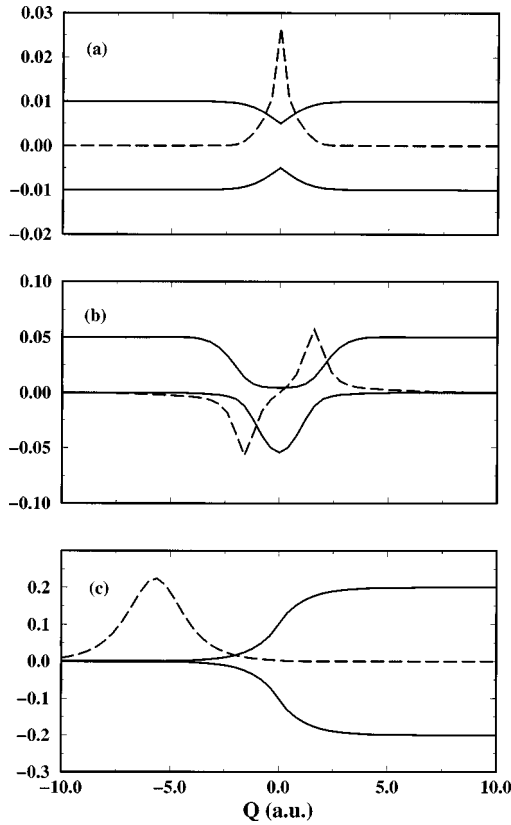


FIG. 1. The adiabatic potential curves (solid line) and the nonadiabatic coupling (dash line) for the three model scattering problems discussed in Sec. IV A. (a) Single avoided crossing. The nonadiabatic coupling is reduced by a factor of 60. (b) Double avoided crossing. The nonadiabatic coupling is reduced by a factor of 15. (c) Extended coupling.

14 and 9 for the specifics of the models and here give only the new features relevant to applying the LSC-IVR to it. Figure 1 shows the two adiabatic potential curves for these three cases.

Equation (3.1) gives the Hamiltonian of the system, with $N=2$ electronic degrees of freedom and one nuclear (translational) degree of freedom (Q, P). The initial nuclear wave function is a minimum uncertainty wave packet

$$\chi(Q) = \left(\frac{\gamma}{\pi}\right)^{1/4} e^{-(\gamma/2)(Q-Q_0)^2 + iP_0 Q/\hbar}, \quad (4.1)$$

with the initial position Q_0 far to the left of the interaction region in Fig. 1 and initial momentum $P_0 > 0$. The quantity of interest is the transmission probability to the right asymptotic region for each final electronic state j as a function of the initial momentum, which is given by

$$P_{j \leftarrow i}(P_0) = \lim_{t \rightarrow \infty} \int_0^\infty |\langle \phi_j, Q | e^{-i\hat{H}t/\hbar} | \chi \phi_i \rangle|^2 dQ. \quad (4.2)$$

This can be written equivalently as

$$P_{j \leftarrow i}(P_0) = \lim_{t \rightarrow \infty} \text{tr} [| \chi \phi_i \rangle \langle \chi \phi_i | e^{i\hat{H}t/\hbar} | \phi_j \rangle \langle \phi_j | e^{-i\hat{H}t/\hbar}], \quad (4.3)$$

so as to be in the form of Eq. (2.12) with

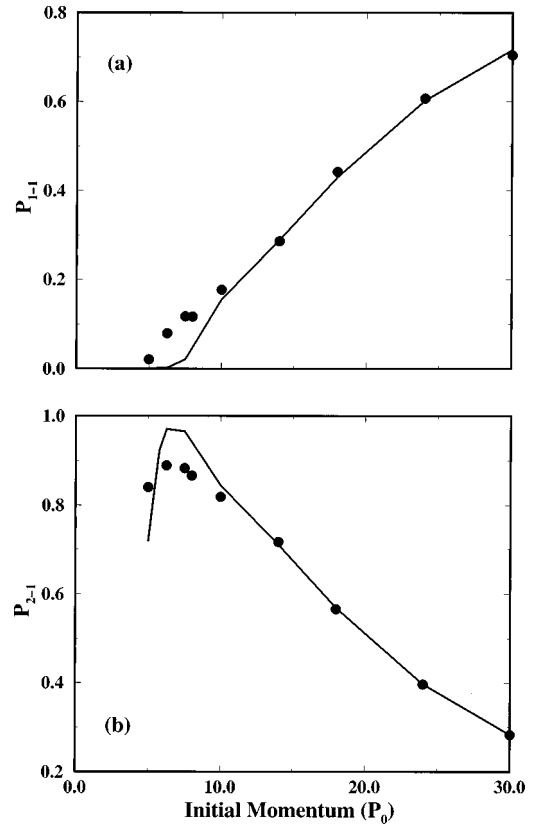


FIG. 2. The transmission probability P_{j-1} as a function of the initial momentum P_0 for the single avoided crossing case. The solid lines are the exact quantum results and the points are the LSC-IVR results. (a) $j=1$, (b) $j=2$.

$$\hat{A} = | \chi \phi_i \rangle \langle \chi \phi_i |, \quad (4.4)$$

$$\hat{B} = | \phi_j \rangle \langle \phi_j | \hat{h}(Q). \quad (4.5)$$

The Wigner functions corresponding to these operators are easily found to be

$$A_w(Q, P, \mathbf{x}, \mathbf{p}) = \rho(Q, P) \rho_i^{\text{el}}(\mathbf{x}, \mathbf{p}), \quad (4.6)$$

$$B_w(Q, P, \mathbf{x}, \mathbf{p}) = h(Q) \rho_j^{\text{el}}(\mathbf{x}, \mathbf{p}), \quad (4.7)$$

where $\rho(Q, P)$ is the Wigner function for the initial nuclear wave function of Eq. (4.1)

$$\rho(Q, P) = 2e^{-\gamma(Q-Q_0)^2 - (P-P_0)^2/\gamma\hbar^2}, \quad (4.8)$$

and $\{\rho_i^{\text{el}}(\mathbf{x}, \mathbf{p})\}$, $i=1,2$ is given by Eq. (3.7) for $N=2$. In actual calculations, these Wigner distributions allow naturally for Monte Carlo importance sampling which we have used for the results presented below.

Figure 2 shows the transmission probability from initial electronic state one to each of the two final electronic states for the first test case, which corresponds to a single avoided crossing [cf. Fig. 1(a)]. The agreement between the LSC-IVR results of Eq. (2.12) and the exact quantum mechanical values is quite good for all energies except those close to the threshold region. Here, quantum mechanical effects such as tunneling through the crossing area are more important, and the classical dynamics in the LSC-IVR is less able to describe this behavior quantitatively.

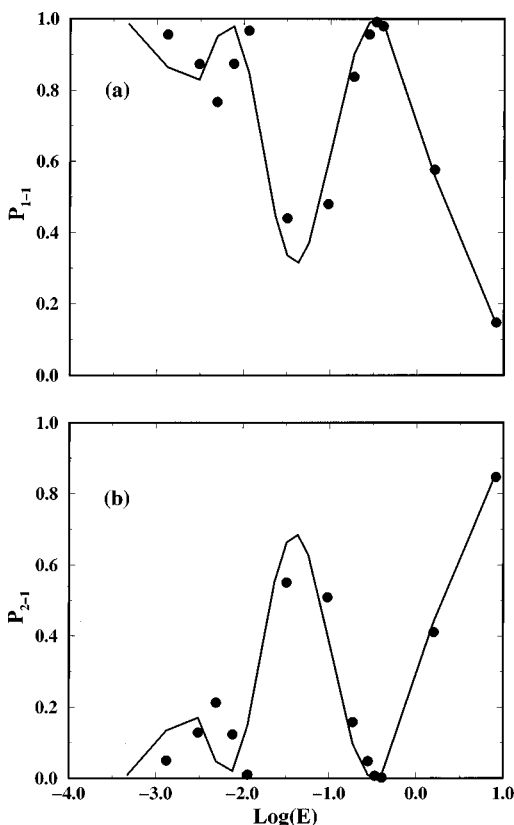


FIG. 3. The transmission probability P_{j-1} as a function of the log of initial energy $E = P_0^2/2m$ for the double crossing case. The solid lines are the exact quantum results and the points are the LSC-IVR results. (a) $j=1$, (b) $j=2$.

Figure 3 shows the same plots as Fig. 2 for the second version of the model, the case of two avoided crossing regions [cf. Fig. 1(b)], where the possibility of Stueckelberg oscillations (i.e., interference effects between the two crossing regions) arises. The LSC-IVR is seen to describe this interference behavior quite well. The most significant error is again seen to be in the low-energy threshold region.

Finally, Fig. 4 shows the transmission probability for the

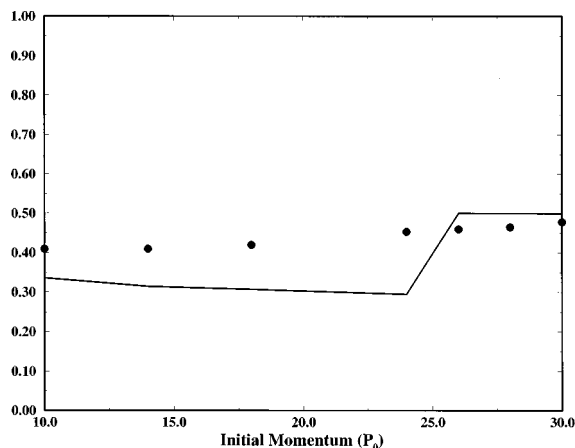


FIG. 4. The transmission probability P_{j-1} as a function of the initial momentum P_0 for the extended coupling case. The solid lines are the exact quantum results and the points are the LSC-IVR results. These results are for $j=1$ and 2.

third case, that with an extended coupling region [cf. Fig. 1(c)]. Since the diabatic states are very close in energy, the transmission probabilities are essentially identical for both final states. This was the case for which Tully's surface-hopping approach gave unphysical oscillations in the transmission probability. The LSC-IVR results do not exhibit this problem, and they do not reproduce the sharp steplike structure in the quantum values for $P_0 \approx 25$ a.u. They do, however, give the correct magnitude of the transmission probability over the whole energy range.

The linearized approximation to the SC-IVR, i.e., the LSC-IVR approximation of Eqs. (2.7) and (2.12), is thus seen to do a reasonably good job for these three model problems which have quite different dynamical features. The results are not quite as good as our previous ones⁹ using the full SC-IVR, but the present LSC-IVR calculation is much easier to carry out than the former.

B. The spin-boson problem

The next test problem we consider is the so-called spin-boson problem,¹⁵ which also consists of $N=2$ electronic states but where the nuclear degrees of freedom are an infinite set of harmonic oscillators. This is about the only example of a system with many degrees of freedom for which accurate quantum mechanical results are available to serve as a benchmark for approximate treatments. It has often been used as a model for two interacting electronic states in a condensed phase medium, e.g., a radiationless transition or electron transfer process in a liquid, a solid, a cluster, or a protein.

The specific form of the 2×2 diabatic electronic matrix $H_{i,j}(\mathbf{Q})$ in this case is

$$\hat{H}_{\text{el}}(\mathbf{Q}) = \begin{pmatrix} H_{11}(\mathbf{Q}) & H_{12}(\mathbf{Q}) \\ H_{21}(\mathbf{Q}) & H_{22}(\mathbf{Q}) \end{pmatrix} = \begin{pmatrix} V_0(\mathbf{Q}) + V_1(\mathbf{Q}) & \Delta \\ \Delta & V_0(\mathbf{Q}) - V_1(\mathbf{Q}) \end{pmatrix}, \quad (4.9)$$

where the off-diagonal electronic coupling Δ is independent of nuclear coordinates, and

$$V_0(\mathbf{Q}) = \sum_{k=1}^F \frac{1}{2} m_k \omega_k^2 Q_k^2, \quad (4.10a)$$

$$V_1(\mathbf{Q}) = \sum_{k=1}^F c_k Q_k. \quad (4.10b)$$

The total Hamiltonian of the spin-boson model

$$\hat{H} = \hat{\mathbf{I}} \sum_{k=1}^F \frac{P_k^2}{2m_k} + \hat{H}_{\text{el}}(\mathbf{Q}), \quad (4.11a)$$

is typically expressed as

$$\hat{H} = H_0 \hat{\mathbf{I}} + V_1(\mathbf{Q}) \hat{\sigma}_z + \Delta \hat{\sigma}_x \quad (4.11b)$$

where

$$H_0 = \sum_{k=1}^F \frac{P_k^2}{2m_k} + V_0(\mathbf{Q}), \quad (4.12)$$

and $\hat{\sigma}_z$ and $\hat{\sigma}_x$ are the Pauli spin matrices. The dynamics of the spin–boson model is fully specified by the combination of the coupling parameters $\{c_k\}$ and the distribution of frequencies that define the spectral density $J(\omega)$

$$J(\omega) = \frac{\pi}{2} \sum_k \frac{c_k^2}{m_k \omega_k} \delta(\omega - \omega_k), \quad (4.13)$$

a common choice for which is the Ohmic case with exponential cutoff

$$J(\omega) = \eta \omega e^{-\omega/\omega_c}. \quad (4.14)$$

This model is thus completely specified by the cutoff parameter ω_c and the coupling coefficient η (or more frequently the Kondo parameter $\alpha = 2\eta/\pi$).

We examine two relevant dynamical quantities of interest for the spin–boson model: The first is the time-dependent electronic population, defined as

$$D(t) = \frac{1}{Z_b} \text{tr}[e^{-\beta(H_0 + V_1)} |1\rangle\langle 1| e^{i\hat{H}t/\hbar} \hat{\sigma}_z e^{-i\hat{H}t/\hbar}] \\ = \bar{P}_{1 \leftarrow 1}(t) - \bar{P}_{2 \leftarrow 1}(t), \quad (4.15)$$

where the initial electronic state is $|1\rangle$ with the nuclear degrees of freedom in Boltzmann equilibrium for the nuclear Hamiltonian of state 1, $H_0 + V_1$ ($Z_b = \text{tr}[|1\rangle\langle 1| e^{-\beta(H_0 + V_1)}]$); the second quantity is the spin correlation function, defined as

$$C(t) = \text{Re} \frac{1}{Z} \text{tr}[e^{-\beta\hat{H}} \hat{\sigma}_z e^{i\hat{H}t/\hbar} \hat{\sigma}_z e^{-i\hat{H}t/\hbar}], \quad (4.16)$$

where the bath and the two-level system are both in thermal equilibrium, and Z is the total partition function of the system and bath. The literature on these quantities for the spin–boson model is vast: Mak and Chandler,¹⁶ for example, performed a systematic study of the spin-correlation function for a wide range of parameters to determine, among other things, the coherent–incoherent transition boundary. They also studied the temperature dependence of the decay rate of $C(t)$ for several sets of parameters. Makri *et al.*³³ performed calculations of the time-dependent electronic population also using path integral methods. These are the primary results to which we shall compare the LSC-IVR approximation.

For the spin–boson Hamiltonian in Eq. (4.11), the MM Hamiltonian of Eq. (3.1) is easily found to be

$$H(\mathbf{x}, \mathbf{p}, \mathbf{Q}, \mathbf{P}) = \sum_{k=1}^F \left[\frac{P_k^2}{2m_k} + \frac{1}{2} m_k \omega_k^2 Q_k^2 \right] \\ + \frac{1}{2} (x_1^2 + p_1^2 - x_2^2 - p_2^2) \sum_{k=1}^F c_k Q_k \\ + \Delta (x_1 x_2 + p_1 p_2). \quad (4.17)$$

It is also immediately clear how to apply the LSC-IVR approximation of Eq. (2.12). For the time-dependent electronic population of Eq. (4.15), the operators \hat{A} and \hat{B} of Eq. (2.12) are

$$\hat{A} = \frac{1}{Z_b} e^{-\beta(H_0 + V_1)} |1\rangle\langle 1|, \quad (4.18)$$

$$\hat{B} = \hat{\sigma}_z = (|1\rangle\langle 1| - |2\rangle\langle 2|), \quad (4.19)$$

so that Eq. (2.12) give $D(t)$ as

$$D(t) = \frac{1}{(2\pi\hbar)^2} \int d\mathbf{x}_0 d\mathbf{p}_0 \int d\mathbf{Q}_0 d\mathbf{P}_0 W_\beta^+(\mathbf{Q}_0, \mathbf{P}_0) \rho_1^{\text{el}}(\mathbf{x}_0, \mathbf{p}_0) \\ \times [\rho_1^{\text{el}}(\mathbf{x}_t, \mathbf{p}_t) - \rho_2^{\text{el}}(\mathbf{x}_t, \mathbf{p}_t)], \quad (4.20)$$

where $W_\beta^\pm(\mathbf{Q}, \mathbf{P})$ is the Wigner transform of $e^{-\beta(H_0 \pm V_1)}/[Z_b(2\pi\hbar)^F]$

$$W_\beta^\pm(\mathbf{Q}, \mathbf{P}) = \prod_{k=1}^F \frac{\tanh(\beta\hbar\omega_k/2)}{\pi\hbar} \\ \times \exp \left\{ \sum_{k=1}^F \frac{2 \tanh(\beta\hbar\omega_k/2)}{\hbar\omega_k} \right. \\ \left. \times \left[\frac{P_k^2}{2m_k} + \frac{1}{2} m_k \omega_k^2 \left(Q_k \pm \frac{c_k}{m_k \omega_k^2} \right)^2 \right] \right\} \quad (4.21)$$

and $\rho_n^{\text{el}}(\mathbf{x}, \mathbf{p})$ is the Wigner transform of $|n\rangle\langle n|$ already given in Eq. (3.7) ($n=1,2$).

For the spin-correlation function of Eq. (4.16), the situation is slightly more complicated. In this case the operators \hat{A} and \hat{B} of Eq. (2.12) are

$$\hat{A} = \frac{1}{Z} e^{-\beta\hat{H}} \sigma_z, \quad (4.22)$$

$$\hat{B} = \hat{\sigma}_z, \quad (4.23)$$

one needs to find the Wigner transform of \hat{A} . It is not possible to obtain this quantity exactly without a fully quantum calculation, but a reasonable approximation can be obtained by using a split operator type approximation for $e^{-\beta\hat{H}}$

$$\exp \begin{pmatrix} -\beta(H_0 + V_1) & -\beta\Delta \\ -\beta\Delta & -\beta(H_0 - V_1) \end{pmatrix} \\ \approx \begin{pmatrix} e^{-\beta(H_0 + V_1)} & 0 \\ 0 & e^{-\beta(H_0 - V_1)} \end{pmatrix} \exp \begin{pmatrix} 0 & -\beta\Delta \\ -\beta\Delta & 0 \end{pmatrix} \\ = \begin{pmatrix} e^{-\beta(H_0 + V_1)} \cosh(\beta\Delta) & -e^{-\beta(H_0 + V_1)} \sinh(\beta\Delta) \\ -e^{-\beta(H_0 - V_1)} \sinh(\beta\Delta) & e^{-\beta(H_0 - V_1)} \cosh(\beta\Delta) \end{pmatrix}. \quad (4.24)$$

The trace of $e^{-\beta\hat{H}}$, which is the partition function Z , is then

$$Z = 2 \cosh(\beta\Delta) \text{tr}(e^{-\beta H_0}) \exp \left[\beta \sum_{k=1}^F \frac{c_k^2}{2m_k \omega_k^2} \right]. \quad (4.25)$$

Multiplying by $\hat{\sigma}_z$ and writing everything in the basis set representation, one obtains

$$\begin{aligned}
e^{-\beta \hat{H}} \hat{\sigma}_z &= \begin{pmatrix} e^{-\beta(H_0+V_1)} \cosh(\beta\Delta) & e^{-\beta(H_0+V_1)} \sinh(\beta\Delta) \\ -e^{-\beta(H_0-V_1)} \sinh(\beta\Delta) & -e^{-\beta(H_0-V_1)} \cosh(\beta\Delta) \end{pmatrix} \\
&= e^{-\beta(H_0+V_1)} \cosh(\beta\Delta) |1\rangle\langle 1| \\
&\quad + e^{-\beta(H_0+V_1)} \sinh(\beta\Delta) |1\rangle\langle 2| \\
&\quad - e^{-\beta(H_0-V_1)} \sinh(\beta\Delta) |2\rangle\langle 1| \\
&\quad - e^{-\beta(H_0-V_1)} \cosh(\beta\Delta) |2\rangle\langle 2|, \quad (4.26)
\end{aligned}$$

so that the final result for the Wigner transform of $e^{-\beta \hat{H}} \hat{\sigma}_z / [Z(2\pi\hbar)^F]$ is

$$\begin{aligned}
&\frac{1}{(2\pi\hbar)^F} A_w(\mathbf{x}, \mathbf{p}, \mathbf{Q}, \mathbf{P}) \\
&= W_\beta^+(\mathbf{Q}, \mathbf{P}) [\cosh(\beta\Delta) \rho_{11}^{\text{el}}(\mathbf{x}, \mathbf{p}) + \sinh(\beta\Delta) \rho_{12}^{\text{el}}(\mathbf{x}, \mathbf{p})] \\
&\quad - W_\beta^-(\mathbf{Q}, \mathbf{P}) [\sinh(\beta\Delta) \rho_{21}^{\text{el}}(\mathbf{x}, \mathbf{p}) \\
&\quad + \cosh(\beta\Delta) \rho_{22}^{\text{el}}(\mathbf{x}, \mathbf{p})], \quad (4.27)
\end{aligned}$$

where ρ_{12}^{el} and ρ_{21}^{el} are the Wigner transform of $|1\rangle\langle 2|$ and $|2\rangle\langle 1|$

$$\begin{aligned}
\rho_{12}^{\text{el}}(\mathbf{x}, \mathbf{p}) &= 2^3 (x_1 - ip_1)(x_2 + ip_2) \\
&\quad \times \exp[-(x_1^2 + x_2^2 + p_1^2 + p_2^2)], \quad (4.28)
\end{aligned}$$

$$\begin{aligned}
\rho_{21}^{\text{el}}(\mathbf{x}, \mathbf{p}) &= 2^3 (x_1 + ip_1)(x_2 - ip_2) \\
&\quad \times \exp[-(x_1^2 + x_2^2 + p_1^2 + p_2^2)], \quad (4.29)
\end{aligned}$$

and $W_\beta^\pm(\mathbf{Q}, \mathbf{P})$ is given in Eq. (4.21). The final result for the LSC-IVR approximation to $C(t)$ is, therefore

$$\begin{aligned}
C(t) &= \text{Re} \frac{1}{(2\pi\hbar)^2} \int d\mathbf{x}_0 d\mathbf{p}_0 \int d\mathbf{Q}_0 d\mathbf{P}_0 \{ W_\beta^+(\mathbf{Q}, \mathbf{P}) \\
&\quad \times [\cosh(\beta\Delta) \rho_{11}^{\text{el}}(\mathbf{x}, \mathbf{p}) + \sinh(\beta\Delta) \rho_{12}^{\text{el}}(\mathbf{x}, \mathbf{p})] \\
&\quad - W_\beta^-(\mathbf{Q}, \mathbf{P}) [\sinh(\beta\Delta) \rho_{21}^{\text{el}}(\mathbf{x}, \mathbf{p}) \\
&\quad + \cosh(\beta\Delta) \rho_{22}^{\text{el}}(\mathbf{x}, \mathbf{p})] \} [\rho_1^{\text{el}}(\mathbf{x}_t, \mathbf{p}_t) - \rho_2^{\text{el}}(\mathbf{x}_t, \mathbf{p}_t)]. \quad (4.30)
\end{aligned}$$

Equations (4.20) and (4.30) are the final LSC-IVR expressions for $D(t)$ and $C(t)$.

For comparison, Stock³² recently carried out calculations for $D(t)$ using the mixed quantum-classical/SC-TDSCF approach, where the electronic transition between the two-level system is treated quantum mechanically but the bath is treated classically. This approximation gives $D(t)$ in a form similar to Eq. (4.20),

$$\begin{aligned}
D(t) &= \frac{1}{2\pi} \int_0^{2\pi} d\theta \int d\mathbf{Q}_0 d\mathbf{P}_0 W_\beta^+(\mathbf{Q}_0, \mathbf{P}_0) \\
&\quad \times [\rho_1^{\text{TDSCF}}(\mathbf{x}_t, \mathbf{p}_t) - \rho_2^{\text{TDSCF}}(\mathbf{x}_t, \mathbf{p}_t)], \quad (4.31)
\end{aligned}$$

where $\rho_{1,2}^{\text{TDSCF}}$ is the probability of being in state 1 or 2. In our language, these probability functions are

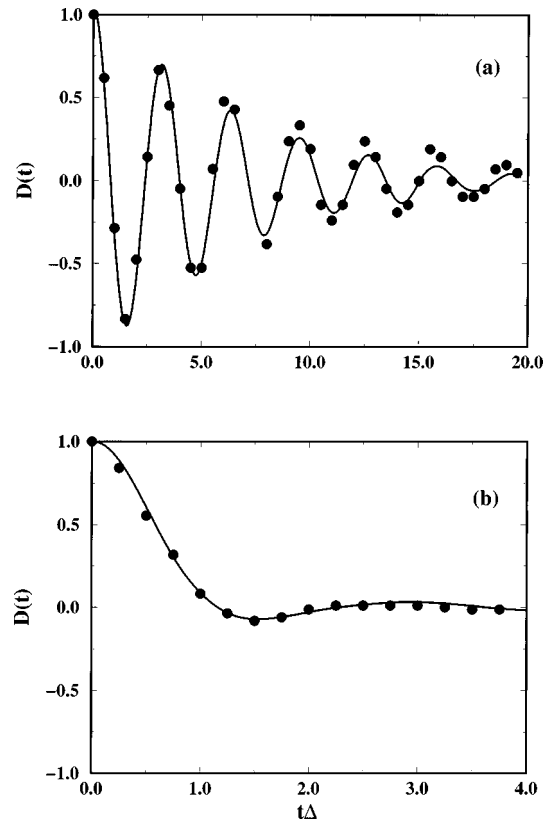


FIG. 5. The time-dependent electronic population, $D(t)$, for two different parameter sets, showing (a) coherent oscillatory behavior and (b) incoherent relaxation behavior. The solid lines are the LSC-IVR results and the points are the exact path integral results. The cutoff frequency is $\omega_c = 2.5\Delta$. (a) $\alpha = 0.09$, $\beta\Delta = 5.0$. (b) $\alpha = 0.09$, $\beta\Delta = 0.1$.

$$\rho_1^{\text{TDSCF}}(\mathbf{x}_t, \mathbf{p}_t) - \rho_2^{\text{TDSCF}}(\mathbf{x}_t, \mathbf{p}_t) = (x_{1t}^2 + p_{1t}^2 - x_{2t}^2 - p_{2t}^2) \quad (4.32)$$

and the initial conditions of the electronic trajectories are

$$\begin{aligned}
x_{10} &= \cos(\theta), \\
p_{10} &= \sin(\theta), \quad (4.33)
\end{aligned}$$

$$x_{20} = p_{20} = 0, \quad (4.34)$$

where the θ ranges from 0 to 2π . It is clear that this is very different from our present approach.

Figure 5 shows the decay of the time-dependent electronic population, $D(t)$, for a ‘coherent’ (i.e., oscillatory) case, Fig. 5(a), and also an ‘incoherent’ (nonoscillatory) one, Fig. 5(b). The LSC-IVR results are seen to be in excellent agreement with Makri *et al.*’s³³ accurate quantum results, showing that the LSC-IVR captures the essential features of the dynamics in both these cases. This also makes it clear that the oscillatory nature in the coherent case [Fig. 5(a)] is of classical rather than quantum mechanical origin. For stronger couplings, i.e., larger α , the LSC-IVR results begin to deviate somewhat from the quantum results, as shown in Fig. 6. However, the differences are still modest, and the LSC-IVR is in somewhat better agreement with the quantum results than the mixed quantum-classical/SC-TDSCF results obtained by Stock.

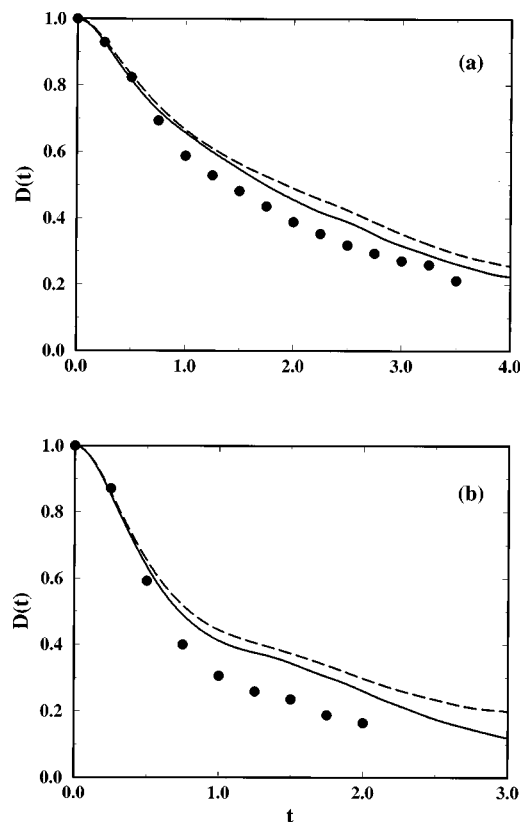


FIG. 6. The time-dependent electronic population, $D(t)$, for higher coupling parameters, comparing the LSC-IVR results (solid line) and the mixed quantum-classical/SC-TDSCF results (dashed line) with the exact quantum results (points). $\alpha=2.0$, $\omega_c=1$ and $\beta=0.25$. (a) $\Delta=0.8$. (b) $\Delta=1.2$.

Mak and Chandler¹⁶ studied the behavior of the spin correlation function, $C(t)$, for a variety of different parameters and determined the boundary between coherent and incoherent behavior. Figure 7 shows the results obtained from the LSC-IVR expression, Eq. (4.30), for three coupling values that span this boundary. One observes reasonably good agreement of the LSC-IVR results with the correct quantum values in all these case. (The approximations made to the Boltzmann operator, Eqs. (4.24)–(4.27), to obtain the Wigner function for the operator in Eq. (4.23) thus apparently cause no significant error.) The results of the LSC-IVR are actually somewhat better than the “noninteracting blip approximation”³⁴ for treating the spin–boson problem.

If coupling to the bath is sufficiently large, then $C(t)$ exhibits exponential decay for the short time regime, i.e.,

$$C(t) \approx A e^{-t/\tau}, \quad (4.35)$$

so that one can define a rate constant τ^{-1} for transitions from one state of the two level system to the other. Figure 8 shows the results given by Eq. (4.30) for τ as a function of temperature for the parameters $\alpha=0.64$, $\omega_c=2.5\Delta$. The decay rate exhibits the correct inverse power-law dependence on temperature, $\tau \sim T^{-\delta}$, and the LSC-IVR results are essentially in quantitative agreement with the exact results of Mak and Chandler. For higher coupling values, however, the procedure outlined in Eqs. (4.24)–(4.27) for obtaining the Wigner transform involving the Boltzmann operator is not valid, so we will not consider this regime. One could, of course, carry

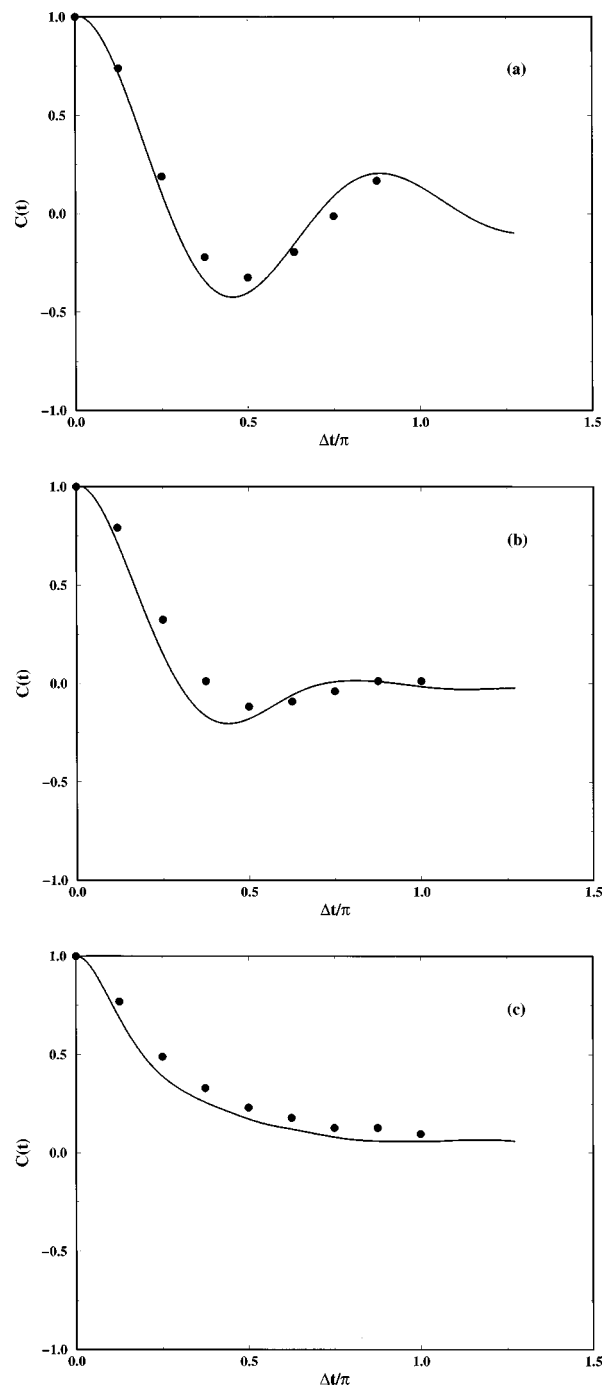


FIG. 7. The spin-correlation function, $C(t)$, for increasing values of the coupling, showing the transition from the coherent to incoherent relaxation. $\omega_c=2.5\Delta$, $\beta=2.5\Delta$. (a) In the coherent relaxation regime, $\alpha=0.13$. (b) Near the coherent–incoherent boundary, $\alpha=0.25$. (c) In the incoherent regime, $\alpha=0.64$. The solid lines are the LSC-IVR results and the points are the exact path integral results.

out a more complete quantum calculation for the Boltzmann operator in order to obtain the Wigner function for the operator in Eq. (4.23), but this is not central to our present discussion of the LSC-IVR.

V. CONCLUDING REMARKS

As shown previously, the semiclassical initial value representation (SC-IVR, summarized in Sec. II) can be general-

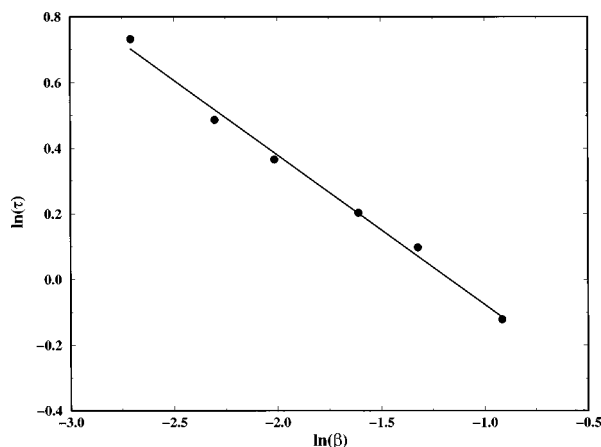


FIG. 8. The temperature dependence of the short time relaxation constant (points) for the spin-correlation function, $C(t)$, obtained with LSC-IVR. $\omega_c = 2.5\Delta$, $\alpha = 0.64$. The temperature dependence follows an inverse power-law, $\tau \approx T^\delta$, indicated by the fitted straight line. The LSC-IVR result for δ is 0.46.

ized to describe electronically nonadiabatic processes in molecular dynamics by utilizing the Meyer–Miller (MM) model to treat electronic and nuclear degrees of freedom on an equivalent footing. The purpose of this paper has been to investigate the usefulness of an approximate version of the SC-IVR for nonadiabatic processes. This LSC-IVR is much easier to apply than the full SC-IVR: As seen from the resulting expressions [Eqs. (2.7) and (2.12)], it involves the overlap of the Wigner distribution function for the initial state (or operator) with the classically time-evolved Wigner distribution for the final state (or operator). The actual dynamics in the LSC-IVR is thus completely classical, the Wigner distribution functions effectively providing the boundary conditions for the classical trajectories.

The LSC-IVR is seen to provide a reasonably good description of the three nonadiabatic scattering problems utilized by Tully, including the effects of Stuckelberg oscillations (interference between nonadiabatic transitions at different times). It also provides a good description of time-dependent transition probabilities in the spin–boson problem (two electronic states coupled to an infinite set of harmonic oscillators), including both coherent and incoherent decay and the transition between them. Altogether, this suggests that the LSC-IVR should be useful for simulating a wide range of nonadiabatic dynamic phenomena in “real” molecular systems.

In conclusion, it should be noted that the LSC-IVR does not describe everything correctly. As seen in our previous work,¹² for example, purely quantum effects in the long time coherent dynamics may not be described correctly. Such effects were apparently not a major contributor in the examples treated in this paper, and this may perhaps often be the case for complex systems, i.e., those with more than a few degrees of freedom.

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