

Forward–backward initial value representation for the calculation of thermal rate constants for reactions in complex molecular systems

Haobin Wang, Michael Thoss, and William H. Miller^{a)}

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

(Received 21 September 1999; accepted 7 October 1999)

The semiclassical (SC) initial value representation (IVR) provides a potentially practical way for including quantum effects into classical molecular dynamics simulations. The forward–backward (FB) version of the IVR provides an especially attractive way for calculating time correlation functions, in particular the reactive flux correlation function which determines chemical reaction rates. This paper presents a further analysis and development of the FB-IVR approach. Applications show that it is feasible and accurate for a reaction coordinate coupled to up to 40 degrees of freedom. © 2000 American Institute of Physics. [S0021-9606(00)01401-X]

I. INTRODUCTION

Although considerable progress has been made over the previous decade in the development of rigorous quantum mechanical methods for calculating thermal (and also micro-canonical) rate constants,¹ they are at present only applicable to relatively small (3–4 atoms) molecular systems. The primary reason is that the finite basis used in these calculations grows exponentially as the number of degrees of freedom increases. Classical molecular dynamics (MD) simulations, on the other hand, are widely used nowadays to describe chemical reactions in quite complex molecular systems, so one inevitably thinks of trying to devise practical ways of incorporating essential quantum effects into classical MD. Semiclassical (SC) initial value representations (IVR)² are currently undergoing a rebirth of interest in this regard,^{3–13} and the present paper is a further development of this methodology and its application. It has been realized for a long time¹ that semiclassical theory is capable of describing essentially all types of quantum effects in molecular dynamics, and a number of recent applications^{3–13} to small molecular systems (and model problems) have shown the IVR version of SC theory to be of good accuracy for a wide variety of phenomena. The primary remaining challenge is to make the SC-IVR approaches practical enough for application to complex molecular systems, and this is the focus of the present paper.

A formally exact expression for the thermal rate constant of a chemical reaction is given in terms of a flux time correlation function,^{14,15}

$$k(T) = Q_r(T)^{-1} \lim_{t \rightarrow \infty} C_{fs}(t), \quad (1.1a)$$

where

$$C_{fs}(t) = \text{tr}[\hat{F}(\beta) e^{i\hat{H}t/\hbar} \hat{h} e^{-i\hat{H}t/\hbar}]. \quad (1.1b)$$

Here, $\beta = (k_B T)^{-1}$, $\hat{F}(\beta)$ is the Boltzmannized flux operator,

$$\hat{F}(\beta) = e^{-\beta\hat{H}/2} \hat{F} e^{-\beta\hat{H}/2}, \quad (1.2a)$$

where the flux operator is given by

$$\hat{F} = \frac{1}{\hbar} [\hat{H}, \hat{h}], \quad (1.2b)$$

\hat{H} is the Hamiltonian operator, \hat{h} the projector that projects the wave functions to the product side, and $Q_r(T)$ is the reactants partition function per unit volume. A semiclassical approximation for $C_{fs}(t)$ can thus be obtained by using the Herman–Kluk or coherent state IVR³ for the time evolution operator of an N -dimensional system,

$$e^{-i\hat{H}t/\hbar} = (2\pi\hbar)^{-N} \int d\mathbf{q}_0 \int d\mathbf{p}_0 C_t(\mathbf{p}_0, \mathbf{q}_0) \times e^{iS_t(\mathbf{p}_0, \mathbf{q}_0)/\hbar} |\mathbf{p}_t, \mathbf{q}_t\rangle \langle \mathbf{p}_0, \mathbf{q}_0|, \quad (1.3)$$

where $(\mathbf{p}_0, \mathbf{q}_0)$ are respectively, initial momenta and coordinates for classical trajectories, $\mathbf{p}_t = \mathbf{p}_t(\mathbf{p}_0, \mathbf{q}_0)$ and $\mathbf{q}_t = \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)$ are the classically time-evolved phase space variables, $S_t(\mathbf{p}_0, \mathbf{q}_0)$ is the classical action integral along the trajectory, and $C_t(\mathbf{p}_0, \mathbf{q}_0)$ is the pre-exponential factor determined by the following combination of the monodromy matrix elements:

$$C_t(\mathbf{p}_0, \mathbf{q}_0) = \sqrt{\det \left[\frac{1}{2} \left(\gamma^{1/2} \frac{\partial \mathbf{q}_t}{\partial \mathbf{q}_0} \gamma^{-1/2} + \gamma^{-1/2} \frac{\partial \mathbf{p}_t}{\partial \mathbf{p}_0} \gamma^{1/2} - i\hbar \gamma^{1/2} \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \gamma^{1/2} + \frac{i}{\hbar} \gamma^{-1/2} \frac{\partial \mathbf{p}_t}{\partial \mathbf{q}_0} \gamma^{-1/2} \right) \right]}. \quad (1.4)$$

^{a)}Electronic mail: miller@neon.cchem.berkeley.edu

In the above expression, γ denotes an N -dimensional diagonal matrix, with element γ_i being the width parameter for the coherent state of the i th dimension. The coordinate space representation of an N -dimensional coherent state is the product of N one-dimensional minimum uncertainty wave packets

$$\langle \mathbf{x} | \mathbf{p} \mathbf{q} \rangle = \prod_{i=1}^N \left(\frac{\gamma_i}{\pi} \right)^{1/4} e^{-(\gamma_i/2)(x_i - q_i)^2 + (i/\hbar)p_i(x_i - q_i)}. \quad (1.5)$$

Since the Heisenberg time evolution in Eq. (1.1b) involves two time evolution operators, use of the IVR of Eq. (1.3) leads to the following double phase space average for the flux correlation function:

$$\begin{aligned} C_{fs}(t) &= (2\pi\hbar)^{-2N} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \int d\mathbf{q}'_0 \int d\mathbf{p}'_0 \\ &\times C_t^*(\mathbf{p}'_0, \mathbf{q}'_0) C_t(\mathbf{p}_0, \mathbf{q}_0) \\ &\times e^{i[S_t(\mathbf{p}_0, \mathbf{q}_0) - S_t(\mathbf{p}'_0, \mathbf{q}'_0)]/\hbar} \langle \mathbf{p}_0 \mathbf{q}_0 | \hat{F}(\beta) | \mathbf{p}'_0 \mathbf{q}'_0 \rangle \\ &\times \langle \mathbf{p}'_0 \mathbf{q}'_0 | \hat{h} | \mathbf{p}_t \mathbf{q}_t \rangle. \end{aligned} \quad (1.6)$$

The practical difficulty with the above formulation is that the integrand in the double phase space average is highly oscillatory and amplified by the large pre-exponential factors $C_t(\mathbf{p}_0, \mathbf{q}_0)$ and $C_t(\mathbf{p}'_0, \mathbf{q}'_0)$. Although various kinds of smoothing methods^{16,8} have been used to damp the phase oscillations, things become increasingly more difficult as the dimension of the integral grows. To side-step this problem, a linearized approximation to the SC-IVR expression in Eq. (1.6), the LSC-IVR, was introduced,¹⁷ whereby all the relevant quantities are expanded to first order in the difference variables $\mathbf{p}_0 - \mathbf{p}'_0$ and $\mathbf{q}_0 - \mathbf{q}'_0$. The integration over these difference variables can be carried out analytically, which yields the following much simpler expression for Eq. (1.1b):

$$C_{fs}(t) = (2\pi\hbar)^{-N} \int d\mathbf{q}_0 \int d\mathbf{p}_0 F_\beta^w(\mathbf{p}_0, \mathbf{q}_0) h^w(\mathbf{p}_t, \mathbf{q}_t), \quad (1.7)$$

where F_β^w and h^w are the Wigner transforms of operators $\hat{F}(\beta)$ and \hat{h} , i.e., this linearization of the SC-IVR leads to the ‘‘classical Wigner’’ model that has arisen before from a variety of approaches.¹⁸ Application of this approximation to several interesting condensed phase problems^{17,19} was quite successful. A more thorough analysis,²⁰ however, showed that though the LSC-IVR is able to describe quantum effects in $C_{fs}(t)$ for short time, $t \sim \hbar\beta$ —and is therefore sufficient for describing quantum effects in transition state theory²¹—it cannot describe quantum effects in the longer time dynamics. It is thus desirable to develop a method that goes beyond this linearized approximation that can capture the important quantum interference effects, but is still more efficient than evaluating Eq. (1.6).

To this end, Sun and Miller have proposed a ‘‘forward–backward’’ (FB) IVR approach for the time correlation function calculation²² (motivated by Makri and Thompson’s use of the FB idea to evaluate anharmonic influence functionals²³). Here, the operator product $e^{i\hat{H}t/\hbar} \hat{h} e^{-i\hat{H}t/\hbar}$ in Eq. (1.1b) is represented by a *single* Herman–Kluk-like IVR, i.e., Eq. (1.3), where the trajectories evolve from time $0 \rightarrow t$

(the action of the operator $e^{-i\hat{H}t/\hbar}$), undergo a momentum jump at time t (the effect of operator \hat{h}), and then evolve backward from $t \rightarrow 0$ (the action of operator $e^{i\hat{H}t/\hbar}$). The benefit gained from the FB-IVR, besides reducing the dimensionality of the phase space integral, is that there is a partial cancellation of the phase in the integrand and the magnitude of the pre-exponential factor, thus greatly improving the numerical property of the integrand.

In this paper, we report a more thorough analysis of the FB-IVR and demonstrate its efficiency by applying it to the case of strong quantum interference and the case of a large number of degrees of freedom. Section II summarizes the FB-IVR approach for calculating time correlation functions; Appendix A gives an alternate derivation of the ‘‘momentum jump’’ condition, and Appendix B discusses some approximate versions of the FB-IVR. The results of numerical tests on the popular model of a double well coupled to harmonic bath are presented in Sec. III, and Sec. IV summarizes and concludes.

II. SUMMARY OF THEORY

Though our interest in this paper is the flux correlation function of Eq. (1.1b), the formulas in this section are written explicitly for the more general correlation function

$$C_{AB}(t) = \text{tr}[\hat{A} e^{i\hat{H}t/\hbar} \hat{B} e^{-i\hat{H}t/\hbar}], \quad (2.1)$$

where operator \hat{B} is assumed to be local (in coordinate space) and to depend on coordinates through a single collective variable $s(\mathbf{q})$, i.e., $\hat{B} = B[\hat{s}(\mathbf{q})]$. Reference 22 shows how more general operators \hat{B} can be treated via this FB approach, but this is not needed for the present.

Operator $\hat{B} = B[\hat{s}(\mathbf{q})]$ is first written as a Fourier integral,

$$B[\hat{s}(\mathbf{q})] = \int_{-\infty}^{\infty} dp_s \tilde{B}(p_s) e^{ip_s \hat{s}(\mathbf{q})/\hbar}, \quad (2.2)$$

e.g., for Eq. (1.1b), $B(s) = h(s)$, and

$$\tilde{B}(p_s) = \lim_{\epsilon \rightarrow 0^+} \frac{1}{2\pi i(p_s - i\epsilon)}. \quad (2.3)$$

The correlation function Eq. (2.1) then becomes

$$C_{AB}(t) = \int_{-\infty}^{\infty} dp_s \tilde{B}(p_s) \text{tr}[\hat{A} \hat{U}(t)], \quad (2.4a)$$

where

$$\hat{U}(t) = e^{i\hat{H}t/\hbar} e^{ip_s \hat{s}(\mathbf{q})/\hbar} e^{-i\hat{H}t/\hbar}. \quad (2.4b)$$

The three operators in Eq. (2.4b) describe, sequentially from right to left, propagation from 0 to t , a momentum jump $\Delta \mathbf{p} = p_s \partial s(\mathbf{q}) / \partial \mathbf{q}$ at time t , and then propagation from t back to 0 ; this was derived one way in Ref. 22, and Appendix A gives an alternate derivation. The Herman–Kluk IVR

for operator $\hat{U}(t)$ thus has the same form as Eq. (1.3), so that the forward-backward (FB) IVR for the correlation function is

$$C_{AB}(t) = \int_{-\infty}^{\infty} dp_s \tilde{B}(p_s) \times (2\pi\hbar)^{-N} \int d\mathbf{p}_0 \int d\mathbf{q}_0 \langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}'_0 \mathbf{q}'_0 \rangle \times C_0(\mathbf{p}_0, \mathbf{q}_0; p_s) e^{iS_0(\mathbf{p}_0, \mathbf{q}_0; p_s)/\hbar}. \quad (2.5)$$

The FB-IVR trajectory involved in Eq. (2.5) begins at $t=0$ with initial condition $(\mathbf{p}_0, \mathbf{q}_0)$ and evolves to time t under the molecular Hamiltonian H ; at time t the momentum is changed to

$$\mathbf{p}_t \rightarrow \mathbf{p}_t + p_s \left[\frac{\partial s(\mathbf{q})}{\partial \mathbf{q}} \right]_{\mathbf{q}=\mathbf{q}_t}, \quad (2.6)$$

and is then evolved back to time 0 via the molecular Hamiltonian H , $(\mathbf{p}'_0, \mathbf{q}'_0)$ being the final phase point. The action integral S_0 has contribution from these three time steps,

$$S_0(\mathbf{p}_0, \mathbf{q}_0; p_s) = \int_0^t d\tau [\mathbf{p}_\tau \cdot \dot{\mathbf{q}}_\tau - H] + p_s s(\mathbf{q}_t) + \int_t^0 d\tau [\mathbf{p}'_\tau \cdot \dot{\mathbf{q}}'_\tau - H] \quad (2.7)$$

and the pre-exponential factor $C_0(\mathbf{p}_0, \mathbf{q}_0)$ has the same form as Eq. (1.4),

$$C_0(\mathbf{p}_0, \mathbf{q}_0, p_s) = \sqrt{\det \left[\frac{1}{2} \left(\gamma^{1/2} \frac{\partial \mathbf{q}'_0}{\partial \mathbf{q}_0} \gamma^{-1/2} + \gamma^{-1/2} \frac{\partial \mathbf{p}'_0}{\partial \mathbf{p}_0} \gamma^{1/2} - i\hbar \gamma^{1/2} \frac{\partial \mathbf{q}'_0}{\partial \mathbf{p}_0} \gamma^{1/2} + \frac{i}{\hbar} \gamma^{-1/2} \frac{\partial \mathbf{p}'_0}{\partial \mathbf{q}_0} \gamma^{-1/2} \right) \right]}. \quad (2.8)$$

The forward-backward nature of the trajectory provides several advantages over the conventional SC-IVR expression, Eq. (1.6): First, for a complex molecular system the dimension of the phase space average is greatly reduced; second, there is a partial cancellation of the phase (those of the action integrals, of the coherent states, and also of the complex pre-exponential factors) which makes the integrand much less oscillatory; third, there is also a partial cancellation of the magnitude of the pre-exponential factor such that it rarely becomes too large, even for a strongly chaotic system. These properties make the FB-IVR integrand for the flux correlation function much better behaved, thus enabling one to study larger systems than those previously attempted by the conventional SC-IVR. The small price paid for these simplifications is that one now has to use separate sets of trajectories for different times t .

An alternate procedure to the above FB approach (but formally equivalent to it) can be obtained by invoking Liouville's theorem, i.e., making the following change in the integration variables:

$$\int d\mathbf{p}_0 \int d\mathbf{q}_0 \rightarrow \int d\mathbf{p}_t \int d\mathbf{q}_t. \quad (2.9)$$

After relabeling the symbols, $(\mathbf{p}_t, \mathbf{q}_t) \rightarrow (\mathbf{p}_0, \mathbf{q}_0)$ and $(\mathbf{p}_0, \mathbf{q}_0) \rightarrow (\mathbf{p}_{-t}, \mathbf{q}_{-t})$, Eq. (2.5) becomes a "double-backward" version (DB-IVR)

$$C_{AB}(t) = \int_{-\infty}^{\infty} dp_s \tilde{B}(p_s) (2\pi\hbar)^{-N} \times \int d\mathbf{p}_0 \int d\mathbf{q}_0 \langle \mathbf{p}_{-t} \mathbf{q}_{-t} | \hat{A} | \mathbf{p}'_{-t} \mathbf{q}'_{-t} \rangle C_0 e^{iS_0/\hbar}. \quad (2.10)$$

Here, one initiates two trajectories at time 0, with initial conditions $(\mathbf{p}_0, \mathbf{q}_0)$ and $(\mathbf{p}'_0, \mathbf{q}'_0)$, respectively, where

$$\mathbf{p}'_0 = \mathbf{p}_0 + p_s \left[\frac{\partial s(\mathbf{q})}{\partial \mathbf{q}} \right]_{\mathbf{q}=\mathbf{q}_0}, \quad \mathbf{q}'_0 = \mathbf{q}_0, \quad (2.11)$$

and integrates them backward in time to $-t$. The action integral S_0 also has contribution from three terms,

$$S_0(\mathbf{p}_0, \mathbf{q}_0; p_s) = - \int_0^{-t} d\tau [\mathbf{p}_\tau \cdot \dot{\mathbf{q}}_\tau - H] + p_s s(\mathbf{q}_0) + \int_0^{-t} d\tau [\mathbf{p}'_\tau \cdot \dot{\mathbf{q}}'_\tau - H], \quad (2.12)$$

and the pre-exponential factor $C_0(\mathbf{p}_0, \mathbf{q}_0)$ is now given as

$$C_0(\mathbf{p}_0, \mathbf{q}_0, p_s) = \sqrt{\det(\mathbf{M})}, \quad (2.13a)$$

$$\mathbf{M} = \begin{bmatrix} \frac{\partial \mathbf{p}'_{-t}}{\partial \mathbf{p}'_0} + \frac{\hbar}{i} \gamma \frac{\partial \mathbf{q}'_{-t}}{\partial \mathbf{p}'_0} & \left[\left(\frac{\partial \mathbf{q}_{-t}}{\partial \mathbf{q}_0} \right)^T - \frac{i}{\hbar} \left(\frac{\partial \mathbf{p}_{-t}}{\partial \mathbf{q}_0} \right)^T \gamma^{-1} \right] \\ \left[\frac{\partial \mathbf{p}'_{-t}}{\partial \mathbf{q}'_0} + \frac{\hbar}{i} \gamma \frac{\partial \mathbf{q}'_{-t}}{\partial \mathbf{q}'_0} \right] & \left[- \left(\frac{\partial \mathbf{q}_{-t}}{\partial \mathbf{p}_0} \right)^T + \frac{i}{\hbar} \left(\frac{\partial \mathbf{p}_{-t}}{\partial \mathbf{p}_0} \right)^T \gamma^{-1} \right] \\ \left[\frac{\partial \mathbf{p}'_{-t}}{\partial \mathbf{p}'_0} + \frac{\hbar}{i} \gamma \frac{\partial \mathbf{q}'_{-t}}{\partial \mathbf{p}'_0} \right] \cdot p_s \left[\frac{\partial^2 s(\mathbf{q}_0)}{\partial \mathbf{q}_0^2} \right] & \left[- \left(\frac{\partial \mathbf{q}_{-t}}{\partial \mathbf{p}_0} \right)^T \right. \\ \left. + \frac{i}{\hbar} \left(\frac{\partial \mathbf{p}_{-t}}{\partial \mathbf{p}_0} \right)^T \gamma^{-1} \right], \end{bmatrix} \quad (2.13b)$$

where the superscript "T" denotes the transpose of a matrix.

The advantage of the DB-IVR, compared with the FB-IVR is that during the backward integration, information on all the intermediate time steps is obtained on the fly, so that one can use the same set of trajectories for all the t -points. The price paid for this is that there is no obvious choice of a weighting function for the initial conditions of the backward classical trajectories. Applications below compare these approaches.

III. APPLICATIONS TO THE SYSTEM-BATH MODEL

In this section, we apply the FB-IVR for the flux correlation function to the model system of a one-dimensional double well linearly coupled to a harmonic bath. The Hamiltonian, written in the mass-weighted coordinates, is

$$H = H_s(p_s, s) + \sum_{i=1}^{N_b} \left[\frac{1}{2} P_i^2 + \frac{1}{2} \omega_i^2 \left(Q_i - \frac{c_i}{\omega_i^2} s \right)^2 \right], \quad (3.1a)$$

where

$$H_s(p_s, s) = \frac{1}{2} p_s^2 - \frac{1}{2} \omega_b^2 s^2 + \frac{\omega_b^4}{16V_0^\ddagger} s^4. \quad (3.2)$$

Here, ω_b is the imaginary frequency at the top of the barrier, and V_0^\ddagger is the barrier height with respect to the bottom of the well. The essential property of the harmonic bath is its spectral density²⁴

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{\omega_j} \delta(\omega - \psi_j), \quad (3.3)$$

which is chosen in the Ohmic form with an exponential cut-off

$$J_o(\omega) = \eta \omega e^{-\omega/\omega_c}. \quad (3.4)$$

The specific parameters we have chosen correspond to the model studied by Topaler and Makri²⁵ using path integral methods, i.e., $\omega_b = 500 \text{ cm}^{-1}$, $V_0^\ddagger = 2085 \text{ cm}^{-1}$, and $\omega_c = 500 \text{ cm}^{-1}$. The continuous bath spectral density of Eq. (3.4) is discretized to the form of Eq. (3.3) via the relation

$$c_j^2 = \frac{2}{\pi} \omega_j \frac{J_o(\omega_j)}{\rho(\omega_j)}, \quad (3.5a)$$

where $\rho(\omega)$ is a density of frequency satisfying

$$\int_0^{\omega_j} d\omega \rho(\omega) = j, \quad j = 1, \dots, N_b. \quad (3.5b)$$

As noted in Ref. 19(b), the precise functional form of $\rho(\omega)$ does not affect the final answer if enough bath modes are included, but it does affect the efficiency of solving the problem (i.e., the number of bath modes needed to represent the continuum). Here, we choose $\rho(\omega)$ as

$$\rho(\omega) = a \frac{J_o(\omega)}{\omega}, \quad (3.6a)$$

with

$$a = \frac{N_b}{\eta \omega_c} \frac{1}{1 - e^{-\omega_m/\omega_c}}, \quad (3.6b)$$

where ω_m is the largest frequency of the bath modes considered in the calculation. With the above scheme of discretization, we found that as few as 40 modes with $\omega_m = 5 \omega_c$ is adequate to describe the condensed phase media of our problem for the time period considered in this paper. Below, various specifics of our calculation are presented.

A. Initial conditions of classical trajectories

The weighting function for the initial conditions of classical trajectories in the FB-IVR expression, Eq. (2.5), can be

obtained from the matrix element $\langle \mathbf{p}_0 \mathbf{q}_0 | \hat{F}(\beta) | \mathbf{p}'_0 \mathbf{q}'_0 \rangle$. Since these matrix elements are not available analytically,²⁶ we have proceeded as before¹⁷ and used a normal mode approximation at the transition state for the Boltzmannized flux operator $\hat{F}(\beta)$; i.e., the Hamiltonian is approximated by

$$H \approx H_f + H_b, \quad (3.7a)$$

where H_f involves one mode with imaginary frequency (the reaction coordinate) and H_b the remaining modes with real frequencies

$$H_f = \frac{1}{2} p_f^2 - \frac{1}{2} \lambda^\ddagger q_f^2, \quad (3.7b)$$

$$H_b = \sum_j \left(\frac{1}{2} p_j^2 + \frac{1}{2} \lambda_j^2 q_j^2 \right), \quad (3.7c)$$

λ^\ddagger and λ_j are the imaginary and real frequencies obtained by diagonalizing the mass-weighted force constant matrix at the saddle point, and q_f , p_f and q_j , p_j are the corresponding coordinates and momenta, respectively. Within this approximation, the coherent state matrix element of $\hat{F}(\beta)$ is (hereafter $\hbar = 1$)

$$\begin{aligned} \langle \mathbf{p}_0 \mathbf{q}_0 | \hat{F}(\beta) | \mathbf{p}'_0 \mathbf{q}'_0 \rangle &= \langle p_{f0} q_{f0} | e^{-\beta \hat{H}_{f/2}} \hat{F} e^{-\beta \hat{H}_{f/2}} | p'_{f0} q'_{f0} \rangle \\ &\times \prod_j \langle p_{j0} q_{j0} | e^{-\beta \hat{H}_{bj}} | p'_{j0} q'_{j0} \rangle, \end{aligned} \quad (3.8a)$$

$$\begin{aligned} \langle p_{f0} q_{f0} | e^{-\beta \hat{H}_{f/2}} \hat{F} e^{-\beta \hat{H}_{f/2}} | p'_{f0} q'_{f0} \rangle &= \frac{1}{8 \cos^2 u^\ddagger} \sqrt{\frac{\gamma^\ddagger}{\pi}} [(p_{f0} + p'_{f0}) + i \gamma^\ddagger (q_{f0} - q'_{f0})] \\ &\times e^{-(\gamma^\ddagger/4)(q_{f0}^2 + q'_{f0}{}^2)} e^{-(p_{f0}^2 + p'_{f0}{}^2)/(4\gamma^\ddagger)} \\ &\times e^{(i/2)(p_{f0} + p'_{f0})(q_{f0} - q'_{f0})}, \end{aligned} \quad (3.8b)$$

$$\begin{aligned} \langle p_{j0} q_{j0} | e^{-\beta \hat{H}_{bj}} | p'_{j0} q'_{j0} \rangle &= e^{-u_j} e^{-(\gamma_j/4)(q_{j0}^2 + q'_{j0}{}^2)} e^{-(p_{j0}^2 + p'_{j0}{}^2)/(4\gamma_j)} \\ &\times e^{(i/2)(p_{j0} + p'_{j0})(q_{j0} - q'_{j0})} \\ &\times \exp \left\{ \frac{1}{2} e^{-2u_j} \left[\gamma_j q_{j0} q'_{j0} + \frac{1}{\gamma_j} p_{j0} p'_{j0} \right. \right. \\ &\left. \left. + i(p'_{j0} q_{j0} - p_{j0} q'_{j0}) \right] \right\}, \end{aligned} \quad (3.8c)$$

where

$$u^\ddagger = \beta \lambda^\ddagger / 2, \quad u_j = \beta \lambda_j / 2, \quad (3.9a)$$

and the width parameters of the coherent states are chosen as

$$\gamma^\ddagger = \lambda^\ddagger \cot u^\ddagger, \quad \gamma_j = \lambda_j. \quad (3.9b)$$

One obvious choice of the weighting function is (the modulus of) the diagonal part of Eq. (3.8), i.e., the Husimi distribution²⁷

$$\begin{aligned}
W(\mathbf{p}_0, \mathbf{q}_0) &= \frac{1}{D} \langle \mathbf{p}_0 \mathbf{q}_0 | \hat{F}(\beta) | \mathbf{p}_0 \mathbf{q}_0 \rangle \\
&= \frac{1}{D} \langle p_{f0} q_{f0} | e^{-\beta \hat{H}_{f/2}} \hat{F} e^{-\beta \hat{H}_{f/2}} | p_{f0} q_{f0} \rangle \\
&\quad \times \prod_j \langle p_{j0} q_{j0} | e^{-\beta \hat{H}_{bj}} | p_{j0} q_{j0} \rangle, \quad (3.10a)
\end{aligned}$$

$$\begin{aligned}
&\langle p_{f0} q_{f0} | e^{-\beta \hat{H}_{f/2}} \hat{F} e^{-\beta \hat{H}_{f/2}} | p_{f0} q_{f0} \rangle \\
&= \frac{1}{4 \cos^2 u^\ddagger} \sqrt{\frac{\gamma^\ddagger}{\pi}} p_{f0} e^{-(\gamma^\ddagger/2) q_{f0}^2} e^{-p_{f0}^2/(2\gamma^\ddagger)}, \quad (3.10b)
\end{aligned}$$

$$\begin{aligned}
&\langle p_{j0} q_{j0} | e^{-\beta \hat{H}_{bj}} | p_{j0} q_{j0} \rangle \\
&= e^{-u_j} \exp \left[-\frac{\gamma_j}{2} (1 - e^{-2u_j}) q_{j0}^2 - \frac{1}{2\gamma_j} (1 - e^{-2u_j}) p_{j0}^2 \right], \quad (3.10c)
\end{aligned}$$

where D is the proper normalization factor.

One thus uses the weighting function $W(\mathbf{p}_0, \mathbf{q}_0)$ to select the initial conditions $(\mathbf{p}_0, \mathbf{q}_0)$ via importance sampling. Though the final phase space variables $(\mathbf{p}'_0, \mathbf{q}'_0)$ are not the same as initial variables $(\mathbf{p}_0, \mathbf{q}_0)$, the forward-backward nature of the classical trajectories makes such differences small so that the diagonal matrix element $\langle \mathbf{p}_0 \mathbf{q}_0 | \hat{F}(\beta) | \mathbf{p}_0 \mathbf{q}_0 \rangle$ represents a large portion of the true matrix element $\langle \mathbf{p}_0 \mathbf{q}_0 | \hat{F}(\beta) | \mathbf{p}'_0 \mathbf{q}'_0 \rangle$. Monte Carlo integration is thus very efficient in this procedure.

For the DB-IVR expressions of the flux correlation function, Eq. (2.10), there is not an obvious choice of a weighting function. The physics behind this is that now the trajectories start from the reactant/product region and move to the transition state, which is a difficult problem for a complex molecular system even at the classical mechanical level. One may use numerical techniques such as a Metropolis walk²⁸ or the rejection method,²⁹ where the modulus of the integrand is used as a sampling function. This, however, makes the weighting function time-dependent and removes the major advantage of the double backward approach. Therefore, we use either simple Monte Carlo procedure (without a weighting function) or insert some Gaussian functions for \mathbf{p}_0 and \mathbf{q}_0 with tunable widths as ‘‘guessed’’ weighting functions to perform the phase space average.

Finally, for the additional integration of the momentum jump variable p_s there is no obvious weighting function in either the FB- or DB-IVR approach. We thus use either simple Monte Carlo or stratified sampling to accomplish this integral. Below, various other specifics of the calculation are presented.

B. Time propagation

The natural way of time propagation is to integrate Hamilton’s equations of motion for a classical trajectory (in a mass-weighted Cartesian system)

$$\dot{\mathbf{q}}_t = \frac{\partial H}{\partial \mathbf{p}_t}, \quad \dot{\mathbf{p}}_t = -\frac{\partial H}{\partial \mathbf{q}_t}, \quad (3.11a)$$

along with the action integral

$$\dot{S}_t = \mathbf{p}_t \cdot \dot{\mathbf{q}}_t - H, \quad (3.11b)$$

and the monodromy matrix (used in the evaluation of the pre-exponential factor)

$$\begin{aligned}
\frac{d}{dt} \begin{pmatrix} \partial \mathbf{q}_t \\ \partial \mathbf{q}_0 \end{pmatrix} &= \frac{\partial \mathbf{p}_t}{\partial \mathbf{q}_0}, \quad \frac{d}{dt} \begin{pmatrix} \partial \mathbf{q}_t \\ \partial \mathbf{p}_0 \end{pmatrix} = \frac{\partial \mathbf{p}_t}{\partial \mathbf{p}_0}, \\
\frac{d}{dt} \begin{pmatrix} \partial \mathbf{p}_t \\ \partial \mathbf{q}_0 \end{pmatrix} &= -\mathbf{K} \times \frac{\partial \mathbf{q}_t}{\partial \mathbf{q}_0}, \quad \frac{d}{dt} \begin{pmatrix} \partial \mathbf{p}_t \\ \partial \mathbf{p}_0 \end{pmatrix} = -\mathbf{K} \times \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0}, \quad (3.11c)
\end{aligned}$$

where \mathbf{K} is the force constant matrix.

The main purpose of an SC-IVR, however, is to construct an accurate approximation for the time evolution operator, $e^{-i\hat{H}t}$, rather than the absolute convergence of various classical quantities. Thus, an alternate time propagation scheme can be designed following the spirit of the split-operator algorithm³⁰ in time-dependent quantum wave packet propagation,

$$e^{-i\hat{H}t} = (e^{-i\hat{H}\Delta t})^n \simeq (e^{-i\hat{H}'\Delta t/2} e^{-i\hat{H}_0\Delta t} e^{-i\hat{H}'\Delta t/2})^n, \quad (3.12)$$

where \hat{H}_0 is a ‘‘zeroth-order’’ Hamiltonian usually chosen in the separable (adiabatic) form and \hat{H}' can be viewed as a nonadiabatic correction to \hat{H}_0 . With an appropriate choice of them the step size Δt can be rather large, as demonstrated in the ‘‘quasiadiabatic’’ propagator approach in the path integral calculation.²⁵ In this picture of an SC-IVR calculation, a classical trajectory is integrated via a time-dependent Hamiltonian: at each time step, the trajectory is first advanced $\Delta t/2$ via H' , then advanced Δt via H_0 , and finally advanced $\Delta t/2$ again via H' .

In our calculation, we choose the normal mode approximation to the original Hamiltonian, Eq. (3.7), as H_0 , and the remainder (simply a nonlinear potential involving all degrees of freedom) as $H'(\mathbf{q})$. Due to its linear nature, the propagation via H_0 is completely analytic in all the desired quantities. The propagation via H' is also very simple

$$\mathbf{q}_{t+\Delta t/2} = \mathbf{q}_t, \quad \mathbf{p}_{t+\Delta t/2} = \mathbf{p}_t - \frac{\partial H'(\mathbf{q}_t)}{\partial \mathbf{q}_t} \frac{\Delta t}{2}, \quad (3.13a)$$

$$S_{t+\Delta t/2} = S_t - H'(\mathbf{q}_t) \frac{\Delta t}{2}, \quad (3.13b)$$

$$\frac{\partial \mathbf{q}_{t+\Delta t/2}}{\partial \mathbf{q}_t} = \mathbf{1}, \quad \frac{\partial \mathbf{q}_{t+\Delta t/2}}{\partial \mathbf{p}_t} = \mathbf{0}, \quad (3.13c)$$

$$\frac{\partial \mathbf{p}_{t+\Delta t/2}}{\partial \mathbf{q}_t} = -\frac{\partial^2 H'(\mathbf{q}_t)}{\partial \mathbf{q}_t^2} \frac{\Delta t}{2}, \quad \frac{\partial \mathbf{p}_{t+\Delta t/2}}{\partial \mathbf{p}_t} = \mathbf{1},$$

where the cumulative monodromy matrix at a certain time can be related to those at each time step via the chain rule.

With the above integration scheme, the step size Δt can be much larger than that used in the usual integrator, thus significantly improving the efficiency of the time propagation.

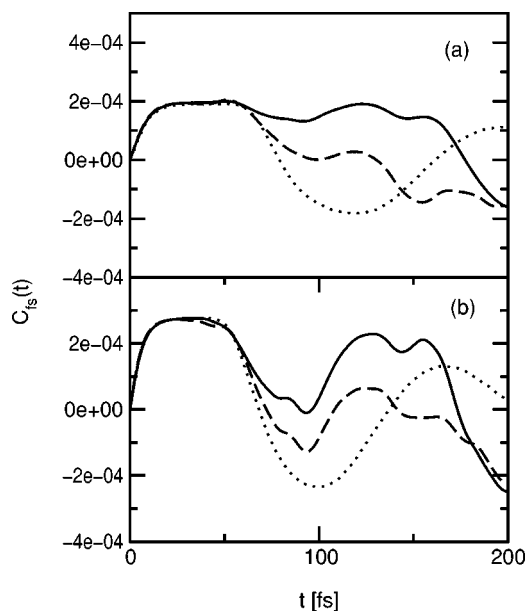


FIG. 1. Flux correlation function of a one-dimensional double well obtained via the DB-IVR (dashed line), the quantum mechanical calculation (solid line), and the LSC-IVR (dotted line): (a) $T=300$ K, (b) $T=500$ K.

C. Results and discussion

1. One-dimensional double well

In the absence of a dissipative bath, the quantum $C_{fs}(t)$ for the double well displays strong coherent structure after reaching its plateau. Such coherence is a pure quantum mechanical result and cannot be described by classical dynamics or by the linearized SC-IVR/classical Wigner model of Eq. (1.7).²⁰ The FB- or DB-IVR, however, is expected to capture some of the quantum interference behavior, and this is indeed what we have found. Figure 1 shows $C_{fs}(t)$ for two temperatures, 300 and 500 K, respectively, obtained from the DB-IVR (the dashed line). Also shown in the figure are the quantum mechanical result (the solid line) and the result from the LSC-IVR/classical Wigner calculation (the dotted line). One sees that the results from DB-IVR are decidedly better than those from the LSC-IVR. For the higher temperature of 500 K, the DB-IVR reproduces quite accurately the phase of oscillations in the flux correlation function, whereas the LSC-IVR completely misses the detailed structures. The DB-IVR is less accurate for the lower temperature of 300 K, but still in reasonable agreement with the quantum result. The FB-IVR gives similar results, but is computationally more expensive in this case. Overall, the agreement between double backward (or forward-backward) IVR and the exact quantum results are quite good, suggesting that they are capable of capturing the important quantum interference effects.

2. The double well coupled to a harmonic bath

When the double well is coupled to a bath of harmonic oscillators, the coherent structure in the flux correlation function is quenched by the bath modes if the coupling is strong enough. In this case, a stable plateau can be maintained and

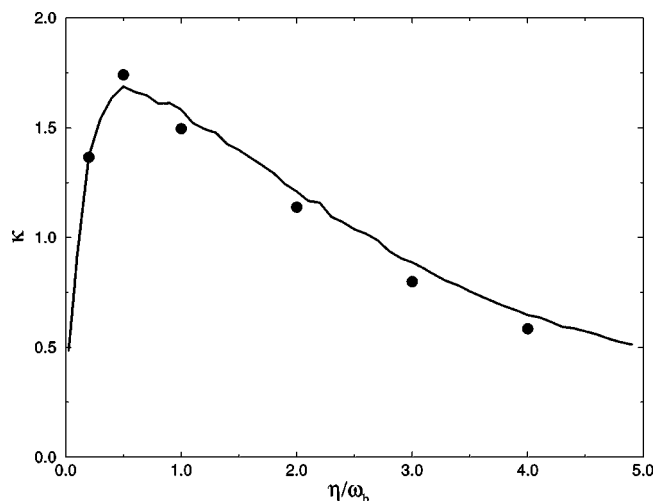


FIG. 2. Transmission coefficient $\kappa = k/k_{\text{TST,CL}}$ as a function of coupling parameter η/ω_b at $T=300$ K; the solid circles are the FB-IVR result, and the solid line is from the accurate quantum path integral calculations, Ref. 25.

the rate constant can be calculated from Eq. (1.1). We now discuss the results obtained with a bath of 40 harmonic oscillators.

Figure 2 shows the rate constants at $T=300$ K obtained via the forward-backward IVR (solid points), Eq. (2.5), compared with the path integral results (solid line).²⁵ As done previously,²⁵ the transmission coefficient κ is plotted, where κ is defined by

$$\kappa = k/k_{\text{TST,CL}}, \quad (3.14a)$$

and $k_{\text{TST,CL}}$ is the classical transition state theory rate constant for the original one-dimensional double well,

$$k_{\text{TST,CL}} = \frac{\omega_{s0}}{2\pi} e^{-\beta V_0^\ddagger}. \quad (3.14b)$$

Overall, the FB-IVR can reproduce quite accurately the quantum “turnover” behavior of the rate constants versus η . This is by far the largest system ever treated by an SC-IVR that involves a complex integrand and demonstrates the potential of the FB-IVR for dealing with complex molecular systems.

Since there is phase (thus possible interference) in the FB-IVR integrand, one still needs a number of trajectories to converge the integral. In the present case, we found that 100 000 trajectories are needed for the time period of ~ 70 fs, and more trajectories for longer time. This is, however, a reasonable amount considering the fact that the previous SC-IVR calculations for much smaller molecular systems usually use as many (or even more) trajectories.

The nature of the dynamics can be examined by looking at the flux correlation function at different coupling strengths. Figure 3 shows $C_{fs}(t)$ at two values of η : for a large coupling parameter ($\eta/\omega_b=1$) the process is the direct barrier crossing, whereas for a small coupling ($\eta/\omega_b=0.3$) recrossing flux is present. The former class can be well described by quantum transition state theory but the latter one needs dynamical corrections. The FB-IVR is seen as capable of describing both of them.

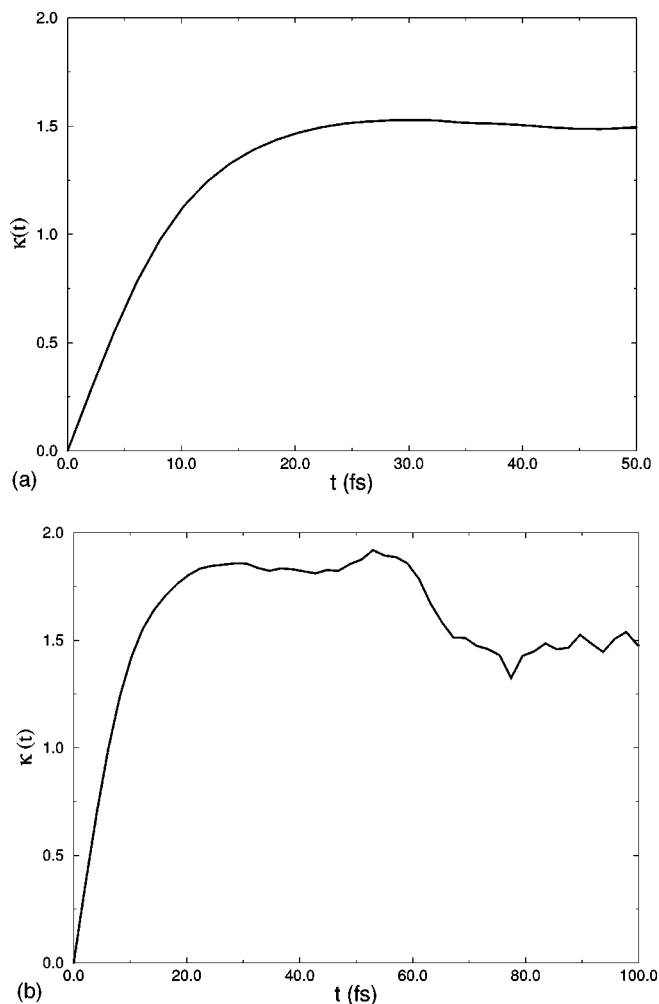


FIG. 3. Flux correlation function for two cases at $T=300$ K: (a) $\eta/\omega_b = 1.0$; (b) $\eta/\omega_b = 0.3$.

Looking at a group of randomly picked trajectories provides further understanding of the efficiency with the FB-IVR: a large portion of overall phase is canceled during the forward–backward integration and, more importantly, the pre-exponential factor C_0 behaves much better than in a conventional SC-IVR calculation. Besides the fact that C_0 is close to 1 at most times, its phase change is also very slow versus time. As a result, the time interval to keep track of the phase [branch in the complex square root, Eq. (2.8)] can be as large as 2 fs in our calculation without introducing significant errors. For a conventional SC-IVR calculation of such a large system, the phase of the pre-exponential factor changes much more rapidly due to the large zero-point energy, and thus severely prohibits the use of a large integration time step even if it is allowed in the classical dynamics simulation.

Finally, we comment on the use of the DB-IVR in this calculation. In a series of calculations we have found that within the first 25 fs or so it can outperform the FB-IVR. However, for longer times, it becomes extremely difficult to converge the integral. This suggests that there appears to be no time-independent weighting function for the DB-IVR. If one uses a time-dependent weighting function, then the DB-IVR becomes similar (in spirit) to the FB-IVR and provides

essentially no advantages. The conclusion is, therefore, that the DB-VR may be preferred for small molecular systems and for short time. In going to longer time dynamics, FB-IVR is a much more favorable choice.

IV. CONCLUDING REMARKS

In this paper, we have applied the forward–backward initial value representation (FB-IVR) to the calculation of reactive flux correlation functions. The system examined via the FB-IVR approach is a double well linearly coupled to a harmonic bath. It is found that when the coupling is zero (i.e., a single double well) the FB-IVR can reproduce reasonably well the quantum interference structure in the flux correlation function, thus going beyond the linearized IVR. For a bath of 40 harmonic oscillators, we have successfully obtained accurate rate constants via the FB-IVR. These encouraging results suggest that the FB-IVR is a potentially powerful approach for describing quantum effects for large molecular systems.

Because of the large number of degrees of freedom considered in this paper, the computational bottleneck is actually evaluating the pre-exponential factor or, more precisely, the determinant of a complex $N \times N$ matrix. This problem has never been addressed before due to the small number of degrees of freedom in previous SC-IVR calculations. One must now focus, therefore, on finding better ways to resolve this problem since it has the unfavorable scaling of N^3 . Several approximations on this subject are being investigated.

ACKNOWLEDGMENTS

We would like to thank Neepa Maitra for several helpful discussions throughout this project. This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and by National Science Foundation Grant No. CHE 97-32758. M. T. gratefully acknowledges a Feodor-Lynen fellowship of the Alexander von Humboldt Foundation.

APPENDIX A: ALTERNATE DERIVATION OF THE FB-IVR

For interest, we give here a different derivation than the original one²² of the basic FB-IVR result summarized in Sec. II.

The three propagators in the product constituting operator $\hat{U}(t)$ of Eq. (2.4b) can be thought of as three sequential time evolution operators,

$$\hat{U}(t) = e^{-i\hat{H}(-t)/\hbar} e^{-i\hat{H}'(1)/\hbar} e^{-i\hat{H}(t)/\hbar}, \quad (\text{A1})$$

where \hat{H} is the usual molecular Hamiltonian, but \hat{H}' is the following rather strange Hamiltonian:

$$\hat{H}' = -\phi(\mathbf{q}). \quad (\text{A2})$$

The Herman–Kluk IVR for $\hat{U}(t)$ thus has the standard form, Eq. (1.3), where the trajectory which begins with initial condition $(\mathbf{p}_0, \mathbf{q}_0)$ evolves via the molecular Hamiltonian $H(\mathbf{p}, \mathbf{q})$ for a time increment (t) , continues via the Hamil-

tonian $H'(\mathbf{p}, \mathbf{q})$ for a unit time increment, and then continues for the time increment $(-t)$ again via the molecular Hamiltonian H . Since Hamilton's equations for the intermediate Hamiltonian $H'(\mathbf{p}, \mathbf{q})$ of Eq. (A2) are

$$\dot{\mathbf{q}} = \frac{\partial H'}{\partial \mathbf{p}} = 0, \quad (\text{A3a})$$

$$\dot{\mathbf{p}} = -\frac{\partial H'}{\partial \mathbf{q}} = \frac{\partial \phi(\mathbf{q})}{\mathbf{q}}, \quad (\text{A3b})$$

integrating them for a unit time increment yields

$$\mathbf{q}_f = \mathbf{q}_i, \quad (\text{A4a})$$

$$\mathbf{p}_f = \mathbf{p}_i + \frac{\partial \phi(\mathbf{q}_i)}{\partial \mathbf{q}_i}, \quad (\text{A4b})$$

where $(\mathbf{p}_i, \mathbf{q}_i) \equiv (\mathbf{p}_t, \mathbf{q}_t)$ is the phase point resulting from the first time increment (t) . The net result of the intermediate time evolution operator is thus the momentum jump at time t as described following Eq. (2.4b) in the text. It is also easy to show from Eqs. (A3) and (A4) that the contribution to the action S from the intermediate time evolution is

$$\int_0^1 dt (\mathbf{p} \cdot \dot{\mathbf{q}} - H') = \phi(\mathbf{q}_i). \quad (\text{A5})$$

APPENDIX B: SOME APPROXIMATIONS TO THE FB-IVR

The discussion related to Eq. (3.10) suggests some systematic approximations that may be utilized to simplify the FB-IVR approach even further. Thus, consider the FB-IVR expression, Eq. (2.5), for the general $A-B$ correlation function. Noting that the Husimi distribution function corresponding to operator \hat{A} is its diagonal coherent state matrix element,

$$\rho_A(\mathbf{p}_0, \mathbf{q}_0) \equiv (2\pi\hbar)^{-N} \langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}_0 \mathbf{q}_0 \rangle, \quad (\text{B1})$$

Eq. (2.5) becomes

$$C_{AB}(t) = \int_{-\infty}^{\infty} dp_s \tilde{B}(p_s) \int d\mathbf{p}_0 \int d\mathbf{q}_0 \times \rho_A(\mathbf{p}_0, \mathbf{q}_0) I_t(\mathbf{p}_0, \mathbf{q}_0; p_s), \quad (\text{B2})$$

where

$$I_t(\mathbf{p}_0, \mathbf{q}_0; p_s) = e^{iS_0(\mathbf{p}_0, \mathbf{q}_0; p_s)/\hbar} C_0(\mathbf{p}_0, \mathbf{q}_0; p_s) \times \langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}'_0 \mathbf{q}'_0 \rangle / \langle \mathbf{p}_0 \mathbf{q}_0 | \hat{A} | \mathbf{p}_0 \mathbf{q}_0 \rangle. \quad (\text{B3})$$

The approximations we consider are suggested by noting that the function $I_t(\mathbf{p}_0, \mathbf{q}_0; p_s)$ is unity for $p_s = 0$ [because in this case the backward trajectory simply retraces the forward trajectory, so that $(\mathbf{p}'_0, \mathbf{q}'_0) = (\mathbf{p}_0, \mathbf{q}_0)$, $S_0 = 0$, and $C_0 = 1$]. If small values of p_s are the most important for the integral over p_s , then a useful approximation for the p_s -dependence of I_t is

$$I_t(\mathbf{p}_0, \mathbf{q}_0; p_s) = \exp \left[\frac{i}{\hbar} \left(ap_s + \frac{b}{2} p_s^2 + \frac{c}{3} p_s^3 + \dots \right) \right], \quad (\text{B4})$$

where the parameters a, b, c are functions of $(\mathbf{p}_0, \mathbf{q}_0)$ and t , i.e., $a = a_t(\mathbf{p}_0, \mathbf{q}_0)$, etc. [For given values of $(\mathbf{p}_0, \mathbf{q}_0)$ and t , the parameters a , b , and c , for example, can be determined by running three "backward" trajectories for three different values of p_s .] With this approximation for the p_s -dependence of I_t , the integral over p_s in Eq. (B2) can be brought inside that over the initial conditions $(\mathbf{p}_0, \mathbf{q}_0)$ and evaluated explicitly,

$$\begin{aligned} & \int_{-\infty}^{\infty} dp_s \tilde{B}(p_s) e^{(i/\hbar)[ap_s + (b/2)p_s^2 + (c/3)p_s^3]} \\ &= \int_{-\infty}^{\infty} ds B(s) \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dp_s \\ & \quad \times e^{(i/\hbar)[(a-s)p_s + (b/2)p_s^2 + (c/3)p_s^3]} \\ & \equiv B(a, b, c), \end{aligned} \quad (\text{B5})$$

so that the FB-IVR expression for the correlation function becomes

$$C_{AB}(t) = \int d\mathbf{p}_0 \int d\mathbf{q}_0 \rho_A(\mathbf{p}_0, \mathbf{q}_0) \times \bar{B}[a_t(\mathbf{p}_0, \mathbf{q}_0), b_t(\mathbf{p}_0, \mathbf{q}_0), c_t(\mathbf{p}_0, \mathbf{q}_0)]. \quad (\text{B6})$$

For example, the lowest order approximation of this type keeps only the *linear* term in Eq. (B4), i.e., assumes $b = c = 0$. In this case, Eq. (B5) becomes

$$\bar{B}(a, 0, 0) = B(a), \quad (\text{B7a})$$

so that Eq. (B6) for the correlation function becomes

$$C_{AB}(t) = \int d\mathbf{p}_0 \int d\mathbf{q}_0 \rho_A(\mathbf{p}_0, \mathbf{q}_0) B[a_t(\mathbf{p}_0, \mathbf{q}_0)], \quad (\text{B7b})$$

which one realizes is very similar to the linearized SC-IVR, or classical Wigner result of Eq. (1.7). It would be exactly the same if the Husimi distribution were the same as the Wigner distribution and if $a_t(\mathbf{p}_0, \mathbf{q}_0) = s[\mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)]$. This linear approximation is also very similar [in fact, identical if $B(s) = s$] to a forward-backward approach utilized recently by Shao and Makri³¹ (and also by Sun and Miller²²), who noted that in their application it gave results essentially indistinguishable from the LSC-IVR/classical Wigner approach. It is thus capable of describing quantum effects only for short time. It should be noted that in contrast to the linearized SC-IVR/classical Wigner model, this linear expansion [Eq. (B7b)] is in general not exact for a quadratic Hamiltonian.

With a quadratic expansion in Eqs. (B2) and (B5)—i.e., a and $b \neq 0$ —one has

$$\bar{B}(a, b, 0) = \int_{-\infty}^{\infty} ds B(s) \sqrt{\frac{i}{2\pi\hbar b}} e^{-i(s-a)^2/(2\hbar b)}, \quad (\text{B8})$$

and if a cubic expansion is retained, this becomes

$$\bar{B}(a, b, c) = \int_{-\infty}^{\infty} ds B(s) e^{i(b/2\hbar c)(s-a+b^2/6c)} (\hbar^2 c)^{-1/3} \text{Ai} \left[-(\hbar^2 c)^{-1/3} \left(s - a + \frac{b^2}{4c} \right) \right], \quad (\text{B9})$$

where Ai is the regular Airy function.³² [One can readily show that Eq. (B9) reduces to Eq. (B8) if $c=0$, and (B8) to (B7a) if $b=c=0$.] For a given function $B(s)$, the integral transforms in Eq. (B8) or Eq. (B9) can thus be evaluated either analytically or efficiently numerically, and the correlation function is then given by the average of it over the Husimi distribution of initial conditions [Eq. (B6)].

The utility of this family of approximations is that it yields in lowest order a result very similar to the linearized approximation that has classical mechanics and short time quantum effects described well, and then higher order expansions systematically go beyond this and begin to introduce true quantum coherence effects.

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