Forward–backward initial value representation for semiclassical time correlation functions

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(Received 27 October 1998; accepted 29 December 1998)

The semiclassical (SC) initial value representation (IVR) for the time evolution operator \( e^{-i\hat{H}t/\hbar} \) involves a phase space integral over the initial conditions of classical trajectories. It is shown in this paper how an IVR for the two \( t \) time evolution operators in a typical quantum mechanical time correlation function, \( C_{AB}(t) = \text{tr}[\hat{A}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}] \), can be combined into one such phase space integral; i.e., time evolution from 0 to \( t \) and from \( t \) to 0 is combined into one overall SC-IVR propagation. This not only reduces the dimensionality of the phase space average, but the forward–backward (FB) nature of the net trajectory has a partial self-cancellation that reduces the oscillatory behavior of the integrand. Several applications of this FB-IVR to reactive flux correlation functions are presented to illustrate its possibilities. © 1999 American Institute of Physics.

I. INTRODUCTION

The semiclassical (SC) initial value representation (IVR), the origin of which goes back many years, \(^1\) is experiencing a rebirth of interest \(^2-5\) as a practical way of incorporating quantum effects into classical molecular dynamics simulations. A number of applications \(^6-8\) have been carried out successfully for small molecular systems, giving one confidence that the SC-IVR will provide an accurate treatment of quantum interference and tunneling effects for a wide range of interesting phenomena (including electronically nonadiabatic processes) \(^5\). The primary remaining challenge is one of implementation; i.e., can one in fact carry out the SC-IVR calculation efficiently enough to make applications practical for complex molecular systems? The purpose of this paper is to describe a procedure that we believe will help make this possible.

The Herman–Kluk (HK) (Ref. 3) or coherent state version of the SC-IVR can be stated as the following approximation for the quantum mechanical time evolution operator,

\[
e^{-i\hat{H}t/\hbar} = (2\pi\hbar)^{-p} \int dp_0 \int dq_0 C_i(p_0, q_0) \times e^{iS(p_0, q_0)/\hbar}\langle p, q\rangle|\langle p_0, q_0\rangle|, \tag{1.1a}
\]

where \( (p_0, q_0) \) are initial momenta and coordinates for classical trajectories, \( p_i = p_i(p_0, q_0) \) and \( q_i = q_i(p_0, q_0) \) are the classically time-evolved variables, \( S(p_0, q_0) \) is the classical action integral along the trajectory, and \( C_i(p_0, q_0) \) is the following combination of the monodromy matrix elements

\[
C_i(p_0, q_0) = \sqrt{\det\left[\frac{1}{2}\begin{bmatrix} \partial q_i/\partial q_0 + \partial q_i/\partial p_0 - i\gamma h/\partial p_0 + i\gamma h/\partial q_0 \end{bmatrix}\right]}, \tag{1.1b}
\]

The wave function of a coherent state is the standard minimum uncertainty wave packet,

\[
\langle q|p'q'\rangle = \left(\frac{\gamma}{\pi}\right)^{\frac{p}{4}} e^{-\frac{(p'q' - q'^2 + i\hbar)}{2\gamma}}, \tag{1.1c}
\]

in the limit that the coherent state parameter \( \gamma \to \infty \). Eq. (1.1c) reverts to the Van Vleck (coordinate space) IVR, and if \( \gamma \to 0 \) becomes the momentum space version. The HK, or coherent state IVR is thus a hybrid representation intermediate between a pure coordinate or momentum representation.

In a complex molecular system, i.e., one with many degrees of freedom, one will almost always be interested in calculating some kind of time correlation function of the form

\[
C_{AB}(t) = \text{tr}[\hat{A}e^{i\hat{H}t/\hbar}\hat{B}e^{-i\hat{H}t/\hbar}], \tag{1.2}
\]

where \( \hat{A} \) and \( \hat{B} \) are various operators and \( \hat{H} \) is the Hamiltonian of the system. [Typically, \( \hat{A} \) will involve the Boltzmann operator, \( e^{\beta\hat{H}} \), and thus all the degrees of freedom of the complete molecular system, while \( \hat{B} \) will involve only the few degrees of freedom of a “probe” molecule or reaction coordinate.] Use of Eq. (1.1a) for each of the time evolution operators in Eq. (1.2) thus leads to the following double phase space average for the correlation function:

\[
C_{AB}(t) = (2\pi\hbar)^{-2p} \int dp_0 \int dq_0 \int dp_0' \int dq_0' \int dp_0'' \int dq_0'' C_i(p_0, q_0) \times C_i(p_0', q_0') \times C_i(p_0'', q_0'') \times \langle p'_0|\hat{p}p'_0|\hat{q}q'_0\rangle \times \langle p'_0|\hat{p}p'_0|\hat{q}q'_0\rangle \times \langle p'_0|\hat{p}p'_0|\hat{q}q'_0\rangle, \tag{1.3}
\]

where \( p'_0 = p_i(p_0', q_0') \) and \( q'_0 = q_i(p_0', q_0') \). For comparison, classical mechanics gives the correlation function as a single phase space average over initial conditions

\[
C_{AB}^{cl}(t) = (2\pi\hbar)^{-p} \int dp_0 \int dq_0 \hat{A}(p_0, q_0)\hat{B}(p_0, q_0), \tag{1.4}
\]
where here $A$ and $B$ are the classical functions of coordinates and momenta corresponding to the operators $\hat{A}$ and $\hat{B}$. The integral in the SC-IVR expression for the correlation function, Eq. (1.3), is thus twice the dimension of the classical expression, Eq. (1.4), but more serious than this is the fact that the integrand of the SC expression is oscillatory due to the phase differences between the trajectories with different initial conditions. Various filtering methods$^{13}$ have been used in applications to date to deal with this troublesome oscillatory behavior, but nothing so far has lead to a procedure that is practical for systems with many degrees of freedom.

To side-step these problems, several applications carried out in our group have used a linearized approximation$^{10-13}$ to Eq. (1.3), whereby the difference in the action integrals is expanded to linear order in $(q_0 - q_0')$ and $(p_0' - p_0)$. With other approximations consistent with this linearization, one obtains the following much simpler result for the correlation function:

$$ C_{AB}(t) = (2\pi\hbar)^{-F} \int dp_0 \int dq_0 A_w(p_0, q_0) B_w(p, q), $$

(1.5a)

where $A_w(p_0, q_0)$ is the Wigner transform of the operator $\hat{A}$,

$$ A_w(p_0, q_0) = \int d\Delta q e^{-i\Delta q p_0} \langle q_0 + \Delta q/2 | \hat{A} | q_0 - \Delta q/2 \rangle, $$

(1.5b)

and similarly for $B_w$. This linearized SC-IVR (LSC-IVR) result thus has the same form as the classical expression, Eq. (1.4), with the Wigner functions replacing the classical functions, a result that has been obtained a number of times previously from a variety of different formulations.$^{14,15}$ Though the LSC-IVR approach has been seen to work extraordinarily well for some important model problems (a reaction coordinate or two level system coupled to an infinite bath of harmonic oscillators$^{12}$), one knows that it is incapable of describing quantum coherence features arising from distinct classical trajectories because the approximation assumes that the initial conditions $(p_0, q_0)$ and $(p_0', q_0')$ in Eq. (1.3) are infinitesimally close to one another.$^{11}$

Another approximation we explored$^{10}$ was to make the linearization approximation only for the less interesting degrees of freedom (the “bath”), retaining the full SC description for the most important degrees of freedom (the “system”). This “mixed semiclassical–classical” approach leads to a single phase space average over the initial conditions of the (many) “bath” degrees of freedom and a double phase space average over the initial conditions of the (few) “system” degrees of freedom.

In this paper we describe a way of evaluating the full SC-IVR expression without invoking the linearization approximation for any of the degrees of freedom. It is based on a generalization of the forward–backward (FB) procedure introduced by Makri and Thompson$^{16,17}$ to evaluate anharmonic influence functionals in their Feynman path integral approaches. The basic idea is to combine the two time evolution operators in Eq. (1.2) into one overall SC-IVR time propagation, so that the double phase space average in Eq. (1.3) becomes a single phase space average (plus a bit more because of the operator $\hat{B}$ which sits between the forward and backward time evolution operators). More important than the reduction of the dimensionality of the integral is that the forward–backward nature of the classical trajectories leads to a partial self-cancellation that makes the integrand less oscillatory. Section II develops this FB-IVR approach in general, and several test applications are presented in Sec. III. It is also shown how an approximate form of the FB-IVR reverts to the LSC-IVR approximation of Eq. (1.5), so that one may think of it as a systematic way of going beyond this linearized approximation. The FB-IVR, unlike the LSC-IVR, is thus able to describe true quantum coherence effects arising from the interference of distinct classical trajectories. Section IV discusses some other applications of the forward–backward idea for quantities other than standard time correlation functions.

II. FORWARD–BACKWARD INITIAL VALUE REPRESENTATION

It is useful to work up to the general result in several stages. First, consider the case that operator $\hat{B}$ is a local (in coordinate space) phase factor,

$$ \hat{B} = e^{i\phi(q)/\hbar}. $$

(2.1)

The operator $\hat{U}$,

$$ \hat{U} = e^{iS_0(q)/\hbar} e^{i\phi(q)/\hbar} e^{-i\hat{H}t/\hbar}, $$

(2.2)

is thus a unitary operator (since it is the product of three unitary operators) and can in fact be thought of as the time-evolution operator forward from $0 \rightarrow t$ and backward from $t \rightarrow 0$ via the time-dependent Hamiltonian,

$$ \hat{H}(t') = \begin{cases} \hat{H} - \delta(t-t')\phi(q), & 0 \rightarrow t \\ \hat{H}, & t \rightarrow 0 \end{cases}, $$

(2.3)

where $\hat{H}$ is the original (time independent) molecular Hamiltonian. Since the semiclassical approximation has the same form also for a time-dependent Hamiltonian, the HK-IVR for operator $\hat{U}$ has the same form as Eq. (1.1a),

$$ \hat{U} = (2\pi\hbar)^{-F} \int dp_0 \int dq_0 C_0(p_0, q_0) $$

$$ \times e^{iS_0(p_0, q_0)/\hbar} \bigg| \bigg| p_0, q_0 \bigg\rangle \bigg\langle p_0, q_0 \bigg|, $$

(2.4)

where the forward–backward classical trajectory that results from the Hamiltonian Eq. (2.3) is as follows: one begins with initial conditions $(p_0, q_0)$ at time 0 and integrates the classical equations of motion—with the molecular Hamiltonian $\hat{H}$—to time $t$, where the momenta and coordinates are $(p_t, q_t)$; here the momenta are changed according to

$$ p_t \rightarrow p_t + \left( \frac{\partial \phi(q)}{\partial q} \right)_{q=q_0}, $$

(2.5)

and one then integrates back to time 0, yielding the final values $p_0' = p_0'(p_0, q_0)$, $q_0' = q_0'(p_0, q_0)$. The action integral in Eq. (2.4) is
and the pre-exponential factor $C_0$ is the same as Eq. (1.1b) with monodromy matrix elements $\partial q^i_0(p_0, q_0)/\partial q_0$, etc. Appendix A also shows how Eqs. (2.5) and (2.6) arise from the “primitive” or stationary phase approximation for matrix elements of the operator $\hat{U}$.

With the operator $\hat{U}=e^{i\hat{H}/\hbar}\hat{B}e^{-i\hat{H}/\hbar}$ given by the FB-IVR of Eq. (2.4) [for $\hat{B}$ of the form of Eq. (2.1)], the correlation function $C_{AB}(t)$ becomes

$$C_{AB}(t)=(2\pi\hbar)^{-F}\int d\mathbf{p}_0\int d\mathbf{q}_0 C_0(p_0, q_0) \times e^{iS_0(p_0, q_0)/\hbar}(\mathbf{p}_0\mathbf{q}_0)^i\hat{A}^{i\prime}0^{i\prime}0\), (2.7)$$

and this exemplifies the basic simplification and efficiency of FB-IVR. By making a SC-IVR for the total operator $\hat{U}$ one has only a single, rather than a double phase space average over initial conditions as in Eq. (1.3). Probably more important than this, however, is the fact that the net phase, i.e., the forward–backward action of Eq. (2.6), has partial cancellation from the forward and backward nature of the trajectory. If, for example, the phase $\phi(q)$ were zero, then the forward and backward parts of the trajectory would cancel exactly, and the net phase of Eq. (2.6) would be zero. The operator $\hat{U}$ would in this case, of course, be the trivial identity operator, but Eq. (2.4) would in fact be an efficient way to represent the identity operator, whereas using two separate IVR’s for $e^{-i\hat{H}/\hbar}$ and $e^{i\hat{H}/\hbar}$, and the resulting double phase space average, would require a great deal of effort to represent the identity operator accurately.

In general of course, operator $\hat{B}$ is not of the simple form in Eq. (2.1). The flux-side correlation function, $C_{fs}(t)$,18–20 which is most important for describing chemical reaction rates, for example, corresponds to operator $\hat{A}$ in Eq. (1.2) being the Boltzmannized flux operator

$$\hat{A}=e^{-\hat{p}\hat{q}/\hbar}\hat{F}e^{-\hat{p}\hat{q}/\hbar}, \quad (2.8a)$$

and $\hat{F}$ being the heaviside function that is 0(1) on the reactant (product) side of a dividing surface which separates reactants and products,

$$\hat{B}=\hat{h}[s(q)], \quad (2.8b)$$

where $s(q)=0$ defines the dividing surface; $\hat{F}$ is the flux operator associated with this dividing surface

$$\hat{F}=i\hbar[\hat{H},\hat{h}(s(q))]. \quad (2.8c)$$

Operator $\hat{B}$ in Eq. (2.8b) is thus not of the simple form in Eq. (2.1), but by Fourier transforming the Heaviside function, one can express it as a one dimensional integral over operators of this form,

$$h[s(q)]=\int_{-\infty}^{\infty} dp\left[2\pi/\hbar(p_s+i\varepsilon)\right]^{-1}e^{ip_s\hat{q}/\hbar}, \quad (2.8d)$$

where $\varepsilon$ is a small positive constant. One thus applies the FB-IVR to the operator $\hat{B}=e^{i\hat{p}\cdot\hat{q}/\hbar}$ and then integrates the result over the Fourier transform parameter $p_s$. The FB-IVR for the flux-side correlation function is therefore given by

$$C_{fs}(t)=\int_{-\infty}^{\infty} dp_s \left(2\pi i/p_s\right)^{-1}(2\pi\hbar)^{-F}\int d\mathbf{p}_0\int d\mathbf{q}_0 \times C_0(p_0, q_0; p_s) e^{iS_0(p_0, q_0; p_s)/\hbar}\langle p_0 q_0|\hat{F}(\beta)|p_0 q_0\rangle, \quad (2.9a)$$

where the “momentum jump” at time $t$ of the FB-IVR [cf. Eq. (2.5)] is

$$p_s\to p_s+p_f\left(\frac{\partial\xi(s)}{\partial q}\right)_{q=q_0}, \quad (2.9b)$$

and the FB action is

$$S_0(p_0, q_0; p_s)=\int_0^t dt'\left[p_s\cdot\hat{q}^i-H(p, q)\right]+p_s\xi(s), \quad (2.9c)$$

Here $p_0=p_0'(p_0, q_0; p_s)$, $q_0=q_0'(p_0, q_0; p_s)$, and the “$i\varepsilon$’’ in Eq. (2.8d) has been dropped since other factors in the integrand are zero if $p_s=0$. [Note that the “momentum jump” defined by Eq. (2.9b) is in the direction normal to the dividing surface.] The FB-IVR result for $C_{fs}(t)$ thus involves only a one-dimensional integral in addition to the single phase space average over initial conditions, only slightly more involved than the linearized SC-IVR expression [Eq. (1.5)].

The above procedure can be generalized to an arbitrary local operator $\hat{B}=\hat{B}(\hat{q})$ by21 writing it as a Fourier integral

$$\hat{B}(\mathbf{q})=\int d\mathbf{p}\hat{B}(\mathbf{p})e^{ip\cdot\hat{q}/\hbar}, \quad (2.10a)$$

where

$$\hat{B}(\mathbf{p})=(2\pi\hbar)^{-F}\int d\mathbf{q}\hat{B}(\mathbf{q})e^{-ip\cdot\hat{q}/\hbar}, \quad (2.10b)$$

and $f$ is the number of coordinates on which $\hat{B}(\mathbf{q})$ depends. The operator $e^{ip\cdot\hat{q}/\hbar}$ is thus of the form of Eq. (2.1), so the FB-IVR, Eq. (2.4), can be applied to it and the result integrated over the Fourier transform variable $\mathbf{p}$. The result for the correlation function $C_{AB}(t)$ is therefore

$$C_{AB}(t)=(2\pi\hbar)^{-F}\int d\mathbf{p}\hat{B}(\mathbf{p})\int d\mathbf{p}_0\int d\mathbf{q}_0 \times C_0(p_0, q_0) e^{iS_0(p_0, q_0; p_f)/\hbar}\langle p_0 q_0|\hat{A}|p_0 q_0\rangle, \quad (2.10c)$$

where the “momentum jump” condition at time $t$ [cf. Eq. (2.5)] is

$$p_f\to p_f+p_f' \quad (2.10d)$$

and the FB action is
\[ S_0(p_0, q_0; p, q) = \int_0^t dt' [p \cdot \dot{q} - H(p, q)] + p \cdot q + \int_t^0 dt' [p \cdot \dot{q} - H(p, q)]; \]

(2.10e)

the final values \((p_f, q_f)\) are functions of the Fourier transform variable \(p\) as well as initial conditions \((p_0, q_0)\). In addition to the phase space average over initial conditions, Eq. (2.10c) also involves an integral over the Fourier transform variable \(p\). It should be emphasized, though, that the operator \(\hat{B}\)—the "probe" operator—will typically involve only a few degrees of freedom, those of a subsystem, even though the complete molecular system involves many degrees of freedom. For the flux-side correlation function, for example, the Fourier transform variable involves only one variable. Thus in general the Fourier transform variable involves only one variable. Thus in general the Fourier transform variable involves only one variable.

Finally, to treat a general operator \(\hat{B}\) we express it in terms of its Weyl ordered product \(^{22}\)

\[ \hat{B} = \int dp \int dq \tilde{B}(p, q)e^{ip\cdot\dot{q}/h}e^{-iq\cdot\dot{q}/h}, \]

(2.11a)

where

\[ \tilde{B}(p, q) = (2\pi\hbar)^{-F} \int dq e^{ip\cdot\dot{q}/h}q[\hat{B}]\left[q^{-}\right] \]

(2.11b)

One can verify Eq. (2.11a) directly by using the fact that matrix elements of the exponential operators are given by

\[ \langle q''|e^{ip\cdot\dot{q}/h}e^{-iq\cdot\dot{q}/h}|q'\rangle = e^{ip\cdot q''/h}\delta(q+q'-q''). \]

(2.11c)

One thus utilizes a SC-IVR for the unitary operator

\[ \hat{U}(p, q) = e^{iHt/h}e^{ip\cdot\dot{q}/h}e^{-iq\cdot\dot{q}/h}e^{-iHt/h}. \]

(2.12)

The FB-IVR for \(\hat{U}(p, q)\) has the same generic form as Eq. (2.4), but as Appendix B shows, there is a "phase space jump" at time \(t\)

\[ p_0 \rightarrow p_0 + p, \]

(2.13a)

\[ q_0 \rightarrow q_0 + q, \]

(2.13b)

and the FB action integral is

\[ S_0(p_0, q_0; p, q) = \int_0^t dt' [p \cdot \dot{q} - H(p, q)] + p \cdot (q + q) + \int_t^0 dt' [p \cdot \dot{q} - H(p, q)]. \]

(2.14)

The general FB-IVR result for the correlation function is therefore

\[ C_{A\beta}(t) = (2\pi\hbar)^{-F} \int dp \int dq \tilde{B}(p, q) \int dp_0 \int dq_0 \times C_{A}(p_0, q_0; p, q)e^{iS_{A}(p_0, q_0; p, q)/\hbar}(p_0, q_0)\hat{A}(p_0, q_0), \]

(2.15)

with \(\tilde{B}(p, q)\) given by Eq. (2.11b). Again it should be emphasized that though the phase space average over initial conditions \((p_0, q_0)\) in Eq. (2.15) involve all the degrees of freedom of the complete molecular system, the dimension of the integrals over the transform variables \((p, q)\) will typically involve only a few degrees of freedom, those in terms of which operator \(\hat{B}\) is expressed.

Several observations about the general FB-IVR result, Eq. (2.15), are in order. First, it is useful to see how Eq. (2.15) reverts to the LSC-IVR expression, Eq. (1.5), with appropriate approximations. One notes that the net FB action integral \(S_0(p_0, q_0; p, q)\) of Eq. (2.14) is zero if \(p = q = 0\); this is because, in this case, the trajectory is continuous at time \(t\) [cf. Eq. (2.13)], so that the forward and backward trajectories are identical and the forward and backward action integrals exactly cancel. Furthermore, from the derivative relations in Appendix B, it is not hard to show that to first order in \(p\) and \(q\), the FB action is given by

\[ S_0(p_0, q_0; p, q) \approx q_0(p_0, q_0) \cdot p - p(p_0, q_0) \cdot q. \]

(2.16)

Since \(p_0(p_0, q_0) \approx p_0\) and \(q_0(p_0, q_0) \approx q_0\) to lowest order in \(p\) and \(q\), and thus \(C_0 \approx 1\), and since one can also show that

\[ \langle p_0, q_0|\hat{A}|p_0, q_0\rangle \approx A_w(p_0, q_0), \]

(2.17)

the general FB-IVR result, Eq. (2.15), becomes

\[ C_{A\beta}(t) = (2\pi\hbar)^{-F} \int dp_0 \int dq_0 A_w(p_0, q_0)(2\pi\hbar)^{-F} \times \int dp \int dq \tilde{B}(p, q)e^{iq \cdot p - p \cdot q}/\hbar. \]

(2.18)

The exact relationship between \(\tilde{B}(p, q)\) and the Wigner function \(B_w(p, q)\) is

\[ B_w(p, q) = \int dp \int dq \tilde{B}(p, q)e^{i(p \cdot q)/\hbar}, \]

(2.19)

but to first order in \(p\) and \(q\) one can drop the phase \(e^{i(p \cdot q)/\hbar}\) in Eq. (2.19), whereby Eq. (2.18) becomes

\[ C_{A\beta}(t) = (2\pi\hbar)^{-F} \int dp_0 \int dq_0 A_w(p_0, q_0)B_w(p, q), \]

(2.20)

precisely the linearized SC-IVR (LSC-IVR) result of Eq. (1.5). Thus, a linearization of the FB-IVR action in the Fourier transform parameters \((p, q)\), as in Eq. (2.16), leads back to the earlier LSC-IVR result.

Second, the general FB-IVR result, Eq. (2.15), bears an interesting relation to our earlier "mixed semiclassical—classical" model.\(^{10}\) To see this, we divide the complete molecular system into an \(f\)-dimensional "system" and a remaining "bath," with \(q = (r, R)\); \((r, p)\) are the coordinates and momenta of the "system" and \((R, P)\) those of the "bath." If operator \(\hat{B}\) depends only on the system degrees of freedom—in fact this would typically be the definition of the system—then Eq. (2.15) reads
\[ C_{AB}(t) = (2\pi\hbar)^{-F} \int dp \int dr \bar{B}(p, r) \int dp_0 \int dr_0 \int dP_0 \times \int dR_0 C_0 e^{iS_0(p_0, r_0, P_0, R_0)} \hat{A}[p_0, r_0, P_0, R_0], \]  \tag{2.21} \]

where \( C_0 \) and \( S_0 \) are functions of all the integration variables. There is thus a double phase space average over the system degrees of freedom, \((p, r)\) and \((p_0, r_0)\), but only a single phase space average over bath degrees of freedom, \((P_0, R_0)\), precisely the same structure as the “mixed semiclassical–classical” approximation. Unlike this previous work,\(^\text{10}\) however, the FB methodology has achieved this form without introducing any linearization approximations to the SC-IVR approach.

Third, it is useful to note that degrees of freedom which are not coupled to the operator \( \hat{B} \) do not contribute to quantum interference structure in the correlation function. To see this, suppose that the “bath” degrees of freedom \((R, P)\) in Eq. (2.21) above were not coupled to the “system” variables \((r, p)\): since the phase jump at time \( t \), Eq. (2.13), involves only system variables (on which \( \hat{B} \) depends), the trajectory of the bath variables would be continuous at \( t \), so that their contribution to the FB action \( S_0 \) would cancel out and thus makes no contribution to the quantum interference in the correlation function. It also follows, of course, that modes that are coupled only weakly to \((r, p)\) make a small contribution to \( S_0 \).

Finally, we note that the only awkward feature of the general FB-IVR result, Eq. (2.15), is the forward–backward aspect of the calculation itself; i.e., one averages over initial conditions for trajectories that go forward, \( 0 \to t \), and then backward, \( t \to 0 \), for a given value of \( t \), so that there is a separate set of such trajectories for each value of \( t \). In a classical (or LSC-IVR) calculation, on the other hand, in Eq. (1.4) [or Eq. (1.5)], one integrates only forward in time and obtains \( C_{AB}(t) \) for all times \( t \) with one set of trajectories. The FB-IVR can actually be cast in this more deterministic form (though not without introducing other inconveniences). This is accomplished by invoking Liouville’s theorem, namely,

\[ \int dp_0 \int dq_0 = \int dp \int dq, \]  \tag{2.22a} \]

so that \((p, q)\) are now the “initial conditions” by which the trajectories are specified. Equation (2.15) thus becomes

\[ C_{AB}(t) = (2\pi\hbar)^{-F} \int dp \int dq \bar{B}(p, q) \int dp \int dq C_0 \times \langle p_0, q_0 | p, q \rangle e^{iS_0(p_0, q_0; p, q) + iS_0(p, q; p_0, q_0)} \hat{A}[p_0, q_0], \]  \tag{2.22b} \]

where here \( p_0 = p_0(p, q), q_0 = q_0(p, q) \) are the momenta and coordinates that result at time 0 by integrating the equations of motion from \( t \to 0 \) with initial conditions \((p_0, q_0)\). Similarly [and in light of the jump conditions in Eq. (2.13)], \((p'_0, q'_0)\) are the variables that result from integrating the equations motion from \( t \to 0 \) with initial conditions \((p, q)\). One can make this look more conventional by now switching time \( t \) and time 0.) The FB trajectory now has the more convenient form of two forward trajectories, but with a less convenient weighting function with which to sample initial conditions for the trajectories. This latter inconvenience can perhaps be overcome by using clever importance sampling techniques, so that it may emerge that Eq. (2.22b) is actually the preferred form of the FB approach.

### III. APPLICATION TO THE FLUX-SIDE CORRELATION FUNCTION

In this section, we apply the FB-IVR approach to the calculation of flux-side correlation functions, Eqs. (2.8)–(2.9), the long time limit of which give the thermal rate constants of chemical reactions. We wish specifically to test the ability of the FB-IVR to describe quantum tunneling and interference effects and to see if it is indeed an improvement upon the LSC-IVR approximation.

Before proceeding, it is useful to note some general properties of \( C_{fs}(t) \) that simplify its evaluation. With the use of Eq. (2.8d), the rigorous expression for the flux-side correlation function is

\[ C_{fs}(t) = \int_{-\infty}^{\infty} dp_s \frac{1}{2\pi i p_s} \text{tr} [ \hat{F}(\beta) \hat{U}(p_s) ], \]  \tag{3.1} \]

where

\[ \hat{U}(p_s) = e^{i\hbar \tilde{H} t S \tau} e^{i\pi p_s \tau} e^{i\hbar \tilde{H} t S \tau} e^{-i\hbar \tilde{H} t S \tau}. \]  \tag{3.2} \]

Since \( \hat{F}(\beta) \) is Hermitian, one has the following relations:

\[ \text{tr} [ \hat{F}(\beta) \hat{U}(p_s) ]^* = \text{tr} [ \hat{F}(\beta) \hat{U}(p_s) ]^t = \text{tr} [ \hat{F}(\beta) i \hat{U}(p_s) ] = \text{tr} [ \hat{F}(\beta) \hat{U}(p_s) ] \]  \tag{3.3} \]

so that the imaginary part of \( \text{tr} [ \hat{F}(\beta) \hat{U}(p_s) ] \) is an odd function of \( p_s \). Therefore the integrand in Eq. (3.1) is an even function of \( p_s \), and one only needs to integrate over positive values of \( p_s \),

\[ C_{fs}(t) = \text{Re} \int_0^{\infty} dp_s \frac{1}{i \pi p_s} \text{tr} [ \hat{F}(\beta) \hat{U}(p_s) ]. \]  \tag{3.4} \]

thus simplifying the calculation.

#### A. 1-d Eckhart barrier

The first example we consider is simple barrier transmission. The specific system is the 1-d Eckhart barrier, for which the Hamiltonian is

\[ H = \frac{p^2}{2m} + V_0 \text{sech}^2(aq), \]  \tag{3.5} \]

with parameters that correspond approximately to the \( \text{H} + \text{H}_2 \) reaction: \( V_0 = 0.425 \text{ eV}, a = 1.36 \text{ a.u.} \) and \( m = 1224 \text{ a.u.} \). To evaluate the matrix element \( \langle p_0 q_0 | \hat{F}(\beta) | p'_0 q'_0 \rangle \) in Eq. (2.9a), we express the Boltzmannized flowed operator by its eigenfunction expansion, i.e.,

\[ \hat{F}(\beta) = \sum_n f_n | u_n \rangle \langle u_n |, \]  \tag{3.6} \]

where

\[ \hat{F}(\beta) | u_n \rangle = f_n | u_n \rangle. \]  \tag{3.7} \]
The matrix element thus becomes

\[ \langle p_0 q_0 | \hat{F} | p'q'_0 \rangle = \sum_n f_n \langle p_0 q_0 | u_n \rangle \langle u_n | p'q'_0 \rangle. \] (3.8)

and the evaluation of Eq. (2.9a) is then accomplished by Monte Carlo sampling of the initial distribution \( \langle p_0 q_0 | u_n \rangle \).

Figure 1 shows the dependence of the integrand of Eq. (3.4) on the momentum jump variable \( p_s \), for \( T = 300 \) K and \( t \approx 10 \) fs, just as it reaches the 'plateau' region. It has some oscillatory character but not of a severe nature. Figure 2 then shows \( C_{fs}(t) \) at several different times, and they are in good agreement with the correct quantum value over the whole time span. For this example \( C_{fs}(t) \) shows the typical behavior of a 'direct' reaction, rising to its plateau value in a time of \( \sim \hbar \beta \). For this temperature the tunneling correction function \( \kappa = k_{QM}/k_{CL} \) is about 2.

B. 1-d double well

A more complicated example is the 1-d double well potential where the Hamiltonian is

\[ H(p_s, s) = \frac{p_s^2}{2m_s} - \frac{1}{2} m_s \omega_p^2 s^2 + \frac{m_s^2 \omega_b^4}{16 V_0} s^4, \] (3.9)

with \( V_0 = 2085 \) cm\(^{-1} \) (\( \sim 6 \) kcal/mol), \( m_s = 1836.1 \) a.u. (that of a H atom), and \( \omega_b = 500 \) cm\(^{-1} \). Unlike the previous example, the flux-side correlation function for this system does not have a well-defined long time limit, and in a previous study\(^{11} \) that carried out both LSC-IVR and SC-IVR calculations, we observed quantum mechanical interference structure that persists to all times. This example thus tests the accuracy of the FB-IVR approach for describing quantum mechanical interference effects. Figure 3 again shows the dependence of the integrand of Eq. (3.4) as a function of \( p_s \), for \( t = 242 \) fs and \( T = 300 \) K. One sees that the integrand is well localized and free of rapid oscillations. This allows us to Monte Carlo sample all of the integration variables, \( (p_0, q_0, p_s) \), together. Figure 4 shows the comparison of the FB-IVR flux-side correlation function for this system at 300 K with the exact quantum mechanical correlation function over a wide time interval. The result here is very good not only because the overall agreement is satisfactory, but also because the longest time we are able to propagate is \( \sim 500 \) fs.
about twice as long as we were able to obtain via the standard SC-IVR. Furthermore, unlike the SC-IVR which becomes drastically more difficult as the time increases, the numerical effort of the FB-IVR for the longest time is not significantly greater than that for the shortest time.

### C. A system coupled to ten bath modes

The final example is the double well potential of the popular system–bath problem, for which the Hamiltonian is

$$H = H_0(p_s, s) + \sum_{i=1}^{10} \frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 \left( q_i - \frac{c_i}{m_i \omega_i} \right)^2,$$  \hspace{1cm} (3.10)

where $H_0(p_s, s)$ is given by Eq. (3.9). The frequencies $\{\omega_i\}$ and coupling constants $\{c_i\}$ are chosen from the usual Ohmic (with exponential cutoff) spectral density

$$J(\omega) = \frac{\pi}{2} \sum_{i=1}^{10} \frac{c_i^2}{m_i \omega_i} \delta(\omega - \omega_i) = \eta \omega e^{-\omega/\omega_c},$$  \hspace{1cm} (3.11)

and their specific values are listed in Table I.

The version of this problem with an infinite bath of harmonic (“bath”) degrees of freedom coupled to it. This is a ten mode version of the popular system–bath problem, for which the Hamiltonian is

$$H = H_0(p_s, s) + \sum_{i=1}^{10} \frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 \left( q_i - \frac{c_i}{m_i \omega_i} \right)^2,$$  \hspace{1cm} (3.10)

and with the Fourier representation of the delta function, this becomes

$$J(\omega) = \frac{\pi}{2} \sum_{i=1}^{10} \frac{c_i^2}{m_i \omega_i} \delta(\omega - \omega_i) = \eta \omega e^{-\omega/\omega_c},$$  \hspace{1cm} (3.11)

where $\omega_c$ is the reactant partition function and

$$k_{\text{TST,CL}} = \frac{\omega_{\omega_c}}{2\pi} e^{-\beta V_0}.$$  \hspace{1cm} (3.13)

The correlation function is seen to rise in typical fashion\(^{12}\) to its transition state value in a time of $\sim \hbar \beta$ and then to show structure due to flux that recrosses the dividing surface. The results of the FB-IVR calculation agree well with those of the LSC-IVR, suggesting that perhaps ten bath modes are sufficient to quench some of the quantum effects in the recrossing region.

### IV. OTHER APPLICATIONS OF THE FORWARD–BACKWARD IDEA

The forward–backward idea can be readily applied to simplify other kinds of semiclassical calculations. For example, the spectral density with respect to some reference state $\langle \chi \rangle$ is defined by

$$I(E) = \langle \chi | \delta(E - \hat{H}) | \chi \rangle,$$  \hspace{1cm} (4.1a)

and with the Fourier representation of the delta function, this becomes

$$I(E) = (\pi \hbar)^{-1} \text{Re} \int_0^\infty dt e^{iEt} \langle \chi | e^{-i\hat{H}t} | \chi \rangle.$$  \hspace{1cm} (4.1b)

The SC-IVR expression for the $t$-dependent survival amplitude is readily obtainable from Eq. (1.1),

$$\langle \chi | e^{-i\hat{H}t} | \chi \rangle = (2\pi \hbar)^{-1} \int d\mathbf{p} \int d\mathbf{q} C_s(\mathbf{p}, \mathbf{q}) \chi(\mathbf{p}, \mathbf{q} | \mathbf{p}_0, \mathbf{q}_0),$$  \hspace{1cm} (4.1c)

Equations (4.1a)–(4.1c) are often used to calculation photon excitation cross section, for which $\langle \chi \rangle$ is the initial state multiplied by the dipole momentum operator, and also to obtain the discrete energy levels of a bound-state system since in this case Eq. (4.1a) can be written as

\[\text{TABLE I. Frequencies and coupling constants (in cm}^{-1}\text{) for the harmonic bath in Sec. III C.}\]

<table>
<thead>
<tr>
<th>$\omega_i$</th>
<th>$c_i/m_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>221.7</td>
<td>0.21</td>
</tr>
<tr>
<td>443.3</td>
<td>0.34</td>
</tr>
<tr>
<td>665.0</td>
<td>0.41</td>
</tr>
<tr>
<td>886.7</td>
<td>0.44</td>
</tr>
<tr>
<td>1108.3</td>
<td>0.44</td>
</tr>
<tr>
<td>1330.0</td>
<td>0.43</td>
</tr>
<tr>
<td>1551.7</td>
<td>0.40</td>
</tr>
<tr>
<td>1773.3</td>
<td>0.36</td>
</tr>
<tr>
<td>1995.0</td>
<td>0.33</td>
</tr>
<tr>
<td>2216.7</td>
<td>0.29</td>
</tr>
</tbody>
</table>

FIG. 5. The flux-side correlation function for the double well potential coupled to ten harmonic modes, the example of Sec. III C, at $T = 300$ K. The solid line is the linearized SC-IVR (LSC-IVR) result and the solid points the FB-IVR results.
\[ I(E) = \sum_i \langle \chi | \psi_i \rangle^2 \delta(E - E_i), \tag{4.1d} \]

where \( \{ E_i \} \) and \( \{ | \psi_i \rangle \} \) are the eigenvalues and eigenstates of \( \hat{H} \); in this latter case \( | \chi \rangle \) can be any convenient reference state.

The forward–backward idea can be implemented if \( | \chi \rangle \) is chosen to be the eigenstate of some zeroth order Hamiltonian \( \hat{H}_0 \), i.e.,

\[ \hat{H}_0 | \chi \rangle = E_0 | \chi \rangle. \tag{4.2} \]

One then has the following elementary identity for the survival amplitude:

\[ \langle \chi | e^{-i\hat{H}_0 t} | \chi \rangle = \langle \chi | e^{-i\hat{H}_0 | \psi_0 \rangle} e^{i\hat{H}_0 | \psi_0 \rangle} e^{-i\hat{H}_0 t} | \chi \rangle \]

\[ = e^{-iE_0 | \psi_0 \rangle} \langle \chi | e^{i\hat{H}_0 | \psi_0 \rangle} e^{-i\hat{H}_0 t} | \chi \rangle, \tag{4.3} \]

so that Eq. (4.1b) becomes

\[ I(E) = (\pi \hbar)^{-1} \text{Re} \int_0^\infty dt e^{i(E - E_0 + 2\hbar \omega) t} \langle \chi | e^{i\hat{H}_0 t} e^{-i\hat{H}_0 t} | \chi \rangle, \tag{4.4} \]

and the FB-IVR is applied to the operator

\[ \hat{U} = e^{i\hat{H}_0 t} e^{-i\hat{H}_0 t}, \tag{4.5} \]

which clearly corresponds to propagation forward \( 0 \to t \) with the Hamiltonian \( \hat{H} \) and then backward \( t \to 0 \) with Hamiltonian \( \hat{H}_0 \). The FB-IVR for the matrix element in Eq. (4.4) is thus given by

\[ \langle \chi | e^{i\hat{H}_0 t} e^{-i\hat{H}_0 t} | \chi \rangle = (2 \pi \hbar)^{-F} \int dp_0 dq_0 C_0(p_0, q_0) \]

\[ \times e^{iS_0(p_0, q_0)/\hbar} \langle \chi | \psi_q \rangle \langle \

\[ \times e^{i\hat{H}_0 (t_1 - 1)} | \psi_q \rangle \langle \psi_q | \chi \rangle, \tag{4.6} \]

where the final values \( (p'_0, q'_0) \) are obtained from the trajectory that begins with initial conditions \( (p_0, q_0) \) at \( t=0 \) and evolves via the full Hamiltonian \( \hat{H} \) to time \( t \), and then back to \( t=0 \) via Hamiltonian \( \hat{H}_0 \), with both the coordinate and momenta being continuous at time \( t \); i.e., there are no coordinate or momentum “jumps” because there is no operator between the two propagators in Eq. (4.5).

The advantage of using Eqs. (4.4) and (4.6), rather than Eqs. (4.1b) and (4.1c) are obvious; the integrand of Eq. (4.6) will be much less oscillatory than that of Eq. (4.1c) because of the partial cancellation of the forward and backward action integrals, i.e., \( S_0(p_0, q_0) \) of Eq. (4.6) is given by

\[ S_0(p_0, q_0) = \int^t_0 dt' \langle p' \cdot q - H \rangle + \int^0_{t'} dt' \langle p' \cdot q - H_0 \rangle. \tag{4.7} \]

This will be increasingly true the better \( H_0 \) approximates \( H \). We have re-done some of the calculations we reported earlier\textsuperscript{8} for eigenvalues of the HCl dimer using Eqs. (4.4) and (4.6) and indeed verified\textsuperscript{24} that they provide an improvement in efficiency over the original calculations base on Eqs. (4.1b) and (4.1c).

Another application of the FB-IVR approach has been Batista et al.’s\textsuperscript{25} treatment of the femtosecond photodetachment of \( I_2 \) as studied by the Neumark group.

\[ I_2(X) + h \nu_1 \to I_2(A), \tag{4.8a} \]

\[ I_2(A) + h \nu_2 \to I_2(K) + e^- (e), \tag{4.8b} \]

where there is a femtosecond time delay between the pump \((h \nu_1)\) and probe \((h \nu_2)\) pulses. The matrix element which describes this process involves a sequence of time evolution operators for the nuclear dynamics on various potential energy surfaces (PES’s),

\[ \langle \chi_g | e^{-i\hat{H}_S(0 - t_1)} e^{-i\hat{H}_S(t_4 - t_3)} e^{-i\hat{H}_S(t_3 - t_2)} e^{-i\hat{H}_S(t_2 - t_1)} \]

\[ \times e^{-i\hat{H}_x (t_1 - 1)} | \chi_g \rangle, \tag{4.9} \]

where \( | \chi_g \rangle \) is the initial vibrational state of the ground (X) state PES. The FB-IVR for this matrix element is of the now standard form of a single phase space average over initial conditions, cf. Eq. (4.6), where here the FB trajectory begins with initial conditions \( (p_0, q_0) \) at \( t=0 \) and evolves on the PES of the X state (of \( I_2 \)) until \( t_1 \), at which time the PES is changed to that of the A state (of \( I_2 \)) and the trajectory evolved to \( t_2 \), at which time the PES is changed again to that of the K state (of \( I_2 \)) and evolved to time \( t_3 \), at which time the PES is changed back to that of the A state (of \( I_2 \)) and evolved to \( t_4 \), at which time the PES is changed finally back to that of the X state (of \( I_2 \)) and evolved back to \( t=0 \). The coordinates and momenta are continuous at each of these times where the PES is changed. The enhanced efficiency of having only a single phase space average over initial conditions, rather than a fivefold such average, is thus amplified for this application. Batista et al.\textsuperscript{25} found the result of the FB-IVR calculation to be in excellent agreement with accurate quantum calculations for the corresponding quantity.

V. CONCLUDING REMARKS

Section II has shown how a SC-IVR of the two time evolution operators that appear in a typical quantum time correlation function can be combined into one overall IVR, involving trajectories that propagate forward from 0 to \( t \) and the backward from \( t \) to 0. This not only reduces the dimensionality of the phase space integral over initial conditions of classical trajectories, but the partial cancellation of the forward–backward trajectory leads to a less oscillatory integrand. Degrees of the freedom not strongly coupled to the “probe” operator are especially cancelled out in the forward–backward trajectory. Section IV shows other examples of how multiple time evolution operators in quantum expressions can also be so combined.

Several applications of the FB-IVR to flux-side correlation functions were presented in Sec. III, with very encouraging results. Together with other approaches for simplifying the SC-IVR calculations—e.g., stationary phase Monte Carlo filtering\textsuperscript{5} and time-averaging of the integrand\textsuperscript{26,27}—the FB-IVR is a significant step toward making these methods useful for describing quantum effects in complex molecular systems.
APPENDIX A

The "primitive" semiclassical approximation for the matrix elements of the operator \(\hat{U}\) of Eq. (2.2) is given by
\[
\langle q'_0 | \hat{U} | q_0 \rangle = \int dq' \langle q'_0 | e^{i \hat{H} \hat{t}/\hbar} | q' \rangle e^{i \phi(q')} \langle q' | e^{-i \hat{H} \hat{t}/\hbar} | q_0 \rangle, \tag{A1}
\]
where the integral over \(q\) is to be evaluated by the stationary phase approximation (SPA). The "primitive" (or Van Vleck) approximation for the individual propagator matrix elements in Eq. (A1) have the standard form
\[
\begin{align*}
\langle q | e^{-i \hat{H} \hat{t}/\hbar} | q_0 \rangle &\sim e^{i S(q, q_0; 0 \rightarrow \tau)/\hbar}, \tag{A2a} \\
\langle q'_0 | e^{i \hat{H} \hat{t}/\hbar} | q \rangle &\sim e^{i S(q'_0, q; t \rightarrow 0)/\hbar}, \tag{A2b}
\end{align*}
\]
where for this qualitative discussion we do not keep track of pre-exponential factors. The stationary phase condition for the integral in Eq. (A1) is
\[
0 = \frac{\partial S(q, q_0; 0 \rightarrow t)}{\partial q} + \frac{\partial \phi(q)}{\partial q} + \frac{\partial S(q'_0, q; t \rightarrow 0)}{\partial q}, \tag{A3}
\]
and the usual derivative relations identify \(\partial S(q, q_0; 0 \rightarrow t)/\partial q = p(q, q_0)\) as the momentum at time \(t\) from the \(0 \rightarrow t\) trajectory, and \(\partial S(q'_0, q; t \rightarrow 0)/\partial q = -p(q'_0, q)\), where \(p(q'_0, q)\) is the momentum at time \(t\) for the \(t \rightarrow 0\) trajectory. Equation (A3) thus gives the "momentum jump" at time \(t\) in Eq. (2.5). Furthermore, the SPA gives the net phase of the matrix element,
\[
\langle q'_0 | \hat{U} | q_0 \rangle \sim e^{i S(q'_0, q_0)/\hbar}, \tag{A4}
\]
as
\[
S(q'_0, q_0) = S(q, q_0; 0 \rightarrow t) + \phi(q) + S(q'_0, q; t \rightarrow 0) \tag{A5}
\]
with \(q = q_f\) evaluated at the stationary phase value determined by Eq. (A3); this is the net forward–backward action given by Eq. (2.6).

APPENDIX B

Here we consider the "primitive" semiclassical approximation for the unitary operator in Eq. (2.12),
\[
\langle q'_0 | \hat{U}(p, q) | q_0 \rangle = \int dq'' \int dq' \langle q'_0 | e^{i \hat{H} \hat{t}/\hbar} | q' \rangle \times \langle q' | e^{i \hat{p} \cdot \hat{q}' \hat{t}/\hbar} | q' \rangle \times \langle q' | e^{-i \hat{H} \hat{t}/\hbar} | q_0 \rangle. \tag{B1}
\]
Utilizing the matrix elements in Eq. (2.11c) gives
\[
\begin{align*}
\langle q'_0 | \hat{U}(p, q) | q_0 \rangle &= \int dq' \langle q'_0 | e^{i \hat{H} \hat{t}/\hbar} | q' \rangle \\
&\quad + \langle q' | e^{i \hat{p} \cdot \hat{q}' \hat{t}/\hbar} \langle q' | e^{-i \hat{H} \hat{t}/\hbar} | q_0 \rangle. \tag{B2}
\end{align*}
\]
and with the primitive semiclassical approximation to the two propagator elements, (again neglecting the pre-exponential factors),
\[
\begin{align*}
\langle q' | e^{-i \hat{H} \hat{t}/\hbar} | q_0 \rangle &\sim e^{i S(q', q_0; 0 \rightarrow \tau)/\hbar}, \tag{B3a} \\
\langle q'_0 | e^{i \hat{H} \hat{t}/\hbar} | q' + q \rangle &\sim e^{i S(q'_0, q'; 0 \rightarrow \tau)/\hbar}. \tag{B3b}
\end{align*}
\]
The stationary phase condition for the integral in Eq. (B2) is
\[
0 = \frac{\partial}{\partial q} S(q'_0, q' + q; t \rightarrow 0) + p + \frac{\partial}{\partial q} S(q', q_0; 0 \rightarrow t). \tag{B4}
\]
Again using the derivative relations of the action integrals,
\[
p(q', q_0) = \frac{\partial S(q', q_0; 0 \rightarrow \tau)/\partial q'}{\partial q} \]
is identified as the momentum at time \(t\) for the forward \(0 \rightarrow t\) trajectory, and \(p(q_0, q + q') = -\frac{\partial S(q'_0, q + q'; t \rightarrow 0)/\partial q'}{\partial q} \)
is the momentum at time \(t\) for the \(t \rightarrow 0\) backward trajectory, so that Eq. (B4) implies the following "momentum jump" at time \(t\):
\[
p_t \rightarrow p_t + p. \tag{B5a}
\]
Also, the coordinate at time \(t\) for the forward \(0 \rightarrow t\) trajectory is \(q'\), and for the backward \(t \rightarrow 0\) trajectory it is \(q' + q\), which is equivalent to the "coordinate jump" at time \(t\),
\[
q_t \rightarrow q_t + q. \tag{B5b}
\]
Finally, the net phase of the matrix element is
\[
S_0(q'_0, q_0) = S(q_0, q + q'; t \rightarrow 0) + p \cdot (q + q') + S(q', q_0; 0 \rightarrow t) \tag{B6}
\]
with \(q' = q_f\), determined by the stationary phase condition Eq. (B4).

The coherent state IVR for \(\hat{U}(p, q)\) therefore has the standard form, Eq. (2.4), where the net trajectory begins at time \(0\) with initial conditions \((p_0, q_0)\) and evolves for time \(t\) to phase point \((p_t, q_t)\); here the momenta and coordinates are changed according to Eq. (B5) and one integrates the classical equations of motion back to \(t = 0\), where the final values
are $p_0' = p_0'(p_0, q_0; p, q)$ and $q_0' = q_0'(p_0, q_0; p, q)$. The action $S_0$ for this forward–backward trajectory is given by Eq. (B6), i.e.,

$$S_0(p_0, q_0; p, q) = \int_0^t dt' \left[ p \cdot q - H(p, q) \right] + p \cdot (q + q)$$

$$+ \int_0^t dt' \left[ p \cdot q - H(p, q) \right]. \quad (B7)$$

21. One can also express the local operator $\hat{B}(q)$ in exponential form by using the identity $\hat{B} = -i(d/dt)e^{i\hat{f}t}$, $\lambda \rightarrow 0$, but we have not found this to work as well as the Fourier representation, at least where $\hat{B}$ is the Heaviside function. It might be useful in other cases.