

# On the semiclassical description of quantum coherence in thermal rate constants

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(Received 6 April 1998; accepted 15 June 1998)

An earlier paper of ours [J. Chem. Phys. **108**, 9726 (1998)] used an approximate (linearized) version of the semiclassical initial value representation (SC-IVR) to calculate reactive flux correlation functions for a model of unimolecular isomerization, namely a 1-*d* double well potential coupled to an infinite set of harmonic oscillators, obtaining excellent agreement with accurate quantum results for this system. Here we analyze this linearized approximation (LA) further, however, and show that it is not capable of describing quantum interference/coherence effects in the longer time recrossing behavior of the isomerization dynamics. (The recrossing effects seen in our earlier work were due to classical mechanics.) To accentuate quantum effects in the recrossing dynamics, the present article considers the double well potential without the harmonic bath, using both the LA and the full SC-IVR. The results of the calculations show that the flux correlation functions given by the LA agrees well with the exact quantum correlation function for times up to  $\approx \hbar\beta$ , meaning that it describes quantum effects in the direct or transition state theory like dynamics accurately. For the longer time recrossing dynamics, however, it agrees with the *classical* rather than the *quantum* correlation function, i.e., it does not describe quantum coherence effects on this time scale. The full SC-IVR calculations, however, are in reasonably good agreement with the quantum correlation function for these longer times. © 1998 American Institute of Physics. [S0021-9606(98)02835-9]

## I. INTRODUCTION

Considerable progress has been made in recent years in the development of rigorous quantum mechanical methods for the efficient calculation of rate constants for chemical reactions in small molecular systems.<sup>1-3</sup> One version of these approaches (actually the original one formulated by one of us some years ago<sup>4</sup>) expresses the thermal rate constant as

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

where  $Q_r(T)$  is the reactant partition function (per unit volume for a bimolecular reaction) and  $C_{fs}(t)$  is the “flux-side” correlation function,<sup>5</sup>

$$C_{fs}(t) = \text{tr}[\hat{F}(\beta)\hat{h}(t)]; \quad (1.2a)$$

here  $\hat{F}(\beta)$  is a combination of the flux operator  $\hat{F}$  and the Boltzmann operator  $\exp(-\beta\hat{H})$ , often taken in the following symmetrized form:<sup>5</sup>

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

and  $\hat{h}(t)$  is a time-evolved projection operator,

$$\hat{h}(t) = e^{i\hat{H}t/\hbar}\hat{h}e^{-i\hat{H}t/\hbar}, \quad (1.2c)$$

where  $h(\mathbf{q})$  is a function of coordinates that is 1(0) on the product (reactant) side of the dividing surface separating the two. [ $\hat{H}$  is the Hamiltonian operator of the molecular system and  $\beta = (k_B T)^{-1}$ .] The efficiency of these approaches is

primarily due to the fact that they focus directly on the rate constant and avoid dealing with the complete state-to-state reactive scattering problem. A variety of applications have been carried out for reactions of three- and four-atom molecular systems.<sup>1-3</sup>

The classical analog<sup>6</sup> of Eqs. (1.1)–(1.2) has been widely used for treating reactions in condensed phases, and it is our goal to develop the quantum version of the theory to be able to describe quantum effects in such systems, e.g., reactions in solutions, clusters, biological environments, or on surfaces. Quantum effects tend to be averaged out in complex systems, but processes that involve the motion of hydrogen atoms—e.g., OH vibrations or bond breaking, H<sub>2</sub>O reorientation, hydrogen bonding, and obviously electronically nonadiabatic processes (in photochemistry)—may often be poorly described by classical molecular dynamics. Furthermore, one can never know the extent to which quantum effects are significant without having a theoretical approach capable of describing them.

One strategy for doing this is to treat only a few degrees of freedom by quantum mechanics and the (many) others by classical mechanics, i.e., the popular mixed quantum-classical (Ehrenfest) model<sup>7</sup> that has been widely used but which can have problems.<sup>8</sup> An alternative approach that we have been pursuing is a semiclassical (SC) approximation to the rigorous quantum dynamics, specifically the semiclassical *initial value representation* (IVR)<sup>9-14</sup> which is a potentially efficient way of implementing semiclassical approximations. Within the framework of the SC-IVR, two of us<sup>15</sup> have recently shown how one can degenerate the description

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of *some* degrees of freedom to the classical level while still retaining the full semiclassical description of the rest—i.e., a mixed *semiclassical*-classical treatment. Ovchinnikov and Apkarian<sup>16</sup> have independently used this idea very effectively in applications to vibrational relaxation processes in clusters and liquids.

The purpose of the present article is to investigate the extent to which the semiclassical initial value representation (SC-IVR) is able to describe quantum interference/coherence effects in thermal rate constants, and also to determine the limitations of a much simpler linearized version of the full SC-IVR approach. In a recent paper<sup>8</sup> we observed that this linearized approximation to the SC-IVR for  $k(T)$  gave excellent results for a model of condensed phase unimolecular isomerization, specifically a 1- $d$  double well potential coupled to an infinite bath of harmonic oscillators for which Topaler and Makri<sup>17</sup> have carried out essentially exact quantum path integral calculations. To accentuate quantum coherence effects, in this article we omit the harmonic bath, which tends to quench them, and consider the 1- $d$  double well potential by itself, a model of unimolecular isomerization of an isolated molecule. In this case  $C_{fs}(t)$  does not reach a limiting value as  $t \rightarrow \infty$  [cf. Eq. (1.1)], i.e.,  $k(T)$  does not exist, for the particle oscillates back and forth in the double well forever. The dynamics of this coherent motion, as it manifests itself in the correlation function  $C_{fs}(t)$ , however, is precisely the phenomenon we are seeking to investigate, so it is an ideal test case for these purposes.

Section II A first summarizes the general SC-IVR approach, and the *linearization approximation* (LA) to the full SC-IVR expression is described in Sec. II B. The Appendix presents a more general, pedagogical discussion of the linearization approximation, showing how it yields precisely the *classical* limit, without any quantum interference/coherence structure. Section II C shows how the LA can also be applied to state-to-state reaction probabilities. The SC approximations in Sec. II all pertain to the time evolution, i.e., the operator  $\hat{h}(t)$  in Eq. (1.2), while the operator  $\hat{F}(\beta)$  is treated via exact quantum mechanics; Sec. III shows how the SC-IVR approach can also be used to approximate the Boltzmann operator in  $\hat{F}(\beta)$ . Section IV then presents and discusses the results of the various approaches to describing the time dependence of  $C_{fs}(t)$  for the double well potential.

Of previous work, this article is most closely related to that of Voth, Chandler, and Miller,<sup>18</sup> who used Eq. (1.2) with various approximations for the time-dependent factor  $\hat{h}(t)$ , applied to barrier crossing dynamics (but not the longer time coherence effects investigated here). The linearization approximation of Sec. II B has been used in various guises by many persons, e.g., Wolynes,<sup>19</sup> Mukamel *et al.*,<sup>20</sup> Cao and Voth,<sup>21</sup> and also recently by Pollak *et al.*<sup>22</sup> who use it with an approximation to the time-dependent factor similar to Voth *et al.*<sup>18</sup> to obtain a “quantum transition state theory.” We also note related work by Filinov *et al.*<sup>23</sup> based on the Wigner representation of Eq. (1.2).

## II. SEMICLASSICAL INITIAL VALUE REPRESENTATION FOR THERMAL RATE CONSTANTS

In this section we assume that the Boltzmannized flux operator  $\hat{F}(\beta)$  is evaluated by exact quantum mechanics, which is trivial for the 1- $d$  problem treated in this article but also feasible by Monte Carlo path integral methods even for complex systems (i.e., those with many degrees of freedom). Also, for the applications below we have used the Kubo version of  $\hat{F}(\beta)$ , which corresponds to *averaging* over how the flux operator is sandwiched between the two Boltzmann operators,

$$\hat{F}_K(\beta) \equiv \frac{1}{\beta} \int_0^\beta d\lambda e^{-\lambda \hat{H}} \hat{F} e^{-(\beta-\lambda)\hat{H}}; \quad (2.1a)$$

since

$$\hat{F} = \frac{i}{\hbar} [\hat{H}, \hat{h}], \quad (2.1b)$$

one can show<sup>18</sup> that this gives

$$\hat{F}_K(\beta) = \frac{i}{\hbar\beta} [\hat{h}, e^{-\beta\hat{H}}], \quad (2.1c)$$

for which the coordinate representation is

$$\langle \mathbf{q}' | \hat{F}_K(\beta) | \mathbf{q} \rangle = \frac{i}{\hbar\beta} [h(\mathbf{q}') - h(\mathbf{q})] \langle \mathbf{q}' | e^{-\beta\hat{H}} | \mathbf{q} \rangle. \quad (2.1d)$$

We also carried out some calculations with the symmetrically split version of  $\hat{F}(\beta)$  in Eq. (1.2b) and found very little difference in the results for the example considered below.

### A. Semiclassical initial value representation for time evolution

In a coordinate representation Eq. (1.2a) becomes

$$C_{fs}(t) = \int d\mathbf{q} \int d\mathbf{q}' \int d\mathbf{q}'' \langle \mathbf{q} | \hat{F}(\beta) | \mathbf{q}' \rangle \times \langle \mathbf{q}' | e^{i\hat{H}t/\hbar} | \mathbf{q}'' \rangle h(\mathbf{q}'') \langle \mathbf{q}'' | e^{-i\hat{H}t/\hbar} | \mathbf{q} \rangle, \quad (2.2)$$

and we utilize the SC-IVR<sup>9-14</sup> for the matrix elements of the time evolution operator,

$$\langle \mathbf{q} | e^{-i\hat{H}t/\hbar} | \mathbf{q}_0 \rangle \equiv (2\pi i\hbar)^{-F/2} \int d\mathbf{p}_0 \delta(\mathbf{q} - \mathbf{q}_t) \times \left[ \det \left( \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \right) \right]^{1/2} e^{-i\pi\nu_t/2} e^{iS_t(\mathbf{p}_0, \mathbf{q}_0)/\hbar}; \quad (2.3)$$

here  $(\mathbf{q}_0, \mathbf{p}_0)$  are the initial conditions for a classical trajectory,  $\mathbf{q}_t = \mathbf{q}(\mathbf{q}_0, \mathbf{p}_0; t)$  is the coordinate at time  $t$  along this trajectory, and  $S_t(\mathbf{q}_0, \mathbf{p}_0)$  the action integral along it:

$$S_t(\mathbf{p}_0, \mathbf{q}_0) = \int_0^t dt' \left[ \frac{\mathbf{p}_{t'}^2}{2m} - V(\mathbf{q}_{t'}) \right]. \quad (2.4)$$

The integer  $\nu_t$ , the Maslov index, is the number of zeros experienced by the Jacobian in the time interval  $(0, t)$ ; i.e., it specifies the particular branch of the square root of the Jacobian.

There are several ways of implementing the semiclassical approximation, Eq. (2.3), in Eq. (2.2). Perhaps the simplest is to choose  $\mathbf{q}''$  in Eq. (2.2) as the initial value  $\mathbf{q}_0$  for both propagators, and using the symmetry relations of the propagator matrix elements

$$\langle \mathbf{q}' | e^{-i\hat{H}t/\hbar} | \mathbf{q} \rangle = \langle \mathbf{q} | e^{-i\hat{H}t/\hbar} | \mathbf{q}' \rangle = \langle \mathbf{q}' | e^{i\hat{H}t/\hbar} | \mathbf{q} \rangle^*, \quad (2.5)$$

one readily obtains the following SC-IVR expression for the correlation function:

$$C_{fs}(t) = \frac{1}{(2\pi\hbar)^F} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \int d\mathbf{p}'_0 \langle \mathbf{q}_t | \hat{F}(\beta) | \mathbf{q}'_t \rangle h(\mathbf{q}_0) \\ \times \left[ \det \left( \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \right) \det \left( \frac{\partial \mathbf{q}'_t}{\partial \mathbf{p}'_0} \right) \right]^{1/2} e^{-i\pi(\nu_t - \nu'_t)/2} \\ \times \exp \left[ \frac{i}{\hbar} (S_t(\mathbf{q}_0, \mathbf{p}_0) - S_t(\mathbf{q}_0, \mathbf{p}'_0)) \right], \quad (2.6)$$

where  $\mathbf{q}'_t = \mathbf{q}_t(\mathbf{q}_0, \mathbf{p}'_0)$ . One thus runs two classical trajectories, both beginning at the same position  $\mathbf{q}_0$  in the product region, with different initial momenta. The only awkward feature of this expression is that the trajectories begin in the product region and must terminate in the transition state region (where  $\langle \mathbf{q} | \hat{F}(\beta) | \mathbf{q}' \rangle$  localizes  $\mathbf{q}$  and  $\mathbf{q}'$ ), and the sampling of initial conditions for this purpose may not be efficient.

A second way of implementing the SC-IVR, in order to have the initial positions  $\mathbf{q}_0$  sampled from the Boltzmannized flux factor, is to choose  $\mathbf{q}$  in Eq. (2.2) to be  $\mathbf{q}_0$ ; then  $\mathbf{q}'' = \mathbf{q}_t(\mathbf{q}_0, \mathbf{p}_0)$ , and  $\mathbf{q}' = \mathbf{q}'_t \equiv \mathbf{q}(\mathbf{q}_t, \mathbf{p}'_0; t)$ . The expression for the correlation function is

$$C_{fs}(t) = \frac{1}{(2\pi\hbar)^F} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \int d\mathbf{p}'_0 \langle \mathbf{q}'_t | \hat{F}(\beta) | \mathbf{q}_0 \rangle h(\mathbf{q}_t) \\ \times \left[ \det \left( \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \right) \det \left( \frac{\partial \mathbf{q}'_t}{\partial \mathbf{p}'_0} \right) \right]^{1/2} e^{-i\pi(\nu_t - \nu'_t)/2} \\ \times \exp \left[ \frac{i}{\hbar} (S_t(\mathbf{q}_0, \mathbf{p}_0) - S_t(\mathbf{q}_t, \mathbf{p}'_0)) \right]; \quad (2.7)$$

i.e., here one begins a trajectory at  $(\mathbf{q}_0, \mathbf{p}_0)$  in the transition state region, runs it for time  $t$  into the product region, then restarts it with a new momentum  $\mathbf{p}'_0$ , runs it for time  $t$ , at which time it must be back in the transition state region. Figure 1 indicates these two possible strategies.

Finally, a third way of implementing the SC approach is to begin both trajectories in the transition state region [cf. Fig. 1(c)], i.e., to choose  $\mathbf{q} = \mathbf{q}_0$  and  $\mathbf{q}' = \mathbf{q}'_0$  in Eq. (2.2), whereby one obtains the following expression for the correlation function,

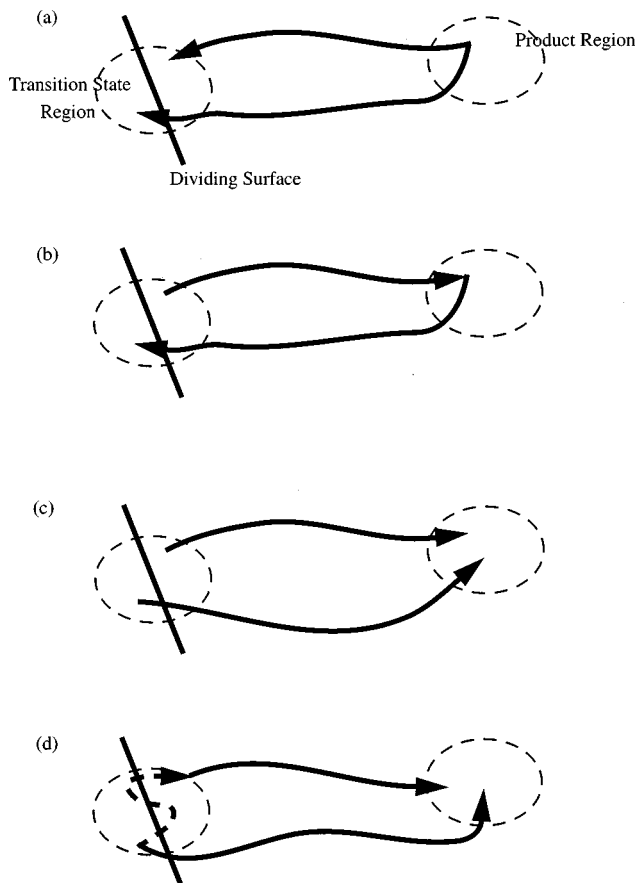


FIG. 1. Sketch of trajectory configurations in coordinate space that have nonzero contributions to the integrand in (a) Eq. (2.6), (b) Eq. (2.7), (c) Eq. (2.11), and (d) Eq. (3.4). The dashed trajectory in (d) is the imaginary time trajectory on the upside down potential.

$$C_{fs}(t) = \frac{1}{(2\pi\hbar)^F} \int d\mathbf{q}_0 \int d\mathbf{q}'_0 \int d\mathbf{p}_0 \int d\mathbf{p}'_0 \langle \mathbf{q}_0 | \hat{F}(\beta) | \mathbf{q}'_0 \rangle \\ \times \delta_F(\mathbf{q}_t - \mathbf{q}'_t) h(\mathbf{q}_t) \left[ \det \left( \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \right) \det \left( \frac{\partial \mathbf{q}'_t}{\partial \mathbf{p}'_0} \right) \right]^{1/2} \\ \times e^{-i\pi(\nu_t - \nu'_t)/2} \exp \left[ \frac{i}{\hbar} (S_t(\mathbf{q}_0, \mathbf{p}_0) - S_t(\mathbf{q}'_0, \mathbf{p}'_0)) \right], \quad (2.8)$$

where  $\mathbf{q}'_t = \mathbf{q}(\mathbf{q}'_0, \mathbf{p}'_0; t)$ . The disadvantages of this approach are clear: one has four (multidimensional) integration variables to integrate over, rather than three as in Eqs. (2.6) and (2.7), and the integral contains a delta function which requires the two trajectories to end at the same point in the product region. This later problem (the delta function) can be ameliorated by switching to a modified version of the generalized Herman-Kluk (coherent state) IVR,<sup>11,12</sup>

$$\langle \mathbf{q}' | e^{-i\hat{H}t/\hbar} | \mathbf{q} \rangle = \frac{1}{(2\pi\hbar)^F} \int d\mathbf{q}_0 d\mathbf{p}_0 C_t(\mathbf{q}_0, \mathbf{p}_0) \\ \times \langle \mathbf{q}' | \mathbf{p}_t, \mathbf{q}_t; \gamma_t \rangle \\ \times \langle \mathbf{p}_0, \mathbf{q}_0; \gamma_0 | \mathbf{q} \rangle e^{iS_t(\mathbf{q}_0, \mathbf{p}_0)/\hbar}, \quad (2.9a)$$

where the coherent state wave functions are

$$\langle \mathbf{q} | \mathbf{p}_0, \mathbf{q}_0; \gamma_0 \rangle = \left( \frac{\gamma_0}{\pi} \right)^{F/4} e^{-\gamma_0/2(\mathbf{q}-\mathbf{q}_0)^2 + i/\hbar \mathbf{p}_0 \cdot (\mathbf{q}-\mathbf{q}_0)}, \quad (2.9b)$$

similarly for  $\langle \mathbf{q}' | \mathbf{p}_t, \mathbf{q}_t; \gamma_t \rangle$ , and the pre-exponential factor is

$$C_t(\mathbf{q}_0, \mathbf{p}_0) = \det \left[ \frac{1}{2} \left( \gamma_t^{1/2} \frac{\partial \mathbf{q}_t}{\partial \mathbf{q}_0} \gamma_0^{-1/2} + \gamma_t^{-1/2} \frac{\partial \mathbf{p}_t}{\partial \mathbf{p}_0} \gamma_0^{1/2} + \frac{i}{\hbar} \gamma_t^{-1/2} \frac{\partial \mathbf{p}_t}{\partial \mathbf{q}_0} \gamma_0^{-1/2} - i\hbar \gamma_t^{1/2} \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \gamma_0^{1/2} \right) \right]^{1/2}. \quad (2.9c)$$

The modification that we use here, the  $\gamma_0 \rightarrow \infty$  limit (which converts the initial coherent state into a coordinate state), gives the following SC-IVR for the propagator

$$\langle \mathbf{q} | e^{-i\hat{H}t/\hbar} | \mathbf{q}_0 \rangle = \frac{1}{(2\pi i \hbar)^{F/2}} \int d\mathbf{p}_0 D_t(\mathbf{q}_0, \mathbf{p}_0) \times \left( \frac{\gamma_t}{4\pi} \right)^{F/4} \langle \mathbf{q} | \mathbf{p}_t, \mathbf{q}_t; \gamma_t \rangle e^{iS_t(\mathbf{q}_0, \mathbf{p}_0)/\hbar}, \quad (2.10a)$$

where

$$D_t(\mathbf{q}_0, \mathbf{p}_0) = \det \left[ \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} + \frac{i}{\hbar} \frac{\partial \mathbf{p}_t}{\partial \mathbf{p}_0} \right]^{1/2}. \quad (2.10b)$$

[The  $\gamma_t \rightarrow \infty$  limit of Eq. (2.10) would convert it into the previously used coordinate space SC-IVR, Eq. (2.3).] Using Eq. (2.10) for the propagator, the following expression is obtained for the correlation function

$$C_{fs}(t) = \frac{1}{(2\pi \hbar)^F} \int d\mathbf{q}_0 \int d\mathbf{q}'_0 \int d\mathbf{p}_0 \int d\mathbf{p}'_0 \langle \mathbf{q}_0 | \hat{F}(\beta) | \mathbf{q}'_0 \rangle \times \langle \mathbf{p}'_t \mathbf{q}'_t | \hat{h} | \mathbf{p}_t \mathbf{q}_t \rangle \left( \frac{\gamma_t}{4\pi} \right)^{F/2} D_t(\mathbf{q}_0, \mathbf{p}_0) D_t(\mathbf{q}'_0, \mathbf{p}'_0)^* \times \exp \left[ \frac{i}{\hbar} (S_t(\mathbf{q}_0, \mathbf{p}_0) - S_t(\mathbf{q}'_0, \mathbf{p}'_0)) \right]. \quad (2.11a)$$

Finally, because the coherent states are localized in position, the following approximation should be reasonable,

$$\langle \mathbf{p}'_t \mathbf{q}'_t | \hat{h} | \mathbf{p}_t \mathbf{q}_t \rangle = h(\mathbf{q}_t) h(\mathbf{q}'_t) \langle \mathbf{p}'_t \mathbf{q}'_t | \mathbf{p}_t \mathbf{q}_t \rangle, \quad (2.11b)$$

where the coherent state overlap is

$$\langle \mathbf{p}'_t \mathbf{q}'_t | \mathbf{p}_t \mathbf{q}_t \rangle = \exp \left[ -\frac{\gamma_t}{4} (\mathbf{q}_t - \mathbf{q}'_t)^2 - \frac{(\mathbf{p}_t - \mathbf{p}'_t)^2}{4\gamma_t \hbar^2} + \frac{i}{2\hbar} (\mathbf{p}_t + \mathbf{p}'_t) \cdot (\mathbf{q}_t - \mathbf{q}'_t) \right]. \quad (2.11c)$$

Comparing Eq. (2.8) to Eq. (2.11), one sees that in the latter the two trajectories are not required to land at the same point but rather that the two final points in phase space,  $(\mathbf{q}_t, \mathbf{p}_t)$  and  $(\mathbf{q}'_t, \mathbf{p}'_t)$ , are required to be in roughly the same phase space cell.

All three strategies of implementing the SC-IVR—Eqs. (2.6), (2.7), or (2.11)—are essentially equivalent; the choice between them is purely one of convenience, and it is not

immediately obvious which will turn out to be most useful in applications to complex systems. For the present 1-*d* application all are possible.

### B. The linearization approximation

The most difficult aspect of a SC-IVR calculation, i.e., the evaluation of Eqs. (2.6), (2.7), or (2.11), is due to the oscillatory character of the integrand, i.e., the difference of the two action integrals in the phase of the integrand. It is thus useful to consider approximations for dealing with this.

The lowest order approximation corresponds to expanding the phase difference in Eqs. (2.6) or (2.7) to *linear* order in  $\mathbf{p}_0 - \mathbf{p}'_0$ ,

$$S_t(\mathbf{q}_0, \mathbf{p}_0) - S_t(\mathbf{q}_0, \mathbf{p}'_0) \approx \frac{\partial S_t(\mathbf{q}_0, \bar{\mathbf{p}}_0)}{\partial \bar{\mathbf{p}}_0} \cdot \Delta \mathbf{p}, \quad (2.12)$$

where  $\bar{\mathbf{p}}_0 = (1/2)(\mathbf{p}_0 + \mathbf{p}'_0)$  and  $\Delta \mathbf{p} = \mathbf{p}_0 - \mathbf{p}'_0$  [or linearly in  $\mathbf{p}_0 - \mathbf{p}'_0$  and  $\mathbf{q}_0 - \mathbf{q}'_0$  in Eq. (2.11)]. By changing integration variables in Eqs. (2.6) or (2.7) from  $\mathbf{p}_0$  and  $\mathbf{p}'_0$  to  $\bar{\mathbf{p}}_0$  and  $\Delta \mathbf{p}$ , with the linearization approximation to the phase difference, Eq. (2.12), the integration over  $\Delta \mathbf{p}$  [ $\Delta \mathbf{p}$  and  $\Delta \mathbf{q}$  for Eq. (2.11)] can be performed analytically. This analysis has been carried out by us before,<sup>15</sup> and the expression for the flux-side correlation function becomes

$$C_{fs}(t) = \frac{1}{(2\pi \hbar)^F} \int d\mathbf{q}_0 \int d\mathbf{p}_0 F_w^\beta(\mathbf{q}_0, \mathbf{p}_0) h(\mathbf{q}_t), \quad (2.13)$$

where here  $\mathbf{p}_0 = \bar{\mathbf{p}}_0$ , with the “bar” having been dropped, and  $F_w^\beta(\mathbf{q}_0, \mathbf{p}_0)$  is the Wigner transform of the Boltzmannized flux operator,

$$F_w^\beta(\mathbf{q}, \mathbf{p}) = \int d\Delta \mathbf{q} e^{-i\mathbf{p} \cdot \Delta \mathbf{q}/\hbar} \langle \mathbf{q} + \Delta \mathbf{q}/2 | \hat{F}(\beta) | \mathbf{q} - \Delta \mathbf{q}/2 \rangle. \quad (2.14)$$

It should be immediately apparent how simple Eq. (2.13) is: it is essentially a classical trajectory calculation with the distribution of initial conditions given by the Wigner transform  $F_w^\beta(\mathbf{q}_0, \mathbf{p}_0)$  rather than by its classical limit,

$$F_w^\beta(\mathbf{q}_0, \mathbf{p}_0) \xrightarrow{\text{CL}} e^{-\beta H(\mathbf{q}_0, \mathbf{p}_0)} \frac{\partial h(\mathbf{q}_0)}{\partial \mathbf{q}_0} \cdot \frac{\mathbf{p}_0}{m}. \quad (2.15)$$

As discussed in detail in the Appendix, however, this linearization approximation produces only *classical* mechanics in the real time dynamics, with no quantum interference/coherence; cf. the classical time-dependent factor  $h(\mathbf{q}_t)$  in Eq. (2.13). The only quantum effects in Eq. (2.13) are from the quantum treatment of the Boltzmannized flux operator and the Wigner transform of it that results from the LA. The consequences of this will be seen in the results discussed in Sec. IV, where  $C_{fs}(t)$  of Eq. (2.13) is observed to be accurate only for times up to  $\approx \hbar \beta$ . This is long enough, however, if the dynamics is simple barrier crossing, with no recrossings involved, as in the assumption of transition state theory. Polak *et al.*<sup>22</sup> have in fact used Eq. (2.13) (with an approximation to the classical time-dependent factor) to define a quantum transition state theory and seen it to work well for examples involving only direct barrier crossing dynamics.

### C. Linearization approximation for state-to-state probabilities

To complete the story of the linearization approximation, we show here how it applies to the state-to-state transition probabilities, first for the time-dependent case,

$$P_{2\leftarrow 1}(t) = |\langle \psi_2 | e^{-i\hat{H}t/\hbar} | \psi_1 \rangle|^2. \quad (2.16)$$

With the SC-IVR of Eq. (2.3) this becomes

$$P_{2\leftarrow 1}(t) = \frac{1}{(2\pi\hbar)^F} \int d\mathbf{p}_0 d\mathbf{q}_0 \int d\mathbf{p}'_0 d\mathbf{q}'_0$$

$$\begin{aligned} & \times \left[ \det \left( \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \right) \det \left( \frac{\partial \mathbf{q}'_t}{\partial \mathbf{p}'_0} \right) \right]^{1/2} \\ & \times \psi_2(\mathbf{q}'_t) \psi_2(\mathbf{q}_t)^* \psi_1(\mathbf{q}_0) \psi_2(\mathbf{q}'_0)^* \\ & \times e^{i(S_t(\mathbf{q}_0, \mathbf{p}_0) - S_t(\mathbf{q}'_0, \mathbf{p}'_0))/\hbar}, \end{aligned} \quad (2.17)$$

where  $\mathbf{q}'_t = \mathbf{q}(\mathbf{q}'_0, \mathbf{p}'_0; t)$ . Changing to sum and difference variables  $\bar{\mathbf{q}} = (1/2)(\mathbf{q}_0 + \mathbf{q}'_0)$ ,  $\Delta \mathbf{q} = (\mathbf{q}_0 - \mathbf{q}'_0)$ ,  $\bar{\mathbf{p}} = (1/2)(\mathbf{p}_0 + \mathbf{p}'_0)$ ,  $\Delta \mathbf{p} = (\mathbf{p}_0 - \mathbf{p}'_0)$ , and expanding linearly in  $\Delta \mathbf{q}$  and  $\Delta \mathbf{p}$  gives

$$\begin{aligned} P_{2\leftarrow 1}(t) = & \frac{1}{(2\pi\hbar)^F} \int d\bar{\mathbf{p}}_0 d\bar{\mathbf{q}}_0 \int d\Delta \mathbf{p} d\Delta \mathbf{q} \det(\mathbf{M}_{\mathbf{qp}}) e^{i(\bar{\mathbf{p}}_t^T \cdot \mathbf{M}_{\mathbf{qq}} - \bar{\mathbf{p}}_0^T \cdot \Delta \mathbf{q} + \bar{\mathbf{p}}_t^T \cdot \mathbf{M}_{\mathbf{qp}} \cdot \Delta \mathbf{p})/\hbar} \psi_2 \left( \bar{\mathbf{q}}_t + \frac{1}{2} \mathbf{M}_{\mathbf{qq}} \cdot \Delta \mathbf{q} + \frac{1}{2} \mathbf{M}_{\mathbf{qp}} \cdot \Delta \mathbf{p} \right)^* \\ & \times \psi_2 \left( \bar{\mathbf{q}}_t - \frac{1}{2} \mathbf{M}_{\mathbf{qq}} \cdot \Delta \mathbf{q} - \frac{1}{2} \mathbf{M}_{\mathbf{qp}} \cdot \Delta \mathbf{p} \right) \psi_1 \left( \bar{\mathbf{q}}_0 + \frac{1}{2} \Delta \mathbf{q} \right) \psi_1 \left( \bar{\mathbf{q}}_0 - \frac{1}{2} \Delta \mathbf{q} \right)^*, \end{aligned} \quad (2.18a)$$

where the various matrices are defined as

$$\mathbf{M}_{\mathbf{qp}} = \frac{\partial \bar{\mathbf{q}}_t}{\partial \bar{\mathbf{p}}_0}, \quad (2.18b)$$

$$\mathbf{M}_{\mathbf{qq}} = \frac{\partial \bar{\mathbf{q}}_t}{\partial \bar{\mathbf{q}}_0}, \quad (2.18c)$$

and  $\bar{\mathbf{q}}_t = \mathbf{q}(\bar{\mathbf{q}}_0, \bar{\mathbf{p}}_0; t)$ . If the integral over  $\Delta \mathbf{p}$  is changed to that over  $\Delta \mathbf{q}'$ , where

$$\Delta \mathbf{q}' = \mathbf{M}_{\mathbf{qq}} \cdot \Delta \mathbf{q} + \mathbf{M}_{\mathbf{qp}} \cdot \Delta \mathbf{p}, \quad (2.19)$$

then Eq. (2.18) becomes

$$P_{2\leftarrow 1}(t) = \frac{1}{(2\pi\hbar)^F} \int d\mathbf{p}_0 d\mathbf{q}_0 \rho_2(\mathbf{q}_t, \mathbf{p}_t)^* \rho_1(\mathbf{q}_0, \mathbf{p}_0), \quad (2.20a)$$

where the ‘‘bars’’ over  $\bar{\mathbf{q}}_0$  and  $\bar{\mathbf{p}}_0$  have been dropped, and  $\rho_n(\mathbf{q}, \mathbf{p})$  is the Wigner function corresponding to state  $n$ ,

$$\rho_n(\mathbf{q}, \mathbf{p}) = \int d\Delta \mathbf{q} e^{-i\mathbf{p} \cdot \Delta \mathbf{q}/\hbar} \psi_n \left( \mathbf{q} + \frac{1}{2} \Delta \mathbf{q} \right) \psi_n \left( \mathbf{q} - \frac{1}{2} \Delta \mathbf{q} \right)^* \quad (2.20b)$$

for  $n = 1$  and  $2$ . Equation (2.20) has the very simple classical structure of the overlap of the initial phase space distribution for state 1 with the time-evolved phase space distribution of state 2.

A similar (but slightly more involved) analysis can be carried out for the energy-dependent transition probability of an isolated bimolecular collision. For a generic inelastic (or reactive) collision the  $F$ -dimensional coordinate space  $(\mathbf{r}, R)$  consists of the translational coordinate  $R$  and the  $(F-1)$  coordinates  $\mathbf{r}$  for the internal degrees of freedom, with corre-

sponding momenta  $(\mathbf{p}, P)$ . The  $S$ -matrix element for the  $1 \rightarrow 2$  transition in the internal degrees of freedom at total energy  $E$  can be expressed as<sup>24</sup>

$$\begin{aligned} S_{2,1} = & -\frac{\hbar}{\mu} \sqrt{k_1 k_2} e^{-i[k_1 R_{\max} + k_2 R'_{\max}]} \int_0^\infty dt \int d\mathbf{r} \int d\mathbf{r}' \\ & \times e^{iEt/\hbar} \phi_2(\mathbf{r}') \langle \mathbf{r}' R'_{\max} | e^{-i\hat{H}t/\hbar} | \mathbf{r} R_{\max} \rangle \phi_1(\mathbf{r}), \end{aligned} \quad (2.21)$$

where  $\{\phi_n\}$  are the wave functions for the asymptotic eigenstates of the internal degrees of freedom,  $R_{\max}$  and  $R'_{\max}$  are large values of the translational coordinate, and  $\{k_n\}$  are the magnitudes of the translational momenta (in units of  $\hbar$ ) determined by energy conservation

$$k_n = \sqrt{2\mu(E - E_n)/\hbar^2}, \quad (2.22)$$

$\{E_n\}$  being the internal energies corresponding to states  $\{\phi_n\}$ . (Note that for a reactive collision  $(\mathbf{r}, R)$  and  $(\mathbf{r}', R')$  are actually different coordinates, but that makes no essential difference in the present development.) It is convenient to turn Eq. (2.21) into a full coordinate space integral by inserting the factor  $\delta(R - R_{\max}) \delta(R' - R'_{\max})$  into the integrand and integrating over  $R$  and  $R'$ ,

$$\begin{aligned} S_{2,1}(E) = & -\frac{\hbar}{\mu} \sqrt{k_1 k_2} e^{-i[k_1 R_{\max} + k_2 R'_{\max}]} \int dt \int d\mathbf{q} \int d\mathbf{q}' \\ & \times e^{iEt/\hbar} \psi_2(\mathbf{q}')^* \langle \mathbf{q}' | e^{-i\hat{H}t/\hbar} | \mathbf{q} \rangle \psi_1(\mathbf{q}), \end{aligned} \quad (2.23a)$$

where here  $\mathbf{q}$  and  $\mathbf{q}'$  denote the full coordinate space, e.g.,  $(\mathbf{r}, R)$ , and

$$\psi_n(\mathbf{q}) = \phi_n(\mathbf{r}) \delta(R - R_{\max}). \quad (2.23b)$$

The SC-IVR, Eq. (2.3), is now used for the matrix element of the propagator in Eq. (2.23a) and the square modulus of the S-matrix element formed to obtain the 1 → 2 transition probability

$$P_{2 \leftarrow 1}(E) = \frac{\hbar^2 k_1 k_2}{\mu^2 (2\pi\hbar)^F} \int dt dt' \int d\mathbf{p}_0 d\mathbf{q}_0 \int d\mathbf{p}'_0 d\mathbf{q}'_0 \times e^{iE(t-t')/\hbar} \psi_2(\mathbf{q}_t)^* \psi_2(\mathbf{q}'_t) \psi_1(\mathbf{q}_0) \psi_1(\mathbf{q}'_0)^* \times \left[ \det \left( \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \right) \det \left( \frac{\partial \mathbf{q}'_t}{\partial \mathbf{p}'_0} \right) \right]^{1/2} \times \exp \left[ \frac{i}{\hbar} (S_t(\mathbf{q}_0, \mathbf{p}_0) - S_t(\mathbf{q}'_0, \mathbf{p}'_0)) \right], \quad (2.24)$$

where  $\mathbf{q}'_t = \mathbf{q}(\mathbf{q}'_0, \mathbf{p}'_0; t)$ . Changing to sum and difference integration variables as in Eq. (2.18) above—and here also for  $\bar{t} = (1/2)(t + t')$  and  $\Delta t = t - t'$ —expanding the difference of the action to first order in  $\Delta \mathbf{q}$ ,  $\Delta \mathbf{p}$ , and  $\Delta t$ , and performing the integral over them as done in going from Eq. (2.18) to (2.20), gives

$$P_{2 \leftarrow 1}(E) = \frac{\hbar^2 k_1 k_2}{\mu^2 (2\pi\hbar)^F} \int_0^\infty dt \int d\mathbf{p}_0 d\mathbf{q}_0 2\hbar \times \frac{\sin([E - H(\mathbf{q}_0, \mathbf{p}_0)]t/2)}{[E - H(\mathbf{q}_0, \mathbf{p}_0)]} \rho_2(\mathbf{q}_t, \mathbf{p}_t)^* \rho_1(\mathbf{q}_0, \mathbf{p}_0), \quad (2.25)$$

where the bars have been dropped from  $\mathbf{p}_0, \mathbf{q}_0, t$ , and we have used the fact that

$$\frac{\partial}{\partial t} S_t(\mathbf{q}, \mathbf{p}) = -H(\mathbf{q}, \mathbf{p}) \quad (2.26)$$

and

$$\int_{-\bar{t}/2}^{\bar{t}/2} d\Delta t e^{i\Delta t[E - H(\mathbf{q}_0, \mathbf{p}_0)]/\hbar} = 2\hbar \frac{\sin([E - H(\mathbf{q}_0, \mathbf{p}_0)]\bar{t}/2)}{[E - H(\mathbf{q}_0, \mathbf{p}_0)]}, \quad (2.27)$$

which if  $\bar{t} \rightarrow \infty$ , it becomes  $2\pi\hbar \delta[E - H(\mathbf{q}_0, \mathbf{p}_0)]$ . In our calculations, we found that it makes little difference whether we take the exact result of Eq. (2.27) or the delta function limit of it, thus for simplicity we shall use the delta function approximation for here on. It is also easy to show that

$$\rho_n(\mathbf{q}, \mathbf{p}) = \rho_n(\mathbf{r}, \mathbf{p}_r) \delta(R - R_{\max}), \quad (2.28)$$

where  $\rho_n(\mathbf{r}, \mathbf{p}_r)$  is the Wigner function corresponding to  $n$ th state of the internal degrees of freedom as defined in Eq. (2.20b). Combining all of these results together and writing the phase space integral in Eq. (2.25) in terms of the internal and translational variables thus gives

$$P_{2 \leftarrow 1}(E) = \frac{\hbar^2 k_1 k_2}{\mu^2 (2\pi\hbar)^{F-1}} \int d\mathbf{r}_0 \int d\mathbf{p}_{r0} \int dR_0 \int dP_0 \times \int dt \delta \left[ E - h(\mathbf{r}_0, \mathbf{p}_{r0}) - \frac{P_0^2}{2\mu} \right] \times \delta(R_0 - R_{\max}) \delta(R_t - R'_{\max}) \times \rho_2(\mathbf{r}_t, \mathbf{p}_{rt})^* \rho_1(\mathbf{r}_0, \mathbf{p}_{r0}), \quad (2.29)$$

where  $h(\mathbf{r}_0, \mathbf{p}_{r0})$  is the asymptotic Hamiltonian of the internal degrees of freedom. The three delta functions in the integrand of Eq. (2.29) allow the integrals over  $R_0$ ,  $P_0$ , and  $t$  to be performed, giving the final result

$$P_{2 \leftarrow 1}(E) = \frac{1}{(2\pi\hbar)^{F-1}} \int d\mathbf{r}_0 d\mathbf{p}_{r0} \frac{\hbar^2 k_1 k_2}{|P_0 P_t|} \rho_2(\mathbf{r}_t, \mathbf{p}_{rt})^* \times \rho_1(\mathbf{r}_0, \mathbf{p}_{r0}). \quad (2.30)$$

Comparing this energy dependent result, Eq. (2.30), to the time-dependent one, Eq. (2.20), one sees that it involves an integral over the initial phase space variables only of the internal degrees of freedom, the initial values of translational variables being given by  $R_0 = R_{\max}$ ,  $P_0 = -\sqrt{2\mu[E - h(\mathbf{r}_0, \mathbf{p}_{r0})]}$ . The classical trajectories which give  $(\mathbf{r}_t, \mathbf{p}_{rt})$  in Eq. (2.30) are of course computed in the full space of all degrees of freedom.

Equation (2.30) was proposed (with some minor differences) some years ago by Lee and Scully<sup>25</sup> and tested for collinear inelastic scattering of  $\text{He} + \text{H}_2(v) \rightarrow \text{He} + \text{H}_2(v')$ , for which they observed reasonably good agreement with quantum coupled channel calculations.

### III. SEMICLASSICAL APPROXIMATION FOR THE BOLTZMANN OPERATOR

In Sec. II A it was assumed that the Boltzmannized flux operator  $\hat{F}(\beta)$  is obtained by fully quantum mechanical methods, and this may indeed be feasible even for complex systems. As an alternative and perhaps more efficient possibility, however, we note that it can also be obtained by a semiclassical approximation. Referring to Eq. (2.1d), one thus needs to construct matrix elements of the Boltzmann operator  $e^{-\beta\hat{H}}$ , which is the same as the time evolution operator  $e^{-i\hat{H}t/\hbar}$  for the imaginary time  $t = -i\hbar\beta$ . It was noted by one of us<sup>26</sup> some years ago, though, that motion in imaginary time is equivalent to motion in real time on the upside-down potential energy surface; e.g., Newton's equation

$$m \frac{d^2}{dt^2} \mathbf{q}(t) = -\frac{\partial V}{\partial \mathbf{q}} \quad (3.1)$$

becomes

$$m \frac{d^2}{d\tau^2} \mathbf{q}(\tau) = +\frac{\partial V}{\partial \mathbf{q}}, \quad (3.2)$$

where  $\tau = it$  is a real timelike variable, which varies from 0 to  $\hbar\beta$  to obtain  $e^{-\beta\hat{H}}$ . The SC-IVR expression for the Boltzmann operator, which is the analog of Eq. (2.3), is therefore

$$\langle \mathbf{q} | e^{-\beta\hat{H}} | \mathbf{q}_0 \rangle \equiv \int d\bar{\mathbf{p}}_0 \delta(\mathbf{q} - \mathbf{q}_\beta) \times \left[ \det \left( \frac{\partial \mathbf{q}_\beta}{\partial \bar{\mathbf{p}}_0} \right) / (2\pi\hbar)^F \right]^{1/2} e^{-S_\beta(\mathbf{q}_0, \bar{\mathbf{p}}_0)/\hbar}, \quad (3.3a)$$

where  $\bar{\mathbf{p}}(\tau) = m\mathbf{q}'(\tau)$  is the real momentumlike variable,  $\mathbf{q}_\beta = \mathbf{q}(\mathbf{q}_0, \bar{\mathbf{p}}_0; \hbar\beta)$  is the coordinate that evolves along the classical trajectory on the upside-down potential energy surface with initial conditions  $(\mathbf{q}_0, \bar{\mathbf{p}}_0)$ , and  $S_\beta$  is the classical action,

$$S_\beta(\mathbf{q}_0, \bar{\mathbf{p}}_0) = \int_0^{\hbar\beta} d\tau \frac{\bar{\mathbf{p}}(\tau)^2}{2m} + V[\mathbf{q}(\tau)]. \quad (3.3b)$$

This semiclassical approximation for the Boltzmann operator is most conveniently implemented via Eq. (2.11) for the flux-side correlation function. Together with Eqs. (3.3a) and (2.1d), it gives the correlation function as

$$C_{\text{fs}}(t) = \frac{1}{(2\pi\hbar)^F} \int d\mathbf{q}_0 \int d\bar{\mathbf{p}}_0 \int d\mathbf{p}_0 \int d\mathbf{p}'_0 \frac{[h(\mathbf{q}_\beta) - h(\mathbf{q}_0)]}{i\hbar\beta} \left[ \det\left(\frac{\partial\mathbf{q}_\beta}{\partial\bar{\mathbf{p}}_0}\right) / (2\pi\hbar)^F \right]^{1/2} e^{-S_\beta(\mathbf{q}_0, \bar{\mathbf{p}}_0)/\hbar} \langle \mathbf{p}'_t \mathbf{q}'_t | \hat{h} | \mathbf{p}_t \mathbf{q}_t \rangle \\ \times \left( \frac{\gamma_t}{4\pi} \right)^{F/2} D_t(\mathbf{q}_0, \mathbf{p}_0) D_t^*(\mathbf{q}_\beta, \mathbf{p}'_0) \exp\left[ \frac{i}{\hbar} (S_t(\mathbf{q}_0, \mathbf{p}_0) - S_t(\mathbf{q}_\beta, \mathbf{p}'_0)) \right]. \quad (3.4)$$

One thus begins a purely imaginary time trajectory (i.e., real trajectory on the upside down potential) with initial conditions  $(\mathbf{q}_0, \bar{\mathbf{p}}_0)$  and integrates it for (imaginary) time  $\hbar\beta$  to position  $\mathbf{q}_\beta$ ;  $\mathbf{q}_0$  and  $\mathbf{q}_\beta$  must be on the opposite sides of the dividing surface. From  $\mathbf{q}_0$  and  $\mathbf{q}_\beta$  one initiates trajectories with momenta  $\mathbf{p}_0$  and  $\mathbf{p}'_0$  and integrates for time  $t$ ; the final coordinate  $\mathbf{q}_t = \mathbf{q}(\mathbf{q}_0, \mathbf{p}_0; t)$  and  $\mathbf{q}'_t = \mathbf{q}(\mathbf{q}_\beta, \mathbf{p}'_0; t)$  must land within the same phase space cell in order to contribute. Figure 1(d) shows this schematically.

The semiclassical Boltzmann operator can also be employed with the linearization approximation for the real time dynamics, i.e., in Eq. (2.13). The necessary steps, indicated below, are straightforward:

$$C_{\text{fs}}(t) = \frac{1}{(2\pi\hbar)^F} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \int d\Delta\mathbf{q} e^{-i\mathbf{p}_0 \cdot \Delta\mathbf{q}/\hbar} \langle \mathbf{q}_0 + \Delta\mathbf{q}/2 | \hat{F}(\beta) | \mathbf{q}_0 - \Delta\mathbf{q}/2 \rangle h(\mathbf{q}_t) \\ = \frac{1}{(2\pi\hbar)^F} \int d\mathbf{q}_0 \int d\mathbf{q}'_0 \int d\mathbf{p}_0 e^{-i\mathbf{p}_0 \cdot (\mathbf{q}'_0 - \mathbf{q}_0)/\hbar} \langle \mathbf{q}'_0 | \hat{F}(\beta) | \mathbf{q}_0 \rangle h\left[\mathbf{q}_t\left(\mathbf{p}_0, \frac{\mathbf{q}_0 + \mathbf{q}'_0}{2}\right)\right] \\ = \frac{1}{(2\pi\hbar)^F} \int d\mathbf{q}_0 \int d\mathbf{p}_0 \int d\bar{\mathbf{p}}_0 \frac{[h(\mathbf{q}_0) - h(\mathbf{q}_\beta)]}{i\hbar\beta} e^{-i\mathbf{p}_0 \cdot (\mathbf{q}_\beta - \mathbf{q}_0)/\hbar} \left[ \det\left(\frac{\partial\mathbf{q}_\beta}{\partial\bar{\mathbf{p}}_0}\right) / (2\pi\hbar)^F \right]^{1/2} \\ \times e^{-S_\beta(\mathbf{q}_0, \bar{\mathbf{p}}_0)/\hbar} h\left[\mathbf{q}_t\left(\mathbf{p}_0, \frac{\mathbf{q}_0 + \mathbf{q}_\beta}{2}\right)\right]. \quad (3.5)$$

Again, the end points of the imaginary time trajectory with initial conditions  $(\mathbf{q}_0, \bar{\mathbf{p}}_0)$  must straddle the dividing surface; however, only one real time trajectory is run, its initial position being the average of the end points of the imaginary time trajectory,  $(\mathbf{q}_0 + \mathbf{q}_\beta)/2$ , with initial momentum  $\mathbf{p}_0$ .

#### IV. RESULTS AND DISCUSSION OF TEST CALCULATIONS

We wish to test the extent to which the SC-IVR of Sec. II A, and the linearized approximation to it in Sec. II B, can describe coherence and other quantum effects in the thermal rate constants. To this end we look at the flux-side correlation function  $C_{\text{fs}}(t)$  for a 1- $d$  double well potential, for which the Hamiltonian is

$$H = \frac{p^2}{2m} - \frac{1}{2}m\omega^\ddagger x^2 + \frac{m^2\omega^\ddagger^4}{16V_0}x^4. \quad (4.1)$$

This is the same system we considered earlier via the linearized approximation to the SC-IVR, but with a harmonic bath coupled to it. As noted in the Introduction, without the bath degrees of freedom  $C_{\text{fs}}(t)$  does not reach a constant value as  $t \rightarrow \infty$ —i.e.,  $k(T)$  does not exist—but the recrossing dynamics manifested in  $C_{\text{fs}}(t)$  should accentuate coherence/

interference effects, and this thus provides an even more stringent test of the SC theories. The mass of the particle is that of a H atom, the barrier height,  $V_0 = 2085 \text{ cm}^{-1}$  ( $\approx 6 \text{ kcal/mol}$ ), is typical of H atom transfer reactions, and the imaginary barrier frequency is  $\omega^\ddagger = 500 \text{ cm}^{-1}$ . The calculations were carried out for  $T = 300$  and  $900 \text{ K}$ .

Figure 2 first shows the results of the linearized approximation (solid points) to the SC-IVR for  $C_{\text{fs}}(t)$  given by Eq. (2.13), compared to the exact quantum (solid line) and the completely classical (open points) results [given by Eq. (2.13) with Eq. (2.15)]. Several observations are apparent. First note that for short times—up to  $\sim 50 \text{ fs}$  at  $300 \text{ K}$  [Fig. 2(a)] and  $\sim 25 \text{ fs}$  at  $900 \text{ K}$  [Fig. 2(b)]— $C_{\text{fs}}(t)$  takes on an approximately constant or plateau value; this is the transition state theory (TST) or barrier crossing rate constant [when divided by the reactant partition function in Eq. (1.1)] that would be the  $t \rightarrow \infty$  limit if there were no recrossing dynamics. The classical correlation function begins at its TST value at  $t = 0$ , but the quantum and semiclassical correlation functions take a time of  $\sim \hbar\beta$  (27 fs for 300 K, 9 fs for 900 K) to reach their plateau values. At 900 K [Fig. 2(b)] one sees that all three curves have approximately the same plateau value, but at 300 K [Fig. 2(a)] the classical plateau value is  $\sim 25\%$  lower than the QM and SC value; this is due to tunneling

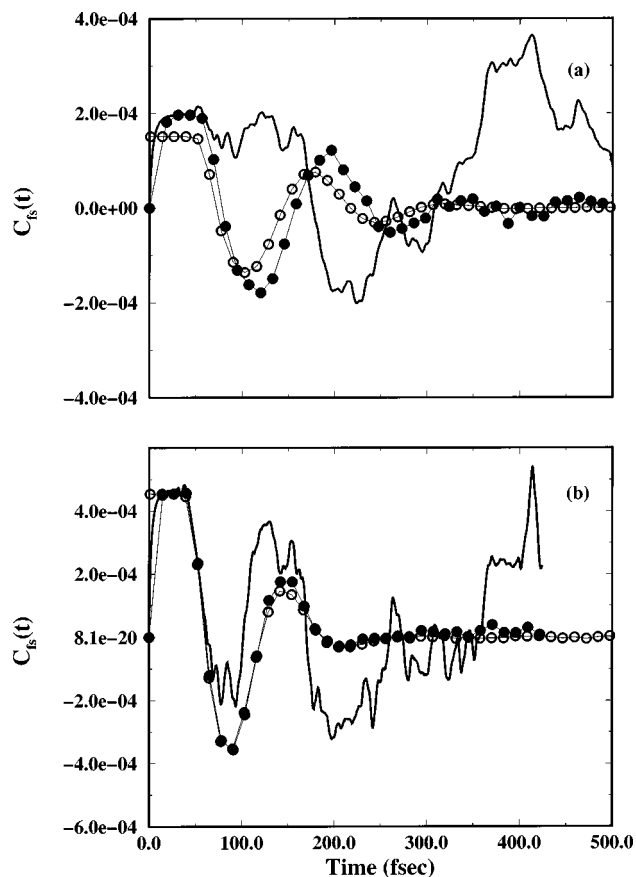


FIG. 2. The correlation function  $C_{fb}(t)$  as given by the exact quantum calculation (solid line), the linearized approximation of Eq. (2.13) (solid points), and the fully classical method of Eq. (2.15) (open points). (a) 300 K and (b) 900 K.

effects in the TST rate constant, and one sees that the linearized SC theory describes this quite well. (This is consistent with earlier work<sup>9c</sup> in our group showing that the SC-IVR is able to describe moderate levels of tunneling—e.g., tunneling probabilities down to  $\sim 10^{-5}$  for H atom motion—though not the “deep” tunneling region that requires explicit use of complex trajectories.<sup>27</sup>)

The time dependence beyond the plateau region in Fig. 2 is the result of recrossing dynamics, and one sees that in this region the linearized SC approximation is essentially the same as the classical result. Furthermore, at 900 K [Fig. 2(b)] the classical and SC correlation functions follow the QM result fairly well up to  $t \approx 150$  fs and then deviate considerably; at 300 K they follow it not well at all past the plateau region. Thus the linearized SC approximation is able to describe quantum effects well in the short time regime of TST-like dynamics, but is not able to describe quantum effects in the longer time recrossing dynamics.

Figure 3 now shows the full SC-IVR results (solid points) for the correlation function [calculated via Eq. (3.4)] compared to the exact quantum (solid line) and linearized SC (open points) values, and one sees that the full SC-IVR indeed does describe the correct quantum behavior for times well into the recrossing regime (up to 200 fs, as long as the SC-IVR calculations were carried out). The comparison is particularly revealing for 300 K [Fig. 3(a)], where the linear-

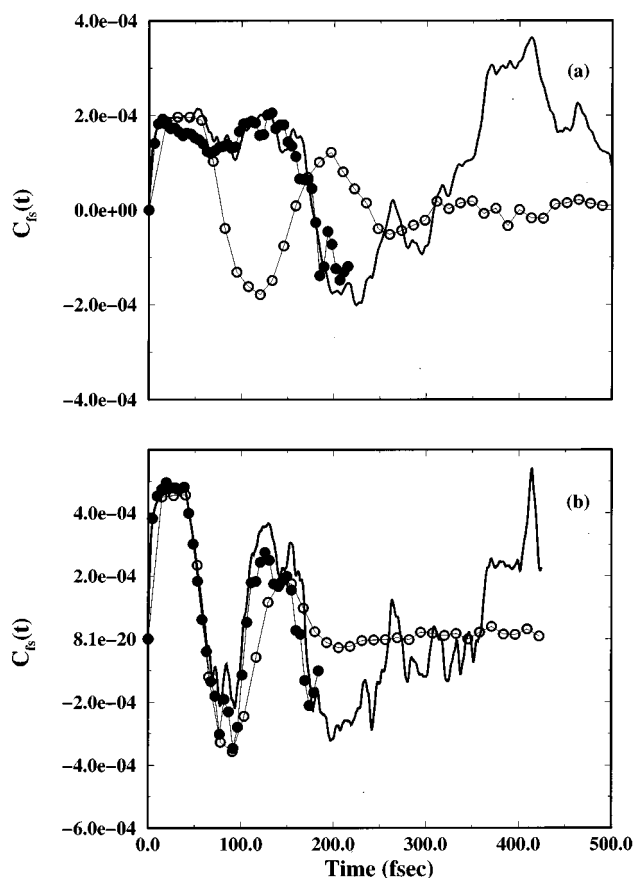


FIG. 3. The correlation function  $C_{fb}(t)$  given by the exact quantum calculation (solid line), the full SC-IVR model of Eq. (3.4) (solid points), and the linearization approximation of Eq. (2.13) (open points). (a) 300 K and (b) 900 K.

ized SC results (open points) deviate drastically from the quantum correlation function for times past the short-time TST plateau region. The effort required for the full SC-IVR calculation, however, is quite large; the integration over the initial conditions were carried out presently by an unweighted Monte Carlo procedure (with finite cutoffs) and required  $\sim 10^6$  trajectories. A more sophisticated Monte Carlo procedure would perhaps make this more efficient.

The SC-IVR results in Fig. 3 used the semiclassical approximation for the Boltzmann operator, Eq. (3.4). To show that this introduces little error, Fig. 4 displays a comparison of the results obtainable with the linearized SC approximation for the real time propagation with the quantum and SC versions of the Boltzmann operator [Eq. (3.5)]. One sees that the results obtained with the SC approximation to the Boltzmann operator are in good agreement with the QM one; little error is introduced by the SC approximation, so that one has a semiclassical description for both the imaginary and real time evolution.

Finally, Fig. 5 shows the results of the state-to-state reaction probability given by the linearized SC approximation, Eq. (2.30). The example is the  $H+H_2(v=0) \rightarrow H_2(v=0) + H$  collinear reaction on the LSTH potential energy surface. One sees that the linearized SC approximation does a good job of describing the *average* energy dependences of the



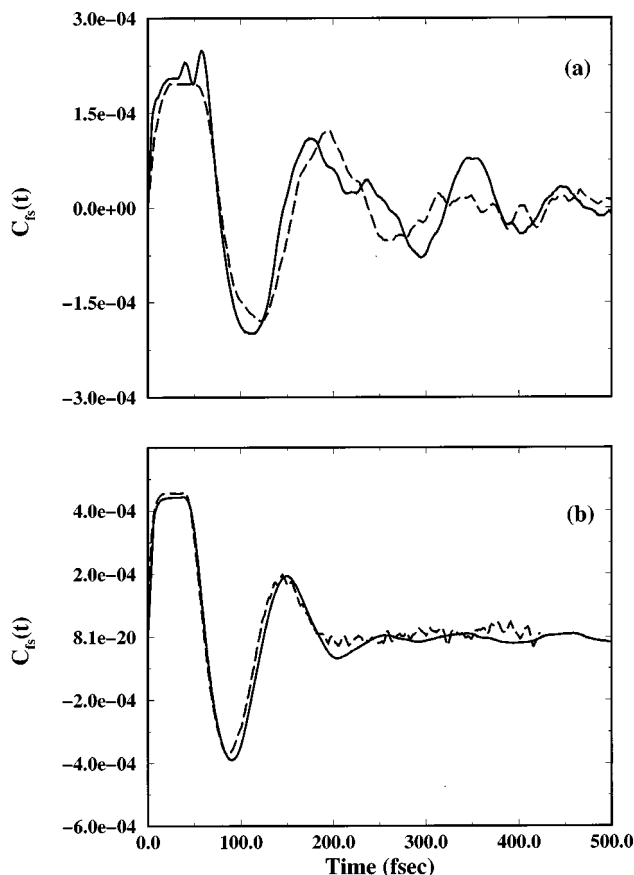


FIG. 4. The correlation function  $C_{fs}(t)$  obtained with the linearization approximation of Eq. (2.13), where the matrix elements of the Boltzmannized flux operator are obtained quantum mechanically (dashed line) and semi-classically via Eq. (3.5) (solid line). (a) 300 K and (b) 900 K.

$P_{0,0}(E)$ , but it misses completely the resonance structure at  $E = 0.85$  and  $1.3$  eV. In light of earlier discussions, this is not surprising since one knows that resonances are an interference effect between difference trajectories that form the collision complex.<sup>28</sup> This is therefore analogous to the inability

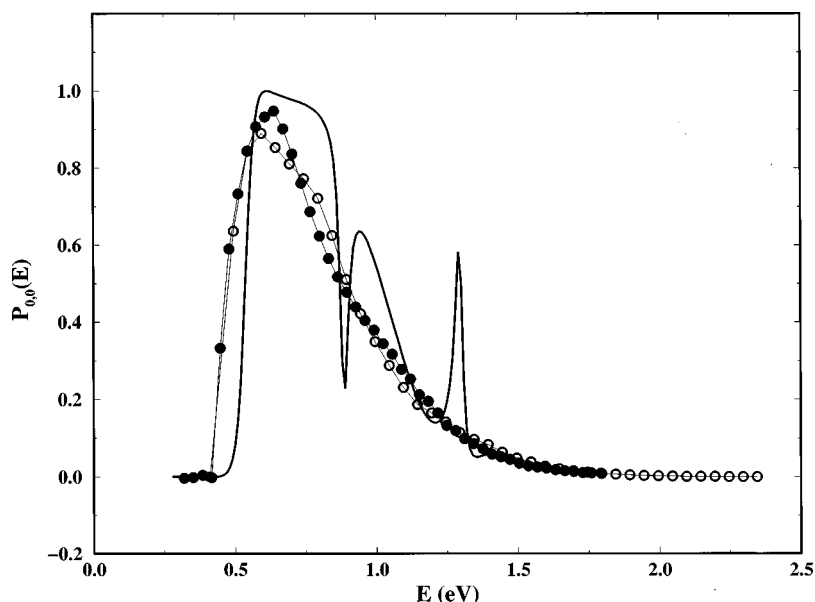


FIG. 5. The state-to-state transition probability,  $P_{0,0}(E)$ , for the collinear  $H + H_2(v=0) \rightarrow H_2(v=0) + H$  reaction, vs the scattering energy. (Note  $v$  is the vibrational quantum number of  $H_2$ .) The exact quantum (solid line) is compared with the linearization approximation of Eq. (2.25) (solid points) and the delta function approximation of Eq. (2.30) (open points).

of the linearized SC theory to describe coherence effects in the longer time recrossing dynamics in  $C_{fs}(t)$  as seen in Fig. 2.

## V. CONCLUDING REMARKS

The goal of this work has been to investigate the extent to which the semiclassical initial value representation, and the linearized approximation to it, are able to describe quantum effects in thermal rate constants. The conclusions are that the linearized approximation to the SC theory is able to describe quantum effects in the short time ( $t \leq \hbar\beta$ ) dynamics that corresponds to direct barrier crossing, i.e., transition state theory like dynamics, but the description of the longer time recrossing dynamics is essentially that given by classical mechanics. The complete SC-IVR treatment, however, is able to describe the quantum effects in the longer time recrossing dynamics, though these calculations become progressively more difficult the longer the time. Also, the SC approximation for the Boltzmann operator introduces essentially no error; one is thus able to have a complete semiclassical theory, i.e., for the imaginary time (Boltzmann operator) as well as real time propagation.

With regard to practical considerations, the linearized approximation to the SC theory is much easier to implement than the full SC-IVR: the real time part of it is a classical molecular dynamics calculation, with the imaginary time part (i.e., the Boltzmann operator) treated either quantum mechanically or semiclassically. The fact that it describes the short time TST-like dynamics correctly, and provides a classical description of the longer time recrossing dynamics, should make it very useful for many applications, particularly for complex molecular systems where quantum effects are often quenched by the many coupled degrees of freedom (as demonstrated in our previous article<sup>8</sup>). The full SC-IVR calculation is considerably more difficult because one has to deal with oscillatory integrands. It does, however, allow one to describe interference/coherence features in the longer time

dynamics, so it behooves one to invest effort in learning how to do these calculations more effectively.

### ACKNOWLEDGMENTS

This work has been supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 and also in part by the National Science Foundation under Grant No. CHE9732758.

### APPENDIX: THE LINEARIZATION APPROXIMATION—A PEDAGOGICAL OVERVIEW

Here we explicitly consider a one dimensional integral of the form

$$I = \int dx e^{iS(x)/\hbar}, \tag{A1}$$

but have in mind multidimensional integrals of this type that represent quantum transition amplitudes. In the applications in this article, the integration is over the phase space  $(\mathbf{q}_0, \mathbf{p}_0)$  of initial conditions for classical trajectories, but a fully quantum path integral representation of the time evolution operator is also a multidimensional integral of this form.

Standard semiclassical approximations<sup>24</sup> result when one evaluates the integral via the stationary phase approximation (SPA),

$$I_{\text{SPA}} = \sum_k \left( \frac{2\pi i \hbar}{S''(x_k)} \right)^{1/2} e^{iS(x_k)/\hbar}, \tag{A2a}$$

where  $\{x_k\}$  are the points of stationary phase, i.e., the roots of the equation

$$S'(x_k) = 0. \tag{A2b}$$

Equation (A2a) is often suggestively written as

$$I_{\text{SPA}} = \sum_k P_k^{1/2} e^{i\phi_k}, \tag{A3a}$$

where

$$P_k = \frac{2\pi\hbar}{|S''(x_k)|}, \tag{A3b}$$

$$\phi_k = S(x_k)/\hbar + \frac{\pi}{4} \text{Sign}[S''(x_k)], \tag{A3c}$$

so that the *probability*, or the observable,  $|I|^2$  has the form

$$\begin{aligned} |I_{\text{SPA}}|^2 &= \sum_k P_k + \sum_{k < k'} 2\sqrt{P_k P_{k'}} \cos(\phi_k - \phi_{k'}) \\ &= |I_{\text{CL}}|^2 + \text{interference}. \end{aligned} \tag{A3d}$$

This is the typical semiclassical result for a transition probability,<sup>24</sup> say, the classical result plus interference, i.e., quantum coherence. If there are no real roots to Eq. (A2b), one may analytically continue the phase function  $S(x)$  and look for complex roots; the approximation for  $|I|^2$  then is<sup>24</sup>

$$|I|^2 \approx \frac{2\pi\hbar}{|S''(x_k)|} e^{-2\text{Im} S(x_k)/\hbar}, \tag{A4}$$

where  $x_k$  is the complex root for which  $S(x_k)$  has the smallest positive imaginary part. In this case the transition is said to be “classically forbidden,” or to proceed by tunneling (or “dynamical tunneling” in the multidimensional case).

One would like to go beyond the stationary phase approximation, e.g., to evaluate integrals of this type numerically, but the oscillatory character of the integrand prevents the straightforward use of Monte Carlo methods. There are ways of converting Eq. (A1) into an integral amenable to Monte Carlo evaluation, such as various filtering methods,<sup>29</sup> but another strategy is to deal directly with the probability,

$$|I|^2 = \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dx' e^{i(S(x) - S(x'))/\hbar}. \tag{A5}$$

(This arises most naturally when using a density matrix formulation.) Changing to sum and difference integration variables  $\bar{x} = (x + x')/2$ ,  $\Delta x = x - x'$ , gives

$$|I|^2 = \int_{-\infty}^{\infty} d\bar{x} \int_{-\infty}^{\infty} d\Delta x e^{i(S(\bar{x} + \Delta x/2) - S(\bar{x} - \Delta x/2))/\hbar}, \tag{A6}$$

and the linearization approximation corresponds to expanding the phase difference to first order in  $\Delta x$ ,

$$S\left(\bar{x} + \frac{\Delta x}{2}\right) - S\left(\bar{x} - \frac{\Delta x}{2}\right) \approx S'(\bar{x})\Delta x. \tag{A7}$$

The integral over  $\Delta x$  is then immediately doable,

$$\int_{-\infty}^{\infty} d\Delta x e^{iS'(\bar{x})\Delta x/\hbar} = 2\pi\hbar \delta[S'(\bar{x})], \tag{A8}$$

so that Eq. (A6) becomes

$$|I|^2 = \int_{-\infty}^{\infty} d\bar{x} 2\pi\hbar \delta[S'(\bar{x})]. \tag{A9}$$

Having approximated the phase difference this way has indeed eliminated the oscillatory problem: the integral over  $\bar{x}$  in Eq. (A9) now involves a positive definite integral, and one can readily proceed by Monte Carlo methods in the multidimensional case. One immediately sees, however, that Eq. (A9) gives only the classical probability: there are contributions to the integral only at values  $\bar{x}$  for which  $S'(\bar{x}) = 0$ , i.e., the stationary phase points, and the evaluation of the delta function integration gives

$$|I|^2 = \sum_k \frac{2\pi\hbar}{|S''(x_k)|}, \tag{A10}$$

the classical part of Eq. (A3d).<sup>30</sup> One may thus say that taking interference [i.e., the phase difference in Eq. (A6)] into account only infinitesimally (i.e., to first order in  $\Delta x$ ) leads only to the classical result; one cannot describe the quantum interference/coherence effects in Eq. (A3d) because these arise from the difference of discrete points of stationary phase,  $\Delta x = x_k - x_{k'}$ .

One systematic approach for improving the linearization approximation is simply to carry the expansion in Eq. (A7) to the next order in  $\Delta x$ , which is  $S'''(x_k)\Delta x^3/24$ . The integral over  $\Delta x$  is then an Airy integral, and in this case Eq. (A6) becomes

$$|I|^2 = \int d\bar{x} \frac{2\pi\hbar}{\epsilon(\bar{x})} \text{Ai}[S'(\bar{x}/\epsilon(\bar{x}))], \quad (\text{A11})$$

where

$$\epsilon(\bar{x}) = \hbar^{2/3} S'''(\bar{x})^{1/3}/2. \quad (\text{A12})$$

The integrand here is also peaked at values of  $\bar{x}$  for which  $S'(\bar{x})=0$ —these are the turning points, or Franck–Condon peaks of the Airy function<sup>31</sup>—but there is some residual interference structure in the integrand. Equation (A11) should indeed be a useful approximation because it is accurate when the two interfering stationary points were not too far apart, which probably is the most important practical situation. (If they are very far apart, the interference is presumably of very high frequency and thus most easily quenched by any averaging that one carries out.) The only problem is that the generalized cubic expansion of the phase difference in the multidimensional case does not yield a separable integrand, so the  $\Delta x$  integration is not easily doable. If one attempts a direct numerical attack on Eq. (A6), this sum and difference analysis suggests that the integration over the sum variable  $\bar{x}$  could be treated by classical (Monte Carlo) methods, while only integration over the difference variable  $\Delta x$  must deal with the interference nature of the problem.

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