Quantum mechanical rate constants for bimolecular reactions

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Several formally exact expressions for quantum mechanical rate constants (i.e., bimolecular reactive cross sections suitably averaged and summed over initial and final states) are derived and their relation to one another analyzed. It is suggested that they may provide a useful means for calculating quantum mechanical rate constants accurately without having to solve the complete state-to-state quantum mechanical reactive scattering problem. Several ways are discussed for evaluating the quantum mechanical traces involved in these expressions, including a path integral evaluation of the Boltzmann operator/time propagator and a discrete basis set approximation. Both these methods are applied to a one-dimensional test problem (the Eckart barrier).

I. INTRODUCTION

The purpose of this paper is to develop several new formally exact quantum mechanical expressions for the Boltzmann rate constant for a bimolecular reaction. (By "Boltzmann rate constant" is meant a Boltzmann average over internal states of the reactants.) The motivation for this is quite practical: one would like to have a systematic and reliable procedure so that, given a Born–Oppenheimer potential energy surface, it is possible to compute the rate. At present the only completely reliable way of doing this is first to solve the coupled channel Schrödinger equation to determine all the individual S-matrix elements, and then state-to-state reaction cross sections, and then to throw away all the state-to-state information by summing over final states of products and Boltzmann averaging over initial states of reactants. It seems intuitively reasonable that if one is interested only in the thermal rate constant, i.e., the net reactive flux, there should be a more economical way to calculate it, i.e., one that circumvents solving for all the state-to-state information first.

Transition state theory is an approximate way of accomplishing this goal, and indeed much of the effort invested in developing ways of computing rate constants has concentrated on refinements and extensions of transition state theory. Transition state theory, however, is inherently approximate. Within the framework of classical mechanics there are corrections due to trajectories which cross the transition state dividing surface more than once (i.e., a nonunit transmission coefficient), and it is difficult to define a completely consistent quantum mechanical version of transition state theory that either does not involve some additional approximations (e.g., separability of motion along a reaction coordinate) or is simply a disguised expression for the formally exact rate. Thus even though some versions of transition state theory are very useful approximations, there is no systematic way of improving it so that with sufficient computational effort one is guaranteed of approaching the correct result.

Within the realm of classical mechanics there actually is a procedure with all the features being sought. Sometimes called the "variational theory of reaction rate" or the "phase space trajectory" method, it is essentially a classical trajectory calculation, but one which begins the trajectories (with initial conditions sampled from a Boltzmann distribution) on a dividing surface in the interaction region, e.g., a dividing surface suggested by transition state theory, and it is then necessary to follow the dynamics forward and backward in time only long enough to determine whether each trajectory is reactive or not. By not following the trajectories all the way from reactants to products one has no state-to-state information about the reaction, and indeed this is the very source of its economy: to determine the net reactive flux, i.e., the rate constant, it is necessary to determine the dynamics of the system for only a relatively short time. If one makes a "zero time" approximation to the dynamics, classical transition state theory results, which is already often a good approximation to the classical rate.

The quantum mechanical rate expressions discussed in this paper are analogous to this classical approach, in that they also require that the (quantum) dynamics of the system be determined for only a short time. Like the above classical approach, they avoid construction of complete state-to-state reactive information, and herein lies their possible economy.

Starting from an expression obtained earlier by one of us, Sec. II first derives several new formally exact expressions for the quantum rate constant. One of these is seen to be similar in form (the rate is given as the time integral of a flux–flux autocorrelation function) to a result obtained still earlier by Yamamoto; the two correlation functions are different, however, and our present result is seen to have some distant advantages. Section II evaluates these rate expressions for a simple analytically solvable example, the one-dimensional parabolic barrier, and shows that it is indeed true that one must follow the (quantum) dynamics for only a short time in order to determine the rate. Several methods are discussed in Sec. IV for evaluating these formally exact rate expressions more generally,
including a path integral evaluation of the quantum propagator and a discrete basis set approximation. Application of these methods to a more realistic one-dimensional problem (the Eckhart barrier) shows the path integral method, in particular, to be excellent. Section V concludes.

II. FORMALLY EXACT RATE EXPRESSIONS

The beginning point for the discussion is a formally exact quantum mechanical rate expression given previously by one of the authors.\(^{4,5}\) To keep the notation as simple as possible, all expressions are written for the case of only one degree of freedom, i.e., the "reaction coordinate"; at the end of the section the explicit multidimensional expression will be noted.

If \(Q\) denotes the partition function (per unit volume for reactions in three dimensions) for reactants and \(k = k(T)\) the Boltzmann rate constant, then the previous expression for \(k\) is

\[
kQ = \text{Re} \left[ \text{tr} \left[ e^{-\beta H} F \sigma \right] \right],
\]

(2.1)

where \(\text{Re}\) denotes the "real part of", \(\text{tr}\) denotes a quantum mechanical trace, \(\beta = 1/(k_b T)\), \(F\) is the flux operator,

\[
F = \delta(s) \left( \frac{p}{m} \right),
\]

(2.2)

\(s\) is the reaction coordinate and \(p\) its conjugate momenta, and \(\sigma\) the projection operator

\[
\sigma = \lim_{t \to \pm\infty} \exp(iHt/k) h(p) \exp(-iHt/k).
\]

(2.3)

The Hamiltonian is of the standard form

\[
H = (p^2/2m) + V(s),
\]

(2.4)

and \(h\) is a step function,

\[
h(t) = \begin{cases} 1, & \xi > 0 \\ 0, & \xi < 0 \end{cases}.
\]

The operator \(\sigma\) projects onto all states that have positive momentum in the infinite future \((t \to \pm\infty)\). (The reactive direction is from \(s = -\infty\) to \(s = +\infty\).)

The first useful modification to Eq. (2.1) is made by noting that \(\sigma = e^{\alpha H}\) commute—this is because \(\sigma\) was originally defined in terms of the eigenstates of \(H^2\)—so that Eq. (2.1) may be written in the more symmetrical form

\[
kQ = \text{Re} \left[ \text{tr} \left[ e^{-(\beta/2) \sigma} \exp(-\beta H/2) \right] \right],
\]

(2.5)

or with \(\sigma\) as given by Eq. (2.3), this becomes

\[
kQ = \lim_{t \to \pm\infty} \text{Re} \left[ \text{tr} \left[ \exp(iHt/k) \exp(-\beta H/2) h(p) \times \exp(-\beta H/2) \exp(-iHt/k) \right] \right].
\]

(2.6)

Since the operator

\[
G = \exp(-\beta H/2) h(p) \exp(-\beta H/2)
\]

is Hermitian (i.e., \(G^\dagger = G\)) one has

\[
\text{tr} \left[ \exp(iHt/k) \exp(-iHt/k) \right] \xrightarrow{t \to \infty} 0.
\]

(2.10a)

so that

\[
\text{Re} \left[ \text{tr} \left[ F \exp(iHt/k) G \exp(-iHt/k) \right] \right] = \text{tr} \left[ F \exp(iHt/k) G \exp(-iHt/k) F^\dagger \right],
\]

where \(F\) is the symmetrized flux operator

\[
F = \frac{1}{2} (F + F^\dagger) = \frac{1}{2} \left[ \delta(s) \frac{p}{m} + \frac{p}{m} \delta(s) \right].
\]

(2.7)

One may also combine the Boltzmann operator and time evolution operator in Eq. (2.6) to write the rate as

\[
kQ = \lim_{t \to \pm\infty} \text{tr} \left[ \exp(iHt_{c}/k) h(p) \exp(-iHt_{c}/k) \right].
\]

(2.8)

where \(t_c\) is the complex time

\[
t_c = t - i\beta/2.
\]

The second modification that is useful to make is to replace \(h(p)\) in Eq. (2.8) by \(h(s)\). The projection operator

\[
lm \exp(iHt/k) h(s) \exp(-iHt/k) = \lim_{t \to \pm\infty} h(s) \exp(iHt_{c}/k).
\]

(2.9)

where \(s(t)\) is the Heisenberg position operator, projects onto states that in the infinite future \((t \to \pm\infty)\) are to the right \((s > 0)\) of the dividing surface \(s = 0\) (i.e., are on the product side). It makes physical sense that the projector given by Eq. (2.9) is equivalent to that of Eq. (2.3), and that this is precisely so is shown in Appendix A. With this modification the expression for the rate becomes

\[
kQ = \lim_{t \to \pm\infty} \text{tr} \left[ \exp(iHt_{c}/k) h(s) \exp(-iHt_{c}/k) \right].
\]

(2.10)

(2.10a)

Note that at this stage it would be possible for the Boltzmann operator to be divided into two factors in the following more general way,

\[
kQ = \lim_{t \to \pm\infty} \text{tr} \left[ \exp(iHt_{c}/k) \exp(-\lambda H) h(s) \times \exp(-\beta - \lambda H) \exp(-iHt/k) \right].
\]

(2.10b)

This is because, as noted above, the Boltzmann operator commutes with the infinite time limit projector. Thus the right-hand side of Eq. (2.10a) is actually independent of \(\lambda\). Some of the desirable properties of the correlation functions to be defined below, however, do not follow unless one makes the symmetrical choice \(\lambda = \beta/2\) (For finite values of \(t\) the right-hand side is not independent of \(\lambda\).

In order to obtain another form of the rate expression note that for \(t = 0\) the trace in Eq. (2.10) is identically zero,\(^s\) so that Eq. (2.10) can also be written as

\[
kQ = \text{tr} \left[ \exp(iHt_{c}/k) h(s) \exp(-iHt_{c}/k) \right] \bigg|_{t=0}^{\infty} = \int_0^{\infty} dt \, C_{f}(t),
\]

(2.11)

where

\[
C_{f}(t) = \frac{d}{dt} \text{tr} \left[ \exp(iHt_{c}/k) h(s) \exp(-iHt_{c}/k) \right].
\]

The time derivative here differentiates only the propagator factors, giving

\[
C_{f}(t) = \frac{i}{k} \text{tr} \left[ \exp(iHt_{c}/k) [H, h(s)] \exp(-iHt_{c}/k) \right],
\]

(2.11a)

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and since

\[
[H, h(s)] = \left[ \frac{p^2}{2m}, h(s) \right] = \frac{1}{2m} \{ p[h(s)], [p, h(s)]p \} \\
= -\hbar \frac{1}{i} \frac{1}{2m} \{ p, \delta(s) \delta(s) p \} \\
= -\hbar \frac{1}{i} \mathcal{F}_{t}
\]

the function \( C_{\beta}(t) \) is seen to be the flux–flux autocorrelation function,

\[
C_{\beta}(t) = \text{tr} \left[ \mathcal{F} \exp(iH_{\beta}/\hbar) \mathcal{F} \exp(-iH_{\beta}/\hbar) \right]. \tag{2.12}
\]

Equations (2.11) and (2.12), expressing the rate constant as the time integral of a flux–flux autocorrelation function, is similar to the result obtained by Yamamoto using Kubo linear response analysis, but there are significant differences. In present notation, Yamamoto's flux–flux correlation function is

\[
\tilde{C}_{\beta}(t) = \frac{1}{\beta} \int_{0}^{\beta} d\lambda \text{tr} \left[ \mathcal{F} \exp(iH_{\beta}/\hbar) \exp(-\lambda H) \mathcal{F} \exp(-\lambda H) \exp(-iH_{\beta}/\hbar) \right] \\
= \frac{1}{\beta} \int_{0}^{\beta} d\lambda \text{tr} \left[ \mathcal{F} \exp(iH_{\beta}/\hbar) \exp(-\lambda H) \mathcal{F} \exp(-\lambda H) \exp(-iH_{\beta}/\hbar) \right]. \tag{2.13a}
\]

As noted with regard to Eq. (2.10a), through the integrand of Eq. (2.13a) is independent of \( \lambda \), so that Eq. (2.13a) reduces to Eq. (2.10a), which is the same rate constant as before. It does not follow, though, that Yamamoto's correlation function, \( \tilde{C}_{\beta}(t) \) of Eq. (2.13), is identical to \( C_{\beta}(t) \) of Eq. (2.12), and in fact the two are not the same, only their integrals are. The fact that \( C_{\beta}(t) \) is simpler to compute than \( \tilde{C}_{\beta}(t) \), e.g., there is no integral over \( \lambda \), thus makes the present rate expressions have some distinct advantage over Yamamoto's.

Finally, there is a third equivalent form of the rate that can be obtained also by using the above relation between the time derivation of the Heisenberg projection operator and the flux operator. From Eq. (2.10), and with a cyclic reordering of operators in the trace, one has

\[
kQ = \lim_{t \to \infty} \text{tr} \left[ \exp(-iH_{t}/\hbar) \mathcal{F} \exp(iH_{t}/\hbar) h(s) \right], \tag{2.14}
\]

and by a calculation similar to that between Eqs. (2.11) and (2.12), one can readily show that

\[
\exp(-iH_{t}/\hbar) \mathcal{F} \exp(iH_{t}/\hbar) h(s) = \frac{d}{dt} \exp(-iH_{t}/\hbar) h(-s) \exp(iH_{t}/\hbar),
\]

so that

\[
kQ = \lim_{t \to \infty} \frac{d}{dt} C_{s}(t), \tag{2.15a}
\]

where the "left–right" spatial correlation function \( C_{s}(t) \) is

\[
C_{s}(t) = \text{tr} \left[ h(-s) \exp(iH_{t}/\hbar) h(s) \exp(-iH_{t}/\hbar) \right]. \tag{2.15b}
\]

The three correlation functions are real, and the above analysis has shown that they are related as follows

\[
C_{\beta}(t) = \tilde{C}_{\beta,s}(t) \Rightarrow C_{s}(t) = \tilde{C}_{s}(t), \tag{2.16}
\]

and the rate is also given by its time integral, as in Eq. (2.11). It is not hard to show that Yamamoto's correlation function gives the same rate as Eqs. (2.11) and (2.12). Integrating Eq. (2.13), and using the reverse of the steps between Eqs. (2.11) and (2.12), gives

\[
kQ = \int_{0}^{\infty} dt \tilde{C}_{\beta}(t)
\]

which one can also show is the negative of the right–right (or left–left) autocorrelation function, i.e.,

\[
C_{s}(t) = -\text{tr} \left[ h(s) \exp(iH_{t}/\hbar) h(s) \exp(-iH_{t}/\hbar) \right]. \tag{2.15c}
\]

To summarize, the three forms for the rate constant we have obtained are the time integral of the flux–flux autocorrelation function (which can easily be shown to be an even function of \( t \)):

\[
kQ = \int_{0}^{\infty} dt C_{s}(t) = \frac{1}{2} \int_{-\infty}^{\infty} dt C_{s}(t), \tag{2.16a}
\]

the long time limit of the time derivative of the left–right correlation function,

\[
kQ = \lim_{t \to \infty} \frac{d}{dt} C_{s}(t), \tag{2.16b}
\]

and the long time limit of the cross correlation function between position and flux,

\[
kQ = \lim_{t \to \infty} C_{s,s}(t), \tag{2.16c}
\]

where

\[
C_{s}(t) = \text{tr} \left[ F \exp(iH_{t}/\hbar) F \exp(-iH_{t}/\hbar) \right], \tag{2.17a}
\]

\[
C_{s}(t) = \text{tr} \left[ h(-s) \exp(iH_{t}/\hbar) h(s) \exp(-iH_{t}/\hbar) \right], \tag{2.17b}
\]

\[
C_{s,s}(t) = \text{tr} \left[ F \exp(iH_{t}/\hbar) h(s) \exp(-iH_{t}/\hbar) \right]. \tag{2.17c}
\]

These three correlation functions are real, and the above analysis has shown that they are related as follows

\[
C_{\beta}(t) = \tilde{C}_{\beta,s}(t) \Rightarrow C_{s}(t) = \tilde{C}_{s}(t), \tag{2.16}
\]

\( C_{\beta} \) and \( C_{s} \) are even functions of \( t \), and \( C_{s,s} \) is odd.
It is also useful to give the explicit expressions obtained if these traces are evaluated in a coordinate representation. Using the fact that

\[ \langle s \mid \exp(\text{i}Ht/\hbar) \mid s' \rangle = \langle s' \mid \exp(-\text{i}Ht/\hbar) \mid s \rangle^* , \quad (2.19) \]

that time-reversal invariance implies the following symmetry:

\[ \langle s \mid \exp(-\text{i}Ht/\hbar) \mid s' \rangle = \langle s' \mid \exp(-\text{i}Ht/\hbar) \mid s \rangle , \quad (2.20) \]

and that the coordinate matrix representation of the symmetrized flux operator is (with the dividing surface at \( s = 0 \))

\[ \langle s \mid \mathcal{F} \mid s' \rangle = \frac{\hbar}{2im} \left[ \delta(s') \delta(s') - \delta(s) \delta(s') \right] , \quad (2.21) \]

it is not hard to show that Eq. (2.17) for the correlation becomes

\[ C_s(t) = \frac{\hbar}{2m} \sum_{q, q'} \left[ \frac{\delta}{\delta q} \langle s' \mid \exp(-\text{i}Ht/\hbar) \mid s \rangle \right]^2 , \]

\[ s = s' = 0 \quad (2.22a) \]

\[ C_s(t) = \int_0^\infty ds \int_0^\infty ds' \left[ \langle s' \mid \exp(-\text{i}Ht/\hbar) \mid s \rangle \right]^2 , \quad (2.22b) \]

\[ C_{s,s}(t) = \frac{\hbar}{m} \int_0^\infty ds \int_0^\infty ds' \left[ \langle s' \mid \exp(-\text{i}Ht/\hbar) \mid s \rangle \right]^2 , \quad \]

\[ s = s' \quad (2.22c) \]

Equation (2.22a) has the desirable feature that one only needs values of the complex time propagator (and its derivatives) at \( s = s' = 0 \), while Eq. (2.22b) has the advantage that no time derivatives are required.

For the general multidimensional case, Eqs. (2.16) and (2.17) apply just as they stand. Equations (2.22) for the coordinate evaluation of the trace are modified by the replacement

\[ \langle s' \mid \exp(-\text{i}Ht/\hbar) \mid s \rangle = \langle s' \mid \exp(-\text{i}Ht/\hbar) \mid s \rangle \delta(q) \delta(q') , \]

where \( \{q, q'\} = q \) denotes the coordinates for all the other degrees of freedom, and there is an integral over \( q \) and \( q' \). Equation (2.22b), for example, becomes

\[ C_s(t) = \int_0^\infty ds \int_0^\infty ds' \int_0^\infty dq \int_0^\infty dq' \left[ \langle s' \mid \exp(-\text{i}Ht/\hbar) \mid s \rangle \delta(q) \delta(q') \right]^2 . \quad (2.23) \]

Finally, it is interesting to note that a formally exact expression for the microcanonical cumulative reaction probability \( N(E) \) can be obtained from the flux-flux version of the rate expression. The rate constant is given in terms of \( N(E) \) by

\[ kQ = (2\pi\hbar)^{-1} \int_0^\infty dE e^{-\text{i}\mathcal{E}} N(E) . \quad (2.24) \]

If one uses the identity

\[ \exp(-\text{i}Ht/\hbar) = \int_0^\infty dE \exp(-\text{i}Et/\hbar) \delta(E-H) , \quad (2.25) \]

then Eqs. (2.16a) and (2.17a) give

\[ \int dt \exp(-\text{i}(E-E')t/\hbar) \delta(E-H) \]

\[ \times \text{tr} \left[ \mathcal{F} \delta(E'-H) \mathcal{F} \delta(E-H) \right] . \quad (2.26) \]

The time integral gives

\[ \int dt \exp[-\text{i}(E-E')t/\hbar] = 2\pi\hbar \delta(E-E') , \quad (2.27) \]

so that Eq. (2.26) becomes

\[ kQ = \pi \hbar \int dE e^{-\text{i}\mathcal{E}} \text{tr} \left[ \mathcal{F} \delta(E-H) \mathcal{F} \delta(E-H) \right] , \quad (2.28) \]

where by one identifies \( N(E) \) as

\[ N(E) = \frac{1}{2} \left( 2\pi\hbar \right)^2 \text{tr} \left[ \mathcal{F} \delta(E-H) \mathcal{F} \delta(E-H) \right] . \quad (2.29) \]

If the trace is evaluated in a coordinate representation, this becomes

\[ N(E) = \frac{1}{2} \left( \frac{\pi\hbar}{m} \right)^2 \left[ \frac{\delta}{\delta q} \langle \langle s' \mid \delta(E-H) \mid s \rangle \left( \frac{\delta}{\delta q} \langle s' \mid \delta(E-H) \mid s \rangle \right) \right] , \quad (2.30) \]

\[ s = s' = 0 . \]

This is an interesting result since it expresses the microcanonical reactive flux in terms of matrix elements of the density operator \( \delta(E-H) \) rather than in terms of the Green's function \( G(t) \), which is usually the case; i.e., one needs only the imaginary part of the Green's function,

\[ \delta(E-H) = -\frac{1}{\pi} \text{Im} G(t) \]

and not its real part. [We note in passing that the second term on the right-hand side of Eq. (2.26) and also of Eq. (2.22a) is zero if the potential surface is symmetric about \( s = 0 \); i.e.,

\[ \delta(E-H) = s = 0 \]

\[ \text{tr} \left( \langle s' \mid \delta(E-H) \mid s \rangle s \right) = \left( \frac{\delta}{\delta q} \langle s' \mid \delta(E-H) \mid s \rangle \right) s \]

at \( s = s' = 0 \) if \( V(s) = V(-s) \). This follows because in such cases all wave functions are even or odd functions of \( s \) (i.e., \( q \) or \( s \) states) so that either the wave function itself or its derivative is zero at \( s = 0 \).]

III. SIMPLE EXAMPLE: THE PARABOLIC BARRIER

To evaluate the rate expressions of the previous section, Eqs. (2.16) and (2.22), it is necessary to determine the matrix elements of the time evolution operator

\[ \langle s' \mid \exp(-\text{i}Ht/\hbar) \mid s \rangle \]

which is tantamount to solving the quantum dynamics of the system. For these expressions to be useful for carrying out calculations it is thus necessary that the infinite time limits in Eq. (2.16) [or the integral over \( t \) from 0 to \( \infty \) as in Eq. (2.16a)] converge rapidly with \( t \). To develop some feeling for whether or not this is actually the case, it is useful to consider a simple, analytically solvable model problem, the one-dimensional parabolic barrier, for which the Hamiltonian is
\[ H = (p^2/2m) - \frac{1}{2} m \omega_s^2 s^2. \]  

(3.2)

In this case the matrix elements of the propagator are
\[ \langle s' | \exp(-iHt_c/\hbar) | s \rangle = \left( \frac{2\pi \hbar}{m \omega_s} \right)^{-1/2} \times \exp \left\{ \frac{im \omega_s}{2\hbar \sinh(\omega_s t_c)} \left( (s^2 + s'^2) \cosh(\omega_s t_c) - 2ss' \right) \right\}, \]  

(3.3)

so that
\[ \left| \langle s' | \exp(-iHt_c/\hbar) | s \rangle \right|^2 = \frac{m \omega_s}{2\hbar} \left| \sinh(\omega_s t_c) \right|^2 \times \exp \left\{ - \frac{m \omega_s \sin(u/2)}{\hbar \left| \sinh(\omega_s t_c) \right|^2} \left( s^2 + s'^2 \right) \times \cos(u/2) - 2ss' \cosh(\omega_s t_c) \right\}, \]  

(3.4)

where
\[ u = n \omega_s \beta \]  

\[ |\sinh(\omega_s t_c)| = |\sinh(\omega_s t - it/2)| \]  

\[ = [\sinh^2(\omega_s t) + \sin^2(u/2)]^{1/2}. \]

It is then a straightforward calculation to show that
\[ C_s(t) = \int_{-\infty}^{\infty} ds \int_{-\infty}^{\infty} ds' \left| \langle s' | \exp(-iHt_c/\hbar) | s \rangle \right|^2 \]  

(3.5a)

\[ = \frac{kT}{\hbar \sin(u/2)} f(t), \]  

(3.5b)

where
\[ f(t) = \ln \left[ \frac{\cos(\omega_s t) + [\sinh^2(\omega_s t) + \sin^2(u/2)]^{1/2}}{\cos(u/2)} \right], \]  

(3.5c)

According to Eq. (2.16b), the rate is then given by
\[ \hbar Q = \frac{kT}{\hbar \sin(u/2)} \lim_{t \to \infty} \frac{d}{dt} f(t), \]  

(3.6)

and from Eq. (3.5c) one calculates
\[ \frac{d}{dt} f(t) = \frac{\sinh(\omega_s t)}{[\sinh^2(\omega_s t) + \sin^2(u/2)]^{1/2}} \]  

(3.7)

\[ = 1 - 2\exp(-2\omega_s t) \sin^2(u/2) + \ldots \]

as \( t \to \infty \). Thus \((d/dt)f(t) \to 1\) as \( t \to \infty \), and one recognizes that Eq. (3.6) is then the correct result. The important observation here is that \((d/dt)f(t)\) approaches unity rapidly (here exponentially) as \( t \to \infty \), in a time of roughly a vibrational period of the inverted potential.

It is also interesting to consider the flux-flux autocorrelation function. According to Eq. (2.18) it is given in this case by
\[ C_f(t) = \frac{kT}{\hbar \sin(u/2)} \frac{d^2}{dt^2} f(t), \]  

(3.8)

\[ = \frac{kT}{\hbar \sin(u/2)} \frac{\omega_s \sin(u/2) \cos(\omega_s t)}{[\sinh^2(\omega_s t) + \sin^2(u/2)]^{3/2}}, \]

which decays to zero as \( \exp(-2\omega_s t) \) as \( t \to \infty \), so that its time integral, which gives the rate constant, would not require it to be determined for more than about one vibrational period of the barrier. Note that in the free particle limit \((\omega_s = 0)\) the correlation function becomes
\[ C_f(t) = \frac{kT}{\hbar} \left( \frac{\beta^2}{2} \right)^2 \left[ \left( t^2 + (\beta/2)^2 \right)^{3/2} \right]. \]  

(3.9)

### IV. MORE GENERAL APPLICATIONS

The example of the parabolic barrier in the previous section suggests the encouraging possibility that the various rate expressions will converge to the correct result rapidly as \( t \) increases, so that it should be necessary to determine the quantum dynamics of the system—i.e., the propagator \( \exp(-iHt_c/\hbar)—\) only for relatively short times. For nontrivial applications, however, one will not have at hand the exact matrix elements of the propagator, so one must consider approximate approaches. It is most desirable, of course, that the approximate method converge to the correct result as the effort put into the approximate calculation (e.g., number of basis functions, number of Monte Carlo samples, etc.) increases in some systematic fashion.

There are at least three approaches that come to mind for evaluating the quantum mechanical trace expressions of Sec. II. One is to solve the time-independent Schrödinger equation, i.e., a coupled-channel scattering calculation in the multidimensional case, in the vicinity of \( s = 0 \). From the two linearly independent translational functions (function matrices in the multidimensional case) one can construct the density operator
\[ \langle s | \delta(E - H) | s' \rangle, \]

and then calculate the microcanonical cumulative reaction probability from Eq. (2.30). Although couched in a different language and formulation, this is essentially the type of calculation carried out by Light and Altenberger-Siczek for a planar version of the \( \text{H} + \text{H}_2 \) reaction. Their results were reasonably encouraging, and there are probably a number of avenues that should be pursued further along these lines.

### A. Path integral approach

Another, quite different approach is to evaluate the coordinate matrix elements of the propagator by a Monte Carlo path integral technique. For matrix elements of the Boltzmann operator, i.e.,
\[ \langle s' | e^{\beta H} | s \rangle, \]  

(4.1)

this is a straightforward calculation, and also one that generalizes to the multidimensional case in an efficient manner. One could utilize an approach based on a Fourier series expansion of the path, as discussed earlier by one of us,\textsuperscript{13} or a Monte Carlo random walk algorithm that is summarized in Appendix B.

Difficulties arise for the present application, though, because one needs the Boltzmann operator at complex values of \( \beta \),
\[ \langle s' | \exp [-iH\beta/\hbar] | s \rangle, \]  

(4.2)

(or equivalently, the propagator in time, \( \exp(-iHt/\hbar) \)).
at complex times). In this case the integrand of the path integral is not a positive definite quantity, and Monte Carlo evaluation of such integrals is in general not successful. Unfortunately, the high dimensionality of a path integral essentially necessitates a Monte Carlo approach, so the possibility of a straightforward evaluation of the path integral for complex $\beta$ does not look promising.

An approach that is successful, though, is to evaluate the path integral representation of the Boltzmann operator for real values of $\beta$ and then to obtain values at $\beta/2 + i\hbar t$ by numerical analytic continuation. To test the feasibility of this we have used it to calculate the one-dimensional rate constant for the symmetric Eckart potential barrier,

$$V(s) = V_0 \text{sech}^2(s/a),$$

(4.3a)

where the two relevant dimensionless parameters are

$$\alpha = \sigma(2mV_0a^2\hbar^2)^{1/2},$$

(4.3b)

$$u = \hbar\beta(2V_0a^2m)^{1/2}.$$

(4.3c)

Specifically, the flux–flux correlation function was computed via Eq. (2.22a), where the Boltzmann matrix elements were determined by the random-walk path integral algorithm described in Appendix B. Equations (B6)–(B8) give these matrix elements as

$$\langle s' | \exp[-i\hbar t \hat{H}/\hbar] | s \rangle = \langle s' | \exp[-\left(\frac{\beta}{2} + i\hbar t/\hbar\right) \hat{H}] | s \rangle$$

(4.4)

$$= \left(\frac{m}{2e\beta t c}\right)^{1/2} \exp\left[\frac{im}{2\hbar t c} \left(s - s' \right)^2\right] \Delta(s, s', \beta/2 + i\hbar t/\hbar),$$

where $\Delta$ is the energy difference element defined by Eq. (B8). $\Delta(s, s', \beta)$ is computed at 10 to 15 real values of $\beta$ via the Monte Carlo algorithm and then numerically analytically continued by Schlessinger's point method to obtain $\Delta(s, s', \beta/2 + i\hbar t/\hbar)$. With Eq. (4.4), it is not hard to show that Eq. (2.22a) then gives

$$C_\Gamma(t) = \frac{kT}{\hbar} \left\{ \frac{(\beta^2/2)}{\beta + (\beta^2/2)} \right\}^{1/2} \left[ \Delta(0, 0; \beta/2 + i\hbar t/\hbar)^2 + \frac{\beta^2}{8s s'} \Delta(s, s', \beta/2 + i\hbar t/\hbar)^2 \right],$$

(4.5)

$$s = s' = 0.$$  

Figure 1 shows the correlation function so obtained for the case $\alpha = 12$, $u = 8$. The time integral of $C_\Gamma(t)$ gives the rate constant, or equivalently the tunneling factor $\Gamma$, which is defined by

$$kQ = \frac{kT}{\hbar} \exp(-\beta V_0)\ .$$

(4.6)

$\Gamma$ has been tabulated by Johnston for various values of $\alpha$ and $u$, and we have reproduced his values for the specific cases $\alpha = 12$, $u = 2, 4, 8, 10$, for which $\Gamma$ ranges from 1.2 to 162. These results are quite stable with respect to the number of real values of $\beta$ used to effect the numerical analytic continuation (~10–15 values), the number (~20) of random walk steps and the number (~500–1000) of Monte Carlo random walks used to evaluate the path integral via the algorithm described in Appendix B.

The significant conclusion of this application is that the analytic continuation from real values of $\beta$ to the complex values $\frac{1}{2} \beta + i\hbar t/\hbar$ is well-behaved. It is clear, of course, that the continuation will be most accurate for short times $t$ because $\frac{1}{2} \beta + i\hbar t/\hbar$ is close to the real $\beta$ axis, and the important observation here is that it is accurate to sufficiently long times to determine the rate constant accurately, even when the quantum correction is large.

In concluding this section, it should be stressed that the correlation function $C_\Gamma(t, \beta)$, as a function of $t$ and $\beta$, is not an analytic function of $\frac{1}{2} \beta + i\hbar t/\hbar$, or $\frac{1}{2} \beta - i\hbar t/\hbar$, or $\frac{1}{2} \beta + i\hbar t/\hbar$, etc., so it itself cannot be analytically continued from values with $t = 0$ to finite $t$. It is the matrix elements of the Boltzmann operator $e^{-\beta \hat{H}}$ that are analytic functions of $\beta$, so that values for complex $\beta$ (i.e., $\frac{1}{2} \beta + i\hbar t/\hbar$) can be obtained by analytic continuation from real $\beta$. The correlation function is then related [Eq. (2.22a)] to the square modulus of these matrix elements.

B. Discrete basis set approach

Finally, there is a third way one can evaluate the quantum mechanical rate expressions, this being a straightforward basis set approximation to the trace. Consider the one-dimensional case and the flux–flux correlation function, Eq. (2.17a). If $\{\phi_i(s)\}$ is a finite set of square integrable basis functions, diagonalizing the matrix of $\hat{H}$ in this basis produces the eigenvalues $\{E_i\}$ and eigenfunctions $\{\phi_i(s)\}$. In this matrix representation it is easy to show that Eq. (2.17a) becomes

$$C_\Gamma(t) = \sum_{i,j} \exp[-\beta(E_i + E_j)/2]|\langle i | \hat{F} | j \rangle|^2,$$

(4.7)

where

$$|\langle i | \hat{F} | j \rangle|^2 = \int ds \int ds' \phi_i(s)^* \langle s | \hat{F} | s' \rangle \phi_j(s')^2 = \left(\frac{\hbar}{2m}\right)^3 |\phi_i(0) \phi_j(0) - \phi_i(0) \phi_j(0)|^2.$$

(4.8)

Integrating this then gives the rate as
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FIG. 2. The tunneling factor for the Eckart potential (with \( \alpha = 12, \mu = 4 \)) as given by the basis set approximation to the flux-flux correlation function [cf. Eq. (4.9)], as a function of the "infinite time" \( t \). (\( t \) is in units of \( 2\pi/\omega_0 \), the harmonic period of the inverted potential barrier.) The solid curve is for a basis set of 50 functions, and the dashed curve for a set of 20 functions.

\[
kQ = \sum_{i,j} \exp\left[-\beta(E_i + E_j)/2\right] \frac{\sin((E_i - E_j)t/\hbar)}{E_i - E_j} \left| \left< i | F | j \right> \right|^2,
\]

(4.9)

with the limit \( t \to \infty \) implied. With a finite, discrete basis, however, this limit does not exist; this is easy to see by noting that the formal \( t \to \infty \) limit is

\[
\lim_{t \to \infty} \frac{\sin((E_i - E_j)t/\hbar)}{E_i - E_j} = \pi \delta(E_i - E_j).
\]

A discrete basis set approximation can thus never describe the very long time limit correctly. For short time, though, discretization of the energy spectrum should not be a major shortcoming, so it is quite possible for Eq. (4.7) or (4.9) to be accurate for short to intermediate times. For Eq. (4.9) to be useful, therefore, the basis set must be sufficiently large—and the energy levels \( E_j \) sufficiently closely spaced—that with increasing \( t \) the right-hand side reaches its effective limit before \( t \) becomes so large that the discreteness of the spectrum makes the approximation inaccurate.

To see how this approach works in practice we have applied it also to the Eckart potential of the previous section, using a standard harmonic oscillator basis set of frequency \( \omega \). For a given number of basis functions there is an optimum range for the frequency \( \omega \) that defines the basis: \( \omega \) must be sufficiently small for the energy levels to be closely spaced enough for the correct long time limit of Eq. (4.9) to be reached, but not too small or else the energy levels will all collapse too much toward zero so that the sum over them in Eq. (4.9) is not convergent.

Figure 2 shows the tunneling factor \( \Gamma \), obtained by equating Eqs. (4.6) and (4.9), as a function of the "infinite" time \( t \), for the parameter values \( \alpha = 12, \mu = 4 \); the dashed curve is with 20 basis functions, and the solid curve with 50. For the smaller basis set there is only a rather short region of time for which the "long time" limit of Eq. (4.9) is reached before the discreteness of the energy spectrum causes erratic behavior, while with the larger basis the long time limit is reached, and maintained, over a much larger region, out to \( t = 3 \) in this case.

For the same set of parameters as the previous section \( (\alpha = 12, \mu = 2, 4, 6, 8, 10) \) a basis set of size 50 gives \( \Gamma \) correct to within 10% for values up to \( \Gamma = 22 \) (\( \mu = 8 \)), but is a factor of 2 too large for the case \( \mu = 10 \) for which \( \Gamma = 162 \). Increasing the basis to 80 functions reduces the error to being a factor of 1.3 too large.

The basis set approach is thus one possible avenue for evaluating the rate expressions of Sec. II, although for large quantum corrections it appears that relatively large basis sets may be required. Equation (4.9) is readily generalizable to the multidimensional case, and since the other degrees of freedom would be rotational and vibrational degrees of freedom, a basis set description of them should be much more efficient than it is for the reaction coordinate. Thus even though this approach does not appear as promising as the path integral method of the previous section, it perhaps merits further exploration before being discarded.

V. CONCLUDING REMARKS

It appears, therefore, that the formal rate expressions discussed in Sec. II may indeed provide a useful means for a direct calculation of the quantum rate constant. The applications described in Secs. III and IV support the feasibility of this, although applications to multidimensional problems are necessary to demonstrate it more convincingly. In one sense these one-dimensional applications are a significant test of the methods, for in a multidimensional case the other degrees of freedom are bound-like, i.e., vibrations and rotations, and these are more easily characterized by the path integral techniques, and also by the discrete basis approximation, than is the translational degree of freedom.

Both the basis set and the path integral methods discussed in Sec. IV for evaluating the trace expressions have the character of being accurate for short times and becoming less so for sufficiently long times. In the spirit of transition state theory, though, it is only the relatively short time dynamics that determines the net reactive flux, i.e., the rate constant, so these approximations have a chance of being adequate for this purpose. This is, of course, the sought for "efficiency" of the overall idea, namely that by asking only for the net reactive flux rather than state-to-state reactive information, a simpler theory should suffice.

Note added in proof: Since completing the work described in this paper, we have seen a preprint by D. Thirumalai and B. J. Berne [J. Chem. Phys. (in press)] on the Monte Carlo path integral evaluation of quantum mechanical dipole autocorrelation functions for bound systems. They have also used a numerical analytic continuation technique to construct the real time propagator which, though different in specifics from our approach, is similar in overall spirit. The interested reader should certainly take note of this work.
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APPENDIX A: EQUIVALENCE OF SPATIAL AND MOMENTUM PROJECTION OPERATORS

The object here is to show explicitly that the two projection operators
\[ \sigma_+ = \exp(iHt/\hbar) \exp(-iHt/\hbar), \]
\[ \sigma_- = \exp(-iHt/\hbar) \exp(iHt/\hbar), \]
are equivalent in the infinite time limit \( t \to \infty \), where \( \hbar \) is the step function
\[ h(\xi) = \begin{cases} 1, & \xi > 0, \\ 0, & \xi < 0. \end{cases} \]

Equation (A1) may be written as
\[ \sigma_+ = \Omega^\dagger \exp(\Omega H_0/\hbar) \exp(-\Omega H_0/\hbar) \Omega, \]
\[ \sigma_- = \Omega \exp(\Omega H_0/\hbar) \exp(-\Omega H_0/\hbar) \Omega, \]
where
\[ \Omega = \exp(iHt/\hbar) \exp(-iHt/\hbar), \]
\[ \Omega^\dagger = \exp(-iHt/\hbar) \exp(iHt/\hbar). \]

\( \Omega \) is a Möller wave operator\(^{16} \) which has a limit as \( t \to \infty \), so that it is sufficient to establish the equivalence of the following two projection operators:
\[ \sigma_+^{(0)} = \exp(iHt/\hbar) \exp(-iHt/\hbar), \]
\[ \sigma_-^{(0)} = \exp(iHt/\hbar) \exp(-iHt/\hbar), \]
as \( t \to \infty \), where \( H_0 = (p^2/2m) \).

Taking a coordinate matrix representation of Eq. (A4b) gives
\[ \langle s' | \sigma_+^{(0)} | s \rangle = \langle s' | \exp[(ip^2/2m)\tau/\hbar] \rangle \langle h(p) \rangle \]
\[ \times \exp[-(ip^2/2m)\tau/\hbar] \]
\[ = \langle s' | h(p) \rangle \langle s \rangle \]
\[ = \int_0^\infty dp \langle s' | p \rangle \langle p | s \rangle \]
\[ = (2\pi)^{-1} \int_0^\infty dp \exp[ip(s' - s)/\hbar], \]
which has the fact been used that
\[ \langle s | p \rangle = (2\pi)^{-1/2} \exp[ip(s'/\hbar)]. \]

For comparison, the coordinate matrix representation of Eq. (A4a) gives
\[ \langle s' | \sigma_-^{(0)} | s \rangle = \langle s' | \exp(iHt/\hbar) \exp(-iHt/\hbar) | s \rangle \]
\[ = \int_0^\infty ds'' \langle s' | \exp(iHt/\hbar) | s'' \rangle \langle s'' | \exp(-iHt/\hbar) | s \rangle, \]
and since
\[ \langle s'' | \exp(-iHt/\hbar) | s \rangle = (2\pi)^{-1} \exp[im(s'' - s)^2/(2\hbar t)], \]
this becomes
\[ \langle s' | \sigma_+^{(0)} | s \rangle = \frac{m}{2\pi \hbar t} \int_0^\infty ds'' \exp \left[ \frac{im}{2\hbar t} (s'' - s)^2 - (s' - s'')^2 \right]. \]

Upon changing integration variables from \( s'' \) to \( p \) in the above equation,
\[ m\tau''/\hbar = p, \]
it becomes
\[ \langle s' | \sigma_+^{(0)} | s \rangle = \exp \left[ \frac{im}{2\hbar t} (s^2 - s''^2) \right] \int_0^\infty dp \exp[ip(s' - s)/\hbar]. \]

As \( t \to \infty \) the exponential factor outside the integral in Eq. (A6) approaches unity, so that Eq. (A6) becomes identical to Eq. (A5), thus establishing the equivalence of the two projection operators.

APPENDIX B: RANDOM WALK ALGORITHM FOR BOLTZMANN PATH INTEGRALS

For a typical one-dimensional Hamiltonian of the form
\[ H = (p^2/2m) + V(x), \]
the standard Feynmann path integral expression for coordinate matrix elements of the Boltzmann operator is\(^{11} \)
\[ \langle x_f | e^{-\beta H} | x_0 \rangle = \int_0^\infty dx_1 \int_0^\infty dx_2 \cdots \int_0^\infty dx_N \exp \left[ -\frac{Nm}{2\hbar^2 \beta} \sum_{k=1}^N \frac{1}{2} (x_k - x_{k-1})^2 - \frac{\beta}{N} \sum_{k=1}^N V \left( \frac{x_k + x_{k-1}}{2} \right) \right]. \]

Since the kinetic energy contribution to the exponent of the integrand is quadratic in the integration variables \( x_1, x_2, \ldots, x_N \), the idea is to change integration variables to new ones \( w_1, w_2, \ldots, w_N \) that incorporate these Gaussian factors. It is also useful to scale the new variables to have the limits \( (0, 1) \) so that Monte Carlo evaluation of the multidimensional integral is then straightforward.

The result of carrying out this change of variables is tedious, but one obtains the following result:
\[ \langle x_f | e^{-\beta H} | x_0 \rangle = \left( \frac{m}{2\pi \hbar^2 \beta} \right)^{1/2} \exp \left[ -\frac{m}{2\hbar^2 \beta} (x_f - x_0)^2 \right] \]
\[ \times \int_0^1 dw_1 \int_0^1 dw_2 \cdots \int_0^1 dw_N \exp[ -\beta V(w) ], \]
with
\[ V(w_1, w_2, \ldots, w_N) = \frac{1}{N} \sum_{k=1}^N V \left( \frac{x_k + x_{k-1}}{2} \right), \]
and where the variables \( x_k \) are given in terms of the variables \( w_k \) by the following recursion relation:
\[ x_1 = \frac{N-1}{N-1+i} x_{i-1} + \frac{x_{i+1}}{N-1+i}, \]
\[ (2\pi \hbar^2 \beta)^{1/2} \left( \frac{N-i}{m} \frac{N-i+1}{N(N-i+1)} \right)^{1/2} z(w_i), \]
\[ i = 1, 2, \ldots, N-1, \]
where \( z(w) \) is the inverse function of \( w(z) \):
\[ w(z) = \int_{a}^{b} dz' \exp(-\pi z'^2) . \]  

(5)

There exists a simple, accurate rational approximation for the function \( w(z) \). \( ^{11} \)

In practice the integral over the variables \( \{w_i\} \) in Eq. (B2) is accomplished by Monte Carlo. Thus the explicit algorithm for computing the matrix element is as follows: the desired matrix element is given by

\[ \langle \phi | e^{-\Delta H} | \chi \rangle = \langle \phi | e^{-\Delta H} | \chi \rangle (e^{-\Delta V}) , \]  

(6)

where the first factor,

\[ \langle \phi | e^{-\Delta H} | \chi \rangle = \left( \frac{m}{2\pi i \hbar} \right)^{1/2} \exp \left[ - \frac{m}{2\pi i \hbar} (\phi - \chi)^2 \right] , \]  

(7)

is the free particle matrix element (i.e., the correct result if \( V = 0 \)), and

\[ (e^{-\Delta V}) = \frac{1}{M} \sum_{k=1}^{M} e^{-\Delta V_k} . \]  

(8)

\( M \) is the number of Monte Carlo "random walks" taken to evaluate the path integral. For the \( k \)th random walk, for example, a random number \( w_1 \) is generated and then \( \chi_1 \) is given by Eq. (B4) (\( \phi_0 \) and \( \chi_0 \) are fixed values); the next random number \( w_2 \) is generated and then \( \chi_2 \) is given by Eq. (B4); and so on, random numbers \( w_3, \ldots, w_{N-1} \) being generated successively and the values \( \chi_1, \chi_2, \ldots, \chi_{N-1} \) determined each time by Eq. (B4). The potential \( V_{\Delta V} \) is

\[ V_{\Delta V} = \frac{1}{N} \sum_{k=1}^{N} \left( \frac{\chi_{k+1} + \chi_{k}}{2} \right) , \]  

or equivalently

\[ V_{\Delta V} = \frac{1}{N} \left[ \frac{1}{2} \Delta V(\chi_0) + \frac{1}{2} \Delta V(\chi_N) \right] + \sum_{k=1}^{N-1} \Delta V(\chi_k) \]  

(9)

This procedure is carried out \( M \) times, and the Monte Carlo approximation to the \((N-1)\) dimensional integral in Eq. (B2) is given by Eq. (B8).

The correct result is given by this procedure in the limit \( N \rightarrow \infty \) and \( M \rightarrow \infty \), but the relevant question is how large \( N \) and \( M \) must be to achieve sufficiently accurate results. For the application reported in Sec. IV the values \( N = 15-20 \) and \( M = 500-1000 \) were used and the results were invariant to increasing them. We did not undertake a systematic study to see how small they could be taken; this will of course depend on the particular application.

This procedure of changing integration variables to incorporate part of the integrand is an example of importance sampling. If possible, it is also useful to include part of the potential energy in the importance sampling. A case for which this can be carried out explicitly is to include the quadratic (i.e., harmonic) part of the potential. Thus suppose

\[ V(x) = V_0(x) + \Delta V(x) , \]  

(10a)

where

\[ V_0(x) = \frac{1}{2} m \omega^2 x^2 , \]  

(10b)

In this case it is clear that the contribution from \( V_0(x) \) to the exponential in Eq. (B1) will also be quadratic in the integration variables \( \{x_i\} \), so that essentially the same kind of change of variables that worked for the free particle can also be carried out here. With a Monte Carlo evaluation of the integral over the new variables \( \{w_i\} \), the result is

\[ \langle \phi | e^{-\Delta H} | \chi \rangle = \langle \phi | e^{-\Delta H} | \chi \rangle (e^{-\Delta V}) , \]  

(11)

where the first factor is the matrix element for the harmonic potential [i.e., \( H_0 = (p^2/2m) + V_0 \)],

\[ \langle \phi | e^{-\Delta H} | \chi \rangle = \left( \frac{m}{2\pi i \hbar} \right)^{1/2} \exp \left[ - \frac{m}{2\pi i \hbar} \left( \frac{\phi^2 - \chi^2}{2} \right) \right] \]  

\[ \times \exp \left[ - \frac{m}{2\pi i \hbar} \left( \frac{\phi^2 - \chi^2}{2} \right) \right] \]  

(12)

\[ u = \hbar \omega , \]  

(13)

and

\[ (e^{-\Delta V}) = \frac{1}{M} \sum_{k=1}^{M} e^{-\Delta V_k} . \]  

(14)

Equation (B13) is analogous to Eq. (B8), and the discussion following it also pertains here. Thus analogous to Eq. (B9) one has

\[ \Delta V_k = \frac{1}{N} \left[ \frac{\Delta V(\chi_0) + \Delta V(\chi_N)}{2} + \sum_{k=1}^{N-1} \Delta V(\chi_k) \right] , \]  

(15)

but the recursion relation which gives \( \{x_i\} \) in terms of the random numbers \( \{w_i\} \) in this case is

\[ x_i = x_{i-1} + \hbar \omega \left( \sinh \left[ (N-1-\ell) u/\hbar \right] - \sinh \left[ (N-1) u/\hbar \right] \right) \]  

\[ + \left( 2\pi i \hbar \sinh \left( \sinh \left[ (N-1-\ell) u/\hbar \right] \right) \right)^{1/2} \]  

(16)

rather than Eq. (B4). [Note that as \( \omega \rightarrow 0 \), \( u \rightarrow 0 \), and \( V_0 \rightarrow 0 \), and Eq. (B15) reduces to Eq. (B4), as it should.] Equation (B15) describes a random walk in a harmonic potential.

When evaluating the trace expressions for the rate constant when there are additional degrees of freedom, many of which will be oscillators, it will be important to use the above procedure to incorporate the harmonic part of the potential for these degrees of freedom explicitly. It is clear, for example, that if \( \Delta V \) is small, then the Monte Carlo average in Eq. (B13) will be rapidly convergent with increasing \( M \).

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This is obvious because the matrix elements of the Boltzmann operators \( \exp(-\frac{1}{2}\beta H) \) are real and the flux operator \( \tilde{F} \) contains the factor \( \sqrt{T} \) explicitly.


For example, Eq. (3.12) of Ref. 13.