"Direct" calculation of quantum mechanical rate constants via path integral methods: Application to the reaction path Hamiltonian, with numerical test for the $H + H_2$ reaction in 3D

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The method recently proposed by Miller, Schwartz, and Tromp for determining Boltzmann rate constants "directly"—by the path integral evaluation of a reactive flux correlation function—is developed within the framework of the reaction path Hamiltonian model for a general polyatomic reaction. The expression for the correlation function, the time integral of which is the rate constant, is reduced to a single path integral over only one degree of freedom (the reaction coordinate). Effects of tunneling, "frictional" effects on the reaction coordinate due to coupling to other degrees of freedom, and the effects of recrossing the transition state dividing surface are all correctly accounted for in the approach. Numerical tests of the formulas for the 3D version of the $H + H_2$ reaction (on the Porter-Karplus potential energy surface) gives excellent agreement with the (known) accurate results for this system.

I. INTRODUCTION

We have recently been exploring the question of whether it is possible, first in principle and then in practice, to determine quantum mechanical rate constants (for bimolecular reactions, say) directly, i.e., without having first to solve the complete state-to-state reactive scattering problem and then Boltzmann average the results. The goal is to be able to do this in a way capable of arbitrary accuracy (given, of course, the potential energy surface for the reaction), e.g., we do not wish to rely on transition state theory or ad hoc corrections thereto.

The answer to the “in principle” aspect of the question was answered in the affirmative in a previous paper$^1$ (paper I). This relies on a formally exact expression for the Boltzmann rate constant derived$^2$ previously by one of the authors. With a few minor manipulations it was seen that this expression gives the rate as the time integral of a flux-flux autocorrelation function, a form closely related to an expression given earlier by Yamamoto$^3$ and recently used by Wolynes$^4$ (Though not applied to flux autocorrelation functions, we note that there has been recent work by Berne et al.$^5$ on quantum time correlation functions that uses methods related to those in paper I). Paper I also treated a simple test problem, a one-dimensional barrier potential, to see if a practical computational scheme could be based on these formally exact rate expressions. The results were quite encouraging.

The purpose of the present paper is to describe some improved procedures for carrying out these calculations and, specifically, to apply the approach to the reaction path Hamiltonian$^6$ model of chemical reactions. The methodology described in this paper is thus applicable to general reactive processes in polyatomic systems (given, of course, the potential energy surface information necessary to characterize the reaction path Hamiltonian). A numerical test is made for the three-dimensional version of the $H + H_2$ reaction (on the Porter-Karplus$^7$ potential energy surface), which shows the approach to be easy to use and capable of quantitative accuracy.

Section II A first describes the improved version of the path integral methodology recently used by Jaquet and Miller,$^6$ and the specific application of it to the reaction path Hamiltonian model is carried out in Sec. II B. Section III describes how nonzero total angular momentum is handled, which is necessary in order to describe reactions in 3D space. Results for application to the three-dimensional $H + H_2$ reaction are described in Sec. IV, and Sec. V concludes with a discussion of the limitations of the present methodology and possible approaches for generalizing the approach to overcome them.

II. SUMMARY OF METHODOLOGY

A. Path integral representation of the flux-flux autocorrelation function

The rate constant is given by the time integral of a flux-flux autocorrelation function

$$k = Z_R^{-1} \int_0^\infty dt \, C_f(t),$$

(2.1)

where $Z_R$ is the partition function (per unit volume) for reactants, and the correlation function is defined by

$$C_f(t) = \text{tr} \left[ e^{-\beta H} e^{-\beta H} \right];$$

(2.2)

"tr" denotes a quantum mechanical trace, $\beta = (k_B T)^{-1}$, $H$ is the full Hamiltonian of the system, and $F$ is the symmetrized flux operator

$$F = \frac{1}{2} \left[ \delta(s) (p_s/m) + (p_s/m) \delta(s) \right],$$

(2.3)

where $s$ is the coordinate normal to the "dividing surface" ($s = 0$ is the equation of the surface) through which the flux is computed. Dynamics enters in this expression for the rate via the time evolution operators, and the anticipated efficiency of this "direct" approach comes about because it is necessary to determine the quantum dynamics only for rela-
tively short times. This is the quantum analog of carrying out a classical trajectory calculation by beginning all the trajectories on a dividing surface in the transition state region and running them forward and backward in time to see which ones are reactive; it is necessary to follow the trajectories for only a short time in order to do so.\textsuperscript{10,12}

To make it possible to deal with systems with many degrees of freedom, the Boltzmann operator/time evolution operators $e^{-(\beta/2 + \gamma/N)t}$ are represented by a Feynman path integral\textsuperscript{13} and the path integral evaluated by a Monte Carlo random walk method. It is in general not feasible to do this for real values of the time $t$, however, because the integrand of the path integral would be oscillatory. (Although see recent work by Dool,\textsuperscript{14} Wolynes et al.,\textsuperscript{15} and Berne et al.,\textsuperscript{5} which suggest otherwise.) We thus first calculate $C_f$ for real values of $\tau=it$, i.e., pure imaginary time,

$$C_f(\tau) = \text{tr} \left[ F_{\beta}^{-1} e^{-(\beta/2 + \gamma/N)t} F_{\beta}^{-1} e^{-(\beta/2 + \gamma/N)t} \right],$$

and then use these calculated values to generate a numerical analytic continuation\textsuperscript{16,17} to obtain $C_f$ for real $t$. Since $C_f$ is an even function of $t$, and thus of $\tau$, one uses the values computed for real $\tau$ to construct a Padé approximant in the variable $\tau^2$; $\tau^2$ is then replaced by $-t^2$ to obtain $C_f(t)$.

If the Hamiltonian of the system has the standard Cartesian form

$$H(p_s, s, P, Q) = \frac{p_s^2}{2m} + \frac{p^2}{2m} + V(s, Q),$$

then writing out Eq. (2.4) in a coordinate representation gives

$$C_f(\tau) = \left( \frac{\hbar}{2m} \right)^2 \left( \frac{\partial^2}{\partial s_N \partial s_s} + \frac{\partial^2}{\partial s_s \partial s_s} - 4 \frac{\partial^2}{\partial s_s \partial \phi_0} \right) \int dQ_0 \int dQ_n \langle s_N, Q_n | e^{-(\beta/2 + \gamma/N)t} | s_s, Q_s \rangle \times \langle s_s, Q_s | e^{-(\beta/2 + \gamma/N)t} | s_0, Q_0 \rangle,$$

where $s_N$, $s_s$, and $s_0$ are set to zero after differentiation. If the reactants and products are equivalent (i.e., a symmetric reaction), then this takes a slightly simpler form

$$C_f(\tau) = \left( \frac{\hbar}{2m} \right)^2 \frac{\partial^2}{\partial s_s \partial \phi_0} \int dQ_0 \int dQ_n \langle s_0, Q_n | e^{-(\beta/2 + \gamma/N)t} | s_s, Q_s \rangle \times \langle s_s, Q_s | e^{-(\beta/2 + \gamma/N)t} | s_0, Q_0 \rangle,$$

with $s_0 = s_s = 0$ after differentiation.

The two Boltzmann operator matrix elements in Eq. (2.6) are now written out as a discretized Feynman path integral,\textsuperscript{13} with the special feature that the same imaginary time increment $\Delta \tau = \hbar \beta / N$ is used in both path integrals. For this to be possible (the imaginary) time $\tau$ must be chosen to be one of the particular values $\tau_n$,

$$\tau_n = \frac{n \hbar \beta}{N}, \quad n = 1, \ldots, N - 1,$$

i.e., one of the intermediate time values in the discretization of the path integrals. [This is no essential restriction since one must evaluate $C_f(\tau)$ for various values of $\tau$ in order to generate the Padé approximant from which $C_f(t)$ is determined.] This leads to the following expression for the correlation function of Eq. (2.6a):

$$C_f(\tau_n) = \left( \frac{\hbar}{2m} \right)^2 \left( \frac{\partial^2}{\partial s_s \partial s_s} + \frac{\partial^2}{\partial s_s \partial \phi_0} \right) \left( \frac{mN}{2\pi \hbar^2} \right)^{N/2} \int d\phi_1 \ldots d\phi_{n-1} d\phi_n \ldots d\phi_N \int dQ_0 \ldots \int dQ_{N-1} \times \exp \left[ - \frac{mN}{2\pi \hbar^2} \sum_{i=1}^{N} (s_i - s_{i-1})^2 - \frac{\beta N}{2} \sum_{i=1}^{N} \left( \frac{Q_i - Q_{i-1}}{2} \right)^2 \right],$$

where $Q_N = Q_0$ and $F - 1$ is the number of $Q$ degrees of freedom. Equation (2.7) has a very useful structure: The two path integrals appear as one overall path integral, from initial position $(s_0, Q_0)$ to final position $(s_N, Q_N)$ in a total imaginary time increment $\hbar \beta$, with the “constraint” that $s(\tau_n) = s_n$. One thinks of the first matrix element, the right-hand factor in Eq. (2.6), as propagation from time $- \hbar \beta / 2$ to time $\tau_n$, and the second matrix element, the left-hand factor in Eq. (2.6), as a propagation from time $\tau_n$ to time $\hbar \beta / 2$. Apart from the $(\hbar / 2m)^2$ factor and the derivatives in Eq. (2.7), the only difference between it and the path integral expression for the quantity

$$\int dQ_n (s_N, Q_n | e^{-(\beta/2 + \gamma/N)t} | s_0, Q_0),$$

is that the intermediate position $s_n = s(\tau_n)$ is not integrated over in Eq. (2.7).

The $Q$ degrees of freedom contribute essentially a partition function-like factor to Eq. (2.7). Thus it is useful to define the partition functional $Z_Q[s(\tau)]$ for the $Q$ degrees of freedom,

$$Z_Q[s(\tau)] = \left[ (\frac{mN}{2\pi \hbar^2})^{N/2} \right]^{-1} \int dQ_0 \ldots \int dQ_{N-1} \times \exp \left[ - \frac{mN}{2\pi \hbar^2} \sum_{i=1}^{N} (Q_i - Q_{i-1})^2 - \frac{\beta N}{2} \sum_{i=1}^{N} \left( \frac{Q_i + Q_{i-1}}{2} \right)^2 \right],$$

which is the partition function for the $\tau$-dependent $Q$ Hamiltonian

$$H_Q(P, Q; \tau) = \frac{P^2}{2m} + V(Q, s(\tau)),$$

i.e., this is the Hamiltonian of Eq. (2.5) with the kinetic energy of the $s$ degree of freedom omitted. $Z_Q$ is clearly a func-
tional of the $s$ path $s(\tau)$, an example of a Feynman influence functional.\textsuperscript{13}

Having performed the Q-path integrals, the complex time correlation function of Eq. (2.7) is now given by

$$
C_f(r_n) = \left(\frac{\hbar}{2m}\right)^2 \left(\frac{\partial^2}{\partial s_i \partial s_n} + \frac{\partial^2}{\partial s_i \partial s_n}\right) - 4 \left(\frac{\partial}{\partial s_i \partial \theta_0}\right)^N \left(2m \hbar^2 \beta \right)^{N/2}$$

$$\times \int ds_1 \cdots \int ds_{n-1} \cdots \int ds_{N-1} \exp \left[-\frac{mN}{2 \hbar^2 \beta} \sum_{i=1}^N (s_i - s_{i-1})^2\right] Z_Q[s(\tau)],
$$

and we use the Monte Carlo random walk algorithm described earlier\textsuperscript{18} to evaluate the s-path integral. The explicit result is [for the symmetric case, Eq. (2.6b)]

$$
C_f(r_n) = \left(\frac{\hbar}{2m}\right)^2 \frac{m}{2\pi \hbar} \sqrt{\frac{(\hbar \theta_0^2)}{2}} - r_n$$

$$\times \frac{\partial}{\partial s_i \partial s_n} \exp \left[-\frac{m \beta}{2} \frac{(s_i - s_n)^2}{(\hbar \theta_0^2)} - r_n^2\right]$$

$$\cdot \int_0^1 dw Z_Q[s(\tau)],
$$

(2.12)

where the $s$ path $[s_i]$ is given in terms of the Monte Carlo integration variables $[w_i], i = 1, ..., N-1, n-1, n$ by

$$
s_i = \frac{(n-i)s_{i-1} + s_i}{n-i+1} + \left(2\frac{\pi \hbar^2 \beta}{mN} s_n - n - 1\right)^{1/2} z(w_i)
$$

(2.13a)

for $i = 1, ..., n-1$, and

$$
s_i = \frac{(N+i)s_{i-1} + s_n}{N-i+1} + \left(2\frac{\pi \hbar^2 \beta}{mN} s_n - n - 1\right)^{1/2} z(w_i)
$$

(2.13b)

for $i = n + 1, ..., N-1$; $s_0$ and $s_n$ are specified values, and the function $z(w)$ is related to the inverse of the error function, an explicit representation for which was given before.\textsuperscript{1} The integration over the variables $[w_i]$ in Eq. (2.8) is done by straightforward Monte Carlo.

The reason the present formulation is so useful is that in many applications the partition functional $Z_Q[s(\tau)]$ can be evaluated explicitly. The most common situation for which this is true is if the potential function $V(s,Q)$ has the form

$$
V(s,Q) = V_0(s) - \sum_{k=1}^{F-1} Q_k f_k(s) + \sum_{k=1}^{F-1} \frac{m \omega_i^2}{2} Q_k^2,
$$

(2.14)

i.e., the Q degrees of freedom are (fixed-frequency) harmonic oscillators that are linearly coupled to the reaction coordinate $s$. As shown before,\textsuperscript{8} $Z_Q[s(\tau)]$ is given in this case by

$$
Z_Q[s(\tau)] = \exp \left[-\frac{1}{\hbar} \int_{-\hbar \theta_0^2}^{\hbar \theta_0^2} d\tau V[s(\tau)]\right] \times \prod_{k=1}^{F-1} \left[2 \sinh(u_k/2)\right]^{-e^{\omega_k}},
$$

(2.15a)

where

$$
\Delta = \sum_{k=1}^{F-1} (4m \hbar \omega_k)^{-1} \int_{-\hbar \theta_0^2}^{\hbar \theta_0^2} d\tau \int_{-\hbar \theta_0^2}^{\hbar \theta_0^2} d\tau' f_k[s(\tau)] f_k[s(\tau')]
$$

$$
\cdot \left[ e^{-u_k |\tau - \tau'|} + e^{-u_k |\tau + \tau'|} \right] (1 - e^{-u_k})^{-1},
$$

(2.15b)

$$
u_k = \hbar \omega_k \beta.
$$

(2.15c)

The product of factors in Eq. (2.15a) is the potential energy Boltzmann factor for $V_0(s)$, the partition function of the free harmonic oscillators, and the factor $e^\omega$ which describes the frictional effects\textsuperscript{18} of coupling between the oscillators and the reaction coordinate. In practice, since the $s(\tau)$ path is discretized by the random walk algorithm [Eq. (2.13)], it is convenient to evaluate the $\tau$ integrals in the expression for $\Delta$ over this same $\tau$ grid. This gives

$$
\Delta = \sum_{k=1}^{F-1} (4m \hbar \omega_k)^{-1} \left(\frac{\hbar \theta_0^2}{N}\right)^2 \sum_{i=1}^{N} \sum_{i=1}^{N} f_k[s_i] f_k[s_i - \tau/N]
$$

$$
\cdot \left[ e^{-u_k |i - i'|/N} + e^{-u_k |i + i'|/N} \right] (1 - e^{-u_k})^{-1}.
$$

(2.16)

B. The reaction path Hamiltonian

We consider first the $J = 0$ version of the reaction path Hamiltonian\textsuperscript{6} for a general polyatomic reaction and include only the linear coupling between the reaction coordinate and the harmonic modes orthogonal to the reaction path. (Appendix A discusses the more general case that retains all the coupling terms.) The Hamiltonian for this system is

$$
H(p_s, s, P, Q) = \frac{1}{2} p_s^2 + \sum_{k=1}^{F-1} \frac{1}{2} P_k^2
$$

$$
- \sum_{k=1}^{F-1} p_k^2 B_{k,s} Q_k + V_0(s)
$$

$$
+ \sum_{k=1}^{F-1} \frac{1}{2} \omega_k (Q_k^2),
$$

(2.17)

where $s$ is the reaction coordinate, the (mass-weighted) distance along the minimum energy path through some transition state, and $[Q_k]$ are the local normal coordinates for vibrations orthogonal to the reaction path. The function $B_{k,s}(s)$ is related to the curvature of the reaction path and how it projects onto the various modes $k$; this and other aspects of the reaction path Hamiltonian are discussed in previous papers.\textsuperscript{6}

This Hamiltonian is very similar to that considered above [Eqs. (2.5) and (2.14)], except that here the frequencies $[\omega_k(s)]$ are functions of the reaction coordinate $s$ and the force $f_k$ in Eq. (2.14) is identified with the quantity $p_k^2 B_{k,s}(s)$, which depends on the momentum of the reaction coordinate as well as its position.

The velocity dependence of the forces $f_k$ causes no difficulty: $f_k[s(\tau)]$ in Eq. (2.15b) is simply replaced by

$$
f_k[s(\tau)] \rightarrow |s(\tau)| B_{k,s}(s) f_k[s(\tau)],
$$

(2.18a)

or in the discretized version [Eq. (2.16)], the equivalent replacement is

$$
f_k[s_i] \rightarrow \left| \frac{s_i - s_{i-1}}{\Delta \tau} \right|^2 B_{k,s}(s_i) + B_{k,s}(s_{i-1}).
$$

(2.18b)

That this is the correct modification can be seen from Ap-
Appendix A, where the rigorous form of path integrals for the reaction path Hamiltonian is described. Equation (2.18) results when only the linear coupling terms are returned.

To deal with the $s$ dependence of the frequencies $\omega_s(s)$ we have employed a WKB-like approximation that is accurate when the fractional variational of the frequencies is small compared to their magnitude, i.e.,

$$\left| \frac{d}{dt} \frac{\omega_s(t)}{\omega_s(t)} \right| \ll \omega_s(t),$$

or

$$\left| \frac{d}{dt} \frac{1}{\omega_s(t)} \right| \ll 1.$$

It would actually not be a great deal of additional effort to eliminate this approximation, but it seems to be sufficiently well justified that we have not done so in applications. Appendix B describes the details of this calculation of the partition functional for the variable frequency case. The result is a rather simple modification to the fixed-frequency case [Eqs. (2.15) and (2.16)]; the quantity $u_k$ of Eq. (2.15c) is redefined by

$$u_k = \frac{1}{\sqrt{2}} \int_{-\frac{\theta}{2}}^{\frac{\theta}{2}} d\tau \omega_s(s[\tau]),$$

and Eq. (2.15b) for $\Delta$ is replaced by (with $m=1$)

$$\Delta = \sum_{k=1}^{N-1} \frac{1}{4\hbar} \int_{-\frac{\theta}{2}}^{\frac{\theta}{2}} d\tau \int_{-\frac{\theta}{2}}^{\frac{\theta}{2}} d\tau' \frac{s(s')^2B_{k,k'}(s[s][s'])s(s')^2B_{k,k'}(s[s'])}{\omega_s(s)[s[s]]\omega_s(s)[s'[s']]} 
\cdot \left[ e^{-u_k(s,s')} + e^{-u_k(s,s')} - e^{-u_k(s,s')}(1 - e^{-u_k})^{-1} \right],$$

where

$$u_k(s,s') = \int_{s}^{s'} d\tau'' \omega_s(s[\tau'']),$$

and where Eq. (2.18) has been used for the force $f_i$. Equations (2.19) clearly revert to their fixed-frequency versions in the limit that $\omega_s(s)$ becomes independent of $s$. The discretized version of Eq. (2.19) is

$$\Delta = \sum_{k=1}^{N-1} \frac{1}{4\hbar} \left( \frac{\beta}{2} \right)^2 \left( \frac{\beta}{2} \right)^2 \frac{\beta}{2} 
\times \exp \left[ -\beta \left( \frac{(s_1-s_0)^2}{2} \right) \right] 
\cdot \int_{0}^{1} dw \prod_{k=1}^{N-1} \left( \frac{1 - e^{-u_k}}{1 - e^{-u_k}} \right) 
\times \exp \left[ \Delta - \beta \sum_{i=1}^{N} (V_{eff}(s_i) - V_{eff}(0)) \right].$$

The partition functional for the "bath" modes of the reaction path Hamiltonian is thus given by Eq. (2.15a) with $|u_k|$ and $\Delta$ redefined by Eq. (2.20).

In writing the final expression for the imaginary time correlation function for the reaction path Hamiltonian, it is useful to factor out the partition function of the "activated complex"

$$Z_{\Delta}^+ = \prod_{k=1}^{N-1} \left( 2 \sinh(u_k/2) \right)^{-1},$$

where

$$u_k = \frac{\theta}{2} \omega_s(s[0]).$$

and also the Boltzmann factor for the barrier height, $e^{-\nu_n}$,$V_0 = V_0(s = 0)$ (and also the thermal frequency factor $kT/h$). Using Eqs. (2.15a) and (2.20) in Eq. (2.12) then gives the correlation function as

$$C_f(s_n) = \frac{kT}{\hbar} Z_{\Delta}^+ e^{-\nu_n} \tilde{C}_f(s_n),$$

where

$$\tilde{C}_f(s_n) = \frac{1}{\beta} \left( \frac{\beta}{2} \right)^2 \frac{\beta}{2} 
\times \exp \left[ -\beta \left( \frac{(s_n-s_0)^2}{2} \right) \right] 
\cdot \int_{0}^{1} dw \prod_{k=1}^{N-1} \left( \frac{1 - e^{-u_k}}{1 - e^{-u_k}} \right) 
\times \exp \left[ \Delta - \beta \sum_{i=1}^{N} (V_{eff}(s_i) - V_{eff}(0)) \right].$$

The effective potential $V_{eff}(s)$ is the "bare" potential along the reaction path $V_0(s)$ plus the adiabatic zero-point energy of the bath modes. The rate constant is then conveniently expressed as a correction to the transition state theory

$$k = \kappa k_{TST},$$

where

$$k_{TST} = \frac{kT}{\hbar} \frac{Z_{\Delta}^+}{Z_{R}} e^{-\nu_n},$$

with

$$\kappa = \int_{0}^{\infty} dt \tilde{C}_f(t).$$

$\kappa$ is thus the correction factor to transition state theory that corrects for tunneling through the barrier, nonseparability of the reaction coordinate from the other degrees of freedom of the system, and recrossing of the transition state dividing surface.
III. INCLUSION OF ROTATION

It is not difficult to extend the methodology of Sec. II B to include rotation in the reaction path Hamiltonian model, in order to be able to treat reactions in 3D space. The Hamiltonian equation (2.17) has added to it the following extra term:

\[ H_{\text{rot}} = A(s)(J^2 - K^2)\sin^2 q_k + B(s)(J^2 - K^2)\cos^2 q_k + C(s)K^2, \]

(3.1)

which is the classical Hamiltonian for an asymmetric rotor with rotational constants \(A, B,\) and \(C\) that here are functions of the reaction coordinate. [There are also rotation-vibration coupling terms in the Hamiltonian, and it would be possible to include the part of these that is linear in the vibrational coordinates \(Q_k\) as part of the linear coupling function \(f(s)\) in Sec. II; for the present simplified discussion, however, we neglect these couplings.] Because rotation is much slower than internal motions, it is reasonable to treat it via a sudden approximation and, furthermore, to calculate the trace over the rotational degrees of freedom classically.

It is easy to see that the development of Sec. II is then modified only in that the vibrational partition functions, i.e., Eq. (2.15a) as generalized in Sec. II B, has the following rotational partition functional as an additional factor:

\[ Z_{\text{rot}}[s(\tau)] = \int_0^\infty dJ \int_0^\pi dK (2\pi)^{-1} \]

\[ \times \int_0^{2\pi} dq_k \exp\left\{ -\beta A(J^2 - K^2)\sin^2 q_k - \beta B(J^2 - K^2)\cos^2 q_k - \beta CK^2 \right\}, \]

(3.2)

where \(A, B,\) and \(C\) are the averages of \(A(s), B(s),\) and \(C(s)\) over the path \(s(\tau) = \{s_i\},\)

\[ A = \frac{1}{\tilde{H}_0} \int_{\tilde{Q}_G^0}^{\tilde{Q}_G^0} \frac{d\tau}{2} A(s(\tau)) \approx \frac{1}{N} \sum_{i=1}^{N} A(s_i) \]

(3.3a)

and similarly

\[ B = \frac{1}{N} \sum_{i=1}^{N} B(s_i), \quad C = \frac{1}{N} \sum_{i=1}^{N} C(s_i). \]

(3.3b)

The vib-rot partition functional is separable, i.e., a product of a vibrational factor and a rotational factor, because rotation-vibration coupling terms in the Hamiltonian have been neglected; it is the classical description of rotation which results in the trace over rotational degrees of freedom being the integral over action-angle variables in Eq. (3.2); and it is the sudden approximation which makes the action-angle variables in the exponent in the integrand of Eq. (3.2) the same as the integration variables. [Without the sudden approximation the action-angle variables in the exponent of the integrand of Eq. (3.2) would be the time-evolved values for which the integration variables are the initial conditions.] The integrals in Eq. (3.2) are doable, giving

\[ Z_{\text{rot}}[s(\tau)] = \left[ \frac{\pi(kT)^3}{ABC} \right]^{1/2}, \]

(3.4)

which is recognized as the standard classical partition function for an asymmetric top in terms of rotation constants \(A, B,\) and \(C.\) If the reaction path is a linear molecular geometry, then there is just one rotation constant \(B(s),\) and \(Z_{\text{rot}}\) is

\[ Z_{\text{rot}}[s(\tau)] = \frac{kT}{B}, \]

(3.5)

where \(B\) is the average of \(B(s)\) as above.

If, as is usual, one includes the rotational partition function \(Z_{\text{rot}}^{\pm},\)

\[ Z_{\text{rot}}^{\pm} = \left[ \frac{\pi(kT)^3}{A^\pm B^\pm C^\pm} \right]^{1/2}, \]

(3.6)

in the definition of the transition state theory rate, then Eq. (2.24a) still applies. Equation (2.24c) also still applies for the correction factor \(\kappa\) with Eq. (2.23) for \(C^\tau_\gamma(t)\) modified by having in its integrand the extra factor

\[ \left( A^\pm B^\pm C^\pm \right)^{1/2}, \]

(3.7)

where \(A, B,\) and \(C\) are the averaged quantities [Eq. (4.3)]. If the reaction path is linear, then this factor is

\[ \left( B^\pm /B \right). \]

(3.8)

IV. NUMERICAL RESULTS FOR \(H + H_2,\) IN 3D

A standard test case for reactive scattering is the \(H + H_2\) reaction on the Porter–Karpplus potential surface, and this is the example we have considered for this initial report. The functions \(V_{\text{eff}}(s), \omega(s)\) (the collinear mode orthogonal to the reaction path), \(\omega_2(s)\) (the doubly degenerate bending mode), \(B(s)\) (the rotation constant along the reaction path), and \(B_{1,2}(s) = \kappa(s)\) (the curvature of the reaction path) have been computed previously for the Porter–Karpplus potential surface and are thus available for the present application. \([B_{1,2}(s)] = 0\) for this system.

The correlation function was computed from Eq. (2.23) (including the rotational factor—see below) for various values of \(\tau,\) and these values were used to generate Padé approximants to \(C^\tau_\gamma(t)\) via Schlessinger’s point method. The tunneling correction factor is then given by Eq. (2.24c).

For the present example, the pre-exponential factor in the integrand of Eq. (2.23) (including rotation) is given explicitly by

\[ \left( \frac{1 - e^{-u^+_t}}{1 - e^{-u^-_t}} \right) \left( \frac{1 - e^{-u^+_t}}{1 - e^{-u^-_t}} \right)^2 \left( B^\pm /B \right), \]

(4.1)

where the various quantities are defined in Secs. II and III.

\[ V_{\text{eff}}(s) = V_0(s) + j\hbar \omega_2(s) + \hbar \omega_2(s). \]

(4.2)

Figure 1 shows the correlation function \(C^\tau_\gamma(t)\) so obtained (for \(T = 300\) K). It falls monotonically to zero, indicating that the dynamics is essentially “direct,” i.e., transition-state-like, with no significant recrossing effects. The time scale for this decay is essentially \(\hbar^2 - 2 \times 10^{-14}\) s. This is well known to be the case for this reaction.

Table I gives the results obtained for the correction factor \(\kappa,\) for various numbers of Monte Carlo random walks. The number of path discretizations (the parameter \(N\) of Sec. II) was \(N = 30;\) some calculations were also carried out for \(N = 20\) and 40 to insure that this was sufficient. Although there is still some statistical scatter, one sees that the result is
in quite good agreement with the direct calculation of $\kappa$ from the results of Schatz and Kuppermann's coupled channel reactive scattering calculations.

This application also illustrates the importance of coupling effects on reaction coordinate motion. Thus if the "frictional" term $\alpha$ in Eq. (2.23) is set to zero, the well-known "vibrationally adiabatic zero-curvature" approximation results, and in this case the value obtained for $\kappa$ is about an order of magnitude too small. This is another illustration of how coupling of reaction coordinate motion to the "bath" can increase tunneling rates.

V. CONCLUDING REMARKS

The methodology described in Sec. II thus provides a powerful way of determining accurate rate constants for a potential energy surface that is characterized via the reaction path model. The correction to the transition state theory rate includes all effects, i.e., tunneling, frictional effects on the reaction coordinate caused by coupling to other degrees of freedom, and dynamical effects due to recrossing of the transition state dividing surface.

There are two primary considerations which will limit the accuracy, and thus usefulness of this approach. First, the curvature of the reaction path should not be too large, so that the coupling elements $B_{k,r}$ are not too large and thus invalidate the linear coupling approximation. (Although see Appendix A, which shows how one can include the coupling correct to all orders.)

![Graph of flux-flux autocorrelation function for the 3D H + H₂ reaction at T = 300 K.](image)

An important case for which the curvature is large is a "heavy plus light-heavy" mass combination, e.g., a H-atom transfer reaction. One way to deal with this situation is to use the "reaction surface" model recently presented by Carrington and Miller. This model utilizes two large amplitude motion, reaction coordinate-like degrees of freedom, which will describe the heavy plus light-heavy situation quite well, and then treats all other degrees of freedom as harmonic displacements away from this 2D reaction surface. With this model, therefore, one can path integrate out the F-2 harmonic modes as in Sec. II and then be left with a two-dimensional path integral that must be treated numerically. By including two large amplitude motion degrees of freedom it should be much better to describe coupling to the remaining F-2 harmonic coordinates within a linear approximation.

The second situation for which the present methodology will have difficulty as if the reaction proceeds via a long-lived collision complex. It will be necessary in such cases to determine the correlation functions $C_\ell(t)$ to longer times (essentially for the lifetime of the complex) in order to determine its integral, and the analytic continuation procedure will have difficulty in this case. To deal with this, one must devise new ways to determine $C_\ell(t)$, ways that do not rely on analytic continuation. There is possibly some progress in this direction, but no completely satisfactory method is yet available.

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APPENDIX A. PATH INTEGRALS FOR THE REACTION PATH HAMILTONIAN

Here we describe the rigorous form of the path integral representation of the propagator (or Boltzmann operator) for the reaction path Hamiltonian. The complete reaction path Hamiltonian for $J = 0$ is given (without making the linear coupling approximation of Sec. II B) by

$$H(p,s,P,Q) = \frac{1}{2} \left[ p_s \cdot Q_s \cdot B(s) \cdot P \right]^2 / [1 + Q \cdot B_P(s)]^2 + \frac{1}{2} P \cdot P + V(s,Q),$$

where $(Q,P) = (Q_k, P_k), k = 1,...,F - 1$ are the coordinates and momenta for the vibrational modes perpendicular to the reaction path; $B(s) = [B_{k,k'}(s)], k,k' = 1,...,F - 1$ are Coriolis-like coupling elements given by

$$B_{k,k'}(s) = \frac{\partial \mathbf{L}_{k'}(s)}{\partial s} \cdot \mathbf{L}_k(s),$$

where $[\mathbf{L}_k(s)], k = 1,...,F - 1$ are the eigenvalues of the projected force constant matrix; $B_P(s) = [B_{k,k'}(s)],$
where
\[ \mathbf{L}_k(s) = \frac{d\mathbf{L}_k}{ds}, \]
and \( V \) is the potential energy
\[ V(s, \mathbf{Q}) = V_0(s) + \sum_{k=1}^{F-1} J \omega_k s^2 Q_k^2. \]

For the purpose of path integration, it is more useful to have the Lagrangian \( \mathcal{L} \) rather than the Hamiltonian \( H \), and this is obtained in the usual way:
\[ \mathcal{L} = \mathbf{P} \cdot \dot{\mathbf{Q}} - H, \]
where the momenta \( \mathbf{P} \) and \( \dot{\mathbf{Q}} \) are determined in terms of the velocities from the equations
\[ \dot{\mathbf{P}} = \frac{\partial H}{\partial \mathbf{Q}}, \quad \dot{\mathbf{Q}} = \frac{\partial H}{\partial \dot{\mathbf{Q}}}. \]

Solving Eq. (A5) for the momenta gives
\[ \mathbf{P} = \mathbf{Q} - i s \mathcal{B}(s) \cdot \mathbf{Q}, \]
\[ \mathbf{p}_k = \dot{\mathbf{Q}}[1 + 2 \mathbf{B}_k(s) \cdot \mathbf{Q} + \mathbf{Q} \cdot \mathbf{C}(s) \cdot \mathbf{Q}] + \mathbf{Q} \cdot \mathbf{B}(s) \cdot \mathbf{Q}, \]
where
\[ C_{k,k'}(s) = \frac{d\mathbf{L}_k}{ds} \cdot \frac{d\mathbf{L}_{k'}}{ds}, \]
and substituting these into Eq. (A4) gives the reaction path Lagrangian
\[ \mathcal{L}(s, \dot{s}, \mathbf{Q}, \dot{\mathbf{Q}}) = \frac{i}{2} \left[ 1 + 2 \mathbf{Q} \cdot \mathbf{B}_k(s) + \mathbf{Q} \cdot \mathbf{C}(s) \cdot \mathbf{Q} \right] + \mathbf{Q} \cdot \dot{\mathbf{Q}} + i s \mathcal{B}(s) \cdot \mathbf{Q} - V. \]

The generic form for the matrix element of the propagator is
\[ \langle s_n \mathbf{Q}_n | e^{-i H \Delta t} | s_0 \mathbf{Q}_0 \rangle = \frac{\sqrt{N}}{2} \int ds_1 \ldots ds_{N-1} \int dQ_1 \ldots dQ_{N-1} \exp \left[ i \frac{\Delta t}{\hbar} \mathcal{L}(t) \right]. \]

The correct expression in terms of the reaction path coordinates \((s, \mathbf{Q})\) is then obtained by using Eq. (A10) to eliminate the variables \( s_n = [s_n(t)], n = 1, \ldots, F \) in Eq. (A11) in favor of the variables \((s_i, \mathbf{Q}_i) = (s_i(t)), (\mathbf{Q}_i(t)), k = 1, \ldots, F - 1 \). Since the Jacobian for the \( s \leftrightarrow \mathbf{Q} \) change of integration variables is
\[ \frac{\partial (s_1, \ldots, s_F)}{\partial (s_i, \mathbf{Q}_i, \mathbf{Q}_1, \ldots, \mathbf{Q}_{F-1})} = 1 + \mathbf{Q} \cdot \mathbf{B}_k(s), \]
Eq. (A11) becomes
\[ \langle s_n \mathbf{Q}_n | e^{-i H \Delta t} | s_0 \mathbf{Q}_0 \rangle = (2\pi i \hbar \Delta t)^{-N} \int ds_1 \ldots ds_{N-1} \int dQ_1 \ldots dQ_{N-1} \exp \left[ i \frac{\Delta t}{\hbar} \mathcal{L}(t) \right]. \]

This is the correct and can be considered the final result. One can obtain the form given by Schumman's procedure by expanding the kinetic energy part of the exponent in Eq. (A13) through the fourth order in the coordinate increments \((s_i - s_{i-1})\) and \((Q_i - Q_{i-1})\). This is rather tedious, but straightforward; for the \(i\)th term in the kinetic energy part of the exponent in Eq. (A13),
\[ |a(s_i) - a(s_{i-1}) + L(s_i) \cdot Q_i - L(s_{i-1}) \cdot Q_{i-1}|^2, \]
but the situation is actually somewhat more complicated because of the curvilinear nature of the reaction path coordinates. Specifically, there are "extra" terms, in addition to the time integral of the Lagrangian, in the exponent of the above integral; they are related to the extra terms that arise in the quantum Hamiltonian operator (constructed from Eq. (A1) by the Podolsky transformation) because the mass tensor is coordinate dependent. Schumman describes one prescription for obtaining the correct expression, but here we give the alternate (though equivalent) way to do that which is in some ways simpler.

To this end it is useful to recall the relation between the Cartesian coordinates of the system \( x = [x_n], n = 1, \ldots, F \) and the reaction path coordinates, \( k, k, k = 1, \ldots, F - 1 \); the explicit relation between the two sets of coordinates is
\[ x = a(s) + \sum_{k=1}^{F-1} L_k(s) Q_k, \]
where \( a(s) = [a_n(s)], n = 1, \ldots, F \) are the Cartesian coordinates of the reaction path as a function of the reaction coordinate (the distance along it). In terms of the Cartesian coordinates the propagator matrix element has the standard discretized expansion (for the mass \( m = 1 \))
\[ \langle x_i | e^{-i H \Delta t} | x_0 \rangle = (2\pi i \hbar \Delta t)^{-N/2} \int dx_1 \ldots \int dx_{N-1} \exp \left[ \frac{i}{\hbar} \int_0^\Delta t dt' \mathcal{L}(t') \right]. \]
\[ + \frac{\Delta s^4}{4} \sum_{k=1}^{F-1} \Delta Q_k \left[ L_k \cdot L_F + \frac{\dot{\mathbf{L}}_F \cdot \dot{\mathbf{L}}_F}{\Delta s} + \frac{1}{2} \mathbf{L}_k \cdot \mathbf{L}_F^* \right] \]
\[ + \sum_{k=1}^{F-1} \Delta Q_k \left[ \dot{L}_k \cdot \mathbf{L}_k^* + \frac{\dot{\mathbf{L}}_k \cdot \dot{\mathbf{L}}_k}{\Delta s} + \mathbf{L}_k^* \cdot \mathbf{L}_k \right] \]
\[ + \frac{\Delta s^4}{4} \sum_{k,k'=1}^{F-1} \Delta Q_k \Delta Q_{k'} \mathbf{L}_k^* \cdot \mathbf{L}_{k'}. \]  

(A15)

where \( \mathbf{L}_k = \mathbf{L}_k(s) \) [\( \mathbf{L}_k(s) = a(s) \)], \( \mathbf{L}_k^\prime = \partial \mathbf{L}_k(s)/\partial s \), \( \mathbf{L}_k^\prime = \partial^2 \mathbf{L}_k(s)/\partial s^2 \), \( Q = |Q| + Q_{-1} \), \( s = s_l \), \( s_{l-1} \), \( \Delta s = s_l - s_{l-1} \). Note that the terms in Eq. (A15) which are quadratic in the coordinate increments, the first three terms
\[ \Delta s^4 [1 + 2Q \cdot \mathbf{B}_F(s) + Q \cdot \mathbf{C}(s) \cdot Q] \]
\[ + \mathbf{L} \cdot \mathbf{L} + 2\Delta s \mathbf{Q} \cdot \mathbf{B}(s) \cdot \mathbf{Q} \]  

(A16)

are precisely the contribution that would be obtained if the time integral of the Lagrangian were used in the exponent of the path integral, as suggested by Eq. (A9), i.e.,
\[ \int_0^t dt' \cdot \mathcal{L}(t') = \frac{1}{2\Delta t} \sum_{i=1}^N \left[ \Delta s_i^4 [1 + 2Q_i \cdot \mathbf{B}_F(s_i) + Q_i \cdot \mathbf{C}(s_i) \cdot Q_i] \right. \]
\[ + \mathbf{L} \cdot \mathbf{L} + 2\Delta s \mathbf{Q} \cdot \mathbf{B}(s_i) \cdot \mathbf{Q} \]
\[ - \Delta t \sum_{i=1}^N \mathbf{V}(s_i, \mathbf{Q}_i) \]  

(A17)

where \( s_i = s_{i-1} \), \( \mathbf{Q}_i = Q_i + Q_{i-1} \), \( \Delta s_i = s_i - s_{i-1} \), \( \Delta \mathbf{Q}_i = (Q_i - Q_{i-1}) \). The last three terms in Eq. (A15), those fourth order in the coordinate increments, are the extra terms referred to above. As discussed by Schulman,24 they do not contribute for "smooth" paths [\( s(t), Q(t) \)], those for which \( \Delta s \) and \( \Delta \mathbf{Q} \) are proportional to \( \Delta t \) [i.e., those for which \( s(t) \) and \( \mathbf{Q}(t) \) exist]. The path integral, however, must also include stochastic-type paths, those for which \( \Delta s \) and \( \Delta \mathbf{Q} \) are proportional to \( \Delta t^{1/2} \), and for these kinds of paths the quartic terms do contribute. Since in practice we expect smooth paths to make the most important contribution to the path integral, particularly so for "heavy particle" (i.e., not electronic) dynamics which is near the semiclassical limit, we do not anticipate that there would be much error induced by neglecting these extra terms in the exponent. For comparison, neglecting the analogous terms in the Hamiltonian operator introduces an error in vibrational eigenvalues of only a few cm\(^{-1}\), which is typically less than 1%. To that extent that these terms are neglected, the exponent in the integrand of the path integral reverts to the "classical" result [Eq. (A17)], i.e., the time integral of the Lagrangian.

Finally, we note that in both the expanded form of the rigorous result [Eq. (A13)] and the expanded version [Eq. (A15)] [and also in the approximate result, Eq. (A17)] the dependence of the exponent on the integral variables is quadratic (recalling that the potential \( V \) of Eq. (A3) is also quadratic in \( Q \). Thus the integral over them in Eq. (A13) can be carried out analytically, without approximation, so that only the path integral over the \( s(t) \) path (i.e., the integrals over \( s_{1,2,...,F-1} \) ) is left to be done numerically, e.g., by the Monte Carlo random walk algorithm or by Fourier path expansion. Without unreasonable additional effort, therefore, it is possible to carry out the procedure described in Sec. II B without making any approximations to the coupling elements in the reaction path Hamiltonian.

APPENDIX B. LINEARLY FORCED HARMONIC OSCILLATOR WITH VARIABLE FREQUENCY

Here we construct the general matrix element of the time evolution operator \( \mathcal{K} \) for the following time-dependent Hamiltonian
\[ H(t) = \frac{P^2}{2m} + \frac{1}{2} m \omega(t)^2 Q^2 - f(t) Q. \]  

(B1)

Once the matrix elements \( \langle Q_2 | \mathcal{K} (t_2, t_1) | Q_1 \rangle \) are known, we can obtain the partition function by
\[ Z_Q = \int dQ_1 \left( Q_1 \left| \mathcal{K} \left( - \frac{i\hbar \partial}{2}, \frac{i\hbar \partial}{2}, \frac{2\pi i}{\hbar} \right) \right| Q_1 \right). \]  

(B2)

Because the Hamiltonian of Eq. (B1) is quadratic in \( P \) and \( Q \), the semicladastic approximation to the propagator is exact.26 One can thus use the general semiclassical expression27
\[ \langle Q_2 | \mathcal{K} (t_2, t_1) | Q_1 \rangle = \left[ - \frac{\partial^2 \phi (Q_2, Q_1)}{\partial Q_2 \partial Q_1} \right] \frac{2\pi i}{\hbar} e^{i\phi (Q_2, Q_1) / \hbar}, \]  

(B3)

where \( \phi (Q_2, Q_1) \) is the classical action
\[ \phi (Q_2, Q_1) = \int_{t_1}^{t_2} dt [\frac{1}{2} m Q(t)^2 - \frac{1}{2} m \omega(t)^2 Q(t)^2 + f(t) Q(t)] \]  

(B4)

computed along the classical trajectory \( Q(t) \) that satisfies the boundary conditions
\[ Q(t_1) = Q_1, \]
\[ Q(t_2) = Q_2. \]  

(B5)

The classical equation of motion for \( Q(t) \) is
\[ \ddot{Q}(t) + \omega(t)^2 Q(t) = f(t) / m, \]  

(B6)

and if \( u(t) \) and \( v(t) \) are the two linearly independent solutions of the homogeneous equation
\[ \frac{d^2 u(t)}{dt^2} + \omega(t)^2 u(t) = 0, \]  

(B7)

with boundary conditions
\[ u(t_1) = 0, \]
\[ v(t) = 0, \]  

(B8)

then the solution of Eq. (B6) with the correct double-ended boundary condition is
\[ Q(t) = u_1 v(t) + u_2 v(t), \]  

(B9)

where \( u_1 = u(t_1), u_2 = u(t_2), w \) is the (time-independent) Wronskian
\[ w = \dot{v} - \dot{u}, \]  

and \( t, t' \) is the lesser (greater) of \( t \) and \( t' \). From the trajectory \( \dot{Q}(t) \) of Eq. (B9) it is not hard to compute the action integral of Eq. (B4), giving

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\[ \phi(Q_{2},Q_{1}) = \frac{m}{2} \left[ -Q_{2}^2 \dot{u}_2 \dot{v}_2 / \omega - Q_{1}^2 \dot{u}_1 \dot{v}_1 / \omega + \frac{2Q_{1}}{\nu_1} \int_{t_1}^{t_2} dt \frac{u(t)}{m} \frac{f(t)}{m} u(t \omega) v(t) \right] \times u(t) + \int_{t_1}^{t_2} dt \frac{f(t)}{m} \left[ u(t) \right]^2 \right]. \] (B12)

This is about as far as one can proceed in general, i.e., without explicitly solving for the functions \( u(t) \) and \( v(t) \). It would not be difficult, however, to do this numerically for any given time-dependent frequency \( \omega(t) \).

A more explicit result can be obtained, however, if we solve Eq. (B7) within a WKB-like approximation; this gives\(^2\)

\[ u(t) = \sin \left[ \int_{t}^{t'} dt' \omega(t') / \omega(t)^{1/2} \right], \] (B13a)

\[ v(t) = \sin \left[ \int_{t}^{t'} dt' \omega(t') / \omega(t)^{1/2} \right]. \] (B13b)

There is no problem with WKB connection formulas in the present application since there will typically be no turning points—i.e., values of \( t \) for which \( \omega(t) = 0 \)—in the interval \( (t_1,t_2) \). The solutions in Eq. (B13) will be most accurate when \( \omega(t) \) is a slowly varying function of \( t \), or stated more precisely, when

\[ \left| \frac{d}{dt} \frac{1}{\omega(t)} \right| = \left| \frac{\omega(t)}{\omega(t)^2} \right| < 1. \] (B14)

Using Eq. (B13) (and with some algebra), one can readily show that the propagator matrix element [Eqs. (B10) and (B11)] becomes

\[ \langle Q_2 | K(t_2,t_1) | Q_1 \rangle = \left( \frac{m \omega_2}{2 \pi \hbar \sin(U)} \right)^{1/2} \exp \left[ \frac{im}{2 \hbar} \left[ \omega_1 Q_1^2 + \omega_2 Q_2^2 \right] \cos(U) - 2\sqrt{\omega_2 \omega_1} Q_1 Q_2 + 2\sqrt{\omega_2 \omega_1} \int_{t_1}^{t_2} \frac{f(t)}{m \omega(t)} \sin \left( \int_{t_1}^{t_2} dt' \omega(t') \right) \right. \]

\[ \left. \times \int_{t_1}^{t_2} dt \frac{f(t)}{m \omega(t)} \sin \left( \int_{t_1}^{t_2} dt' \omega(t') \right) \right] \sin \left[ \int_{t_1}^{t_2} dt' \omega(t') \right] \right], \] (B15)

where \( \omega_1 = \omega(t_1), \omega_2 = \omega(t_2) \), and

\[ U = \int_{t_1}^{t_2} dt \omega(t). \]

It is easy to see that Eq. (B15) reduces to that in Feynman and Hibbs\(^7\) in the limit of a \( t \)-independent frequency \( \omega(t) \rightarrow \omega \).

Similarly, one obtains the following explicit result for the trace of the propagator [Eq. (B12)]:

\[ Z_{Q} = \left[ 2 \sinh(U/2) \right]^{-1} \exp \left[ \frac{i}{2 \hbar} \int_{t_1}^{t_2} dt \int_{t_1}^{t_2} dt' \right. \]

\[ \times \frac{f(t)}{\sqrt{\omega(t)}} \frac{f(t')}{\sqrt{\omega(t')}} \cos \left( \frac{U}{2} - \int_{t_1}^{t_2} dt' \omega(t') \right) \left. \right] \right]. \] (B16)

Finally, the partition function is obtained from Eq. (B16) by making the replacement \( t_1 = +i \hbar \beta / 2, t_2 = -i \hbar \beta / 2, t = -i \tau \):

\[ Z_{Q} = \left[ 2 \sinh(u/2) \right]^{-1} \exp \left[ \frac{1}{2 \hbar} \int_{-\hbar \beta / 2}^{\hbar \beta / 2} dt \int_{-\hbar \beta / 2}^{\hbar \beta / 2} dt' \frac{f(t)}{\sqrt{\omega(t)}} \frac{f(t')}{\sqrt{\omega(t')}} \right]. \] (B17)

where

\[ u = \int_{-\hbar \beta / 2}^{\hbar \beta / 2} dt \omega(t). \]

The exponent of Eq. (B17) may also be expressed as

\[ \frac{1}{4 \hbar m (1 - u)} \int_{-\hbar \beta / 2}^{\hbar \beta / 2} dt \int_{-\hbar \beta / 2}^{\hbar \beta / 2} dt' \frac{f(t)}{\sqrt{\omega(t)}} \frac{f(t')}{\sqrt{\omega(t')}} \left[ e^{-i \omega(t') \tau} + e^{-i \omega(t') \tau} \right], \]

where

\[ \omega(t', \tau) = \int_{-\hbar \beta / 2}^{\hbar \beta / 2} dt'' \omega(t''). \] (B18)


\(^3\)T. Yamamoto, J. Chem. Phys. 33, 281 (1960); (b) see also, S. F. Fischer, ibid. 53, 3195 (1970).
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19Note that here it is overall rotation of the H$_2$--H complex that is being described via the sudden approximation, and not H$_2$ rotation itself (which has turned into the bending vibration in the transition state region).
20See, for example, D. G. Truhlar and R. E. Wyatt, Annu. Rev. Phys. Chem. 27, 1 (1976).
28See, for example, L. I. Schiff, Quantum Mechanics (McGraw-Hill, New York, 1968), p. 270.
29Reference 13, p. 64.

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