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Publication Date

1975-03-01

Submitted to Journal of Chemical Physics

LBL-3788
Preprint c.1

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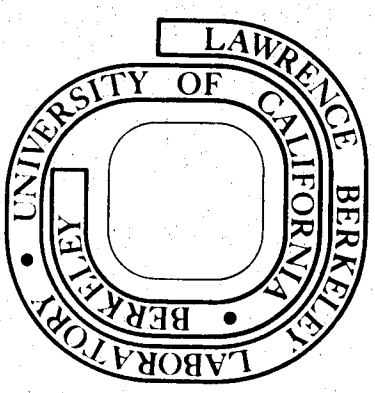
March 1975

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48



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LBL-3783

PATH INTEGRAL REPRESENTATION OF THE REACTION RATE CONSTANT IN QUANTUM MECHANICAL TRANSITION STATE THEORY*

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ABSTRACT

Feynman's path integral representation of the Boltzmann operator, $e^{-\beta H}$, is used to express the rate constant of a recently formulated quantum mechanical version of transition state theory. By evaluating the path integral in two separate stages, one is able to interpret the result as a generalization of a model suggested several years ago by Johnston and Rapp for handling the non-separable aspect of tunneling in transition state theory. A Fourier series expansion of the path integral is also developed, and this approach has promise for direct numerical evaluation of the quantum rate expression.

I. INTRODUCTION

This paper is a continuation of recent work on quantum mechanical transition state theory.[1-3,4] The basic idea motivating this development is the thesis that the "fundamental assumption"[5] of transition state theory--namely, that all flux through a particular surface in coordinate space can be identified as reactive flux--is a good approximation for describing the threshold behavior of a chemical reaction with activation energy. It is reasoned that the shortcomings[6] of conventional transition state theory[7] stem from additional assumptions--such as separability of the potential energy surface about its saddle point, vibrationally adiabatic motion along a reaction coordinate, etc.--which are not necessarily valid in the threshold region. The goal, then, has been to implement this "fundamental assumption" of transition state theory quantum mechanically (since quantum effects are very important in the threshold region) without incorporating any form of these additional separability approximations.

Earlier work has given a formal solution[1] to the problem and derived its semiclassical limit.[2] Numerical application[3] to the collinear $H + H_2$ reaction shows that the semiclassical approximation to quantum transition state theory gives a good description of the threshold behavior. The semiclassical approximation[2,3] involves the classical path approximation to the Boltzmann operator, but does not introduce any assumptions of separability.

The present paper, however, develops a different approach to evaluating the quantum rate expression in Reference 1, namely use

of a path integral representation[8] of the Boltzmann operator, $e^{-\beta H}$. This path integral formulation has a two-fold utility. First, the path integral version of the quantum mechanical expression has an intuitive physical structure that can perhaps lead to new useful models and approximations; this has certainly been the case regarding the path integral representation of the quantum propagator, $e^{-iHt/\hbar}$, and its use in scattering theory.[9,10] Second, unlike the situation with the quantum propagator, the "integrand" of the path integral for $e^{-\beta H}$ is not an oscillatory function, and it thus appears that the path integral approach may actually be an efficient way of carrying out the quantum mechanical calculation for the rate constant.

The path integral representation of the Boltzmann operator is introduced in Section II, and the rate constant written in terms of it. By evaluating the path integral in two distinct stages, an interesting interpretation of the result emerges, namely an exact version of a model postulated several years ago by Johnston and Rapp[11] for dealing with non-separable aspects of tunneling in transition state theory. A particularly convenient way of carrying out the path integral--a Fourier series expansion of the path--is developed in Section III, and Section IV shows how an exactly solvable "reference potential" can be used to accelerate the rate of convergence of the path integral. Section V gives the final expressions for the rate constant which result from the path integral expansion of $e^{-\beta H}$; this expression for the rate constant has the form of conventional transition state theory but with a generalized "tunneling factor" which includes corrections due to non-separability as well as

tunneling. For completeness, the path integral representation of the microcanonical density operator, $\delta(E-H)$, is given in the Appendix.

II. GENERAL FORMULATION

The quantum transition state rate expression derived previously[1] is

$$k_{b\leftarrow a} = \mathrm{tr}(e^{-\beta H} f)/Q_a \quad , \tag{2.1}$$

where a and b denote reactant and product arrangements, respectively, Q_a is the partition function per unit volume for separated reactants, H is the total Hamiltonian, and f is a special one-dimensional flux operator. To keep the notation simple all expressions will pertain to a collinear A + BC → AB + C reaction; in most cases it should be obvious what the more general equations are.

If the "dividing surface" of transition state theory is a straight line and s the coordinate that measures distance from the dividing surface (see Figure 1 of Reference 1), then the flux operator f is given in transition state theory by[1]

$$f = \delta(s) \frac{p_s}{m} h(p_s) \quad , \tag{2.2}$$

where p_s is the momentum operator conjugate to s and h is the step-function:

$$h(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0 \end{cases} \quad .$$

As discussed in Reference 1, one actually wants the version of operator f given by the Weyl correspondence rule;[12] the coordinate

matrix elements of the Weyl version of f are given by

$$\langle s'|f|s\rangle = -\frac{\hbar}{\pi m}\,\frac{\delta(s+s')}{(s-s')^2} \quad . \tag{2.3}$$

If the trace in Eq. (2.1) is evaluated in a coordinate representation, therefore, one has

$$k_{b\leftarrow a}\,Q_a = \int ds' \int ds \int du\, \langle u,s|e^{-\beta H}|u,s'\rangle \langle s'|f|s\rangle \quad , \tag{2.4}$$

where u is the other coordinate in the collinear A + BC system, the one which measures distance parallel to the dividing surface; in conventional language s is the "reaction coordinate" and u is the symmetric stretch coordinate of the "activated complex". Substitution of Eq. (2.3) into (2.4) and an integration by parts gives

$$k_{b\leftarrow a}\,Q_a = \frac{\hbar}{4\pi m}\int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} ds\; (-\frac{1}{s})\,\frac{\partial}{\partial s}\,\langle u,s|e^{-\beta H}|u,-s\rangle \quad . \tag{2.5}$$

Feynman's path integral representation[8] is now introduced for matrix elements of the Boltzmann operator:

$$\langle u,s|e^{-\beta H}|u',s'\rangle = \int_{u'}^{u} Du \int_{s'}^{s} D\underline{s}$$

$$\exp\{-\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau\, [\frac{1}{2}\,m(\frac{ds(\tau)}{d\tau})^2 + \frac{1}{2}\,m(\frac{du(\tau)}{d\tau})^2 + V(s(\tau),\, u(\tau))]\}, \tag{2.6}$$

where V(s,u) is the potential energy surface, and the integral notation

$$\int_{u'}^{u} Du$$

denotes Feynman's "sum" over all paths $u(\tau)$ which satisfy the boundary conditions $u(0) = u'$ and $u(\hbar\beta) = u$; the integral

$$\int_{s'}^{s} Ds$$

denotes a similar path integral over all paths $s(\tau)$ for which $s(0) = s'$ and $s(\hbar\beta) = s$. τ is a time-like parameter that varies from 0 to $\hbar\beta$; it is the same parameter which is the imaginary time in the semiclassical limit[2] of quantum transition state theory. Section III undertakes an explicit evaluation of the path integral, but for now it will be left at this rather symbolic level.

With this path integral representation for the Boltzmann operator, Eq. (2.4) thus becomes

$$k_{b\leftarrow a}\, Q_a = \int ds' \int ds \int du \, \langle s' | f | s \rangle \int_{u'}^{u} Du \int_{s'}^{s} Ds \qquad (2.7)$$

$$\exp\{-\frac{1}{\hbar}\int_{0}^{\hbar\beta} d\tau \, [\frac{1}{2} m s'(\tau)^2 + \frac{1}{2} m u'(\tau)^2 + V(s(\tau), u(\tau))]\},$$

and since the flux operator f involves only the s degree of freedom it is convenient to perform the $s(\tau)$ path integral first. Thus Eq. (2.7) is equivalent to

$$k_{b\leftarrow a}\, Q_a = \frac{kT}{h} \int_{-\infty}^{\infty} du \int_{u}^{u} Du \;\; P[u] \exp\{-\frac{1}{\hbar} \int_0^{\hbar\beta} d\tau \; [\frac{1}{2} mu'(\tau)^2 + V_0(u(\tau))]\}, \quad (2.8)$$

where the P is a functional of the path $u(\tau)$:

$$P[u] = 2\pi\hbar\beta \int_{-\infty}^{\infty} ds' \int_{-\infty}^{\infty} ds \; \langle s'|f|s\rangle \int_{s}^{s'} Ds$$

$$\exp\{-\frac{1}{\hbar} \int_0^{\hbar\beta} d\tau \; [\frac{1}{2} ms'(\tau)^2 + V(s(\tau), u(\tau)) - V_0(u(\tau))]\}. \quad (2.9)$$

The rate constant is formally independent of the reference potential $V_0(u)$ which is introduced purely for convenience. Similarly, the factor $\frac{kT}{h} \equiv (2\pi\hbar\beta)^{-1}$ is introduced by Eq. (2.8) and in the definition of P for interpretational reasons.

Eqs. (2.8) and (2.9) have a simple and physically intuitive interpretation. The functional P[u] is the one-dimensional tunneling probability for the s degree of freedom with the u coordinate following the fixed path $u(\tau)$; since $u(\tau)$ is a fixed function, P[u] is the probability for tunneling in the s-degree of freedom through the <u>one-dimensional</u> "<u>time</u>"-<u>dependent potential barrier</u> $v(s,\tau)$,

$$v(s,\tau) \equiv V(s,u(\tau)) - V_0(u(\tau)) \quad . \quad (2.10)$$

The path integral over $u(\tau)$ paths in Eq. (2.8) is simply Boltzmann average over all $u(\tau)$ paths; i.e., one notes that

$$\int_{-\infty}^{\infty} du \int_{u}^{u} Du \exp\{-\frac{1}{\hbar}\int_{0}^{\hbar\beta} d\tau \quad [\frac{1}{2} mu'(\tau)^2 + V_0(u(\tau))]\} \tag{2.11}$$

is a path integral expression for the quantum mechanical partition function for the u-degree of freedom with potential function $V_0(u)$. Eqs. (2.8) and (2.9) express the rate constant, therefore, as $\frac{kT}{h}$ times the probability of tunneling through the one-dimensional time dependent potential barrier in the s-direction--the time dependence arising because the path $u(\tau)$ is fixed--with a subsequent Boltzmann average over all paths $u(\tau)$.

The description in the above paragraph has much of the character of the ad hoc model suggested a number of years ago by Johnston and Rapp[11] for treating the non-separable aspect of tunneling in transition state theory. The Johnston-Rapp model essentially corresponds to Eqs. (2.8)-(2.9) with the crudest possible approximation to the $u(\tau)$ path integral, namely the inclusion of only the constant path

$$u(\tau) = u \quad ; \tag{2.12}$$

including only this path in the "sum over paths" gives (apart from multiplicative factors)

$$k_{b\leftarrow a}\, Q_a \sim \int_{-\infty}^{\infty} du\, e^{-\beta V_0(u)} P(u) \quad , \tag{2.13}$$

where here $P(u)$ is simply a function of u, namely the 1-dimensional tunneling probability through the s-potential barrier $V(s,u) - V_0(u)$, which depends parametrically on u. Eqs. (2.8)-(2.9) are thus an exact formulation of Johnston and Rapp's important qualitative idea.

The reader will recognize that the development leading to Eqs. (2.8) and (2.9) is an example of Feynman's discussion of the "path integral as functional".[13] This is also the same methodology used in describing electronic transitions in atom-atom and atom-molecule collisions;[14,15] here one imagines performing the path integral over electronic degrees of freedom for a fixed nuclear path, with a subsequent semiclassical approximation for the path integral over nuclear degrees of freedom.

Eqs. (2.8) and (2.9) may be a useful starting point for exploring other approaches to quantum mechanical transition state theory. One can investigate various approximations, for example, for determining the one-dimensional tunneling probability through a time-dependent potential barrier. To whatever level of accuracy this one-dimensional time-dependent problem is solved, the final step is simply a Boltzmann average over all paths for the remaining degree of freedom, the symmetric stretch u-motion. The case with more than two degrees of freedom is an obvious generalization of Eqs. (2.8) and (2.9): P is still the probability of tunneling through a one-dimensional time-dependent potential barrier for the s-degree of freedom, but there are more degrees of freedom of the u-type, so that Eq. (2.8) would involve a multiple path integral over paths of the remaining degrees of freedom.

III. PATH INTEGRALS BY FOURIER SERIES

This Section develops a procedure for evaluating Boltzmann path integrals which has a number of desirable features. The idea itself is suggested by Feynman.[16]

For simplicity of notation, consider a one-dimensional Boltzmann path integral,

$$\langle x_2|e^{-\beta H}|x_1\rangle = \int_{x_1}^{x_2} Dx \exp\{-\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau\ [\frac{1}{2}mx'(\tau)^2 + V(x(\tau))]\} \quad . \quad (3.1)$$

One way of representing "all paths" $x(\tau)$ that satisfy $x(0) = x_1$, $x(\hbar\beta) = x_2$, is by a Fourier series

$$x(\tau) = x_1 + (x_2-x_1)(\tau/\hbar\beta) + \sum_{n=1}^{N} c_n \sin(n\pi\tau/\hbar\beta) \quad . \quad (3.2)$$

The first two terms in Eq. (3.2) are the "straight line" path connecting x_1 and x_2, and the remaining terms are harmonic perturbations about it. Summing over "all paths" that connect x_1 and x_2 is equivalent to integrating over all possible values of the Fourier coefficients $\{c_n\}$; i.e.,

$$\int_{x_1}^{x_2} Dx \sim \int_{-\infty}^{\infty} dc_1 \int_{-\infty}^{\infty} dc_2 \cdots \int_{-\infty}^{\infty} dc_N \quad , \quad (3.3)$$

where the limit $N \to \infty$ must be taken. Eq. (3.3) cannot be written as an equality, however, since there is a yet undertermined Jacobian factor relating the "change of variables" from Dx to $dc_1 dc_2 \ldots dc_N$.

With the Fourier series expansion for $x(\tau)$ given by Eq. (3.2), the "kinetic energy" part of the exponent in Eq. (3.1) can be evaluated explicitly:

$$\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau \ \frac{1}{2}mx'(\tau)^2 = \frac{m}{2\hbar^2\beta}\left[(x_2-x_1)^2 + \frac{1}{2}\sum_{n=1}^{N}(n\pi)^2 c_n^2\right]. \quad (3.4)$$

For reasons that will be clear below it is convenient to rescale the Fourier coefficients $\{c_n\}$ by defining the new integration variables $\{z_n\}$:

$$z_n = c_n\, n\left(\frac{m\pi}{4\hbar^2\beta}\right)^{1/2} ,$$

and one notes that

$$dc_1 dc_2 \ldots dc_N = (\text{constant}) \times dz_1 dz_2 \ldots dz_N .$$

With this change of variables, and with Eq. (3.4), Eq. (3.1) becomes

$$\langle x_2|e^{-\beta H}|x_1\rangle = J \exp\left[\frac{m}{2\hbar^2\beta}(x_2-x_1)^2\right]$$

$$\times \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \cdots \int_{-\infty}^{\infty} dz_N \ e^{-\pi(z_1^2+z_2^2+\ldots+z_N^2)} \exp\left[-\beta\int_0^1 d\xi\ V(x(\xi))\right], \quad (3.5)$$

where J is the undetermined constant Jacobian factor, $\xi = \tau/\hbar\beta$, and the path $x(\xi)$ is

$$x(\xi) = x_1 + (x_2-x_1)\xi + \left(\frac{4\hbar^2\beta}{m\pi}\right)^{1/2} \sum_{n=1}^{N} \frac{z_n}{n} \sin(n\pi\xi) \quad . \qquad (3.6)$$

The Jacobian factor J is determined by realizing that it is a property only of function space itself and must thus be independent of the particular potential function V(x). For the case V(x) = 0, i.e., a free particle, one knows that

$$\langle x_2|e^{-\beta H_0}|x_1\rangle = \left(\frac{m}{2\pi\hbar^2\beta}\right)^{1/2} \exp\left[-\frac{m}{2\hbar^2\beta}(x_2-x_1)^2\right] \quad , \qquad (3.7)$$

where $H_0 = p^2/2m$, and since

$$\int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \cdots \int_{-\infty}^{\infty} dz_N \; e^{-\pi(z_1^2+z_2^2+\ldots+z_N^2)} = 1 \quad ,$$

this implies that

$$J = \left(\frac{m}{2\pi\hbar^2\beta}\right)^{1/2} \quad .$$

Finally, then, one has

$$\langle x_2|e^{-\beta H}|x_1\rangle = \langle x_2|e^{-\beta H_0}|z_1\rangle \int_{-\infty}^{\infty} d\underset{\sim}{z} \; e^{-\pi \underset{\sim}{z}^2} \, e^{-\beta\bar{V}} \quad , \qquad (3.8)$$

where the first factor is the "unperturbed" Boltzmann matrix element, given by Eq. (3.7), and

$$\int_{-\infty}^{\infty} d\underset{\sim}{z} = \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \cdots \int_{-\infty}^{\infty} dz_N$$

$$\underset{\sim}{z}^2 = z_1^2 + z_2^2 + \ldots + z_N^2$$

$$\bar{V} = \int_0^1 d\xi \; V(x(\xi)) \quad ,$$

with $x(\xi)$ given by Eq. (3.6).

Since the integrand in Eq. (3.8) is positive for all $\{z_n\}$, one can imagine evaluating this multi-dimensional integral by Monte Carlo methods. To do this it is convenient to change variables of integration from $\{z_n\}$ to integration variables which go from 0 to 1. Thus let the integration variables $\{w_n\}$ be defined by

$$\int_{-\infty}^{z_n} dz'_n \; e^{-\pi z'^2_n} = w_n \quad , \tag{3.9}$$

so that

$$dz_n \; e^{-\pi z_n^2} = dw_n \quad ;$$

it is clear that $w_n = 0 \to 1$ as $z_n = -\infty \to +\infty$. Eq. (3.8) then becomes

$$\langle x_2 | e^{-\beta H} | x_1 \rangle = \langle x_2 | e^{-\beta H_0} | x_1 \rangle \int_0^1 d\underset{\sim}{w} \; e^{-\beta \bar{V}} \quad , \tag{3.10a}$$

where

$$\int_0^1 d\underset{\sim}{w} = \int_0^1 dw_1 \int_0^1 dw_2 \cdots \int_0^1 dw_N \qquad (3.10b)$$

$$\bar{V} = \int_0^1 d\xi \; V(x(\xi)) \quad , \qquad (3.10c)$$

with the path $x(\xi)$ given by

$$x(\xi) = x_1 + (x_2 - x_1)\xi + \left(\frac{4\hbar^2\beta}{m\pi}\right)^{1/2} \sum_{n=1}^{N} \frac{Z(w_n)}{n} \sin(n\pi\xi) \quad . \qquad (3.10d)$$

The function $Z(w)$ which appears in Eqs. (3.10d) is determined implicitly by the relation

$$\int_{-\infty}^{Z} dz \; e^{-\pi z^2} = w \quad , \qquad (3.11)$$

and closed form rational approximations are readily available for it; for example, for $\frac{1}{2} \leq w \leq 1$,

$$Z(w) = (2\pi)^{-1/2} \left[t - \frac{a_0 + a_1 t}{1 + b_1 t + b_2 t^2} \right] \quad , \qquad (3.12)$$

where

$$t = [-2 \ln (1-w)]^{1/2} \quad ,$$

amd where the coefficients $\{a_i\}$, $\{b_i\}$ are tabulated.[17] For the range $0 \leq w \leq \frac{1}{2}$, one can use the symmetry relation

$$Z(w) = -Z(-w)$$

in conjunction with Eq. (3.12).

A Monte Carlo evaluation of Eq. (3.10) is now straight forward: The variables $\{w_n\}$, n = 1,...N are chosen as random numbers in (0,1), $\bar{V}$ calculated for the corresponding path $x(\xi)$, and this is repeated M times, say. Then

$$\int_0^1 dw_1 \int_0^1 dw_2 \cdots \int_0^1 dw_N \; e^{-\beta\bar{V}} \simeq \frac{1}{M} \sum_{k=1}^{M} e^{-\beta\bar{V}_k} \quad , \tag{3.13}$$

where $\bar{V}_k$ is the value of $\bar{V}$ for the k^{th} selection of the random variables $\{w_n\}$. One particularly attractive feature of this approach is that one need not be too concerned about the choice of N, the number of Fourier terms kept in the expansion of the path [Eq. (3.10d), so long as enough terms are included; i.e., it is in the nature of the Monte Carlo integration process that there is no wasted effort if many extra terms are included.

IV. HARMONIC REFERENCE POTENTIAL

This Section is a continuation of the previous one but involves a procedure which is of particular utility. Any quantum mechanical expansion method can be made more efficient if the potential V(x)--for a one-dimensional system, for example--can be divided into a zero$^{\text{th}}$ order part which is exactly solvable plus a (hopefully small) remainder. This Section shows how this idea can be carried out in the path integral version of quantum mechanics.

One thus writes

$$V(x) = V_0(x) + \Delta V(x) \quad , \tag{4.1}$$

where $\Delta V(x) \equiv V(x) - V_0(x)$, and where $V_0(x)$ is an exactly solvable potential which is chosen to make $\Delta V(x)$ as small as possible. Within the path integral version of quantum mechanics "exactly solvable" essentially means "harmonic oscillator", and V_0 is thus chosen as

$$V(x) = \frac{1}{2} m\omega^2 x^2 \quad . \tag{4.2}$$

Eq. (3.8) can then be written as

$$\langle x_2 | e^{-\beta H} | x_1 \rangle = \left(\frac{m}{2\pi\hbar^2\beta}\right)^{1/2} \exp\left[-\frac{m}{2\hbar^2\beta}(x_2-x_1)^2\right]$$

$$\chi \int d\underset{\sim}{z}\; e^{-\pi \underset{\sim}{z}^2}\; e^{-\beta \bar{V}_0}\; e^{-\beta \Delta \bar{V}} \quad , \tag{4.3}$$

where

$$\bar{V}_0 = \int_0^1 d\xi \; V_0(x(\xi))$$

$$\Delta\bar{V} = \int_0^1 d\xi \; \Delta V(x(\xi)) \quad ,$$

with $x(\xi)$ given by Eq. (3.6). Since V_0 is a simple function of x, $\bar{V}_0$ can be calculated explicitly:

$$\bar{V}_0 = \frac{1}{2} m\omega^2 \int_0^1 d\xi \; x(\xi)^2$$

$$= \frac{1}{2} m\omega^2 \int_0^1 d\xi \; [x_1 + (x_2-x_1)\xi + (\frac{4\hbar^2\beta}{m\pi})^{1/2} \sum_{n=1}^{N} \frac{z_n}{n} \sin(n\pi\xi)]^2$$

$$= \frac{1}{2} m\omega^2 \{\frac{1}{3}(x_1^2 + x_2^2 + x_1x_2) + \frac{2\hbar^2\beta}{m\pi} \sum_{n=1}^{N} \frac{z_n^2}{n^2}$$

$$+ \frac{4}{\pi}(\frac{\hbar^2\beta}{m\pi})^{1/2} \sum_{n=1}^{N} \frac{z_n}{n^2}[x_1 - (-1)^n x_2]\} \quad . \qquad (4.4)$$

Substituting this result into Eq. (4.3) gives

$$\langle x_2|e^{-\beta H}|x_1\rangle = (\frac{m}{2\pi\hbar^2\beta})^{1/2} \exp[-\frac{m(x_2-x_1)^2}{2\hbar^2\beta} - \frac{\beta m\omega^2}{6}(x_1^2 + x_2^2 + x_1x_2)]$$

$$\times \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \cdots \int_{-\infty}^{\infty} dz_N \; e^{-\beta\Delta\bar{V}} \exp\{ - \sum_{n=1}^{N} (\pi z_n^{\,2} + \frac{u^2 z_n^{\,2}}{\pi n^2}$$

$$+ \frac{2uz_n}{\pi n^2} (\frac{\beta m\omega^2}{\pi})^{1/2} [x_1 - (-1)^n x_2])\} \quad , \qquad (4.5)$$

where $u = \hbar\omega\beta$. Since the variables $\{z_n\}$ appear in the exponent of Eq. (4.5) quadratically, it is useful to complete the square and make the appropriate change of integration variables; thus let

$$\bar{z}_n = (1 + \frac{u^2}{n^2\pi^2})^{1/2} [z_n + u (\frac{\beta m\omega^2}{\pi})^{1/2} \frac{x_1 - (-1)^n x_2}{(n\pi)^2 + u^2}] \quad , \qquad (4.6)$$

and then

$$d\bar{z}_n = (1 + \frac{u^2}{n^2\pi^2})^{1/2} dz_n \quad ,$$

so that Eq. (4.5) becomes

$$\langle x_2 | e^{-\beta H} | x_1 \rangle = (\frac{m}{2\pi\hbar^2\beta})^{1/2} \prod_{n=1}^{N} \frac{1}{(1 + \frac{u^2}{n^2\pi^2})^{1/2}}$$

$$\cdot \exp\left[- \frac{m(x_2 - x_1)^2}{2\hbar^2\beta} - \frac{\beta m\omega^2}{6} (x_1^{\,2} + x_2^{\,2} + x_1 x_2) + \right.$$

$$\left. u^2 \frac{\beta m\omega^2}{} \sum_{n=1}^{N} \frac{x_1^{\,2} + x_2^{\,2} - 2(-1)^n x_1 x_2}{(n\pi)^2 (n^2\pi^2 + u^2)} \right]$$

$$\chi \int_{-\infty}^{\infty} d\bar{z}_1 \int_{-\infty}^{\infty} d\bar{z}_2 \cdots \int_{-\infty}^{\infty} d\bar{z}_N \quad e^{-\pi \underset{\sim}{\bar{z}}^2} \quad e^{-\beta \Delta \bar{V}} \quad , \tag{4.7}$$

where the path $x(\xi)$ is given in terms of the integration variables $\{\bar{z}_n\}$ as

$$x(\xi) = x_1 + (x_2 - x_1)\xi - \frac{2u^2}{\pi} \sum_{n=1}^{N} \frac{x_1 - (-1)^n x_2}{n^2\pi^2 + u^2} \frac{\sin(n\pi\xi)}{n}$$

$$+ \left(\frac{4\hbar^2\beta}{m\pi}\right)^{1/2} \sum_{n=1}^{N} \frac{\bar{z}_n \sin(n\pi\xi)}{(n^2 + u^2/\pi^2)^{1/2}} \quad . \tag{4.8}$$

Eqs. (4.7) and (4.8) can be simplified a great deal by making use of certain summation and product formulae.[18] Thus one finds that

$$\prod_{n=1}^{N} \frac{1}{\left(1 + \frac{u^2}{n^2\pi^2}\right)^{1/2}} = \left(\frac{u}{\sinh u}\right)^{1/2}$$

$$- \frac{m(x_2 - x_1)^2}{2\hbar^2\beta} - \frac{\beta m\omega^2}{6}(x_1^2 + x_2^2 + x_1x_2) + u^2\beta m\omega^2 \sum_{n=1}^{N} \frac{x_1^2 + x_2^2 - 2(-1)^n x_1x_2}{n^2\pi^2(n^2\pi^2 + u^2)}$$

$$= -\frac{m\omega}{2\hbar}\left[(x_1^2 + x_2^2)\coth u - \frac{2x_1x_2}{\sinh u}\right] \quad ,$$

and

$$x_1 + (x_2 - x_1)\xi - \frac{2u^2}{\pi} \sum_{n=1}^{N} \frac{x_1 - (-1)^n x_2}{n^2\pi^2 + u^2} \frac{\sin(n\pi\xi)}{n}$$

$$= \frac{x_1 \sinh\ [u(1-\xi)] + x_2 \sinh(u\xi)}{\sinh u} \quad .$$

With these results Eqs. (4.7) and (4.8) take on a very simple form

$$\langle x_2|e^{-\beta H}|x_1\rangle = \langle x_2|e^{-\beta H_0}|x_1\rangle \int_{-\infty}^{\infty} d\underset{\sim}{z}\ e^{-\pi \underset{\sim}{z}^2}\ e^{-\beta \Delta \bar{V}} \quad , \tag{4.9}$$

where the "bar" has been removed from the integration variables $\{z_n\}$, and where

$$\langle x_2|e^{-\beta H_0}|x_1\rangle = \left(\frac{m}{2\pi\hbar^2\beta}\ \frac{u}{\sinh u}\right)^{1/2} \exp\left\{-\frac{m\omega}{2\hbar}\left[(x_1^2 + x_2^2)\coth u - \frac{2x_1x_2}{\sinh u}\right]\right\} \quad ; \tag{4.10}$$

the quantity in Eq. (4.10) is the matrix representation of the Boltzmann operator for a harmonic oscillator, i.e., for the unperturbed Hamiltonian

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

$$= \frac{p^2}{2m} + V_0(x) \quad .$$

The path $x(\xi)$, furthermore, is given by

$$x(\xi) = x_0(\xi) + \left(\frac{4\hbar^2\beta}{m\pi}\right)^{1/2} \sum_{n=1}^{N} \frac{z_n \sin(n\pi\xi)}{(n^2 + u^2/\pi^2)^{1/2}} \tag{4.11a}$$

where

$$x_0(\xi) = \frac{x_1 \sinh [u(1-\xi)] + x_2 \sinh (u\xi)}{\sinh u} \quad ; \qquad (4.11b)$$

$x_0(\xi)$ is the classical path from x_1 to x_2 followed by a particle which experiences only the harmonic potential $V_0(x)$, i.e., it is the "unperturbed path" from x_1 to x_2.

Eqs. (4.9)-(4.11) thus have a simple intuitive structure; they may be thought of as the path integral version of the "distorted wave"[19] representation familiar in scattering theory. A matrix element of the Boltzmann operator $e^{-\beta H}$ is the matrix element of the "unperturbed" Boltzmann operator $e^{-\beta H_0}$ multiplied by a correction factor involving the perturbation ΔV; the correction factor is an average of $e^{-\beta \Delta \hat{V}}$ over all Fourier deviations of the path $x(\xi)$ about the unperturbed path $x_0(\xi)$.

One can also imagine a Monte Carlo evaluation of the integrals in Eq. (4.9) along the same lines discussed at the end of the previous section. One would change integration variables from $\{z_n\}$ to $\{w_n\}$ in exactly the same manner. To the extent that ΔV is small, the integrand $e^{-\beta \Delta \bar{V}}$ is a slowly varying function, so that Monte Carlo evaluation of the integral would be expected to be efficient.

V. FINAL RATE EXPRESSION

With the Fourier expansions of the path integral developed in Sections III and IV, one can now return to the quantum mechanical expression for the transition state theory rate constant, Eq. (2.5). For the $s(\xi)$ path it is convenient to use the Fourier series representation with no reference potential [Eqs. (3.6)-(3.8)], and for the $u(\xi)$ path to use the Fourier series representation with a harmonic reference potential [Eqs. (4.9)-(4.11)]. This gives

$$k_{b\leftarrow a}\, Q_a = \frac{kT}{h}\, \frac{e^{-\beta V_{sp}}}{4\pi} \left(\frac{\hbar\omega\beta}{\sinh\ (\hbar\omega\beta)}\right)^{1/2} \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} ds\ (+\tfrac{1}{s})\ \frac{\partial}{\partial s}$$

$$\exp\left[-\frac{2ms^2}{\hbar^2\beta} - \frac{m\omega}{\hbar}\ \tanh\ (\tfrac{\hbar\omega\beta}{2})(u-u_0)^2\right] \int_{-\infty}^{\infty} d\underset{\sim}{z} \int_{-\infty}^{\infty} d\underset{\sim}{y}\ e^{-\pi(\underset{\sim}{z}^2+\underset{\sim}{y}^2)}\ e^{-\beta\Delta\bar{V}}\ , \tag{5.1}$$

where ω is the frequency for the reference potential for the u-degree of freedom (i.e., the symmetric stretch frequency), and

$$\int_{-\infty}^{\infty} d\underset{\sim}{z} = \int_{-\infty}^{\infty} dz_1 \int_{-\infty}^{\infty} dz_2 \cdots \int_{-\infty}^{\infty} dz_N$$

$$\int_{-\infty}^{\infty} d\underset{\sim}{y} = \int_{-\infty}^{\infty} dy_1 \int_{-\infty}^{\infty} dy_2 \cdots \int_{-\infty}^{\infty} dy_N$$

$$\Delta V(s,u) = V(s,u) - V_{sp} - \tfrac{1}{2}\, m\omega^2\, (u-u_o)^2 \quad ,$$

$$\Delta\bar{V} = \int_0^1 d\xi\ \Delta V(s(\xi),\, u(\xi)) \quad ,$$

and the paths are

$$s(\xi) = (2\xi - 1)s + \left(\frac{4\hbar^2\beta}{m\pi}\right)^{1/2} \sum_{n=1}^{N} \frac{z_n}{n} \sin(n\pi\xi)$$

$$u(\xi) = u_0 + u \frac{\sinh(\hbar\omega\beta\xi) + \sinh[\hbar\omega\beta(1-\xi)]}{\sinh(\hbar\omega\beta)}$$

$$+ \left(\frac{4\hbar^2\beta}{m\pi}\right)^{1/2} \sum_{n=1}^{N} \frac{y_n \sin(n\pi\xi)}{\left[n^2 + \left(\frac{\hbar\omega\beta}{\pi}\right)^2\right]^{1/2}} ,$$

where u_0 is the equilibrium value of the u-coordinate. $V_{sp} = V(0,u_0)$ is the saddle point of the potential surface and is inserted purely for convenience, (i.e., it cancels out identically in Eq. (5.1)).

The derivative with respect to s in Eq. (5.1) can be carried out, and the result is simplified if one then changes the integration variables s and u to z_0 and y_0, defined by

$$z_0 = \left(\frac{2m}{\hbar^2\beta\pi}\right)^{1/2} s$$

$$y_0 = \left[\frac{m\omega}{\pi\hbar} \tanh\left(\frac{\hbar\omega\beta}{2}\right)\right]^{1/2} u \quad .$$

Eq. (5.1) then takes the familiar form of conventional transition state theory

$$k_{b\leftarrow a} = \Gamma \frac{kT}{h} \frac{Q^{\dagger}_{vib}}{Q_a} e^{-\beta V_{sp}} , \qquad (5.2)$$

where $Q^{\dagger}_{vib}$ is the harmonic oscillator partition function for the u-degree of freedom,

$$Q^{\dagger}_{vib} = \frac{1}{2 \sinh\left(\frac{\hbar\omega\beta}{2}\right)} \quad , \tag{5.3}$$

and Γ is a generalized non-separable tunneling correction:

$$\Gamma = \int_{-\infty}^{\infty} dz_0 \int_{-\infty}^{\infty} dz_1 \cdots \int_{-\infty}^{\infty} dz_N \int_{-\infty}^{\infty} dy_0 \int_{-\infty}^{\infty} dy_1 \cdots \int_{-\infty}^{\infty} dy_N$$

$$\times \quad e^{-\pi(z_0^2+z_1^2+\ldots+z_N^2+y_0^2+y_1^2+\ldots+y_N^2)}$$

$$\times \quad e^{-\beta\Delta\bar{V}} \left[1 + \left(\frac{\hbar^2\beta^3}{2\pi m}\right)^{1/2} \frac{1}{z_0} \int_0^1 d\xi \left(\xi - \frac{1}{2}\right) \Delta V_s(s(\xi), u(\xi))\right] , \tag{5.4}$$

where

$$\Delta V_s(s,u) = \frac{\partial \Delta V(s,u)}{\partial s} = \frac{\partial V(s,u)}{\partial s} \quad ,$$

and where the paths $s(\xi)$ and $u(\xi)$ are given in terms of the integration variables by

$$s(\xi) = \left(\frac{2\pi\hbar^2\beta}{m}\right)^{1/2} \left(\xi - \frac{1}{2}\right) z_0 + \left(\frac{4\hbar^2\beta}{m\pi}\right)^{1/2} \sum_{n=1}^{N} \frac{z_n}{n} \sin(n\pi\xi) \tag{5.5a}$$

$$u(\xi) = u_0 + y_0 \left[\frac{\pi\hbar}{m\omega \tanh\left(\frac{\hbar\omega\beta}{2}\right)}\right]^{1/2} \frac{\sinh\left(\hbar\omega\beta\xi\right) + \sinh\left[\hbar\omega\beta(1-\xi)\right]}{\sinh\left(\hbar\omega\beta\right)}$$

$$+ \left(\frac{4\hbar^2\beta}{m\pi}\right)^{1/2} \sum_{n=1}^{N} \frac{y_n \sin(n\pi\xi)}{\left[n^2 + \left(\frac{\hbar\omega\beta}{\pi}\right)^2\right]^{1/2}} \quad . \tag{5.5b}$$

Eq. (5.2), with Γ given by Eqs. (5.4)-(5.5), is the final result. If $\Delta V = 0$, then clearly $\Gamma = 1$. It is also easy to see that $\Gamma = 1$ in the classical, high temperature limit, $\hbar\beta \to 0$. Following the discussion at the end of Sections III and IV, one can see how Eq. (5.4) could be evaluated by Monte Carlo: One would change from the $2N + 2$ integration variables $\{z_n\}$, $\{y_n\}$, $n = 0,1,...N$, to $2N + 2$ w-like variables defined in Eqs. (3.11)-(3.12).

VI. CONCLUDING REMARKS

The path integral representation of the Boltzmann operator thus leads to a very useful formulation of quantum mechanical transition state theory. It is particularly illuminating to view it as a generalization of the Johnston-Rapp model for taking into account the effects of non-separability in the tunneling correction to transition state theory.

The Fourier series representation of the path integral seems to have many desirable features to suggest it as a possible computational procedure, but this, of course, can only be verified by actual numerical calculation. Furthermore, since the Boltzmann operator arises in many applications other than transition state theory, the methodology developed in Sections III and IV has relevance to a much wider class of problems than just the present one.

APPENDIX. PATH INTEGRAL REPRESENTATION OF THE MICROCANONICAL DENSITY MATRIX.

In some cases it may be desirable to calculate the average of the flux operator f [Eq. (2.3)] with a microcanonical density operator first before Boltzmann averaging it. One thus observes that the transition state theory rate constant of Eq. (2.1),

$$k_{b\leftarrow a}\, Q_a = \mathrm{tr}(e^{-\beta H} f) \quad ,$$

can be written in the form

$$k_{b\leftarrow a}\, Q_a = (2\pi\hbar)^{-1} \int dE\; e^{-\beta E}\, N(E) \quad , \tag{A.1}$$

where N(E) is defined by

$$N(E) = 2\pi\hbar\; \mathrm{tr}[\delta(E-H)f] \quad . \tag{A.2}$$

This is often a useful way to express the rate constant since many other kinds of approaches give a result in this form. The exact rate constant obtained from quantum scattering theory, for example, is given by Eq. (A.1) with

$$N(E) = \sum_{n_a, n_b} |S_{n_b, n_a}(E)|^2 \quad , \tag{A.3}$$

where $S_{n_b, n_a}(E)$ is the reactive S-matrix connecting reactant quantum state n_a to product quantum state n_b. With Eq. (2.3) the quantum transition state approximation to N(E), Eq. (A.2), becomes

$$N(E) = \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} ds \left(\frac{-1}{s}\right) \frac{\partial}{\partial s} \langle u,s|\delta(E-H)|u,-s\rangle \quad , \tag{A.4}$$

so that it is necessary to consider matrix elements of the micro-canonical density operator $\delta(E-H)$.

For simplicity of notation consider a one-dimensional system and the matrix elements

$$\langle x_2|\delta(E-H)|x_1\rangle \quad . \tag{A.5}$$

A formal identity gives $\delta(E-H)$ in terms of $e^{-\beta H}$,

$$\delta(E-H) = \mathrm{Re}\, \frac{1}{i\pi} \int_0^{\infty} d\beta \; e^{\beta E} e^{-\beta H} \quad , \tag{A.6}$$

so that the matrix elements in Eq. (A.5) are given by

$$\langle x_2|\delta(E-H)|x_1\rangle = \mathrm{Re}\, \frac{1}{i\pi} \int_0^{\infty} d\beta \; e^{\beta E} \langle x_2|e^{-\beta H}|x_1\rangle \quad . \tag{A.7}$$

By using the Fourier path integral expansion for matrix elements of the Boltzmann operator, Eqs. (3.6)-(3.8), this becomes

$$\langle x_2|\delta(E-H)|x_1\rangle = \int_{-\infty}^{\infty} d\underset{\sim}{z} \; \mathrm{Re}\, \frac{1}{i\pi} \int_0^{\infty} d\beta \left(\frac{m}{2\pi\hbar^2\beta}\right)^{\frac{N+1}{2}} \exp\left[\frac{-m(\Delta x^2+\underset{\sim}{z}^2)}{2\hbar^2\beta}\right]$$

$$\times \; e^{\beta(E-\bar{V})} \quad , \tag{A.8a}$$

where

$$\Delta x = x_2 - x_1$$

$$\bar{V} = \int_0^1 d\xi \; V(x(\xi)) \quad ,$$

and where the path $x(\xi)$ is

$$x(\xi) = x_1 + (x_2-x_1)\xi + \frac{\sqrt{2}}{\pi} \sum_{n=1}^{N} \frac{z_n}{n} \sin(n\pi\xi) \quad . \tag{A.8b}$$

[The integration variables $\{z_n\}$ in Eq. (A.8) have been scaled differently from those in Eqs. (3.6)-(3.8) in order to remove the β-dependence from $x(\xi)$ and thus from $\bar{V}$.] The integral over β in Eq. (A.8) can now be evaluated, and one obtains

$$\langle x_2 | \delta(E-H) | x_1 \rangle = \frac{2m}{\hbar^2} \frac{1}{2\pi^2} \int_{-\infty}^{\infty} d\underset{\sim}{z} \left[\frac{2m}{\hbar^2} \frac{(E-\bar{V})}{4\pi^2(\Delta x^2 + \underset{\sim}{z}^2)}\right]^{\frac{N-1}{4}}$$

$$\times J_{\frac{N-1}{2}}\left(\sqrt{\frac{2m}{\hbar^2}(\Delta x^2 + \underset{\sim}{z}^2)(E-\bar{V})}\right) h(E-\bar{V}) \quad , \tag{A.9}$$

where J is the regular Bessel function and h the step-function.

Use of a two-dimensional version of Eq. (A.9) in Eq. (A.4) thus gives a path integral representation for N(E).

The path integral representation of the microcanonical density matrix, Eq. (A.9), is considerably more complicated than its canonical counterpart, Eqs. (3.6)-(3.8). This greater complexity in the path integral representation of the microcanonical density operator has been noted before[20] in other contexts.

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* Supported in part by the U. S. Energy Research and Development Administration, and by the National Science Foundation under grant GP-41509X.

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