Evaluation of microcanonical rate constants for bimolecular reactions by path integral techniques

D. Thirumalai
Department of Chemistry and Institute for Physical Sciences and Technology, University of Maryland, College Park, Maryland 20742

B. C. Garrett
Chemical Dynamics Corporation, 1550 West Henderson Road, Columbus, Ohio 43220

B. J. Berne
Department of Chemistry, Columbia University, New York, New York 10027

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An expression for the microcanonical rate constant that can be conveniently evaluated by path integral techniques is proposed. The efficacy of the method is illustrated by obtaining accurate transmission probabilities as a function of energy for a particle tunneling through an Eckart barrier. The application of the method to systems involving many degrees of freedom is discussed.

INTRODUCTION

One of the important achievements in bimolecular reaction dynamics has been the investigation of state-to-state reaction cross sections[1–3] as a function of energy of the colliding partners. Very recently Marinero, Rettner, and Zare[4] and Gerrity and Valentini[5] were successful in studying the reaction dynamics of $H + D_2$ as a function of collision energy. Undoubtedly these results will prove to be of great importance in constructing approximate theories of reaction dynamics. Thus the task of a theoretician is to calculate microcanonical rate constants as a function of energy for a given Born–Oppenheimer potential energy surface. This is a well posed problem in reactive scattering theory and the solution can be reduced to a set of N coupled channel Schrödinger equations.[6] The solution to the N-channel problem yields the S matrix from which the state-to-state reaction cross section can be obtained. This procedure was followed by Schatz and Kuppermann[7–9] for the reaction $H + H_2$; however, this task is impractical for more complicated reactions. The difficulty in calculating the quantum mechanical microcanonical rate constant $k(E)$ as a function of energy has led to the exploration of classical trajectory methods.[10] Although this approach has indeed met with much success, it is not applicable to the many bimolecular reactions of interest in which tunneling dominates the reaction rate. Thus in this paper a formulation of the problem that enables us to directly evaluate $k(E)$ for a given potential energy surface is suggested. The range of applicability of this formulation will eventually depend on the development of efficient Monte Carlo algorithms. Given the current attention to the development of simulation techniques,[11] it is hoped that the scheme outlined here will indeed be practical for systems of chemical interest.

MICROCANONICAL RATE CONSTANTS IN TERMS OF PATH INTEGRALS

We begin by deriving formal expressions for the microcanonical rate constant in terms of path integrals. The starting point of our formulation is explicitly found in the work of Miller[12] and has been reproduced more recently by Miller, Schwartz, and Tromp.[13] To keep the notation simple we consider the case of one degree of freedom, namely the reaction coordinate. The generalization to many dimensions and the associated difficulties in evaluating the resultant expression are dealt with at the end of the section. Starting from an explicit and formally exact expression for the quantum mechanical rate constant, Miller *et al.*[12,13] have shown that the canonical rate constant k can be written as

$$kQ = \frac{1}{2}\int_{-\infty}^{\infty} C_f(t)\,dt, \tag{1}$$

where the flux–flux correlation function $C_f(t)$ is given by

$$C_f(t) = \mathrm{tr}\,\{F e^{-H\tau} F e^{-H\tau^*}\}. \tag{2}$$

In Eq. (2) H is the Hamiltonian of the system, F is the flux operator given by

$$F = \tfrac{1}{2}[\delta(x)(P/m) + (P/m)\delta(x)], \tag{3}$$

where P is the momentum conjugate to x, and $\tau = \beta/2 - it/\hbar$. In order to obtain the microcanonical cumulative reaction probability $N(E)$ it is observed that k is given by[12]

$$k = \frac{1}{2\pi\hbar}\int_0^{\infty} e^{-\beta E} N(E)\,dE. \tag{4}$$

Substituting the identity

$$e^{-H\tau} = \int_{-\infty}^{\infty} e^{-E\tau}\delta(E - H)\,dE$$

in Eq. (2), it is a simple matter to show that

$$kQ = \pi\hbar\int_{-\infty}^{\infty} dE\, e^{-\beta E}\,\mathrm{tr}\,[F\delta(E - H)F\delta(E - H)]. \tag{5}$$

Comparison of Eq. (5) and Eq. (4) allows one to identify $N(E)$ as

$$N(E) = \tfrac{1}{2}(2\pi\hbar)^2\,\mathrm{tr}\,[F\delta(E - H)F\delta(E - H)]. \tag{6}$$

This formally exact expression for the microcanonical rate constant was first obtained by Miller.[12] In the coordinate representation Eq. (6) becomes[13]

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$$N(E)=\frac{1}{2}\left(\frac{\pi\hbar^2}{m}\right)\left[\frac{\partial}{\partial x\partial x'}(\langle x'|\delta(E-H)|x\rangle)^2 - 4\left(\frac{\partial}{\partial x'}\langle x'|\delta(E-H)|x\rangle\right)^2\right] \quad (7)$$

evaluated at $x=x'=0$. Notice that the second term in Eq. (7) vanishes for potentials that are symmetric about $x=0$.

The task of calculating $N(E)$ is thus reduced to evaluating the matrix elements of $\delta(E-H)$ in the coordinate representation. This is accomplished by using the method suggested by Hirsch and Schrieffer[14] in the context of the evaluation of ground state dynamic correlation functions in quantum systems and it springs from the fact that $\delta(E-H)$ can be expressed as

$$\delta(E-H)=\lim_{\bar\beta\to\infty}\left(\frac{\bar\beta}{\pi}\right)^{1/2}e^{-\bar\beta(H-E)^2}, \quad (8a)$$

so that

$$\langle x|\delta(E-H)|x'\rangle=\lim_{\bar\beta\to\infty}\left(\frac{\bar\beta}{\pi}\right)^{1/2}\langle x|e^{-\bar\beta(H-E)^2}|x'\rangle. \quad (8b)$$

Substitutions of Eq. (8) into Eq. (7) gives the following expression for $N(E)$:

$$N(E)=\frac{1}{2}\left(\frac{\pi\hbar^2}{m}\right)^2\frac{\bar\beta}{\pi}\left[\langle 0|e^{-\bar\beta(H-E)^2}|0\rangle \times\left(\frac{\partial^2}{\partial x\partial x'}\langle x|e^{-\bar\beta(H-E)^2}|x'\rangle\right) - \left(\frac{\partial}{\partial x'}\langle x'|e^{-\bar\beta(H-E)^2}|x\rangle\right)^2\right], \quad (9)$$

evaluated at $x=x'=0$, and where it is understood that $\bar\beta\to\infty$. The computation of $N(E)$ has been reduced to calculating the matrix elements of the Gaussian operator in the coordinate representation. This is accomplished by exploiting the discretized path integral representation of such operators. To proceed we observe that

$$e^{-\bar\beta(H-E)^2}=e^{[-\bar\beta/L(H-E)^2]L} \quad (10)$$

and therefore $\langle x|e^{-\bar\beta(H-E)^2}|x'\rangle$ in the coordinate representation becomes

$$\langle x|e^{-\bar\beta(H-E)^2}|x'\rangle = \int dx_2\ldots dx_L\prod_{t=1}^{L}\langle x_t|e^{-\bar\beta/L(H-E)^2}|x_{t+1}\rangle \quad (11)$$

with the condition $x_1=x$ and $x_{L+1}=x'$. Although this formulation for the evaluation of $N(E)$ is formally exact in the limit of $\bar\beta\to\infty$ in practice one chooses a sufficiently large (but finite) value of $\bar\beta$ so that the Gaussian function adequately represents the delta function. Thus for a given value of $\bar\beta$ if L is large enough so that $\bar\beta/L\equiv\epsilon$ is small then we can use the Trotter formula to evaluate $e^{-\epsilon(H-E)^2}$:

$$e^{-\epsilon(H-E)^2}\approx\exp\left[\frac{-\epsilon(V-E)^2}{2}\right]\exp-\left[\frac{P^4}{4m^2}+\frac{P^2}{2m}(V-E)+(V-E)\frac{P^2}{2m}\right]\times\exp\left[\frac{-\epsilon(V-E)^2}{2}\right]+O(\epsilon^2). \quad (12)$$

Using Eq. (12) the matrix element $\langle x_t|e^{-\epsilon(H-E)^2}|x_{t+1}\rangle$ can be shown to be[14,15]

$$\langle x_t|e^{-\bar\beta/L(H-E)^2}|x_{t+1}\rangle \approx e^{-\bar\beta/2L[V(x_t)-E]^2}g(x_t,x_{t+1})e^{-\bar\beta/2L[V(x_{t+1})-E]^2}, \quad (13)$$

where

$$g(x_t,x_{t+1})=\frac{1}{\pi}\int_0^\infty dP\cos P(x_t-x_{t+1}) \times\exp\left(\frac{-\bar\beta}{L}\left\{\frac{P^4}{4m^2}+\frac{P^2}{2m}[V(x_t)+V(x_{t+1})-E]\right\}\right). \quad (14)$$

We have not been able to evaluate Eq. (14) in a closed form so that it has to be calculated numerically. Substituting Eqs. (11), (13), and (14) into Eq. (9) yields a complicated multidimensional integral which, in general, has to be evaluated by a Monte Carlo algorithm suitably designed to account for the negative weights that could arise from the short time approximation to the Gaussian operator.

For systems which involve only a few degrees of freedom it proves to be convenient to calculate $N(E)$ using Eq. (9) by the numerical matrix multiplication method[16] suitably adopted for Gaussian operators. The NMM method exploits the group property for the Gaussian operators, i.e.,

$$e^{-\epsilon(H-E)^2}e^{-\epsilon(H-E)^2}=e^{-2\epsilon(H-E)^2}, \quad (15a)$$

so that in the coordinate representation

$$\langle x|e^{-2\epsilon(H-E)^2}|x'\rangle = \int dx''\langle x|e^{-\epsilon(H-E)^2}|x''\rangle\langle x''|e^{-\epsilon(H-E)^2}|x'\rangle. \quad (15b)$$

Having obtained $\langle x|e^{-2\epsilon(H-E)}|x'\rangle$ one can substitute it in Eq. (15b) and obtain $\langle x|e^{-4\epsilon(H-E)}|x'\rangle$. This process can be repeated and after n iterations this would yield $\langle x|e^{-2^n\epsilon(H-E)}|x'\rangle$ for all x and x'. If 2^n is chosen so that $2^n\epsilon=\bar\beta(L=2^n)$, then after n matrix multiplications one arrives at the desired matrix elements of the Gaussian operator. Given this, $N(E)$ can be evaluated using Eq. (9), where derivatives are obtained by finite difference. The ultimate usefulness of our formulation however, will depend upon efficient Monte Carlo methods to calculate $N(E)$.

Before closing we make a few remarks about extending the above formulation to multidimensional systems. Substituting Eqs. (11) and (12) into Eq. (9) it can be readily shown that $N(E)$ can be written as

$$N(E)=\int d\mathbf{R}\,P[\mathbf{R}]F(\mathbf{R}),$$

where $\mathbf{R}$ denotes collectively all the coordinates in the isomorphic system obtained by making the short time approximation to the Gaussian operator, $P[\mathbf{R}]$ is the probability distribution for the configuration and $F(\mathbf{R})$ is the residue. This is precisely the form that is amenable to Monte Carlo evaluation. The strategy is to sample from $P(\mathbf{R})$ and average the quantity $F(\mathbf{R})$. It should be pointed out that there is considerable freedom in the choice of $P(\mathbf{R})$ which can be optimized to obtain convergence. Because the short time approximation

to the Gaussian operator can sometimes be negative one might require many configurations to achieve convergence.

CALCULATIONS AND RESULTS

In order to test the feasibility of our approach we have calculated the one-dimensional reaction probability for the symmetric Eckart potential[17]

$$V(x)=\frac{4V_0e^{2\alpha x}}{(1+e^{2\alpha x})^2}, \tag{16}$$

where we have taken $V_0=0.02$ Hartree and $\alpha=2.0$ (a.u.)$^{-1}$. Since this is a one-dimensional problem we can profitably use NMM to evaluate $N(E)$. In particular, the integral in Eq. (15b) which gives the matrix $\langle x|e^{-2\epsilon(H-E)}|x'\rangle$ starting from $\langle x|e^{-\epsilon(H-E)}|x'\rangle$ is approximated by

$$\langle i\Delta|e^{-2\epsilon(H-E)^2}|j\Delta\rangle \approx \Delta\sum_{k=-M}^{M}\langle i\Delta|e^{-\epsilon(H-E)^2}|k\Delta\rangle\langle k\Delta|e^{-\epsilon(H-E)^2}|j\Delta\rangle, \tag{17}$$

where $x=i\Delta, x'=j\Delta, x''=k\Delta$, and Δ is the lattice spacing. The spacing Δ and the upper (lower) limit $M\Delta$ ($-M\Delta$) are chosen to ensure the convergence of the integral.[18] Thus the calculation of the matrix elements of the Gaussian operator for a given $\bar{\beta}$ is reduced to n matrix multiplications. The integral in Eq. (14) which is needed to calculate the short time aproximation to the Gaussian operator was evaluated by Gauss–Hermite quadrature for sufficiently small values of (x_t-x_{t+1}) and by repeated Gauss–Legendre quadrature for large (x_t-x_{t+1}).

In order to accelerate the convergence of the matrix multiplication scheme we note that the matrix $\mathbf{G}$ whose elements $\langle i\Delta|e^{-\epsilon(H-E)}|j\Delta\rangle$ are given by Eqs. (13) and (14), is a real symmetric and banded matrix. Consequently, one can diagonalize $\mathbf{G}$ using an orthogonal matrix $\mathbf{U}$, i.e.,

$$\mathbf{U}^T\mathbf{G}\mathbf{U}=\lambda^2\mathbf{I}, \tag{18}$$

where λ^2 are the eigenvalues of $\mathbf{G}$ and $\mathbf{I}$ is the unit matrix. It can be readily seen that $\mathbf{U}$ also diagonalizes the matrix $\mathbf{G}^{(1)}$, obtained after the first iteration [cf. Eq. (17)], i.e.,

$$\mathbf{U}^T\mathbf{G}^{(1)}\mathbf{U}=\Delta\mathbf{U}^T\mathbf{G}\mathbf{G}\mathbf{U}=\Delta\mathbf{U}^T\mathbf{G}\mathbf{U}\mathbf{U}^T\mathbf{G}\mathbf{U}=\Delta(\lambda^2)^2\mathbf{I}. \tag{19}$$

The matrix $\mathbf{G}^{(n)}$ of the Gaussian operator (obtained after n iterations) for a given $\bar{\beta}$ is easily obtained from

$$\mathbf{G}^n=\Delta^n\mathbf{U}(\lambda^2)^{n+1}\mathbf{U}^T. \tag{20}$$

Thus the desired matrix after n iterations may be obtained by diagonalizing the short time approximation to the Gaussian operator, multiplying a diagonal matrix n times, and finally using the inverse transformation in accordance with Eq. (20). This additional simplification proves to be about twice as fast as the straightforward iteration scheme using Eq. (17).

We note that the matrix elements of the Gaussian operator can be rewritten as

$$\langle x|e^{-\bar{\beta}(H-E)^2}|x'\rangle = e^{-\bar{\beta}E^2}\int dx''\langle x|e^{-\bar{\beta}H^2}|x''\rangle\langle x''|e^{2\bar{\beta}EH}|x'\rangle, \tag{21}$$

and hence $\langle x|e^{-\beta H^2}|x''\rangle$ which is independent of energy need be evaluated just once. The operator $e^{2\beta EH}$ is the inverse of the operator $e^{-2\beta EH}$ and has matrix elements in the coordinate representation which can be readily calculated using NMM. When doing problems involving multidimensions, the inverse has to be updated every pass and this is most easily accomplished by the method introduced by Von Neuman and Ulam[19] and more recently used by Kuti[20] in lattice gauge calculations involving fermionic degrees of freedom.

Before presenting the results, we plot the short time approximation to $\langle x|e^{-\epsilon(H-E)^2}|x'\rangle$ for $x'=-1$, $E=0.018$ a.u., and $\epsilon=100$ as a function of x in Fig. 1. The solid line represents the real values of the function and it is quite evident that there are small regions where the matrix elements becomes negative. In order to focus on the magnitude of the negative weights the ordinate has been scaled for various regions of the x axis. For example, the short-, intermediate-, and long-dashed lines are scaled by 10, 100, and 1000, respectively, to accentuate the region $0.25<|x-x'|>1.0$. Comparison of the two peaks near $x=-0.3$ and $x=-1.2$ clearly shows the asymmetry of the curve about $x=-1$. The negative weights are most prominent in the region $0.2<|x-x'|>0.7$.

The results for the transmission probability $N(E)$, as a function of energy is presented in tabular form. For each energy, $N(E)$ was calculated at five large values of $\bar{\beta}$. The results were then fitted to a polynomial in $1/\bar{\beta}$ and $N(E)$ was extrapolated as $\bar{\beta}\to\infty$ or $1/\bar{\beta}\to 0$. In Table I we compare the present calculations with the exact results. The exact expression for $N(E)$ for the symmetric Eckart potential is given by[17]

$$N(E)=\frac{\cosh(2a)-1}{\cosh(2a)+\cosh(b)}, \tag{22}$$

where

$$a=\frac{2\pi}{\hbar\alpha}(2mE)^{1/2}, \qquad b=\frac{2\pi}{\hbar\alpha}\left[8mV_0-\left(\frac{\hbar\alpha}{2}\right)^2\right]^{1/2}. \tag{23}$$

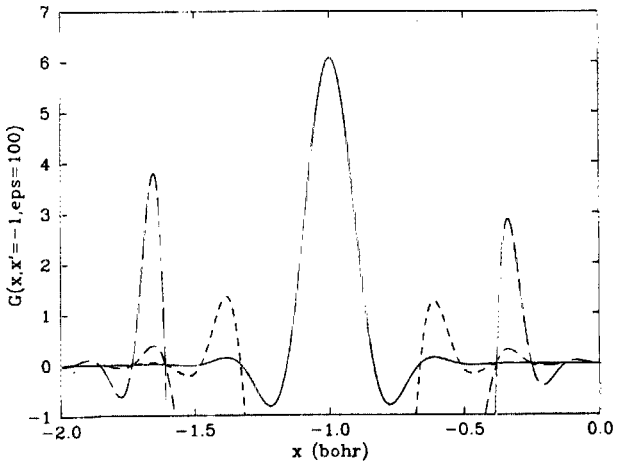

FIG. 1. Short time approximation to the matrix elements of the Gaussian operator $\exp[-\epsilon(H-E)^2][G(x,x')]$ as a function of the coordinate x for fixed $x'=1.0$ bohr and $\epsilon=100$ a.u. $G(x,x')$ is given in atomic units for tunneling at a total energy of 0.018 hartree through a symmetric Eckart barrier with maximum of 0.02 hartree at $x=0$ and a range parameter of 2 bohr^{-1}. The solid line is $G(x,x')$ and the short-, intermediate-, and long-dashed lines are $G(x,x')$ scaled by 10, 100, and 1000, respectively.

TABLE I. Microcanonical reaction probability as a function of energy for the Eckart potential. The exact result is also shown for comparison.

Energy (a.u.)	$N(E)$	
	Present	Exact[a]
0.005	1.93(− 6)[b]	1.71(− 6)
0.010	4.60(− 4)	4.51(− 4)
0.015	3.13(− 2)	3.15(− 2)
0.018	2.33(− 1)	2.32(− 1)

[a] Calculated using Eq. (22).
[b] Figures in parentheses refer to powers of 10.

It is seen that the present calculations are in excellent agreement with the exact answers. The maximum deviation of about 12% occurs at the lowest energy considered where $N(E)$ is quite small. It is well known that convergence of small quantum mechanical probabilities is difficult to achieve. Our result for this energy can definitely be improved by using smaller lattice spacing. Nevertheless, for energies of practical interest (obtainable in beam experiments), the present calculations are very encouraging.

CONCLUSIONS

We have presented an algorithm that may be useful in the direct calculation of quantum microcanonical rate constants. The method avoids the calculation of state-to-state rate constants, which are often extremely difficult to obtain. The application to a one-dimensional problem demonstrates the usefulness of our method. However, we emphasize that the practicability of the formulation for multidimensional problems will undoubtedly depend on Monte Carlo algorithms to evaluate $k(E)$. It should be recalled that in multidimensional problems the degrees of freedom besides the reactive coordinate are bound-like and in a sense are easier to treat than the translational motion. In fact our formulation can be easily applied to the reaction path Hamiltonian[21,22] model for a polyatomic reaction. This and other generalizations will be presented elsewhere.[23]

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