

Evaluation of Microcanonical Rate Constants by Semiclassical Boundary Conditions: Early Asymptotic Analysis

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An approximate scheme for evaluating total reaction probability is proposed. Semiclassical boundary conditions are imposed well before the asymptotic region in the reactant and product channels to calculate the Green's function and its derivatives. Propagations are confined to a limited regime near the activated complex. Calculations are made for one dimensional Eckart barrier model of $H+H_2$ reaction. Implications of the procedure in multi-dimensional systems are discussed.

Introduction

The rate constants of chemical reactions are one of the most important properties of chemical systems. It is the ultimate goal of molecular reaction dynamics to evaluate the rate constants when the potential surfaces for the reacting species are given. Many different approaches have been used to calculate this important quantities in various situations.

Exact evaluation of the rate constants is quite involved. One has to solve the close-coupled equations that include many channels (elastic, inelastic and reactive), calculate state-to-state cross sections from the S-matrix elements, which can be combined to give the total reaction cross sections.¹⁻³ Even for atom-diatom reactions, the efforts for solving these close-coupled equations are sometimes prohibitive. If one is interested only in the thermal rate constants, *i.e.*, the net reactive flux, there should be a more economical way of calculating it, without solving for all the state-to-state information first.

Choosing appropriate coordinate systems for describing reactive scattering processes is another serious problem. In $A+BC \rightarrow AB+C$ type rearrangement processes, it is well known⁴ that different coordinate systems should be employed to describe reactants and products. For the asymptotic analysis, different sets of Jacobi coordinates are used for the reactants and products, respectively, while other types of coordinates are more convenient for regimes near the activated complexes. The transformations between these coordinate systems are not trivial. These problems arise from the necessity of asymptotic analysis that should be performed when the reacting species are far apart. If we can confine the calculation to a limited region near the transition state, we may not have to deal with the coordinate transformations, since the asymptotic analysis can be obviated.

Several methods that avoid the asymptotic analysis have been proposed. Transition state theory has been used to calculate approximate rate constants, and considerable effort has been directed to improving the accuracy of the method.⁵⁻⁷ While it is difficult to systematically improve the accuracy of transition state theory, its advantage is obvious: We only need information on the potential surface near the transition state. Finite difference methods and path integral techniques have been proposed by McCurdy *et al.*⁸ and by Miller *et al.*⁹ respectively, for evaluating total reaction probability for one-dimensional reacting systems, but extensions to multidimensional systems are not straightforward in their procedures.

Park and Light¹⁰ and Day and Truhlar¹¹ have evaluated accurate thermal rate constants for three-dimensional reactions by evaluating the time correlation function in a localized bases, but so far their approaches have not been widely exploited. Time-dependent wavepacket propagation is another popular method of solving dynamical problems without doing asymptotic analysis.¹²⁻¹⁴ These approaches usually assume short-time approximations. A popular application is to photodissociation in an excited electronic state. Here one propagates the wavepackets along the excited state surfaces until they reach the asymptotic region. Since the propagation is performed with respect to time, not spatial coordinates, such methods are efficient when the excited potential surfaces are repulsive. When the wavepackets return to the Franck-Condon region long after the excitation, as in predissociating systems, the short-time approximations fail, and the time-dependent methodologies become inefficient.

Singer *et al.* have developed¹⁵ an efficient algorithm that combines the advantages of the time-independent and time-dependent methods and applied it to Raman scattering problems. The algorithm, called early asymptotic analysis, employs semiclassical boundary conditions, based on the WKB approximation, that are imposed well before the asymptotic region. Since the semiclassical boundary conditions depend *locally* on the matching point, information on the potential surfaces beyond the matching point is not needed. The propagation is performed with respect to the spatial coordinates, not time, and consequently the algorithm can be applied to any kind of system. Singer *et al.* have shown that the method gives Raman scattering amplitudes accurate to 3 or more significant figures when the semiclassical boundary conditions are imposed at 1-3 Å beyond the classical turning points for Na dimer (single channel problem) and Br₂ (multi-channel problem) molecules, well before the asymptotic region. We propose here to extend these ideas to reactive scattering problems. The total reaction probability is expressed in terms of the Green's function and its derivatives,⁹ and the semiclassical boundary conditions are derived in section II. Approximate reaction probabilities are evaluated for a one dimensional model $H+H_2$ system in section III.

Theory

Thermal rate constants $k(T)$ can be written as the thermal

trace of the microcanonical reaction probability $P(E)$ as^{16,17}

$$k(T) = \{1/h Z(T)\} \int dE P(E) \exp(-E/k_B T) \equiv [P(E)]_T$$

where E is the total energy, h is the Planck constant, $k_B(T)$ is the Boltzmann constant, and $Z(T)$ is the partition function of the reaction system. Microcanonical rate constants are given as^{8,9,18}

$$P(E) = 2\pi^2 h^2 \text{tr}[F \delta(E-H) F \delta(E-H)], \quad (1)$$

where $[\dots]$ represents the quantum mechanical trace, F is the symmetrized flux operator, $\delta(E-H)$ is the density operator at the energy of E , H is the Hamiltonian. The density operator $\delta(E-H)$ is related to the Green's operator as

$$\delta(E-H) = -\text{Im} G^{(+)}(E)/\pi, \quad (2)$$

and the reaction probability for a one dimensional barrier penetration problem is given as

$$P(E) = (h/\mu)^2 [\text{Im}[G^{(+)}(x, x')] \text{Im}[\partial^2 G^{(+)}(x, x')/\partial x \partial x'] - [\text{Im} \partial G^{(+)}(x, x')/\partial x]^2]_{x=x'=x_s} \quad (3)$$

where x_s is the position of the matching point. The Green's function $G^{(+)}(x, x')$ satisfies the equation.

$$[E-H(x)] G^{(+)}(x, x') = \delta(x-x'). \quad (4)$$

Here $H(x)$ is the Hamiltonian of the system. For a one dimensional problem, $G^{(+)}(x, x')$ can be expressed in terms of the solutions $h^{(-)}(x)$ and $h^{(+)}(x)$,

$$G^{(+)}(x, x') = \begin{cases} h^{(-)}(x) (2\mu/W) h^{(+)}(x'), & x < x' \\ h^{(+)}(x) (2\mu/W) h^{(-)}(x'), & x > x' \end{cases} \quad (5)$$

$$(6)$$

where $h^{(-)}(x)$ and $h^{(+)}(x)$ are eigenfunctions of $H(x)$ that have boundary conditions at $x \rightarrow -\infty$ and at $x \rightarrow \infty$, respectively,

$$h^{(-)}(x) \rightarrow e^{-ikx} \quad (7)$$

$$h^{(+)}(x) \rightarrow e^{+ikx} \quad (8)$$

μ is the reduced mass and W is the Wronskian of $h^{(+)}(x)$ and $h^{(-)}(x)$,

$$W \equiv (h^{(-)}, h^{(+)} = h^{(-)}(x) [d/dx h^{(+)}(x)] - [d/dx h^{(-)}(x)] h^{(+)}(x) \quad (9)$$

where t denotes transposition. Using this definition of the Wronskian W , $G^{(+)}(x, x')$ can be expressed as, at $x=x'=x_s$,

$$G^{(+)}(x, x') = h^{(-)}(x_s) (2/W) h^{(+)}(x_s) = 2\mu \{ [h^{(+)}_R]^{-1} - [h^{(-)}_R]^{-1} \} \quad (10)$$

where $h^{(+)}_R(x)$ and $h^{(-)}_R(x)$ are the log-derivative matrices

$$h^{(+)}_R(x) = h^{(+)}(x)/h'^{(+)}(x) \quad (11)$$

$$h^{(-)}_R(x) = h^{(-)}(x)/h'^{(-)}(x). \quad (12)$$

Similarly, the first derivative and mixed second derivative of the Green's function can be obtained as

$$\partial/\partial x G^{(+)}(x, x') = 2\mu \{ [h^{(-)}_R]^{-1} - [h^{(+)}_R]^{-1} \} \quad (13)$$

$$\partial^2/\partial x \partial x' G^{(+)}(x, x') = 2\mu \{ h^{(-)}_R - h^{(+)}_R \}. \quad (14)$$

Log-derivatives $h^{(+)}_R(x)$ and $h^{(-)}_R(x)$ have boundary conditions at $x \rightarrow \infty$ and $x \rightarrow -\infty$,

$$h^{(+)}_R(x) \rightarrow 1/ik_{\infty} \quad (15)$$

$$h^{(-)}_R(x) \rightarrow -i/k_{-\infty} \quad (16)$$

where k_{∞} , $k_{-\infty}$ are wave vectors at $x \rightarrow \infty$, $x \rightarrow -\infty$, respectively.

Semiclassical boundary conditions of $h^{(+)}_R(x)$ and $h^{(-)}_R(x)$ are obtained, using WKB approximations.

$$h^{(+)}_{R, \text{WKB}}(x) = 1/(2k(x)) d/dx(k(x)) + i k(x) \quad (17)$$

$$h^{(-)}_{R, \text{WKB}}(x) = -1/(2k(x)) d/dx(k(x)) - i k(x) \quad (18)$$

These approximate boundary conditions depend *locally* on the matching point x_s , and are independent of the potential surfaces beyond x_s . When these boundary conditions are imposed well before the asymptotic region to evaluate the Green's function and its derivatives at the matching point, the reaction probability can be evaluated by using the limited portion of the potential surfaces near the transition states, and the asymptotic analysis is not needed.

Results and Discussion

Numerical Results for a One Dimensional Eckart Barrier. We examine the efficiency of these procedures for evaluating the reaction probability for a one dimensional problem. Test calculations are performed for the Eckart barrier^{18,19}

$$V(x) = y\Delta V/(1+y) + By/(1+y)^2,$$

where

$$y = \exp[\alpha(x-x_0)],$$

$$B = [(V_{\max})^{1/2} + (V_{\max} - \Delta V)^{1/2}]^2.$$

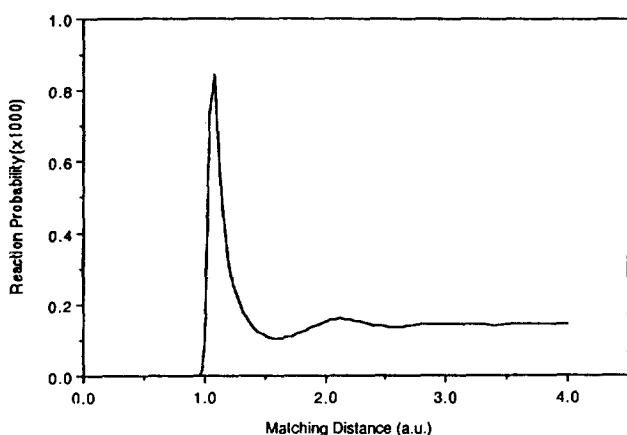
The zero of energy is at $x = -\infty$, ΔV is the value of the potential at $x = +\infty$, V_{\max} is the value of the potential at its maximum, and the constant x_0 is arbitrary and chosen to give the maximum of the potential at $x=0$. We perform the calculation for the one dimensional Eckart model of $H+H_2$ reaction. The reason for this choice is twofold. First, $H+H_2$ is the most fundamental reaction in the molecular reaction dynamics. Secondly, it is the severest system for checking the accuracy of our procedure, since it is well known that the WKB approximation becomes worse for lighter systems. Appropriate parameters for the $H+H_2$ system^{8,9,20} are $V_{\max} = 6.6$ kcal/mol, $\Delta V = 0$, $\alpha = 1.6$ bohr⁻¹. These parameters give a one dimensional system that mimics tunneling through the ground state, minimum energy path vibrationally adiabatic potential curve of the $H+H_2$ reaction. Propagation for $h^{(-)}_R(x)$ is performed from $x = -\infty$ to $x=0$, while $h^{(+)}_R(x)$ is propagated *backward* from $x = +\infty$ to $x=0$. The renormalized Numerov method^{21,22} is modified to accommodate the backward propagation for $h^{(+)}_R(x)$. The numerical error thus varies as the fourth power of the stepsize.

Table 1 presents the approximate reaction probabilities at selected energies. Approximate boundary conditions for $h^{(-)}_R(x)$ and $h^{(+)}_R(x)$ are imposed at matching points of $+R_{\max}$ and $-R_{\max}$, respectively. When $R_{\max} \rightarrow \infty$, our formalism should give exact reaction probabilities presented in column 2 of Table 1. Columns 3 and 4 present the approximate reaction probabilities for $R_{\max} = 5$ a.u. and 3 a.u., respectively. Results for $R_{\max} = 5$ a.u. are a little better than those

Table 1. Comparison of the Semiclassical Approximation with Exact Results

E (Kcal)	Exact ^a	Numerical ^b	
		$R_{max}=5$ a.u.	$R_{max}=3$ a.u.
6.60	5.3090 (-1)	5.3087 (-1)	5.2734 (-1)
4.28	1.6550 (-2)	1.6559 (-2)	1.6461 (-2)
2.96	1.4169 (-4)	1.4191 (-4)	1.4539 (-4)
1.64	4.9030 (-7)	4.9196 (-7)	4.8568 (-7)
0.32	3.0432 (-10)	3.0756 (-10)	2.6981 (-10)

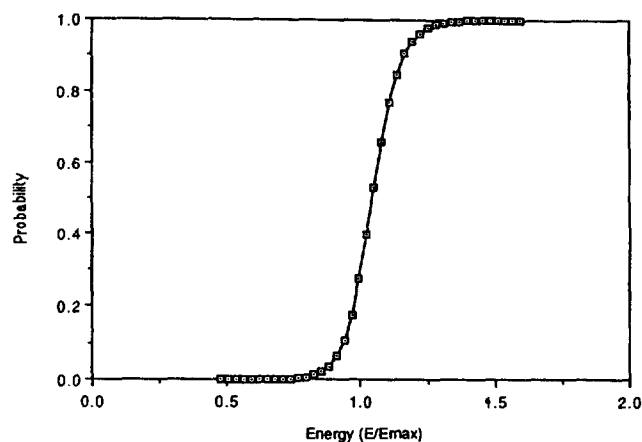
^aC. W. McCurdy and B. C. Garrett, *J. Chem. Phys.*, **84**, 2630 (1986). ^bPropagation is from $-R_{max}$ to $+R_{max}$ with 320 integration steps.

**Figure 1.** Convergence of the reaction probability.

for $R_{max}=3$ a.u., but overall, the convergence is very good for all the cases, the errors being less than 3%. The exception is the probability at $E=0.32$ kcal/mol evaluated with $R_{max}=3$ a.u. Inaccuracy in this case results from the fact that the energy is only 1/20 of the barrier height (6.6 kcal/mol), and that the difference of the energy and the value of the potential at the matching point of 3 a.u. is only 0.1 kcal/mol, which is too small for the WKB approximation to hold. Actually, the tunneling probability at this energy is only about 10^{-10} . Hence matching point of $R_{max}=3$ a.u. is sufficient for all purposes for H+H₂ system.

Figure 1 shows the convergence of the reaction probability as a function of the position of the matching point at the energy of $E=2.96$ kcal. The classical turning point at this energy is 0.95 a.u. The reaction probability evaluated by our formalism converges at about $R_{max}=2$ a.u. Figure 2 presents the reaction probability as a function of energy. The reaction probability is a monotonic increasing function of E , and at the energy of 6.6 kcal/mol, which is the barrier height of the system, the reaction probability is about 0.53. At the energy of $E/V_{max}=1.5$, the reaction probability is essentially unity. Although we choose an Eckart Barrier model for H+H₂ system for convenience, our procedure can be employed for any kind of potential surfaces. Also we believe that the accuracy of our formalism should be better for reactions between heavier systems.

Extensions to Multidimensional Systems. For multidimensional reacting systems, the computations become

**Figure 2.** Reaction probability as a function of the energy.

much more complicated. Besides the problem of increasing number of channels, the choice of the coordinates for describing the reactive scattering systems is a difficult problem. Even for the simplest multidimensional system, the collinear atom-diatom reactive collision, the "natural" reaction coordinates are not obvious at all. For chemical reactions the use of Jacobi coordinates yields a diagonal form for the kinetic energy, but in those coordinates the Hamiltonian is not separable in both the reactant and product channels.⁸ Natural reaction coordinates used by Marcus *et al.*^{23,24} approach the Jacobi coordinates for reactant and product channels, but result in the first derivative terms that are awkward to deal with, in addition to being difficult to generalize to higher dimensional systems. On the other hand, when one tries to solve Schrodinger equations in different regimes of the configuration space using the locally appropriate coordinates, the procedure introduces a complicated wave function matching procedure into the calculation. These problems arise from the necessity of the asymptotic analysis. The Jacobi coordinates are the most appropriate coordinate systems for the asymptotic analysis and different Jacobi coordinates must be used for reactants and product channels.

Since our approximate boundary conditions are *locally* determined to be imposed well before the asymptotic region, asymptotic analyses are not needed in our formalism to evaluate the reaction probability. For collinear reactive scattering system $A+BC \rightarrow AB+C$, for instance, propagation of $h^{(-)}_{R,WKB}(x)$ is performed *forward* from a matching point in the reactant side to the activated complex region with respect to R_{A-BC} , while $h^{(+)}_{R,WKB}(x)$ is propagated *backward* from a matching point in the product side with respect to R_{AB-C} . Here R_{A-BC} is the distance of the atom A to the center of mass of BC, and similarly for R_{AB-C} . Approximate boundary conditions developed by Singer *et al.*,¹³ based on the multi-channel WKB methods, may be very useful for these multidimensional systems. Alternatively, one can use the coordinates most appropriate for regimes near the activated complex for the propagations of $h^{(-)}_{R,WKB}(x)$ and $h^{(+)}_{R,WKB}(x)$, although this choice may result in nondiagonal form for the kinetic energy operator. In any cases, neither the transformations between the coordinate systems nor the complicated matching procedures are needed in our formalism. Also our procedure only needs informations on the potential surfaces

near the activated complex region, since the semiclassical boundary conditions are imposed well before the asymptotic region. Optimal basis sets for reactant and product can be employed separately. As the matching points (where approximate boundary conditions are imposed) move toward the asymptotic regime, the accuracy of the reaction probability is systematically improved, an obvious advantage over the transition state theory, for which there is no systematic way of improving the accuracy so that with sufficient computational efforts one is guaranteed of approaching the correct results.

Our procedure is similar to the detailed quantum transition state theory (DQTST) developed by Light and Altenberger-Siczek^{25,26} for reactive cross sections. They have replaced the product side potential surfaces by several model potentials to evaluate the reaction probability. Although their results were good, the question remains in their procedure as to what kind of model potentials should be used. On the other hand, our approximate boundary conditions depends locally on the matching point, being *independent of the potential surfaces beyond it*. Hence we confine the quantum calculations to a limited region near the activated complex, while DQTST still necessitates propagation in the asymptotic region.

Conclusion

Our approximate scheme, in the spirit of early asymptotic analysis, has been shown to be a highly accurate procedure for obtaining the matrix elements of Green's operator and its derivatives for evaluating the total reaction probability. Propagations are confined to a limited region near the activated complex. It is suggested that coordinates most appropriate for reactants and products can be used separately for a two-way propagation towards the activated complex region for multidimensional reactive scattering problems, obviating the need for coordinate transformation and complicated matching procedures. Results for collinear atom-diatom reactions will be published in a separate work.

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