Semiclassical transition state theory for nonseparable systems: Application to the collinear H+H₂ reaction

Sally Chapman, Bruce C. Garrett, and William H. Miller

Department of Chemistry and Inorganic Materials Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720
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Two different kinds of semiclassical approximations are used to evaluate a previously obtained quantum mechanical transition state theory rate expression. No assumptions, however, such as separability of the Hamiltonian, vibrationally adiabatic motion along a reaction coordinate, etc., are incorporated. Application is made to the collinear H+H₂ reaction, and agreement with accurate quantum scattering calculations is found to be reasonably good. The results indicate that transition state theory—provided no assumptions of separability are included—is probably as accurate quantum mechanically as it has been found to be classically for describing the threshold of chemical reactions with an activation barrier.

I. INTRODUCTION

The accurate description of the threshold region of a chemical reaction with an activation barrier is one of the few important features of chemical reaction dynamics that can not be adequately described by the usual classical trajectory methods. Because of the importance of this region for determining the thermal rate constant, however, this is a serious shortcoming of a completely classical description. The complex-valued classical trajectory approach of classical S-matrix theory² has shown that it can describe this tunneling region well, but it is often a difficult calculation to carry out and one desires simpler models which are accurate.

There have been several recent studies which indicate that the "fundamental assumption" of transition state theory—i.e., the identification of all flux through a specially chosen surface in coordinate space as reactive flux—is quite accurate for energies in the threshold region. Pechukas and McLaugherty,³ for example, have shown that within the realm of classical mechanics transition state theory is exact for sufficiently low energy; for collinear systems they have also found a simple geometrical criterion to determine a lower limit to this energy below which transition state theory is exact. Also, Chapman, Horstein, and Miller⁴ have compared the microcanonical version of classical transition state theory with a microcanonical classical trajectory calculation for the collinear and for the three-dimensional H⁺H₂ reaction. In the three-dimensional case, for example, they find that transition state theory is in essentially exact agreement with the trajectory results for energies up to about 0.3 eV above the height of the activation barrier, and even at the relatively high energy of 1 eV above the barrier height it is only 10% larger than the exact trajectory result. This means that in a strictly classical world transition state theory would give the rate constant for this reaction essentially exactly for temperatures up to thousands of degrees.

Work by Marcus⁵ and by Morokuma and Karplus⁶ has also indicated that classical transition state theory is a good approximation to classical dynamics for collision energies not too far above the barrier height.

As noted above, however, quantum effects are important in the threshold region, so that a quantum mechanical version of transition state theory is required. Previous quantum mechanical versions of transition state theory,⁷,⁸ however, incorporate other approximations—e.g., separability of the Hamiltonian about the saddle point of the potential surface, vibrationally adiabatic motion along a reaction coordinate, etc.—in addition to the fundamental assumption itself. It is our hypothesis that these additional dynamical approximations are the reason that transition state theory has given poor agreement with accurate quantum scattering calculations⁹, i.e., we believe that the fundamental assumption of transition state theory is itself accurate—as in the classical examples described above—but that it must be implemented quantum mechanically and without introducing any dynamical approximations, such as separability.

Such a theory has recently been formulated,¹⁰ i.e., a fully quantum mechanical theory which invokes the fundamental assumption of transition state theory but makes no other dynamical approximations. By introducing a semiclassical approximation for the Boltzmann operator,¹¹ the semiclassical limit of this quantum mechanical transition state theory has also been derived.¹² The "semiclassical transition state theory"¹³ leads to a very interesting and physically intuitive picture of the tunneling dynamics which characterizes the threshold region: The tunneling takes place along a periodic classical trajectory on the upside-down potential surface, and the stability parameters¹⁴ which characterize the periodic orbit appear in the theory as the generalization of the normal mode frequencies of the "activated complex."

It is important that although this model invokes a semiclassical approximation to the quantum transition state rate expression obtained in Ref. 10, no approximations such as separability, or vibrational adiabaticity, are introduced.

This paper presents the first numerical results of this semiclassical limit of quantum transition state theory, here for the simplest possible example, the collinear H⁺H₂ reaction. The agreement with quantum scattering calculations is reasonably good, and one sees, for example, how the tunneling "cuts the corner" increasingly as the energy is decreased. Section II summarizes the semiclassical limit of quantum transition state theory, and the results of the calculations are presented in Sec. IV.

Section III describes another kind of semiclassical approach to evaluating the quantum rate expression, this
based on a semiclassical approximation for the quantum mechanical phase space distribution function. The results of calculations based on this model are also presented in Sec. IV, and they too are in good agreement with accurate scattering calculations. It is important that this approach is relatively simple to implement, so that it may be a practical procedure for treating reactive systems in three dimensions.

II. SUMMARY OF PERIODIC ORBIT THEORY

The rate constant for a collinear A + BC reaction is given by

$$k_{2s}(T) = Q_s(T)^{-1}(2\pi \hbar)^{-1} \int e^{\Delta E} N(E),$$

(2.1)

where $E$ is a total energy and $Q_s(T)$ is the partition function per unit volume (actually per unit length for a collinear system) for noninteracting reactants. $N(E)$ is the "cumulative reaction probability" that was designated $P(E)$ in Ref. 12; we have made this change in notation in order to conform more closely with previous work of other researchers. Equation (2.1) is no approximation itself, and to see how the semiclassical "periodic orbit" result of Ref. 12 relates to other theories, it is illustrative to review the form taken by $N(E)$ in various quantum mechanical and classical approximations.

The dynamically exact quantum mechanical rate constant, for example, corresponds to Eq. (2.1) with $N(E)$ given in terms of reactive $S$-matrix elements which come from a quantum scattering calculation:

$$N_{QM}(E) = \sum_{n_s n_g} |S_{n_s n_g}(E)|^2,$$

(2.2)

where $n_s$ and $n_g$ denote the quantum state of the reactant and product molecules, BC and AB, respectively.

Dynamically exact classical mechanics corresponds to Eq. (2.1) with $N(E)$ given by

$$N_{CL}(E) = 2\pi \hbar \int dp \int d\mathbf{q} \delta(E - H) \delta[f(\mathbf{q})]$$

$$\times \frac{1}{2} \left[ \frac{\partial f}{\partial \mathbf{p}} \cdot \mathbf{p} / m \right] \frac{1 + (-1)^M}{2(M + 1)},$$

(2.3)

where $F$ is the number of degrees of freedom ($F = 2$ in the collinear case), $f(\mathbf{q})$ is the function of coordinates which defines the surface in configuration space, $f(\mathbf{q}) = 0$, which divides reactants and products, and $M$ is the number of time a trajectory which begins with initial conditions $(p, \mathbf{q})$ on the dividing surface re-crosses this surface as time is run forward to $+\infty$ and backward to $-\infty$. $N_{CL}(E)$ is independent of the particular choice of the dividing surface.

Classical transition state theory corresponds to Eq. (2.1) with $N(E)$ given by Eq. (2.3) with the assumption $M = 0$, i.e., the assumption that there are no trajectories which re-cross the dividing surface;2,3 this result, of course, is not invariant to the choice of the dividing surface. Thus,

$$N_{CL,TST}(E) = 2\pi \hbar \int dp \int d\mathbf{q} \delta(E - H) \frac{1}{2} \left[ \frac{\partial f}{\partial \mathbf{p}} \cdot \mathbf{p} / m \right].$$

(2.4)

If the coordinate $q_F$ measures distance normal to the dividing surface, then

$$f(q) = q_F,$$

and it is not hard to show that Eq. (2.4) then becomes

$$N_{CL,TST}(E) = h^{-1/2} \int dp_{F1} \int d\mathbf{q}_{F1} h(E - H_{F1})$$

(2.5)

where $h(s)$ is the step function

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

and the $F - 1$ dimensional phase space average is over all degrees of freedom other than $q_F$; $H_{F1}$ is the Hamiltonian for the remaining $F - 1$ degrees of freedom with the potential energy surface evaluated at $q_F = 0$. For the collinear case, Eq. (2.5) reads

$$N_{CL,TST}(E) = \int dp_{F1} \int du \left( \int d\mathbf{u} \left( E - \frac{p_{F1}^2}{2m} - V(u, 0) \right) \right),$$

(2.6)

where $u$ is the coordinate along the dividing surface (actually a dividing line in the collinear case) and $V(u, s)$ is the total potential energy function; $s$ is the coordinate perpendicular to the dividing surface. (See Fig. 1 of Ref. 10.) It is clear from Eqs. (2.5) and (2.6) that $N_{CL,TST}(E)$ is the classical approximation to the number of quantum states for the system with $F - 1$ degrees of freedom which have energy less than or equal to $E$.

The conventional quantum mechanical version of transition state theory is meaningful only if the potential is assumed to be separable;

$$V(u, s) = V_1(u) + V_2(s);$$

(2.7)

$V_1(u)$ is a potential well, and $V_2(s)$ a potential barrier. If $P_{tot}(E_s)$ is the one-dimensional tunneling probability for the $s$ degree of freedom with translational energy $E_s$, and if $\{\epsilon_n\}, n = 0, \ldots$ are the vibrational eigenvalues for the potential well $V_1$, then $N(E)$ is given in the separable limit of quantum mechanical transition state theory by

$$N_{sep,QM,TST}(E) = \sum_n P_{tot}(E - \epsilon_n).$$

(2.8)

Although the vibrationally adiabatic model does not assume separability in precisely the same form as Eq. (2.7), it leads to a function $N(E)$ of the same form as Eq. (2.8).

The more general quantum mechanical transition state theory derived in Ref. 10 corresponds to Eq. (2.1) with $N(E)$ given by

$$N_{QM,TST}(E) = 2\pi \hbar \int \left[ \delta(E - H) \delta(s) \frac{1}{2} \left| \frac{\partial q_F}{\partial \mathbf{p}} \right| \right],$$

(2.9)

which one recognizes as the obvious quantum mechanical version of Eq. (2.4). The semiclassical limit of this expression involves a periodic trajectory on the upside-down potential surface. If $\theta(E)$ is the classical action integral (in units of $\hbar$) along this periodic trajectory with energy $E$ and $u(E)$ the stability parameter which characterizes it (it is an unstable periodic trajectory), then the semiclassical limit of Eq. (2.9) is...
\[ N_{\text{sc}} \cdot \text{tst}(E) = \sum_{n=0}^{\infty} \frac{1}{1 + \exp[2\theta(E) + (n + \frac{1}{2})\hbar \omega(E)]]} \] 

The period of the periodic trajectory is related to the action integral by
\[ \tau(E) = -2\hbar \theta'(E), \]
and it is useful to define the frequency \( \omega(E) \) by
\[ \omega(E) = \frac{\dot{u}(E)}{\tau(E)}; \]

Eq. (2.10) then reads
\[ N_{\text{sc}} \cdot \text{tst}(E) = \sum_{n=0}^{\infty} \frac{1}{1 + \exp[2\theta(E) + 2\theta'(E)\hbar \omega(E)(n + \frac{1}{2})]} \]

If the potential function is separable, as in Eq. (2.16), then the action integral \( \theta(E) \) is the ordinary one-dimensional barrier penetration integral for the potential barrier \( V_1(s) \), and \( \omega \)—which is not a function of energy in this case—is the harmonic frequency for the potential well \( V_1(u) \).

Equation (2.11), however, actually gives poor agreement with the exact quantum mechanical \( N_{\text{qm}}(E) \) of Eq. (2.2), and this can be understood in the following way. For a separable potential function [Eq. (2.7)] Eq. (2.8) is the correct result for quantum mechanical transition state theory. The one-dimensional WKB approximation for the tunneling probability is
\[ P_{\text{tst}}(E) = \frac{1}{1 + \exp[2\theta(E)]}, \]

where \( \theta \) is the barrier penetration integral for the potential barrier \( V_1(s) \) with translational energy \( E \). With this semiclassical approximation for the one-dimensional tunneling probability and with a harmonic approximation to the energy levels of the potential well \( V_1(u) \),
\[ \epsilon_n = (n + \frac{1}{2})\hbar \omega, \]

Eq. (2.8) becomes
\[ N_{\text{exp \cdot \text{tst}}}(E) \approx \sum_{n=0}^{\infty} \frac{1}{1 + \exp[2\theta(E) + (n + \frac{1}{2})\hbar \omega]} \]

This is seen to be identical to Eq. (2.11) if one makes the approximation
\[ \theta(E - (n + \frac{1}{2})\hbar \omega) \approx \theta(E) - \theta'(E)\hbar \omega(n + \frac{1}{2}), \]
i.e., if one keeps only the lowest order term in an expansion in powers of \( \hbar \). The approximation in Eq. (2.15) is certainly consistent with the semiclassical nature of the theory, but for very quantumlike systems, such as \( \text{H} + \text{H}_2 \), the frequency \( \omega \) is large enough to make Eq. (2.15) a poor approximation.

The idea for correcting Eq. (2.11), therefore, is to identify the exponent as the first two terms of a Taylor series expansion in powers of \( \hbar \) and then to “unexpand” it. One thus defines the energy \( E_n \) so that
\[ \theta(E_n) = \theta(E) - \theta'(E)\hbar \omega(E)(n + \frac{1}{2}), \]

to lowest order in \( \hbar \), and this leads to the choice
\[ E_n = E - \hbar \omega(E_n)(n + \frac{1}{2}); \]
i.e., \( E_n \) is the root of this equation (which is easily solved by successive substitution). The interpretation is that \( E_n \) is the translational energy for motion along the “reaction coordinate”—i.e., the periodic path—if the transverse degree of freedom is in vibrational quantum state \( n \). The modified expression for semiclassical transition state theory becomes
\[ N_{\text{sc}} \cdot \text{tst}(E) = \sum_{n=0}^{\infty} \frac{1}{1 + \exp[2\theta(E_n)]}, \]

with \( E_n \) determined for a given value of \( E \) by Eq. (2.16).

In the separable limit the frequency \( \omega(E) \) becomes energy independent, and Eqs. (2.16) and (2.17) give Eq. (2.14); the only approximation in this case is the WKB approximation for one-dimensional tunneling, and one knows this to be quite adequate. The interest in the semiclassical version of transition state theory, however, is for the nonseparable case, and Sec. IV gives numerical results for the comparison of Eqs. (2.16) and (2.17) with the exact quantum result for \( N(E) \), Eq. (2.2).

### III. A SEMICLASSICAL PHASE SPACE DISTRIBUTION

The quantum mechanical rate expression of transition state theory obtained in Ref. 10 was shown to be equivalent to the completely classical expression if the classical distribution function \( h^n e^{-\hbar H'/\hbar} \), replaced by the Wigner distribution function \( W(p, q) \).

\[ W(p, q) = h^n \int \frac{dq}{q} e^{i(p \cdot q) / \hbar / 2} \left(q + \frac{1}{2} \frac{q \cdot q}{2} + |q| e^{i\hbar H'} - q - \frac{1}{2} q' \right) \]

That is, the rate constant of quantum transition state theory \( k_{\text{qm}} \) is
\[ k_{\text{qm}}(T) = N_q(T) \int dp \int dq W(p, q) \frac{1}{2} \left| \frac{\delta f(q)}{\delta q} \right| \frac{p}{m} \]

\[ f(q) = 0 \text{ defining the “dividing surface” in the usual way.} \]

This section describes another kind of semiclassical approximation for the rate constant which is obtained by introducing a semiclassical approximation for the quantum mechanical phase space distribution function. The distribution function we use is suggested by expressions which arose in considering the classical path approximation for the Boltzmann operator. Thus the quantum partition function, which is given in terms of the distribution function by
\[ Q = \int dq_0 \int dq_0 W(p_0, q_0), \]

is also given by
\[ Q = \int dq_0 \left| \langle q_0 | e^{-\hbar H/\hbar} | q_0 \rangle \right|^2 \]

Using the classical path approximation for the matrix elements in Eq. (3.4) and changing variables of integration (see Ref. 11 for more details) gives the following semiclassical approximation for the partition function:
\[ Q = h^n \int dp \int dq_0 \exp \left( - \frac{2}{\hbar} \int_0^{\hbar / \hbar} dt H'(t) \right) \]

where \( H'(t) = H(p(t), q(t)) \) is the value of the Hamiltonian
at "time" \( \tau \), with \( q(\tau) \) and \( p(\tau) \) determined by the equations of motion
\[
q'(\tau) = \mathcal{H}/\hbar p = p/m, \quad (3.6a)
\]
\[
p'(\tau) = \mathcal{H}/\hbar q = -\hbar V/\hbar q \quad (3.6a)
\]
[note the + sign in Eq. (3.6b)] with initial conditions
\[
q(0) = q_0, \quad (3.7a)
\]
\[
p(0) = p_0. \quad (3.7b)
\]

Equation (3.6) describes a classical trajectory in the time variable \( \tau \) on the upside-down potential surface \(-V(q)\).

Comparing Eqs. (3.3) and (3.5), the temptation is to identify the integrand of Eq. (3.5) as an approximation to the Wigner distribution function. Liouville's theorem, however, implies that
\[
|dp_0 dq_0| = dp(\tau) dq(\tau),
\]
for any \( \tau \), so it follows simply that
\[
Q = \int dq_0 \left| dp_0 \right| \exp \left( -\frac{\hbar}{\mathcal{H}} \int_{t_0}^{t_0 + \hbar/\mathcal{H}} d\tau \mathcal{H}(\tau) \right), \quad (3.8)
\]
for any value of \( t_0 \), with \( (q(\tau), p(\tau)) \) still determined by Eq. (3.6) with the initial conditions in Eq. (3.7). Although \( Q \) is independent of the choice for \( t_0 \) in Eq. (3.8), the integrand—the function of \( p_0 \) and \( q_0 \) which one wishes to identify as the distribution function—is not.

The choice for \( t_0 \) which seems most justified is the one which is most symmetrical,
\[
\tau_0 = \hbar \beta/4; \quad (3.9)
\]
one then identifies the integrand of Eq. (3.8) as the semiclassical distribution function:
\[
W(p_0, q_0) = \exp \left( -\frac{\hbar}{\mathcal{H}} \int_{t_0}^{t_0 + \hbar/\mathcal{H}} d\tau \mathcal{H}(\tau) \right), \quad (3.10)
\]
where the trajectory \((p(\tau), q(\tau))\) is determined by Eqs. (3.6) and (3.7). This choice for \( \tau_0 \) is reinforced by the fact that for a one-dimensional parabolic barrier,
\[
V(x) = -\frac{1}{2} m \omega^2 x^2, \quad (3.11)
\]
the one-dimensional tunneling coefficient \( \Gamma \),
\[
\Gamma = 2 \pi \hbar \beta \chi(x^2)^{-\chi} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp \ W(p, x) \delta(x) \frac{1}{2} \left| \frac{1}{2} \right| \quad (3.12)
\]
which one obtains with the distribution function in Eq. (3.10) is found to be
\[
\Gamma = \frac{\hbar}{2} \hbar \omega \beta / \sin(\hbar \omega \beta), \quad (3.13)
\]
which is the exact result for this case. The choice \( \tau_0 = \hbar \beta/4 \) is the only one which gives the correct tunneling coefficient, Eq. (3.13), for the parabolic barrier. One can also show that Eq. (3.10) gives the exact partition function for a harmonic oscillator, but any value of \( \tau_0 \) in Eq. (3.8) will do this.

One already knows that the distribution function of Eq. (3.10) gives partition functions quite well,¹¹ and the only other feature that it must describe for the present application is tunneling. It was noted above that it gives the exact result for a one-dimensional parabolic barrier, but to get a more revealing measure of its accuracy in this regard we have considered tunneling through the one-dimensional Eckart barrier,
\[
V(x) = V_0 \operatorname{sech}^2(x/\alpha). \quad (3.14)
\]
This is a convenient test case, since Johnston¹⁶ has tabulated the exact value of \( \Gamma \) for the potential for a wide range of the two dimensionless parameters
\[
u = \frac{\hbar \beta}{\alpha} \left( \frac{2 V_0}{m} \right)^{1/2}, \quad (3.15a)
\]
\[
\alpha = \pi \hbar \left( \frac{2 m V_0}{\mathcal{H}} \right)^{1/2}; \quad (3.15b)
\]
\( \nu \) is proportional to \( 1/T \), \( T \) the temperature, and \( \alpha \) is a measure of how quantalike the system is (the smaller \( \alpha \), the more quantalike).

Figure 1 shows the comparison between the exact tunneling factor \( \Gamma \) (solid line) and the result given by Eqs. (3.10) and (3.12) (broken line) as a function of \( \nu \) for two values of \( \alpha \). (Note that
\[
\lim_{\nu \to 0} \Gamma = 1
\]
in all cases.) The one-dimensional barrier for the \( H + H_2 \) reaction, for example, corresponds to \( \alpha \approx 10-12 \), so that \( \alpha = 4 \) is considerably more quantalike than the \( H + H_2 \) system, and \( \alpha = 20 \) is more classical-like. These one-dimensional results are therefore quite encouraging and suggest that the distribution function in Eq. (3.10) is sufficiently accurate so far as the one-dimensional aspect of tunneling is concerned.

For the collinear \( H + H_2 \) reaction, Eq. (3.2), with Eq. (3.10) for the distribution function, gives the rate constant as
\[
k_{\text{a} = 4} = \left( \frac{2 \pi \hbar}{m} \right)^{\alpha} \int_{-\infty}^{\infty} dp \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dp \left| \frac{1}{2} \right| \quad (3.16)
\]
\[
\times \exp \left( -\frac{\hbar}{\mathcal{H}} \int_{-\infty}^{\infty} d\tau \mathcal{H}(\tau) \right). \quad (3.16)
\]
where \( H(t) \) is evaluated along the classical trajectory that evolves on the upside-down potential surface with initial conditions
\[
s(0) = 0, \quad u(0) = u, \quad p_x(0) = p_x, \quad p_y(0) = p_y; \quad (3.17)
\]
one integrates the equations of motion forward from \( \tau = 0 \) to \( \tau = \hbar / 4 \), and backward from \( \tau = 0 \) to \( \tau = -\hbar / 4 \), in order to compute the exponent in the integrand of Eq. (3.16). The three-dimensional integral is evaluated numerically, and in higher-dimensional systems one would probably resort to Monte Carlo integration methods.

Finally, it should be noted that within this model it is a trivial matter to include the full classical dynamics of the reaction in real time, eliminating the need to make the fundamental assumption itself; this follows from the discussion in Sec. V of Ref. 10. For the collinear \( \text{H} + \text{H}_2 \) reaction, for example, the necessary modification to Eq. (3.16) is simply to insert in the integrand the factor
\[
\frac{1 + (-1)^M}{2(M+1)}, \quad (3.18)
\]
where \( M \) is the number of times the trajectory, with the initial conditions of Eq. (3.17), crosses the line \( s = 0 \) as \( \text{real} \) time is run forward to \( +\infty \) and backward to \( -\infty \).
(Note that this trajectory is on the ordinary, right-side up potential surface.) This procedure essentially amounts to a Keck-type\textsuperscript{17} classical trajectory calculation with the modification that the classical distribution function is replaced by the above semiclassical one. One thus carried out a classical trajectory calculation in real time to determine the “transmission coefficient,” Eq. (3.18), and then with the same initial conditions carries out another trajectory calculation on the upside-down potential surface to determine the value of the semiclassical distribution function for the given initial point in phase space. The reader should recognize that a calculation such as this should be quite practical even for three-dimensional \( \text{A} + \text{BC} \) collision systems.

IV. RESULTS

Consider first the results of the periodic orbit model described in Sec. II. Calculations were carried out for the collinear reaction
\[
\text{H} + \text{H}_2 \rightarrow \text{H}_3 + \text{H} \quad (4.1)
\]
using the Trauhar–Kuppermann\textsuperscript{18} potential surface for \( \text{H}_2 \) (a Wall–Porter\textsuperscript{19} fit to the scaled Shavitt–Stevens–Minn–Karplus\textsuperscript{20} potential surface) and also for the Porter–Karplus\textsuperscript{21} potential surface.

Figure 2 shows the periodic trajectory for two different energies \( E \), one just below the barrier and one far below it. So long as \( E < V_{SP} \) (the only region considered in this paper) the trajectories are all real valued and relatively easy to find because of their high symmetry. There is only one such trajectory for a given energy. As \( E = V_{SP} \), the trajectory becomes infinitesimally short in length and moves to the saddle point of the
potential surface; for lower energies the periodic trajectory cuts the corner of the potential surface, the more so the lower the energy.

Figures 3 and 4 show the action integral $\theta(E)$ and the stability parameter $\omega(E)$ as a function of the total energy for the Truhlar–Kuppermann potential surface. One notes that

\[
\lim_{E \to E_{sp}} \theta(E) = 0, \quad (4.2a)
\]

\[
\lim_{E \to E_{sp}} \omega(E) = \omega^s, \quad (4.2b)
\]

where $\omega^s$ is the symmetric stretch frequency at the saddle point, the quantity which appears in conventional transition state theory. It is tempting to suspect that the zero energy limit of $\omega(E)$ might be $\omega_{H_2}$, the vibrational frequency of the isolated $H_2$ molecule:

\[
\lim_{E \to 0} \omega(E) = \omega_{H_2}. \quad (4.3)
\]

Although this is clearly the trend seen in Fig. 4, it does not appear to be quantitatively true.

The cumulative reaction probability for the two potential surfaces is shown in Figs. 5 and 6. The solid lines are the exact quantum mechanical values, Eq. (2.2), and the dashed lines are the semiclassical transition state theory approximation given by Eq. (2.17). The agreement between the two is seen to be reasonably good. The accuracy of this semiclassical transition state theory is, in fact, almost as good as the results of classical $S$-matrix theory.\(^1\)

The results based on the semiclassical phase space distribution of Sec. III are shown in Figs. 7 and 8; the quantity shown is the rate constant for Reaction (4.1) as a function of temperature on the Truhlar–Kuppermann\(^18\) and Porter–Karplus\(^21\) potential surfaces, respectively. For comparison the rate constant of conventional transition state theory,

\[
k_{3-2} = Q_{e} \frac{kT}{h} \left[ 2 \sinh \left( \frac{\hbar \omega^s \beta}{2} \right) \right]^{-1}, \quad (4.4)
\]

where $\omega^s$ is the symmetric stretch frequency at the saddle point, is also shown (the lower solid line). No tunneling factor is included in Eq. (4.4), since Truhlar and Kuppermann\(^5\) find that the use of any of the variety of one-dimensional tunneling corrections tends to do more harm than good. One sees that this semiclassical approximation to quantum transition state theory has gone a long way toward correcting the deficiencies of conventional transition state theory. At 200°K, for example, conventional transition state theory is about a factor of 30 and 70 too small, respectively, for the Truhlar–Kuppermann and Porter–Karplus potential surfaces, while this semiclassical approximation to
quantum transition state theory is correspondingly a factor of 1.6 and 2.3 too small.

Note added in proof. The rate constant for the D+H$_2$ → DH + H reaction in full 3-D has been computed at 300 and 1000 °K using the semiclassical phase space distribution of Sec. III. The Yates–Lester [A. C. Yates and W. A. Lester, Chem. Phys. Lett. 24, 305 (1974)] fit to Liu’s [B. Liu, J. Chem. Phys. 58, 1925 (1973)] potential surface was used, and the preliminary results agree well with the measurements of Mitchell and Le Roy [D. N. Mitchell and D. J. Le Roy, J. Chem. Phys. 58, 3449 (1973)]; log k (cm$^3$/molecule·sec) = 3.2 ± 0.2 (8.26) at 300 °K, and log k = 12.1 ± 0.2 (12.04) at 1000 °K, the experimental results being the values in parenthesis and the error estimates being the residual error in the Monte Carlo evaluation of the phase space integrals.

V. CONCLUDING REMARKS

The results of both of the semiclassical approximations to the quantum transition state theory rate constant are in reasonably good agreement with the corresponding quantum scattering calculations. The indication is, therefore, that the fundamental assumption of transition state theory is valid in the threshold region of this reaction quantum mechanically, just as it has been seen to be classically. It is not possible to say whether the remaining discrepancy is due to transition state theory itself or to the approximations used to evaluate the quantum expression. Others ways of evaluating the quantum rate expression are being explored, and it may be that they can help answer this question.

The semiclassical limit summarized in Sec. II is the theoretically more appealing of the two approaches described in this paper. It is obtained from a well established prescription—the stationary phase approximation—and the resulting periodic trajectory and its stability parameters have interesting physical interpretations. The approach based on the semiclassical distribution function of Sec. III, however, is clearly the more practical of the two, and it seems to be no less accurate. It would certainly seem that calculations of this type are feasible for three-dimensional A + BC reactive systems, and applications such as these are planned.

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2E. Wigner, Trans. Faraday Soc. 34, 29 (1938). Wigner refers to what we call the “fundamental assumption” as the third assumption; in the classical version of the theory it is the assumption that no trajectories cross the dividing surface more than once.


7See, for example, H. Eyring, Trans. Faraday Soc. 34, 41 (1938), or any textbook on chemical kinetics.

8A. Marcus, J. Chem. Phys. 45, 2630 (1966); 46, 959 (1967); see also Ref. 5.

9See, for example, D. G. Truhlar and A. Kuppermann, Chem. Phys. Lett. 9, 269 (1971).


16H. S. Johnston, Gas Phase Reaction Rate Theory (Ronald, New York, 1966), p. 44.


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