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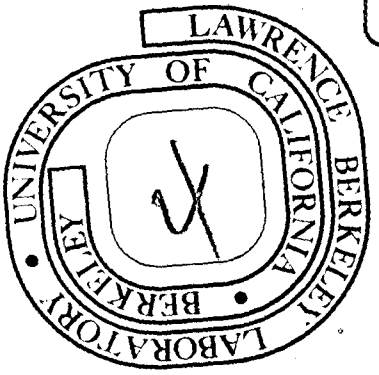

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QUANTUM MECHANICAL TRANSITION STATE THEORY AND A NEW SEMICLASSICAL MODEL FOR REACTION RATE CONSTANTS*

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ABSTRACT

An "exact" quantum mechanical transition state theory is defined, i.e., a model which invokes the basic transition state idea to calculate the rate of a chemical reaction but which is free of any auxiliary approximations. Most importantly, for example, it is not necessary to assume that the Hamiltonian is separable about the saddle point. It is argued that this model should provide an accurate description of the threshold region of the reaction where quantum effects are most significant. Finally, an even more general model, a new kind of semiclassical approximation, is presented which is essentially a synthesis of this quantum mechanical transition state model and the completely classical trajectory procedure for determining the rate constant; at sufficiently high temperatures quantum effects become neglible, so that the correct rate constant is obtained, while at low temperature the correct result is obtained because the transition state model becomes valid.

I. INTRODUCTION

For many purposes classical trajectory calculations[1] provide as complete a solution to molecular collision dynamics as is ever called for under practical experimental conditions. True, there are quantum effects, such as interference and tunneling, which can only be described by quantum mechanical[2] or semi-classical[3] collision theories, but if the process of interest is "classically allowed"--i.e., has a cross section (or rate constant) which is not too small--these are usually quenched by averaging over scattering angle, collision energy, and/or quantum states which pertains to anything other than the perfect experiment (a completely state-selected differential cross section measurement).

Classical trajectory methods are in general not useful, however, for treating "classically forbidden" processes,[4] i.e., those which do not take place via ordinary classical mechanics. One of the most important examples of such a process is tunneling in the threshold region of a chemical reaction which has an activation barrier. Since it is this threshold region of the cross section which is most important for determining the rate constant at temperatures comparable to and below the barrier height, this short-coming of standard trajectory methods leaves an important gap in one's ability to treat kinetic phenomena theoretically.

Low collision energy and a high activation barrier, however, are the ideal conditions for the applicability of transition

state theory.[5] The cases in which transition state theory has been compared[6] with accurate quantum scattering calculations, though, show quite poor agreement in the low temperature region where quantum effects are important, even when tunneling corrections are applied in any of several different ways. The reason for this failure of transition state theory is, in my opinion, the failure of the assumption of separability of the Hamiltonian about the saddle point, a feature which is an inherent part of standard transition state theory; arguments supporting this point of view are presented below.

The goal of this paper, therefore, is to obtain an "exact" quantum mechanical transition state theory, i.e., an approximation to the reaction rate constant which invokes the transition state approximation but no subsidiary ones (such as separability); surprisingly, no such formulation has previously been given.[7,8] It is suggested that this should provide an accurate description of the threshold region of a chemical reaction. In the process there will also emerge a semiclassical approximation for the rate constant which goes beyond this quantum transition state approximation, incorporating the full classical dynamics of the reaction within a quantum framework.

One of the motivating factors in our pursuit of a correct quantum mechanical transition state theory has been the observation of how well classical transition state theory agrees with classical dynamics, i.e., trajectory calculations. For

the collinear H + H_2 reaction, for example, classical transition state theory agrees exactly with completely classical (not quasi-classical) trajectory calculations in the energy region just above the classical threshold;[9] this conclusion also follows from the work of Pechukas and McLafferty.[10] Quantum effects in this energy region are enormous, however, so that classical mechanics is a poor approximation to reality. The implication, nevertheless, is that the transition state idea is a good one provided it can be implemented quantum mechanically.

Another indication that the transition state idea may be valid--but that the separability approximation is poor--comes from the quantum scattering calculations of Kuppermann, Adams, and Truhlar[11] and the "classical S-matrix calculation of George and Miller,[12] both for the collinear H + H_2 system. The streamlines of quantum flux[11] show smooth flow at low energies from the reactant to product regions of configuration space, implying that the dynamics is "straight through" the transition region. (At high energies the streamlines become contorted.) This same inference comes from the classical S-matrix calculations,[12] where the complex-valued trajectory which tunnels from reactants to products move monotonically through the transition region. Classical transition state theory is exact, however, if all trajectories move through the transition region without re-crossing the dividing surface,[10] so the fact that the quantum and semiclassical calculations show this "straight through" dynamics suggests the transition

state model is a valid one at these energies. The quantum[11] and semiclassical[12] calculations also show, however, that the tunneling does not take place through the saddle point itself but severely "cuts the corner",[13] implying that separability of the Hamiltonian is a poor approximation at these energies.

The organization of the paper is as follows: Section II begins with the quantum mechanical expression for the rate constant as obtained from quantum scattering theory and through a sequence of manipulations casts it into a form as close as possible to transition state theory, i.e., in the form of a Boltzmann average of a flux operator. Section III discusses the classical expression for the rate constant and observes a strikingly simple relation between the classical and quantum rate expressions. Section IV introduces the transition state approximation, first classically and then quantum mechanically, obtaining the desired quantum mechanical transition state rate expression; it is seen that the traditional expression[5] involving quantum partition functions and tunneling correction factor is obtained if the separability approximation is made. Section V then presents a new kind of semiclassical model which has several quite attractive features: it is essentially a synthesis of this quantum transition state model and numerically exact classical dynamics, and thus provides another way--other than classical S-matrix theory[3]--of using numerically computed classical trajectories as input to a quantum mechanical theory.

II. RATE EXPRESSION FROM QUANTUM SCATTERING THEORY

For simplicity of presentation I treat a collinear A + BC → AB + C reaction explicitly, but it should be clear that with fairly obvious generalizations of notation the results apply to bimolecular reactive systems in general. If "a" denotes the initial arrangement, A + BC, and "b" the final arrangement, AB + C, then the standard expression for the equilibrium rate constant (i.e., the rate summed over final vibrational states of AB, and Boltzmann averaged over initial vibrational states of BC and over initial translational energy) is

$$k_{b\leftarrow a}(T) = (2\pi\mu kT)^{-1/2}\, Q_{BC}^{-1} \sum_{n_a,n_b} \int_0^\infty dE_1\, e^{-\beta(E_1 + \varepsilon_{n_a})} \times |S_{n_b,n_a}(E_1)|^2 \quad , \tag{2.1}$$

where $\beta \equiv (kT)^{-1}$, μ is the reduced mass for translation in arrangement a, n_a (n_b) is the vibrational quantum number of BC (AB), E_1 is the initial translational energy, $S_{n_b,n_a}(E_1)$ is the S-matrix for the reactive process (obtained from a quantum scattering calculation), and Q_{BC} the vibrational partition function of BC:

$$Q_{BC} = \sum_{n_a} e^{-\beta\varepsilon_{n_a}} \quad , \tag{2.2}$$

ε_{n_a} denoting the vibrational energy levels of BC. An equivalent, but more suggestive expression for the rate is

$$k_{b\leftarrow a}(T) = \frac{kT}{h} Q_a^{-1} \sum_{n_a,n_b} \int_o^\infty d(\beta F_1)\, e^{-\beta(E_1 + \varepsilon_{n_a})}$$

$$\times \left|S_{n_b,n_a}(E_1)\right|^2 \quad , \tag{2.3}$$

where Q_a is the total partition function per unit volume (actually per unit length for this collinear system) for the unperturbed A + BC system; i.e.,

$$Q_a \equiv \mathrm{tr}\,(e^{-\beta H_o}) \tag{2.4a}$$

$$= Q_{BC}\,(2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dP\, \exp(-\beta P^2/2\mu) \quad , \tag{2.4b}$$

"tr" denoting a quantum mechanical trace. [For the A + BC → AB + C reaction in three dimensions the rate expression is the natural extension of Eq. (2.3) and (2.4):

$$k_{b\leftarrow a}^{3d} = \frac{kT}{h} Q_a^{-1} \sum_{\substack{n_a,j_a,\ell_a,\\ n_b,j_b,\ell_b,J}} (2J+1) \int_o^\infty d(\beta E_1)\, e^{-\beta(E_1 + \varepsilon_{n_a,j_a})}$$

$$\times \left|S_{n_b\, j_b\, \ell_b, n_a\, j_a\, \ell_a}(J,E_1)\right|^2 \quad , \tag{2.5a}$$

where

$$Q_a = Q_{BC}\,(2\pi\hbar)^{-3} \int d_3\underset{\sim}{P}\, e^{-\beta P^2/2\mu} \tag{2.5b}$$

$$Q_{BC} = \sum_{n_a,j_a} (2j_a + 1)\, e^{-\beta\varepsilon_{n_a,j_a}} \quad , \tag{2.5c}$$

where the indices denote the usual[14] quantities.]

The first step in re-writing Eq. (2.3) in a more convenient form is to introduce the idea of flux through a surface.[15] Consider

first the surface S_1 (a "surface" in two-dimensional coordinate space is actually a line) shown in Figure 1 and defined by the equation

$$R_o - R = 0 \quad , \tag{2.6}$$

R_o being some asymptotically large value of the translational coordinate R; r is the vibrational coordinate of BC. For a wavefunction $\Psi(r,R)$ the flux through surface S_1 is

$$- \mathrm{Re} \int_{-\infty}^{\infty} dr \;\; \Psi(r,R)^* \frac{\hbar}{i\mu} \frac{\partial}{\partial R} \Psi(r,R) \Big| R = R_o \quad , \tag{2.7}$$

where Re denotes "real part of", and where positive flux is associated with decreasing R; i.e., the positive direction of flux is chosen in the "direction of reaction". The scattering wavefunction $\Psi_{p_1 n_a}(r,R)$, the solution of the Schrödinger equation--

$$(H - E) \Psi_{p_1 n_a} = 0 \tag{2.8}$$

with

$$E = P_1^2/2\mu + \varepsilon_{n_a}$$

--which corresponds to an incident wave in arrangement a with initial vibrational state n_a, has the asymptotic form

$$\Psi_{p_1 n_a}(r,R) \sim - \frac{e^{-ik_{n_a} R}}{(2\pi\hbar)^{1/2}} \phi_{n_a}(r)$$

$$+ \sum_{n_a'} \frac{e^{ik_{n_a'} R}}{(2\pi\hbar)^{1/2}} \phi_{n_a'}(r) \left(\frac{v_{n_a}}{v_{n_a'}} \right)^{1/2} S_{n_a', n_a}(E_1) \quad , \tag{2.9}$$

where

$$E_1 = P_1^2/2\mu$$

$$k_n = [2\mu(E - \varepsilon_n)]^{1/2}/\hbar$$

$$v_n = \hbar k_n/\mu \quad ;$$

v_n is the asymptotic velocity for channel n. (This normalization for the translational functions corresponds to delta function normalization on the momentum scale.) Since Eq. (2.9) is valid for large R, it can be used to compute the flux through surface S_1; by making use of the fact that the vibrational functions $\{\phi_n(r)\}$ are orthonormal, it is then a simple matter to show that Eqs. (2.7) and (2.9) give

$$-\mathrm{Re} \int_{-\infty}^{\infty} dr\ \Psi_{P_1 n_a}(r,R)^* \frac{\hbar}{i\mu} \frac{\partial}{\partial R} \Psi_{P_1 n_a}(r,R)$$

$$= v_{n_a} (2\pi\hbar)^{-1} \left[1 - \sum_{n_a'} |S_{n_a', n_a}(E_1)|^2\right] \quad . \tag{2.10}$$

In the asymptotic region of arrangement b, the product region, the wavefunction $\Psi_{P_1 n_a}$ --since it corresponds to an incident wave in arrangement a--has only outgoing waves:

$$\Psi_{P_1 n_a} \sim \sum_{n_b} \frac{e^{ik_{n_b} R_b}}{(2\pi\hbar)^{1/2}} \phi_{n_b}(r_b) \left(\frac{v_{n_a}}{v_{n_b}}\right)^{1/2} S_{n_b, n_a}(E_1) \quad , \tag{2.11}$$

where R_b and r_b are the translational and vibrational coordinates, respectively, of arrangement b, AB + C. (The subscript "a" was omitted from the coordinates of that arrangement to keep the notation uncluttered.) It is easy to show that the flux from this wavefunction

through surface S_2 (see Figure 1) defined by

$$R_o - R_b = 0 \quad , \tag{2.12}$$

is given by

$$v_{n_a} (2\pi\hbar)^{-1} \sum_{n_b} |S_{n_b,n_a}(E_1)|^2 \quad . \tag{2.13}$$

Unitarity, however--i.e., the fact that

$$1 = \sum_{n'_a} |S_{n'_a,n_a}(E_1)|^2 + \sum_{n_b} |S_{n_b,n_a}(E_1)|^2 \tag{2.14}$$

--shows that the flux through surfaces S_1 and S_2, Eqs. (2.10) and (2.13), are the same. In fact, the flux through <u>any</u> surface which divides reactant and product configuration space is the same; this follows because the flux from a time-independent wavefunction through a <u>closed</u> surface is zero (the quantum mechanical continuity equation)[15]

$$\mathrm{Re} \oint d\vec{S} \cdot \psi^* \frac{\hbar}{i\mu} \vec{\nabla} \psi = 0 \quad . \tag{2.15}$$

Since surfaces S_1 and S_2 can be made into one closed surface by joining them with segments at infinity, and since there is no flux through these segments at infinity, the flux into the closed "volume" through S_1 must equal to the flux out of the closed "volume" through S_2. Thus the flux in the reactive direction through any surface which divides reactant and product configuration space in this manner must be the same.

It is convenient to write the flux integral as a volume, rather than a surface integral. If the surface is defined more generally by the equation

$$f(r,R) = 0 \quad , \tag{2.16}$$

with $f(r,R) < 0$ (>0) being the reactant (product) region of configuration space, then the flux through this surface can be written as the volume integral

$$\mathrm{Re} \int d\underset{\sim}{q}\ \delta[f(\underset{\sim}{q})]\ \Psi^*(\underset{\sim}{q})\ \frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{v}\ \Psi\ (\underset{\sim}{q}) \tag{2.17}$$

$$\equiv \mathrm{Re} \langle \Psi | F | \Psi \rangle \quad ,$$

where $\underset{\sim}{q} \equiv (r,R)$, and the components of the velocity operator are $v_k = \frac{\hbar}{i m_k} \frac{\partial}{\partial q_k}$, $k = 1, 2$; the operator F is thus defined by

$$F = \delta[f(\underset{\sim}{q})]\ \frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{v} \quad . \tag{2.18}$$

Eqs. (2.10) and (2.13) can now be written as

$$(2\pi\hbar)^{-1} \sum_{n_b} \left| S_{n_b,n_a}(E_1) \right|^2 = v_{n_a}^{-1}\ \mathrm{Re} \langle \Psi_{P_1 n_a} | F | \Psi_{P_1 n_a} \rangle \quad , \tag{2.19}$$

and substitution of this into Eq. (2.1) or (2.3) gives

$$k_{b \leftarrow a} = Q_a^{-1} \sum_{n_a} \int_0^\infty dE_1\ e^{-\beta(E_1 + \varepsilon_{n_a})}\ v_{n_a}^{-1} \langle \Psi_{P_1 n_a} | F | \Psi_{P_1 n_a} \rangle \; ; \tag{2.20}$$

where the real part of the RHS is to be taken, and where it is important to emphasize that the flux operator F [Eq. (2.18)] is independent of the particular surface which is used to divide reactant and product configuration space. By virtue of the Schrödinger equation, Eq. (2.8), one has

$$e^{-\beta(E_1 + \varepsilon_{n_a})}\ \Psi_{P_1 n_a} = e^{-\beta H}\ \Psi_{P_1 n_a} \quad , \tag{2.21}$$

and since

$$E_1 = P_1^2/2\mu$$

$$dE_1 = \frac{P_1}{\mu}\, dP_1 = v_{n_a}\, dP_1 \quad ,$$

Eq. (2.20) becomes

$$k_{b\leftarrow a} = Q_a^{-1} \sum_{n_a} \int_{-\infty}^{0} dP_1 \; \langle \psi_{P_1 n_a} | F\, e^{-\beta H} | \psi_{P_1 n_a} \rangle \quad , \tag{2.22}$$

where $P_1 \equiv -(2\mu E_1)^{1/2}$.

Eq. (2.22) is almost in the desired form, namely a quantum mechanical trace: the sum over $\{n_a\}$ is a complete set in the space of the vibrational coordinate, but translational scattering wavefunctions are complete only if the integral over P_1 covers <u>all</u> momenta, positive and negative. If the projection operator $\mathcal{P}$ is defined by

$$\mathcal{P}\psi_{P_1 n_a} = \psi_{P_1 n_a} \quad , P_1 < 0$$

$$= 0 \quad , P_1 > 0 \quad , \tag{2.23}$$

then Eq. (2.22) can be written as

$$k_{b\leftarrow a} = Q_a^{-1} \sum_{n_a} \int_{-\infty}^{\infty} dP_1 \; \langle \psi_{P_1 n_a} | F\, e^{-\beta H}\, \mathcal{P} | \psi_{P_1 n_a} \rangle \quad ; \tag{2.24}$$

the sum over states is now complete,[16] so that this becomes

$$k_{b\leftarrow a} = Q_a^{-1}\, \mathrm{tr}\, [F\, e^{-\beta H}\, \mathcal{P}] \quad ,$$

or since P and H commute,

$$k_{b\leftarrow a} = Q_a^{-1} \text{ tr } (e^{-\beta H} FP) \quad . \tag{2.25}$$

The rate constant is thus the quantum mechanical Boltzmann average of the reactive flux operator FP. Up until this point the fact has been used that the basis functions $\{\psi_{P_1 n_a}\}$ are the eigenfunction of the Schrödinger equation, i.e., the exact scattering states; quantum mechanical traces are independent of the representation in which they are carried out, however, so that in Eq. (2.25) there is no longer any explicit reference to the scattering wavefunctions.

It is illustrative to write the projection operator P in a more physically meaningful form. P, defined by Eq. (2.23), can be written explicitly as

$$\begin{aligned} P &= \sum_{n_a} \int_{-\infty}^{0} dP_1 \; |\psi_{P_1 n_a}\rangle \langle \psi_{P_1 n_a}| \\ &= \sum_{n_a} \int_{-\infty}^{\infty} dP_1 \; h(-P_1) \; |\psi_{P_1 n_a}\rangle \langle \psi_{P_1 n_a}| \quad , \end{aligned} \tag{2.26}$$

where $h(x)$ is the step function:

$$h(x) = 1, \; x > 0$$

$$= 0, \; x < 0 \quad .$$

By invoking the "formal theory of scattering" (see Appendix I) it is possible to write $\psi_{P_1 n_a}$ in terms of the unperturbed function $\Phi_{P_1 n_a}$,

$$\Phi_{P_1 n_a}(r,R) = \phi_{n_a}(r) \frac{e^{iP_1 R/\hbar}}{(2\pi\hbar)^{1/2}} \quad . \tag{2.27}$$

This relation is

$$\Psi_{P_1 n_a} = \lim_{t\to-\infty} e^{iHt/\hbar}\, e^{-iH_0 t/\hbar}\, \Phi_{P_1 n_a} \quad , \tag{2.28}$$

so that Eq. (2.26) becomes

$$P = e^{iHt/\hbar}\, e^{-iH_0 t/\hbar}\, P_0\, e^{iH_0 t/\hbar}\, e^{-iHt/\hbar} \quad , \tag{2.29}$$

where $t \to -\infty$, and where

$$P_0 = \sum_{n_a} \int_{-\infty}^{\infty} dP_1\, h(-P_1)\, |\Phi_{P_1 n_a}\rangle\langle\Phi_{P_1 n_a}|$$

or

$$P_0 = h(-P) \quad , \tag{2.30}$$

P being the translation momentum operator for arrangement a.

Since H_0 commutes with P_0, Eq. (2.29) becomes

$$P = \lim_{t\to-\infty} e^{iHt/\hbar}\, h(-P)\, e^{-iHt/\hbar} \quad ; \tag{2.31}$$

i.e., the projector P is the Heisenberg transform of the projector h(-P). In Heisenberg notation, therefore, the projector P is

$$P = h[-P(-\infty)] \quad , \tag{2.32}$$

where

$$P(-\infty) = \lim_{t\to-\infty} P(t) \quad ,$$

P(t) being the Heisenberg transform of the translational momentum operator. P, therefore, projects onto that part of Hilbert space which in the infinite past had negative translational momentum in arrangement a.

The final, formally exact expression for the rate constant thus becomes

$$k_{b\leftarrow a} = Q_a^{-1}\ \mathrm{tr}\{e^{-\beta H}\ F\ h[-P(-\infty)]\} \quad , \tag{2.33}$$

with F defined by Eq. (2.18). As emphasized above, this result is independent of the choice of surface which divides reactant and product configuration space. For the discussion in later sections, however, the surface S_3 in Figure 1 is of special interest; in terms of the coordinates (s,u) of Figure 1 this surface is defined by

$$\begin{aligned} f(s,u) &\equiv s \\ &= 0 \quad , \end{aligned} \tag{2.34}$$

so that for this choice of the surface Eq. (2.33) becomes

$$k_{b\leftarrow a} = Q_a^{-1}\ \mathrm{tr}\{e^{-\beta H}\ \delta(s)\ \frac{p_s}{m_s}\ h[-P(-\infty)]\} \quad , \tag{2.35}$$

where m_s is the reduced mass for the s degree of freedom and p_s is its momentum operator.

III. THE CLASSICAL RATE CONSTANT

It is interesting to compare the quantum mechanical rate expression obtained in the previous section with the analogous expression of classical mechanics. The correspondence is strikingly direct.

The transcription from quantum to classical mechanics is accomplished by the rules that a quantum mechanical trace becomes a classical phase space integral, and quantum mechanical operators become the corresponding classical function of coordinates and momenta. The quantum mechanical expression of Eq. (2.33) thus becomes

$$k_{b\leftarrow a}^{CL} = Q_a^{-1} h^{-2} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\, e^{-\beta H(\underset{\sim}{p},\underset{\sim}{q})} F(\underset{\sim}{p},\underset{\sim}{q}) h[-P(\underset{\sim}{p},\underset{\sim}{q};-\infty)] \quad , \tag{3.1}$$

where $H(\underset{\sim}{p},\underset{\sim}{q})$ is the classical Hamiltonian, $F(\underset{\sim}{p},\underset{\sim}{q})$ is the function

$$F(\underset{\sim}{p},\underset{\sim}{q}) = \delta[f(\underset{\sim}{q})] \frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot (\underset{\sim}{p}/m) \quad , \tag{3.2}$$

Q_a is classical partition function for the non-interacting reactants

$$Q_a = h^{-2} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\, e^{-\beta H_o(\underset{\sim}{p},\underset{\sim}{q})} \quad , \tag{3.3}$$

and $P(\underset{\sim}{p},\underset{\sim}{q};t)$ is the translational momentum of arrangment a at time t which results from a trajectory beginning with initial conditions $(\underset{\sim}{p},\underset{\sim}{q})$ at $t = 0$; $P(\underset{\sim}{p},\underset{\sim}{q};-\infty)$ is the $t \to -\infty$ limit of $P(\underset{\sim}{p},\underset{\sim}{q};t)$. The step-function in the integrand of Eq. (3.1) is 1, therefore, if the trajectory has come in the infinite past from arrangement a, and zero otherwise; it is equivalent to the characteristic function $\chi(\underset{\sim}{p},\underset{\sim}{q})$ of Pechukas and McLafferty.[10]

If the dividing surface is taken to be S_1 (see Fig. 1)--i.e.,

$$f(r,R) = R_o - R$$

--then it is easy to show that Eq. (3.1) becomes the traditional classical rate expression:

$$k_{b\leftarrow c}^{CL} = Q_{BC}^{-1} (2\pi\mu kT)^{-1/2} \int_0^\infty dE_1 \, e^{-\beta E_1} (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dr \int_{-\infty}^{\infty} dp \, e^{-\beta h(p,r)} \chi(p,r,E_1) \quad , \tag{3.4}$$

where $h(p,r)$ is the vibrational Hamiltonian of BC, Q_{BC} is the classical vibrational partition function,

$$Q_{BC} = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dr \int_{-\infty}^{\infty} dp \, e^{-\beta h(p,r)} \quad , \tag{3.5}$$

and $\chi(p,r,E_1)$ is 1 if the trajectory beginning with initial conditions

$$\begin{aligned} R_1 &= R_o \\ P_1 &= -(2\mu E_1)^{1/2} \\ r_1 &= r \\ p_1 &= p \end{aligned} \tag{3.6}$$

is reactive, and is zero otherwise. (A non-reactive trajectory crosses surface S_1 twice, once on the way in and once on the way out, and thus gives a net flux of zero.) The integrals over p,r, and E_1 in Eq. (3.4) are usually evaluated by Monte Carlo methods.[1]

It has been emphasized by Keck,[17] however, that this choice of the dividing surface can be quite inefficient because many of the

trajectories beginning in the asymptotic region may be non-reactive. Since Eq. (3.1) is invariant to where the surface is chosen,[18] one does better to choose it so that most of the trajectories beginning on it are reactive, i.e., so that the function $\chi(\underset{\sim}{p},\underset{\sim}{q})$ is 1 for most values of $(\underset{\sim}{p},\underset{\sim}{q})$. For a symmetric system, such as depicted in Figure 1, the obvious choice for this "best" surface is S_3 as defined by Eq. (2.34); with this choice for the dividing surface Eq. (3.1) becomes

$$k_{b\leftarrow a}^{CL} = Q_a^{-1} h^{-2} \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dp_u \int_{-\infty}^{\infty} dp_s \left(\frac{p_s}{m_s}\right) e^{-\beta H(p_u,p_s,u,0)} \chi(p_u,p_s,u,0) \quad , \tag{3.7}$$

where χ is 1 only if the trajectory with initial conditions

$$\begin{aligned} s_1 &= 0 \\ u_1 &= u \\ p_{s_1} &= p_s \\ p_{u_1} &= p_u \end{aligned} \tag{3.8}$$

is reactive in the direction of arrangement a to arrangement b. By following Keck's[17] arguments it is possible to re-write Eq. (3.7) in an equivalent form which involves an integral over only positive values of p_s:

$$k_{b\leftarrow a}^{CL} = Q_a^{-1} h^{-2} \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dp_u \int_{0}^{\infty} dp_s \left(\frac{p_s}{m_s}\right) e^{-\beta H(p_u,p_s,u,0)} \times \frac{1 + (-1)^N}{2\,(N+1)} \quad , \tag{3.9}$$

where N is the number of additional times that the trajectory which begins with the initial conditions of Eq. (3.8) crosses the surface s = 0 as time is run forward and backward.

For purposes of calculating a classical rate constant it is clear that Keck's choice of the dividing surface is superior, for (1) most of the trajectories beginning on it are reactive, and (2) it is not necessary to carry the numerical integration to long times in the past or future to see if the trajectory is indeed going to be a reactive one. If information concerning the distribution of initial or final internal states is desired, it is of course necessary to follow the trajectory all the way into the initial or final asymptotic region; here the trajectory can be assigned to quantum number "boxes" in the usual manner. However a word of caution is necessary: if zero point energy effects are important this procedure of "boxing" the initial and final quantum numbers does not seem to work as well in practice as the quasi-classical procedure[1] of beginning the trajectory in the initial asymptotic region with a quantum energy level and "boxing" only the final quantum numbers. Appendix II discusses this point in more detail.

IV. THE TRANSITION STATE APPROXIMATION

All discussion of the quantum and classical rate expressions so far has been dynamically exact, the only assumption being that the internal states of the separated reactants and their relative translational energy are in Boltzmann equilibrium. (There are, of course, non-equilibrium effects--i.e., perburbations of the Boltzmann distribution--that result if the rate of reaction from some internal states is much faster than inelastic rates which maintain Boltzmann equilibrium of the reactants. These non-equilibrium effects have been studied in great detail[19] and in most cases are quite small, certainly so in the region of the reaction threshold.) Now we wish to inject the transition state approximation.

a. Classical Case

Considering the classical case first and following Pechukas and McLafferty,[10] the transition state approximation to Eq. (3.7) corresponds to the replacement

$$\chi(p_u,p_s,u,0) \to h(p_s) \quad , \tag{4.1}$$

h being the step function; i.e., transition state theory assumes that any trajectory beginning on the surface $s = 0$ with positive momentum p_s is reactive, that it does not turn around and become a non-reactive one. In terms of Eq. (3.9), the transition state approximation is that $N \equiv 0$, again that there are no trajectories that re-cross the dividing surface. The important simplifying feature of transition state theory is, of course, that this

approximation [Eq. (4.1)] eliminates all reference to dynamics.

For the general classical rate expression, Eq. (3.1) - (3.3), involving the general dividing surface $f(\underset{\sim}{q}) = 0$, the transition state approximation is

$$h[-P(\underset{\sim}{p},\underset{\sim}{q};-\infty)] \rightarrow h[\frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{p}] \quad , \tag{4.2}$$

and the general transition state rate expression is

$$k_{b\leftarrow a}^{\text{CL TST}} = Q_a^{-1} h^{-2} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\, e^{-\beta H(\underset{\sim}{p},\underset{\sim}{q})} \delta[f(\underset{\sim}{q})] \frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot (\underset{\sim}{p}/m)\, h[\frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{p}] \quad . \tag{4.3}$$

For the case of the surface S_3, Eq. (2.34), this becomes

$$k_{b\leftarrow a}^{\text{CL TST}} = Q_a^{-1} h^{-2} \int_{-\infty}^{\infty} dp_u \int_{-\infty}^{\infty} du \int_{0}^{\infty} dp_s \, (\frac{p_s}{m_s})\, e^{-\beta H(p_u,p_s,u,0)} \quad , \tag{4.4}$$

and since

$$H(p_u,p_s,u,0) = \frac{p_s^2}{2m_s} + \frac{p_u^2}{2m_u} + V(u,0) \quad ,$$

Eq. (4.4) becomes the usual classical transition state expression:

$$k_{b\leftarrow a}^{\text{CL TST}} = \frac{kT}{h} \frac{Q_u}{Q_a} \quad , \tag{4.5}$$

where Q_u is the partition function for the symmetric stretch vibration

$$Q_u = h^{-1} \int_{-\infty}^{\infty} dp_u \int_{-\infty}^{\infty} du \exp\{-\beta\, [\frac{p_u^2}{2m_u} + V(u,0)]\} \quad . \tag{4.6}$$

Although the dynamically exact rate expressions of Sections II and III are invariant to the choice of dividing surface, it is

clear that the transition state rate expression depends on where the surface is taken. To make Eq. (4.2) as accurate as possible one wishes to choose the surface to be the one for which most trajectories beginning on it are reactive. For a symmetric system such as $H + H_2$, as depicted in Figure 1, it is clear that surface S_3 is the best choice. At low collision energies one certainly expects most trajectories beginning on this surface to be reactive. Pechukas and McLafferty[10] have given a beautiful analysis of the situation, obtaining a simple geometrical criterion for deciding under what conditions transition state theory will be exact, i.e., under what conditions all trajectories beginning on the dividing surface $s = 0$ will be reactive.

In any event, the transition state rate expression is an upper bound to the dynamically exact rate; this is most easily seen from Keck's[17] version of the rate expression, Eq. (3.9), where the transition approximation is $N \equiv 0$. Since

$$\frac{1 + (-1)^N}{2\ (N + 1)} \leq 1 \tag{4.7}$$

for $N = 0, 1, 2, \ldots$, the bounding relation follows. Keck[17] thus emphasizes that the dividing surface should be chosen to minimize the transition state rate constant. If the function $f(q)$, which defines the dividing surface, is chosen in the form

$$f(q) = y - Y(x) = 0 \quad , \tag{4.8}$$

where x and y are the scaled coordinates in Figure 1, then the function $Y(x)$ which minimizes the rate can be determined[20] by the condition

$$\delta\, k_{b\leftarrow a}^{\text{CL TST}} = 0 \quad . \tag{4.9}$$

Substituting Eq. (4.8) into Eq. (4.3) and carrying out this variation leads to the following Euler equation

$$\frac{\partial V(x,Y(x))}{\partial y} - Y'(x)\,\frac{\partial V(x,Y(x))}{\partial x} + kT\,\frac{Y''(x)}{1 + Y'(x)^2} = 0 \tag{4.10}$$

for the "best" function Y(x), i.e., the "best" dividing surface. One interesting observation which follows from Eq. (4.10) is that for high temperature, $T \to \infty$, the best dividing surface (or line for this collinear system) is straight, i.e., $Y''(x) = 0$.

b. Quantum Mechanical Case

The quantum mechanical transition state approximation is now defined as an approximation to the dynamically exact quantum rate expression, Eq. (2.35), which is analogous to the classical approximation in Eq. (4.1). In terms of the dividing surface S_3, defined by Eq. (2.34), therefore, the transition state approximation results from the replacement

$$h[-P(-\infty)] \to h(p_s) \tag{4.11}$$

in Eq. (2.35), where p_s is the momentum operator corresponding to coordinate s (see Figure 1). The projection operator $h(p_s)$ projects onto that part of Hilbert space which has positive momentum in the s-direction, and the assumption of transition state theory is that positive momentum at the dividing surface implies negative translational momentum in the infinite past.

The physical meaning of the approximation is the same as in the classical case, and one thus expects that if the quantum dynamics is "direct"--corresponding to the classical situation of no re-crossing trajectories--then the transition state approximation will be a good one.

The quantum transition state expression for the rate is thus given from Eqs. (2.35) and (4.11) as

$$k_{b\leftarrow a}^{\text{QM TST}} = Q_a^{-1} \, \text{tr}[e^{-\beta H} \, \delta(s) \, \frac{p_s}{m_s} \, h(p_s)] \quad . \tag{4.12}$$

There is one complication which arises, however: The approximate projection operator $h(p_s)$, unlike the dynamically exact one, does not commute with the total Hamiltonian H; with the dynamically exact projector P one thus has

$$\text{tr}[e^{-\beta H} \, \delta(s) p_s \, P] = \text{tr}[e^{-\beta H} \, P \, \delta(s) p_s] \quad , \tag{4.13}$$

but for the approximate projector $h(p_s)$

$$\text{tr}[e^{-\beta H} \, \delta(s) p_s \, h(p_s)] \neq \text{tr}[e^{-\beta H} \, h(p_s) \, \delta(s) p_s] \quad . \tag{4.14}$$

The ordering of the operators that one should choose in Eq. (4.12), therefore, is not obvious.

The most general prescription available for constructing the physically meaningful ordering of a product of several hermitian operators is given by the Weyl correspondence rule[21] (see Appendix III). If the trace in Eq. (4.12) is evaluated in a coordinate representation, then one has (taking the coordinates to be (s,u) in Figure 1)

$$k_{b\leftarrow a}^{\text{QM TST}} = Q_a^{-1} \int_{-\infty}^{\infty} ds \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} ds' \int_{-\infty}^{\infty} du' \; \langle su|e^{-\beta H}|s'u'\rangle$$

$$\langle s'u'|R|su\rangle \quad , \tag{4.15}$$

where R is the Weyl operator corresponding to $\delta(s)\ (p_s/m_s)\ h(p_s)$; from Appendix III one finds the coordinate matrix R to be

$$\langle s'u'|R|su\rangle = \delta(u'-u)\ \delta\left(\frac{s'+s}{2}\right)\ (2\pi\hbar)^{-1} \int_0^{\infty} dp_s \left(\frac{p_s}{m_s}\right)$$

$$\times \exp\left[\frac{i}{\hbar}\, p_s\, (s'-s)\right]$$

$$= \delta(u'-u)\ \delta\left(\frac{s'+s}{2}\right)\ \frac{\hbar}{2\pi m_s}\ \frac{-1}{(s'-s)^2} \quad . \tag{4.16}$$

Substitution of Eq. (4.10) into (4.15) and an integration by parts gives

$$k_{b\leftarrow a}^{\text{QM TST}} = Q_a^{-1}\ \frac{\hbar}{4\pi m_s} \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} ds\ \left(-\frac{1}{s}\right) \frac{\partial}{\partial s}\ \langle su|e^{-\beta H}|-s,u\rangle \quad . \tag{4.17}$$

Since the matrix element $\langle su|e^{-\beta H}|-s,u\rangle$ is an even function of s, its derivative is odd, so the factor $(-1/s)$ causes no difficulty in the integrand of Eq. (4.17).

Eq. (4.17) is the desired quantum mechanical transition state rate expression,[22] and one can easily verify that it reproduces traditional transition state theory[5] in the separable limit. Suppose, therefore, that the Hamiltonian H is separable in s and u variables:

$$H = h_u + h_s \quad .$$

where h_u and h_s are one-dimensional Hamiltonians describing the u-motion (symmetric stretch vibration) and s-motion (translation along the reaction coordinate). It is easy to see that Eq. (4.17) becomes

$$k_{b\leftarrow a}^{QM\ TST} = \Gamma \frac{kT}{h} \frac{Q_u}{Q_a} \quad , \tag{4.18}$$

where

$$Q_u = \int_{-\infty}^{\infty} du \ \langle u|e^{-\beta h_u}|u\rangle$$

$$= tr\ (e^{-\beta h_u}) \quad ,$$

and

$$\Gamma = \frac{\hbar^2\beta}{2m_s} \int_{-\infty}^{\infty} ds \ (-\frac{1}{s}) \frac{d}{ds} \langle s|e^{-\beta h_s}|-s\rangle \quad ; \tag{4.19}$$

Q_u is the quantum mechanical partition function for the symmetric stretch vibration, and Γ is the tunneling correction for motion along the reaction coordinate. If h_s is the free particle Hamiltonian,

$$h_s = p_s^2/2m_s \quad , \tag{4.20}$$

then

$$\langle s|e^{-\beta h_s}|-s\rangle = \left(\frac{m_s}{2\pi\hbar^2\beta}\right)^{1/2} \exp\left(-\frac{2m_s}{\hbar^2\beta} s^2\right) \quad , \tag{4.21}$$

and one finds that Eq. (4.19) gives

$$\Gamma = 1 \quad ,$$

the expected result. If h_s is chosen to have a parabolic potential barrier about the saddle point,

$$h_s = p_s^2/2m_s - \tfrac{1}{2} m_s \omega^2 s^2 \quad , \tag{4.22}$$

then[24]

$$\langle s|e^{-\beta h_s}|-s\rangle = \left[\frac{m_s\omega}{2\pi\hbar \sin(\hbar\omega\beta)}\right]^{1/2} \exp\left[-\frac{m_s\omega}{\hbar}\cot(\tfrac{\hbar\omega\beta}{2})s^2\right] , \tag{4.23}$$

and in this case Eq. (4.19) gives

$$\Gamma = \tfrac{1}{2}\hbar\omega\beta \,/\, \sin(\tfrac{1}{2}\hbar\omega\beta) \quad , \tag{4.24}$$

the Wigner tunneling correction[7] which is known to be correct for the parabolic barrier.

This separable approximation, however, is the precisely what we do <u>not</u> wish to introduce, for--as discussed in the Introduction--the system is quite non-separable over the regions of configuration space which are important in the low energy region near threshold where tunneling is significant. To evaluate Eq. (4.17) in general it may be most convenient to introduce a discrete set of square integrable basis functions. With regard to the u-dependence of the kernel

$$\langle su|e^{-\beta H}|-s,u\rangle \tag{4.25}$$

it is clear that a basis set description is adequate, for the u-motion is bound state-like. As a function of s it is also localized because it is off-diagonal with regard to the s coordinate; the above separable approximations, Eqs. (4.21) and (4.23), show it to be gaussian about s = 0, and one expects this to be qualitatively the same for the non-separable case. If $\{\Phi_i(s,u)\}$, i = 1,...., N is a discrete basis set[25] and $\{\psi_i(s,u)\}$ the particular linear

combinations of the $\{\Phi_i\}$ which diagonalize the finite matrix $H_{i,j} \equiv \langle\Phi_i|H|\Phi_j\rangle$, then the basis set evaluation of Eq. (4.17) gives

$$k_{b\leftarrow a}^{QM\ TST} = Q_a^{-1} \sum_i e^{-\beta E_i} R_i \quad , \tag{4.26}$$

where $\{E_i\}$ are the eigenvalues of the matrix $H_{i,j}$, and

$$R_i = \langle\psi_i|R|\psi_i\rangle$$

$$= \frac{\hbar}{4\pi m_s} \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} ds \left(-\frac{1}{s}\right) \frac{\partial}{\partial s} \psi_i(s,u)\psi_i(-s,u),$$

or

$$R_i = \frac{-\hbar}{2\pi m_s} \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} ds \left(-\frac{1}{s}\right) \psi_i(-s,u) \frac{\partial\psi_i(s,u)}{\partial s} \quad , \tag{4.27}$$

where the $\{\psi_i\}$ have (without restriction) been chosen to be real.

V. A NEW KIND OF SEMICLASSICAL MODEL

Although the transition state approximation is expected to be good at low energy for cases where there is a well-defined activation barrier, it is clear that it will become poor at sufficiently high energy; the energy at which it begins to fail is presumably lower the lower the activation barrier. In the language of classical mechanics this failure is due to trajectories which cross the dividing surface more than once, and quantum mechanically it is manifest in streamlines of flux[11] which have whirlpool effects, etc., at high energy. It would clearly be desirable to have one model which incorporates the simplifying features of quantum mechanical transition state theory at low energies where quantum effects are expected to be important, and which also takes account of these dynamical effects at the higher energies where transition state theory fails. This section shows how such an expression can be constructed.

If the trace in the dynamically exact quantum mechanical rate expression, Eq. (2.35), is carried out in the (s,u) coordinate representation, then it reads

$$k_{b\leftarrow a} = Q_a^{-1} \int_{-\infty}^{\infty} ds \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} ds' \int_{-\infty}^{\infty} du' \; \langle su|e^{-\beta H}|s'u'\rangle$$

$$\langle s'u'|\delta(s)\left(\frac{p_s}{m_s}\right) h\,[-P(-\infty)]|su\rangle \quad . \tag{5.1}$$

The present semiclassical model is obtained by using the Weyl rule[21] (see Appendix III) to approximate the matrix elements of

the operator $\delta(s)\ p_s\ h\ [-P(-\infty)]$; from Appendix III one sees that this gives

$$\langle s'u'|\delta(s)\left(\frac{p_s}{m_s}\right) h[-P(-\infty)]|su\rangle$$

$$\simeq (2\pi\hbar)^{-2}\ \delta\left(\frac{s'+s}{2}\right)\ \int_{-\infty}^{\infty}dp_u\ \int_{-\infty}^{\infty}dp_s\ \left(\frac{p_s}{m_s}\right)$$

$$\times\ \exp\{\frac{i}{\hbar}\ [p_s(s'-s) + p_u(u'-u)]\}\ \ h[-P(p_u,p_s,\frac{u'+u}{2},\ \frac{s'+s}{2};-\infty)], \quad (5.2)$$

where $P(p_u,p_s,u,s;-\infty)$ is the $t \to -\infty$ limit of the translational momentum of arrangement a that results from a trajectory beginning at $t = 0$ with the indicated initial conditions. With this approximation Eq. (5.1) can be written as

$$k_{b\leftarrow a}^{SC} = Q_a^{-1} \int_{-\infty}^{\infty}dp_u \int_{-\infty}^{\infty}du \int_{-\infty}^{\infty}dp_s \left(\frac{p_s}{m_s}\right) W(p_u,p_s,u,0)$$

$$\times\ h[-P(p_u,p_s,u,0;-\infty)] \quad , \qquad (5.3)$$

where $W(p_u,p_s,u,s)$ is the Wigner distribution function[26]

$$W(p_u,p_s,u,s) = (2\pi\hbar)^{-2} \int_{-\infty}^{\infty}du' \int_{-\infty}^{\infty}ds'\ \exp[\frac{i}{\hbar}\ (p_s s' + p_u u')]$$

$$\langle s - \frac{s'}{2},\ u - \frac{u'}{2}\ |e^{-\beta H}|\ s + \frac{s'}{2},\ u + \frac{u'}{2}\rangle \quad , \quad (5.4)$$

here with $s = 0$.

In the limit that transition state theory is a good approximation, i.e., at low temperatures, one has

$$h[-P(p_u,p_s,u,0;-\infty)] \to h(p_s) \quad , \qquad (5.5)$$

and it is not hard to show that Eq. (5.3) then becomes identical to quantum transition state theory, Eq. (4.17). In the high

temperature limit quantum effects become neglible, so that the Wigner distribution function of Eq. (5.4) takes on its classical limit

$$W(p_u,p_s,u,0) \rightarrow (2\pi\hbar)^{-2} e^{-\beta H(p_u,p_s,u,0)} , \qquad (5.6)$$

and one sees that Eq. (5.3) becomes identical to the dynamically exact classical rate, Eq. (3.7), in this case. Eq. (5.3) thus has the desired property of combining the quantum transition state rate expression and the dynamically exact classical rate expression into one unified model.

If the Weyl correspondence rule[21] always produced the exactly correct quantum mechanical operator, then Eq. (5.3) would be the dynamical exact quantum mechanical rate constant. This is not true (see Appendix III), but the arguments in the above paragraph suggest that it may indeed provide an excellent approximation. Another insight into why this should be so is the following: The dynamically exact rate expressions of both classical and quantum mechanics involve an infinite time limit. In the classical case, however, it is clear that a trajectory need not be run to particularly long times in order to see if it will be reactive or not. Analogously, one expects that a short time approximation to the projection operator $h[-P(t)]$ is sufficient to determine the reactive flux if the dividing surface is chosen, as it is, in the optimum location. As is shown in Appendix III, the Weyl rule does indeed describe the quantum propagator correctly for short times, thus implying that Eq. (5.2)

is a good approximation for purposes of determining the net rate constant.

With regard to the evaluation of Eqs. (5.3) and (5.4), a basis set evaluation is also possible here. If

$$\psi_i(s,u) = \sum_{n,m} U_{i,mn}\, \phi_n(u)\, \chi_m(s) \tag{5.7}$$

is the set of linear combinations of basis functions $\{\phi_n\chi_m\}$ which diagonalize the Hamiltonian matrix, then the rate constant is given by Eq. (4.26) but where R_i is now given by

$$R_i = \sum_{m,n,m',n'} U_{i,mn}\, U_{i,m'n'} \int_{-\infty}^{\infty} dp_u \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dp_s \left(\frac{p_s}{m_s}\right) \times h[-P(p_u,p_s,u,0;-\infty)]\; J_{n,n'}(p_u,u)\; K_{m,m'}(p_s,0) \quad , \tag{5.8}$$

where

$$J_{n,n'}(p_u,u) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} du'\; \exp(ip_u u'/\hbar)\; \phi_n(u-\tfrac{u'}{2})\; \phi_{n'}(u+\tfrac{u'}{2}) \tag{5.9a}$$

$$K_{m,m'}(p_s,s) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} ds'\; \exp(ip_s s'/\hbar)\; \chi_m(s-\tfrac{s'}{2})\; \chi_{m'}(s+\tfrac{s'}{2}), \tag{5.9b}$$

It is also interesting to note how different this semiclassical model is from "classical S-matrix" theory[3] where classical trajectories are used to construct amplitudes for transitions between specific initial and final quantum states. The semiclassical model described above also uses exact classical mechanics within a quantum mechanical framework, but the rate constant itself is constructed without going through the intermediate use of amplitudes. It is clear that the present semiclassical model will be much easier to implement than classical S-matrix theory, primarily because much more limited information is being sought, namely

the net reaction rate constant rather than complete information about initial and final state distributions.

Finally, it is worthwhile to note that the semiclassical rate expression, Eq. (5.3), and its transition state approximation, Eq. (4.17), can both be obtained directly from the corresponding classical rate expressions, Eqs. (3.1) and (4.4) respectively, simply by replacing the classical distribution function by the Wigner[26] distribution function:

$$h^{-N} e^{-\beta H(\underset{\sim}{p},\underset{\sim}{q})} \rightarrow W(\underset{\sim}{p},\underset{\sim}{q})$$

where $W(\underset{\sim}{p},\underset{\sim}{q})$ is defined by Eq. (5.4). Use of the Weyl flux operator in quantum mechanical rate expressions is thus equivalent to use of the Wigner distribution function in classical expressions, and any shortcomings of one approach are present in the other.

VI. SUMMARY AND CONCLUDING REMARKS

In obtaining a quantum mechanical transition state theory which is free of any additional approximations it was first useful to write the dynamically exact quantum mechanical rate in the form of a Boltzmann average of a flux operator. This is given by Eq. (2.33) and is quite an interesting expression itself, being a verbatim transcription of the dynamically exact classical rate expression, Eq. (3.1).

The quantum rate expression, Eq. (2.33), involves the total Hamiltonian H in two ways, one in the Boltzmann operator $\exp(-\beta H)$, and the other through the projection operator

$$h[-P(-\infty)] = \lim_{t\to-\infty} e^{iHt/\hbar}\, h(-P)\, e^{-iHt/\hbar} \quad , \tag{6.1}$$

P being the translation momentum operator of arrangement a. It is the infinite time limit of this projection operator that can only be handled completely correctly by a quantum scattering calculation.

The transition state approximation, in either the quantum or classical framework, circumvents the need to know the full scattering dynamics by invoking the approximation $h[-P(-\infty)] \simeq h(p_s)$ quantum mechanically, or $h[-P(\underset{\sim}{p},\underset{\sim}{q};-\infty)] \simeq h(p_s)$ classically; the full Hamiltonian is retained with no approximation in the Boltzmann operator. Physically, this approximation assumes that if the momentum in the s-direction at the dividing surface $s = 0$ is positive, then the system must have come from arrangement a in the infinite past. This will be exact classically at sufficiently low energy.

The quantum mechanical transition state rate expression, Eq. (4.17), is seen to reduce to the standard transition state expression if separability of the Hamiltonian is assumed; the indications are, however, that this is not a good assumption in the threshold region where tunneling is important. For a collinear A + BC → AB + C reaction the evaluation of the quantum transition state expression via Eq. (4.26) - (4.27), for example, should be relatively easy, and may even be quite tractible for such a system, and larger ones, in full three dimensional space.

To overcome the failure of the transition state approximation at higher energies Section V shows how classical trajectory information can be combined with the quantum transition state model by use of the Weyl correspondence rule to approximate the projector in Eq. (6.1). Although the projector is defined as a limit $t \to -\infty$, one expects that it is actually necessary to describe the time evolution only for reasonably short times; this is by analogy with the classical case where one knows that a trajectory need be followed over only a short time internal to determine from which arrangement it originates. Since the Weyl approximation is correct for short times, the implication is that it should provide a good approximation to the projector.

In any event, for temperatures high enough that quantum effects are neglible the semiclassical model of Section V becomes the dynamically exact classical rate expression and therefore correct. The model is thus completely correct of temperatures sufficiently high that quantum effects are neglible and at temperatures sufficiently

low for transition state theory (our quantum mechanical version of it) to be valid; if these two temperature regions overlap or if the Weyl approximation to the projector operator is good, then this semiclassical model will provide a complete description of the reaction rate constant for all temperatures.

To answer these questions as to absolute accuracy, ease of application, etc., it is clear that numerical applications are required. Some of these are now in progress.

APPENDIX I. STEPS LEADING TO EQ. (2.28)

Here we show how Eq. (2.28) follows from the formal theory of scattering.[27,28] Since the manipulations are standard, they are given without comment.

$$\Psi_{P_1 n_a} \equiv \Psi^{(+)}_{P_1 n_a}$$

$$= [1 + (E - H + i\varepsilon)^{-1} V] \Phi_{P_1 n_a}$$

$$= [1 + (E - H + i\varepsilon)^{-1} (H - E)] \Phi_{P_1 n_a}$$

$$= i\varepsilon (E - H + i\varepsilon)^{-1} \Phi_{P_1 n_a} \quad ,$$

where $V = H - H_o$. The green's function $(E - H + i\varepsilon)^{-1}$ can be expressed as the "half Fourier transform" of the propagator, so that this becomes

$$\Psi_{P_1 n_a} = (i\varepsilon)\ (i\hbar)^{-1} \int_0^\infty dt\ e^{-\varepsilon t/\hbar}\ e^{iEt/\hbar}\ e^{-iHt/\hbar}\ \Phi_{P_1 n_a}$$

$$= (\varepsilon/\hbar) \int_0^\infty dt\ e^{-\varepsilon t/\hbar}\ e^{-iHt/\hbar}\ e^{iH_o t/\hbar}\ \Phi_{P_1 n_a}$$

$$= \int_0^\infty dx\ e^{-x}\ e^{-iHx/\varepsilon}\ e^{iH_o x/\varepsilon}\ \Phi_{P_1 n_a}$$

$$= \int_0^\infty dx\ e^{-x}\ [\lim_{t\to\infty} e^{-iHt/\hbar}\ e^{iH_o t/\hbar}]\ \Phi_{P_1 n_a}$$

$$\Psi_{P_1 n_a} = \lim_{t\to-\infty} e^{iHt/\hbar}\ e^{-iH_o t/\hbar}\ \Phi_{P_1 n_a} \quad .$$

APPENDIX II. AVERAGED CLASSICAL TRANSITION PROBABILITY

Consider for simplicity the collinear A + BC collision system; the following discussion can easily be extended[29] to the three-dimensional case. The $n_1 \to n_2$ transition probability, either reactive or non-reactive, is given classically by[30]

$$P_{n_2,n_1} = \left[2\pi \left| \frac{\partial n_2(q_1,n_1)}{\partial q_1} \right| \right]^{-1} , \qquad \text{(II.1)}$$

where $n_2(q_1,n_1)$ is the final vibrational quantum number that results from the trajectory with initial conditions (n_1,q_1), n and q being the action and angle variables for the vibrational degree of freedom; q_1 in Eq. (II.1) is determined by the condition[30]

$$n_2(q_1,n_1) = n_2 , \qquad \text{(II.2)}$$

where n_1 and n_2 are integers.

Although Eq. (II.1) is the formally exact classical transition probability--and thus, for example, satisfies microscopic reversibility, $P_{n_2,n_1} = P_{n_1,n_2}$--it is awkward to apply directly because of the necessity of solving Eq. (II.2), a non-linear boundary value problem. The now standard "quasi-classical" procedure[1] corresponds to averaging Eq. (II.1) over a quantum number width about the final quantum number:

$$\bar{P}_{n_2,n_1} \equiv \int_{n_2 - \frac{1}{2}}^{n_2 + \frac{1}{2}} dn_2 \; P_{n_2,n_1} \qquad \text{(II.3)}$$

$$= \int_{n_2 - \frac{1}{2}}^{n_2 + \frac{1}{2}} dn_2 \; (2\pi)^{-1} \left| \frac{\partial n_2}{\partial q_1} \right|^{-1} ,$$

or

$$\bar{P}_{n_2,n_1} = \int d(q_1/2\pi)\ \chi(n_1,q_1) \quad , \tag{II.4}$$

where $\chi(n_1,q_1) = 1$ if

$$n_2 - \tfrac{1}{2} \le n_2(q_1,n_1) \le n_2 + \tfrac{1}{2} \quad , \tag{II.5}$$

and is zero otherwise. The integral over q_1 in Eq. (II.4) is most efficiently carried out by Monte Carlo, or other sampling methods, particularly so for systems with more internal degrees of freedom.

Although the quasi-classical transition probability, Eq. (II.4), is simpler to evaluate, it has the undesirable feature of not being microscopically reversible, i.e.,

$$\bar{P}_{n_2,n_1} \neq \bar{P}_{n_1,n_2} \quad .$$

A microscopically reversible result can be regained by the more democratic procedure of averaging over the initial, as well as final, quantum number:

$$\begin{aligned} \bar{\bar{P}}_{n_2,n_1} &\equiv \int_{n_2-\frac{1}{2}}^{n_2+\frac{1}{2}} dn_2 \int_{n_1-\frac{1}{2}}^{n_1+\frac{1}{2}} dn_1\ P_{n_2,n_1} \\ &= \int_{n_1-\frac{1}{2}}^{n_1+\frac{1}{2}} dn_1 \int d(q_1/2\pi)\ \chi(n_1,q_1) \quad , \end{aligned} \tag{II.6}$$

where $\chi(n_1,q_1)$ is the same as above. (The average over n_1 is done holding the <u>total</u> energy constant.) This "double-averaged" transition probability is the quantity which is obtained in a Keck-type[17]

Monte Carlo calculation, i.e., by beginning the trajectory in the interaction region, integrating forward and backward in time, and assigning initial and final quantum numbers to "quantum number boxes".

Although this double averaging procedure seems more internally consistent (and is no more difficult to apply) than the singly-averaged, quasi-classical approach, it is interesting that it does not necessarily give better agreement with quantum mechanical calculations. For the collinear $H + H_2$ reaction, for example, Figure 2 shows the singly-averaged [Eq. (II.4)] and doubly-averaged [Eq. (II.6)] results, compared to the numerically exact quantum mechanical result;[31] the singly averaged result is seen to mimic the quantum mechanical behavior more closely. This is probably due to the fact that at these low energies this system is highly vibrationally adiabatic. The vibrational zero point energy with which the quasi-classical trajectory begins is thus not all available to motion along the reaction coordinate, and this corresponds well to the quantum mechanical situation.

APPENDIX III. THE WEYL CORRESPONDENCE RULE

The Weyl correspondence rule[21] gives a prescription for constructing the hermitian operator F_{op} that corresponds to the classical function of coordinates and momenta $F_{CL}(\underset{\sim}{p},\underset{\sim}{q})$. For the general case of N degrees of freedom the rule is

$$F_{op} = (2\pi\hbar)^{-2N} \int d\underset{\sim}{p} \int d\underset{\sim}{q} \int d\underset{\sim}{p}' \int d\underset{\sim}{q}' \; F_{CL}(\underset{\sim}{p},\underset{\sim}{q})$$

$$\exp[-i(\underset{\sim}{p}'\cdot\underset{\sim}{q} + \underset{\sim}{p}\cdot\underset{\sim}{q}')/\hbar] \exp[i(\underset{\sim}{p}'\cdot\underset{\sim}{q}_{op} + \underset{\sim}{q}'\cdot\underset{\sim}{p}_{op})/\hbar] \quad , \text{(III.1)}$$

where $(\underset{\sim}{q},\underset{\sim}{p})$ are cartesian coordinates and momenta and $\underset{\sim}{q}_{op}$ and $\underset{\sim}{p}_{op}$ are the coordinate and momentum operators. Using the fact that

$$\exp[i(\underset{\sim}{p}'\cdot\underset{\sim}{q}_{op} + \underset{\sim}{q}'\cdot\underset{\sim}{p}_{op})/\hbar] = \exp(i\,\underset{\sim}{p}'\cdot\underset{\sim}{q}_{op}/h) \exp(i\,\underset{\sim}{q}'\cdot\underset{\sim}{p}_{op}/\hbar) \times \exp(\tfrac{1}{2}\, i\,\underset{\sim}{p}'\cdot\underset{\sim}{q}'/\hbar) \quad , \qquad \text{(III.2)}$$

one can readily show that the coordinate matrix representation of F_{op} is

$$\langle \underset{\sim}{q}_2 | F_{op} | \underset{\sim}{q}_1 \rangle = (2\pi\hbar)^{-N} \int d\underset{\sim}{p} \exp[i\,\underset{\sim}{p}\cdot(\underset{\sim}{q}_2 - \underset{\sim}{q}_1)/\hbar] \times F_{CL}\left(\underset{\sim}{p}, \frac{\underset{\sim}{q}_2 + \underset{\sim}{q}_1}{2}\right) \quad . \qquad \text{(III.3)}$$

One can verify that Eq. (III.1), or (III.3), gives the correct quantum mechanical result if F_{CL} is a function only of coordinates or only of momenta (or a sum of such functions); for example, if F_{CL} is a function only of coordinates, $F_{CL}(\underset{\sim}{q})$, then Eq. (III.1) gives the obvious result

$$F_{op} = F_{CL}\,(\underset{\sim}{q}_{op}) \quad .$$

For the case that F_{CL} is a non-additive function of coordinates and momenta the operator $F_{CL}(\underset{\sim}{p}_{op}, \underset{\sim}{q}_{op})$ is not well-defined due to lack of commutivity of the operators $\underset{\sim}{p}_{op}$ and $\underset{\sim}{q}_{op}$; Eq. (III.1) thus defines a unique ordering of these non-commuting operators. If

$$F_{CL}\,(\underset{\sim}{p},\underset{\sim}{q}) = \underset{\sim}{p}\cdot\underset{\sim}{q} \quad ,$$

for example, then Eq. (III.1) gives the symmetrized product

$$F_{op} = \frac{1}{2}\,(\underset{\sim}{p}_{op}\cdot\underset{\sim}{q}_{op} + \underset{\sim}{q}_{op}\cdot\underset{\sim}{p}_{op}) \quad ,$$

the intuitively reasonable choice. More generally, if F_{CL} is a product of a function of coordinates and a function of momenta,

$$F_{CL}(\underset{\sim}{p},\underset{\sim}{q}) = f(\underset{\sim}{p})\; g(\underset{\sim}{q}) \quad , \tag{III.4}$$

Eq. (III.3) gives

$$\langle \underset{\sim}{q}_2 | F_{op} | \underset{\sim}{q}_1 \rangle = \bar{f}(\underset{\sim}{q}_2 - \underset{\sim}{q}_1)\; g\left(\frac{\underset{\sim}{q}_2 + \underset{\sim}{q}_1}{2}\right) \quad , \tag{III.5}$$

where $\bar{f}$ is the Fourier transform of f.

Although the Weyl rule is the most general prescription available for constructing the appropriate quantum mechanical operator from an arbitrary classical function of coordinates and momenta--or, equivalently, for uniquely defining the appropriate ordering of coordinate and momentum operators in $F_{CL}(\underset{\sim}{p}_{op}, \underset{\sim}{q}_{op})$--it unfortunately does not always produce the correct quantum mechanical result. For the propagator,

$$F_{op} = e^{-iHt/\hbar} \quad ,$$

for example, the corresponding classical function is clearly

$$F_{CL}(\underset{\sim}{p},\underset{\sim}{q}) = e^{-iH(\underset{\sim}{p},\underset{\sim}{q})t/\hbar}$$

$$= \exp\left(-i\frac{p^2}{2\mu}\,t/\hbar\right)\exp[-iV(\underset{\sim}{q})t/\hbar] \quad ,$$

so that Eq. (III.5) gives

$$\langle \underset{\sim}{q}_2 | e^{-iHt/\hbar} | \underset{\sim}{q}_1 \rangle = (2\pi i\hbar t/\mu)^{-N/2} \exp\left[\frac{i\mu}{2\hbar t}\,|\underset{\sim}{q}_2 - \underset{\sim}{q}_1|^2 - i\,V\left(\frac{\underset{\sim}{q}_2 + \underset{\sim}{q}_1}{2}\right) t/\hbar\right] \quad ,$$

which is recognized[32] as a short time approximation to the coordinate representation of the propagator. The implied warning is that one should invoke the Weyl correspondence rule with caution. In Section IV it was used to define a unique ordering of the non-commuting operators $\delta(s)p_s$ and $h(p_s)$; since no other basis for choosing the ordering is apparent, it seems to be the most justifiable procedure.

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FIGURE CAPTIONS

1. Sketch of a collinear potential energy surface for a symmetric $A + BC \rightarrow AB + C$ reaction (i.e., $A \equiv C$). x and y are mass weighted, or "skewed" coordinates that diagonalize the kinetic energy: $x = R(\mu/M)^{1/2}$, $y = r(m/M)^{1/2}$, where R and r are the translational and vibrational coordinates, respectively, and μ and m the corresponding reduced masses [$m = BC/(B+C)$, $\mu = A(B+C)/(A+B+C)$]. M is any arbitrary mass, and the classical kinetic energy is $\frac{1}{2} M(\dot{x}^2 + \dot{y}^2)$. s and u are the linear combinations of x and y which diagonalize the potential energy at the saddle point. S_1, S_2, and S_3 indicate the "surfaces" which are referred to in the text.

2. Reaction probability for the collinear $H + H_2 \rightarrow H_2 + H$ reaction on the Porter-Karplus potential surface [R. N. Porter and M. Karplus, J. Chem. Phys. 40, 1105 (1964)] as a function of relative collision energy. The dotted and dashed lines are the singly and doubly averaged classical trajectory results, Eqs. (II.4) and (II.6), respectively, and the solid line the quantum mechanical values of ref. 31.

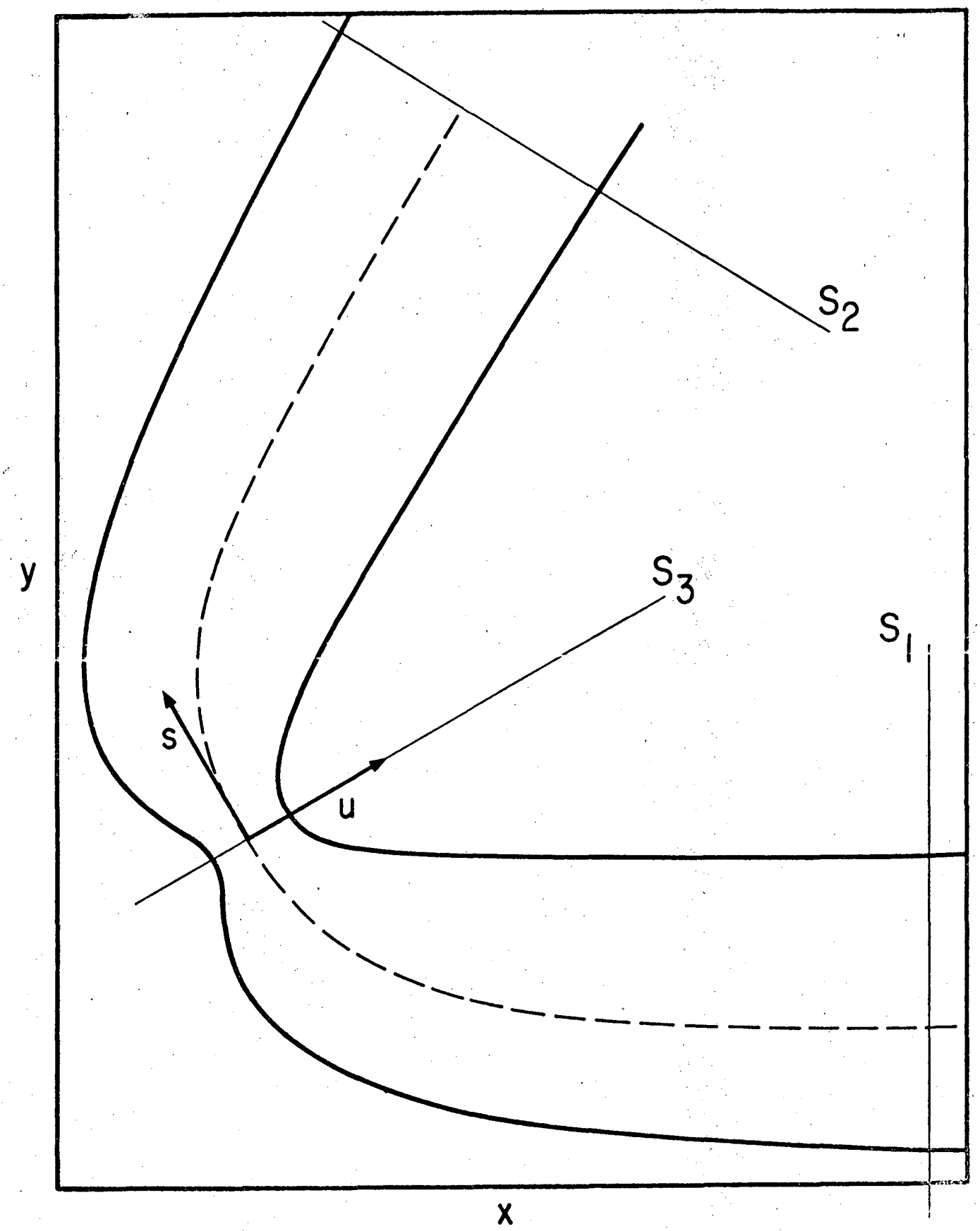

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Figure 1

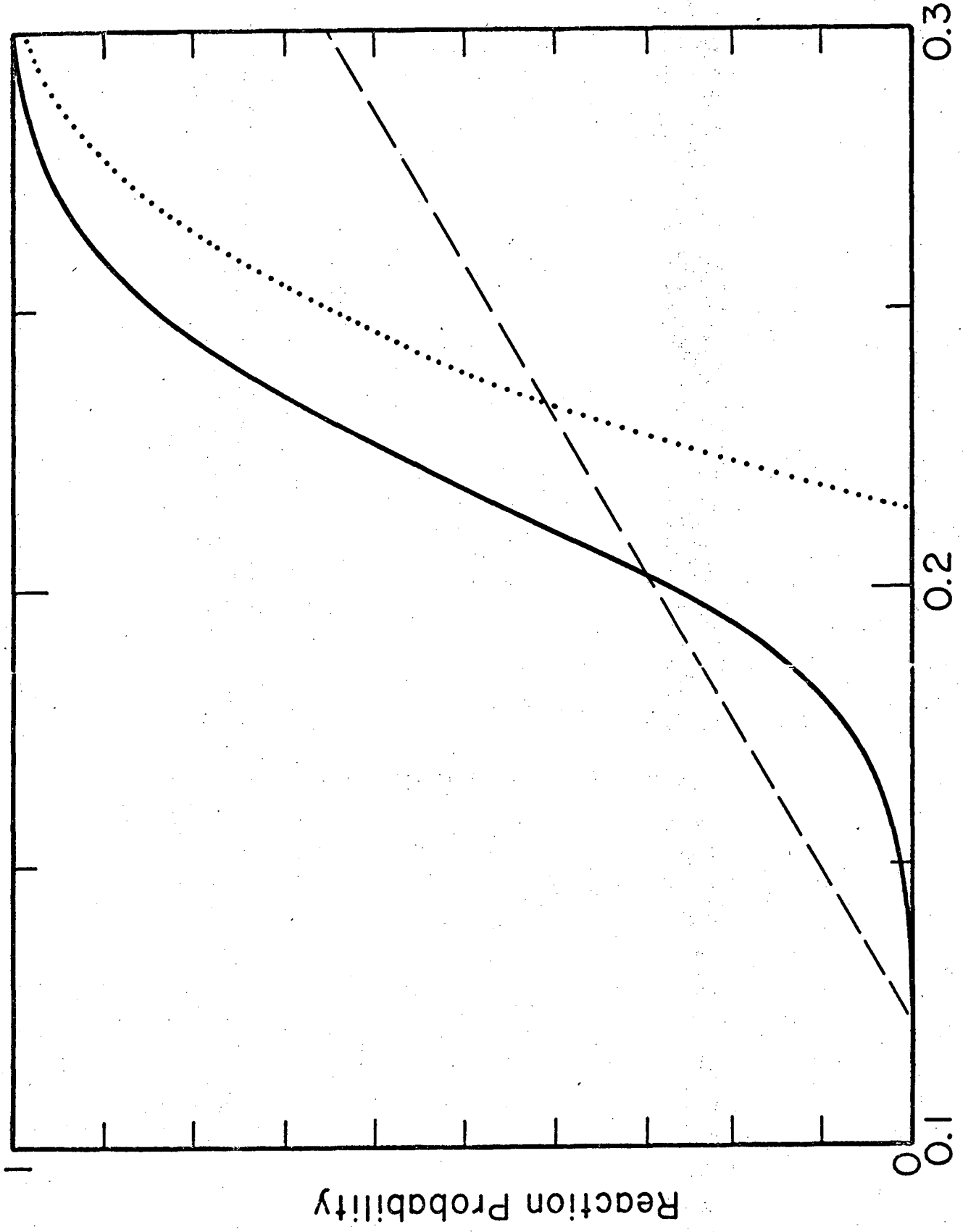

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Fig. 2

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