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SEMICLASSICAL METHODS IN REACTIVE AND NON-REACTIVE COLLISIONS
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I. INTRODUCTION

Semiclassical methods have a long history of application in the field of
atomic and molecular collisions. For the simplest case, namely that of elastic
scattering (1-3), the well-known analysis of Ford and Wheeler (1) has been
immensely important, both as a method for carrying out calculations and, even
more importantly, in providing an interpretation of the quantum effects in
elastic scattering.

Inelastic collisions have also been treated by a variety of semiclassical
approximations. Perhaps the simplest examples of such an approach are the
"impact parameter", or classical path methods (4) which assume a classical tra­
jectory for the translational motion and then solve a time-dependent quantum
mechanical problem for the internal degrees of freedom. The time-dependent
quantum mechanical problem may be solved exactly (i.e., numerically), but is
usually treated approximately, e.g., via perturbation theory. The translational
motion is most often assumed to follow a straight line, constant velocity tra­
jectory, but this is not a fundamental limitation.

The inherent shortcoming of these classical path approaches is that they
are unable to describe the translational dynamics correctly; i.e., it is not
possible to take adequate account of the effect on the translational motion
caused by the inelastic transition in the internal degrees of freedom. These
methods have thus found their greatest utility in treating high energy collision
processes for which the translational dynamics is relatively unimportant.

Another class of semiclassical treatments begins from a more rigorous start­
ing point, namely the quantum mechanical coupled channel expansion of the wave­
function,

$$\psi(r,q) = \sum_i \phi_i(q) f_i(r),$$  \hspace{1cm} (1.1)

where q and r denote the internal and translational coordinates, respectively,
{\phi_i} are the internal eigenfunctions, and {f_i} the translational, or radial
functions. The radial functions are determined by coupled channel Schrödinger
equations of the form

$$\left(\frac{-\hbar^2}{2\mu} \frac{d^2}{dr^2} - E_i\right) f_i(r) + \sum_j V_{ij}(r) f_j(r) = 0,$$  \hspace{1cm} (1.2)

and here one introduces semiclassical approximations to effect the solution of
these equations. Progress can only be made semiclassically, however, if (a) there are only a few channels involved and the transitions between them are localized, or (b) explicit dynamical approximations are incorporated in the treatment. The Landau-Zener-Stuckelberg (5) description of electronic transitions in atom-atom collisions is the best-known example of the first situation. The introduction of dynamical approximations is necessary if there are a large number of strongly coupled channels, as is typically the case if the internal states correspond to heavy particle degrees of freedom (i.e., rotation and vibration), or if the transition is not localized. For rotational/vibrational excitation in molecular collisions useful semiclassical analyses have been based on the distorted wave Born approximation (6,7) and on the sudden approximation (7), and the Eikonal approximation (8) has been used to describe electronic transitions in atomic collisions semiclassically.

This paper reviews a recently developed semiclassical theory (9,10) designed primarily for treating molecular collisions which take place on one electronically adiabatic potential energy surface; i.e., all degrees of freedom, internal as well as translation, are heavy particle degrees of freedom. Section IV discusses the extension to describe electronic transitions between different potential surfaces.) Its principal distinction from the semiclassical procedures noted above is that the dynamics of all degrees of freedom is treated classically, the only vestige of quantum mechanics which is retained being the quantum principle of superposition. The power of such an approach is that the full dynamics of all degrees of freedom can be treated exactly (i.e. numerically) via computation of the classical trajectories of the system; quantization of the internal degrees of freedom is achieved by supplying the appropriate boundary conditions to the classical equations of motion. Furthermore, since all intrinsic quantum effects – interference, tunneling, selection rules, resonances, and quantization itself – are actually a direct consequence of the superposition of probability amplitudes, this combination of "classical dynamics plus quantum superposition" contains all these effects at least qualitatively. It will be seen, too, that they are often described even quantitatively.

The net result, therefore, is that one has a prescription for using numerically computed classical trajectories for an atom-diatom collision system, say, to construct the probability amplitudes (i.e., S-matrix elements) for transitions between specific quantum states of the collision partners. The utility of purely classical trajectory methods in reactive and non-reactive molecular collisions is well-established (12,13) and "classical S-matrix" theory thus provides the possibility of incorporating many of the essential quantum effects within the overall classical trajectory approach.

The following sections first summarize without derivation the general theoretical results and then discuss a few simple examples to illustrate the
primary features of the theory. The topic of "classically forbidden" phenomena is given special emphasis, and the last section discusses how electronic transitions between different adiabatic electronic states can be described within this semiclassical theory.

II. THE CLASSICAL S-MATRIX

A. General Formulae

The general semiclassical theory has been derived in detail elsewhere (9, 10, 14). Here we wish to summarize the basic results as they apply to scattering systems and then illustrate the theory with several examples.

Consider first a non-reactive collision system with \( N \) degrees of freedom, one being radial translation of the collision partners and \((N-1)\) "internal" degrees of freedom which are quantized in the asymptotic regions. The Hamiltonian operator is

\[
H = \frac{p^2}{2\mu} + h + V
\]

where \( h \) is the Hamiltonian for the internal degrees of freedom and \( V \) is the interaction, which vanishes as the translational coordinate \( R \) becomes large. The internal Schrödinger equation

\[
\hbar \frac{d}{dt} |n> = \varepsilon_n |n>
\]

defines the internal states \( |n> \) and the internal energies \( \varepsilon_n \); there are \((N-1)\) quantum numbers, \( n = n_1, n_2, \ldots, n_{N-1} \) for the \((N-1)\) quantized degrees of freedom. The quantities of interest in a scattering problem are the on-shell S-matrix elements

\[
S_{n_2, n_1}(E)
\]

which are the transition amplitudes describing transitions between quantum states of the internal Hamiltonian; as indicated, the S-matrix elements depend on the value of the total energy.

The classical limit of the S-matrix, i.e., the "classical S-matrix", is constructed in the following manner. Let \( H(P, R, n, q) \),

\[
H(P, R, n, q) = \frac{p^2}{2\mu} + \varepsilon(n) + V(R, n, q)
\]

be the classical Hamiltonian function for the dynamical system, where \((n, q) = (n_1, q_1), i = 1, 2, \ldots, N-1\), are the action-angle variables (15) for the internal degrees of freedom; \( \varepsilon(n) \) is the LKB eigenvalue function for the internal degrees of freedom. (This form for the Hamiltonian can be obtained by carrying out a
canonical transformation from ordinary cartesian coordinates $R, x$ and momenta $P, p$. As $R \to \infty$, the interaction $V \to 0$, so that the "quantum numbers" $n(t)$ become constant in the asymptotic regions. The classical S-matrix element for the $n_1 \rightarrow n_2$ transition is constructed from the classical trajectory (or trajectories) with initial conditions at time $t_1$ given by

\begin{align}
n(t_1) &= n_1 \quad \text{(a specific set of integers)} \tag{2.4a} \\
R(t_1) &= \text{large} \tag{2.4b} \\
P(t_1) &= -\{2\mu[E - \epsilon(n_1)]\}^{1/2} \tag{2.4c} \\
q(t_1) &= \bar{q}_1 + \frac{3\epsilon(n_1)}{\partial n_1} R(t_1)/P(t_1) \tag{2.4d}
\end{align}

and with final conditions at time $t_2$ given by

\begin{align}
n(t_2) &= n_2 \quad \text{(another set of integers)} \tag{2.5a} \\
R(t_2) &= \text{large} \tag{2.5b} \\
P(t_2) &= +\{2\mu[E - \epsilon(n_2)]\}^{1/2} \tag{2.5c} \\
q(t_2) &= \text{anything} \tag{2.5d}
\end{align}

i.e., it is integer values of the action variables, or quantum numbers $n$ which are the classical counterpart to a quantum state, and the transition amplitude between quantum states is related to the trajectory (or trajectories) for which the action variables $n(t)$ are integers in the initial and final asymptotic regions.

To find those trajectories which satisfy the above double-ended boundary conditions it is useful to introduce the quantum number function $n_2(\bar{q}_1, n_1; E)$, the final value of the quantum numbers, not necessarily integral, which result from the classical trajectory with the initial conditions in Equation (2.4).

[Note: The second term in Equation (2.4d) is inserted as a matter of convenience so that $\bar{q}_1 = q(t_1) - \frac{3\epsilon(n_1)}{\partial n_1} R(t_1)/P(t_1)$ is time independent at $t_1 \rightarrow \infty$.]

This function $n_2(\bar{q}_1, n_1; E)$ is evaluated simply by numerically integrating the classical equations of motion with the indicated initial conditions. For a given total energy $E$ and a given set of initial quantum numbers $n_1$, the task is to find the particular values of the angle variables $\bar{q}_1$ for which $n_2(\bar{q}_1, n_1; E)$ turns out to be the specific integers $n_2$; i.e., suppressing the arguments $n_1$ and $E$, one must solve the equations

\begin{align}
n_2(\bar{q}_1) &= n_2 \quad \tag{2.6}
\end{align}

where $n_2$ on the RHS is a specific set of integers. This is a set of $(N-1)$ nonlinear equations in $(N-1)$ unknowns.

The classical S-matrix element for the $n_1 \rightarrow n_2$ transition is then given by
where $\partial n_2 / \partial q_1$ is the N-1 dimensional Jacobian determinant evaluated at the root of Equation (2.6), and $\phi$ is the classical action integral evaluated along the classical trajectory satisfying the above initial and final boundary conditions. If there is more than one trajectory at this energy corresponding to the same initial and final quantum numbers $n_1$ and $n_2$, Equation (2.7) is a sum of similar terms, one for each such trajectory.

Equation (2.7) is an asymptotic approximation to the S-matrix, in the same spirit as the WKB approximation (16) for systems with one degree of freedom. Thus the phase $\phi$ may be thought of as coming from the solution of a Hamilton-Jacobi-like equation and the pre-exponential Jacobian factor from the solution of a classical continuity equation (17). To see the physical meaning of the pre-exponential factor more clearly, note that for fixed $n_1$ the square modulus of the S-matrix element in Equation (2.7) gives the probability distribution in the final quantum number:

$$|S_{n_2, n_1}|^2 = \text{Prob}(n_2).$$

(2.9)

With $n_1$ fixed, however, the initial angles $\varphi_1$ and final quantum numbers $n_2$ are functionally related by the classical equations of motion; their probability distributions are thus related by

$$\text{Prob}(n_2) dn_2 = \text{Prob}(\varphi_1) d\varphi_1.$$  

(2.10)

With $n_1$ specified, though, the probability distribution in $\varphi_1$ is random (cf. the uncertainty principle), meaning that

$$\text{Prob}(\varphi_1) = \text{constant},$$

(2.11)

so that Equation (2.10) gives

$$\text{Prob}(n_2) = \text{constant} / \left(\frac{\partial n_2}{\partial \varphi_1} \right)_{n_1}.$$  

(2.12)

i.e.,
\[ |S_{n_2, n_1}|^2 = \text{constant} \left( \frac{3n_2}{\sqrt{2q_1 n_1}} \right) \]

which is pre-exponential factor in Equation (2.7).

B. Example: Vibrational Excitation

The simplest non-trivial example which illustrates the above formalism is the non-reactive collinear atom-diatom collision (18,19). Describing the vibrational degree of freedom by its action-angle variables, the classical Hamiltonian for this system is

\[ H(P, R, n, q) = \frac{P^2}{2\mu} + \varepsilon(n) + V(R, n, q) \]

If the oscillator is harmonic, the cartesian coordinate and momenta for vibration are expressed in terms of the action-angle variables by

\[ r(n, q) = r_0 + \left( \frac{2n + 1}{m\omega} \right)^{1/2} \sin q \]
\[ p(n, q) = \left[ m\omega(2n + 1) \right]^{1/2} \cos q \]

and the vibrational eigenvalue function is

\[ \varepsilon(n) = (n + \frac{1}{2})\omega \]

units being used such that \( \hbar = 1 \). For the application to be discussed (20) the interaction potential is an exponential repulsion between the atom and the closest end of the diatom, so that

\[ V(R, n, q) = V[R, r(n, q)] \]

where

\[ V(R, r) = \exp[\alpha(r-R)] \]

\( \alpha \) being a parameter of the potential.

According to the general prescription of the previous section, one considers classical trajectories characterized by initial conditions

\[ n(t_1) = n_1, \text{ an integer} \]
\[ R(t_1) = \text{large} \]
\[ P(t_1) = -\left\{ 2\mu (E - \epsilon(n_1)) \right\}^{1/2} \]
The function \( n_2(q_1, n_1) \) is the final vibrational quantum number that results from numerical integration of the equations of motion with these initial conditions. To describe a particular vibrational transition one looks for roots of the equation

\[
n_2(q_1, n_1) = n_2
\]

(2.18)

for a 0 \( \rightarrow \) 1 excitation, for example, Equation (2.18) reads

\[
n_2(q_1, 0) = 1
\]

Figure 1 shows an example of \( n_2(q_1, n_1) \) for the case \( n_1 = 1 \) and where the masses and potential parameters correspond roughly to \( \text{He} + \text{H}_2 \) at a total energy \( E = 10\hbar\omega_j = 5\text{eV} \). The horizontal line at \( n_2 = 2 \) indicates the two roots of the equation

\[
n_2(q_1, 1) = 2
\]

i.e., there are two classical trajectories which contribute to the 1 \( \rightarrow \) 2 vibrational transition at this energy.

The S-matrix element for such a transition is thus the sum of two terms,

\[
S_{n_2, n_1} = p^{1/2}_I \exp(i\frac{\Phi}{\hbar}) + p^{1/2}_{II} \exp(i\frac{\Phi}{\hbar})
\]

(2.19)

where \( \Phi \) is the classical action integral

\[
\Phi = \int_{-\infty}^{\infty} dt [R(t) \dot{P}(t) + q(t) \dot{\Delta}(t)]
\]

(2.20)

and the pre-exponential factor is

\[
p = [2\pi |n_2'(q_1)|]^{-1}
\]

(2.21)

for the two trajectories satisfying Equation (2.18). The transition probability is

\[
P_{n_2, n_1} = |S_{n_2, n_1}|^2 = p_I + p_{II} + 2(p_I p_{II})^{1/2} \sin[(\Phi_{II} - \Phi_I)/\hbar]
\]

(2.22)

If \( \hbar \) were actually set to zero, the interference term in Equation (2.22) would be infinitely oscillatory and thus absent, whereby Equation (2.22) would reduce to the completely classical result

\[
P_{n_2, n_1}^{CL} = p_I + p_{II}
\]

(2.23)

If interference is neglected, therefore, nature reverts to classical superposition, as in Equation (2.23), simply the sum of the probabilities associated...
Figure 2 shows the vibrational transition probabilities which correspond to Figure 1. The broken lines connect points which are the completely classical result, Equation (2.23), while the solid lines connect the semiclassical values (actually, the uniform (18) semiclassical values), and it is seen that the interference structure is quite prominent. These semiclassical values are in excellent agreement (within a few %) with essentially exact quantum mechanical calculations (20), showing that the semiclassical theory is an accurate description of the quantum effects for this system. In one sense, therefore, the system is highly quantum-like, in that the purely classical transition probabilities are poor; the quantum effects are chiefly of an interference nature, however, so that "classical dynamics plus quantum superposition" provides an accurate description.

The completely classical transition probability, Equation (2.23), is poor, however, only so long as one looks at transitions between individual quantum states. It is clear from Figure 2 that the purely classical transition probabilities will be much more satisfactory if one considers quantities which sum over a number of final quantum states. The average energy transfer, for example, is defined quantum mechanically as

$$\Delta \varepsilon_{n_1} = \sum_{n_2} P_{n_2,n_1} [\varepsilon(n_2) - \varepsilon(n_1)]$$

Upon summing over $n_2$ the interference term in the semiclassical transition probability essentially averages to zero, and if in addition the sum over $n_2$ is replaced by an integral, Equation (2.25) becomes

$$\Delta \varepsilon_{n_1} = \int d\bar{q}_1 \left( \frac{32\pi}{\hbar^2} \right)^{-1} \varepsilon(n_2) - \varepsilon(n_1)$$

and changing variables of integration from $n_2$ to $\bar{q}_1$ gives

$$\Delta \varepsilon_{n_1} = (2\pi)^{-1} \int_{0}^{2\pi} d\bar{q}_1 \{\varepsilon(n_2(\bar{q}_1,n_1)) - \varepsilon(n_1)\}$$

The average energy transfer is thus simply the energy transfer for the trajectory with initial conditions $n_1$ and $\bar{q}_1$, averaged over $\bar{q}_1$. In systems with more degrees of freedom integrals such as that in Equation (2.26) are conveniently performed by Monte Carlo, or other sampling methods (12,21).

Thus, if one is not interested in completely "state selected" information, but rather quantities that involve a sum or average over at least a few quantum states, then a purely classical treatment is probably completely adequate.

During the discussion of this example the reader may have noticed many analogies of this semiclassical theory of inelastic scattering to the semiclassical description of elastic scattering (1-3); indeed, this analogy was most
helpful in developing the concepts for the more general collision processes. The function \( n_2(\bar{q}_1) \), for example, plays the same role in inelastic scattering as does the classical deflection function \( \theta(b) \) of elastic scattering, and Equation (2.18) is analogous to the equation

\[
\theta(b) = \pm \theta
\]

which is central to the analysis of elastic scattering. The multiple roots of Equation (2.18), which give rise to the interference structure in the vibrational transition probabilities, are likewise analogous to the multiple roots of Equation (2.27) which are the origin of interference structure in elastic scattering. Finally, just as an extremum in \( \theta(b) \) leads to a "rainbow" in the differential elastic cross section, it will be seen in the next section that extrema in \( n_2(\bar{q}_1) \) (cf. Figure 1) give rise to similar structure in the vibrational translation probabilities.

III. CLASSICALLY FORBIDDEN PROCESSES

A. General Description: Vibrational Excitation.

As seen graphically in Figure 1, there are two roots of the equation

\[
n_2(\bar{q}_1,1) = n_2 \text{ for } n_2 = 1, 2, 3, 4.
\]

The equation

\[n_2(\bar{q}_1,1) = 5\]

however, has no roots, for the maximum of \( n_2(\bar{q}_1,1) \) is less than 5. The \( 1 \rightarrow 5 \) vibrational transition is thus classically forbidden (18) at this energy, the \( 1 \rightarrow 0, 1 \rightarrow 2, 1 \rightarrow 3, \) and \( 1 \rightarrow 4 \) transitions all being classically allowed.

It is important at the outset to recognize that the terms "classically allowed" and "classically forbidden" are dynamical concepts and distinct from "energetically allowed" or "energetically forbidden". In Figure 1, for example, the total energy being \( 10\hbar\omega \) implies that final vibrational states up to \( n_2 = 9 \) are energetically allowed; as seen, however, only final quantum numbers up to \( n_2 = 4 \) are accessible via classical dynamics from the initial state \( n_1 = 1 \).

To describe the \( 1 \rightarrow 5 \) classically forbidden transition semiclassically one notes that although Equation (3.1) has no real roots, there are nevertheless complex roots. This is easy to see in an approximate fashion by expanding \( n_2(\bar{q}_1) \) quadratically about its maximum:

\[n_2(\bar{q}_1) = n_2^{\text{max}} + 0 + \frac{1}{2} n_2''(\bar{q}_x)(\bar{q}_1 - \bar{q}_x) + \ldots\]

where \( \bar{q}_x \) is the position of the maximum (i.e., \( n_2'(\bar{q}_x) = 0 \)); the roots of Equation (3.1) are thus approximated by

\[\bar{q}_1 = \bar{q}_x \pm 1 \left[ \frac{2(n_2^{\text{max}} - 5)}{|n_2''(\bar{q}_x)|} \right]^{1/2}\]
The evaluation of $n_2(\bar{q}_1)$ for complex values of $\bar{q}_1$ is accomplished more generally (22,23) by actually numerically integrating the classical equations of motion with the initial conditions in Equation (2.17), with $\bar{q}_1$ complex. During the course of the trajectory all the coordinates and momenta of course become complex, so that the final values at time $\tilde{t}_2 - R(\tilde{t}_2)$, $P(\tilde{t}_2)$, $n(\tilde{t}_2)$, and $q(\tilde{t}_2)$ are in general complex. The value $n(\tilde{t}_2)$ can be made real, however, by the proper choice of the initial value $\bar{q}_1$ [i.e., $\bar{q}_1$ is chosen to satisfy Equation (3.1)], and with $n(\tilde{t}_2) \equiv n_2$ real, the final value of the translational momentum,

$$P(\tilde{t}_2) \equiv P_2 = \pm (2\mu(E - \epsilon(n_2)))^{1/2}$$

is automatically real. The final value of the translational coordinate is also a physical observable and should be real, and can be made so by integrating the equations of motion from $\tilde{t}_2$ to $t_2$,

$$t_2 = \tilde{t}_2 - (\mu/p_2) \text{Im} R(\tilde{t}_2),$$

at which time the trajectory is terminated; it is easy to see that $R(t_2)$ is real. (Note that this final pure imaginary time increment in the asymptotic region does not alter the final values of $n$ or $P$, for these quantities are time-independent in the asymptotic regions.)

Classically forbidden transitions are thus described by complex-valued classical trajectories (22,23) for which the total time increment $(t_2 - t_1)$ must also be complex. For the real part of the time increment one has the usual scattering limit

$$\text{Re}(t_2 - t_1) \rightarrow + \infty,$$

but the imaginary part of $(t_2 - t_1)$ is uniquely determined by the physically appropriate boundary conditions.

It should be clear that this numerical integration of complex-valued classical trajectories is essentially accomplishing an analytic continuation of classical mechanics in a manner analogous to the way the WKB approximation is used to describe tunneling in one-dimensional systems. It is possible, in fact, to cast the WKB approximation for one-dimensional tunneling into precisely the present language of complex-valued trajectories and complex time (22,24,25). Thus classically forbidden processes are a generalization of the concept of tunneling to dynamical systems with more than one degree of freedom.

Regarding the notion of complex time it is important to point out that the final values of the coordinates and momenta depend only on the time increment $(t_2 - t_1)$ and not on the particular path in the complex time path along which one numerically integrates the equations of motion from $t_1$ to $t_2$; this is true because the coordinates and momenta are analytic functions of time (because they
are generated by analytic continuation). One is at liberty, therefore, to choose any convenient time contour in order to integrate the equations of motion. [This statement must be modified when branch points exist (26)].

Along a complex-valued trajectory the action integral $\Phi$ in Equation (2.20) is also complex. If $\tilde{q}_I$ is a complex root of Equation (3.1), however, it is easy to show that $\tilde{q}_{II} = \tilde{q}_I^*$ is also a root; the phases $\Phi_I$ and $\Phi_{II}$ associated with these two complex trajectories are also complex conjugates of one another, $\Phi_{II} = \Phi_I^*$. If the root at $\tilde{q}_I$ corresponds to an exponential damping in the S-matrix, i.e., $\text{Im} \Phi_I > 0$, then it is clear that the second root at $\tilde{q}_{II}$ corresponds to an exponential enhancement, $\exp(\text{Im} \Phi/h)$, in the S-matrix. It is intuitively clear on physical grounds, and can be concluded more rigorously, that the exponentially large term should be discarded (it would go to $\pm \infty$ as $h \rightarrow 0$), so that the S-matrix element is just the single term

$$S_{n_2, n_1} = [-2\pi n_2'(\tilde{q}_I)]^{-1/2} \exp(i \Phi_I/h) \quad (3.4)$$

so that

$$P_{n_2, n_1} = [2\pi |n_2'(\tilde{q}_I)|^{-1} \exp(-2\text{Im} \Phi_I/h) \quad (3.5)$$

The transition probability thus has the exponential damping which is reminiscent of the WKB expression for one-dimensional tunneling.

The above theory has been applied (22,23) to the non-reactive collinear systems and excellent results have been achieved for vibrational probabilities as small as $10^{-11}$; the agreement with exact quantum mechanical values (20) is within a few percent, the same level of accuracy observed for classically allowed processes. The dynamics of even these weak classically forbidden transitions is still essentially classical, therefore, all the quantum effects arising from superposition; i.e., tunneling is simply an analytically continued interference effect.

Referring to Figure 1 again, it has been seen that the classical S-matrix is an accurate description of transitions to quantum numbers above or below the maximum of $n_2(\tilde{q}_I)$. The only situation in which the semiclassical theory has difficulty is when the final quantum number is close to $n_2^\text{max}$, i.e., when the transition is "just" allowed or forbidden. It is easy to see that the "primitive" semiclassical expressions, Equations (2.19)-(2.22) and Equation (3.4), become invalid in this case, for the pre-exponential factor becomes infinite [because $n_2'(\tilde{q}_I) \rightarrow 0$ as $\tilde{q}_1 \rightarrow \tilde{q}_x$]. This situation is precisely analogous to the breakdown of the WKB wavefunction near classical turning points, and to the rainbow infinity in the classical differential cross section for elastic scattering (1-3) there is always such a classical infinity at a boundary between classically
allowed and classically forbidden regions. For the present case the situation is easily remedied by invoking a uniform semiclassical expression (18,19,27) which makes a smooth transition through the allowed/forbidden boundary. In more complicated situations it is more difficult to discover the proper uniform semiclassical expressions, although considerable progress is being made in this regard (38-30). In some cases there may actually be no uniform asymptotic treatment which is possible (31,32).

B. Reactive Tunneling.

One of the most interesting examples of a classically forbidden process is tunneling in reactive systems which have activation barriers. The practical importance of this process lies in the fact that the energy region near the threshold for reaction, where tunneling effects are most significant, often dominates the thermal energy kinetics, particularly so if the transferred atom is hydrogen.

To describe rearrangement processes the theoretical expressions given above need simple modifications that are discussed in detail elsewhere (9,14). The essential ideas are unchanged except in an obvious manner; thus, to describe the reactive transition

\[ A + BC(n_1) \rightarrow AB(n_2) + C \]  \hspace{1cm} (3.6)

one must find the reactive trajectories corresponding to the initial and final quantum conditions for the internal degrees of freedom of the appropriate arrangement.

This section describes results (33) obtained for the collinear \( H + H_2 \) reaction at collision energies below the classical threshold for reaction, i.e., at energies for which all ordinary (i.e., real-valued) trajectories are non-reactive. The most novel feature of such a calculation is that one must take advantage of the flexibility described in the previous section regarding the choice of the complex time path in order to "make" the trajectory react. More details of this procedure are described elsewhere.

Figure 3 shows the ground state to ground state reaction probability for the collinear \( H + H_2 \rightarrow H_2 + H \) reaction on the Porter-Karplus (34) potential surface. Also shown are the results of quantum mechanical calculations (35,36) and purely classical Monte Carlo calculations (37), all for this same potential energy surface. One sees that there is a considerable amount of tunneling for this model system and that it is quite accurately described by classical S-matrix theory. Figure 4 shows the same results on a log scale, showing again that the dynamics is still essentially classical-like even at energies for which the transition is extremely weak.

Figure 5 shows the reactive trajectory which satisfies the \( n_1 = 0, n_2 = 0 \) quantization conditions for two different collision energies. The most significant qualitative feature here is that the tunneling dynamics "cuts the corner"
(38-41), i.e., does not follow the adiabatic path of least potential energy. This feature would seem to invalidate many approximate treatments of tunneling which reduce the problem to a one-dimensional one by invoking vibrational adiabaticity (42,43).

A dramatic illustration of the practical significance of reactive tunneling, as well as an interesting interpretation of the imaginary part of the time increment, is revealed by considering a thermal average of the reactive probability:

\[ \overline{P}(T) \equiv \beta \int_0^\infty dE \exp(-\beta E) P(E) \]  

(3.7)

where \( \beta = (kT)^{-1} \); \( \overline{P}(T) \) is the one-dimensional analog of the thermal rate constant for a three-dimensional system. Since there is just one complex-valued trajectory that contributes to the \( 0 \rightarrow 0 \) reaction, \( P(E) \) is of the form given by Equation (3.5) so that Equation (3.7) becomes

\[ \overline{P}(T) = \beta \int_0^\infty dE \left( 2\pi \left| \frac{\partial \phi}{\partial q_1} \right| \right)^{-1} \exp[-\beta E - 2\text{Im}\phi(E)/\hbar] \]  

(3.8)

Evaluating Equation (3.8) by the method of steepest descent (which is consistent with the general semiclassical theory) gives

\[ \overline{P}(T) = A(T) \exp(-\beta E - 2\text{Im}\phi(E)/\hbar) \]  

(3.9)

where \( A(T) \) is a slowly varying pre-exponential factor and \( E = E(T) \) is determined by the steepest descent condition

\[ \frac{d}{dE}[-\beta E - 2\text{Im}\phi(E)/\hbar] = 0 \]

or

\[ \text{Im}\phi'(E) = -\frac{1}{2} \hbar \beta \]  

(3.10)

The energy derivative of the classical action, however, is the time increment, so that the steepest descent condition is equivalently expressed as

\[ \text{Im}(t_2-t_1) = -\frac{1}{2} \hbar \beta \]  

(3.11)

From the imaginary part of the time increment for the complex-valued trajectory at energy \( E \), therefore, one associates a temperature according to Equation (3.11); the physical meaning is that this is the temperature for which the energy region about \( E \) makes the dominant contribution to the Boltzmann average for this temperature.
Figure 6 shows the $E$ versus $T$ relation given by Equation (3.11) for the present $H + H_2$ reaction. For a given temperature $T$ this graph gives the energy $E$ which is the most important for this temperature. Since the classical threshold for reaction is slightly above $E = 0.21$ eV (cf. Figure 3), Figure 6 shows that for temperatures below 1000°K the most important region for the Boltzmann average is below the classical threshold, demonstrating the importance of tunneling in this system. The temperature-dependent reaction probability is shown in Figure 7 as an Arrhenius plot, i.e., $\log \tilde{F}(T)$ vs. $T^{-1}$; the pronounced curvature below 1000°K is also a result of tunneling.

Another interesting interpretation of the $E$ vs. $T$ relation of Equation (3.11) (and shown in Figure 6) is obtained by considering the activation energy for the reaction. The activation energy, which is in general a function of temperature, is defined by

$$E_{\text{act}}(T) = -\frac{d}{dB} \ln \tilde{F}(T) \quad \text{(3.12)}$$

or from Equation (3.9)

$$E_{\text{act}}(T) = \frac{d}{dB}\{BE(B) + 2\text{Im}[E(B)]/\hbar\} \quad \text{(3.13)}$$

where $E(B) \equiv E(T)$ is the function defined implicitly by Equation (3.11) and where the $T$-dependence of the pre-exponential factor $A(T)$ has been ignored. It is easy to show that Equation (3.13) gives

$$E_{\text{act}}(T) = E(B) \quad \text{(3.14)}$$

i.e., the $E$ vs. $T$ relation defined by Equation (3.11) and shown in Figure 6 has the interpretation of the temperature-dependent activation energy. At high temperature it becomes constant, as expected, but because of tunneling falls considerably below the high temperature limit at low temperatures. It is interesting that this semiclassical theory leads to a definition of the activation energy in terms of purely dynamical quantities, with the imaginary part of the time increment playing a central role.

C. Applications to Three-Dimensional Collision Systems.

The discussion in Sections IIB, IIIA, and IIIB have all referred to collinear $A + BC$ collision systems since they are the simplest models which illustrate the essential features of the present semiclassical theory. Applications have also been made, however, to three-dimensional $A + BC$ collision systems, both reactive and non-reactive (26, 28, 44).

The most important feature of three-dimensional collisions which distinguishes them from the collinear models discussed above is the additional
degrees of freedom corresponding to rotational and orbital angular momentum. Because of this, one is almost always interested in cross sections that are summed and/or averaged over some of the quantum numbers; an ambitious goal, for example, would be to select the initial and final vibrational/rotational states (but not the projection quantum numbers), and this still involves a sum over three quantum numbers:

\[
\sigma_{n_2J_2 + n_1J_1} = \frac{\pi}{k_1^2(2j_1+1)} \sum_{J} \sum_{m_2,m_1} |S_{n_2J_2,m_2,n_1J_1,m_1}(E,J)|^2.
\]

These sums tend to quench the interference structure which the semiclassical theory provides and thus reduce the averaged cross section to that which would be calculated by the usual Monte Carlo procedures. This tendency is even further accentuated by the fact that with three internal degrees of freedom there will typically be more than two classical trajectories which contribute to a single S-matrix element (28); there will thus be more than one interference term, meaning that the interference will be even more easily quenched.

For the above reasons one expects a completely classical treatment to be adequate in most cases if the process of interest is classically allowed. The most practically important contribution of classical S-matrix theory is thus expected to be the ability to describe classically forbidden processes for which completely classical approaches are obviously inadequate. [The most useful version of the theory for application to three-dimensional collisions turns out to be a "hybrid" approach (26, 44, 45) in which the classical-like degrees of freedom (e.g., rotation), which have many quantum states strongly coupled, are treated within the usual Monte Carlo framework, while the quantum-like degrees of freedom (e.g., vibration) are quantized semiclassically via the boundary conditions of the trajectories; this is all accomplished without introducing any dynamical approximations.] Vibrational excitation, typically a weak transition, and reactive tunneling are two important examples of classically forbidden processes which have been discussed above, and the next section discusses another class of phenomena which are of this type, namely electronic transitions between different adiabatic potential energy surfaces.

IV. ELECTRONIC TRANSITIONS IN LOW ENERGY MOLECULAR COLLISIONS.

The description of inelastic and reactive scattering in Sections II and III had been relatively simple because no coupled channel expansion [Equations (1.1) and (1.2)] in the internal quantum states was made. A coupled channel expansion in internal states imposes an intrinsically quantum dynamical description of the internal degrees of freedom, and difficulties thus arise when one attempts to treat the translational dynamics classically. The problems related to mixing quantum and classical dynamics per se were avoided in the previous sections by treating the dynamics of all degrees of freedom classically and
quantizing the internal degrees of freedom by use of action-angle variables and asymptotic boundary conditions for the classical trajectories.

Describing electronic transitions in a molecular collision, such as A + B, presents an especially difficult problem to a semiclassical theory which wishes to refrain from incorporating any intrinsic dynamical approximations, for it is clear that the electronic degrees of freedom must be described by an expansion in electronic states while one at the same time wishes to retain the advantages of treating the dynamics of all heavy particle degrees of freedom classically. It is necessary, therefore, to deal with an explicit mixture of classical and quantum dynamics, not simply a combination of classical dynamics and quantum superposition. (One obvious way to avoid having to mix classical and quantum dynamics is to treat all internal degrees of freedom quantum mechanically, i.e., perform a coupled channel expansion in rotational/vibrational, as well as electronic, states. This is fruitless, however, for one cannot deal semiclassically with the large number of coupled channels without incorporating intrinsic dynamical approximations.)

In the following paragraphs we sketch (without derivation) the semiclassical model which emerges from classical S-matrix theory (46, 14). Although the description is certainly not an exact quantum mechanical treatment, the model is "dynamically exact" in that it does not incorporate any intrinsic approximations regarding the heavy particle dynamics. The model is essentially an extension of Stuckelberg's (5c,47) semiclassical treatment of electronic transitions in atomic collisions, and as such, the principal physical requirement is that the possibility of electronic transitions be localized.

The first point to be made is that the semiclassical solution of a coupled channel problem, such as Equation (1.2), results in classical motion on the adiabatic potential surfaces (48). If the channel indices i in Equation (1.2) denote electronic states and \( r = (r_1, r_2, \ldots, r_N) \) denotes all heavy particle coordinates, therefore, the potential matrix \( V_{ij}(r) \) is the matrix of the molecular electronic Hamiltonian in some molecular electronic basis set, and its eigenvalues \( \{\mathcal{W}_i(r)\} \) are the adiabatic potential surfaces which determine the classical motion of the nuclei.

Electronic transitions from one potential surface to another appear in classical S-matrix theory as a classically forbidden process in the sense that complex-valued classical trajectories are needed to describe them. To see this, note that the adiabatic potential surfaces \( \{\mathcal{W}_i(r)\} \) are the roots of the electronic secular equation

\[
\text{det}|V_{ij}(r) - \delta_{ij}\mathcal{W}| = 0
\]

(4.1)

i.e., the roots of an \( M^{th} \) order polynomial, \( M \) being the number of electronic
basis functions. The M different roots of an \( M^{\text{th}} \) order polynomial, however, are simply the M different branches of the same analytic function. For the two channel case, for example, the eigenvalues of the two-by-two potential matrix are given explicitly by

\[
W_i(t) = \frac{1}{2}(V_{11} + V_{22}) \pm \frac{1}{2}(V_{11} - V_{22})^2 + 4V_{12}^2)^{1/2}, \tag{4.2}
\]

\( i = 1, 2 \), showing that the two roots are a direct result of the double valuedness of the square root function. The three roots of a three-by-three secular equation are a result of the triple valuedness of the cube root function, and in general, the M roots of an M-by-M secular equation result from the M-fold multivaluedness of the M\(^{\text{th}}\) root function.

Transitions from one adiabatic surface to another are described by complex-valued classical trajectories which change from one branch or Riemann sheet, of the multivalued electronic potential function to another. Thus with initial conditions of the trajectory specified, the nuclear coordinates \( r(t) \) are functions only of the time, and the adiabatic potential surfaces are likewise functions only of time,

\[
W(t) = W[r(t)] \quad . \tag{4.3}
\]

Considered as a function of the complex time variable, \( W(t) \) has branch points in the time plane as a result of the multivalued character of the roots of a secular equation. For the two channel case, for example, the condition

\[
0 = W_2(t) - W_1(t) = [(V_{11} - V_{22})^2 + 4V_{12}^2]^{1/2} \tag{4.4}
\]

defines the branch points \( t_* \); these are also recognized as the complex times at which the adiabatic potentials intersect. If \( \text{Im} t_* > 0 \), choosing the time path in the complex \( t \)-plane to pass below \( t_* \) will cause the trajectory to terminate on the same adiabatic surface on which it began; choosing the time contour to pass above \( t_* \), however, will cause the trajectory to emerge on another branch of the potential energy surface, i.e., in another adiabatic electronic state, meaning that an electronic transition has occurred.

Classical S-matrix elements describing a transition from an initial rotational/vibrational/electronic state to a particular final rotational/vibrational/electronic state is constructed from the appropriate complex-valued trajectories in an analogous manner to that described in Sections II and III. Thus if \( \alpha \) and \( \beta \) denote the electronic states and \( n \) the heavy particle quantum numbers, the appropriate generalization of Equation (2.7) is (45)
\[ S_{\beta n_2, \alpha n_1} (E) = \left[ \frac{(\alpha n_1)^{\beta} \alpha \alpha (q_1, n_1 \alpha)}{\alpha \alpha (q_1, n_1 \alpha)} \right]^{-1/2} \times \exp \left[ i \Phi (n_2 \beta, n_1 \alpha; E)/\hbar \right] \], \hspace{1cm} (4.5) \]

where the quantum number function
\[ n_2 \beta (q_1, n_1 \alpha) \]
is the final quantum number which results from a complex-valued trajectory beginning on Riemann sheet \( \alpha \) of \( \mathcal{H}(r) \), i.e., electronic state \( \alpha \), with the indicated initial conditions and with the complex time path chosen so that the trajectory terminates on Riemann sheet \( \beta \). The initial angle variables are determined by the usual conditions
\[ n_2 \beta (q_1, n_1 \alpha) = n_2 \], \hspace{1cm} (4.6) \]
and the action integral is
\[ \Phi (n_2 \beta, n_1 \alpha) = \int_{t_0}^{t_1} dt [-R(t) \dot{q}(t) - \dot{q}(t) n_2 \alpha (t)] + \int_{t_1}^{t_2} dt [-R(t) \dot{q}(t) - \dot{q}(t) n_2 \alpha (t)] \]
\[ + \int_{t_2}^{t_0} dt [-R(t) \dot{q}(t) - \dot{q}(t) n_2 \alpha (t)] \], \hspace{1cm} (4.7) \]
where \( F_4 (n_2 \beta, n_1 \alpha) \) is the classical generating function for the canonical transformation from the action-angle variables of potential surface \( \alpha \) to those of potential surface \( \beta \). (The action integral \( \Phi \) can be shown to be independent of the time \( t_0 \) at which this transformation is carried out.) Since \( \Phi \) is in general complex, the \( S \)-matrix elements have an exponential damping characteristic of classically forbidden processes.

One can show that the above model reproduces several well-known approximate results in the appropriate simplifying limits: the Landau-Zener-Stückelberg approximation (5) for avoided crossings of adiabatic potential curves, the Demkov approximation (49) for transitions between nearly parallel potential curves, and Nikitin's formula (50) for fine structure transitions in \( ^2P \) atoms. Another approximate version of the theory which involves only real-valued trajectories and discards all interference terms is essentially equivalent to Tully and Preston's (51) "trajectory surface hopping" model which has been successfully employed by them to describe non-adiabatic transitions in the \( \text{H}^+ + \text{H}_2 \) system; more recently Chapman and Preston (52) have carried out similar calculations for the \( \text{Ar}^+ + \text{H}_2 \to \text{ArH}^+ + \text{H}, \text{Ar} + \text{H}_2^+ \) system, also with good agreement with experimental results.
To the extent that electronic transitions are reasonably localized, therefore, it is possible to formulate a semiclassical theory which is free of any intrinsic approximations regarding the heavy particle dynamics. The nuclear dynamics is described by the classical equations of motion with the potential energy being the adiabatic electronic energy; electronic transitions result because the potential energy function is multivalued and there exists complex-valued classical trajectories which begin on one Riemann sheet of the potential energy function and terminate on another. The quantum principle of superposition is incorporated in the description in the same manner as with a single potential energy surface.

V. CONCLUDING REMARKS

It appears, therefore, that the semiclassical model of "classical dynamics plus quantum superposition" accurately describes many of the quantum effects in molecular collision phenomena. As such, methods based on this semiclassical theory may prove to be a useful way to carry out calculations, particularly so for three-dimensional collision systems for which the large number of quantum states associated with the heavy particle degrees of freedom obviates a quantum mechanical coupled channel description. As with the semiclassical treatment of elastic scattering, however, perhaps the most important contribution of the approach is the physical picture it provides, i.e., the realization that the heavy particles dynamics is essentially classical, with all significant quantum effects arising from the superposition of semiclassical probability amplitudes.

VI. REFERENCES

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(48) To show this one writes the radial function matrix $f_{1+k}(r)$ in the form $f(r) = \hat{A}(r) \cdot \exp[i\hat{S}(r)/\hbar]$, substitutes into Equation (1.1), and solves for $\hat{A}(r)$ and $\hat{S}(r)$ to lowest order in $\hbar$.

FIGURE CAPTIONS:

**Figure 1:** An example of the quantum number function $n_{2}(\hat{q}_{1},n_{1})$ here with $n_{1} = 1$. The ordinate is the final value of the vibrational quantum number as a function of the initial phase $\hat{q}_{1}$ of the oscillator, along a classical trajectory with the initial conditions in Equation (2.17). The dotted line at $n_{2} = 2$ indicates the graphical solution for the two roots of the equation $n_{2}(\hat{q}_{1},1) = 2$.

**Figure 2:** Vibrational transition probabilities for collinear He + H$_{2}$ at total energy $E = 10$ h$\omega$, for initial vibrational states $n_{1} = 0$ (top), 1, 2 (bottom). The dotted lines connect the completely classical transition probabilities, Equation (2.23), and the solid lines connect the semiclassical results (which, on the scale of the drawing, are essentially the same as the exact quantum mechanical values of ref. 20.)

**Figure 3:** Reaction probability for the ground state to ground state H + H$_{2}$ + H$_{2}$ + H reaction (collinear) as a function of the relative collision energy $E_{c}$. The crosses and circles are the quantum mechanical
results of Diestler (35) and Wu and Levine (36), and the broken line is the purely classical Monte Carlo result (37), all for the same [Porter-Karplus (34)] potential surface.

**Figure 4:** Same as Figure 3, but with a log scale for the ordinate.

**Figure 5:** Trajectories for reactive tunneling in the ground state to ground state $H + H_2$ reaction at a collision energy $E_o = 0.20$ eV (dotted line) and $E_o = 0.02$ eV (dash-dot line). The dashed line is the "reaction coordinate", i.e., the path of minimum potential energy. $R_a$ and $r_a$ are the real parts of the complex translational and vibrational coordinates, respectively, for arrangement A + BC.

**Figure 6:** The energy-temperature relation determined by the steepest descent condition, Equation (3.10) or (3.11), for the Boltzmann average of the $H + H_2$ reaction probability. For a given temperature $T$ the corresponding energy $E$ is the value which makes the dominant contribution to the Boltzmann average at that temperature. $E(T)$ can also be interpreted as the temperature-dependent activation energy.

**Figure 7:** The temperature-dependent reaction probability for the ground state to ground state $H + H_2$ reaction. The present semiclassical treatment is only valid for $T \leq 1000^\circ$K, so the dashed part of the curve is simply an extrapolation to unit probability at infinite temperature.
Fig. 1
Fig. 2
Fig. 5
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