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COMPLEX-VALUED CLASSICAL TRAJECTORIES FOR REACTIVE TUNNELING IN THREE-
DIMENSIONAL COLLISIONS OF H AND H₂^{††}

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ABSTRACT

Complex-valued classical trajectories for three dimensional reactive collisions of H + H₂ have been calculated at collision energies below the classical threshold for reaction, and from such trajectories classical S-matrix elements for the 0 → 1 rotational transition have been constructed. Comparison with available quantum mechanical results for the same system are encouraging and suggest that this semiclassical theory is capable of accurately describing reactive tunneling in a physically realistic model of a chemical reaction. Ways of simplifying the practical aspects of applying classical S-matrix theory to three dimensional reactive systems are also described.

I. INTRODUCTION

The utility of classical trajectory methods for studying the dynamics of chemical reactions is well-established¹. Recent work²⁻⁴ has shown how classical mechanics (i.e., numerically computed trajectories) can also be used semiclassically by incorporating the quantum principle of superposition, and it has been seen in a number of examples² that this "classical S-matrix" theory is an accurate description of the quantum effects in molecular collisions.

A most important recent development^{2f-2h,3g} has been the ability to analytically continue classical dynamics in such a way as to be able to describe processes which do not take place via ordinary classical mechanics. A common example of such "classically forbidden" processes is reactive tunneling in chemical reactions (e.g., $A + BC \rightarrow AB + C$) for which an activation barrier exists. In such cases it is well-known⁵ that the threshold, or tunneling region dominates the rate of the reaction at low and moderate temperatures, particularly so if the transferred atom is hydrogen. The ability of these semiclassical, complex-valued classical trajectory methods to describe reactive tunneling is thus an important step forward.

Another reason for our concentration on classically forbidden processes is that under most conditions one expects the interference effects predicted by the semiclassical theory for classically allowed transitions to be largely quenched by the averagings that are present for a realistic collision system in three-dimensional space^{2d}. [Note that even the perfect $A + BC$ experiment - selection of n , j , and m quantum numbers initially and finally - still involves an average over

one variable, the total angular momentum:

$$\sigma_{n_2 j_2 m_2 \leftarrow n_1 j_1 m_1} = \frac{\pi}{k_1^2} \sum_J (2J+1) |S_{n_2 j_2 m_2, n_1 j_1 m_1}(J)|^2 \quad (1)$$

A much more realistic experiment, which is still quite ambitious, would omit selection of the m -components of the rotational state, and this involves sums over three variables:

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1} = \frac{\pi}{k_1^2 (2j_1 + 1)} \sum_{J m_2 m_1} (2J+1) |S_{n_2 j_2 m_2, n_1 j_1 m_1}(J)|^2 \quad (2)$$

When interference effects present in classically allowed transitions are quenched, however, it has been argued, and demonstrated, that strictly classical trajectory methods¹ (e.g., Monte Carlo averaging) are quite adequate^{2d}. These strictly classical methods cannot give a meaningful description of classically forbidden processes, however, so it is this case for which classical S-matrix theory makes a unique and important contribution.

An earlier paper^{2g} has reported the results of a classical S-matrix calculation for the $H + H_2$ reaction on the Porter-Karplus⁶ potential surface within a co-linear model. Comparison of these results with accurate quantum mechanical calculations in the tunneling region indicated the semiclassical theory to be an accurate description of reaction tunneling for this co-linear system.

This paper reports the results of analytically continued classical S-matrix theory applied to the three-dimensional $H + H_2$ reaction on the Porter-Karplus surface. This paper may thus be viewed as a synthesis of the complex-valued classical trajectory procedures developed in reference 2g for dealing with the reactive co-linear $A + BC$ system and those developed

in reference 2h for dealing with the non reactive A + BC system in three dimensions.

Section II first summarizes the general theory briefly and discusses some of the practical aspects of the calculation that arise for the reactive A + BC system in three dimensions. The results of the calculation are presented in Section III and compared with available quantum mechanical work on the same potential surface; the agreement is seen to be quite encouraging. Section IV concludes by discussion ways of simplifying the semiclassical calculation and thus making it more practical for general applicability. Some of the more subtle theoretical features that arise in the analytic continuation of classical mechanics for reactive systems are discussed in Appendix A, and Appendix B summarizes the cross section formulas that pertain to the A + BC collision when some, or all, of the atoms are identical.

II. GENERAL THEORY AND ASPECTS OF THE CALCULATION

The general expressions for the classical limit of S-matrix elements for a specific quantum transition of the three-dimensional reactive A + BC collision system have been given previously^{2a}. Thus, if n_1^a, j_1^a, ℓ_1^a are the initial vibrational, rotational, and orbital angular momentum quantum numbers of arrangement a (A + BC), and n_2^c, j_2^c, ℓ_2^c are the analogous quantities for final arrangement c (AB + C), then the classical S-matrix element for the transition is

$$S_{n_2^c j_2^c \ell_2^c, n_1^a j_1^a \ell_1^a}(J, E) = \sum D^{-1/2} \exp[i\phi(n_2^c j_2^c \ell_2^c, n_1^a j_1^a \ell_1^a)], \quad (3)$$

where D is proportional to the determinant of the three-dimensional Jacobian

$$D = (2\pi)^3 \left[\frac{\partial(n_2^c j_2^c \ell_2^c)}{\partial(q_{n_1}^a q_{j_1}^a q_{\ell_1}^a)} \right] ; \quad (4)$$

J and E are the total angular momentum and total energy, and units are used throughout such that $\hbar = 1$.

The summation in Equation (3) is over all those classical trajectories for which the quantum numbers (i.e., the action variables of the pair of action-angle variables for each internal degree of freedom) are n_1^a, j_1^a, ℓ_1^a initially and n_2^c, j_2^c, ℓ_2^c finally; i.e., for the fixed initial integer values n_1^a, j_1^a, ℓ_1^a one must find the initial values of the conjugate angle variables $q_{n_1}^a, q_{j_1}^a, q_{\ell_1}^a$ for which the final quantum numbers come out to be the desired final integer values. Stated another way, one must solve the following three non-linear equations simultaneously:

$$\begin{aligned} n_2^c(q_{n_1}^a, q_{j_1}^a, q_{\ell_1}^a) &= n_2^c \\ j_2^c(q_{n_1}^a, q_{j_1}^a, q_{\ell_1}^a) &= j_2^c \\ \ell_2^c(q_{n_1}^a, q_{j_1}^a, q_{\ell_1}^a) &= \ell_2^c \end{aligned} , \quad (5)$$

where the LHS of Equation (5) denotes the final quantum numbers (not necessarily integral) that result from the classical trajectory with the indicated initial conditions, and the RHS of Equation (5) are specific integers. The determinant in Equation (4) is the determinant of the matrix of partial derivatives of the LHS of Equation (5) evaluated at the values of $q_{n_1}^a, q_{j_1}^a, q_{\ell_1}^a$ that satisfy Equation (5). The summation

in Equation (3) is thus a sum over the various sets of triples $(q_{n_1}^a, q_{j_1}^a, q_{\ell_1}^a)$ that satisfy Equation (5).

The $n_1^a, j_1^a, \ell_1^a \rightarrow n_2^c, j_2^c, \ell_2^c$ transition is said to be classically forbidden if there are no real values of the angle variables that satisfy Equation (5). Even in this case, however, there will be complex roots, and along such complex-valued trajectories the action integral ϕ is complex, leading to the exponential damping factor $\exp(-\text{Im}\phi/\hbar)$ in Equation (3) that is characteristic of classically forbidden, or tunneling precesses.

The quantum number functions in Equation (5) are evaluated for complex $(q_{n_1}^a, q_{j_1}^a, q_{\ell_1}^a)$ by actually numerically integrating the classical equations of motion with the indicated complex initial conditions. The precise manner of specifying the complex initial conditions is the same as has been described in detail before^{2d,2h} for the non-reactive A + BC collision in three dimensions; briefly, one specifies the initial values $n_1^a, j_1^a, \ell_1^a, q_{n_1}^a, q_{j_1}^a, q_{\ell_1}^a$, and J and E (which are conserved), transforms these initial values into initial values for the Cartesian coordinates of the A + BC system in its center of mass, carries out the numerical integration of the complex-valued trajectory in Cartesian coordinates, and at the end of the trajectory transforms the final values of the complex Cartesian coordinates into final values of the action-angle variables for the final arrangement.

For a given set of complex initial conditions the classical trajectory is "made" to react by the same procedure that was used before^{2g} for the co-linear H + H₂ calculation, i.e., by the choice of the complex time path. Thus with the numerical integration begun in the manner discussed above (i.e., just as for the non-reactive 3-d case^{2h}) the time increments are

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chosen real and positive until the time that the turning point in the relative A + BC motion is reached; from this point the complex time path is chosen to force atoms A and B together. The time increments are then chosen predominantly real and positive until AB and C have separated sufficiently far. As has been pointed out before^{2f-2h}, the classical S-matrix is invariant to the particular choice of the complex time path (but see Appendix A for a caution regarding this point), so there is no loss of generality in our choosing the time path in this manner.

The calculation of the action integral ϕ is simplified, as before for the non-reactive 3-d case^{2h}, by beginning and ending the numerical integration at a time when the diatomic molecule is at an inner radial turning point of its motion. The precise expression for the action integral for the reactive A + BC system in three-dimensions is then a simple extension of the expression for the non-reactive case^{2d,2h},

$$\begin{aligned} \phi(n_2^c j_2^c \ell_2^c, n_1^a j_1^a \ell_1^a) = & \frac{\pi}{2}(\ell_1^a + \ell_2^c) - [Jq_{J_2} + \ell_2^c q_{\ell_2^c} \\ & + j_2^c q_{j_2^c} + p_2^c R_2^c + \frac{\pi}{2}(j_2^{c^2} - \ell_2^{c^2})/J] \\ & + [Jq_{J_1} + \ell_1^a q_{\ell_1^a} + j_1^a q_{j_1^a} + p_1^a R_1^a \\ & + \frac{\pi}{2}(j_1^{a^2} - \ell_1^{a^2})/J] + \int_{t_1}^{t_2} dt \, 2T, \quad (6) \end{aligned}$$

where T is the total kinetic energy, expressed in the Cartesian variables of either arrangement.

The most difficult aspect of applying the above expressions for the classically forbidden reactive case is in finding the complex roots of

Equation (5). Unlike the non-reactive case^{2h} there is no simple way to obtain an initial guess for the root by carrying out a preliminary sweep of the angle variables through their classically allowed (i.e., real) domains; i.e., since the reactive transition is classically forbidden at the collision energy of interest, all real trajectories are non-reactive and thus provide no information as to what complex values of the angle variables are most likely to lead to reactive trajectories with the correct final integer values of the quantum numbers.

To find the correct roots, therefore, we resorted to a general search procedure⁷ designed to minimize a function of many variables. Defining

$$\begin{aligned} f(q_{n_1}^a, q_{j_1}^a, q_{l_1}^a) \equiv & |n_2^c(q_{n_1}^a, q_{j_1}^a, q_{l_1}^a) - n_2^c|^2 \\ & + |j_2^c(q_{n_1}^a, q_{j_1}^a, q_{l_1}^a) - j_2^c|^2 \\ & + |l_2^c(q_{n_1}^a, q_{j_1}^a, q_{l_1}^a) - l_2^c|^2, \end{aligned} \quad (7)$$

this search routine was applied to the function f , the values of $q_{n_1}^a, q_{j_1}^a, q_{l_1}^a$ for which f takes on its minimum value of zero being a root of Equation (5). This search routine has the advantage of being extremely general (i.e., successive iterations almost always move toward a root no matter what the initial guess), but it is extremely slowly convergent. Thus it was found to be most efficient to use this minimization routine⁷ to begin the search for a root of Equation (5), but when it was deemed that one was sufficiently close to a root a switch was made to a multi-dimensional Newton iteration procedure that then converged to the root quite rapidly.

At best, however, this way of finding the roots of Equation (5) is awkward and would be difficult to automate and apply on a large scale. It was feasible, however, to carry out a limited number of calculations in order to get a reasonable comparison of the semiclassical theory with quantum mechanical calculations. The possibility of simplifying these practical difficulties of the semiclassical calculation through use of the "partial averaging" trick described before^{2h} for non-reactive $A + BC$ collisions in three dimensions is discussed in Section IV.

III. RESULTS

In order to observe a purely reactive process in $H + H_2$ collisions one must consider a change in the parity of the rotational quantum number of H_2 . Thus we have considered the transition $(n_1, j_1) = (0, 0)$ to $(n_2, j_2) = (0, 1)$, which is also the transition studied in most detail quantum mechanically by Wolken and Karplus⁸.

In carrying out the semiclassical calculation the three H atoms are, of course, distinguishable, and we have calculated the S-matrix element for reaction with one of the H atoms in H_2 , i.e., $H_A + H_B H_C \rightarrow H_A H_B + H_C$. The correctly symmetrized reaction probability is given by multiplying the distinguishable probability by 3,

$$P_{\text{sym}} = 3|S|^2 \quad ; \quad (8)$$

the factor is 3, not 2 as one would naively guess. Appendix B summarizes the cross section formulas for the $A + BC$ collision system that pertain to various combinations of identical atoms.

For the transitions discussed in this section we found four roots to

Equation (5), i.e., four different complex-valued trajectories that satisfied the appropriate double-ended boundary conditions. Although we are reasonably confident that these are all the trajectories that contribute significantly, it is difficult to be absolutely certain because the angle variables for the different roots do not fall in any simple pattern as they do for the non-reactive case^{2d,2h}. These four roots of Equation (5) were found simply by starting the root-search procedure described above with a number of different initial values to see how many different trajectories it could find which satisfied these boundary conditions. Once such a trajectory was found it was possible to "follow" it as one continuously changed the total energy E and/or total angular momentum J . In no case did we see evidence of more than these four roots.

The first series of calculations investigated the energy dependence of the reaction probability for total angular momentum $J \neq 0$. Since the classical threshold for reaction on the Porter-Karplus surface is ~ 0.25 eV collision energy^{1b} — i.e., there are no ordinary (real-valued) classical trajectories below this energy that react — we are primarily interested in the energy region just below this value. Figure 1 shows the transition probability in this region of collision energy. The solid line is the semiclassical result obtained⁹ by forming the square modulus of Equation (3), and the broken line is the result obtained if the interference terms are omitted. The two points are the quantum mechanical results of Wolken and Karplus⁸ for the same quantity.

The agreement of the quantum and semiclassically reaction probabilities is quite reasonable, although not as precise as one might have hoped. One must keep in mind, however, that although these quantum mechanical

calculations should be the most accurate yet carried out for this system, it is probably not realistic to say that they are the "final word" on it, their primary shortcoming being (as discussed by the authors⁸) the lack of any excited vibrational states in the coupled channel expansion. It should be noted, nevertheless, that Wolken and Karplus⁸ quantum mechanical results and those of classical S-matrix theory, as compared in Figure 1, agree much more closely with one another than either do with the distorted wave calculations of Tang and Karplus¹⁰; these latter quantum calculations appear to be about a factor of 50 or 60 smaller than that of Wolken and Karplus⁸ at 0.20 eV, for example, whereas our semiclassical value is less than a factor of 2 smaller.

Another possible cause for the lack of more precise agreement in Figure 1 is that one does not know how to construct a uniform semiclassical approximation for the present case of a reactive system; the four term formula^{2d,2h} used previously for non-reactive systems is not applicable. If one were able to discover the proper uniform semiclassical expression for the present situation, then the agreement in Figure 1 might be improved.

In addition to these results for the energy dependence of the $J = 0$ reaction probability a series of calculations was carried out to learn about the dependence on J for a fixed collision energy. Because of the difficulty of the calculations, however, this was done for only one of the four roots to Equation (5); since the J -dependence of all four roots was similar, this is not a serious shortcoming for the purpose of drawing qualitative conclusions.

Figure 2 shows the J-dependence of the reaction probability (resulting from one of the complex trajectories at each J) for a collision energy of 0.20 eV, the solid line being the sum of the two branches $\ell_2 = J + 1$ and $J - 1$. Figure 3 shows the center of mass scattering angle that results from this trajectory as a function of J, again for the two branches $\Delta\ell = +1, -1$.

From these quantities in Figures 2 and 3 it is possible to construct a semiclassical approximation to the angular distribution of the reactive scattering. This is given by

$$\sigma(\theta) = \sigma_+(\theta) + \sigma_-(\theta) \quad (9)$$

the $\pm$ referring to $\Delta\ell = \pm 1$, where

$$\sigma_{\pm}(\theta) = (J_{\pm} + 1/2) [k_1^2 \sin\theta |\Theta_{\pm}'(J_{\pm})|]^{-1} P_{\pm}(J_{\pm}) \quad , \quad (10)$$

where $P_{\pm}(J)$ and $\Theta_{\pm}(J)$ are the two branches of the reaction probability and classical deflection function shown in Figures 2 and 3, respectively, and where $J_{\pm}$ is determined by the classical relation

$$\Theta_{\pm}(J) = \theta \quad . \quad (11)$$

Figure 4 shows this angular distribution. Since only one of the four reactive trajectories was used to construct it, absolute values of the differential cross section are not meaningful (a rough approximation to the absolute values can be obtained by multiplying by ~ 5), but the relative angular distribution should be. Although the experimental results of Geddes, Krause, and Fite¹¹ pertain to a different isotopic combination, $D + H_2 \rightarrow DH + H$, it is interesting to note that their center of mass differential cross section agrees extremely well with Figure 4,

both falling to zero at about 120° .

IV. CONCLUDING REMARKS

Classical S-matrix elements for the $0 \rightarrow 1$ rotational transition in three dimensional $H + H_2$ reactive collisions have been calculated in the energy region below the classical threshold. Comparison with available quantum mechanical calculations are encouraging, suggesting that reactive tunneling in a physically realistic system can be accurately described within the framework of this semiclassical theory.

The practical aspects of applying the theory to reactive systems in three dimensions are difficult, however, and one seeks alternative procedures that would make the theory of more general applicability. The most promising avenue for such simplifications is the "partial averaging" trick that has been described earlier^{2h} for the non-reactive $A + BC$ collision system in three dimensions and which is currently giving excellent results for this case¹².

To summarize the approach briefly, one assumes that there are at least a few final values j_2^c and ℓ_2^c that have comparable probability so that these degrees of freedom can be treated in a "unquantized" manner, i.e., so that a sum over them can be replaced by an integral. Specifically, one averages the square modulus of the classical S-matrix element of Equation (3) over a quantum number width about j_2^c and ℓ_2^c (hence the term "partial averaging")

$$\begin{aligned}
 & |S_{n_2^c j_2^c \ell_2^c, n_1^c j_1^c \ell_1^c}|^2 \text{ averaged} \\
 &= \int_{\ell_2^c - 1/2}^{\ell_2^c + 1/2} d\ell_2^c \int_{j_2^c - 1/2}^{j_2^c + 1/2} dj_2^c |S_{n_2^c j_2^c \ell_2^c, n_1^c j_1^c \ell_1^c}|^2 \quad (12)
 \end{aligned}$$

The integrals over j_2^c and ℓ_2^c are then converted into ones over the conjugate initial variables, $q_{j_1}^a$ and $q_{\ell_1}^a$, and the Jacobian resulting from this change of integration variables combines with that in Equation (4) to give^{2h}

$$|S_{n_2^c j_2^c \ell_2^c, n_1^a j_1^a \ell_1^a}|^2_{\text{averaged}} = \int d(q_{j_1}^a/2\pi) \int d(q_{\ell_1}^a/2\pi) \times \left[2\pi \left| \frac{\partial n_2^c}{\partial q_{n_1}} \right| \right]^{-1} \exp(-2\text{Im}\phi) \quad (13)$$

where interference terms in the integrand of Equation (13) have been discarded; i.e., it is assumed that they are quenched by the averaging procedure. The integrals over $q_{j_1}^a$ and $q_{\ell_1}^a$ are over those values for which j_2^c and ℓ_2^c come out in the interval $(j_2^c - 1/2, j_2^c + 1/2)$ and $(\ell_2^c - 1/2, \ell_2^c + 1/2)$; the most practical way of carrying out this would be to sweep $q_{j_1}^a$ and $q_{\ell_1}^a$ through their entire domains for which reactive trajectories can be obtained¹³ and place the numerical value of the integrand of Equation (13) in the appropriate "box" labeled by the closest integer values of j_2^c and ℓ_2^c .

In practice, of course, one is actually not interested in individual S-matrix elements but in cross sections, and usually cross sections that involve an average and sum over some of the quantum number labels of the collision partners; cf. Equation (2) of the INTRODUCTION. The total reactive cross section from a given n_1^a, j_1^a state of BC to a final n_2^c state of AB, summed over final rotational states, and summed and averaged over m-components of molecular rotation, for example, is given in the

"partial averaging" framework by

$$\sigma_{n_2^c \leftarrow n_1^a j_1^a}(E_1) = \frac{\pi}{k_1^2 (2j_1^a + 1)} \int dJ (2J + 1) \int d\ell_1^a \frac{1}{2\pi} \int_0^{2\pi} dq_{j_1^a} \frac{1}{2\pi} \int_0^{2\pi} dq_{\ell_1^a} P_{n_2^c, n_1^a}(j_1^a, \ell_1^a, q_{j_1^a}, q_{\ell_1^a}; J, E) \quad (14)$$

where $P_{n_2^c, n_1^a}$, the integrand of Equation (14), is essentially a one dimensional-like reaction probability for the specific initial and final states n_1^a and n_2^c :

$$P_{n_2^c, n_1^a} \equiv [2\pi \left| \frac{\partial n_2^c}{\partial q_{n_1}} \right|]^{-1} \exp(-2\text{Im}\phi) \quad (15)$$

Thus for the fixed initial values $j_1^a, \ell_1^a, q_{j_1^a}, q_{\ell_1^a}$, J , and E , one must solve only the one non-linear equation

$$n_2^c(q_{n_1}^a) = n_2^c \quad (16)$$

and from this one-dimensional trajectory relation one constructs the one-dimensional-like reaction probability in Equation (15) and averages it (via Monte Carlo sampling, say) over the initial conditions as in Equation (14).

The primary feature of this partial averaging approach is that one quantizes only that (or those) degree of freedom that is highly quantum-like, vibration in this case. (It is clear that one cannot also "partially average" the vibrational degree of freedom, for there is only one vibrational state energetically accessible.) The other internal degrees of freedom, which have a number of final quantum numbers comparably populated,

are not quantized in the final asymptotic region. The important practical advantage of this is that one must deal with double-ended boundary conditions for only that (or those) degree of freedom that is quantized; the unquantized degrees of freedom enter only through a phase space average over their initial conditions [as in Equation (14)].

Many of the most difficult aspects of applying classical S-matrix theory to three dimensional reactive systems are thus eliminated through use of the partial averaging trick. Work is under way to implement it in further studies of this and other reactive systems.

APPENDIX A

Branch Point Structure in the Analytic Continuation of Classical Mechanics for Classically Forbidden Rearrangement Processes

One of the most elementary notions concerning classical mechanics is its determinism: if the coordinates and momenta are specified at time t_1 then their values at time t_2 are uniquely determined, i.e., they are single-valued function of t_2 . Moreover, they are functions only of $t_2 - t_1$ if the Hamiltonian contains no explicit time dependence (as is assumed).

In ordinary classical mechanics the coordinates and momenta, and the time, are all real-valued quantities, but in dealing with semiclassical approximations to quantum mechanics it is necessary to analytically continue $q(t)$ and $p(t)$ in the complex variable t ¹⁴. For systems with more than one degree of freedom it is in general not possible to know explicit analytic expressions for $q(t)$ and $p(t)$, so analytic continuation must be numerical. In this and earlier papers^{2f-2h,3g} it has been shown that

this analytic continuation of $\underline{q}(t)$ and $\underline{p}(t)$ in complex time can be achieved simply by integrating the equations of motion step-by-step in complex time in a manner¹⁵ quite similar to the numerical integration of ordinary real-valued trajectories. It is interesting to note, in fact, that numerical integration of the equations of motion is precisely the "textbook"¹⁶ procedure of analytic continuation: knowing $\underline{q}(t)$, $\underline{p}(t)$, and (approximations for) a number of their derivatives at complex time t_i , the numerical integration procedure effectively expands $\underline{q}(t)$ and $\underline{p}(t)$ in a power series about t_i and extrapolates these expansions to complex time $t_i + 1$ and here re-expands in a power series about $t_i + 1$ and extrapolates to complex time $t_i + 2$, etc. Thus numerical integration of the equations of motion along any curve C in the complex t -plane generates the analytic continuation of the coordinates and momenta in complex time.

Analytic continuation of a function leads in general, however, to a multivalued function. Thus if one analytically continues (i.e., numerically integrates the equations of motion) from t_1 to t_2 along two different paths in the complex t -plane, the values $\underline{q}(t_2)$ and $\underline{p}(t_2)$ from these two different choices of the time path will be the same provided no branch points lie between the two curves connecting t_1 and t_2 . In complex analysis one usually defines a particular single-valued branch of a multi-valued function by drawing branch lines from all branch points to infinity, say, and not allowing any path of analytic continuation to cross a branch line. Other single-valued branches of the multivalued function are then defined by drawing the branch lines in different ways.

In Section II and in earlier papers^{2f-2h} the statement has been made, and the fact exploited, that the final values of the coordinates and momenta (and the classical action and, therefore, the classical S-matrix elements) do not depend on the particular complex time path along which one chooses to integrate the equations of motion. The purpose of this Appendix is therefore to qualify this statement somewhat by noting that this is true provided no branch lines are crossed, or stated equivalently, provided one considers only time paths that pass on the same side of any branch points that may exist.

The remainder of this Appendix will discuss some exactly solvable one dimensional examples in order to illustrate some of the analytic properties we expect to be characteristic of the general situation. Since there is no evidence to suggest that there are any branch points that play a role in non-reactive scattering, the one dimensional examples are those which are proto-type of reactive tunneling, i.e., tunneling through a one-dimensional potential barrier¹⁷.

Consider first the parabolic potential barrier that has been discussed before¹⁸ in some detail, $V(x) = -(1/2)m\omega^2 x^2$. If the energy E is negative (i.e., below the top of the barrier) and the particle to the left of the barrier for real time, then the trajectory is easily found to be

$$x(t) = -x_0 \cosh(\omega t) \quad , \quad (A.1)$$

where

$$x_0 = (2|E|/m)^{1/2}/\omega \quad ,$$

and where the zero of time has been chosen (without restriction) as the

time that the particle is at its classical turning point. Here $x(t)$ is manifestly a single-valued function of t , i.e., there are no branch points in the finite t -plane; thus the position at time t is the same for any path along which one imagines integrating from $t_1 = -\infty$ to t . As discussed before¹⁸, a tunneling trajectory results if one chooses $t = +\infty + i\pi/\omega$. The simplest coordinate trajectory results if one chooses the time path to be a sequence of straight line segments from $-\infty$ to 0 , 0 to $i\pi/\omega$, and $i\pi/\omega$ to $+\infty + i\pi/\omega$; for this time path $x(t)$ moves monotonically from $-\infty$ to $+\infty$ on the real x -axis. Some rather bizarre coordinate trajectories result if the time path is chosen, for example, along straight line segments from $-\infty$ to $-\infty + i\pi/\omega$ and then from $-\infty + i\pi/\omega$ to $+\infty + i\pi/\omega$, or from $-\infty$ to $+\infty$ and then from $+\infty$ to $+\infty + i\pi/\omega$; the reader may find it amusing to trace out the motion in the x -plane that results from these time paths. The final position and momentum, and the classical action integral along the trajectory and thus the semiclassical tunneling probability, are the same, however, for all three of these time paths.

The parabolic barrier is actually atypical, however, because it has no asymptotic regions, i.e., no regions where the particle is free of the potential. For the more realistic case for which the potential goes asymptotically to zero as $x \rightarrow \pm\infty$, it will be seen that there are indeed branch points in the finite t plane.

Consider now a symmetrical Eckart potential barrier,

$$V(x) = V_0 \operatorname{sech}^2(\alpha x) \quad , \quad (\text{A.2})$$

which does have the property $V(x) \rightarrow 0$ as $x \rightarrow \pm \infty$. If $E \equiv (1/2)mv^2 < V_0$ and if the particle is to the left of the barrier for real time, then one finds the trajectory to be

$$x(t) = \frac{-1}{\alpha} \sinh^{-1}[\lambda \cosh(\alpha vt)], \quad (A.3)$$

where

$$\lambda = (V_0/E - 1)^{1/2},$$

and where the zero of time has again been chosen so that $x(0)$ is the classical turning point. The analytic properties of $x(t)$ derive from those of the inverse hyperbolic sine. Since $\sinh^{-1}(z)$ has branch points¹⁹ at $z = \pm i$, $x(t)$ has branch points at values of t for which

$$\lambda \cosh(\alpha vt) = \pm i,$$

i.e., the branch points are the values t_n ,

$$t_n = \pm t_* + in\pi/\alpha v, \quad (A.4)$$

when $n = \pm 1/2, \pm 3/2, \dots$, and

$$t_* = (\alpha v)^{-1} \tanh^{-1}[(E/V_0)^{1/2}]. \quad (A.5)$$

The layout of these branch points is shown in Figure 5.

$x(t)$ in Equation (A.3) is thus a multivalued function of time t . The principal tunneling trajectory corresponds to the time path C_1 in Figure 5; for this time path $x(t)$ moves monotonically from $-\infty$ to $+\infty$ along the real x -axis; the semiclassical probability for the tunneling transition associated with this trajectory is the standard WKB result²⁰,

$$P_{\text{tunnel}} = e^{-2\theta} \quad , \quad (A.6)$$

where θ is the imaginary part of the classical action along the trajectory i.e., the "barrier penetration" integral; for the present case

$$\theta = \frac{\pi}{\alpha} [(2mV_0)^{1/2} - (2mE)^{1/2}] \quad . \quad (A.7)$$

Precisely the same result is obtained for any other time path that is any distortion of curve C_1 that does not move it through any of the branch points; i.e., the curve C_1 , and any distortion of it that doesn't cross branch points, defines one of the single-valued branches of $x(t)$, the principal tunneling branch. Alternatively, this principal tunneling branch of $x(t)$ can be defined by drawing branch lines from all the branch points to infinity in a way that does not cross C_1 ; e.g., branch lines could be drawn vertically upward (downward) from all the branch points above (below) curve C_1 .

The time path C_2 in Figure 5 connects the same points t_1 and t_2 as curve C_1 , but one can easily verify that following $x(t)$ continuously along curve C_2 leads to a non-reactive, or reflective transition. In fact, the branch of $x(t)$ defined by curve C_2 (or any distortion thereof that doesn't cross branch points) is the principal reflective trajectory that corresponds to a purely real time path.

It is seen from curves C_1 and C_2 , therefore, that it matters at what real value of the time the imaginary time increments are made: if the imaginary time increment is made in one of the asymptotic regions (curve C_2), no tunneling occurs, but tunneling does result if the imaginary time increment is made while the particle is in the "interaction

region". More precisely, tunneling will occur if the imaginary time increment takes place when the real part of the time satisfies

$$-t_* < \text{Ret} < t_*,$$

with t_* given by Equation (A.5) for the present case of the Eckart barrier. It is clear that this feature will be general for any kind of potential barrier: imaginary time increments in the asymptotic regions will not cause tunneling, but an imaginary time increment taken when the collision partners are sufficiently close together will cause tunneling. (For the parabolic barrier tunneling occurs no matter when the imaginary time increment is taken, but this is because there is no asymptotic region for this potential; i.e., the value of t_* for this case is ∞).

In addition one can easily identify other branches of the function $x(t)$ of Equation (A.3): the time paths that pass above the branch points $t_* + i(3/2)\pi/\alpha v$, $t_* + i(5/2)\pi/\alpha v$, etc., correspond to a reflective trajectory with a passage back and forth inside the barrier, a tunneling trajectory with an additional reflection inside the barrier, etc., respectively. The probability of the transitions associated with these time paths is $\exp(-4\theta)$, $\exp(-6\theta)$, etc., respectively.

One last observation regarding the solution for the Eckart barrier: it is easy to show that the coordinate $x(t)$ at the branch point times themselves are those for which

$$V(x) = \infty.$$

This is also a general feature for any potential barrier, for the equation of motion for $x(t)$ is

$$m\ddot{x}(t) = -V'(x) \quad ,$$

showing that derivatives of $x(t)$ will fail to exist whenever $V'(x)$ is divergent.

To conclude this Appendix we summarize those features we expect to be generally valid. (1) The final properties of any analytically continued trajectory, and the classical S-matrix element associated with it, are independent of the particular complex time path along which time is incremented, provided any branch points are passed by in the same manner. (2) The existence of more than one energetically open asymptotic arrangement implies the existence of branch points in the finite t -path. (3) Branch points in the t -plane correspond to coordinates for which the potential or some of its partial derivatives are divergent. (4) In order to cause a classically forbidden rearrangement transition the imaginary part of the time increment should be made predominantly when the collision partners are closest together.

APPENDIX B

Symmetry Considerations for the Case of Identical Atoms

In a paper dealing with the quantum mechanical description of the reactive $A + BC$ collision system Miller²¹ defined a set of reduced scattering amplitudes which take proper account of symmetry if any of the atoms A, B, or C are identical, and it was noted that the quantum mechanical coupled channel calculation is simplified considerably if one formulates the problem in such a way as to calculate these reduced amplitudes directly. Expressions for the various observable cross

sections were given in terms of these reduced amplitudes.

When dealing with a classical or semiclassical theory, however, the amplitudes that one obtains directly from a calculation are the ones that refer to distinguishable atoms, so-called "direct" and "exchange" amplitudes. Thus it is most convenient in this case to express the observable cross sections in terms of these distinguishable amplitudes. This is easily accomplished by inverting the relations in Reference 21 and first expressing the reduced amplitudes in terms of the distinguishable amplitudes, and then using the previous formulas to obtain the observable cross sections in terms of the direct and exchange amplitudes. The resulting expressions are summarized below, some of which have also been given by Tang and Karplus¹⁰.

All quantum number labels will be suppressed in the following expressions, but it should be understood that the amplitudes and cross sections correspond to a specific set of initial and final quantum numbers $(n_1 j_1 m_1)$ and $(n_2 j_2 m_2)$, respectively. For the case of three identical atoms $(A + A_2 \rightarrow A + A_2)$, let f be the amplitude for a direct, or non-reactive transition, and g be the amplitude for an exchange, or reactive transition. If "even" and "odd" refer to the rotational quantum number j , then the observable cross sections (i.e., summed and averaged over all nuclear spin states consistent with the rotational states) are given in terms of the direct and exchange amplitudes by

$$\sigma_{\text{even} \leftarrow \text{even}} = \frac{1}{3} (1 + 2\lambda) |f + 2g|^2 + \frac{2}{3} (1 - \lambda) |f - g|^2 \quad (\text{B.1})$$

$$\sigma_{\text{odd} \leftarrow \text{odd}} = \frac{1}{3} (1 - 2\lambda) |f + 2g|^2 + \frac{2}{3} (1 + \lambda) |f - g|^2 \quad (\text{B.2})$$

$$\sigma_{\text{odd} \leftarrow \text{even}} = 2(1 - \lambda)|g|^2 \quad (\text{B.3})$$

$$\sigma_{\text{even} \leftarrow \text{odd}} = 2(1 + \lambda)|g|^2 \quad (\text{B.4})$$

where

$$\lambda = (-1)^{2s}/(2s + 1) \quad ,$$

s being the nuclear spin of the atom. For the case $\text{H} + \text{H}_2$, for example, $s = 1/2$ and Equations (B.1)-(B.4) are

$$\sigma_{\text{even} \leftarrow \text{even}} = |f - g|^2$$

$$\sigma_{\text{odd} \leftarrow \text{odd}} = \frac{2}{3} |f + 2g|^2 + \frac{1}{3} |f - g|^2$$

$$\sigma_{\text{odd} \leftarrow \text{even}} = 3|g|^2$$

$$\sigma_{\text{even} \leftarrow \text{odd}} = |g|^2$$

There are more possibilities to consider for the case that two of the atoms are the same, $\text{B} + \text{A}_2 \rightarrow \text{B} + \text{A}_2$, $\text{BA} + \text{A}$, and $\text{A} + \text{AB} \rightarrow \text{A} + \text{AB}$, $\text{A}_2 + \text{B}$. Let f_B be the non-reactive amplitude for direct scattering of B and A_2 ($\text{B} + \text{A}_2 \rightarrow \text{B} + \text{A}_2$), f_A be the non-reactive amplitude for direct scattering of A and AB ($\text{A} + \text{A}'\text{B} \rightarrow \text{A} + \text{A}'\text{B}$), g_A be the reactive amplitude for exchange of atom A ($\text{B} + \text{A}_2 \rightarrow \text{BA} + \text{A}$), and g_B be the reactive amplitude for exchange of atom B ($\text{A} + \text{BA}' \rightarrow \text{AB} + \text{A}'$). Again suppressing the quantum number labels, the expressions for the observable cross sections are

$$\sigma_{\text{B} + \text{A}_2 \leftarrow \text{B} + \text{A}_2} = |f_B|^2 \quad (\text{B.5})$$

$$\sigma_{A + AB \leftarrow B + A_2} = 2|g_A|^2 \quad (B.6)$$

$$\sigma_{A + BA \leftarrow A + BA} = \frac{1}{2} (1 + \lambda) |f_A + g_B|^2 + \frac{1}{2} (1 - \lambda) |f_A - g_B|^2 \quad (B.7)$$

$$\sigma_{B + A_2 \leftarrow A + BA} = \frac{1}{2} [1 + \lambda(-1)^{j_2}] |g_A|^2, \quad (B.8)$$

where λ is the same as above with s being the nuclear spin of atom A, and where j_2 in Equation (B.8) is the final rotational quantum number of A_2 .

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FIGURE CAPTIONS

FIGURE 1: The square modulus of $S_{n_2 j_2 \ell_2, n_1 j_1 \ell_1}(J)$ as a function of the initial translational energy for $n_1 = j_1 = \ell_1 = 0$, $n_2 = 0$, $j_2 = \ell_2 = 1$, $J = 0$. The solid line is the semiclassical result (note reference 9), and the dotted line is the result if the interference terms from the four trajectories are discarded. The two points are the quantum mechanical coupled channel calculations of Wolken and Karplus (ref. 8).

FIGURE 2: The square modulus of $S_{n_2 j_2 \ell_2, n_1 j_1 \ell_1}(J)$ (resulting from only one of the four reactive trajectories) as a function of total angular momentum J for relative collision energy $E_0 = 0.20$ eV, and $n_1 = n_2 = j_1 = 0$, $\ell_1 = J$, $j_2 = 1$, and $\ell_2 = J - 1$ (upper dotted line) or $J + 1$ (lower dotted line). The solid line connects points that are the sum of the two branches.

FIGURE 3: The center of mass scattering angle that results for one of the four reactive trajectories (the same one as for Figure 2) as a function of total angular momentum J ; the lower curve corresponds to $\ell_2 = J + 1$ and upper curve $\ell_2 = J - 1$.

FIGURE 4: The differential cross section for the $H + H_2 (j_1 = 0) \rightarrow H_2(j_2 = 1) + H$ reaction as calculated semiclassically from Equations (9)-(11). For the reasons discussed in the text the absolute values of this differential cross section are not as meaningful as the relative angular distribution; a rough estimate of the absolute values can be obtained by multiplying these results ~ 5 .

FIGURE 5: The layout of branch points of the function $x(t)$ given by Equation (A.4); their locations are given algebraically by Equations (A.5)-(A.6). Curve C_1 consists of the straight line segments $t_1 \equiv -\infty \rightarrow 0$, $0 \rightarrow i\pi/\alpha v$, $i\pi/\alpha v \rightarrow +\infty + i\pi/\alpha v \equiv t_2$, and Curve C_2 the straight line segments $t_1 \equiv -\infty \rightarrow +\infty$, $+\infty \rightarrow +\infty + i\pi/\alpha v \equiv t_2$.

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Fig. 1

Fig. 2

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Fig. 3

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Fig. 4

Fig. 5

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