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ANALYTIC CONTINUATION OF CLASSICAL MECHANICS FOR CLASSICALLY FORBIDDEN COLLISION PROCESSES*

by

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Abstract

Classically forbidden processes are those than cannot take place via ordinary classical dynamics. Within the framework of classical S-matrix theory, however, classical mechanics can be analytically continued and classical-limit approximations obtained for these classically forbidden, or weak transition amplitudes (i.e., S-matrix elements). The most powerful and general way of analytically continuing classical mechanics for a complex dynamical system is to integrate the equations of motion themselves through the classically inaccessible regions of phase space. Success in calculating these analytically continued trajectories is reported in this work; with certain special features of these complex-valued trajectories recognized and taken account of, it is seen that they are essentially as easy to deal with numerically as ordinery (i.e., real) classical trajectories. Application to the linear A + BC collision (vibrational excitation) gives excellent results; transition probabilities as small as 10^{-11} (the smallest ones available for comparison) have been obtained, agreement with the exact quantum mechanical values being within a few percent.

I. Introduction

Recent work has shown how exact classical mechanics (i.e., numerically computed classical trajectories) for a complex collision system, such as A + BC, can be used semiclassically to construct the classical limit of the quantum mechanical S-matrix for transitions between specific quantum states[1-3]. This use of classical mechanics to construct classical-limit approximations for transition amplitudes (rather than transition probabilities themselves) properly incorporates quantum superposition, and this appears often to be the principal contribution of quantum mechanics to the dynamics of molecular collisions.

One of the most intriguing aspects of this "classical S-matrix" theory is the possibility of using classical trajectories to obtain transition probabilities (or cross sections) for <u>classically forbidden</u> processes[1b, 1c, 2a]. By "classically forbidden" one does not mean that the transition is forbidden by any conservation law, such as being energetically forbidden, but rather that classical dynamics simply does not lead to the transition. Although it may at first seem self-contradictory that classically forbidden processes can be in any way described by a classical-limit theory, there is actually a familiar example of this, namely the WKB approximation for one-dimesional barrier penetration[4] (i.e., tunneling): the barrier penetration integral θ is the classical action integral along a classical trajectory, the transmission probability being $\exp(-2\theta)$. (See also Appendix A).

Not only is the classically forbidden, or weak transition problem intrinsically interesting from a theoretical point of view, though, it has quite important practical aspects. Thus while the interference features that are seen when a number of transitions are classically

allowed are extremely interesting – and it is exciting to see that they can be accurately described by classical dynamics plus quantum superposition – it has been observed[1d] that they tend to be averaged out quite readily under any conditions except complete state selection. Consequently, a purely classical approach (with the usual Monte Carlo sampling methods) will likely be adequate for most practical purposes when many transitions are classically allowed. When all transitions are classically forbidden, however, a purely classical calculation of some collision property, such as the average energy transfer, is in general completely meaningless[1d]. (Under certain special conditions this may not be true[1d].) Classical S-matrix theory, however, shows how classical trajectories can be used to describe these weak transitions[1b, 1c].

Another useful point regarding the situation when all transitions of interest are classically forbidden is that one is typically interested in only a few transitions, namely the ones that are least forbidden classically and therefore have the largest probabilities. In the case of vibrational excitation of H_2 or N_2 at low collision energy, for example, one is primarily interested only in the $0 \rightarrow 1$ vibrational transition.

Other examples of classically forbidden processes that are extremely important are reactive tunneling near the threshold of rearrangement processes, such as $A + BC \rightarrow AB + C$, and electronic transitions between adiabatic electronic states; a recent formulation[5] of this latter problem has emphasized the fact that it is a special case of a classically forbidden process.

Section II summarizes classical S-matrix theory in general, with a detailed discussion of the description of classically forbidden processes. The treatment of classically forbidden processes within the framework of

classical S-matrix theory is seen to be a problem of analytic continuation — the analytic continuation of classical mechanics through classically inaccessible regions of coordinate and momentum space. A procedure for numerical analytic condition of the trajectory functions (via a rational approximation) is developed in Section III; this is much more powerful than the methods used previously[1c], and excellent results are achieved for transition probabilities as small as 10^{-5}. There are, however, fundamental limitations to the degree that any such extrapolation method can be usefully continued into the classically forbidden domain; in addition, there are severe practical limitations because of the extreme accuracy required for the "input" functional values.

The "ultimate solution", however, is achieved in Section IV, where it is shown how the equations of motion can themselves be integrated directly through classically inaccessible regions of coordinate and momentum space. This is the most general way of analytically continuing classical mechanics; e.g., it is the only one capable of describing reactive tunneling. The key element for the success of this procedure is the realization that analytically continued classical trajectories are in general unstable, and this feature has been overcome by integrating such trajectories from both ends; i.e., one begins in the initial and final asymptotic regions and integrates both branches of the trajectory toward the interaction region, joining the two at some appropriate point. Integrated in this manner, these analytically continued trajectories are quite well-behaved from a numerical point of view, and excellent results have been obtained; transitions with probabilities as small as 10^{-11} (the smallest available for comparison) have been obtained, with agreement within a few percent of the exact quantum values.

II. Summary of Classical S-Matrix Theory for Classically Forbidden Transitions.

The expressions defining the classical S-matrix are summarized below, where the system is taken to be the linear non-reactive A + BC collision (i.e., vibrational excitation); in addition to the translational degree of freedom, therefore, there is just one internal degree of freedom, vibration. This choice is purely for notational convenience, the expressions appropriate to several degrees of freedom being obvious generalizations that have been given previously[1a].

The translational degree of freedom is described by its center of mass coordinate and momentum R and P, and the vibrational degree of freedom by its action-angle variables[6] n and q; n, the action variable of the vibrational degree of freedom, is the classical counterpart of the vibrational quantum number, and in the asymptotic regions ($R \to \infty$) it must be an integer (the semiclassical quantum condition). The $n_1 \to n_2$ vibrational transition probability is given by

$$P_{n_2,n_1} = |S_{n_2,n_1}|^2, \tag{II.1}$$

where the classical S-matrix element is

$$S_{n_2,n_1} = \left[-\frac{\partial^2 \phi(n_2,n_1)}{\partial n_2 \, \partial n_1} \Big/ 2\pi i\hbar \right]^{1/2} \exp\left[i\phi(n_2,n_1)/\hbar \right] , \tag{II.2}$$

$\phi(n_2,n_1)$ being the (total) action integral along the classical trajectory determined by the double-ended boundary conditions $n(t) = n_1$ initially and n_2 finally; in this quantum number representation the action integral is

$$\phi(n_2,n_1) = -\int_{t_1}^{t_2} dt\,[R(t)\,\dot{P}(t) + q(t)\,\dot{n}(t)] \quad . \qquad \text{(II.3)}$$

If there is more than one trajectory with initial and final integer values n_1 and n_2, then Equation (II.2) is a sum of similar terms, one for each such trajectory.

To find the desired trajectories for a specific $n_1 \rightarrow n_2$ transition (a non-linear boundary-value problem), it is convenient to introduce the classical trajectory function $n_2(q_1,n_1)$, the final value of the quantum number for the classical trajectory with initial conditions[7] q_1 and n_1. (Initial values for the translational coordinate and momentum are always determined implicitly by those of the internal degrees of freedom, total energy conservation, and the scattering boundary condition: R_1 = large, $P_1 = -\left\{2\mu[E - \epsilon(n_1)]\right\}^{1/2}$, where $\epsilon(n)$ is the semiclassical eigenvalue function and E the total energy). One thus looks for values of q_1 which satisfy the equation

$$n_2(q_1,n_1) = n_2 \quad . \qquad \text{(II.4)}$$

[It is hoped that this notation is not confusing; when n_1 and n_2 are written without arguments, they denote some integer value of the quantum number. Written with arguments, $n_2(q_1,n_1)$ is the final quantum number, not necessarily integral, that results from the classical trajectory with initial integral quantum number n_1 and conjugate angle q_1. For the $0 \rightarrow 1$ vibrational transition, for example, Equation (II.4) reads $n_2(q_1,0) = 1$.] The phase $\phi(n_2,n_1)$ is the time integral in Equation (II.3) along the trajectory with initial values n_1 and q_1 equal to the root of Equation (II.4). The pre-exponential factor in Equation (II.2) is equivalently (and more

conveniently) evaluated by noting that

$$\frac{\partial^2 \phi(n_2,n_1)}{\partial n_2 \partial n_1} = \left[\frac{\partial n_2(q_1,n_1)}{\partial q_1}\right]^{-1} , \qquad \text{(II.5)}$$

with q_1 evaluated at the root of Equation (II.4).

The $n_1 \to n_2$ transition is <u>classically forbidden</u> if there is no value of q_1 in its complete interval $(0, 2\pi)$ for which Equation (II.4) is satisfied. There will in general, however, be complex values of q_1 that satisfy Equation (II.4). The task, therefore, is to analytically continue $n_2(q_1,n_1)$ as a function of q_1 (for fixed n_1) so that it can be evaluated for complex q_1 and the roots of Equation (II.4) thus found. To construct the S-matrix element in Equation (II.2) it is also necessary to analytically continue the phase $\phi(n_2(q_1,n_1),n_1)$ as a function of q_1 so that it can be evaluated at the complex q_1 determined by Equation (II.4). Since q_1 is complex, ϕ will also be complex, and it is the imaginary part of ϕ that leads to damping of the transition probability:

$$P_{n_2,n_1} = \left[2\pi\hbar\left|\frac{\partial n_2(q_1,n_1)}{\partial q_1}\right|\right]^{-1} \exp\left[-2\mathrm{Im}\phi/\hbar\right] ; \qquad \text{(II.6)}$$

this exponential damping is the characteristic feature of classically forbidden (i.e., tunneling) transitions.

Just as for classically allowed transitions, there may be more than one complex root of Equation (II.4), and the S-matrix element would then be a sum of several terms. [Since $n_2(q_1,n_1)$ is a real analytic function of q_1, the complex conjugate of a root is also a root. The phase ϕ is also a real analytic function of q_1, however, so that $\phi(q_1^*) = \phi(q_1)^*$, and if $\mathrm{Im}\ \phi(q_1) > 0$, then $\mathrm{Im}\ \phi(q_1^*) < 0$; the root q_1^* would thus give an

exponential enhancement to the transition probability, rather than a damping. It is thus obvious on physical grounds that one is only interested in roots for which Im $\phi > 0$ and thus always only one of a given pair q_1 and q_1^*.] One expects, however, the particular complex root for which $|\mathrm{Im}\phi|$ is smallest to dominate the sum, so that one will normally need to analytically continue $n_2(q_1,n_1)$ only so far as the root of Equation (II.4) that lies closest to the real q_1-axis.

At this point some discussion is in order regarding the justification of our proceeding somewhat naively to analytically continue Equation (II.2). One way of developing the theory is via an asymptotic evaluation of the path integral representation of the propagator. [The S-matrix is immediately obtainable from the propagator[1a].] Thus the exact quantum expression for the propagator in the coordinate representation is[8]

$$< x_2|\exp[-iH(t_2-t_1)/\hbar]|x_1 > = \int_{x_1}^{x_2} Dx(t)\, \exp\left\{i\phi[x(t)]/\hbar\right\}, \quad \text{(II.7)}$$

where x denotes all the coordinates of the system, $Dx(t)$ is an integral over all paths[8] which connect the space time points x_1t_1 and x_2t_2, and ϕ is the classical action functional:

$$\phi[x(t)] = \int_{t_1}^{t_2} dt\, [\tfrac{1}{2}m\dot{x}(t)^2 - V(x(t))] \quad . \quad \text{(II.8)}$$

Asymptotic evaluation of the path integral is analogous to the asymptotic evaluation of an ordinary integral of the form

$$A = \int_{x_1}^{x_2} dx\, \exp\,[if(x)/\hbar]. \quad \text{(II.9)}$$

In this latter case one looks for points of stationary phase, i.e., values

of x which satisfy

$$f'(x) = 0. \qquad \text{(II.10)}$$

If there are no roots to Equation (II.10) in the interval (x_1, x_2), then A will be exponentially small. There may be complex roots to Equation (II.10), however; let x_o be one such complex root. According to the method of steepest descent[9], one deforms the path of integration from the real x-axis to a contour which passes through the point x_o, and the result is

$$A = [2\pi i\hbar/f''(x_o)]^{\frac{1}{2}} \exp[if(x_o)/\hbar] \; ; \qquad \text{(II.11)}$$

this is exactly the same form as if x_o were real.

Asymptotic evaluation of the path integral would proceed analogously[8,10,11]; one would look for "paths of stationary phase", i.e., paths x(t) which connect x_1 and x_2 and satisfy

$$\delta\phi[x(t)] = 0 \quad . \qquad \text{(II.12)}$$

The path (or paths) which satisfy Equation (II.12) are, of course, those which satisfy the classical equations of motion[12]. If there are no real paths, the transition is classically forbidden and its probability thus exponentially small. There will in general, however, be complex paths that connect x_1 and x_2 and which satisfy the classical equations of motion. Analogous to the steepest descent integration in the previous paragraph, one thus needs to deform the path integral to include the complex path $x_o(t)$. Although the mathematics of path integration over complex paths has not to our knowledge been developed, it should be fairly clear that the asymptotic value of the path integral in Equation (II.7) is of the desired form

$$< x_2|\exp[-iH(t_2-t_1)/\hbar]|x_1 > \sim \exp\,[i\phi(x_2,x_1)/\hbar] \quad ,$$

where $\phi(x_2,x_1)$ is the action function of Equation (II.8) evaluated along the complex path $x_o(t)$ which is determined by the classical equations of motion with boundary conditions x_1 and x_2.

Another way of arriving at this same result, but by more conventional methods, is to use the fact[8] that the propagator in Equation (II.7) satisfies the time-dependent Schrodinger equation in the variables x_2 and t_2. Writing (for fixed x_1,t_1)

$$< x_2|\exp[-iH(t_2-t_1)/\hbar]|x_1 > = \exp\,[iS(x_2,t_2)/\hbar] \quad ,$$

substituting into the Schrodinger equation, and expanding

$$S(x_2,t_2) = S_o(x_2,t_2) + (\hbar/i)\, S_1(x_2,t_2) + \cdots \quad ,$$

leads in the usual way[13] to the Hamilton-Jacobi equation for S_o and the continuity equation for S_1. (This is essentially the route used by Marcus[2a] in his development of classical-limit theory.) Since a solution to the Hamilton-Jacobi equation is the action computed along a trajectory determined by the classical equations of motion[14], one has that $S_o = \phi(x_2,x_1)$. Complex solutions to the Hamilton-Jacobi equation (which is what S_o is if the transition is classically forbidden) are ignored in ordinary classical mechanics, but the classical-limit of quantum mechanics gives meaning to them.

In concluding this section it is interesting to see how the boundary conditions work out for an analytically continued classical trajectory; in addition to allowing coordinates and momenta to be complex, it will be seen that one must also allow the time to be complex. (Appendix A discusses

the role of complex time in more detail by way of a simple exactly solvable example.)

For a system of N degrees of freedom, let R and P denote the translational coordinate and momentum, and $\underset{\sim}{n}$ and $\underset{\sim}{q}$ the set of (N-1) action-angle variables for the (N-1) internal degrees of freedom. The problem is to find the trajectory that has initial conditions

$$\underset{\sim}{n}_1 = \text{specified integers} \tag{II.13a}$$

$$\underset{\sim}{q}_1 = \text{anything} \tag{II.13b}$$

$$R_1 = \text{large (positive) and real} \tag{II.13c}$$

$$P_1 = -\left\{2\mu[E - \epsilon(\underset{\sim}{n}_1)]\right\}^{\frac{1}{2}} , \tag{II.13d}$$

and final conditions

$$\underset{\sim}{n}_2 = \text{specified integers} \tag{II.14a}$$

$$\underset{\sim}{q}_2 = \text{anything} \tag{II.14b}$$

$$R_2 = \text{large (positive) and real} \tag{II.14c}$$

$$P_2 = +\left\{2\mu[E - \epsilon(\underset{\sim}{n}_2)]\right\}^{\frac{1}{2}} , \tag{II.14d}$$

and it is assumed that there are no ordinary (i.e., real) trajectories that satisfy these boundary conditions; i.e., the $\underset{\sim}{n}_1 \rightarrow \underset{\sim}{n}_2$ transition is classically forbidden. One begins the trajectory at time t_1 (which may be taken real) with the initial conditions in Equation (II.13), where $\underset{\sim}{q}_1$ is in general complex, and may at this stage without restriction increment the time along the real time axis. During the trajectory there is coupling between all degrees of freedom and all the coordinates and momenta become complex; thus the final values $\underset{\sim}{n}_2$, R_2, etc., are in general complex. The classical trajectory relation $\underset{\sim}{n}_2(\underset{\sim}{q}_1, \underset{\sim}{n}_1) = \underset{\sim}{n}_2$, however, is a set of 2N-2 equations

$$\text{Im } \underset{\sim}{n}_2(\underset{\sim}{q}_1, \underset{\sim}{n}_1) = 0$$

$$\text{Re } \underset{\sim}{n}_2(\underset{\sim}{q}_1, \underset{\sim}{n}_1) = \text{specified integers,}$$

in terms of the 2N-2 unknowns Re $\underset{\sim}{q}_1$, Im $\underset{\sim}{q}_1$; the final boundary conditions in Equation (II.14a) can therefore be satisfied by a specific choice of the variables $\underset{\sim}{q}_1$. The problem remains, however, that R_2 is complex, but this is taken care of by the choice of t_2. Thus, if the trajectory is initially terminated in the final asymptotic region at the real time $\bar{t}_2$ (i.e., the integration from t_1 to $\bar{t}_2$ has been along the real time axis), $\bar{R}_2 \equiv R(\bar{t}_2)$ is in general complex; since the trajectory is in the asymptotic region, however, $\underset{\sim}{n}_2$ and P_2 are constant in time, so that

$$R(t) = \bar{R}_2 + (P_2/\mu)(t-\bar{t}_2) \quad ,$$

and the choice[15]

$$t_2 = \bar{t}_2 - i(\mu/P_2)\, \text{Im } \bar{R}_2$$

makes $R_2 \equiv R(t_2)$ real (equal to Re $\bar{R}_2$).

Since $\underset{\sim}{n}_2$ and P_2 are constant in the final asymptotic region, this last time increment from $\bar{t}_2$ to t_2 actually has no effect on anything of interest [i.e., the quantum number $\underset{\sim}{n}_2$ or the phase $\phi(\underset{\sim}{n}_2, \underset{\sim}{n}_1)$ of Equation (II.3)]: it is necessary only to obtain a consistent description of the analytically continued trajectories. Furthermore, it is important to realize that the final values $\underset{\sim}{n}_2$, R_2, etc., <u>depend only on the total time difference</u> (t_2-t_1) and not on the path in the complex time plane along which the trajectory is integrated (this follows because the classical Hamiltonian is not an explicit function of time); as will be seen in Section IV, for example, it is useful to exploit this fact and choose

the path in the complex t-plane in such a way as to facilitate the calculation.

Finally, for reasons to be discussed in Section IV, it is actually not possible in practice to integrate these analytically continued trajectories from the initial asymptotic region straight through to the final asymptotic region; one must begin at both ends of the trajectory and integrate toward the middle. The above discussion concerning the nature of the boundary conditions, however, is unchanged.

III. Numerical Analytic Continuation.

The first procedure we discuss for analytically continuing the function $n_2(q_1)$ (where, for convenience, the dependence on n_1 is not indicated explicitly) might more descriptively be referred to as "curve-fitting"; i.e., $n_2(q_1)$ is computed for real values of q_1 in the interval $(0,2\pi)$ by integrating ordinary classical trajectories, these values are used to fit the function to some analytical form, and this analytical fit to $n_2(q_1)$ is used to evaluate the function for complex values of q_1.

In earlier work[1c], for example, the periodic nature of $n_2(q_1)$ $[n_2(q_1 + 2\pi) \equiv n_2(q_1)]$ was taken into account, expanding it in a Fourier series

$$n_2(q_1) = \sum_{k=0}^{N} a_k \, u_k(q_1) \quad , \tag{III.1}$$

where the basis functions $u_k(q_1)$ are

$$u_k(q_1) = \begin{cases} \cos(kq_1/2) & , \ k \text{ even} \\ \\ \sin\,[(k+1)q_1/2], & k \text{ odd} \ , \end{cases} \tag{III.2}$$

and N is an even integer. The N+1 coefficients $\{a_k\}$ are determined by Hildebrand's method[16] from the values of $n_2(q_1)$ computed at the N equally spaced points $q_1 = k(2\pi/N)$, k = 1,...,N. With the coefficients thus determined, Equation (III.1) was then used to find the complex roots of Equation (II.4); the phase $\phi(q_1) \equiv \phi(n_2(q_1,n_1),n_1)$ was similarly[17] analytically continued as a function of q_1, and the transition probability evaluated from Equation (II.1), (II.2), and (II.5). To guarantee that $n_2(q_1)$ was being accurately represented by Equation (III.1), the calculation was repeated with successively larger values of N until the resulting transition probabilities were unchanged.

This Fourier series representation of $n_2(q_1)$ gave good results[1c] if the transition was not too forbidden classically, i.e., if the imaginary part of q_1, the root of Equation (II.4), was not too large; in practice this meant that one was unable to describe transitions with a probability smaller than about 10^{-3}. It was noted that the origin of the difficulty is that for large $|\text{Im } q_1|$ the Fourier series becomes a power series in the variable $\exp(|\text{Im } q_1|)$ and appears to be only <u>asymptotically convergent</u>. Thus if $|\text{Im } q_1|$ is not too large, successive terms in Equation (III.1) decrease rapidly in magnitude, so that the series can be truncated (before it begins to diverge) and accurate results obtained; if $|\text{Im } q_1|$ is too large, however, the series begins to diverge before it has "settled down", the typical phenomenon for asymptotic series outside their domain of utility.

Due to recent advances[18] there are now much more powerful methods available for numerical analytic continuation; these methods all employ a <u>ratio</u> of polynomials in some variable and are referred to as rational approximations, Padé approximants, etc.[18]. The practical element gained

by using a ratio of polynomials is that polar singularities in the function can be explicitly accounted for, so that useful results can be obtained beyond such singularities; a power series would of course fail to converge passed its first singularity.

In place of Equation (III.1), therefore, $n_2(q_1)$ is represented as a ratio of polynomials in the variable $\exp(iq_1)$. This variable has the advantage of incorporating the periodic nature of the function, and it is also the most natural extension of a Fourier series [which is a polynomial in $\exp(iq_1)$ and $\exp(-iq_1)$]. A ratio of polynomials in $\exp(iq_1)$, however, is equivalent to a ratio of polynomials in $\exp(iq_1)$ and $\exp(-iq_1)$, which in turn is equivalent to a ratio of Fourier series. Thus the desired expansion by which Equation (III.1) is replaced is[19]

$$n_2(q_1) = P_N(q_1)/Q_M(q_1) \quad , \tag{III.3}$$

where

$$P_N(q_1) = \sum_{k=0}^{N} a_k \, u_k(q_1) \tag{III.4a}$$

$$Q_M(q_1) = 1 + \sum_{k=1}^{M} b_k \, u_k(q_1) \quad , \tag{III.4b}$$

with the basis functions $u_k(q_1)$ defined as in Equation (III.2). For large $|\mathrm{Im}\ q_1|$ there are now large terms of the form $\exp(k|\mathrm{Im}\ q_1|)$ in the denominator to balance those in the numerator.

To determine the coefficients $\{a_k\}$ and $\{b_k\}$ in Equation (III.4) it is convenient to use the "moment method" as described by Schlessinger[20]; this is also the most natural extension of Hildebrand's method[16] for determining the Fourier coefficients in Equation (III.1). Thus one

writes Equation (III.3) as

$$n_2(q_1)\, Q_M(q_1) - P_N(q_1) = 0 \quad ,$$

multiplies by a typical basis function $u_j(q_1)$, $j = 0,\ldots, M + N$, and integrates over q_1. Since the basis functions are trigonometric functions, one can replace the integral over q_1 by a sum over the equally spaced points

$$q_1^{(r)} = r\, 2\pi/(N + M) \quad , \tag{III.5}$$

$r = 1,\ldots, N + M$, and use the orthogonality relations[16]

$$\sum_{r=1}^{N+M} u_j(q_1^{(r)})\, u_i(q_1^{(r)}) = \delta_{i,j}\left(\frac{N+M}{2}\right)\left[1 + \delta_{i,0} + \delta_{i,N+M}\right] \quad , \tag{III.6}$$

for $i,j = 0,\ldots,N+M$. The resulting equations that determine $\{a_k\}$ and $\{b_k\}$ are

$$\sum_{k=1}^{M} n_{j,k}\, b_k = -n_{j,0} \quad , \tag{III.7}$$

$j = N+1,\ldots,N+M$,

$$a_j = \frac{(1 + \delta_{j,0})}{N+M}\left[n_{j,0} + \sum_{k=1}^{M} n_{j,k}\, b_k\right] \quad , \tag{III.8}$$

$j = 0,\ldots,N$, where

$$n_{i,j} = \sum_{r=1}^{N+M} u_i(q_1^{(r)})\, n_2(q_1^{(r)})\, u_j(q_1^{(r)}). \tag{III.9}$$

Thus one first evaluates the "matrix elements" $n_{i,j}$ defined by Equation (III.9), solves the set of linear equations in Equation (III.7) for the coefficients $\{b_k\}$, and then determines the coefficients $\{a_k\}$ from

Equation (III.8).

Table I shows results of the above procedure applied to the linear non-reactive A + BC collision[21,22]; the quantum calculations are those of Secrest and Johnson[23]. All of the transitions listed in Table I are too weak to be treated by the Fourier series method of reference 1c; nevertheless, it is seen that classical dynamics, used in the framework of the classical S-matrix, is as accurate for these very weak transitions as it is for classically allowed transitions. In addition to the smallness of the transition probability the large imaginery part of q_1 (shown in Table I), the root of Equation (II.4), is another measure of the degree to which these transitions are classically forbidden.

In obtaining the results in Table I it was found best in all cases to take N = M in Equation (III.4). Convergence was always achieved by the value N = 12; i.e., calculations were also performed with N = 14 and N = 16, with no change in the transition probabilities.

As an interesting check on the results, some of the reverse transitions were computed; e.g., the $4 \rightarrow 2$ transition was computed and compared to the $2 \rightarrow 4$ transition in the top line of Table I. The values of q_1 which satisfy the trajectory equations $n_2(q_1,2) = 4$ and $n_2(q_1,4) = 2$ are of course different ($q_1 = 4.66 + 1.07i$ and $1.75 + 2.38i$, respectively), but the two transition probabilities were equal; this is as it should be for the classical S-matrix satisfies microscopic reversibility identically.

Even though numerical analytic continuation via the ratio of Fourier series in Equation (III.3) is much more powerful than by the Fourier series itself of Equation (III.1), it is only capable of going so far into the classically forbidden domain. The limitation is the accuracy required in the "input"; i.e., the further from the real q_1-axis that it is necessary

to analytically continue $n_2(q_1)$ the greater is the accuracy required in the values of $n_2(q_1)$ computed for real q_1. In order to obtain converged values for the transitions in Table I, for example, it was necessary to compute the classical trajectories with an error parameter of 10^{-12} or 10^{-13}, whereas for ordinary purposes it is only necessary to use a value 10^{-6}. This, of course, increases the time necessary to integrate the equations of motion.

This sensitivity of the analytically continued functional values to the "input" is certainly not unexpected and is typical of any situation in which one attempts to extrapolate far from the region in which the functional values are known. So long as one computes only ordinary (i.e., real) classical trajectories, there appears to be little possibility of overcoming this fundamantal difficulty.

Fortunately, however, the next section shows how it is now possible to integrate the equations of motion directly through classically forbidden regions and thus evaluate the functions $n_2(q_1,n_1)$ and $\phi(n_2(q_1,n_1),n_1)$ directly for any complex values of q_1.

IV. Direct Integration of the Equations of Motion.

The most general way of computing $n_2(q_1,n_1)$ for complex values of q_1 is actually to integrate the equations of motion themselves with complex initial conditions. During the course of such a trajectory all the coordinates and momenta become complex, but the discussion in Section II has shown that there are precisely the number of variables at ones disposal so that all physical observables can be made to have real values in the initial and final asymptotic regions.

This direct approach was attempted in our first work[1c] on the classically forbidden problem, but it was only successful for "slightly forbidden" transitions, the reason being that the trajectories diverged if Im q_1 was taken larger than ~0.1. The origin of this divergence is now understood: The usual way of solving Equation(II.4) is to set n_1 equal to an integer, make a guess at q_1, and calculate $n_2(q_1,n_1)$ by calculating the trajectory with these initial conditions; the resulting value for $n_2(q_1,n_1)$ will in general be complex if q_1 is, but one iterates the procedure until the "correct" complex value of q_1 if found, i.e., the value for which $n_2(q_1,n_1)$ equals the desired integer. Trajectories for which $n_2(q_1,n_1)$ is not real, however, are <u>divergent</u> (as shown below), so that the iteration procedure just described is not possible; i.e., the trajectory exists if q_1 is a particular complex value for which $n_2(q_1,n_1)$ turns out to be real[24], but diverges for other values of q_1 in the immediate neighborhood.

To see that trajectories with complex quantum numbers in the final asymptotic region are divergent, note that the solution for the angle variable in the final asymptotic region is

$$q(t) = \text{constant} + \epsilon'(n_2)t \quad ;$$

thus, if n_2 is not real the imaginary part of $q(t)$ increases with t. The physical vibrational coordinate, however, is

$$r(t) \sim \cos\,[q(t)] \quad ,$$

so that $|r(t)|$ becomes infinite if Im $q(t)$ increases without limit. If n_2 is real, only Re $q(t)$ increases as $t \to \infty$, and this obviously causes no problem in $r(t)$.

Because of this unstable situation it is therefore not possible to integrate the equations of motion from the initial asymptotic region through a classically forbidden region and to the final asymptotic region. The way out of this predicament is to integrate the trajectory from both ends and match the two branches somewhere in the middle. Thus the inward branch is begun with the boundary conditions of Equation (II.13) and integrated forward in time, and the outward branch is begun in the final asymptotic region with the boundary conditions in Equation (II.14) and integrated backward in time. The initial and final values of the quantum number are taken as the desired integers (and this solves the stability problem in the asymptotic regions), and the initial and final angle variables, q_1 and q_2, are chosen iteratively so that all the coordinates and momenta of the two branches are equal at some intermediate point, i.e., so that the inward and outward branches meet to form one complete trajectory with the boundary conditions in Equations (II.13) and (II.14). More of the details of this matching procedure are given in Appendix B.

Because of the necessity of using complex time increments in the numerical integration of the equations of motion (see Appendix B), it was advantageous to use an integration algorithm that permits an arbitrary step-size for the independent variable at each step of the integration. Runge-Kutta algorithms[25] do this, but are notoriously slow because a number of derivative evaluations are required for each step. Therefore we derived Adams-Moulton-like formulas by using backward difference expansions[26] for arbitrarily spaced values of the independent variable; Appendix C gives these predictor-corrector formulas. Since this routine can choose a near-to-optimum step-size for each step of the integration (for a given error limit), it was observed that this integrater was

actually several times faster than a fixed step-size Adams-Moulton routine (of the same order) that can only halve or double the step-size. The most important feature of this routine from our point of view, however, is that since the step-size is arbitrary at each step, it can just as well be complex. The only modification of the numerical integration routine required for these complex trajectories, therefore, is the definition of the coordinate and momentum variables, and the time increment, as complex variables.

Once the instability problem was eliminated by starting the trajectory at both ends with real (and integer) quantum numbers and integrating toward the interaction region, these complex classical trajectories were found to be no more difficult to integrate than ordinary (i.e., real) trajectories. [The term "complex trajectory" is used to mean one for which coordinates, momenta, and time may be complex valued; it does not mean that the trajectory is complicated.] They require approximately the same amount of computing time, and no more than the usual accuracy requirement is necessary to attain comparable accuracy in the final results.

All the transitions given in Table I of the previous section were also computed by direct integration of the equations of motion, and precisely the same values were obtained for both the transition probabilities and the complex values of q_1 that satisfy Equation (II.4). This must be true formally, of course, since the numerical analytic continuation of Section III and the direct integration method of this section are simply different ways of analytically continuing the same functions. When one considers what extremely different methods these two are, however, it is gratifying to see that they are consistent.

Table II gives additional results obtained by direct integration for transitions that are too weak to be treated by the method in Section III; they are the smallest transition probabilities given by Secrest and Johnson[23]. Agreement with the quantum values is remarkably good, and it appears that the dynamics of even these extremely weak transitions are accurately described by classical S-matrix theory. The trajectories associated with even the weakest of the transitions in Table II were well-behaved and proceeded much as ordinary trajectories.

V. Concluding Remarks.

The methods of numerical analytic continuation in Section III are essentially made obsolete by the success in direct integration of the equations of motion as discussed in Section IV. Direct integration is easier to apply than the procedures of Section III even for only slightly forbidden transitions and is no more difficult for the most strongly forbidden transitions (for which the methods of Section III are completely inadequate).

Even more important, particularly with regard to other applications, is the generality afforded by the ability to integrate the equations of motion through classically forbidden domains. Thus it is not possible even in principle to apply the methods of Section III to the problem of tunneling in reactive collisions, for below the classical threshhold for reaction there is no reactive trajectory function on which to base a numerical analytic continuation (i.e., it is not possible to analytically continue nothing). By direct integration of the equations of motion, however, it should be possible to treat such processes. In fact, any classically forbidden process, including electronic transitions between

adiabatic electronic potential energy surfaces[5], should be amenable to this description.

The scope of problems to which semiclassical theories that incorporate exact classical dynamics can be applied is thus greatly expanded by this demonstrated feasibility of calculating classical trajectories through classically forbidden regions of phase space. As systems with more degrees of freedom (e.g., A + BC in three dimensions) are examined and as different types of classically forbidden processes are explored, it will be interesting and important to see if such future work continues to support the thesis that the dynamics of molecular collisions is primarily classical dynamics plus quantum superposition.

Table I. Numerical Analytic Continuation[a]

E, m, α[b]	n_1, n_2[c]	q_1[d]	Semiclassical[e]	Uniform[f]	Quantum[g]
6, $\frac{2}{3}$, 0.3	2, 4	4.66 + 1.07i	6.64×10^{-3}	6.11×10^{-3}	6.00×10^{-3}
4, $\frac{2}{3}$, 0.3	1, 3	4.66 + 1.92i	1.57×10^{-5}	1.51×10^{-5}	1.46×10^{-5}
2.47275, $\frac{5}{4}$, 0.2973	0, 1	3.35 + 3.87i	1.31×10^{-4}	1.22×10^{-4}	1.12×10^{-4}
3.47275, $\frac{5}{4}$, 0.2973	1, 2	3.46 + 3.31i	2.68×10^{-4}	2.57×10^{-4}	2.30×10^{-4}
4.47275, $\frac{5}{4}$, 0.2973	2, 3	3.56 + 3.04i	4.12×10^{-4}	3.95×10^{-4}	3.52×10^{-4}

a. Transition probabilities were computed by the procedure described in Section III.

b. The total energy E (in units of $\hbar\omega$, and therefore $\frac{1}{2}$ the corresponding numerical value in reference 23), mass parameter m, and potential parameter α for the linear A + BC collision system of Secrest and Johnson.

c. The initial and final vibrational quantum numbers.

d. The complex root of Equation (II.4).

e. The semiclassical transition probability as given by Equation (II.6).

f. The uniform semiclassical transition probability, which is given by Equation (II.6) with the replacement $\exp(-2\mathrm{Im}\phi/\hbar) \rightarrow 4\pi z^{\frac{1}{2}} \mathrm{Ai}^2(z)$, where $z = (\frac{3}{2}\ \mathrm{Im}\phi/\hbar)^{\frac{2}{3}}$; for details of this procedure see reference 1b.

g. The (exact) quantum mechanical transition probability calculated by Secrest and Johnson.

Table II. Direct Integration[a]

E, m, α[b]	n_1, n_2[c]	q_1[d]	q_2[d]	Semiclassical[e]	Uniform[f]	Quantum[g]
3, 0.2, 0.114	1, 2	3.74 + 4.33i	4.28 + 9.28i	5.95×10^{-6}	5.80×10^{-6}	5.11×10^{-6}
3, 0.2, 0.114	0, 2	3.72 + 3.97i	4.29 + 9.98i	9.28×10^{-10}	9.14×10^{-10}	9.03×10^{-10}
3.47275, $\frac{5}{4}$, 0.2973	0, 2	3.31 + 3.47i	5.47 + 6.24i	1.73×10^{-7}	1.70×10^{-7}	1.69×10^{-7}
4.47275, $\frac{5}{4}$, 0.2973	1, 3	3.40 + 2.91i	5.34 + 6.06i	5.64×10^{-7}	5.52×10^{-7}	5.29×10^{-7}
3.8, 0.5, 0.114	0, 2	1.43 + 5.38i	1.71 + 9.08i	1.42×10^{-11}	1.40×10^{-11}	1.28×10^{-11}

a. Transition probabilities were computed by the procedure described in Section IV.

b, c, e, f, g. Same as for Table I.

d. The initial (q_1) and final (q_2) complex values of the angle variable.

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5. W. H. Miller and T. F. George, "Semiclassical Theory of Electronic Transitions in Low Energy Atomic and Molecular Collisions Involving Several Nuclear Degrees of Freedom", to be published.

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7. Although we think of the internal (i.e., quantized) degrees of freedom semiclassically in terms of their action-angle variables, the numerical integration of the equations of motion is actually carried out in ordinary cartesian coordinates. For the linear A + BC system, of reference 23, for example, if n_1 and q_1 are the initial action-angle variables, one converts these into initial conditions for the cartesian variables

$$r_1 = (2n_1 + 1)^{\frac{1}{2}} \cos q_1$$

$$p_1 = -(2n_1 + 1)^{\frac{1}{2}} \sin q_1 \quad ,$$

and the trajectory is integrated with the classical Hamiltonian $H(P, R, p, r) = P^2/2m + p^2/2 + r^2/2 + \exp[\alpha(r-R)]$. At the conclusion of the trajectory the final values r_2 and p_2 are used to construct the final values of the action-angle variables

$$n_2 = \tfrac{1}{2}(p_2^2 + r_2^2) - \tfrac{1}{2}$$

$$q_2 = -\tan^{-1}(p_2/r_2) \quad .$$

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15. It is easy to see that the "formal theory of scattering" requires only that $\mathrm{Re}(t_2-t_1) \to +\infty$, $\mathrm{Im}(t_2-t_1)$ finite, in defining the operator S,

$$S = \exp(iH_o t_2/\hbar)\exp[-iH(t_2-t_1)/\hbar]\exp(-iH_o t_1/\hbar) \quad ;$$

see, for example, R. G. Newton, Scattering Theory of Waves and Particles, McGraw-Hill, New York, 1966, pp. 167-175. Furthermore, since for the pair of action-angle variables (n,q) it is n that is the observable and must therefore be real, q is completely unspecified and may therefore be complex.

16. F. B. Hildebrand, Introduction to Numerical Analysis, McGraw-Hill, New York, 1956, pp. 373-375.

17. The phase $\phi[n_2(q_1,n_1),n_1] \equiv \phi(q_1)$ is actually not periodic: $\phi(q_1 + 2\pi) = \phi(q_1) - 2\pi[n_2(q_1,n_1) - n_1]$, but $\chi(q_1) \equiv \phi(q_1) + q_1[n_2(q_1,n_1) - n_1]$ is; therefore it is the function $\chi(q_1)$ that is actually numerically analytically continued, and then ϕ is calculated by $\phi(q_1) = \chi(q_1) - (n_2 - n_1)q_1$.

18. G. A. Baker and J. L. Gammel, Eds., The Padé Approximant in Theoretical Physics, Academic Press, New York, 1970.

19. Periodic functions such as $n_2(q_1)$ can also be represented by the point method using continued fractions; see, for example, reference 20. The basis functions must be chosen, however, so that their zeros occur only at the ends of the region of periodicity. Thus we found that $n_2(q_1)$ could be represented by a linear combination of the basis functions $u_k(x) = \sin^k(x/2)$. The differences $x-x_i$ in the continued fraction expressions [see Equations (2.9) and (2.10) of Schlessinger, reference 20] are replaced by $\sin[(x-x_i)/2]$, where x_i is an input point. The procedure described in the text, however, being a more natural extension of the well-known Fourier series, seemed preferable to us.

20. L. Schlessinger, Phys. Rev., 167, 1411 (1968).

21. All of the classically forbidden transitions of reference 1c were also re-calculated using the procedure of this section, and the earlier results were confirmed to within at least one unit in the last significant figure reported there.

22. For derivation and discussion of the uniform semiclassical formulas, see references 1b and 2c.

23. D. Secrest and B. R. Johnson, J. Chem. Phys., 45, 4556 (1966).

24. The equation $\mathrm{Im}\, n_2(q_1,n_1) = 0$ defines a line in the complex q_1-plane. There is thus zero probability that successive q_1 iterates give final values $n_2(q_1)$ that are real.

25. See, for example, F. B. Hildebrand, ibid. pp. 233-239.

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27. C. Garrod, Rev. Mod. Phys., 38, 483 (1966).

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33. R. Van Wyk, "Variable Mesh Methods for Differential Equations", NASA Report CR-1247, November 1968.

Appendix A: One Dimensional Tunneling Through a Parabolic Barrier.

To illustrate some points regarding classically forbidden processes that are typical of the general situation, it is illustrative to consider a simple example, the tunneling of a particle through a one-dimensional parabolic barrier.

The potential is

$$V(x) = -\frac{1}{2} m\omega^2 x^2, \tag{A.1}$$

m being the mass of the particle, and the classical trajectory of the particle is easily found to be

$$x(t) = x_1 \cosh(\omega T) + (p_1/m\omega) \sinh(\omega T) \quad , \tag{A.2}$$

where x_1 and p_1 are the position and momentum at t_1, and $T = t - t_1$. The choice

$$x_1 = -a$$
$$p_1 = \left\{2m[E - V(x_1)]\right\}^{\frac{1}{2}}$$
$$V(x_1) < E < 0$$

describes a particle initially to the left of the barrier, moving toward it, but with insufficient energy to surmount it. Equation (A.2) becomes

$$x(t) = -a \cosh(\omega T) + a' \sinh(\omega T) \tag{A.3}$$

where $a' = (a^2 - a_o^2)^{\frac{1}{2}}$ and $a_o^2 = 2|E|/m\omega^2$; as $T \to +\infty$. This gives

$$x(t) \simeq \frac{1}{2}(a' - a)e^{\omega T} \to -\infty \quad ;$$

i.e., as expected, the particle is reflected by the barrier.

The particle is reflected by the barrier, however, only so long as the time is required to be real. If time is allowed to be complex

$$T \equiv r + is \quad ,$$

then Equation (A.3) becomes

$$x(t) = [-a \cosh(\omega r) + a' \sinh(\omega r)] \cos(\omega s) + i[a \sinh(\omega r) + a' \cosh(\omega r)] \sin(\omega s) \quad , \tag{A.4}$$

and as $\mathrm{Re}T \equiv r \to +\infty$, this is

$$x(t) = \frac{1}{2} e^{\omega r} [(a'-a) \cos(\omega s) + i(a'+a) \sin(\omega s)]. \tag{A.5}$$

If $\mathrm{Im}\, T \equiv s = \pm \pi/\omega$, for example, then it is clear from Equation (A.5) that $x(t) \to +\infty$, i.e., that the particle has tunneled through the barrier.

Since we have been dealing strictly with classical trajectories with energy $E < 0$ (and E is conserved), one may ask how did the particle get through the barrier; i.e., what trajectory did it follow. This is somewhat of an ambiguous question for the following reason: $x(t)$, the position of the particle at time t, is a function only of the time difference $t - t_1$, and does not in any way depend on the path in the complex t-plane along which the time is incremented from t_1 to t; this is true for all dynamical systems, of any number of degrees of freedom, for which the classical Hamiltonian is not an explicit function of time. Thus the trajectory swept out in the x-plane from x_1 to $x(t)$ depends on how the time is incremented from t_1 to t, but the final position $x(t)$ does not.

The simplest physical picture results, however, if one chooses a particular curve in the complex t-plane along which to increment time from t_1 to t. Namely, time is initially incremented along the real time

axis from t_1 to $\bar{t}$,

$$\bar{t} = t_1 + \cosh^{-1}(a/a_o) \quad ,$$

and the particle moves from $x_1 = -a$ to the classical turning point $x(\bar{t}) = -a_o$. Time is then incremented in the imaginary direction of the t-plane from $\bar{t}$ to $\bar{t} + i\pi/\omega$, and from Equation (A.4) one can see that $x(t)$ varies from $-a_o$ to $+a_o$; i.e., it is during this interval that the particle tunnels through the barrier. Further increments to the time are all real, and the particle moves from a_o to the right on the real x-axis.

To give a precise meaning to such a trajectory, and to determine the probability of the tunneling transition, one needs to look at matrix elements of the fixed-energy propagator, i.e., the Green's function[27-30]

$$< x_2|G(E)|x_1 > \equiv < x_2|(E-H)^{-1}|x_1 >$$

$$= (i\hbar)^{-1} \int_o^\infty dT \exp(iET/\hbar) < x_2|\exp(-iHT/\hbar)|x_1 > \quad ; \text{(A.6)}$$

the square modulus of this matrix element is the probability that a particle with energy E goes from x_1 to x_2. The time propagator is given in the classical-limit by

$$< x_2|\exp[-iH(t_2-t_1)/\hbar]|x_1 > = \left[- \frac{\partial^2 \phi(x_2, x_1; T)}{\partial x_2 \partial x_1} \Big/ 2\pi i\hbar \right]^{\frac{1}{2}}$$

$$\times \exp\left[i\phi(x_1, x_2; T)/h\right] \quad , \qquad \text{(A.7)}$$

where $T = t_2 - t_1$, and ϕ is the classical action

$$\phi(x_2, x_1; T) = \int_{t_1}^{t_2} dt \, \tfrac{1}{2} m \dot{x}(t)^2 - V(x(t)) \quad . \qquad \text{(A.8)}$$

Within the classical limit it is consistent to evaluate the time integral in Equation (A.6) by the stationary phase approximation, and this gives

$$< x_2|G(E)|x_1 > = (i\hbar)^{-1}\left[\frac{-\partial^2\phi}{\partial x_2 \partial x_1} \Big/ \frac{\partial^2\phi}{\partial T^2}\right]^{\frac{1}{2}} \times \exp\left\{i[ET + \phi(x_2,x_1;T)]/\hbar\right\} \quad , \tag{A.9}$$

where T in Equation (A.9) is the value determined by the stationary phase condition

$$E + \frac{\partial\phi(x_2,x_1;T)}{\partial T} = 0 \quad . \tag{A.10}$$

This overall procedure is well-known[28,29], and it is not difficult to show that Equations (A.9) and (A.10) give the final result

$$< x_2|G(E)|x_1 > = \left\{i\hbar[v(x_1)v(x_2)]^{\frac{1}{2}}\right\}^{-1} \times \exp\left[\frac{i}{\hbar}\int_{x_1}^{x_2} dx \left\{2m[E-V(x)]\right\}^{\frac{1}{2}}\right] \quad , \tag{A.11}$$

where $v(x) = \left\{2[E-V(x)]/m\right\}^{\frac{1}{2}}$ is the local velocity. Equation (A.11) is simply the WKB approximation for the Green's function.

For the case of the parabolic barrier, with $x_1 = -a$ and $x_2 = a$, the stationary phase condition in Equation (A.10) is easily shown to be

$$\sinh^2(\omega T/2) = \tfrac{1}{2}m\omega^2 a^2/E \quad ,$$

so that if $E < 0$, it is clear that T has to be complex. Evaluation of the time integral in Equation (A.6) would then proceed by the method of steepest descent[9]; i.e., the path of the time integral is distorted from the real time axis to a contour in the complex t-plane that passes through the complex point of "stationary phase". The final result of

this procedure is identical to Equation (A.11). The exponent in Equation (A.11) now has an imaginary part, however, and this of course is what gives the usual WKB tunneling factor:

$$|< x_2|G(E)|x_1 >|^2 = |v(x_1)v(x_2)|^{-1} \exp\left\{ - \frac{2}{\hbar} \mathrm{Im} \int_{x_1}^{x_2} dx \left\{ 2m[E-V(x)] \right\}^{\frac{1}{2}} \right\} \quad (A.12)$$

The complex time difference T that was seen earlier to lead to a classical trajectory that tunnels through the barrier is thus seen to be the complex time that is the point of stationary phase in the time integral in Equation (A.6). One again sees that the stationary phase approximation is the classical limit of quantum mechanics.

In conclusion, however, one must refrain from leaning too heavily on analogies with one-dimensional examples, for they can sometimes be misleading with regard to the general situation of several degrees of freedom. In one dimension, for example, it is always possible to keep the coordinate x(t) real (as was done above) by the proper choice of the contour in the complex t-plane along which time is incremented. For a system with more than one degree of freedom, however, there is more than one coordinate but still only one time variable; i.e., one can choose the time contour to keep <u>one</u> of the coordinates real, but not all of them. Thus there is no way to avoid having to deal with the full complexity of the situation.

Appendix B. Matching Procedure for Double-Ended Trajectories.

There are undoubtedly a number of equivalent ways of connecting the two branches of the complex trajectory discussed in Section IV. The procedure described below seemed to be quite fool-proof for the present application, but other procedures will be necessary for other types of classically forbidden processes.

Consider the inward branch of the trajectory. The time is first incremented from t_1 to the time t_1' (with Re $t_1' = t_1$) such that $q(t_1')$ is purely real. The reason for this is that if Im q_1 is large, as it is for very weak transitions, and if t is incremented along the real times axis, it is easy to show that the unperturbed motion of the vibrational coordinate $r(t)$ = constant x $\cos[q(t)]$ is approximately a circle in the complex r-plane with a radius proportional to $\exp(|\text{Im } q_1|)$. Since $r(t)$ makes a pass about this circle with each time increment of a vibrational period, $r(t)$ changes quite rapidly with time and is thus difficult to treat numerically. Since the trajectory in the initial asymptotic region is

$$\begin{aligned} P(t) &= P_1 \\ n(t) &= n_1 \\ R(t) &= R_1 + (P_1/\mu)(t-t_1) \\ q(t) &= q_1 + \epsilon'(n_1)(t-t_1) \quad , \end{aligned} \tag{B.1}$$

where P_1, R_1, q_1, n_1 are the boundary conditions in Equation (II.13), it is easy to see that the choice for t_1' that makes Im q = 0 is

$$t_1' = t_1 - i(\text{Im } q_1)/\epsilon'(n_1) \quad ;$$

the values of the coordinates and momenta at t_1' are

$$
\begin{aligned}
n_1' &= n_1 \\
P_1' &= P_1 \\
q_1' &= \mathrm{Re}\ q_1 \\
R_1' &= R_1 - i(P_1/\mu)(\mathrm{Im}\ q_1)/\epsilon'(n_1)
\end{aligned}
\qquad \text{(B.2)}
$$

The numerical integration of the equations of motion is thus actually begun with the primed initial conditions in Equation (B.2), and the time is incremented in the real time direction. The vibrational coordinate r(t) now carries out ordinary vibrational motion initially and remains approximately real; the translational coordinate R(t) may have a large imaginary part, but this causes no numerical difficulties since R(t) is not oscillatory.

Integration of the inward branch of the trajectory is continued, with time incremented along the real time axis, until the real part of P(t) is observed to go through zero (i.e., changes sign). [Since $P_1 < 0$ and $P_2 > 0$, it is clear that such a point must be passed.] The inward branch of the trajectory is stopped at this point.

The outward branch of the trajectory is then begun with the boundary conditions in Equation (II.14) and, just as for the inward branch, one first increments the time to the value at which q(t) is real. Thus the boundary conditions with which the trajectory is actually begun are analogous to Equation (B.2):

$$
\begin{aligned}
n_2' &= n_2 \\
P_2' &= P_2 \\
q_2' &= \mathrm{Re}\ q_2 \\
R_2' &= R_2 - i(P_2/\mu)(\mathrm{Im}\ q_2)/\epsilon'(n_2)
\end{aligned}
$$

The time is now incremented along the real time axis (in the negative direction) until the real part of $P(t)$ is observed to change sign. From this point one chooses successive time increments in order to integrate to that (complex) time at which $P(t)$ exactly equals the final value of P from the inward branch of the trajectory. [Since the numerical integration routine allows for a continuously variable time increment, this is quite simple to do.] Integration of the outward branch of the trajectory is stopped at this point.

Let the values of the coordinates and momenta from the inward and outward branches of the trajectory at this intermediate point be denoted at P_{in}, R_{in}, p_{in}, r_{in} and P_{out}, R_{out}, p_{out}, r_{out}, respectively. As discussed above, the intermediate point is chosen so that $P_{in} = P_{out}$. The differences between the internal variables, $\Delta r \equiv r_{out} - r_{in}$ and $\Delta p = p_{out} - p_{in}$, are functions of the initial and final angle variables q_1 and q_2 (for fixed quantum numbers n_1 and n_2), and one solves the following equations simultaneously:

$$\Delta r(q_2, q_1) = 0 \qquad \text{(B.4a)}$$

$$\Delta p(q_2, q_1) = 0 \quad . \qquad \text{(B.4b)}$$

[Since Δr, Δp, q_2, and q_1 are all complex-valued, Equations (B.4) are actually four equations in four unknowns.] With the particular values of q_1 and q_2 that satisfy Equations (B.4) one then has that $P_{in} = P_{out}$, $r_{in} = r_{out}$, $p_{in} = p_{out}$; furthermore, since both branches of the trajectory have the same total energy, it must also be true that $R_{in} = R_{out}$. All the coordinates and momenta are thus equal at this intermediate point, so that the two branches form one continuous trajectory.

The argument in the above paragraph that energy conservation implies that $R_{in} = R_{out}$ assumes that the equation

$$H(R_{in}, P, r, p) = H(R_{out}, P, r, p) \qquad (B.5)$$

(where P,p,r are equal to their common intermediate values) implies the result

$$R_{in} = R_{out} \ ;$$

this will strictly be true only if the Hamiltonian is a monotonic function of R (when P, p, r equal their intermediate values). Although this is the case for the present physical system, there will be cases for which this is not true, and one would need to account for this in carrying out the matching procedure.

For the case of N degrees of freedom (translation, with variables R and P, and N-1 internal degrees of freedom with variables $\underset{\sim}{q}$ and $\underset{\sim}{n}$) the arguments are quite similar. One can always choose the stopping place for the inward and outward branches to make one variable continuous, say P. The 2N-2 variables $\underset{\sim}{q}_1$ and $\underset{\sim}{q}_2$ can then be chosen iteratively (with fixed quantum numbers $\underset{\sim}{n}_1$ and $\underset{\sim}{n}_2$) to make the 2N-2 coordinates and momenta of the internal degrees of freedom continuous at the intermediate point. Finally, energy conservation will then insure that R is also continuous at this point.

Appendix C. Variable Step-Size Adams-Moulton Integrater.

Consider the set of (non-linear) first order differential equations

$$y'(x) = f(x,y) \quad ,$$

where x is the independent variable, and y and f are understood to be vectors. The formulas below are derived analogously to the standard procedures[32], except that divided difference expansions[26] are used that do not require the independent variable to be at equally spaced points. There has been previous work dealing with these variable mesh methods[33], but they were not of sufficiently high order for our purposes.

Let x_i denote the points of the independent variable and h_i the i^{th} step-size

$$h_i = x_{i+1} - x_i \quad ;$$

also

$$y_i \equiv y(x_i)$$

$$f_i \equiv f(x_i, y_i) \quad .$$

If p^{th} order differences are retained, then the Adams-like predictor formula is found to be

$$y_{n+1}^{(0)} = y_n + \sum_{s=0}^{p} C_s \, f[x_n, x_{n-1}, \cdots, x_{n-s}] \quad ,$$

where the notation for the divided differences is that of Hildebrand[26]; i.e.,

$$f[x_n] = f_n$$

$$f[x_n, x_{n-1}] = \frac{f[x_n] - f[x_{n-1}]}{x_n - x_{n-1}}$$

$$\vdots$$

$$f[x_n, \ldots, x_{n-s}] = \frac{f[x_n, \ldots, x_{n+1-s}] - f[x_{n-1}, \ldots, x_{n-s}]}{x_n - x_{n-s}} \quad .$$

The coefficients C_s are

$$C_s = \int_{x_n}^{x_{n+1}} dx\, (x-x_n)(x-x_{n-1})\ldots(x-x_{n+1-s}) \quad ,$$

and the first few are

$$C_0 = 1$$

$$C_1 = \tfrac{1}{2} h_n^2$$

$$C_2 = h_n^2(\tfrac{1}{3} h_n + \tfrac{1}{2} h_{n-1})$$

$$C_3 = h_n^2[h_n(\tfrac{1}{4} h_n + \tfrac{2}{3} h_{n-1} + \tfrac{1}{3} h_{n-2}) + \tfrac{1}{2} h_{n-1}(h_{n-1} + h_{n-2})]$$

$$\begin{aligned} C_4 = h_n^2\{&h_n^2(\tfrac{1}{5} h_n + \tfrac{3}{4} h_{n-1} + \tfrac{1}{2} h_{n-2} + \tfrac{1}{4} h_{n-3}) \\ &+ \tfrac{1}{3} h_n[(2h_{n-1} + h_{n-2})(h_{n-1} + h_{n-2} + h_{n-3}) \\ &+ h_{n-1}(h_{n-1} + h_{n-2})] \\ &+ \tfrac{1}{2} h_{n-1}(h_{n-1} + h_{n-2})(h_{n-1} + h_{n-2} + h_{n-3})\} \quad . \end{aligned}$$

The p^{th} order Moulton-like corrector formula is most conviently given in the form

$$\begin{aligned} y_{n+1} = y_{n+1}^{(0)} + C_p \{&f_{n+1} - f[x_n] - (h_n) f[x_n, x_{n-1}] \\ &- (h_n)(h_n + h_{n-1})\, f[x_n, x_{n-1}, x_{n-2}] - \ldots - (h_n)(h_n + h_{n-1}) \\ &\ldots(h_n + h_{n-1} + \ldots + h_{n+1-p})\, f[x_n, \ldots, x_{n-p}]\} \\ &\div [(h_n)(h_n + h_{n-1})\ldots(h_n + h_{n-1} + \ldots + h_{n+1-p})] \quad , \end{aligned} \qquad (C.2)$$

where C_p is the coefficient defined above.

An optimum step-size selector is easily devised for a predictor-corrector routine such as this. It is based on the fact that the truncation error[32] for the p^{th} order case is of order h^{p+2}, and a measure of the actual truncation error in the $x_n \to x_{n+1}$ step is the difference of the predicted and corrected functional values, $y_{n+1} - y_{n+1}^{(0)}$. If ϵ is the specified error limit (e.g., $\epsilon \sim 10^{-6}$), therefore, the step $x_n \to x_{n+1}$ is accepted if

$$\text{Error} \equiv \left| \frac{y_{n+1} - y_{n+1}^{(0)}}{y_{n+1}} \right| \leq \epsilon \quad , \tag{C.3}$$

and the step-size h_{n+1} for the next step is chosen as

$$h_{n+1} = h_n \left(\frac{1}{3} \epsilon/\text{Error} \right)^{1/(p+2)} \tag{C.4}$$

[If Equation (C.3) is not fulfilled, then the step is repeated with a new value of h_n given by RHS of Equation (C.4)]. If the error behaved exactly as h^{p+2}, then the choice of h_{n+1} in Equation (C.4) would make the error in the $x_{n+1} \to x_{n+2}$ step exactly $\epsilon/3$. The $\frac{1}{3}$ is a safety factor to prevent the need for frequent repetitions of a step; for the case $p = 4$, the order of the formulas we used, the factor $3^{1/6} \simeq 1.2$ means that the step size is chosen $\sim 20\%$ smaller than would ideally be the case.

If one chooses a constant step size, $h_i \equiv h$ for all i, then it is easy to verify that Equations (C.1) and (C.2) give the usual Adams-Moulton prediction and corrector expressions[32]. From our observations, however, it appears that the additional algebraic complexity of the variable step-size formula is off-set by the more efficient choice of step size that is possible; thus a fewer total number of steps is required, and this means a fewer number of derivative evaluations, normally the most time consuming part of the calculation.

Appendix D. The Total Initial Value Representation.

Another way of attempting to describe classically forbidden transitions is via an integral representation. Although we have not pursued this direction (for reasons discussed below), it may nevertheless be of interest to see this particular version of such procedures.

As has been noted previously[1a], making the classical-limit approximation to the S-matrix in one representation is equivalent to making it in any other representation provided one transforms between representations by the ordinary stationary phase approximation. If one carries out the integrations that change representations more accurately than by stationary phase, then all representations are no longer equivalent. If there is some representation in which the dynamics is most classical-like, therefore, one should make the classical-limit approximation to S in that representation and transform to any others by carrying out the necessary integrations as accurately as desired.

A trivial example in fact shows that there is one representation in which the classical-limit approximation is exact. If $\underset{\sim}{P}$ is the complete set of constants of the motion of the Hamiltonian H, then the matrix elements of the propagator in this representation are

$$< P_2|\exp[-iH(t_2-t_1)/\hbar]|P_1 > = \delta(P_2-P_1)\exp[-iE(P_1)(t_2-t_1)/\hbar] \quad (D.1)$$

both quantum mechanically and in the classical limit; E(P) is simply H(P), the energy expressed in terms of the constants of the motion. Matrix elements in some other coordinate representation, for example, are obtained by

$$< q_2|\exp[-iH(t_2-t_1)/\hbar]|q_1 > = \int dP_2 \int dP_1 < q_2|P_2 >$$

$$< P_2|\exp[-iH(t_2-t_1)/\hbar]|P_1> < P_1|q_1 >$$

$$= \int dP <q_2|P > \exp[-iE(P)(t_2-t_1)/\hbar] < P|q_1 > . \qquad (D.2)$$

Equation (D.2) is a well-known formal expression for the exact quantum propagator, being "formal" because the transformation elements $< q|P >$ are the exact wavefunctions and thus unknown. This example does show, however, that there are some representations in which it is better to make the classical-limit approximation than others.

Following the discussion of the "initial value representation" in reference 1b, one can write the S-matrix in the quantum number representation as

$$< n_2|S|n_1 > = \int dq_2 \int dq_1 \ < n_2|q_2 > < q_2|S|q_1 > < q_1|n_1 > . \quad (D.3)$$

Using the classical-limit approximation for $< q_2|S|q_1 >$ and changing variables of integration from q_2 to n_1 (for fixed q_1), it is not difficult to show that Equation (D.3) can also be written as

$$S_{n_2',n_1'} = (2\pi\hbar)^{-1} \int_0^{2\pi} dq_1 \int_0^{} dn_1 \left[\frac{\partial q_2(q_1,n_1)}{\partial n_1} \Big/ 2\pi\hbar \right]^{\frac{1}{2}}$$

$$\exp\left[\frac{i}{\hbar}\Big\{\phi[n_2(q_1,n_1),n_1] + q_2(q_1,n_1)[n_2(q_1,n_1) - n_2'] - q_1(n_1 - n_1')\Big\}\right] , \qquad (D.4)$$

where n_2' and n_1' are fixed integers. Equation (D.4) is an integral over initial values q_1 and n_1 (and not just q_1 as in reference 1b) and might thus be called the <u>total</u> initial value representation. The $n_1' \to n_2'$

transition is classically forbidden if there are no points of stationary phase in the integral over initial values, but the integral could nevertheless be evaluated numerically.

One attractive feature of Equation (D.4) is that one never has trouble with "coalescing points of stationary phase" that need to be "uniformized"[1b, 1d]; this is true because the initial values q_1 and n_1 determine a unique classical trajectory. [The integrand in Equation (D.3) may actually contain several terms since q_2 and q_1 do not necessarily determine a unique trajectory. With q_1 fixed, however, the change of variables from q_2 to n_1 eliminates such a sum; i.e., integrating over n_1 integrates over all the multiple branches of q_2.] Lastly, one can see that Equation (D.4), unlike the initial value representation of reference 1b, satisfies microscopic reversibility identically; this follows since Equation (D.4) is equivalent to Equation (D.3) (they are related simply by a change of variables of integration), and Equation (D.3) is manifestily symmetric in n_1 and n_2.

Our reasons for not pursuing this procedure are two-fold. The first is practical; there are two integrations for each internal degree of freedom. For A + BC in three dimensions there are three internal degrees of freedom and Equation (D.4) would thus be a six-fold integral. In addition, the integrand is highly oscillatory and thus cannot be evaluated by Monte Carlo integration methods.

The more fundamental shortcoming of Equation (D.4) is its <u>lack of uniqueness</u>. Thus the integral over n_1 and q_1 is essentially a phase space integral, and one would like for the expression to be canonically invariant to a change of canonical variables from (n,q) to (p,r), say;

i.e., one would like Equation (D.4) to be the result if one had begun in Equation (D.3) with S in the r-representation, for example. Unfortunately, one can verify that this is not the case. Depending on what representation is chosen as the one in which to make the classical limit approximation, a different classical S-matrix results in the quantum number representation.

The analytic continuation procedures of Sections III and IV, on the other hand, are unique and unambiguous; they are exact classical dynamics, analytically continued.

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