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The Classical S-Matrix: A More Detailed Study of Classically Forbidden Transitions in Inelastic Collisions‡

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ABSTRACT

Procedures are investigated for describing classically forbidden collision processes within the framework of the classical limit of quantum mechanics. The goal is to use exact classical mechanics (numerically computed trajectories) to treat classically forbidden transitions in a complex collision (such as an atom plus diatom) in a manner analogous to the way one uses it to treat barrier transmission by a single particle in one dimension (a classically forbidden process); in this latter example the transmission coefficient is $\exp(-2\theta)$, θ being the classical action integral through the barrier (a classically forbidden region). Numerical application of these procedures is made to the linear atom – diatom collision system (without reaction), and the resulting vibrational transition probabilities for the classically forbidden transitions are in as good agreement with the exact quantum mechanical values as are the transition probabilities for classically allowed transitions. It appears, therefore, that the dynamics of even these classically forbidden transitions is accurately described in this semiclassical framework.

I. INTRODUCTION

It has recently been shown [1-3] how one can use exact classical mechanics (numerically computed trajectories) to obtain the classical limit of the time-independent quantum mechanical S-matrix for a given collision system. Numerical application was made in II to the linear atom-diatom collision system (without reaction), and the resulting vibrational transition probabilities were of such accuracy as to suggest that classical mechanics may indeed be sufficiently accurate to describe the dynamics of complex heavy particle collisions - provided one makes the classical approximation to the appropriate transition amplitude (i.e., S-matrix element) and takes account of interferences which appear in the resulting transition probability (or cross section, for a three-dimensional system).

In the present work we wish to explore more fully the question of classically forbidden transitions (a term explained precisely in II), in particular, how one can use exact[4] classical mechanics to obtain results for classically forbidden processes.[5] At first glance this may seem self-contradictory, but consider the simple example of barrier transmission (tunneling) by a single particle in one dimension.[6] Although the strictly classical limit ($\hbar = 0$) for the transmission coefficient is zero, the WKB approximation gives $\exp(-2\theta)$, θ being the phase integral through the barrier. This WKB result, however, is actually obtainable classically, for θ is a classical quantity (the classical action integral through a classically forbidden region). From another point of view one may note that the Hamilton-Jacobi equation (which is equivalent to the classical equations of motion) does possess solutions in classically forbidden regions; classical mechanics ordinarily ignores these solutions since here the momentum is imaginary, but the classical limit of quantum mechanics (in one dimension the WKB approximation) shows that they do have significance (cf. the WKB wave function in a classically forbidden region).

The goal, then, is to show how exact classical mechanics can be used to treat classically forbidden processes for multi-dimensional systems (such as an atom-diatom collision) in a manner analogous to the way one uses it in the above mentioned one particle problem; the matter is greatly complicated, of course, by the fact that one does not possess closed form

solutions for the classical trajectories (as one does for one particle in one dimension.) This author is of the opinion that this "zeroth order" treatment of classically forbidden processes, if it can be effected, will be of useful accuracy; the numerical results presented below (see Table I) certainly support this thesis.

Sections II and III present two approaches to the problem, with specific reference to (and numerical results for) the linear atom-diatom system. These results are considerably more accurate than the rather crude parabolic approximation used in paper II for the classically forbidden transitions. Although there are some practical problems associated with the procedures presented in Sections II and III (which are discussed below), the numerical results indicate that this semiclassical treatment is as accurate for classically forbidden processes as it is for classically allowed ones.

II. CLASSICALLY FORBIDDEN TRANSITIONS BY ANALYTIC CONTINUATION

Although we now consider specifically the linear atom-diatom collision system as in II [and one should consult this work for a more detailed description of the procedure summarized below by Eqs. (1)-(6)], the basic result applies to more general systems with obvious generalizations.

The uniform semiclassical expression for the transition probability developed in II is

$$P_{n_2,n_1} = \pi|z|^{\frac{1}{2}} \mathrm{Ai}^2(-z)[p_I^{\frac{1}{2}} + p_{II}^{\frac{1}{2}}]^2 + \pi|z|^{\frac{1}{2}} \mathrm{Bi}^2(-z)[p_I^{\frac{1}{2}} - p_{II}^{\frac{1}{2}}]^2 , \tag{1}$$

where n_1 and n_2 are the initial and final vibrational quantum numbers; p_I and p_{II} are probabilities associated with the two independent trajectories which contribute to the $n_1 \rightarrow n_2$ transition:

$$p = \left[2\pi \left|\frac{\partial n_2(\bar{q}_1, n_1)}{\partial \bar{q}_1}\right|\right]^{-1} \tag{2}$$

with $\bar{q}_1$ equal to $\bar{q}_I$ (for p_I) or $\bar{q}_{II}$ (for p_{II}); $\bar{q}_1$ is the initial phase of the oscillator (the diatom) and the function $n_2(\bar{q}_1, n_1)$ (the final vibrational quantum number as a function of the initial vibrational quantum number and initial phase) is actually evaluated by specifying values for $\bar{q}_1$ and n_1, and integrating the classical equations of motion to determine n_2; the particular values $\bar{q}_I$ and $\bar{q}_{II}$ are the two roots of

$$n_2(\bar{q}_1, n_1) = n_2 \; ; \tag{3}$$

Ai and Bi in Equation (1) are the regular and irregular Airy functions[7], with z defined by

$$z = (\tfrac{3}{4}\Delta\phi)^{2/3} \tag{4}$$

where

$$\Delta\phi = \phi(\bar{q}_{II}, n_1) - \phi(\bar{q}_I, n_1) \tag{5}$$

is the phase difference of the two trajectories. For large phase differences Equation (1) takes on the "primitive" semiclassical form

$$P_{n_2,n_1} = p_I + p_{II} + 2(p_I p_{II})^{\frac{1}{2}} \sin(\Delta\phi). \tag{6}$$

As noted in II, the $n_1 \rightarrow n_2$ transition is <u>classically forbidden</u> if there is no value of $\bar{q}_1$ in its $(0,2\pi)$domain for which Equation (3) is satisfied. There will in general, however, be <u>complex</u> roots of Equation (3); suppose $\bar{q}_I$ is one such complex root

$$n_2(\bar{q}_I) = n_2 \; , \tag{3^1}$$

where we have suppressed the argument n_1 since it is constant throughout. Assuming that $n_2(\bar{q}_1)$ is an analytic function of $\bar{q}_1$ (which is certainly true for some region about the real $\bar{q}_1$ - axis), one has

$$n_2(\bar{q}_1)^* = n_2(\bar{q}_1^*),$$

so that complex conjugation of Equation (3^1) gives (since n_2 on the RHS is

some real integer)

$$n_2(\bar{q}_I^{\,*}) = n_2 \quad ;$$

i.e., the second root $\bar{q}_{II}$ is the complex conjugate of $\bar{q}_I$,

$$\bar{q}_{II} \equiv \bar{q}_I^{\,*} \,. \tag{7}$$

It follows, then, that

$$\left|n_2'(\bar{q}_I)\right| = \left|n_2'(\bar{q}_I^{\,*})\right| = \left|n_2'(q_{II})\right| \quad ,$$

so that the probabilities p_I and p_{II} are equal; the second term in Equation (1) is therefore absent. Furthermore, since $\phi(\bar{q}_1)$ is also (assumed to be) an analytic function of $\bar{q}_1$,

$$\begin{aligned} \Delta\phi &\equiv \phi(\bar{q}_{II}) - \phi(\bar{q}_I) \\ &= \phi(\bar{q}_I^{\,*}) - \phi(\bar{q}_I) \\ &= \phi(\bar{q}_I)^* - \phi(\bar{q}_I), \end{aligned}$$

or

$$\Delta\phi = -2i \ \mathrm{Im}\ \phi(\bar{q}_I); \tag{8}$$

i.e., $\Delta\phi$ is pure imaginary.

Substituting these results into Equation (1) gives

$$P_{n_2,n_1} = 4\pi \left|z\right|^{\frac{1}{2}} \mathrm{Ai}^2(z)\, p \tag{1^1}$$

for the classically forbidden transition $n_1 \to n_2$, where

$$p = \left[2\pi \left|n_2'(\bar{q}_I)\right|\right]^{-1} \tag{2^1}$$

$$z = \left[3/2 \ \mathrm{Im}\ \phi\ (\bar{q}_I)\right]^{2/3} \,. \tag{4^1}$$

For large z one may invoke the asymptotic form of the Airy function and obtain the "primitive" semiclassical expression

$$P_{n_2,n_1} = p \exp\left[-\left|\mathrm{Im}\,\phi(\bar{q}_I)\right|\right] \quad . \qquad (9)$$

It is Equation (9) that is the most readily interpretable physically - it is the precise generalization of the exp (-2θ) transmission coefficient for one-dimensional tunneling by a single particle; the factor p in Equation (9) is simply a Jacobian (the Jacobian for a single particle in one dimension is always unity). Two other illuminating analogies to Equations (6) and (9) are the WKB wave-function in classically allowed and forbidden regions, respectively, and the rainbow effect in potential scattering[8] - in all such situations the classically allowed region has oscillatory structure [Equation (6)] and the classically forbidden region is damped [Equation (9)]. The uniform semiclassical expression, Equation (1)[and Equation (1^1) which is just Equation (1) written out explicitly for a classically forbidden transition], is valid even through the region of the classical/non-classical boundary and reduces to Equations (6) and (9) in the appropriate limits.

The question now is, how does one apply Equations (1^1) or (9). In II a parabolic approximation to $n_2(\bar{q}_1)$ was made at its extrema, but here we wish to apply Equations (1^1) and (9) <u>exactly</u>, to see the limit of accuracy of these semiclassical expressions.

Our first approach was naively straight-forward: the initial phase $\bar{q}_1$ was allowed to be complex (with appropriate COMPLEX designations inserted into the Fortran programs) and the equations of motion integrated as usual. Surprisingly, this worked - at least sometimes. If $\mathrm{Im}\bar{q}_1$ becomes too large, though, the trajectory diverges. The procedure described in the following section is more satisfactory, and since it can be applied in all those situations in which the present approach is successful, no numerical results will be quoted for the present procedure. In those cases for which this method does work, however, it gives exactly the same numerical results as the method of Section III; this must be true, of course, since they both are the direct application of Equations (1^1) and (9) - they differ only in the method used to find the complex root of Equation (3).

III. ANALYTIC CONTINUATION BY FOURIER SERIES

The method described here is in the same spirit as the original parabolic approximation used in II; namely, one computes $n_2(\bar{q}_1)$ for a sample

of real $\bar{q}_1$ values in the $(0,2\pi)$ interval and uses these values to fit some analytic form for $n_2(\bar{q}_1)$. The natural extension of the parabolic approximation is to expand $n_2(\bar{q}_1)$ about an extremum in a Taylor series of higher order. We found it much more convenient (and accurate), however, to take advantage of the periodic nature of $n_2(\bar{q}_1)$ [i.e., $n_2(\bar{q}_1 + 2\pi) = n_2(\bar{q}_1)$] and expand it as a Fourier series:

$$n_2(\bar{q}_1) = a_o + \sum_{k=1}^{N} a_k \cos(k\bar{q}_1) + b_k \sin(k\bar{q}_1); \qquad (10)$$

$n_2(\bar{q}_1)$ was computed at $(2N + 1)$ equally spaced points in the interval $(0,2\pi)$ and standard procedures[9] used to obtain the coefficients $\{a_k\}$ and $\{b_k\}$ from this input. Since $n_2(\bar{q}_1)$ is naturally periodic [see II for figures showing $n_2(\bar{q}_1)$ for typical cases], the coefficients decrease rapidly with increasing k.

With the coefficients in Equation (10) thus determined, one solves numerically for the complex root of Equation (3), using Equation (10) for $n_2(\bar{q}_1)$. The phase $\phi(\bar{q}_1)$ is also expanded in a Fourier series[10], so that all the quantities required in Equations (1^1) and (9) are obtained. In practice we performed the calculation for a sequence of N-values [N being the number of terms in Equation (10)], starting with small N and increasing it until there was no significant change in the transition probabilities being computed ($N \simeq 5$-10 was normally sufficient).

Table I shows the numerical results obtained for the parameters $\alpha = .3$, $m = 2/3$ (which correspond roughly to H_2 + He), compared to the exact quantum mechanical results of Secrest and Johnson[11]; all the transitions in Table I are classically forbidden. It is seen that the uniform semiclassical results [Equation (1^1)] are in excellent agreement with the exact quantum values, considerably more so than the parabolic approximation used with Equation (1^1) in II. The results with the "primitive" semiclassical expression [Equation (9)] are less accurate, being better the smaller the transition probability; this is as it should be, for the primitive semiclassical expressions are most accurate far from the classical/non-classical boundary.

There are some problems, however, in applying this procedure; in particular, if $\mathrm{Im}\bar{q}_1$ is too large, the series is divergent. It is easy to see that this will happen, since it becomes effectively a power series in

$\exp[\,|\mathrm{Im}\bar{q}_1|\,]$. Just as with the direct method outlined at the end of Section II, therefore, this Fourier series procedure fails if $\bar{q}_1$ wanders too far from the real axis; thus one is unable to treat transitions that are too highly forbidden classically. The 4; 1-3 transition (see Table I for an explanation of this labeling) in Table I is an example of this failure; footnote e shows that the transition probability does not take on a consistent value as N is increased (although it is nevertheless of the correct order of magnitude).

The basic reason for this failure is that one is attempting to describe the function $n_2(\bar{q}_1)$ for values of $\bar{q}_1$ (large $\mathrm{Im}\bar{q}_1$) far removed from the "imput" values of $\bar{q}_1$ (real values). What is needed is a practical method for integrating Hamilton's equations through a classically forbidden region.

IV. CONCLUSIONS

It has been demonstrated that one can use exact classical mechanics to describe classically forbidden processes, even for complex collisions; the numerical results indicate this treatment of classically forbidden transitions to be as accurate as the analogous treatment of classically allowed transitions.

There are practical problems, however, in applying Equations (11) and (9) to highly forbidden transitions; these problems stem from the fact that one does not possess closed form expressions for the trajectories and must integrate Hamilton's equations numerically to obtain them. For tunneling by a single particle in one dimension, the transmission coefficient is accurately given by $\exp(-2\theta)$ even though θ is extremely large; no trouble arises for this highly forbidden process because one has an explicit expression for the classical action integral through the classically forbidden region.

It is clear that the general problem of applying classical mechanics to classically forbidden processes requires much further research. The indications are, however, that this semiclassical treatment of classically forbidden processes is of quite useful accuracy.

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1. W. H. Miller, J. Chem. Phys. 53, 1949 (1970).
2. W. H. Miller, J. Chem. Phys. 53, 000 (1970); This paper is hereafter referred to as II.
3. Some of the general results in reference 1 have been independently obtained by R. A. Marcus, J. Chem. Phys., to be published.
4. In reference 2, classically forbidden transitions were treated via a parabolic approximation to the classical trajectory functions.
5. One particular classically forbidden process of extreme importance is tunneling in reactive atom-diatom collisions near threshold; see D. Russell and J. C. Light, J. Chem. Phys. 51, 1720 (1969).
6. See any quantum mechanics text; e.g., L. I. Schiff, Quantum Mechanics (Mc-Graw-Hill Book Company, New York, 1955) pp. 278-279.
7. M. Abramowitz and I. A. Stegun, Handbook of Mathematical Functions, (U.S. Government Printing Office, Washington, D.C., 1964), pp. 446-452.
8. See, for example, R. B. Bernstein, Adv. Chem. Phys. 10, 75(1966).
9. The routine used was based on the method in F. B. Hildebrand, Introduction to Numerical Analysis, (Mc-Graw-Hill Book Company, New York, 1956) pp. 373-378.
10. The phase $\phi(\bar{q}_1)$ is actually not periodic, $\phi(\bar{q}_1 + 2\pi) = \phi(\bar{q}_1) - 2\pi [n_2(\bar{q}_1) - n_1]$, but $\chi(\bar{q}_1) \equiv \phi(\bar{q}_1) + \bar{q}_1 [n_2(\bar{q}_1) - n_1]$ is; therefore χ was actually approximated by a Fourier series, and then $\phi(\bar{q}_I) = \chi(\bar{q}_I) - (n_2 - n_1)\bar{q}_I$.
11. D. Secrest and B. R. Johnson, J. Chem. Phys. 45, 4556 (1966).

TABLE I

Transitions Probabilities for

Classically Forbidden Transitions

Transition [a]	Semiclassical [b]	Uniform [c]	Quantum [d]
3; 1-0	2.5×10^{-2}	2.3×10^{-2}	2.2×10^{-2}
3; 1-2	1.1×10^{-3}	1.0×10^{-3}	0.9×10^{-3}
4; 1-2	5.1×10^{-2}	4.4×10^{-2}	4.2×10^{-2}
4; 1-3	-	e	1.5×10^{-5}
6; 0-2	8.5×10^{-2}	6.6×10^{-2}	6.8×10^{-2}
6; 1-3	4.4×10^{-2}	3.7×10^{-2}	3.7×10^{-2}
6; 2-4	6.7×10^{-3}	6.2×10^{-3}	6.0×10^{-3}
10; 0-0	5.0×10^{-2}	4.1×10^{-2}	(6.0×10^{-2})
10; 0-4	14.9×10^{-2}	8.6×10^{-2}	8.9×10^{-2}
10; 1-5	13.8×10^{-2}	7.6×10^{-2}	7.7×10^{-2}
10; 2-6	4.8×10^{-2}	3.7×10^{-2}	3.7×10^{-2}

a. The notation is E; n_1-n_2, where E is the total energy (in units of $\hbar\omega$) and n_1 and n_2 are the initial and final vibrational quantum numbers (or vice-versa since $P_{n_2,n_1} = P_{n_1,n_2}$);all of these results pertain to the Secrest-Johnson parameters $\alpha = .3$, $m = 2/3$ (corresponding roughly to H_2 + He).

b. Results are from the "primitive" semiclassical expression, Equation (9)

c. Results are from the uniform semiclassical expression, Equation (11).

d. Essentially exact quantum mechanical results of Secrest and Johnson[11]; the figure in parenthesis is actually only an upper bound to the exact diagonal transition probability.

e. The values $5.9, 2.6, 2.2, 1.3, 0.7 \times 10^{-5}$ were obtained for 4, 6, 8, 10, and 12 terms, respectively, in Equation (10); see text for a discussion of this failure.

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