Title
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Publication Date
1970-06-01

Submitted to Journal of
Chemical Physics

UCRL-19659
Preprint
c.2

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June 1970

AEC Contract No. W-7405-eng-48

UCRL-19659

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

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The Classical S-Matrix: Numerical Application to Inelastic Collisions

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Abstract

A previously developed semiclassical theory of molecular collisions based on exact classical mechanics is applied to the linear atom-diatom collision (vibrational excitation). Classical, semiclassical, and uniform semiclassical results for individual vibrational transition probabilities corresponding to the H_2 + He system are presented and compared to the exact quantum mechanical results of Secrest and Johnson. The purely classical results (the classical limit of the exact quantum mechanical transition probability) are seen to be accurate only in an average sense; the semiclassical and uniform semiclassical results, which contain interference effects omitted by the classical treatment, are in excellent agreement (within a few percent) with the exact quantum transition probabilities. An integral representation for the S-matrix elements is also developed which, although it involves only classical quantities, appears to have a region of validity beyond that of the semiclassical or uniform semiclassical expression themselves. The general conclusion seems to be that the dynamics of these inelastic collisions is basically classical, with all quantum mechanical structure being of a rather simple interference nature.

I. INTRODUCTION

In an earlier paper[1] (referred to hereafter as I) it has been shown how the classical limit of the time-independent quantum mechanical S-matrix (i.e., the classical S-matrix) can be expressed in terms of quantities directly obtainable from the solution of the classical equations of motion for the collision system under consideration. The basic approach in I is that one employs classical dynamics (equation of motion), but quantum mechanical superposition (addition of probability amplitudes for indistinguishable processes rather than probabilities themselves[2]). In light of what has been learned about the semiclassical nature of simple elastic scattering[3], it was argued that many, if not all, of the quantum mechanical features in atomic and molecular collisions should be accurately contained within this framework. The general results of I apply to systems of any number of degrees of freedom, and detailed considerations were made for the atom-diatom collision system.

In the present paper we present the numerical results of this approach as applied to the linear atom-diatom collision (without reaction); with just one internal degree of freedom (that of vibration) this is the simplest prototype inelastic collision. The system is precisely that for which accurate quantum mechanical calculations have been carried out by Secrest and Johnson[4], and it is these essentially exact quantum mechanical results to which we compare.

In order to provide a severe test for the various semiclassical expressions, the mass ratio and potential parameters were chosen to correspond to a highly quantum-like system, H_2 + He. The results are presented and discussed in following sections, and uniform, or extended, semiclassical expressions are developed; in Sec. IV an integral representation for the S-matrix is obtained which appears to have an even wider region of validity.

To summarize our findings briefly, there are typically two independent classical trajectories which contribute to a particular "classically allowed" transition (a term which will become clear in Sec. II); the purely classical approximation to the transition probability is the sum of a probability associated with each of these two trajectories, and is accurate only in an average sense. Figure 1 shows typical results, and one sees quite clearly the failure of the classical approximation to account for individual transition probabilities. The semiclassical treatment takes account of quantum mechanical interference between the two trajectories and accurately reproduces the exact quantum mechanical values, except for final states near the "classically forbidden" region; the uniform semiclassical expressions are valid even through this transition region, so that on the scale of Fig. 1 there is essentially no difference between the uniform semiclassical and exact quantum results; Table I gives the numerical values corresponding to Fig. 1. The conclusion seems to be, therefore, that the dynamics of these inelastic collisions is essentially classical, and all quantum mechanical structure is due to interference between the several classical-like terms.

II. Description of the Collision System and Classical Results.

The linearly constrained atom-diatom collision system has been studied by a number of authors[4,5], using a variety of techniques. The particular version of the model we choose is that used by Secrest and Johnson[4], and one should consult their paper for details, such as reduction to dimensionless variables, etc. The principal features of this version of the model are that the diatom is taken as a harmonic oscillator, and the interaction is an exponential repulsion between the atom and the closest end of the diatom.

The translational, or scattering degree of freedom is characterized by canonical variables R and P, where R is the usual center of mass scattering coordinate and P is its conjugate momentum. Following the procedure in I, the canonical variables for the vibrational degree of freedom are chosen to be action-angle variables[6,7] q and n; q is the phase of the oscillator, and n is its conjugate momentum (the classical counterpart to the vibrational quantum number[8]). The relation between the physical vibrational coordinate and these canonical variables can be worked out from the expressions in I, but is well-known[6] for the harmonic oscillator:

$$r - r_{eq} = [(2n + 1)/m\omega]^{\frac{1}{2}} \cos q , \tag{1}$$

where m is the reduced mass for the oscillator and ω the vibrational frequency.[9,10]

In terms of these canonical variables, and for the dimensionless system of ref. 4, the classical Hamiltonian is

$$H(P, R, n, q) = P^2/2\mu + (n + \tfrac{1}{2}) + V, \tag{2a}$$

where the interaction V is

$$V = \exp\left[-\alpha R + \alpha(2n + 1)^{\frac{1}{2}} \cos q\right]; \tag{2b}$$

α and μ are the only two parameters of the model. Most of the results of this paper use the values $\mu = \frac{2}{3}$, $\alpha = .3$, which Secrest and Johnson indicate correspond to the H_2 + He system; Sec. IV presents some results for $\mu = \frac{1}{2}$, $\alpha = .1287$. The classical equations of motion for these canonical variables are

$$\dot{R} = P/\mu \tag{3a}$$

$$\dot{P} = \alpha V \tag{3b}$$

$$\dot{q} = 1 + \alpha V (2n + 1)^{-\frac{1}{2}} \cos q \tag{3c}$$

$$\dot{n} = \alpha V (2n + 1)^{\frac{1}{2}} \sin q , \tag{3d}$$

where V is given by Eq. (2b).

According to I, initial values R_1, P_1, q_1, n_1 are assigned the canonical variables, and Eq. (3) integrated numerically. The particular initial value R_1, however, is unimportant and only need be taken sufficiently large so that $V \sim 0$. Also, the value P_1 is automatically determined by energy conservation and the initial values of the internal variables; e.g., for fixed total energy[11] E, P_1 must be taken as

$$P_1 = P_1(n_1) = -\left[2\mu\,(E - n_1 - \tfrac{1}{2})\right]^{\frac{1}{2}} , \tag{4}$$

so that only the initial values q_1, n_1 remain to be chosen.

The phase variable q, however, is actually not a convenient one by which to specify the initial condition, the reason being that $q(t)$ does not take on a constant value as $t_1 \rightarrow -\infty$ (before collision) or $t_2 \rightarrow +\infty$ (after collision) - this is easily seen from Eq. (3c) since the unperturbed ($V = 0$) solution for $q(t)$ is

$$q(t) = t + \text{constant}.$$

To eliminate this unperturbed time dependence we define the vibrational phase <u>shift</u> $\bar{q}$ by

$$q \equiv \bar{q} + \mu R/P \; ; \tag{5}$$

since

$$R(t) = Pt/\mu + \text{constant}$$

is the solution for R in the asymptotic region, it is clear that $\bar{q}(t)$ does take on a constant value as $t \rightarrow \pm\infty$.

In summary, then, the initial values for the canonical variables are

$$R_1 \quad \text{large} \tag{6a}$$

$$P_1 = -[2\mu(E - n_1 - \tfrac{1}{2})]^{\frac{1}{2}} \tag{6b}$$

$$q_1 = \bar{q}_1 + \mu R_1/P_1 \tag{6c}$$

$$n_1 = n_1 \; ; \tag{6d}$$

$\bar{q}_1$ and n_1, therefore, are the independent variables by which the trajectory is specified (E is a fixed parameter throughout the entire problem). With these initial conditions Eqs. (3) are integrated numerically[12] from some initial time until the collision is over -- i.e., until $P > 0$ and R is sufficiently large so that $V \sim 0$ and thus $\bar{q}$ and n have taken on constant values; the final values for $\bar{q}$ and n, designated $\bar{q}_2$ and n_2, are independent of the particular time t_2 or distance R_2 at which the trajectory is terminated, just as they are independent of the initial time t_1 and initial distance R_1 -- provided only that R_1 and R_2 are sufficiently large. We write, therefore,

$$n_2 = n_2 (\bar{q}_1 , n_1) \tag{7a}$$

$$\bar{q}_2 = \bar{q}_2 (\bar{q}_1 , n_1) , \tag{7b}$$

to indicate that the final values of these quantities depend only on the independent variables $\bar{q}_1$ and n_1 (and, of course, the fixed total energy E). The functional relations in Eq. (7) and the role played by the two functions are analogous to that for the classical deflection function familiar in potential scattering[3], in that the functional dependence is determined by the classical trajectory connecting the initial and final values of the classical quantities.

The purely classical result[13] for the transition probability is expressed in terms of the function $n_2(\bar{q}_1 , n_1)$ alone:

$$P_{n_2 , n_1} = \sum \left[2\pi \left| \frac{\partial n_2 (\bar{q}_1 , n_1)}{\partial \bar{q}_1} \right| \right]^{-1} , \tag{8}$$

where n_2 and n_1 are integers (vibrational quantum numbers) and $\bar{q}_1$ is equal to that value for which

$$n_2 = n_2 (\bar{q}_1 , n_1) ; \tag{9}$$

the sum in Eq. (8) is a sum over all different values of $\bar{q}_1$ (in its domain 0 to 2π) for which Eq. (9) is satisfied. Figure 2 shows the function $n_2(\bar{q}_1 , n_1)$ for the typical case $n_1 = 1$ and $E = 10$ (for H_2 + He this is ~ 5 eV total energy); a dotted line at $n_2 = 2$ intersects the curve at two points, indicating that there are two values of $\bar{q}_1$ which satisfy Eq. (9). (It is clear that there will always be an even number of terms contributing in Eq. (8); this follows since $\bar{q}_1 = 0$ and $\bar{q}_1 = 2\pi$ are physically the same, so that

$$n_2 (0 , n_1) = n_2 (2\pi , n_1) .$$

Note that this must be the case for any type of internal degree of freedom since these properties of the action-angle variables for a periodic degree of freedom are quite general[6].) From the slope of the curve at these two points the 1 → 2 transition probability is evaluated according to Eq. (8); the classical transition probabilities for $1 \rightarrow n_2$, $n_2 = 0$ to 4, are all constructed similarly.

Referring to Fig. 2, one sees that the 1 → 5 transition is not possible since there is no value of $\bar{q}_1$ for which $n_2 = 5$ is reached; this transition is therefore classically forbidden, whereas those mentioned above are classically allowed[14]. Suppose for the moment that n_2 is a continuous variable, rather than quantized. Figure 3a indicates the general character of the transition probability for fixed n_1 and continuously variable n_2. The infinities occur because the zero slope of the function $n_2(\bar{q}_1 , n_1)$ at its extrema appears in the denominator in Eq. (8). This is a very typical "classical catastrophe" (cf. the WKB wavefunction near a classical turning point and the classical rainbow effect in potential scattering[3]); in fact, Fig. 3a looks very much like the classical probability distribution for a particle in a potential well[15], the classically "allowed" and "forbidden" terminology being completely analogous. It is not surprising, therefore, that the semiclassical, or uniform semiclassical treatment will replace Fig. 3a by Fig. 3b--the classically forbidden region being not completely forbidden, and the classically allowed region having interference features.

Figure 1 shows the numerical results actually obtained for P_{n_2, n_1} in this classical limit with $n_1 = 0, 1, 2$ at $E = 10$, as compared to the exact quantum mechanical values (which are essentially indistinguishable on the scale of the drawing from the uniform semiclassical results); Table I gives the numerical values corresponding to Fig. 1, and Table II gives similar results for the lower energy $E = 6$. Although the classical approximation does indeed describe the exact transition probability on the average, it is clear from Fig. 1 just how important are the interference features which are omitted in the purely classical treatment. If, however, the particular experimental conditions do not select individual quantum states and the observed transition probabilities (or cross sections) are thus averaged quantities, then it is of course quite possible that the classical result will be all that is actually required. If one is interested in the magnitude and trends of individual transition probabilities, though, it is clear that the purely classical results are completely unsatisfactory.

III. Semiclassical and Uniform Semiclassical Results.

The basic reason for the failure of the purely classical approximation is that classical superposition is built into it; i.e., in Eq. (8) one adds the probabilities associated with the two independent trajectories which contribute to the $n_1 \rightarrow n_2$ transition. The semiclassical result is obtained by using classical quantities still, but quantum superposition.

According to I, the transition probability is the square modulus of a transition amplitude, or S-matrix element:

$$P_{n_2, n_1} = | S_{n_2, n_1} |^2 , \qquad (10)$$

where

$$S_{n_2, n_1} = \sum \left[2\pi \frac{\partial n_2 (\bar{q}_1, n_1)}{\partial \bar{q}_1} \right]^{-\frac{1}{2}} e^{i\phi(\bar{q}_1, n_1)} , \qquad (11)$$

and, as above, the sum in Eq. (11) is a sum over all the independent values of $\bar{q}_1$ which satisfy Eq. (9) (two for the typical situation); the magnitude of each term in Eq. (11) is the square root of the corresponding term in the classical expression [Eq. (8)], and the phase[16] is given by

$$\phi(\bar{q}_1, n_1) \equiv - \int_{t_1}^{t_2} dt\ (R\dot{P} + q\dot{n}). \qquad (12)$$

Just as the classical functions in Eq. (7) are independent of t_1, t_2, R_1, and R_2, so is the phase function in Eq. (12); this is easily seen since $\dot{P} = \dot{n} = 0$ in the asymptotic region.

Combining Eqs. (10) - (12), the semiclassical expression for the transition probability is

$$P_{n_2, n_1} = p_1 + p_2 + 2\ (p_2\ p_1)^{\frac{1}{2}} \sin\ (\Delta\phi) ; \qquad (13)$$

p_1 and p_2 are the square modulus of each term in Eq. (11), and $\Delta\phi$ is their phase difference; $p_1 + p_2$ is the classical result of Eq. (8). The interference term is proportional to sin $(\Delta\phi)$, rather than cos $(\Delta\phi)$, due to the $\frac{\pi}{2}$ phase difference resulting because $\partial n_2 (\bar{q}_1, n_1)/\partial \bar{q}_1$ has a different sign for the two terms in Eq. (11). The sign of

$\Delta\phi$ may be determined unambiguously by the method of Pechukas[17], but a simpler procedure is possible on the basis of results to be developed below.

Tables I and II display the results of Eq. (13) for energies $E = 10$ and $E = 6$; except for the largest and smallest classically allowed value of n_2, the semiclassical results are within a few percent of the exact quantum results; the transition probability to all classically forbidden final states is still identically zero. These results are entirely consistent with one's previous knowledge of semiclassical phenomena and the correspondence principle in general. The "breakdown" of results near classically forbidden regions is expected; it is analogous to the "primitive" semiclassical description of the rainbow effect in potential scattering[3] -- the interference effects not too close to the rainbow angle (the classical/non-classical boundary) are treated correctly, but not the transition region itself. It is clear, therefore, that "special techniques" must be introduced to handle the transition and classically forbidden regions correctly. Here we give a heuristic presentation of the uniform, or extended semiclassical expressions; a rigorous derivation is possible by using the integral representation for the S-matrix developed in Sec. IV and the general results of the Appendix. The presentation below is useful in showing how one can essentially guess the appropriate uniformly valid expression from the primitive semiclassical result itself.

Since

$$\sin(\Delta\phi) = \sin^2\left(\frac{\Pi}{4} + \frac{\Delta\phi}{2}\right) - \cos^2\left(\frac{\Pi}{4} + \frac{\Delta\phi}{2}\right)$$

$$1 = \sin^2\left(\frac{\Pi}{4} + \frac{\Delta\phi}{2}\right) + \cos^2\left(\frac{\Pi}{4} + \frac{\Delta\phi}{2}\right),$$

The semiclassical expression in Eq. (13) is equivalent to

$$P_{n_2, n_1} = (p_1 + p_2) \left[\sin^2\left(\frac{\Pi}{4} + \frac{\Delta\phi}{2}\right) + \cos^2\left(\frac{\Pi}{4} + \frac{\Delta\phi}{2}\right)\right] + 2(p_1 p_2)^{\frac{1}{2}} \left[\sin^2\left(\frac{\Pi}{4} + \frac{\Delta\phi}{2}\right) - \cos^2\left(\frac{\Pi}{4} + \frac{\Delta\phi}{2}\right)\right]. \qquad (14)$$

The oscillatory functions in Eq. (14) may be recognized, however, as the asymptotic forms of the two kinds of Airy function[18]:

$$\sin^2\left(\frac{\Pi}{4} + \frac{\Delta\phi}{2}\right) \simeq \pi z^{\frac{1}{2}} \mathrm{Ai}^2(-z)$$

$$\cos^2\left(\frac{\Pi}{4} + \frac{\Delta\phi}{2}\right) \simeq \pi z^{\frac{1}{2}} \mathrm{Bi}^2(-z),$$

where

$$z = \left(\frac{3}{4} \Delta\phi\right)^{2/3} . \qquad (15)$$

For large $\Delta\phi$ (or z), therefore, Eq. (14) is equivalent to

$$P_{n_2, n_1} = (p_1 + p_2) \left[\pi z^{\frac{1}{2}} \mathrm{Ai}^2(-z) + \pi z^{\frac{1}{2}} \mathrm{Bi}^2(-z)\right] + 2(p_1 p_2)^{\frac{1}{2}} \left[\pi z^{\frac{1}{2}} \mathrm{Ai}^2(-z) - \pi z^{\frac{1}{2}} \mathrm{Bi}^2(-z)\right] \qquad (16a)$$

or

$$P_{n_2, n_1} = (p_1^{\frac{1}{2}} + p_2^{\frac{1}{2}})^2 \; \pi z^{\frac{1}{2}} \mathrm{Ai}^2(-z) + (p_1^{\frac{1}{2}} - p_2^{\frac{1}{2}})^2 \; \pi z^{\frac{1}{2}} \mathrm{Bi}^2(-z). \qquad (16b)$$

Not only is Eq. (16) equivalent to the semiclassical expression for large phase differences, however, but it is also well-behaved in the transition region and is actually the uniform semiclassical expression we seek.

In the transition region (n_2 near an extremum of $n_2(\bar{q}_1, n_1)$) $p_1 \simeq p_2$, so that Eq. (16b) becomes

$$P_{n_2, n_1} = 4 p \pi z^{\frac{1}{2}} \mathrm{Ai}^2(-z), \tag{17}$$

where p is the common value of p_1 and p_2. As n_2 approaches an extremum of $n_2(\bar{q}_1, n_1)$, p becomes infinite, as discussed above; the phase difference $\Delta\phi$, however, goes to zero, and the zero of $\Delta\phi$ (and thus z) in Eq. (17) exactly cancels the infinity in p. The appropriate limiting expression can be derived by approximating $n_2(\bar{q}_1, n_1)$ as a quadratic about its extremum and $\phi(\bar{q}_1, n_1)$ as a cubic about this particular value of $\bar{q}_1$; if use is made of Eq. (23a) in Sec. IV, the result is

$$P_{n_2, n_1} = \frac{\mathrm{Ai}^2\left[(n_2^x - n_2)/a^{1/3}\right]}{|q_2'|\,|a|^{2/3}}, \tag{18}$$

where

$$a = n_2''/2 q_2'^2,$$

and

$$n_2'' = \frac{\partial^2 n_2(\bar{q}_1, n_1)}{\partial \bar{q}_1^2}$$

$$\bar{q}_2' = \frac{\partial \bar{q}_2(\bar{q}_1, n_1)}{\partial \bar{q}_1},$$

with the derivatives evaluated at the extremum of $n_2(\bar{q}_1, n_1)$; this result is valid for n_2^x a maximum or minimum.

Eq. (18) clearly exhibits the transition from oscillatory character in the classically allowed region to exponentially decaying character in the classically forbidden region; this is directly analogous to the rainbow effect in potential scattering[3], near the rainbow angle.

The results in Tables I and II under the "Uniform" column were all obtained from Eq. (16) for the classically allowed transitions, and Eq. (18) for the classically forbidden transitions. The semiclassical and uniform semiclassical results are, as expected, essentially the same for classically allowed transitions not close to the transition region; the general agreement between the uniform semiclassical and exact quantum mechanical results has been noted above.

The values in Tables I and II for the classically forbidden transitions, while quite good, are not of as high accuracy as for the classically allowed transitions. One reason for this lower accuracy is that Eq. (18) is an approximation to the uniform expression in Eq. (16). One may apply Eq. (16) more accurately to obtain better results for the classically forbidden transitions. Although for classically forbidden transitions there are no <u>real</u> values of $\bar{q}_1$ which satisfy Eq. (9), there are <u>complex</u> roots; Eq. (18) may be obtained by approximating $n_2(\bar{q}_1 , n_1)$ as a quadratic at its extremum, solving for the complex roots of Eq. (9), and then applying Eq. (16). One can solve Eq. (9) for its complex roots more accurately, however, by expanding $n_2(\bar{q}_1 , n_1)$ as a polynomial of higher order[19], or by fitting $n_2(\bar{q}_1 , n_1)$ to some functional form and solving the transcendental equations numerically. In either event the two roots of Eq. (9) will be complex conjugates of each other, and the second term in Eq. (16b) will be absent (it would be exponentially increasing if it were present). This more accurate treatment for the classically forbidden transitions has not been carried out, but would certainly be expected to give results improved over Eq. (18).

In concluding this section we point out that even Eq. (16) fails (or at best becomes difficult to apply) in the case that all transitions are highly forbidden classically. Figure 4 shows the function $n_2(\bar{q}_1, n_1)$ for $n_1 = 1$ at energy $E = 3$; classically the vibrational quantum number can change from its initial value only a small fraction of a whole quantum, so that all transitions are forbidden. The extrema are so far from $n_2 = 0$ and 2 that the quadratic approximation to $n_2(\bar{q}_1, n_1)$ at its extrema is quite poor; Table III shows the classical, semiclassical, and uniform semiclassical results for this case, as compared to the exact quantum results. The procedure introduced in the next section, however, is successful in describing even these highly non-classical transitions.

IV. The Initial Value Representation.

Here we derive an expression for the S-matrix in terms of classical quantities which is more general than any yet presented; on the basis of it the uniform semiclassical expressions of the previous section can be rigorously obtained, and the highly non-classical transitions discussed above are more accurately treated.

Consider first some properties of the phase function defined by Eq. (12); as pointed out[16], this is actually the phase of the propagator in the momentum representation[1]. If all four momenta (two initial and two final) are considered to be independent variables, therefore, the phase satisfies the following general relations[1,20]

$$\frac{\partial}{\partial n_2} \phi(n_2, P_2, n_1, P_1) = -q_2 \qquad (19a)$$

$$\frac{\partial}{\partial n_1}\ \phi(n_2\ ,\ P_2\ ,\ n_1\ ,\ P_1) = q_1 \qquad (19b)$$

$$\frac{\partial}{\partial P_2}\ \phi(n_2\ ,\ P_2\ ,\ n_1\ ,\ P_1) = -\ R_2 \qquad (19c)$$

$$\frac{\partial}{\partial P_1}\ \phi(n_2\ ,\ P_2\ ,\ n_1\ ,\ P_1) = R_1\ , \qquad (19d)$$

where the quantities on the RHS of Eqs.(19) are functions of these four independent variables. As was noted in Sec. II, however, if one enforces energy conservation (as we do), then

$$P_1 = P_1\ (n_1) = -\ \left[2\mu(E - n_1 - \tfrac{1}{2})\right]^{\frac{1}{2}} \qquad (20a)$$

$$P_2 = P_2\ (n_2) = \left[2\,\mu\,(E - n_2 - \tfrac{1}{2})\right]^{\frac{1}{2}}\ , \qquad (20b)$$

so that the phase is a function only of n_2 and n_1 :

$$\phi\,(n_2\ ,\ n_1) \equiv \phi\left[n_2\ ,\ P_2\ (n_2)\ ,\ n_1\ ,\ P_1\ (n_1)\ \right]\ ; \qquad (21)$$

furthermore, Eqs. (19) - (21) and the chain rule imply

$$\frac{\partial}{\partial n_2}\ \phi\,(n_2\ ,\ n_1) = -\ q_2 + \mu\ R_2/P_2 \qquad (22a)$$

$$\frac{\partial}{\partial n_1}\ \phi(n_2\ ,\ n_1) = q_1 - \mu\ R_1/P_1\ . \qquad (22b)$$

Recalling the definition of the phase <u>shift</u> in Eq. (5), Eqs. (22) become

$$\frac{\partial}{\partial n_2}\ \phi(n_2\ ,\ n_1) = -\ \bar{q}_2 \qquad (23a)$$

$$\frac{\partial}{\partial n_1}\ \phi(n_2\ ,\ n_1) = \bar{q}_1\ . \qquad (23b)$$

In Sec. II n_1 and $\bar{q}_1$, rather than n_2 and n_1, were chosen as the two independent variables, and the phase $\phi(\bar{q}_1, n_1)$ is more precisely designated by

$$\phi(\bar{q}_1, n_1) = \phi(n_2(\bar{q}_1, n_1), n_1) . \tag{24}$$

Eq. (23) is the basic relation we sought[21]; it has the form of the usual canonical transformation [20] but is actually somewhat different. The variable $\bar{q}(t)$ is not conjugate to $n(t)$ in the usual sense (the variable $q(t)$ is). Using energy conservation to eliminate the canonical variables of the translational degree of freedom as independent variables, however, has the effect of causing $\bar{q}$ to behave in the asymptotic region as though it were the variable conjugate to n (in the sense of Eq. (23)).

On the basis of Eq. (23) one may define the S-matrix in the $\bar{q}$ representation

$$S_{\bar{q}_2, \bar{q}_1} \equiv \int dn_2 \int dn_1 \frac{e^{i\bar{q}_2(n_2+\frac{1}{2})}}{(2\pi)^{\frac{1}{2}}} S_{n_2, n_1} \frac{e^{-i\bar{q}_1(n_1+\frac{1}{2})}}{(2\pi)^{\frac{1}{2}}} ; \tag{25}$$

the inverse transformation is

$$S_{n_2, n_1} = \int d\bar{q}_2 \int d\bar{q}_1 \frac{e^{-i\bar{q}_2(n_2+\frac{1}{2})}}{(2\pi)^{\frac{1}{2}}} S_{\bar{q}_2, \bar{q}_1} \frac{e^{i\bar{q}_1(n_1+\frac{1}{2})}}{(2\pi)^{\frac{1}{2}}} . \tag{26}$$

If the integrals in Eq. (25) are evaluated by stationary phase, then in view of Eq. (23) one obtains

$$S_{\bar{q}_2,\bar{q}_1} = \left[\frac{\partial n_2(\bar{q}_2, \bar{q}_1)}{\partial \bar{q}_1}/2\pi\right]^{\frac{1}{2}} e^{i\left[\phi(n_2, n_1) + \bar{q}_2(n_2 + \frac{1}{2}) - \bar{q}_1(n_1 + \frac{1}{2})\right]} , \tag{27}$$

where $n_1 = n_1(\bar{q}_2, \bar{q}_1)$, $n_2 = n_2(\bar{q}_2, \bar{q}_1)$ ($\bar{q}_2$ and $\bar{q}_1$ are the independent variables of the trajectory in this case). If Eq. (27) is substituted into Eq. (26) and integration over $\bar{q}_2$ and $\bar{q}_1$ performed by stationary phase, then it is clear that Eq. (11) is recovered. Suppose, however, only the integration over $\bar{q}_1$ is performed by stationary phase; the result is

$$S_{n_2, n_1} = \frac{1}{2\pi} \int d\bar{q}_2 \left[\frac{\partial \bar{q}_1(\bar{q}_2, n_1)}{\partial \bar{q}_2}\right]^{\frac{1}{2}} \cdot e^{i\left\{\phi(n_2(\bar{q}_2, n_1), n_1) + \bar{q}_2\left[n_2(\bar{q}_2, n_1) - n_2\right]\right\}} , \tag{28}$$

where $\bar{q}_2$ and n_1 are the independent variables specifying the trajectory in the integrand. With n_1 fixed one can use the relations

$$\bar{q}_2 = \bar{q}_2(\bar{q}_1, n_1)$$

$$\frac{d\bar{q}_2}{d\bar{q}_1} = \frac{\partial \bar{q}_2(\bar{q}_1, n_1)}{\partial \bar{q}_1}$$

to change variables of integration, so that Eq. (28) becomes

$$S_{n_2, n_1} = \frac{1}{2\pi} \int_0^{2\pi} d\bar{q}_1 \left[\frac{\partial \bar{q}_2 (\bar{q}_1, n_1)}{\partial \bar{q}_1} \right]^{\frac{1}{2}} e^{i\{\phi(\bar{q}_1, n_1) + \bar{q}_2 (\bar{q}_1, n_1)[n_2 (\bar{q}_1, n_1) - n_2]\}} ; \tag{29}$$

the independent variables specifying the trajectory in the integrand of Eq. (29) are $\bar{q}_1$ and n_1.

Eq. (29) is the desired integral representation, and we refer to it as the <u>initial value representation</u>[22] of the S-matrix. Why is it any better than any of the other representations discussed? In short, it is because the initial values $\bar{q}_1$ and n_1 must necessarily determine a <u>unique</u> classical trajectory; this is not so for other pairs of boundary conditions (n_2 and n_1, $\bar{q}_2$ and $\bar{q}_1$, and $\bar{q}_1$ and n_2). Thus in Eq. (11) one must sum over several (i.e., two) terms corresponding to different values of $\bar{q}_1$ which satisfy Eq. (9); i.e., $\bar{q}_1$ (n_2, n_1) is a multivalued function, which is another way of saying that n_2 and n_1 do not determine a unique classical trajectory. In like manner, n_2 $(\bar{q}_2, \bar{q}_1)$ can be multivalued, so that Eq. (27) would have to contain several terms, one for each branch of this multivalued function. It is interference between these several terms, however, which causes problems--particularly so when two terms coalesce, as they do in the transition region. The important feature of Eq. (29) is that all the functions which appear in the integrand are necessarily single-valued (since $\bar{q}_1$ and n_1 determine a unique trajectory), so that there is just the one term in the integrand.

If one proceeds to evaluate Eq. (29) by stationary phase, the stationary phase requirement is

$$\frac{d}{d\bar{q}_1}\left\{ \phi(\bar{q}_1 , n_1) + \bar{q}_2 (\bar{q}_1 , n_1) \left[n_2 (\bar{q}_1 , n_1) - n_2 \right] \right\} = 0 ;$$

but from Eq. (23) one sees that[23]

$$\frac{\partial}{\partial\bar{q}_1} \Phi (\bar{q}_1 , n_1) = - \bar{q}_2 (\bar{q}_1 , n_1) \frac{\partial n_2 (\bar{q}_1 , n_1)}{\partial\bar{q}_1} , \qquad (30)$$

so that this requirement is equivalent to Eq. (9) and one recovers Eq. (11). This must be true since, as pointed out in I, all semiclassical representations of the S-matrix are equivalent provided one uses the stationary phase approximation to transform from one representation to another. If one evaluates the integrals more accurately than by stationary phase, however, all representations are no longer equivalent. On the basis of the above arguments we have chosen Eq. (29) to be the more fundamental representation of the S-matrix in terms of the classical trajectory functions.

The uniform semiclassical expressions [Eq. (16)] can be obtained by a straight-forward application of the techniques[24-26] for evaluating an integral which contains two possibly coalescing points of stationary phase; details of this technique are given in the Appendix. Eq. (18), which is valid for n_2 not too far from an extremum of $n_2 (\bar{q}_1 , n_1)$, is readily obtained from Eq. (29) by expanding $n_2(\bar{q}_1 , n_1)$ as a quadratic at its extremum and $\bar{q}_2(\bar{q}_1 , n_1)$ as a linear function.

In the case that all transitions are highly forbidden classically it has been noted that Eqs. (16) and (18) are not useful. One may ask if this is due to the complete invalidity of classical dynamics under these conditions, or if Eq. (29) is still valid and the failure of Eqs. (16) and (18) due only to the inaccurate evaluation of the integral in Eq. (29). When many final states are classically allowed, direct numerical integration of Eq. (29) would be extremely difficult because the phase of the integrand is large and quite rapidly varying--which is why, of course, the uniform stationary phase evaluation is accurate in this case. When all transitions are highly forbidden, however, the phase varies much more moderately, so that direct numerical integration is feasible; Table IV shows the results of this procedure applied to several situations in which all, or most, of the transitions are classically forbidden. Except for transitions with extremely small probability, the accuracy of the results indicates that Eq. (29) does indeed have a range of validity beyond the semiclassical and uniform semiclassical expressions.

One may observe that Eq. (29) does not identically obey microscopic reversibility (the property $P_{n_2, n_1} \equiv P_{n_1, n_2}$); the degree of this failure can be used in practice to estimate the overall accuracy one expects for the numerical results obtained from Eq. (29). It is interesting to note, and may be significant, that in Table IV the agreement with the quantum results is best when the initial quantum number is the larger of the two.

In concluding this section we would like to suggest that it may often be quite useful to employ <u>approximate</u> classical dynamics (e.g., sudden, impulse,[5d] or adiabatic[7] approximations) to generate the trajectory functions $n_2(\bar{q}_1, n_1)$ and $\bar{q}_2(\bar{q}_1, n_1)$ (and thus ϕ [23]), and then use Eq. (29) to obtain the S-matrix. For example, for low energies the trajectory functions are often well approximated by

$$\bar{q}_2(\bar{q}_1, n_1) \simeq \bar{q}_1 + \text{constant}$$

$$n_2(\bar{q}_1, n_1) \simeq n_1 + A(E) \cos(\bar{q}_1 + \text{constant}),$$

from which $\phi(\bar{q}_1, n_1)$ may be obtained[23]. With these approximations Eq. (29) is recognized as an integral representation for a Bessel function of order $|n_2 - n_1|$, and the transition probability becomes

$$P_{n_2, n_1}(E) = J^2_{|n_2 - n_1|}[A(E)] ;$$

this does indeed approximate the transition probability for this case reasonably well.

V. Systems with More than One Internal Degree of Freedom.

Many features of the present problem carry over quite directly to general collision problems with more than one internal degree of freedom[27]. The reason is that all internal degrees of freedom are quantized (quantum mechanically), or periodic (classically), and in terms of action-angle variables all such degrees of freedom are essentially of the same type[6]; the canonical momentum for each degree of freedom is the corresponding quantum number, and the canonical coordinate is the phase of the periodic motion. For the ith internal degree of freedom the canonical coordinate $q_i(t)$ has the asymptotic solution

$$q_i(t) = \omega_i t + \text{constant} ,$$

and this unperturbed time dependence can be removed by defining the phase shift for each degree of freedom, $\bar{q}_i(t)$, just as in Sec. II. The total phase in Eq. (12) and the derivative relations in Eq. (23) are generalized in the obvious manner.

The classical [Eq. (8)] and semiclassical [Eq. (11)] expressions for the S-matrix apply for systems with more degrees of freedom with obvious generalizations, but not so for the uniform semiclassical results--the reason being that there may be more than two terms in Eq. (11). If only two of these terms are coalescent (i.e., in the transition region), however, one can still use Eq. (16) to handle this pair-wise coalescense of terms. It does not appear, though, that one would be able to treat the situation in which three or more terms are simultaneously in the same transition region[28].

The initial value representation in Eq. (29) is also generalizable in the obvious manner; it is now a multi-dimensional integral, however, so that direct numerical integration will be of more limited use.

Acknowledgements

A grant of computation time from the University Computing Center is gratefully acknowledged.

This work supported, in part, by the U. S. Atomic Energy Commission.

Appendix: Uniform Stationary Phase Integration.

The following procedure is essentially that due to Carrier[24]. Consider an integral I of the form

$$I = \int dx\, g(x)\, e^{if(x)} \quad , \tag{A1}$$

and suppose that there exist two points of stationary phase--i.e., that there are two roots of the equation

$$f'(x) = 0 \quad , \tag{A2}$$

designated x_1 and x_2; $f''(x_1)$ and $f''(x_2)$ must have different signs, and for definiteness we take the former to the positve and the latter negative.

If the usual method of stationary phase is used separately at x_1 and x_2, then

$$I = I_1 + I_2 \tag{A3}$$

where

$$I_k = g_k \left(\frac{2\pi i}{f_k''}\right)^{\frac{1}{2}} e^{if_k} \quad , \tag{A4}$$

$k = 1, 2$, and $f_k = f(x_k)$, $g_k = g(x_k)$, $f_k'' = f''(x_k)$; for the present case

$$I_1 = g_1 \mid 2\pi/f_1'' \mid^{\frac{1}{2}} e^{i(f_1 + \frac{\pi}{4})} \tag{A5a}$$

$$I_2 = g_2 \mid 2\pi/f_2'' \mid^{\frac{1}{2}} e^{i(f_2 - \frac{\pi}{4})} \quad . \tag{A5b}$$

These results come about by expanding $f(x)$ as a quadratic about each extremum; if it is expanded as a cubic, Eq. (A3) pertains but with Eq. (A5) replaced by

$$I_1 = g_1 \left| 2\pi/f_1'' \right|^{\frac{1}{2}} 2\pi^{\frac{1}{2}} z_1^{\frac{1}{4}} e^{i(f_1 + \xi_1)} \mathrm{Ai}(-z_1) \qquad \text{(A6a)}$$

$$I_2 = g_2 \left| 2\pi/f_2'' \right|^{\frac{1}{2}} 2\pi^{\frac{1}{2}} z_2^{\frac{1}{4}} e^{i(f_2 - \xi_2)} \mathrm{Ai}(-z_2) \ , \qquad \text{(A6b)}$$

where Ai is the regular Airy function[18], and

$$z_k = \left(\frac{f_k''}{2}\right)^2 \left(\frac{2}{f_k'''}\right)^{4/3} \qquad \text{(A7)}$$

$$\xi_k = \frac{2}{3} z_k^{3/2} \ , \qquad \text{(A8)}$$

for $k = 1, 2$. For large z_k one may employ the asymptotic form of the Airy function, and Eq. (A6) becomes

$$\begin{aligned} I_1 \simeq\ & g_1 \left|2\pi/f_1''\right|^{\frac{1}{2}} e^{i(f_1 + \frac{\pi}{4})} \\ & + g_1 \left|2\pi/f_1''\right|^{\frac{1}{2}} e^{i(f_1 + 2\xi_1 - \frac{\pi}{4})} \end{aligned} \qquad \text{(A9a)}$$

$$\begin{aligned} I_2 \simeq\ & g_2 \left|2\pi/f_2''\right|^{\frac{1}{2}} e^{i(f_2 - \frac{\pi}{4})} \\ & + g_2 \left|2\pi/f_2''\right|^{\frac{1}{2}} e^{i(f_2 - 2\xi_2 + \frac{\pi}{4})} \ ; \end{aligned} \qquad \text{(A9b)}$$

i.e., Eq. (A5) is recovered, plus a spurious, highly oscillatory term. In Eq. (A9a), for example, the second term in the expression for I_1 is actually a crude approximation to I_2, and one does better by simply discarding it. This can be accomplished more generally by writting the Airy functions in Eq. (A6) as the sum of two terms,

$$Ai(-z) = \tfrac{1}{2}\left[Ai(-z) + i\ Bi(-z)\right] + \tfrac{1}{2}\left[Ai(-z) - i\ Bi(-z)\right] \quad ; \qquad \text{(A10)}$$

since for large z

$$\pi^{\frac{1}{2}} z^{\frac{1}{4}} \left[Ai(-z) \pm i\ Bi(-z)\right] \simeq e^{\pm i(\frac{\Pi}{4} - \xi)} \ , \qquad \text{(A11)}$$

one can identify the spurious term and discard it. The result is that Eq. (A6) is replaced by

$$I_1 = g_1 \left| 2\pi/f_1'' \right|^{\frac{1}{2}} \pi^{\frac{1}{2}} z_1^{\frac{1}{4}} e^{i(f_1 + \xi_1)} \left[Ai(-z_1) + i\ Bi(-z_1)\right] \qquad \text{(A12a)}$$

$$I_2 = g_2 \left| 2\pi/f_2'' \right|^{\frac{1}{2}} \pi^{\frac{1}{2}} z_2^{\frac{1}{4}} e^{i(f_2 - \xi_2)} \left[Ai(-z_2) - i\ Bi(-z_2)\right] \ . \qquad \text{(A12b)}$$

Eq. (A12), with Eq. (A3), is a uniform approximation to the integral I, but is actually not the most useful result--the reason being that it is necessary to evaluate the third derivatives of $f(x)$ at x_1 and x_2 in order to obtain the quantities z_k and ξ_k, defined by Eqs. (A7) and (A8), which are required in Eq. (A12). The fact is, however, that these third derivatives are not needed with high accuracy unless z_1 and z_2 are small; this follows since Eq. (A12) reduces to Eq. (A5) if z_1 and z_2

are large, irrespective of their specific values. It is only when x_2 and x_1 begin to coalesce that Eq. (A12) differs significantly from Eq. (A5)

The third derivatives are therefore approximated by

$$f_1''' \simeq f_2''' \simeq (f_2'' - f_1'')/(x_2 - x_1) \qquad \text{(A13)}$$

which implies that $f'''(x)$ is constant, or that $f(x)$ is a cubic; it is clear that Eq. (A13) is essentially exact for small $| x_2 - x_1 |$. Within this approximation it is easy to show that

$$f_1'' = -f_2'' = \frac{3}{2} (f_2 - f_1)/(x_2 - x_1)^2$$

$$f_1''' = f_2''' = -3 (f_2 - f_1)/(x_2 - x_1)^3 ,$$

from which it follows that

$$z_1 = z_2 = \left[\frac{3}{4} (f_2 - f_1)\right]^{2/3} \qquad \text{(A14)}$$

$$\xi_1 = \xi_2 = \frac{1}{2} (f_2 - f_1) \quad . \qquad \text{(A15)}$$

With Eqs. (A14) and (A15) replacing (A7) and (A8), the final result becomes

$$I_1 = g_1 \,|\, 2\pi/f_1'' \,|^{\frac{1}{2}} \, \pi^{\frac{1}{2}} z^{\frac{1}{4}} e^{i(f_2 + f_1)/2} \left[Ai(-z) + i\, Bi(-z)\right] \qquad \text{(A16a)}$$

$$I_2 = g_2 \,|\, 2\pi/f_2'' \,|^{\frac{1}{2}} \, \pi^{\frac{1}{2}} z^{\frac{1}{4}} e^{i(f_2 + f_1)/2} \left[Ai(-z) - i\, Bi(-z)\right] , \qquad \text{(A16b)}$$

where

$$z = \left[\frac{3}{4} (f_2 - f_1)\right]^{2/3} \quad . \qquad \text{(A17)}$$

The virtue of Eq. (A16) over (A12) is that no quantities are required in Eq. (A16) other than those which are needed in the simplest approximation, Eq. (A5); the accuracy of Eq. (A16) is essentially equal to that of Eq. (A12) since the approximation of the third derivatives by Eq. (A13) is poor only when z is large and not accurately required. For $(x_2 - x_1)$ small both of these uniform approximations reduce to

$$I = g_0\, e^{if_0}\, 2\pi \, | 2/f_0''' |^{1/3} \; \mathrm{Ai}\left[f_0 \,(2/f_0''')^{1/3} \right] , \qquad \text{(A18)}$$

where x_0 is the value of x for which $f''(x) = 0$ (the coalesced value of x_1 and x_2).

Application of these results to the integral representation of the S-matrix in Sec. IV gives the uniform semiclassical expressions in Sec. III. One word of caution is necessary, however; the primitive semiclassical expression in Eq. (11) is invariant to the replacements

$$\Delta\phi \rightarrow \Delta\phi + 2k\pi \qquad \text{(A19a)}$$

$$\Delta\phi \rightarrow (2k + 1)\pi - \Delta\phi \quad , \qquad \text{(A19b)}$$

where k is any integer; the value of $z = (3\Delta\phi/4)^{2/3}$, of course, is <u>not</u> invariant to such a replacement. To obtain the proper value of z it is sometimes necessary to use Eq. (A19) to modify the value of $\Delta\phi$ obtained directly from the calculation. The reason for this is that for some trajectories, particularly those at high energy, the function $\bar{q}_2(\bar{q}_1, n_1)$ changes abruptly by ± 2π (as a function of $\bar{q}_1$), and the phase $\phi(\bar{q}_1, n_1)$ undergoes a corresponding jump of $\pm 2\pi\left[n_2(\bar{q}_1, n_1) + \frac{1}{2}\right]$ at the same point. This causes no real problems, however, for

$n_2(\bar{q}_1, n_1)$ is completely smooth at this point, so that the phase of the integrand in Eq. (29) changes by $\mp 2\pi (n_2 - n_1)$, which has no effect on the integrand because

$$e^{\pm 2\pi i(n_2 - n_1)} = 1.$$

The magnitude of the integrand in Eq. (29) behaves like $\left[\delta(\bar{q}_1 - a)\right]^{\frac{1}{2}}$, where a is the point of discontinuity in $\bar{q}_2(\bar{q}_1, n_1)$, and since

$$\int_{-\epsilon}^{\epsilon} dx\ \delta(x)^{\frac{1}{2}} = 0$$

as $\epsilon \to 0$, the region of the discontinuity makes no contribution to the integral. The phase difference $\Delta\phi$ is modified according to Eq. (A19), therefore, to make it a continuous function of $\bar{q}_1$; this is appropriate in the sense that $\Delta\phi$ is actually being used to approximate higher derivatives of the phase of the integrand. One can avoid this problem of identifying the proper $\Delta\Phi$ by using Eq. (A12) which employs the higher derivatives themselves; for Eq. (29) of Sec. IV the higher derivatives of the phase of the integrand are given by

$$f'' = q_2{}'\, n_2{}'$$

$$f''' = q_2{}'\, n_2{}'' + 2q_2{}''\, n_2{}' .$$

In practice, however, we found it easier to identify the proper $\Delta\Phi$ than to evaluate these derivatives.

Table I.

Transition Probabilities for
$\mu = 2/3$, $\alpha = 0.3$, E = 10

Transition[a]	Classical[b]	Semiclassical[c]	Uniform[d]	Quantum[e]
0 - 0	0	0	0.058	(0.060)
0 - 1	0.356	0.422	0.211	0.218
0 - 2	0.212	0.416	0.381	0.366
0 - 3	0.232	0.359	0.266	0.267
0 - 4	0	0	0.075	0.089
1 - 0	0.356	0.423	0.211	0.218
1 - 1	0.158	0.290	0.287	(0.286)
1 - 2	0.130	0.009	0.011	0.009
1 - 3	0.128	0.168	0.174	0.170
1 - 4	0.159	0.285	0.240	0.240
1 - 5	0	0	0.062	0.077
2 - 0	0.212	0.416	0.381	0.366
2 - 1	0.130	0.009	0.011	0.009
2 - 2	0.109	0.208	0.206	(0.207)
2 - 3	0.105	0.020	0.017	0.018
2 - 4	0.114	0.165	0.170	0.169
2 - 5	0.169	0.262	0.194	0.194
2 - 6	0	0	0.045	0.037

[a] These are the initial and final vibrational quantum numbers, $n_1 - n_2$.

[b] Results are all from Eq. (8).

[c] Results are all from Eqs. (10), (11), and (13).

[d] Results are from Eq. (16) for the classically allowed transitions and Eq. (18) for the classically forbidden transitions.

[e] Results of Secrest and Johnson, ref. 4; the figures in parenthesis were obtained by subtracting from 1 the sum of transition probabilities for all possible transitions out of the initial state, and thus is an upper bound to the correct diagonal transition probability.

Table II.

Transition Probabilities for

$\mu = 2/3$, $\alpha = 0.3$, $E = 6$

Transition[a]	Classical[b]	Semiclassical[c]	Uniform[d]	Quantum[e]
0 - 0	0.401	0.672	0.534	(0.538)
0 - 1	0.360	0.546	0.397	0.394
0 - 2	0	0	0.059	0.068
1 - 0	0.360	0.546	0.397	0.394
1 - 1	0.228	0.210	0.223	(0.224)
1 - 2	0.302	0.470	0.349	0.345
1 - 3	0	0	0.061	0.037
2 - 0	0	0	0.059	0.068
2 - 1	0.302	0.470	0.349	0.345
2 - 2	0.242	0.333	0.344	(0.348)
2 - 3	0.607	0.659	0.239	0.233
2 - 4	0	0	0.029	0.006

[a, b, c, d, e] See the notes at the bottom of Table I.

Table III.

Transition Probabilities for
$\mu = 2/3$, $\alpha = 0.3$, $E = 3$

Transition[a]	Classical[b]	Semiclassical[c]	Uniform[d]	Quantum[e]
1 - 0	0	0	0.012	0.022
1 - 1	1.633	2.251	1.457	(0.977)
1 - 2	0	0	0.013	0.001

[a, b, c, d, e] See the notes at the bottom of Table I.

Table IV.

Transition Probabilities via the Initial Value Representation

Transition[a]	IVR[b]	Quantum[c]
	$\mu = 2/3$, $\alpha = 0.3$, $E = 6$	
1 - 0	0.025	0.022
1 - 1	0.973	(0.977)
1 - 2	0.0016, 0.0004	0.0009
	$\mu = 2/3$, $\alpha = 0.3$, $E = 8$	
1 - 0	0.117	0.108
1 - 1	0.826	(0.856)
1 - 2	0.052, 0.044	0.042
1 - 3	2.1×10^{-4}	1.5×10^{-5}
	$\mu = 1/2$, $\alpha = 0.1287$, $E = 12.8365$	
0 - 0	0.974	(0.986)
0 - 1	0.019, 0.016	0.014
0 - 2	2.1×10^{-5}, 3.4×10^{-5}	3.2×10^{-5}

Table IV. (continued)

Transition[a]	IVR[b]	Quantum[c]
$\mu = 1/2$, $\alpha = 0.1287$, $E = 16.8365$		
1 - 0	0.069	0.063
1 - 1	0.860	(0.874)
1 - 2	0.069	0.063
2 - 0	0.0015	0.0011
2 - 1	0.067	0.063
2 - 2	0.886	(0.896)
2 - 3	0.045	0.040

[a] See note a at the bottom of Table I.

[b] These values were obtained by numerical integration of the initial value representation, Eq. (29). Where there are two values, the second is for the inverse transition; these should be equal, of course, but Eq. (29) does not exactly obey this microscopic reversibility requirement.

[c] See note e at the bottom of Table I.

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2. R. P. Feynman and A. R. Hibbs, Quantum Mechanics and Path Integrals (McGraw-Hill Book Company, New York, 1965).
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6. H. Goldstein, Classical Mechanics (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1950), pp. 288-307.
7. Action-angle variables have also been used in the linear atom-diatom problem by M. Attermeyer and R. A. Marcus, J. Chem. Phys. 52, 393 (1970).
8. Units with $\hbar = 1$ are always used so that there is not this constant of proportionality between the classical action and the quantum mechanical quantum number.
9. The classical action is assigned half-integral values $(n + \frac{1}{2})$; this is in keeping with the semiclassical quantum condition for oscillators.
10. The relation corresponding to Eq. (1) can also be obtained in closed form for the Morse oscillator $\Big[$i.e., the potential $v(r) = D \left\{ e^{-2a(r - r_o)} - 2e^{-a(r - r_o)} \right\}\Big]$ and is $r - r_{eq} = -\frac{1}{a} \ln (1 - \frac{2n+1}{k})^2 / \left\{ 1 + \cos q \left[1 - (1 - \frac{2n+1}{k})^2 \right]^{\frac{1}{2}} \right\}$; the eigenvalue expression

which correspondsto $\omega(n+\frac{1}{2})$ is $-D(1 - \frac{2n+1}{k})^2$, where $k = 2(2mD/a^2)^{\frac{1}{2}}$.

11. Our energy E is in units of $\hbar\omega$, while that of ref. 4 is in units of $\frac{1}{2}\hbar\omega$; for H_2, $\hbar\omega \simeq \frac{1}{2}$ eV.

12. A standard fifth-order, variable step-size Runge-Kutta routine was used.

13. There are, of course, many ways of using classical mechanics to obtain properties of collisions (such as average energy transfer); see, for example, J. D. Kelley and M. Wolfsberg, J. Chem. Phys. 44, 324 (1966); see also ref. 7. What we mean by the classical result is the exact classical limit ($\hbar = 0$) of the exact quantum mechanical transition probability.

14. Note that the "forbidden" and "allowed" designations used here are quite distinct from the term energetically forbidden and allowed; for example, with $E = 10$ and $n_1 = 1$, values of n_2 from 0 to 9 are energetically allowed, but only values from 0 to 4 are allowed by classical dynamics.

15. See, for example, L. Pauling and E. B. Wilson, Jr., Introduction to Quantum Mechanics (McGraw-Hill Book Company, Inc., New York, 1935), pp. 74-76.

16. The independent variables of the trajectory are indicated as the arguments of Φ, whereas this phase is actually the phase of the S-matrix in the momentum representation [1], and is more rigorously designated as $\Phi(P_2, n_2, P_1, n_1)$, where $P_2 = P_2(n_2)$, $P_1 = P_1(n_1)$, and $n_2 = n_2(\bar{q}_1, n_1)$; see Eq. (24) and the discussion preceeding it.

17. P. Pechukas, Phys. Rev. 181, 166 (1969).

18. M. Abramowitz and I. A. Stegun, Handbook of Mathemetical Functions (U. S. Government Printing Office, Washington, D. C., 1964), pp. 446-452.

19. This approach has been used to evaluate barrier penetration integrals; see W. H. Miller, J. Chem. Phys. 48, 1651 (1968).

20. Ref. 6, pp. 237-244.

21. It was with these derivative relations in mind that $\bar{q}(t)$ was defined precisely as it was.

22. An important invariance property of Eq. (29) is that the particular 2π-length interval of $\bar{q}_1$ over which the integral is evaluated is unimportant; i.e.,

$$\int_0^{2\pi} d\bar{q}_1 = \int_A^{A+2\pi} d\bar{q}_1 \quad ,$$

where the integrand is that of Eq. (29), and A is any real number. This property can be demonstrated quite simply by using the fact that

$$n_2(\bar{q}_1 + 2\pi, n_1) = n_2(\bar{q}_1, n_1)$$

$$\bar{q}_2(\bar{q}_1 + 2\pi, n_1) = \bar{q}_2(\bar{q}_1, n_1) + 2\pi$$

$$\phi\left[n_2(\bar{q}_1 + 2\pi, n_1), n_1\right] = \phi\left[n_2(\bar{q}_1, n_1), n_1\right] - 2\pi\left[n_2(\bar{q}_1, n_1) - n_1\right] \quad .$$

23. Eq. (30) shows that the three trajectory functions n_2, $\bar{q}_2$, and ϕ are not independent; in fact, it provides an alternate way of computing ϕ:

$$\phi(\bar{q}_1, n_1) = \text{constant} - \int_0^{\bar{q}_1} d\bar{q}_1' \, \bar{q}_2(\bar{q}_1', n_1) \frac{\partial n_2(\bar{q}_1', n_1)}{\partial \bar{q}_1'} .$$

24. G. F. Carrier, J. Fluid Mech. 24, 641 (1966).
25. W. H. Miller, J. Chem. Phys. 48, 464 (1968).
26. M. V. Berry, Proc. Phys. Soc. (London) 89, 479 (1966); J. Phys. B 2, 381 (1969).
27. One important such system is the atom-diatom system in three dimensional space, for which there are three internal degrees of freedom; this has been discussed in some detail in I.
28. See R. J. Cross, Jr., J. Chem. Phys. to be published, where a similar problem has been noted.

Figure Captions

1. Transition probabilities for $\mu = 2/3$, $\alpha = 0.3$ (corresponding to H_2 + He) at $E = 10$ (~ 5 eV total energy for H_2 + He) with the initial vibrational quantum number $n_1 = 0$ (top), 1, and 2 (bottom). The dotted lines connect the results of the purely classical approximation [Eq. (8)], and the solid lines connect the exact quantum results of ref. 4; on the scale of the drawing these quantum results are essentially the same as the uniform semiclassical results of Eqs. (16) and (18). The numerical values corresponding to this Figure are contained in Table I.

2. The trajectory function $n_2(\bar{q}_1, n_1)$ for $\mu = 2/3$, $\alpha = 0.3$, with $E = 10$ and initial vibrational quantum number $n_1 = 1$; this function is the final vibrational quantum number of the classical trajectory with initial conditions $(\bar{q}_1, n_1)$. The dotted line at $n_2 = 2$ indicates the graphical solution for the two values of the multi-valued function $\bar{q}_1(n_2, n_1)$, here with $n_2 = 2$, $n_1 = 1$.

3. (a) A sketch of the classical approximation for the transition probability [Eq. (8)] for continuously variable n_2, at fixed n_1; n_2^{min} and n_2^{max} indicate the extrema of the function $n_2(\bar{q}_1, n_1)$ for fixed n_1 (such as in Fig. 2). (b) A sketch of the uniform semiclassical result for the transition probability [Eqs. (16) and (18)].

4. Same as Fig. 2, except for total energy $E = 3$. There are no classical trajectories at this energy for which the quantum number can change by an integral amount from it initial $(n_1 = 1)$ value; all transitions are therefore classically forbidden.

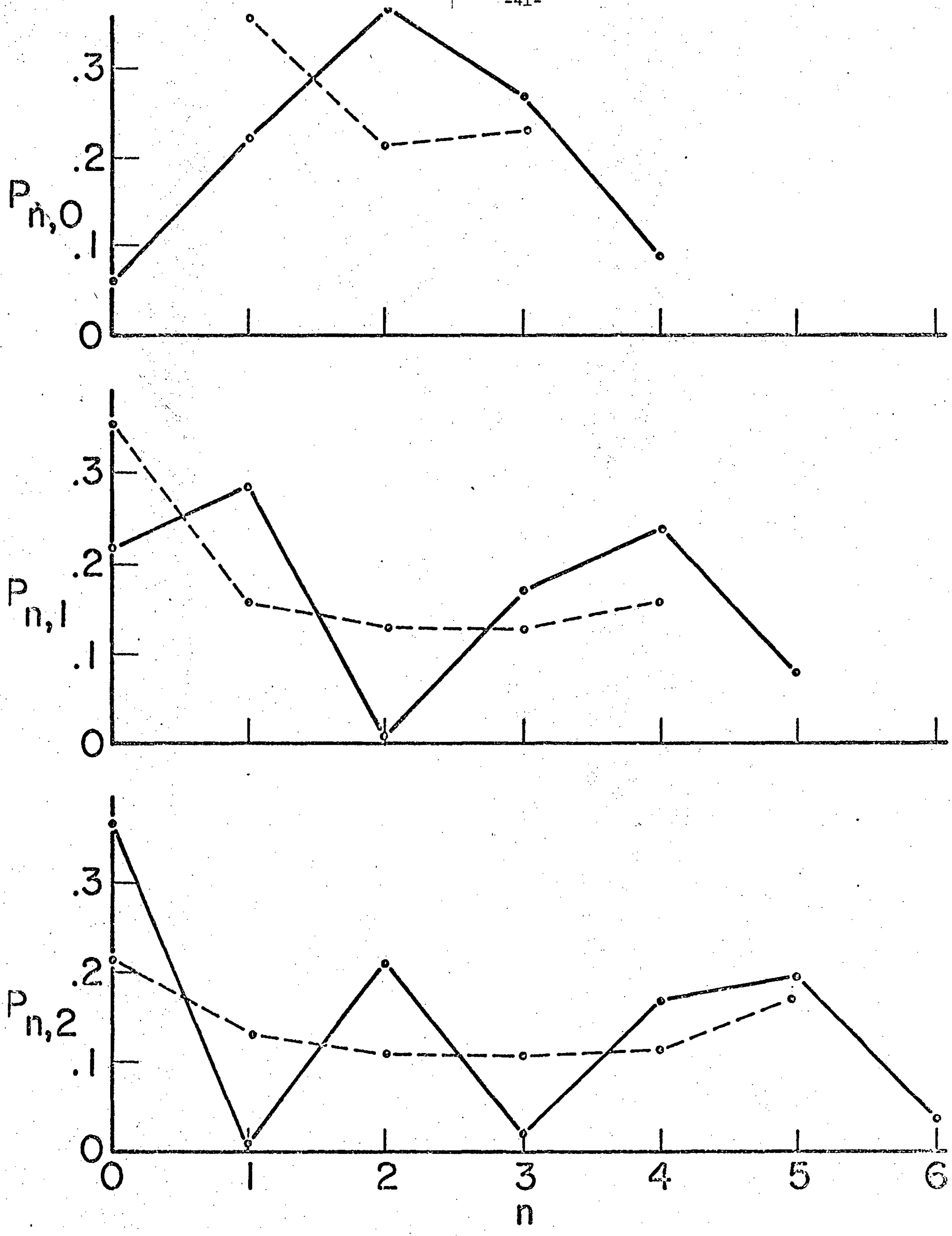

Fig. 1

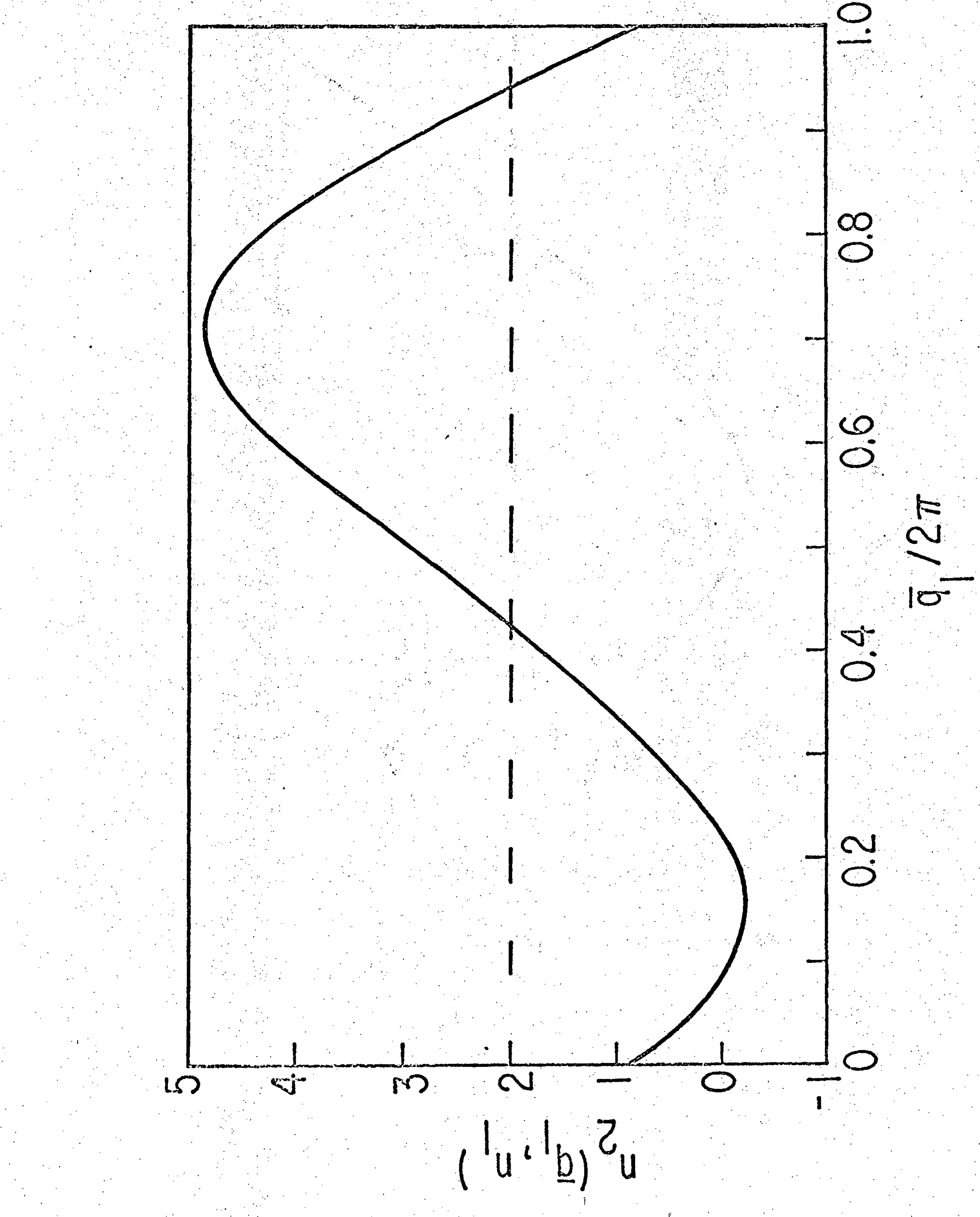

Fig. 2

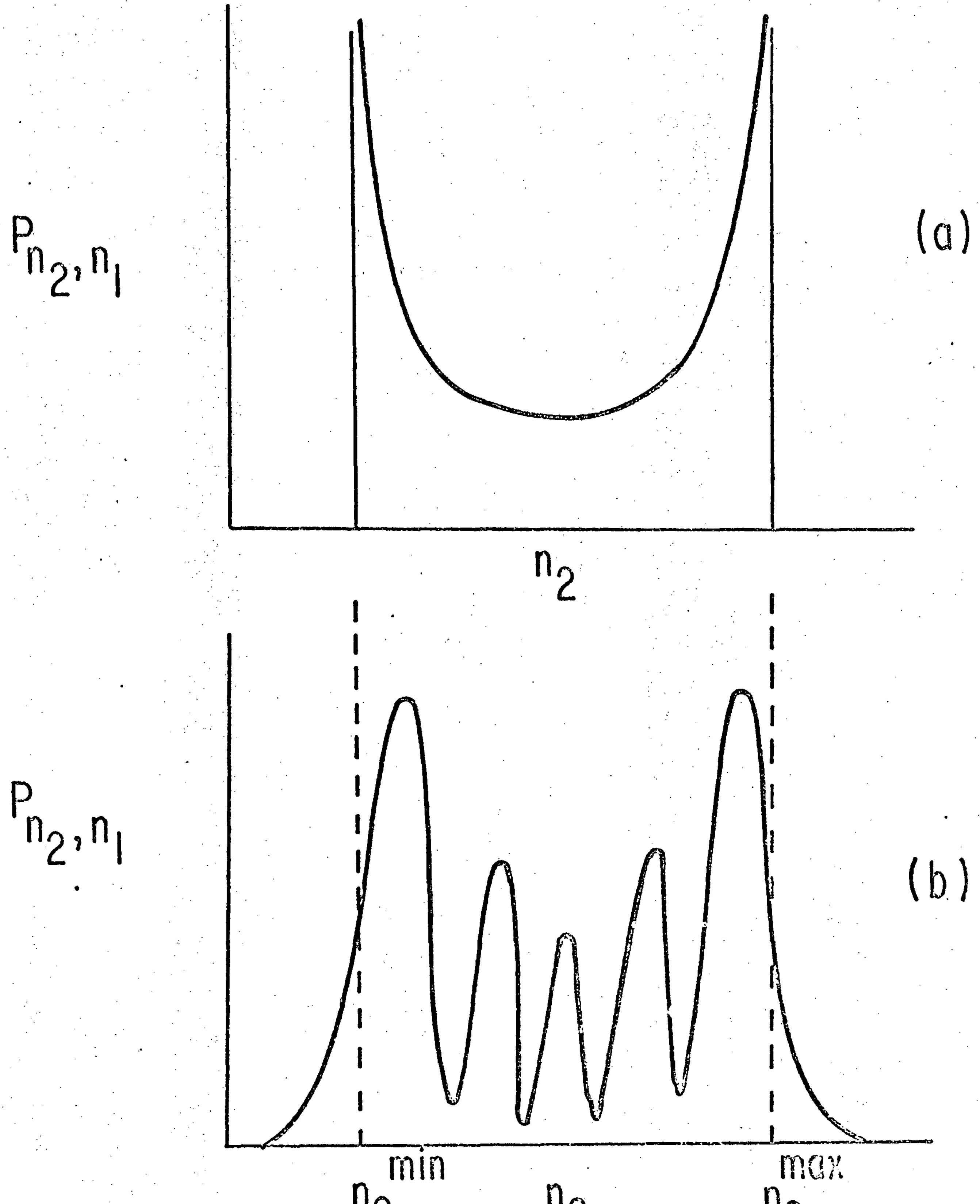

Fig. 3

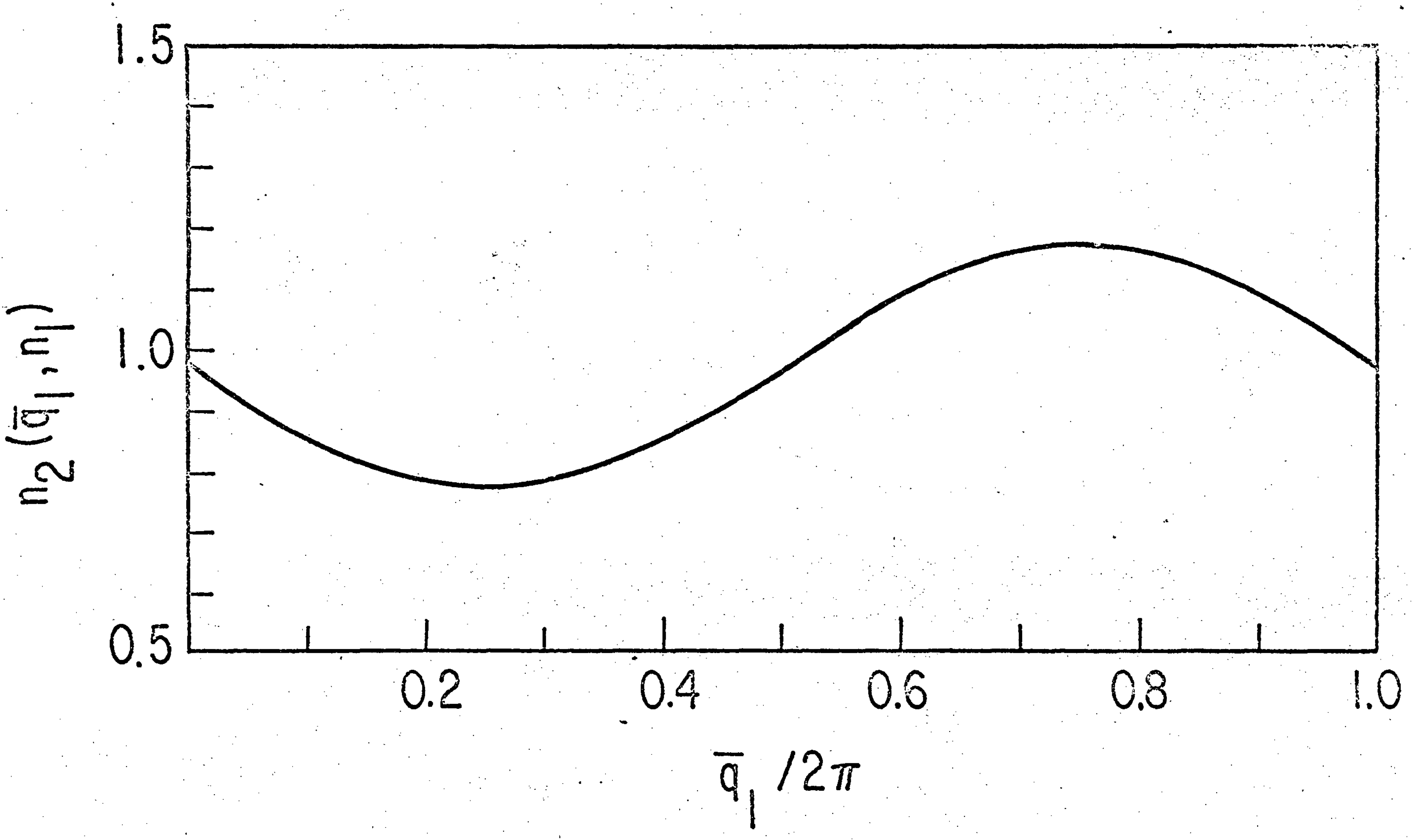

Fig. 4

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