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THE CLASSICAL S-MATRIX IN MOLECULAR COLLISIONS*

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I. INTRODUCTION

The last three years have seen considerable interest in the development of semiclassical methods for treating complex molecular collisions, i.e., those which involve inelastic or reactive processes. One of the reasons for this activity is that the recent work, primarily that of Miller[1] and that of Marcus,[2] has shown how numerically computed classical trajectories can be used as input to the semiclassical theory, so that it is not necessary to make any dynamical approximations when applying these semiclassical approaches to complex collision processes. There is thus the possibility of being able to augment purely classical (i.e. Monte Carlo) trajectory calculations,[3,4] which have proved extremely powerful and useful in their own right, with many of the quantum effects that may be important in molecular collision phenomena.

Another motivation for pursuing these semiclassical approaches to inelastic and reactive scattering is the well-known success that semiclassical theory has had in describing quantum effects in simpler elastic (potential) scattering.[5,6] Here one now knows that essentially all quantum effects can be adequately described in a semiclassical framework.

This paper reviews this "classical S-matrix" theory, i.e., the semiclassical theory of inelastic and reactive scattering which combines exact classical mechanics (i.e. numerically computed trajectories) with the quantum principle of superposition. It is always possible, and in some applications may even be desirable, to apply the basic semiclassical model with approximate dynamics; Cross[7] has discussed the simplifications that result in classical S-matrix theory if one treats the dynamics within the sudden approximation, for example, and shown how this relates to some of his earlier work[8] on inelastic scattering. For the most part, however, this review will emphasize the use of exact classical dynamics and avoid discussion of various dynamical models and approximations, the reason being to focus on the nature and validity of the basic semiclassical idea itself, i.e., classical dynamics plus quantum superposition. Actually, all quantum effects - being a direct result of the superposition of probability amplitudes - are contained (at least qualitatively) within the semiclassical model, and the primary question to be answered regards the quantitative accuracy of the description.

Since I have reviewed certain aspects of semiclassical, or classical-limit quantum mechanics only a year ago,[9] this presentation will summarize the general theory only briefly and concentrate more on specific applications. The results of various calculations utilizing classical S-matrix theory are reviewed, and the semiclassical description of several different physical processes - scattering resonances, scattering of atoms from surfaces, and photodissociation of polyatomic molecules - is developed to illustrate more fully how one can translate between classical, semiclassical, and quantum mechanical versions of a theory. The semiclassical theory of elastic scattering itself will not be discussed explicitly since this has been the subject of a recent review by Berry and Mount.[10] An understanding of the semiclassical techniques used in elastic scattering has, of course, been essential in extending semiclassical ideas to more general collision processes.

It should be noted that there are a number of other treatments of inelastic scattering, which will not be reviewed here, to which the term "semiclassical" is also applied. The oldest and most common of these is the "classical path model":[11] here a trajectory is assumed for the translational motion, this causing a time-dependent perturbation on the internal degrees of freedom which are treated quantum mechanically, i.e., via the time-dependent Schrödinger equation. The simplest version of this approach[11] assumes a straight line, constant velocity trajectory and applies first order perturbation theory to solve the time-dependent Schrödinger equation for the internal degrees of freedom; neither of these assumptions is necessary, however, and there have been applications that invoke neither of them.[12] The fundamental distinction between this class of approximations and classical S-matrix theory is that in the former some degrees of freedom, namely translation, are treated classically and the others quantum mechanically, while classical S-matrix theory treats all degrees of freedom classically, superposition being the only element of quantum mechanics contained in the model. In classical S-matrix theory, therefore, it is completely straight-forward to include the full dynamics exactly - by calculation of classical trajectories - while classical path models have inherent dynamical approximations embedded in them.

The remarks in the previous paragraph apply, of course, only to the case of electronically adiabatic molecular collisions for which all degrees of freedom refer to the motion of nuclei (i.e., translation, rotation, and vibration); if transitions between different electronic states are also involved, then there is no way to avoid dealing with an explicit mixture of a quantum description of some degrees of freedom (electronic) and a classical description of the others.[9] The description of such non-adiabatic electronic transitions within the framework of classical S-matrix theory has been discussed at length in the earlier review[9] and is not included here.

II. FUNDAMENTAL CORRESPONDENCE RELATIONS.

The basic semiclassical idea is that one uses a quantum mechanical description of the process of interest but then invokes classical mechanics to determine all dynamical relationships. A transition from initial state i to final state f, for example, is thus described by a transition amplitude, or S-matrix element S_{fi}, the square produlus of which is the transition probability: $P_{fi} = |S_{fi}|^2$. The semiclassical approach uses classical mechanics to construct the classical-limit approximation for the transition amplitude, i.e., the "classical S-matrix"; the fact that classical mechanics is used to construct an amplitude means that the quantum principle of superposition is incorporated in the description, and this is the only element of quantum mechanics in the model. The completely classical approach would be to use classical mechanics to construct the transition probability directly, never alluding to an amplitude.

One thus needs a prescription for constructing the classical-limit approximation to quantum mechanical amplitudes, or transformation elements. This is given most generally by establishing the correspondence of canonical transformations between various coordinates and momenta in classical mechanics to unitary transformations between various sets of states in quantum mechanics. These correspondence relations have been derived earlier[1,9] and are summarized below.

A. Summary of General Formulae.

Let (p, q) be one set of canonically conjugate coordinates and momenta (the "old" variables) and (P, Q) be another such set (the "new" variables.)[13] (P, Q, p, and q are N-dimensional vectors for a system with N degrees of freedom, but for the sake of clarity multidimensional notation will not be used; the explicitly multidimensional expressions are in most cases obvious.) In classical mechanics P and Q may be considered as functions of p and q, or inversely, P and Q may be chosen as the independent variables with p and q being functions of them. To carry out the canonical transformation between these two sets of variables, however, one must rather choose one "old" variable and one "new" variable as the independent variables, the remaining two variables then being considered as functions of them. The canonical transformation is then carried out with the aid of a generating function, or generator, which is some function of the two independent variables, and two equations which express the dependent variables in terms of the independent variables.[13]

If, for example, the "old" coordinate q and the "new" coordinate Q are chosen as the independent variables, and if $F_1(q,Q)$ is the generator, then the two equations which define p and P are

$$p(q,Q) = \frac{\partial F_1(q,Q)}{\partial q} \tag{2.1a}$$

$$P(p,Q) = -\frac{\partial F_1(q,Q)}{\partial Q} \quad . \tag{2.1b}$$

To express P and Q explicitly in terms of p and q it would be necessary to solve Eq. (2.1a), i.e.

$$p = \frac{\partial F_1(q,Q)}{\partial q} \quad . \tag{2.1a'}$$

for $Q(p,q)$ and then substitute this into Eq. (2.1b) to obtain $P(p,q)$. There are clearly three other combinations of "one old variable and one new variable": (q,P), (p,Q), and (p,P). Equivalently, the generators $F_2(q,P)$, $F_3(p,Q)$, or $F_4(p,P)$ may be used in a similar manner, along with the appropriate pair of differential equations analogous to Eq. (2.1), to effect the transformation.

Quantum mechanically, the objects of interest are the elements of the unitary transformation from the "old" states $|q\rangle$ and $|p\rangle$ to the "new" states $|Q\rangle$ and $|P\rangle$. [The unitary transformation elements relating any canonically conjugate pair is always given by

$$\langle q|p\rangle = (2\pi i\hbar)^{-1/2} \exp(ipq/\hbar) \tag{2.2a}$$

$$\langle Q|P\rangle = (2\pi i\hbar)^{-1/2} \exp(iPQ/\hbar) \quad .] \tag{2.2b}$$

There are, just as in classical mechanics, four ways of choosing "one old variable and one new variable", so there are four equivalent sets of unitary transformation elements connecting the "old" and "new" representations: $\langle q|Q\rangle$, $\langle q|P\rangle$, $\langle p|Q\rangle$, and $\langle p|P\rangle$. The fundamental correspondence relations express the classical limit of these unitary transformation elements in terms of the classical generating functions for the related classical canonical transformation:

$$<q|Q> = [-\frac{\partial^2 F_1(q,Q)}{\partial q\partial Q} / 2\pi i\hbar]^{1/2} \quad \exp\ [iF_1(q,Q)/\hbar] \qquad (2.3a)$$

$$<q|P> = [\frac{\partial^2 F_2(q,P)}{\partial q\partial P} / 2\pi i\hbar]^{1/2} \quad \exp\ [iF_2(q,P)/\hbar] \qquad (2.3b)$$

$$<p|Q> = [\frac{\partial^2 F_3(p,Q)}{\partial p\partial Q} / 2\pi i\hbar]^{1/2} \quad \exp\ [iF_3(p,Q)/\hbar] \qquad (2.3c)$$

$$<p|P> = [-\frac{\partial^2 F_4(p,P)}{\partial p\partial P} / 2\pi i\hbar]^{1/2} \quad \exp\ [iF_4(p,P)/\hbar) \quad . \qquad (2.3d)$$

In applications it is usually convenient to make use of the derivative relations of the generator[13] to express the pre-exponented factors above in a less symmetrical, but more useful form. If use is made of Eq. (2.1b), for example, it is easy to show that Eq. (2.3a) can be written as

$$<q|Q> = [2\pi i\hbar\left(\frac{\partial q}{\partial P}\right)_Q]^{-1/2} \quad \exp\ [iF_1(q,Q)/\hbar] \quad . \qquad (2.3a')$$

The derivation of these fundamental correspondence relations, Eq. (2.3), has been given previously,[9] and one should see reference 9 for a more detailed discussion. To obtain the results it is necessary to assume only Eq. (2.2) (which is essentially a statement of the uncertainty principle), make use of classical mechanics itself, and invoke the stationary phase approximation[14] to evaluate all integrals for which the phase of the integrand is proportional to $\hbar^{-1}$. Since the stationary phase approximation[14] is an asymptotic approximation which becomes exact as $\hbar \to 0$, this is the nature of the classical-limit approximations in Eq. (2.3). In a very precise sense, therefore, classical-limit quantum mechanics is the stationary phase approximation to quantum mechanics.

B. Example: Franck-Condon Factors.

Several examples of the basic correspondence relations [Eq. (2.3)] have been worked out in reference 9, and here another one is considered. For brevity the following discussion assumes some familiarity of Section II of reference 9.

Let $V_a(x)$ and $V_b(x)$ be two one-dimensional potential wells with eigenstates (labeled by their vibrational quantum numbers) $|n_a>$ and $|n_b>$, respectively. A Franck-Condon factor is the square modulus of the amplitude $<n_b|n_a>$, i.e., $|<n_b|n_a>|^2$. Thinking semiclassically, one notes that n_a is the generalized momentum of the action-angle variables[15] (n_a,q_a) for the potential V_a; n_b is similarily the generalized momentum of the action-angle variables (n_b,q_b) that are defined with respect to V_b. The amplitude $<n_b|n_a>$ is thus a matrix element between momentum states of different representations, so that its classical limit is given by Eq. (2.3d):

$$<n_b|n_a> = \left[-\frac{\partial^2 F_4(n_b,n_a)}{\partial n_b \partial n_a} \Big/ 2\pi i\hbar\right]^{1/2} \exp\,[iF_4(n_b,n_a)/\hbar] \quad , \qquad (2.4)$$

where $F_4(n_b,n_a)$ is the F_4 - type generator of the $(n_a,q_a) \leftrightarrow (n_b,q_b)$ classical canonical transformation.

To discover the appropriate F_4 generator for Eq. (2.4) it is useful first to consider the canonical transformation from (n_a,q_a) to ordinary cartesian variables (p,x), and then from (p,x) to the canonical set (n_b,q_b). As shown before,[9] the F_2 - type generator for the $(n_a,q_a) \leftrightarrow (p,x)$ transformation is

$$F_2^{\,a}(x,n_a) = \int dx\{2m[\varepsilon_a(n_a) - V_a(x)]\}^{1/2} \quad , \tag{2.5}$$

and of a similar form for the $(n_b,q_b) \leftrightarrow (p,x)$ transformation:

$$F_2^{\,b}(x,n_b) = \int dx\{2m[\varepsilon_b(n_b) - V_b(x)]\}^{1/2} \quad , \tag{2.6}$$

where $\varepsilon_a(n_a)$ and $\varepsilon_b(n_b)$ are the WKB eigenvalue functions. Since

$$\langle n_b|n_a\rangle = \int dx\ \langle n_b|x\rangle\langle x|n_a\rangle \quad , \tag{2.7}$$

use of Eq. (2.3b) for the matrix elements on the integrand of Eq. (2.7) and stationary phase evaluation of the integral over x shows that

$$F_4(n_b,n_a) = F_2^{\,a}(x,n_a) - F_2^{\,b}(x,n_b) \quad . \tag{2.8}$$

where $x \equiv x(n_b,n_a)$ is defined implicitly by the stationary phase condition

$$0 = \frac{\partial F_2^{\,a}(x,n_a)}{\partial x} - \frac{\partial F_2^{\,b}(x,n_b)}{\partial x} \quad . \tag{2.9}$$

Because of the following derivation relation for an F_2 - type

$$\frac{\partial F_2(x,n)}{\partial x} = p(x,n) \quad ,$$

Eq. (2.9) may also be written as

$$0 = p(x,n_a) - p(x,n_b) \quad . \tag{2.10}$$

Thus the position x at which the $n_a \leftrightarrow n_b$ Franck Condon – transition occurs is the one (or ones) for which the Cartesian momentum is conserved; this is, of course, a statement of the Franck Condon principle.[16] Since

$$p(x,n) = \{2m[\varepsilon(n) - V(x)]\}^{1/2} \quad ,$$

$x(n_b,n_a)$ is equivalently defined as the solution of

$$\varepsilon_a(n_a) - V_a(x) = \varepsilon_b(n_b) - V_b(x) \quad . \tag{2.11}$$

The pre-exponential factor in Eq. (2.4) can be evaluated explicitly by making use of Eqs. (2.8) and (2.9). Differentiation of Eq. (2.8) gives

$$\frac{\partial F_4(n_b,n_a)}{\partial n_a} = \left[\frac{\partial F_2{}^a(x,n_a)}{\partial x} - \frac{\partial F_2{}^b(x,n_b)}{\partial x}\right] \frac{\partial x(n_b,n_a)}{\partial n_a} + \frac{\partial F_2{}^a(x,n_a)}{\partial n_a} \quad , \tag{2.12}$$

and by virtue of Eq. (2.9) the first term vanishes. Differentiation of Eq. (2.12) with respect to n_b thus gives

$$\frac{\partial^2 F_4(n_b,n_a)}{\partial n_b \partial n_a} = \frac{\partial^2 F_2{}^a(x,n_a)}{\partial x \partial n_a} \frac{\partial x(n_b,n_a)}{\partial n_b} \quad , \tag{2.13}$$

and from Eq. (2.5) one can show that

$$\frac{\partial^2 F_2^{\,a}(x,n_a)}{\partial x \partial n_a} = \frac{m\,\varepsilon_a{}'(n_a)}{p} \quad , \tag{2.14}$$

where $p \equiv p(x,n_a) = p(x,n_b)$. Furthermore, differentiation of Eq. (2.11) with respect to n_b gives

$$[V_b{}'(x) - V_a{}'(x)]\,\frac{\partial x(n_b,n_a)}{\partial n_b} = \varepsilon_b{}'(n_b) \quad ,$$

or

$$\frac{\partial x(n_b,n_a)}{\partial n_b} = \varepsilon_b{}'(n_b)\ /\ \Delta V'(x) \tag{2.15}$$

where $\Delta V(x) = V_b(x) - V_a(x)$. Eqs. (2.13) - (2.15) thus give the pre-exponential factor as

$$\frac{\partial^2 F_4(n_b,n_a)}{\partial n_b \partial n_a}\ /\ 2\pi\hbar = \frac{m\varepsilon_a{}'(n_a)\ \varepsilon_b{}'(n_b)}{2\pi\hbar\ p\ \Delta V'(x)} \quad . \tag{2.16}$$

If there is one value of x which satisfies Eq. (2.11), then there will be two terms contributing to Eq. (2.4), one corresponding to $p > o$ and one to $p < o$. With Eqs. (2.8) and (2.16), Eq. (2.4) finally gives the Franck Condon amplitude as

$$\langle n_b | n_a \rangle = \left[\frac{m\ \varepsilon_a{}'(n_a)\varepsilon_b{}'(n_b)}{2\pi\hbar|p|\ \ |\Delta V'(x)|}\right]^{1/2}$$

$$\times\ 2\cos\left[\frac{\pi}{4} + F_2{}^a(x,n_a) - F_2{}^b(x,n_b)\right] \quad , \tag{2.17}$$

where the F_2 - generators are given by Eq. (2.5) and (2.6) and x is evaluated at the "crossing point" [the root of Eq. (2.11)]. This result has been obtained before[17-19] from other more traditional approaches, but it is interesting to see that it results directly from the general correspondence relations. If there is more than one value of x which satisfies Eq. (2.11), then Eq. (2.17) is a sum of similar terms, one for each such value of x.

If one discards the interference term between the two terms that contribute to Eq. (2.17), then the classical Franck-Condon factor is obtained:

$$|\langle n_b|n_a\rangle|^2 = 2\,\frac{m\,\varepsilon_a{}'(n_a)\ \varepsilon_b{}'(n_b)}{2\pi\hbar\ |p|\ |\Delta V'(x)|} \quad , \tag{2.18}$$

the factor of 2 appearing because of the two terms that contribute equally. It is interesting (and useful) to show that this purely classical expression can also be obtained from simpler phase space considerations. The Franck-Condon factor in Eq. (2.18) is the joint probability that n_a and n_b have certain specific values; it can thus be written as the following phase space integral:

$$P(n_b,n_a) = (2\pi\hbar)^{-1} \int dP \int dQ\ \delta[n_b - n_b(P,Q)]$$

$$\times\ \delta[n_a - n_a(P,Q)] \quad , \tag{2.19}$$

where P and Q are any set of canonically conjugate variables (since phase space integrals are invariant to a canonical transformation), and $n_b(P,Q)$ and $n_a(P,Q)$ are these variables expressed in terms of P and Q. Choosing (P,Q) to be the variables (n_a,q_a), for example, leads to

$$
\begin{aligned}
P(n_b,n_a) &= (2\pi\hbar)^{-1}\int dq_a\,\delta[n_b - n_b(n_a,q_a)] \\
&= (2\pi\hbar)^{-1}\left|\left(\frac{\partial n_b}{\partial q_a}\right)_{n_a}\right|^{-1} \\
&= (2\pi\hbar)^{-1}\left|\frac{\partial q_a(n_b,n_a)}{\partial n_b}\right| \quad .
\end{aligned}
\tag{2.20}
$$

Since one of the derivative relations for an F_4 - type generator is[13]

$$q_a(n_b,n_a) = \frac{\partial F_4(n_b,n_a)}{\partial n_a} \quad ,$$

one sees that

$$\frac{\partial q_a(n_b,n_a)}{\partial n_b} = \frac{\partial^2 F_4(n_b,n_a)}{\partial n_b \partial n_a} \quad , \tag{2.21}$$

so that Eq. (2.20) thus becomes

$$P(n_b,n_a) = \left|\frac{\partial^2 F_4(n_b,n_a)}{\partial n_b \partial n_a} \Big/ 2\pi\hbar\right| \quad , \tag{2.22}$$

which is the same pre-exponential factor as in Eq. (2.4) and thus the same classical Franck-Condon factor as Eq. (2.18).

C. Matrix Elements.

The correspondence relations summarized in Section IIA show how any unitary transformation element can be evaluated within the classical limit. Sometimes, however, one is interested in matrix elements of operators which are not unitary. Consider, for example, the one-dimensional system discussed in the previous section; if A is some operator, the question is how does one obtain the classical limit of the matrix element $<n_b|A|n_a>$.

Let $|\xi>$ be some yet unspecified set of states; then

$$<n_b|A|n_a> = \int d\xi \int d\xi' <n_b|\xi'> <\xi'|A|\xi> <\xi|n_a> \quad . \tag{2.23}$$

To evaluate this semiclassically one should choose the basis $|\xi>$ so that the representation of A is local and multiplicative,

$$<\xi'|A|\xi> = \delta(\xi' - \xi) A(\xi) \quad , \tag{2.24}$$

and where $A(\xi)$ is non-singular as $\hbar \to 0$. If A is an operator with a simple classical analog, as is usually the case, then the choice of the basis $|\xi>$ is obvious. If A is the kinetic energy, $A = p^2/2m$, for example, the basis should be chosen to be the cartesian momentum states $|p>$. If A is a simple function of the cartesian coordinates, $A = A(x)$, then one should use a cartesian coordinate representation.

In this latter case, for example, Eq. (2.23) becomes

$$<n_b|A|n_a> = \int dx <n_b|x> A(x) <x|n_a> \quad , \tag{2.25}$$

stationary phase evaluation of which clearly gives

$$<n_b|A|n_a> = A(x) <n_b|n_a> \quad , \tag{2.26}$$

where $x = x(n_b, n_a)$ and $<n_b|n_a>$ is the Franck-Condon factor discussed in the previous section. Probably the most common example of this result is the case the A is the dipole operator, $A(x) = ex$, e being the electron charge; this is the application made in discussing photodissociation in Section III E below.

III. CLASSICAL S-MATRIX: CLASSICALLY ALLOWED PROCESSES.

In a collision system such as an atom A colliding with a diatomic molecule BC, one is interested in the transition amplitudes, or S-matrix elements, which describe transitions between specific quantum states of the molecule BC. From the S-matrix elements one can construct scattering amplitudes for any collision process resulting from A + BC, the square modulus of the amplitudes being the cross sections.

Several derivations of the classical limit of the S-matrix, the "classical S-matrix", for complex collisions (i.e. those for which the collision partners have internal degrees of freedom) have been given;[1,2,9] the results follow almost directly from the fundamental correspondence relations, Eq. (2.3), the only modifications being those required to factor out an energy-conserving delta function. This section first summarizes the general expression and then discusses their application.

A. Basic Formulae.

For ease of presentation a non-reactive collision is considered first; the modifications required to include reactive processes are straight-forward and simple.[1,9] The general system consists of N degrees of freedom, one being relative translation of the collision partners and the other (N-1) being internal degrees of freedom which are quantized in the asymptotic regions. The translational degree of freedom is described by the center of mass coordinate R and momentum P, while the internal degrees of freedom are described by their action angle variables $(\underset{\sim}{n},\underset{\sim}{q}) \equiv (\underset{\sim}{n}_i,\underset{\sim}{q}_i)$, i = 1,2, ..., N-1. The action variables $\{n_i\}$ are the classical counterpart of the quantum numbers for these degrees of freedom and will thus be referred to simply as the "quantum numbers" although classically, of course, they are continuous functions of time like any other (generalized) momenta; in the asymptotic regions ($R \to \infty$) before and after collision they are required to be integers.[20]

The classical Hamiltonian function for the system is given in terms of these variables by

$$H(P,R,\underset{\sim}{n},\underset{\sim}{q}) = P^2/2\mu + \varepsilon(\underset{\sim}{n}) + V(R,\underset{\sim}{n},\underset{\sim}{q}) \quad , \qquad (3.1)$$

where μ is the reduced mass of relative motion, $\varepsilon(\underset{\sim}{n})$ is the WKB eigenvalue function for the internal degrees of freedom, and V is an interaction which vanishes as $R \to \infty$. It is the dependence of V on R and $\underset{\sim}{q}$ which prevents P and $\underset{\sim}{n}$ from being constants of the motion; since $V \to 0$ as $R \to \infty$, P and $\underset{\sim}{n}$ are conserved asymptotically, and as noted above the asymptotically constant values of $\underset{\sim}{n}$ must be integers.

The quantities of interest are the on-shell S-matrix elements,

$$S_{\underset{\sim}{n}_2,\underset{\sim}{n}_1}(E) \quad ,$$

which are the probability amplitudes for the $\underset{\sim}{n}_1 \to \underset{\sim}{n}_2$ transition. Their classical-limit approximation, the classical S-matrix, is constructed from the classical trajectory (or trajectories) with initial conditions[21] at time t_1 ($t_1 \to -\infty$)

$$\underset{\sim}{n}(t_1) = \underset{\sim}{n}_1 \text{ (a specific set of integers)} \qquad (3.2a)$$

$$R(t_1) = \text{large} \qquad (3.2b)$$

$$P(t_1) = -\{2\mu[E - \varepsilon(n_1)]\}^{1/2} \tag{3.2c}$$

$$\underset{\sim}{q}(t_1) = \underset{\sim}{\bar{q}}_1 + \frac{\partial\varepsilon(\underset{\sim}{n}_1)}{\partial\underset{\sim}{n}_1}\,\mu R(t_1)/P(t_1) \quad , \tag{3.2d}$$

and with final conditions at time t_2 ($t_2 \to +\infty$)

$$\underset{\sim}{n}(t_2) = \underset{\sim}{n}_2 \text{ (another set of integers)} \tag{3.3a}$$

$$R(t_2) = \text{large} \tag{3.3b}$$

$$P(t_2) = +\{2\mu[E - \varepsilon(\underset{\sim}{n}_2)]\}^{1/2} \tag{3.3c}$$

$$\underset{\sim}{q}(t_2) = \text{anything} \tag{3.3d}$$

For a system with several degrees of freedom the trajectories must, of course, be determined by numerical integration of Hamilton's equations step by step in time. To find the trajectory (or trajectories) which obey the boundary conditions in Eq. (3.2) and (3.3) it is convenient to introduce the function $\underset{\sim}{n}_2(\underset{\sim}{\bar{q}}_1,\underset{\sim}{n}_1;E)$, the final value of the quantum numbers that result from a trajectory with the initial conditions of Eq. (3.2); in general, of course, $\underset{\sim}{n}_2(\underset{\sim}{\bar{q}}_1,\underset{\sim}{n}_1;E)$ is non-integral. For a given total energy E and a given set of initial integral quantum numbers $\underset{\sim}{n}_1$, the task is to find the particular values of the angle variables $\underset{\sim}{\bar{q}}_1$ for which $\underset{\sim}{n}_2(\underset{\sim}{\bar{q}}_1,\underset{\sim}{n}_1;E)$ turn out to be the specific set of integers $\underset{\sim}{n}_2$;i.e., suppressing the arguments $\underset{\sim}{n}_1$ and E, one must solve the equations

$$\underset{\sim}{n}_2(\underset{\sim}{\bar{q}}_1) = \underset{\sim}{n}_2 \quad , \tag{3.4}$$

where $\underset{\sim}{n}_2$ on the RHS is a given set of integers. This is a set of (N-1) equations in N-1 unknowns.

The classical S-matrix element for the $\underset{\sim}{n}_1 \rightarrow \underset{\sim}{n}_2$ transition is then given by[22]

$$S_{\underset{\sim}{n}_2,\underset{\sim}{n}_1}(E) = \left[(-2\pi i)^{N-1} \frac{\partial \underset{\sim}{n}_2(\underset{\sim}{\bar{q}}_1,\underset{\sim}{n}_1;E)}{\partial \underset{\sim}{\bar{q}}_1}\right]^{-1/2} \exp[i\Phi(\underset{\sim}{n}_2,\underset{\sim}{n}_1;E)/\hbar], \qquad (3.5)$$

where $\partial \underset{\sim}{n}_2/\partial \underset{\sim}{\bar{q}}_1$ is the determinant of the N-1 Jacobian, $\underset{\sim}{\bar{q}}_1$ is evaluated at the root of Eq. (3.4), and Φ is the classical action integral

$$\Phi(\underset{\sim}{n}_2,\underset{\sim}{n}_1;E) = -\int dt[R(t)\ \dot{P}(t) + \underset{\sim}{q}(t) \cdot \dot{\underset{\sim}{n}}(t)] \qquad (3.6)$$

evaluated along the trajectory which satisfies the above double-ended boundary conditions. If there is more than one trajectory at this energy corresponding to the same initial and final quantum numbers $\underset{\sim}{n}_1$ and $\underset{\sim}{n}_2$, Eq. (3.5) is a sum of similar terms, one for each such trajectory.

Before proceeding to discuss more substantive examples it is interesting to see that the above expressions do reproduce the standard WKB results for one-dimensional dynamical systems. For a system with only a translational degree of freedom, i.e. no internal degrees of freedom, the pre-exponential factor in Eq. (3.5) is unity and the phase Φ is

$$\begin{aligned}\Phi(E) &= -\int_{t_1}^{t_2} dt\ R(t)\ \dot{P}(t) \\ &= -(R_2P_2 - R_1P_1) + \int_{t_1}^{t_2} dt\ P(t)\ \dot{R}(t) \qquad . \qquad (3.7)\end{aligned}$$

If the interaction potential $V(R)$ has a repulsive core and $R_<$ is the classical turning point, then Eq. (3.7) becomes

$$\Phi(E) = -2RP + 2\int_{R_<}^{R} dR'\; P(R') \quad , \tag{3.8}$$

where $R \equiv R_1 \equiv R_2 \to \infty$, $P \equiv -P_1 = P_2 = (2mE)^{1/2}$, and $P(R) = \{2m[E - V(R)]\}^{1/2}$.

The S-matrix is thus

$$\begin{aligned} S(E) &= \exp\,[i\Phi(E)/\hbar] \\ &= \exp\,[2i\eta(E)] \quad , \end{aligned} \tag{3.9}$$

where the phase shift $\eta(E)$ is given by the usual WKB expression:

$$\eta(E) = \lim_{R\to\infty}\; [-kR + \int_{R_<}^{R} dR'\; k(R')] \quad , \tag{3.10}$$

where $k = (2mE/\hbar^2)^{1/2}$ and

$$k(R) = \{2m[E - V(R)]/\hbar^2\}^{1/2} \quad .$$

For a single particle moving in three dimensions under the influence of a spherically symmetric potential $V(R)$, the classical Hamiltonian is

$$H(P,R,\ell,q_\ell,m,q_m) = (2\mu)^{-1}(P^2 + \ell^2/R^2) + V(R) \quad , \tag{3.11}$$

and one sees that the quantum numbers ℓ (orbital angular momentum) and m (its z-componant) for the two "internal" degrees of freedom are conserved since their conjugate variables q_ℓ and q_m do not appear in the Hamiltonian. The dynamical system thus reduces to a one-dimensional one with a Hamiltonian

$$H_\ell(P,R) = (2\mu)^{-1}(P^2 + \ell^2/R^2) + V(R) \tag{3.12}$$

that depends parametrically on ℓ. Because of the centrifugal term $\ell^2/2\mu R^2$, however, the Hamiltonian in Eq. (3.12) is not precisely of the form in Eq. (3.1). To remedy this one transforms from variables P and R to the new variables $\bar{P}$ and $\bar{R}$, where

$$\bar{P}^2 = P^2 + \ell^2/R^2 \quad . \tag{3.13}$$

The classical generator which effects this canonical transformation is

$$\begin{aligned} F_2(R,\bar{P}) &= \int dR\ (\bar{P}^2 - \ell^2/R^2)^{1/2} \\ &= R(\bar{P}^2 - \ell^2/R^2)^{1/2} \\ &\quad - \ell \cos^{-1}(\ell/\bar{P}R) \end{aligned} \tag{3.14}$$

By invoking the derivation relations for an F_2 - type generator,

$$P = \frac{\partial F_2(R,\bar{P})}{\partial R} \tag{3.15a}$$

$$\bar{R} = \frac{\partial F_2(R,\bar{P})}{\partial \bar{P}} \quad , \tag{3.15b}$$

one can easily verify that Eq. (3.13) is fulfilled and that R is given in terms of the new variables by

$$R = (\bar{R}^2 + \ell^2/\bar{P}^2)^{1/2} \quad . \tag{3.16}$$

The Hamiltonian thus takes the desired form in terms of the new variables

$$H_\ell(\bar{P},\bar{R}) = \bar{P}^2/2\mu + V([\bar{R}^2 + \ell^2/\bar{P}^2]^{1/2}) \quad , \tag{3.17}$$

and the S-matrix in this angular momentum representation has the one-dimensional form

$$S_\ell(E) = \exp\,[i\Phi_\ell(E)/\hbar] \quad , \tag{3.18}$$

where

$$\Phi_\ell(E) = -\int_{t_1}^{t_2} dt\ \bar{R}(t)\,\frac{d\bar{P}(t)}{dt} \quad . \tag{3.19}$$

Use of Eq. (3.15) shows that

$$\frac{d}{dt}\,F_2(R,\bar{P}) = \frac{\partial F_2(R,\bar{P})}{\partial R}\,\dot{R} + \frac{\partial F_2(R,\bar{P})}{\partial \bar{P}}\,\dot{\bar{P}}$$

$$= P\dot{R} + \bar{R}\dot{\bar{P}} \quad , \tag{3.20}$$

so that the phase in Eq. (3.19) is equivalently given by

$$\Phi_\ell(E) = -F_2(R,\bar{P})\Big|_{t_1}^{t_2} + \int_{t_1}^{t_2} dt\ P(t)\ \dot{R}(t) \quad . \tag{3.21}$$

By eliminating t in favor of R in the usual way it is then easy to show that

$$\Phi_\ell(E) = 2\hbar\eta_\ell(E) \quad ,$$

i.e.,

$$S_\ell(E) = \exp\,[2i\eta_\ell(E)] \quad , \tag{3.22}$$

where the phase shift is given by the standard WKB expression

$$\eta_\ell(E) = \frac{\pi}{2}\ell - kR + \int_{R_<}^{R} dR'\ k_\ell(R') \quad , \tag{3.23}$$

where $R \to \infty$ and $k_\ell(R) = \{2\mu[E - V(R)] - \ell^2/R^2\}^{1/2}/\hbar$; in practice[6] the replacement $\ell \to \ell+1/2$ is usually made.

B. Applications.

The first calculations using the theory described in the preceeding section were carried out by Miller[23] for the non-reactive collinear A + BC collision system for which Secrest and Johnson[24] had earlier obtained accurate quantum mechanical transition probabilities. Since this is a system of two degrees of freedom, and thus only one internal degree of freedom, Eq. (3.1) - (3.6) apply with the vector designation removed from the pair of action-angle variables (n,q).

Thus the $n_1 \to n_2$ vibrational transition is constructed from those trajectories which satisfy

$$n_2(\bar{q}_1) = n_2 \quad , \tag{3.24}$$

where $n_2(\bar{q}_1)$ (with the arguments n_1 and E suppressed) is the final vibrational quantum number, not necessarily integral, which result from the trajectory with the initial conditions in Eq. (3.2). Figure 1 shows this function for the case $n_1 = 1$, $E = 10\hbar\omega$, and for the potential parameters chosen to correspond to a He + H_2 collision. It is clear from the figure that there are two roots to Eq. (3.24) for the case $n_2 = 2$, for example, i.e., there are two classical trajectories that contribute to the 1 → 2 vibrational transition. The classical S-matrix element [Eq. (3.5)] for it is thus the sum of two terms

$$S_{n_2,n_1}(E) = [2\pi|n_2'(\bar{q}_I)|]^{-1/2} \exp(i\tfrac{\pi}{4} + i\Phi_I/\hbar)$$

$$+ [2\pi|n_2'(\bar{q}_{II})|]^{-1/2} \exp(-i\tfrac{\pi}{4} + i\Phi_{II}/\hbar) \quad , \tag{3.25}$$

where $\bar{q}_I$ and $\bar{q}_{II}$ are the two roots of Eq. (3.24), and Φ_I and Φ_{II} are the action integrals for these two trajectories. The transition probability,

$$P_{n_2,n_1}(E) \equiv |S_{n_2,n_1}(E)|^2 \quad , \tag{3.26}$$

is therefore the sum of the probabilities associated with the two trajectories plus an interference between the two:

$$P_{n_2,n_1}(E) = p_I + p_{II} + 2(p_I p_{II})^{1/2} \sin[(\Phi_{II} - \Phi_I)/h], \tag{3.27}$$

where

$$p_K = [2\pi|n_2{}'(\bar{q}_K)|]^{-1} \quad ,$$

K = I,II. The situation is quite analogous to the usual discussion[25] of the "two slit experiment", and just as there, it is not proper to say that the $n_1 \to n_2$ transition takes place via trajectory I or trajectory II, for logic would then demand that the probabilities add; rather there is a probability amplitude for the trajectory being I or II, and these amplitudes add.[25]

The calculations[23,26] show the semiclassical results to be in excellent agreement with the accurate quantum mechanical values. Furthermore, the interference term in Eq. (3.27) is quite significant in that the completely classical transition probability,

$$P_{n_2,n_1}{}^{CL}(E) \equiv p_I + p_{II} \quad , \tag{3.28}$$

gives poor results for individual transition probabilities. On the average, however, the classical transition probability [Eq. (3.28)] is correct, as seen in Figure 2, so that the purely classical treatment is adequate if one is interested in collision properties that involve an average over some initial and/or final quantum states.

The atom-rigid rotor collision in three-dimensions has also been treated by Miller[27], and the comparison with accurate quantum mechanical values is similar to the collinear results discussed above: individual S-matrix elements are described accurately only by proper inclusion[28] of interference between the various trajectories which contribute to the transition. If the transition probabilities are summed over several quantum states, however, the interference effects are quenched and the purely classical probability gives accurate results.

The conclusion which seems to be emerging from these examples, therefore, is that individual S-matrix elements, and thus the transition probability between a complete set of initial and final quantum numbers, cannot be described accurately without proper inclusion[28] of the interference terms provided by the classical S-matrix approach. If the transition probabilities or cross sections of interest are summed and/or averaged over some of the final or initial quantum numbers, however, the interference terms tend to average to zero so that the completely classical treatment becomes adequate.

The fact which makes interference effects so "fragile" is that there can be interference only between those processes which are <u>in principle indistinguishible</u>.[25] This means that only the transition probability, or cross section, for a <u>completely state-selected</u> quantity is given by the square modulus of an amplitude; an averaged cross section is not given by the square modulus of an average amplitude but rather by the average of the square modulus of the completely state-selected amplitude -- i.e.

$$\begin{aligned} \langle\sigma\rangle &= \langle|f|^2\rangle \\ &\neq |\langle f\rangle|^2 \quad . \end{aligned}$$

With regard to simple potential (elastic) scattering, for example, since there are no internal degrees of freedom the "completely state-selected" quantity is the differential cross section; thus

$$\sigma_E(\theta) = |f_E(\theta)|^2 \quad , \tag{3.29}$$

and $f_E(\theta)$ is constructed semiclassically[5,6,29] from the trajectories which satisfy the appropriate double-ended boundary conditions (i.e., that the energy be E and that the scattering angle be θ). Interference structure is thus readily observed in $\sigma_E(\theta)$, whereas it is usually quenched in the total cross section:

$$\begin{aligned}\sigma(E) &\equiv 2\pi \int_0^\pi d\theta \, \sin\theta \, \sigma_E(\theta) \\ &= \frac{\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell + 1) \, |S_\ell(E) - 1|^2 \quad ;\end{aligned} \tag{3.30}$$

i.e., even though the individual "transition probabilities"

$$|S_\ell(E) - 1|^2 \equiv 4 \sin^2[\eta_\ell(E)] \tag{3.31}$$

show prominent interference between the scattered particle and its "shadow", the sum over ℓ quenches it. (Under certain conditions a residual oscillatory term in σ(E) does survive the average over ℓ; this is the "glory" effect.[6])

For three-dimensional A + BC collisions[1] the completely state-selected quantity is the differential cross section from a given initial state $|n_1 j_1 m_1>$ to a specific final state $|n_2 j_2 m_2>$; it is thus given by the square modulus of an amplitude

$$\sigma_{n_2 j_2 m_2 \leftarrow n_1 j_1 m_1}(\theta) = |f_{n_2 j_2 m_2 \leftarrow n_1 j_1 m_1}(\theta)|^2 \quad , \qquad (3.32)$$

where the "classical amplitude" is constructed from the trajectories with the appropriate initial and final boundary conditions.[1,9] There should undoubtedly be significant interference effects in these completely state-selected differential cross sections, but any less detailed quantity, being an average of Eq. (3.32), will have the interference more or less quenched.

Although the practical difficulty of observing quantum interference effects on complex collisions is discouraging from one point of view (because a completely state-selected experiment is clearly quite difficult), it is encouraging to one who desires a relatively easy way of calculating observed scattering properties, for if interference is neglected the semiclassical expressions degenerate to purely classical ones. For classically allowed processes which involve an average over some of the initial or final quantum numbers, and/or the scattering angle, one therefore expects a purely classical (e.g. Monte Carlo) treatment to be adequate. This conclusion has been one of the reasons that most of the recent semiclassical work has dealt with classically forbidden processes (see Section IV) for which purely classical treatments are inapplicable.

With regard to reactive processes, there have been several attempts at applying classical S-matrix theory to the

$$H + H_2\ (n_1 = 0) \rightarrow H_2\ (n_2 = 0) + H \tag{3.32}$$

reaction in the energy region above the classical threshold.[30] Bowman and Kuppermann[31] and Wu and Levine[32] have treated it within the collinear model, and Tyson, Saxon, and Light[33] have considered the coplanar model. (George and Miller[34] and Doll, George, and Miller[35] have treated this same process within a collinear and fully three-dimensional models, respectively, in the energy region below the classical threshold for reaction, but this "classically forbidden" case will be discussed in Section IV.) For the collinear model the quantity of interest is the reaction probability as a function of collision energy; both groups of workers[31,32] find rough agreement between the semiclassical transition probability and their quantum mechanical results (apart from a resonance structure which is not reproduced semiclassically) for energies not too close to the classical threshold, with the semiclassical values becoming poor as the energy decreases to the classical threshold. The coplanar calculations of Tyson et al[33] are at one collision energy, for $j_1 = j_2 = 0$, and the differential, as well as total cross section has been considered; they also find rough agreement between the "primitive" semiclassical and quantum mechanical cross sections.

In neither the collinear nor the coplanar cases, however, is the agreement as quantitative as for the non-reactive applications discussed above. The difficulty lies in applying the appropriate <u>uniform</u> semiclassical expression, for the small differences between action integrals of the various trajectories which contribute to the 0 → 0 transition makes the "primitive" semiclassical expressions inaccurate. For the collinear case, for example, Figure 3 shows the reactive quantum number function $n_2(\bar{q}_1)$ of Wu and Levine[32] for the case $n_1 = 0$ and a total energy of 14.7 kcal/mole. Because the function is so "flat", i.e.,

$$|n_2(\bar{q}_1) - n_1| << 1$$

for all $\bar{q}_1$, the uniform semiclassical expression based on Airy functions[23] (which was used by Bowman and Kuppermann[31] and Wu and Levine[32]) is not applicable. (This is also true for an elastic non-reactive transition when all inelastic transitions are classically forbidden; this is of little concern, however, since one is usually not interested in the elastic transition probability in such cases.) A uniform semiclassical expression based on Bessel functions[36,37] is the appropriate one for this case, and one would expect it to give much more satisfactory results than those reported.[31,32]

[Briefly, the Bessel function uniform expression is generated from the primitive semiclassical expression

$$P_{n_2,n_1} = (p_I^{1/2} + p_{II}^{1/2})^2 \sin^2\left(\frac{\pi}{4} + \frac{\Delta\Phi}{2}\right)$$
$$+ (p_I^{1/2} - p_{II}^{1/2})^2 \cos^2\left(\frac{\pi}{4} + \frac{\Delta\Phi}{2}\right) \qquad (3.33)$$

by the replacement

$$\sin^2\left(\frac{\pi}{4} + \frac{\Delta\Phi}{2}\right) \rightarrow \frac{\pi}{2}(z^2 - n^2)^{1/2} J_n(z)^2 \qquad (3.34a)$$
$$\cos^2\left(\frac{\pi}{4} + \frac{\Delta\Phi}{2}\right) \rightarrow \frac{\pi}{2}(z^2 - n^2)^{1/2} J_n'(z)^2/\left(1 - \frac{n^2}{z^2}\right) \quad , \qquad (3.34b)$$

where $n = |n_2 - n_1|$ and z is defined by the equation

$$(z^2 - n^2)^{1/2} - n \cos^{-1}(n/z) = \frac{\Delta\Phi}{2} \quad . \qquad (3.35)$$

See reference 37 for a derivation. In cases where the Airy function expression is valid, the two uniform semiclassical expressions are essentially equivalent. For the case of present interest, $n_1 = n_2 = 0$, and Eqs. (3.33) and (3.34) become

$$P_{n_2,n_1}^{UN} = \frac{\pi}{4} \Delta\Phi \left[(p_I^{1/2} + p_{II}^{1/2})^2 J_o\left(\frac{\Delta\Phi}{2}\right)^2\right.$$
$$\left. + (p_I^{1/2} - p_{II}^{1/2})^2 J_1\left(\frac{\Delta\Phi}{2}\right)^2 \right] \quad , \qquad (3.36)$$

where the fact has been used that $J_o'(z) = -J_1(z)$.]

Figure 4 shows another example of the collinear reactive quantum number function $n_2(\bar{q}_1)$ from the paper of Wu and Levine,[32] this one also for $n_1 = 0$ and for a total energy of 13.7 kcal. Here the function is considerably more complicated than those of Figure 1 or Figure 3, there being four trajectories that contribute to the $0 \rightarrow 0$ reaction. At first glance one might expect no semiclassical treatment to be possible; Connor,[38] however, has developed more general uniform semiclassical formulae which take account of four terms, and it would clearly be desirable to see if these expressions give more accurate results for this application.

In highly quantum-like situations such as these, therefore, it is necessary to use the appropriate uniform semiclassical expressions to obtain quantitative results for transitions between individual quantum states. There will, too, undoubtedly be cases for which the quantum number function is too highly structured for any semiclassical treatment to be quantitatively useful.

Finally, I would like to discuss briefly the bi-modal structure that has been observed recently in product vibrational state distributions in three-dimensional classical trajectory calculations.[39] It is illustrative to see how this arises even in the simplest situation, the non-reactive collinear model. Within a completely classical framework, neglecting semiclassical interference terms, the $n_1 \rightarrow n_2$ vibrational transition probability of Eq. (3.28) is

$$P_{n_2,n_1}{}^{CL} = [2\pi\ |n_2{}'(\bar{q}_I)|]^{-1}$$

$$+ [2\pi\ |n_2{}'(\bar{q}_{II})|]^{-1} \qquad , \tag{3.37}$$

where $\bar{q}_I$ and $\bar{q}_{II}$ are the roots of Eq. (3.24). Considering n_2 for the moment to be a continuous variable, as n_2 approaches the maximum or the minimum of $n_2(\bar{q}_1)$ (See Figure 1) it is clear that the transition probability in Eq. (3.37) becomes infinite (because $n_2{}'(\bar{q}_1) \to 0$.) As a continuous function of n_2, the $n_1 \to n_2$ transition probability will thus have the qualitative shape sketched in Figure 5 (which also shows the semiclassical interference).

In a Monte Carlo calculation the classical probability of Eq. (3.37) is actually not the quantity calculated, but rather this transition probability averaged over the final quantum number:

$$P_{n_2 \leftarrow n_1}{}^{AV} \equiv \int_{n_2 - 1/2}^{n_2 + 1/2} dn_2 \quad P_{n_2,n_1}{}^{CL} \qquad , \tag{3.38}$$

and one can easily see that this gives

$$P_{n_2 \leftarrow n_1}{}^{AV} = \Delta q_1/2\pi \qquad , \tag{3.39}$$

where Δq_1 is the increment of the $\bar{q}_1$ interval for which

$$n_2 - \frac{1}{2} \leq n_2(\bar{q}_1) \leq n_2 + \frac{1}{2} \qquad . \tag{3.40}$$

This averaging procedure rounds off the two classical infinites, leaving finite peaks; for the case $n_1 = 0$ the two peaks usually overlap so that there is just one peak, but this need not always be the case.

The bimodal structure of the vibrational state distribution is thus simply a result of the fact that $n_2(\bar{q}_1)$ has one maximum and one minimum. The effect is entirely analogous to the classical rainbow[5,6] in elastic scattering which results because the deflection function $\Theta(b)$ has a minimum. It is possible, too, that $n_2(\bar{q}_1)$ could have more than one relative maximum and minimum, hence the classical vibrational state distribution would have more than two maxima. If semiclassical interference is taken account of, then there can of course be any number of peaks in the vibrational state distribution even though $n_2(\bar{q}_1)$ has just one maximum and one minimum (cf. Figure 2).

C. Complex Formation; Resonances.

As noted in the Introduction, all quantum effects are a direct result of the superposition principle and must therefore be contained, at least qualitatively within the semiclassical model. This section discusses more explicitly how scattering resonances arise semiclassically.

Consider first the case of a potential, or "single particle" resonance which results from one-dimensional tunneling through a potential barrier (see Figure 6). T, the probability of tunneling through the barrier, is given by[40]

$$T = e^{-2\theta}/(1 + e^{-2\theta}) \quad , \tag{3.41}$$

where θ is the barrier penetration integral

$$\theta = \int_{r_2}^{r_3} dr\ \{2m[V(r)-E]/\hbar^2\}^{1/2} \quad ; \tag{3.42}$$

$R \equiv 1-T$, the probability of reflection from the barrier, is

$$R = (1 + e^{-2\theta})^{-1} \quad .$$

The one-dimensional S-matrix is given by a sum of amplitudes, one for each possible trajectory. (There is more than one trajectory because tunneling is being allowed for.) The simplest possible trajectory is one that comes in from large r and is reflected at $r = r_3$; the amplitude associated with this is

$$R^{1/2}\ e^{\frac{-i\pi}{2}\ 2i\eta_o} \quad , \tag{3.43}$$

where

$$\eta_o = \lim_{r \to \infty} [-kr + \int_{r_3}^{r} dr'\ k(r')] \tag{3.44}$$

$$k(r) = \{2m[E - V(r)]/\hbar^2\}^{1/2}$$

$$k = k(\infty) \quad .$$

The pre-exponential factor is the square root of the probability for this trajectory (a reflection at the barrier), the phase $-\frac{\pi}{2}$ results any time a reflection occurs, and the phase η_o is the usual semiclassical phase shift for motion from $r = \infty$ to $r = r_3$ and back to $r = \infty$.

Another possible trajectory is one that comes in from infinity, travels through the barrier, moves across the potential well and back, and then tunnels back out through the barrier. The amplitude associated with this trajectory is

$$(T^{1/2})^2 \; e^{-i\frac{\pi}{2}} \; e^{2i\phi} \; e^{2i\eta_o} \qquad , \tag{3.45}$$

where ϕ is the phase integral across the potential well

$$\phi = \int_{r_1}^{r_2} dr\, k(r) \qquad ;$$

the probability factor corresponds to the fact that two tunnelings are required. A third possible trajectory is similar to the previous one except that instead of tunneling back out of the potential well, it is reflected at the barrier and makes an additional passage back and forth across the well before tunneling out. This trajectory involves two tunnelings, one barrier reflection, and two reflections at $r = r_1$, so that the amplitude associated with it is

$$(T^{1/2})^2 \; R^{1/2} \; (e^{-i\frac{\pi}{2}})^3 \; e^{4i\phi} \; e^{2i\eta_o} \qquad . \tag{3.46}$$

These three trajectories are depicted schematically in Figure 7. Clearly there are an infinite number of possible trajectories arising from the various number of oscillations the particle may make back and forth across the well before it tunnels back out through the barrier. The amplitude for the trajectory that makes N round trips across the well is

$$(T^{1/2})^{2} \quad (R^{1/2})^{N-1} \quad (e^{-i\frac{\pi}{2}})^{2N-1} \quad e^{2iN\phi} \quad e^{2i\eta_o} \quad . \tag{3.47}$$

The S-matrix, being the sum of the amplitudes for all possible trajectories, is thus given by

$$S = R^{1/2} \, e^{\frac{-i\pi}{2}} \, e^{2i\eta_o} + (T^{1/2})^{2} \, e^{2i\eta_o} \sum_{N=1}^{\infty} (R^{1/2})^{N-1} (e^{-i\frac{\pi}{2}})^{2N-1} \, e^{2iN\phi} \quad , \tag{3.48}$$

and this geometric series can be summed to give

$$S = -ie^{2i\eta_o} \left[R^{1/2} + \frac{Te^{2i\phi}}{1 + R^{1/2} \, e^{2i\phi}} \right] \tag{3.49}$$

$$= -ie^{2i\eta_o} \left[\frac{R^{1/2} + e^{2i\phi}}{1 + R^{1/2} e^{2i\phi}} \right] \quad . \tag{3.50}$$

Furthermore, it is not difficult to show that

$$\frac{R^{1/2} + e^{2i\phi}}{1 + R^{1/2} e^{2i\phi}} = e^{2i\eta_r} \quad , \tag{3.51}$$

where

$$\eta_r = \tan^{-1}\left\{\tan\phi\left[\frac{(1 + e^{-2\theta})^{1/2} - 1}{(1 + e^{-2\theta})^{1/2} + 1}\right]\right\} , \tag{3.52}$$

so that the net phase shift is

$$\eta = \eta_o + \eta_r \quad . \tag{3.53}$$

Eqs. (3.52) and (3.53) are the semiclassical result that has been obtained previously by a number of other approaches.[5,41,42]

A "resonance" thus occurs from the constructive interference of the many trajectories which contribute to the process (elastic scattering in this case). To see this more explicitly, suppose the energy E is far below the top of the barrier so that

$$R \simeq 1$$
$$T << 1 \quad ;$$

the sum of multiply reflected terms in Eq. (3.48) is then given approximately by

$$i\ T\ e^{2i\eta_o} \sum_{N=1}^{\infty} e^{2iN(\phi - \frac{\pi}{2})} \quad . \tag{3.54}$$

Each term contributes very little (since $T << 1$), but there are many of them. If $\phi \equiv \phi(E)$ is such that

$$\phi(E) - \frac{\pi}{2} = n\pi \quad , \tag{3.55}$$

n being an integer, then

$$e^{2iN(\phi - \frac{\pi}{2})} = 1 \qquad (3.56)$$

for all N, and the sum in Eq. (3.54) is infinite. Eq. (3.55) is thus the condition that all the terms in Eq. (3.54) add up in phase and cause a resonance; it is also recognized as the WKB (Bohr-Sommerfeld) quantum condition[43] for the potential well.

Proceeding more formally,[44] the definition of a resonance is that the S-matrix, considered as a function of the (complex-valued) energy, have a pole; the real part of this complex pole is the energy at which the resonance occurs, and its imaginary part is the width of the resonance, or reciprocal lifetime of the collision complex. Referring to Eq. (3.50), the semiclassical S-matrix has a pole if

$$1 + R^{1/2}\, e^{2i\phi} = 0 \quad ,$$

or

$$(1 + e^{-2\theta})^{1/2} + e^{2i\phi} = 0 \quad ,$$

or

$$\phi = \frac{1}{2i}\, \ell n\, [-(1 + e^{-2\theta})^{1/2}] \quad ,$$

or

$$\phi(E) = (n + \frac{1}{2})\pi - \frac{i}{4}\, \ell n[1 + e^{-2\theta(E)}] \quad , \qquad (3.57)$$

where it has been emphacized that ϕ and θ are both functions of E. For the case that the energy is far below the top of the barrier,

$$e^{-2\theta} \ll 1 \quad ,$$

and one can write

$$E = E_r - i\Gamma/2$$

with

$$\Gamma \ll E_r \quad ;$$

thus

$$\phi(E) = \phi(E_r - i\frac{\Gamma}{2})$$

$$\simeq \phi(E_r) - i\frac{\Gamma}{2}\,\phi'(E_r)$$

and

$$\ell n(1 + e^{-2\theta}) \simeq e^{-2\theta} \quad ,$$

so that from these approximations and Eq. (3.57) one identifies E_r as determined by the quantum condition of Eq. (3.55) with Γ given by

$$\Gamma = \frac{1}{2}\, e^{-2\theta}/\phi'(E_r) \quad . \tag{3.58}$$

The potential resonances discussed above are "classically forbidden" processes (see Section IV) in that they involve tunneling. "Classically allowed" complex formation is possible only for systems that have internal degrees of freedom in addition to translation; i.e., classically allowed resonances must be "multiparticle resonances". These internal excitation, or Feshbach resonances result from an energy transfer mechanism: if the interaction between A and BC is attractive, when they collide more energy may be transferred into excitation of the internal degrees of freedom than is energetically possible when A and BC are infinitely separated. As A and BC attempt to separate, therefore, a translational turning point is encountered so that A and BC suffer another collision, and so forth, until the internal degrees of freedom loose sufficient energy for A and BC (or AB and C, for example, if reactive processes are possible) to separate.

Classical complex formation such as outlined above has been observed in a number of classical Monte Carlo trajectory studies,[45] and Brumer and Karplus[46] have recently reported an extensive study of alkali halide - alkali halide reactions which involve long-lived collision complexes. These purely classically studies cannot, of course, describe the resonance structure in the energy dependence of scattering properties, but rather give an average energy dependence; the resonance structure, a quantum effect, is described only by a theory which contains the quantum principle of superposition.

To see how Feshbach resonances appear in classical S-matrix theory, consider the collinear H + $C\ell_2$ collision as studied by Rankin and Miller.[47] Figure 8 shows the quantum number function $n_2(\bar{q}_i)$; for one region of $\bar{q}_1$ the function is smooth, these trajectories being "direct". The remaining interval of $\bar{q}_1$ leads to complex trajectories, those which spend a number of additional vibrational periods in the interaction region; for this region of $\bar{q}_1$ values the final vibrational quantum number changes dramatically with small changes in $\bar{q}_1$. The S-matrix for the particular transition indicated in Figure 8 thus has the form

$$S = S_D + S_R \quad , \tag{3.59}$$

where S_D is the "direct" contribution which is constructed in the usual semiclassical fashion from the two direct trajectories; the "complex" contribution is the sum of many terms

$$S_R = \sum_K [2\pi i \; n_2'(\bar{q}_K)]^{-1/2} \exp(i\Phi_K/\hbar) \quad . \tag{3.60}$$

Analogous to Eq. (3.54) in the discussion of potential resonances, each term in Eq. (3.60) makes a small contribution (because $n_2'(\bar{q}_K)$ is very large), but there are many such terms. Since the various complex trajectories differ from one another essentially by the number of oscillations of the collision complex before it decomposes, the action integrals Φ_K differ roughly by integer multiples of the action integral for an oscillation of the complex. Thus if the energy is such that

$$\Phi_K - \Phi_{K'} = 2\pi \times \text{integer},$$

the terms in Eq. (3.60) will add up in phase to cause a resonance in the scattering; at other energies the interference is destructive and $S_R \simeq 0$. The "average" resonance contribution to the transition probability--i.e., the quantity obtained in classical Monte Carlo trajectory calculations[45,46]--results if one discards interference terms in $|S_R|^2$ (since they are quenched by averaging over an energy interval larger than the resonance widths) and averages over the final vibrational quantum number (cf. the discussion related to Eqs. (3.38) - (3.40)):

$$
\begin{aligned}
|S_R|^2 &\simeq \int_{n_2 - \frac{1}{2}}^{n_2 + \frac{1}{2}} dn_2 \sum_K [2\pi|n_2'(\bar{q}_K)|]^{-1} \\
&= \Delta q_1/2\pi \quad ,
\end{aligned}
$$

Δq_1 being the increment of the $\bar{q}_1$ interval for which $n_2(\bar{q}_1)$ is in the interval $(n_2 - \frac{1}{2}, n_2 + \frac{1}{2})$. This average probability is also the quantity for which statistical approximations are often good.[46,47]

The reader will recognize that the semiclassical origin of the resonance, namely the constructive interference of the amplitudes associated with the many trajectories that arise from a collision complex, is the same for Feshbach (multiparticle) resonances as for potential (single-particle) resonances. The physical mechanism causing the collision complex is quite different, however, being barrier tunneling for the case of a single degree of freedom and an energy transfer between degrees of freedom for the Feshbach case.

From the point of view of numerical calculations it would appear that the semiclassical treatment of Feshbach resonances is quite impractical. By looking at Figure 8 it is clear the difficulty one would have in finding all the roots of the semiclassical relation

$$n_2(\bar{q}_1) = n_2$$

which are needed to construct the resonance contribution to the S-matrix [Eq. (3.60)]. Recently Marcus[48] has developed a semiclassical treatment of Feshbach resonances that attempts to go beyond the "primitive" semiclassical description outlined above. It may be that this could turn out to have some practical utility.

D. Atom-Surface Scattering.

As another application of classical S-matrix theory it is interesting to see how the scattering of atoms from a solid surface is described. (The extension to scattering of molecules should also be clear.) This has been worked out by Doll[49] and closely parallels Wolken's[50] quantum mechanical formulation of the problem.

By "solid surface" one means that the surface is being represented by a potential, $V(\vec{r})$, so that the Hamiltonian for the particle is

$$H(\underset{\sim}{p},\underset{\sim}{r}) = p^2/2\mu + V(\underset{\sim}{r}) \quad , \tag{3.61}$$

where $\underset{\sim}{r} = (x,y,z)$ and $\underset{\sim}{p} = p_x,p_y,p_z)$. z is the direction perpendicular to the surface, i.e.,

$$\lim_{z\to\infty} V(x,y,z) = 0$$

$$\lim_{z\to-\infty} V(x,y,z) = +\infty \quad ,$$

and the surface periodicity is

$$V(x,y,z) = V(x + ma_x, y + na_y, z) \quad , \tag{3.62}$$

where m and n are integers of (a_x,a_y) are the unit cell dimensions.

If $\underset{\sim}{k}_1$ is the initial wave vector of the particle, i.e., $\hbar\underset{\sim}{k}_1$ is the initial momentum, then the quantity of interest is

$$P_{\underset{\sim}{k}_2 \leftarrow \underset{\sim}{k}_1}$$

the probability that the final wave vector is $\underset{\sim}{k}_2$; quantum mechanically, this is given by the square modulus of a probability amplitude, or S-matrix element

$$P_{\underset{\sim}{k}_2 \leftarrow \underset{\sim}{k}_1} = \left| S_{\underset{\sim}{k}_2 \leftarrow \underset{\sim}{k}_1} \right|^2 \quad .$$

Since internal degrees of freedom of the surface are being neglected, the scattering of the atom must be elastic, i.e.

$$\underset{\sim}{k}_1 \cdot \underset{\sim}{k}_1 = \underset{\sim}{k}_2 \cdot \underset{\sim}{k}_2 \quad , \tag{3.63}$$

so that only two components of the wave vector can change independently, k_x and k_y, say. Thus one actually seeks the S-matrix on the "energy shell"

$$S_{k_{x_2} \; k_{y_2} \leftarrow k_{x_1} \; k_{y_1}}(E) \quad . \tag{3.64}$$

Since the desired S-matrix element is in a cartesian momentum representation, it is clear from the general prescription outlined in Section III A that the <u>classical</u> S-matrix is given by

$$S_{k_{x_2} k_{y_2} \leftarrow k_{x_1} k_{y_1}}(E) = C \left[\frac{\partial(k_{x_2}, k_{y_2})}{\partial(\bar{x}_1, \bar{y}_1)} \right]^{-1/2} \exp[i\Phi(\underset{\sim}{k}_2, \underset{\sim}{k}_1)/\hbar] \tag{3.65}$$

where the action integral Φ is

$$\Phi(\underset{\sim}{k}_2,\underset{\sim}{k}_1) = -\int_{t_1}^{t_2} dt\ (\underset{\sim}{r} \cdot \dot{\underset{\sim}{p}})$$

$$= -\int_{t_1}^{t_2} dt\ (x\dot{p}_x + y\dot{p}_y + z\dot{p}_z) \quad . \tag{3.66}$$

The meaning of Eq. (3.65) is analogous to Eq. (3.5): the initial conditions for a trajectory are specified as[51]

$$\begin{aligned} p_{x_1} &= \hbar k_{x_1} \\ p_{y_1} &= \hbar k_{y_1} \\ p_{z_1} &= -(2mE - p_{x_1}^2 - p_{y_1}^2)^{1/2} \\ z_1 &= \text{large and positive} \\ y_1 &= \bar{y}_1 + p_{y_1} z_1/p_{z_1} \\ x_1 &= \bar{x}_1 + p_{x_1} z_1/p_{z_1} \quad ; \end{aligned} \tag{3.67}$$

$K_{x_2}(\bar{x}_1,\bar{y}_1)$ and $K_{y_2}(\bar{x}_1,\bar{y}_1)$ are the final values of k_x and k_y that result from this trajectory, and the S-matrix element in Eq. (3.65) is constructed from the trajectory (or trajectories) which satisfies

$$\begin{aligned} K_{x_2}(\bar{x}_1,\bar{y}_1) &= k_{x_2} \\ K_{y_2}(\bar{x}_1,\bar{y}_1) &= k_{y_2} \quad . \end{aligned} \tag{3.68}$$

The constant C in Eq. (3.65) is a normalization factor that will be specified below. As usual, if there is more than one root to Eq. (3.68), Eq. (3.65) is a sum of terms, one for each such trajectory.

Let $\overset{o}{S}_{k_{x_2} k_{y_2} \leftarrow k_{x_1} k_{y_1}}(E)$ be the S-matrix of Eq. (3.65) that is constructed from all roots of Eq. (3.68) for which $\bar{x}_1$ and $\bar{y}_1$ lie in one unit cell:

$$\begin{aligned} 0 &\leq \bar{x}_1 \leq a_x \\ 0 &\leq \bar{y}_1 \leq a_y \end{aligned} \tag{3.69}$$

If $\bar{x}_1$ and $\bar{y}_1$ satisfy Eq. (3.68), then it is clear from the symmetry of the potential energy function [Eq. (3.62)] that a root to Eq. (3.68) will also result if one makes the replacement

$$\begin{aligned} \bar{x}_1 &\rightarrow \bar{x}_1 + ma_x \\ \bar{y}_1 &\rightarrow \bar{y}_1 + na_y \quad , \end{aligned} \tag{3.70}$$

where m and n are integers. The resulting trajectory is identical to the original one, simply shifted an integral number of unit cell dimension parallel to the surface:

$$\begin{aligned} x(t) &\rightarrow x(t) + ma_x \\ y(t) &\rightarrow y(t) + na_y \\ z(t) &\rightarrow z(t) \\ \underset{\sim}{p}(t) &\rightarrow \underset{\sim}{p}(t) \end{aligned}$$

for all t. The pre-exponential factor in Eq.(3.65) is the same for the two symmetrically related trajectories, but the phase, defined by Eq. (3.66), is changed according to

$$\phi(\underset{\sim}{k}_2,\underset{\sim}{k}_1) \to -\int_{t_1}^{t_2} dt\{[x(t) + ma_x]\,\dot{p}_x + [y(t) + na_y]\dot{p}_y + z(t)\,\dot{p}_z\}$$

$$= \phi(\underset{\sim}{k}_2,\underset{\sim}{k}_1) - ma_x(p_{x_2} - p_{x_1}) - na_y(p_{y_2} - p_{y_1}) \ . \qquad (3.71)$$

The contribution to the S-matrix from this new trajectory is therefore given by

$$S_{k_{x_2}k_{y_2} \leftarrow k_{x_1}k_{y_1}}(E) = S^{0}_{k_{x_2}k_{y_2} \leftarrow k_{x_1}k_{y_1}}(E) \exp\,(-ima_x\Delta k_x - ina_y\,\Delta k_y) \quad , \qquad (3.72)$$

where $\Delta k_x = k_{x_2} - k_{x_1}$, $\Delta k_y = k_{y_2} - k_{y_1}$.

Since the above arguments are valid for any integers m and n, the S-matrix element that results from all roots,

$$-\infty < \bar{x}_1 < \infty$$

$$-\infty < \bar{y}_1 < \infty$$

is

$$S_{k_{x_2}k_{y_2} \leftarrow k_{x_1}k_{y_1}}(E) = S^{o}_{k_{x_2}k_{y_2} \leftarrow k_{x_1}k_{y_1}} \sum_{m,n=-\infty}^{\infty} \exp[-ima_x\Delta k_x -ina_y\Delta k_y]$$

$$= S^{o}_{k_{x_2}k_{y_2} \leftarrow k_{x_1}k_{y_1}}(E) \left(\sum_{m=-\infty}^{\infty} \exp(-ima_x\Delta k_x)\right) \times \left(\sum_{n=-\infty}^{\infty} \exp(-ina_y\Delta k_y)\right) \quad . \qquad (3.73)$$

If

$$a_x\Delta k_x = 2\pi \times (\text{integer}) \quad ,$$

then the sum over m will be infinite (since all the terms are unity); it vanishes otherwise. Stated more precisely, the Poisson sum formula implies that

$$\sum_{m=-\infty}^{\infty} \exp(-ima_x\Delta k_x) = \sum_{m=-\infty}^{\infty} \delta\left(m - \frac{a_x\Delta k_x}{2\pi}\right) \quad , \qquad (3.74)$$

and similarly for the sum over n:

$$\sum_{n=-\infty}^{\infty} \exp(-ina_y\Delta k_y) = \sum_{n=-\infty}^{\infty} \delta\left(n - \frac{a_y\Delta k_y}{2\pi}\right) \quad . \qquad (3.75)$$

The interference of all symmetrically related trajectories, i.e., the quantum principle of superposition, thus leads to the Bragg diffraction law which allows only certain discrete changes in the x and y components of momentum. The S-matrix element S^o, which is constructed from those trajectories with initial values $\bar{x}_1$ and $\bar{y}_1$ restricted to one cell, is the S-matrix on the "diffraction spot shell".

To summarize in more convenient notation, let E be the initial translational energy and (θ_i,ϕ_i) the polar and azimuthal angles of incidence. The initial conditions for a trajectory are specified by

$$p_{x_1} = \hbar k \sin\theta_i \cos\phi_i$$

$$p_{y_1} = \hbar k \sin\theta_i \sin\phi_i$$

$$p_{z_1} = -\hbar k \cos\theta_i \quad ; \tag{3.76}$$

where $\hbar k = (2mE)^{1/2}$, and with (x_1,y_1,z_1) given as in Eq. (3.67). From the final values of the x and y components of momentum one defines the "diffraction order" functions

$$M(\bar{x}_1,\bar{y}_1) = (k_{x_2} - k_{x_1})\, a_x/2\pi$$

$$N(\bar{x}_1,\bar{y}_1) = (k_{y_2} - k_{y_1})\, a_y/2\pi \quad . \tag{3.77}$$

The relative intensity of the (m,n) diffraction spot is then given by

$$P_{mn}(E) = |S_{mn}(E)|^2 \quad , \tag{3.78}$$

where

$$S_{mn}(E) = \Sigma \left[a_x\ a_y \frac{\partial(M,N)}{\partial(\bar{x}_1,\bar{y}_1)} \right]^{-1/2} \exp(i\Phi_{mn}/\hbar), \qquad (3.79)$$

with $\bar{x}_1$ and $\bar{y}_1$ determined by the "quantum conditions"

$$M(\bar{x}_1,\bar{y}_1) = m$$

$$N(\bar{x}_1,\bar{y}_1) = n \quad , \qquad (3.80)$$

and where Φ_{mn} is given by Eq. (3.66); the sum in Eq. (3.79) is over all the roots $\bar{x}_1$ and $\bar{y}_1$ in the intervals $(0,a_x)$ and $0,a_y)$, respectively. The proper constants have been supplied in Eq. (3.79) so that the relative intensities are normalized to unity within the usual classical limit:

$$\begin{aligned} \sum_{m,n} P_{mn} &\simeq \int dm \int dn\ |S_{mn}|^2 \\ &\simeq \int dm \int dn\ (a_x a_y)^{-1} \left| \frac{\partial(M,N)}{\partial(\bar{x}_1,\bar{y}_1)} \right|^{-1} \\ &= (a_x a_y)^{-1} \int_0^{a_x} d\bar{x}_1 \int_0^{a_y} d\bar{y}_1 \qquad (1) \\ &= 1 \quad . \end{aligned}$$

With a semiclassical description such as this it is possible to discuss rainbow phenomena[53] in a manner parallel to the treatment in elastic scattering.[5,6] Doll[49] has also discussed the "quenching" of the diffraction spots which results when imperfect periodicities of the lattice are taken into account.

E. Photodissociation.

The final application of classical S-matrix theory to be discussed is the description of photodissociation of a complex (e.g., triatomic) molecule. The completely classical description, essentially the "half-collision" model of Holdy, Klutz, and Wilson,[54] is discussed first, and then the semiclassical version of the theory is presented. A completely quantum mechanical description of the process has been developed in detail recently by Shapiro.[55]

The quantity of interest is the transition dipole,

$$\langle E_2\ \underset{\sim}{n}_2 | \vec{\mu} | \underset{\sim}{N}_1 \rangle \quad , \tag{3.81}$$

which describes the process

$$\mathrm{ABC}\ (\underset{\sim}{N}_1) + h\nu \rightarrow \mathrm{A} + \mathrm{BC}\ (\underset{\sim}{n}_2) \quad , \tag{3.82}$$

where the total energy of the final (dissociated) state, E_2, is related to the photon's energy by

$$E_2 - E_1\ (\underset{\sim}{N}_1) = h\nu \quad ; \tag{3.83}$$

from this dipole matrix element the absorption coefficient is given by standard formulae.[56] The classical Hamiltonian for the ground electronic state is of the form

$$H_1(\mathbf{p},\mathbf{r}) = \mathbf{p}^2/2m + V_1(\mathbf{r}) \quad , \tag{3.84}$$

where $(\mathbf{p},\mathbf{r})$ are the cartesian coordinates and momenta of the system. To define the initial state $|\mathbf{N}_1>$ semiclassically, however, it is necessary to introduce the action-angle variables $(\mathbf{N},\mathbf{Q})$ for the ground state potential energy surface V_1; this requires that $V_1(\mathbf{r})$ be separable, and in most applications one would probably go further and assume it to be harmonic. A particular set of integer values of the action variables $\mathbf{N}$, $\mathbf{N}_1$, is the classical, or semiclassical equivalent of the quantum state $|\mathbf{N}_1>$, and the energy $E_1(\mathbf{N}_1)$ is simply the Hamiltonian H_1 expressed in terms of the action-angle variables:

$$\begin{aligned} E_1(\mathbf{N}_1) &= H_1\ (\mathbf{p}(\mathbf{N}_1,\mathbf{Q}_1)\ ,\ \mathbf{r}(\mathbf{N}_1,\mathbf{Q}_1)) \\ &= H_1(\mathbf{N}) \quad . \end{aligned} \tag{3.85}$$

(Note that rotational effects are being neglected in this simplified discussion; if one assumes that rotation and vibration are separable, then it is a trivial matter to incorporate rotation explicitly.) The state $|E_2\mathbf{n}_2>$ in Eq. (3.81) is a scattering state on the excited electronic potential surface $V_2(\mathbf{r})$, the state corresponding to total energy E_2 and to BC being asymptotically in state $|\mathbf{n}_2>$; since the quantum numbers $\mathbf{n}_2$ refer to the diatomic fragment BC with A infinitely separated, no assumptions about the potential surface $V_2(\mathbf{r})$ are required.

It is simplest first to use the phase space approach discussed in Section II B to construct the purely classical expression for the square modulus of the dipole matrix element in Eq. (3.81). Thus if M denotes the total number of degrees of freedom, one has

$$|\langle E_2\mathbf{n}_2|\vec{\mu}|\mathbf{N}_1\rangle|^2 = (2\pi\hbar)^{-M} \int d\bar{\mathbf{p}} \int d\bar{\mathbf{p}}_1 \;\; \mu(\mathbf{r}(\bar{\mathbf{p}}_1,\bar{\mathbf{q}}_1))^2$$

$$\times\, \delta_M[\mathbf{N}_1 - \mathbf{N}(\bar{\mathbf{p}}_1,\bar{\mathbf{q}}_1)]\;\; \delta_{M-1}[\mathbf{n}(\bar{\mathbf{p}}_1,\bar{\mathbf{q}}_1) - \mathbf{n}_2]\;\; \delta[E_2 - H_2(\bar{\mathbf{p}}_1,\bar{\mathbf{q}}_1)], \quad (3.86)$$

where $(\bar{\mathbf{p}}_1,\bar{\mathbf{q}}_1)$ is an arbitrary set of canonical variables (since phase space integrals are invariant to a canonical transformation), $\mathbf{n}(\bar{\mathbf{p}}_1,\bar{\mathbf{q}}_1)$ is the set of M-1 quantum numbers of BC that result from a (dissociative) trajectory that begins on the excited potential surface $V_2(\mathbf{r})$ with initial conditions $(\bar{\mathbf{p}}_1,\bar{\mathbf{q}}_1)$, and $\mathbf{N}(\bar{\mathbf{p}}_1,\bar{\mathbf{q}}_1)$ is the set of M vibrational quantum numbers of the ground state potential surface expressed in terms of the variables $(\bar{\mathbf{p}}_1,\bar{\mathbf{q}}_1)$; the subscripts on the delta functions denote their dimensionality. $H_2(\bar{\mathbf{p}}_1,\bar{\mathbf{q}}_1)$ is the classical Hamiltonian for the excited potential surface expressed in terms of $(\bar{\mathbf{p}}_1,\bar{\mathbf{q}}_1)$, and $\vec{\mu}(\mathbf{r})$ is the transition dipole function.[57] In terms of cartesian coordinates and momenta the Hamiltonian H_2 is

$$H_2(\mathbf{p},\mathbf{r}) = \mathbf{p}^2/2m + V_2(\mathbf{r}) \quad , \qquad (3.87)$$

but in order to evaluate Eq. (3.86) it is most convenient to choose $(\bar{\mathbf{p}},\bar{\mathbf{q}})$ to be the action-angle variables $(\mathbf{N},\mathbf{Q})$; Eq. (3.86) then becomes

$$|\langle E_2 \underset{\sim}{n}_2|\vec{\mu}|\underset{\sim}{N}_1\rangle|^2 = (2\pi\hbar)^{-M} \int d\underset{\sim}{Q}_1 \; \mu(\underset{\sim}{r}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1))^2$$

$$\times\, \delta_{M-1}[\underset{\sim}{n}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1) - \underset{\sim}{n}_2] \;\; \delta[E_2 - H_2(\underset{\sim}{N}_1,\underset{\sim}{Q}_1)] \quad . \tag{3.88}$$

Since

$$\begin{aligned} H_2 &= \underset{\sim}{p}^2/2m + V_2(\underset{\sim}{r}) \\ &= \underset{\sim}{p}^2/2m + V_1(\underset{\sim}{r}) + V_2(\underset{\sim}{r}) - V_1(\underset{\sim}{r}) \\ &= H_1 + \Delta V(\underset{\sim}{r}) \\ &= E_1(\underset{\sim}{N}_1) + \Delta V(\underset{\sim}{r}(\underset{\sim}{N}_1\underset{\sim}{Q}_1)) \quad , \end{aligned}$$

where $\Delta V = V_2 - V_1$, Eq. (3.88) becomes

$$|\langle E_2 \underset{\sim}{n}_2|\vec{\mu}|\underset{\sim}{N}_1\rangle|^2 = (2\pi\hbar)^{-M} \int d\underset{\sim}{Q}_1 \; \mu(\underset{\sim}{r}_1)^2$$

$$\delta_{M-1}[\underset{\sim}{n}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1) - \underset{\sim}{n}_2] \;\; \delta[E_2 - E_1 - \Delta V(\underset{\sim}{r}_1)] \quad , \tag{3.89}$$

where $\underset{\sim}{r}_1 = \underset{\sim}{r}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1)$. Because of the M delta function factors in Eq. (3.89), the M-fold integral over Q_1 can be carried out, giving the final result

$$|\langle E_2 \underset{\sim}{n}_2|\vec{\mu}|\underset{\sim}{N}_1\rangle|^2 = \mu(\underset{\sim}{r}_1)^2 \left[(2\pi\hbar)^M \left|\frac{\partial(\underset{\sim}{n},\Delta V)}{\partial \underset{\sim}{Q}_1}\right|\right]^{-1} \quad , \tag{3.90}$$

where the M-dimensional Jacobian determinant is evaluated at the values of $Q_1 \equiv \{Q_i(t_1)\}$ determined by the M equations

$$\underset{\sim}{n}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1) \tag{3.91a}$$

$$\Delta V(\underset{\sim}{r}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1)) = E_2 - E_1(\underset{\sim}{N}_1) \quad ; \tag{3.91b}$$

$\underset{\sim}{n}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1)$ is the set of M-1 asymptotic quantum numbers of BC that result from a dissociative trajectory beginning on potential surface $V_2(\underset{\sim}{r})$ with initial conditions

$$\underset{\sim}{r}_1 = \underset{\sim}{r}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1) \tag{3.92a}$$

$$\underset{\sim}{p}_1 = \underset{\sim}{p}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1) \quad . \tag{3.92b}$$

If there is more than one root to Eq. (3.91), then Eq. (3.90) is a sum of such terms over all roots.

The physical picture which may be attached to Eq. (3.90) and (3.91) is as follows:[54] up until time t_1, say, the system is in state $|\underset{\sim}{N}_1>$, i.e., the action variables have these particular integer values and the conjugate angle variables at time $t_1,\underset{\sim}{Q}_1$, have random values in the internal $(0,2\pi)$; the corresponding values of the cartesian coordinates and momenta at t_1 are $\underset{\sim}{r}_1 \equiv \underset{\sim}{r}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1)$, $\underset{\sim}{p}_1 = \underset{\sim}{p}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1)$. A photon is absorbed at time t_1, which changes the potential function from $V_1(\underset{\sim}{r})$ to $V_2(\underset{\sim}{r})$, but which conserves the instantaneous values of the cartesian coordinates and momenta. Since the absorption process conserves the cartesian variables, the kinetic energy, $p^2/2m$, cannot change, so that the photon's energy $h\nu \equiv E_2 - E_1$ must be matched exactly by the instantaneous change in the potential energy [Eq. (3.91 b)]. A classical trajectory begins at time t_1 on the excited potential surface with initial conditions $(\underset{\sim}{r}_1, \underset{\sim}{p}_1)$, leading to dissociation of ABC into A + BC$(\underset{\sim}{n})$. In order for the M-1 quantum numbers of BC to turn out to be the specific integer values $\underset{\sim}{n}_2$, and for the potential energy difference ΔV to be exactly $h\nu$, the M variables $\underset{\sim}{Q}_1 \equiv \{Q_i(t_1)\}$, $i = 1, \ldots, M$, must be chosen to be certain specific values [Eq. (3.91)]. The intensity of the transition is the square modulus of the transition dipole function at $\underset{\sim}{r}_1$, weighted by the Jacobian which maps the initial random variables $\underset{\sim}{Q}_1$ onto specific final values of $\underset{\sim}{n}$ and ΔV.

It would not be practical or even desirable, however, to carry out a classical calculation in the above framework. The practical difficulty would be related to finding the roots of Eq. (3.91), the usual multi-dimensional root-search problem, and the result would be undesirable because zeros in the Jacobian determinant cause singularities, classical "rainbows", in the classical probability distribution in Eq. (3.90). To remedy both of these features one averages the classical expression over a quantum number increment about $\underset{\sim}{n}_2$ and over some increment about E_2:

$$\overline{|\langle E_2 \underset{\sim}{n}_2|\vec{\mu}|N_1\rangle|^2} \equiv \frac{1}{\varepsilon}\int_{E_2-\frac{1}{2}\varepsilon}^{E_2+\frac{1}{2}\varepsilon} dE_2 \int_{\underset{\sim}{n}_2-\frac{1}{2}}^{\underset{\sim}{n}_2+\frac{1}{2}} d\underset{\sim}{n}_2 \; |\langle E_2 \underset{\sim}{n}_2|\vec{\mu}|\underset{\sim}{N}_1\rangle|^2, \qquad (3.93)$$

and from Eq. (3.88) this is seen to give

$$|\langle E_2\underset{\sim}{n}_2|\vec{\mu}|\underset{\sim}{N}_1\rangle|^2 = (2\pi\hbar)^{-M} \int d\underset{\sim}{Q}_1 \, \frac{\mu(\underset{\sim}{r}_1)^2}{\varepsilon} \, \chi(\underset{\sim}{Q}_1;\underset{\sim}{N}_1,\underset{\sim}{n}_2,E_2), \quad (3.94)$$

where

$$\chi = 1$$

if

$$E_2 - E_1 - \frac{\varepsilon}{2} \leq \Delta V(\underset{\sim}{r}_1) \leq E_2 - E_1 + \frac{\varepsilon}{2}$$

and

$$\underset{\sim}{n}_2 - \frac{1}{2} \leq \underset{\sim}{n}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1) \leq \underset{\sim}{n}_2 + \frac{1}{2}$$

and $\chi = 0$ otherwise. A Monte Carlo procedure would probably be the most efficient way to carry out such a calculation;[54] thus with $\underset{\sim}{N}_1$ fixed, $\underset{\sim}{Q}_1$ would be chosen at random

$$Q_i(t_1) = 2\pi\xi_i \quad ,$$

where $\{\xi_i\}$ are random numbers in (0,1). $\Delta V(\underset{\sim}{r}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1))$ and $\underset{\sim}{n}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1)$

are then determined and the value of $\mu(\mathbf{r}_1)^2/\varepsilon$ added to the appropriate quantum number and energy "box", with the procedure repeated many times.

The semiclassical version of the above classical description is fairly obvious; the matrix element itself (i.e. the amplitude) is constructed first and then the square modulus formed. The classical limit of the amplitude is the square root of the classical expression in Eq. (3.90) times a phase factor, and analogous to the discussion in Section II B one can see that the appropriate phase is

$$\Phi\,(E_2\mathbf{n}_2,\mathbf{N}_1) = F_2^{(1)}(\mathbf{r}_1,\mathbf{N}_1) - F_2^{(2)}\,(\mathbf{r}_1,\mathbf{n}_2E_2) \quad , \qquad (3.95)$$

where $F_2^{(i)}$ is the F_2-type generator for potential surface i. Since $\mathbf{r}_1$ and $\mathbf{N}_1$ refer to the same time, t_1, and since $V_1(\mathbf{r})$ is separable, the first term in Eq. (3.95) is simply the sum of one dimensional generators of the form in Eq. (2.5) for each vibrational mode. In the second term of Eq. (3.95), however, $\mathbf{r}_1$ and $\mathbf{n}_2E_2$ refer to different times, so it is convenient to think first of a canonical transformation from $\mathbf{r}_1$ to $\mathbf{r}_2$, the cartesian coordinates at time t_2, and then a transformation from $\mathbf{r}_2$ to $(\mathbf{n}_2,E_2)$; by the general prescription for combining successive canonical transformations,[1,9] one has

$$F_2^{(2)}(\mathbf{r}_1,\mathbf{n}_2E_2) = F_1^{(2)}(\mathbf{r}_1,\mathbf{r}_2) + F_2^{(2)}(\mathbf{r}_2,\mathbf{n}_2E_2) \quad , \qquad (3.96)$$

and the first term here, the generator of the dynamical transformation from $\mathbf{r}_1$ to $\mathbf{r}_2$, is known[58] to be the action integral along the trajectory

$$F_1^{(2)}(\mathbf{r}_1,\mathbf{r}_2) = -F_1^{(2)}(\mathbf{r}_2,r_1)$$

$$= -\int_{t_1}^{t_2} dt\ \mathbf{p}\cdot\dot{\mathbf{r}} \quad . \tag{3.97}$$

in the second term of Eq. (3.96) $\mathbf{r}_2$ and $(\mathbf{n}_2,E_2)$ both refer to time t_2, so that it is simply the F_2-generator for potential surface $V_2(\mathbf{r})$ at time t_2; i.e.,

$$F_2^{(2)}(\mathbf{r}_2,\mathbf{n}_2E_2) = P_2R_2 + f_2^{BC}(\mathbf{r}_2^{M-1},\mathbf{n}_2) \quad , \tag{3.98}$$

where f_2^{BC} is the F_2-type generator for diatomic molecule BC.

The semiclassical expression for the dipole matrix element is therefore given by

$$\langle E_2\mathbf{n}_2|\vec{\mu}|\mathbf{N}_1\rangle = \vec{\mu}(\mathbf{r}_1)\left[(2\pi i)^M\frac{\partial(\mathbf{n},\Delta V)}{\partial\mathbf{Q}_1}\right]^{-1/2}$$

$$\times\exp\left[i\Phi(\mathbf{n}_2E_2,\mathbf{N}_1)/\hbar\right] \quad , \tag{3.99}$$

where

$$\Phi(\mathbf{n}_2E_2,\mathbf{N}_1) = \int_{t_1}^{t_2} dt\ \mathbf{p}\cdot\dot{\mathbf{r}} + F_2^{(1)}(\mathbf{r}_1,\mathbf{N}_1)$$

$$- F_2^{(2)}(\mathbf{r}_2,\mathbf{n}_2E_2) \quad . \tag{3.100}$$

There will typically be more than one trajectory that obeys the appropriate double-ended boundary conditions, i.e., more than one root to Eq. (3.91), so that Eq. (3.99) will be the sum of several such terms.

If the excited state potential surface is repulsive, so that the dissociative trajectories are "direct", the dipole matrix element will be a smooth function of E_2, i.e., the absorption spectrum is "continuous". If, on the other hand, $V_2(\underset{\sim}{r})$ is attractive so that the complex ABC lives a long time before dissociating into A and BC, the quantum number function $\underset{\sim}{n}(\underset{\sim}{N}_1,\underset{\sim}{Q}_1)$ will be highly structured (cf. Figure 8) and thus a large number of terms will contribute to Eq. (3.99). Analogous to the semiclassical discussion of resonances in Section II D, these many terms will interfere destructively at all but certain specific values of E_2 at which the interference is constructive and the matrix element extremely large. In such cases, therefore, there will be a "line spectrum", with the width of the absorption lines related to the time the excited state lives before dissociating.

IV. CLASSICAL S-MATRIX: CLASSICALLY FORBIDDEN PROCESSES.

Classically forbidden processes are those that do not take place via ordinary classical dynamics. The simplest example of such a process is one-dimensional tunneling through a potential barrier, and the "classically forbidden" concept is essentially a generalization of tunneling to dynamical systems of more than one degree of freedom. In addition to being one of the most intrinsically interesting aspects of classical S-matrix theory, the ability to describe classically forbidden processes - for which a completely classical theory is obviously inadequate - provides an extension of classical trajectory methods that may have practical utility, particularly the "partial averaging" mode of calculation discussed in Section IV C.

A. Introductory Discussion.

The essential idea is that classical forbidden transitions are treated by analytic continuation. To motivate the approach, consider evaluation of the definite integral

$$I = \int_{-\infty}^{\infty} dt\ g(t) \exp\left[if(t)/\hbar\right] \tag{4.1}$$

by the method of stationary phase;[14] this is an asymptotic approximation which becomes exact as $\hbar \to 0$ and which is the basic semiclassical approximation. If t_0 is the point of stationary phase, i.e., the root of the equation

$$f'(t) = 0 \quad , \tag{4.2}$$

then this approximation gives[14]

$$I \simeq g(t_o) \left[\frac{2\pi i\hbar}{f''(t_o)}\right]^{1/2} \exp[if(t_o)/\hbar] \quad . \qquad (4.3)$$

If there is more than one point of stationary phase, i.e., more than one root to Eq. (4.2), then Eq. (4.3) is a sum of similar terms, one for each such root.

If there are no roots to Eq. (4.2), then the "primitive" stationary phase approximation implies

$$I \simeq 0 \quad ;$$

although it is true that in such cases the value of the integral is small, one often wishes to know <u>how</u> small - 10^{-2}, say, or 10^{-4}. To determine the asymptotic approximation to the integral in such cases one analytically continues Eq. (4.3), the mathematical apparatus for which is the "method of steepest descent".[59] This approach notes that although there are no <u>real</u> values of t which satisfy Eq. (4.2), there will in general be complex values which do so - provided, of course, that it is possible to analytically continue the function f(t) into the complex t-plane. The method of steepest descent then deforms the path of integration in Eq. (4.1) from the real t-axis,

$$I = \int_C dt\, g(t) \exp[if(t)/\hbar] \quad , \qquad (4.4)$$

where C is a contour in the complex t-plane which pases through the "complex point of stationary phase" t_o. The resulting approximation[59] for the integral is exactly the same as Eq. (4.3), the only difference being that t_o, the root of Eq. (4.2), is now complex, and $g(t_o)$ and $f(t_o)$ are the (unique) analytic continuations of g(t) and f(t). Since t_o is complex, $g(t_o)$ and $f(t_o)$ are in general also complex, so that the square modulus of the integral, which is usually the quantity of interest, is given by

$$|I|^2 \simeq |g(t_o)|^2 \frac{2\pi\hbar}{|f''(t_o)|} \exp[-2\mathrm{Im} f(t_o)/\hbar] \quad . \tag{4.5}$$

The original integral in Eq. (4.1) requires the functions f(t) and g(t) only at real values of t, and it is the asymptotic approximation to the integral which introduces their analytic continuation to complex t.

To illustrate how classically forbidden processes are described with this type of approximation, consider tunneling through a one-dimensional potential barrier as sketched in Figure 9. Apart from some irrelevant constants, the amplitude for the particle going from the left to the right of the barrier at fixed energy E is a matrix element of the green's function, which in turn is a Fourier transform of the propagator:

$$\langle x_2| G(E)|x_1\rangle = (i\hbar)^{-1} \int_0^\infty dt\, e^{iEt/\hbar} \langle x_2|e^{-iHt/\hbar}|x_1\rangle \quad . \tag{4.6}$$

$$\simeq (i\hbar)^{-1} \int_0^\infty dt \left[\frac{\partial^2 \phi(x_2,x_1;t)}{\partial x_2 \, \partial x_1} / (-2\pi i\hbar) \right]^{-1/2}$$

$$\times \exp \left\{ \frac{i}{\hbar} [Et + \phi(x_2,x_1;t)] \right\} \tag{4.7}$$

where the classical-limit propagator has been invoked in Eq. (4.7). Consistent with classical-limit quantum mechanics,[9] the integral over t is evaluated by stationary phase, the time of stationary phase being determined by

$$0 = E + \frac{\partial \phi(x_2,x_1;t)}{\partial t} \quad . \tag{4.8}$$

But classical mechanics implies that the time derivative of the action integral along a trajectory is the negative of the energy of the trajectory:

$$\frac{\partial \phi(x_2,x_1;t)}{\partial t} \equiv -E(x_2,x_1;t) \quad , \tag{4.9}$$

$E(x_2,x_1;t)$ being the energy of the trajectory that goes from x_1 to x_2 in time t. It is clear intuitively (and can be shown rigorously) that the trajectory which connects x_1 and x_2 in a very short time must correspond to a very high energy, and the one that takes a long time to go from x_1 to x_2 corresponds to an energy just slightly above V_{max}; i.e.,

$$\lim_{t \to 0} E(x_2,x_1;t) = +\infty \tag{4.10a}$$

$$\lim_{t\to\infty} E(x_2,x_1;t) = V_{max} \quad . \tag{4.10b}$$

Thus for any value of E on the range

$$V_{max} < E < \infty$$

there is a real value of t, $0 < t < \infty$, which satisfies the stationary phase condition, Eq. (4.8); this corresponds to the ordinary classical trajectory which goes from x_1 to x_2 if $E > V_{max}$. For $E < V_{max}$, however, it is clear from Eq. (4.10) that no real value of t satisfies Eq. (4.8), and the transition is thus classically forbidden, i.e., there is no real-valued trajectory at this energy which obeys the appropriate double-ended boundary conditions. It is possible to analytically continue $\phi(x_2,x_1;t)$, however, and find a complex value of t which satisfies Eq. (4.8); the stationary phase approximation then proceeds in the manner discussed above, and the resulting expression from the transition amplitude is the same as if the transition were classically allowed.

$$<x_2|G(E)|x_1> \sim \exp\{\frac{i}{\hbar}[Et_o + \phi(x_2,x_1;t_o)]\} \tag{4.11}$$

except that the time t_o, the root of Eq. (4.8), is complex.

The action integral $\phi(x_2,x_1;t)$ is the time integral of the Lagrangian

$$\phi(x_2,x_1;t) = \int_0^t dt' \left[\frac{1}{2}\mu\, \dot{x}(t')^2 - V(x(t'))\right] \quad , \tag{4.12}$$

where x(t') is the trajectory determined by solving the equations of motion with the boundary conditions $x(0) = x_1$, $x(t) = x_2$. In order to analytically continue ϕ to complex time, therefore, it is necessary to analytically continue the trajectory x(t') itself to complex time. For systems with more than one degree of freedom trajectories must of course be determined by numerical integration of the classical equations of motion step by step in time, so that the analytic continuation of a trajectory (and therefore the action integral) to complex values of time in general proceeds as follows: rather than incrementing the time variable along the real t-axis, one increments it along the desired contour in the complex t plane. Since numerical integration of the equations of motion[3] amounts to approximating the coordinates and momenta at each integration step by polynomials in t - a manifestly analytic representation - it is clear that numerical integration step by step along a complex time contour does indeed generate the analytic continuation of the coordinates and momenta, and thus the action integral, from which the classical S-matrix is constructed. The expression for the classical S-matrix element for a classically forbidden process is the same as for a classically allowed one [Eq. (3.5)], the only difference being that the appropriate trajectory is complex-valued.

Analogous to the present use of complex time to construct amplitudes which refer to a definite energy is the more familiar use of complex energy to describe time dependence. The most common example of this occurs when considering the decay of a prepared state;[60] The probability amplitude that the system has not decayed from its initial state $|\phi\rangle$ is a diagonal matrix element of the propagator, which is conveniently written as a transform of the green's function [essentially the inverse of Eq. (4.6)];

$$\langle\phi|e^{-iHt/\hbar}|\phi\rangle = (-2\pi i\hbar)^{-1} \int_{-\infty}^{\infty} dE \quad e^{-iEt/\hbar} \langle\phi|G^{+}(E)|\phi\rangle \quad . \quad (4.13)$$

Clearly only real values of E appear in this expression, but since the analytic continuation of the green's function $G^{+}(E)$ into the lower half E-plane often has a pole in that region,

$$\langle\phi|e^{-iHt/\hbar}|\phi\rangle \simeq A/(E - E_r + i\Gamma/2) \quad , \quad (4.14)$$

it is convenient to convert the above real integral into a contour integral enclosing the lower half E-plane.[60] If there is only the one such pole, then evaluation of this contour integral is trivial, giving

$$\langle\phi|e^{-iHt/\hbar}|\phi\rangle \simeq A\ e^{-iE_r t/\hbar}\ e^{-\Gamma t/2\hbar} \quad , \quad (4.15)$$

the square modulus of which gives the probability that the system has not yet left its initial state;

$$|\langle\phi|e^{-iHt/\hbar}|\phi\rangle|^2 \simeq |A|^2 e^{-\Gamma t/\hbar} \quad . \tag{4.16}$$

Thus although energy and time are obviously real physical quantities, it is a useful mathematical devise to invoke the idea of complex energy (a "complex eigenvalue" or complex pole of the green's function) when considering time evolution, and conversely, the notion of complex time when constructing amplitudes that refer to processes at a definite energy.

B. Applications.

Classical S-matrix theory has been applied to classically forbidden processes in A + BC collision systems, both collinear and three-dimensional models, reactive as well as non-reactive processes having been studied. This section discusses some of these results.

Consider first the simplest case, the non-reactive collinear system, for which there is just one internal degree of freedom. To construct the classical S-matrix for the $n_1 \to n_2$ transition one must find the roots of the equation

$$n_2(\bar{q}_1) = n_2 \quad , \tag{4.17}$$

where the meaning of the quantities is the same as discussed in Section III B. Figure 10 shows the function $n_2(\bar{q}_1)$ for $n_1 = 1$ and for an energy such that all inelastic transitions are classically forbidden, meaning simply that they have small probabilities; this is actually the typical situation for vibrationally inelastic processes in thermal energy kinetics. For $n_2 \neq n_1$ there are thus no real values of $\bar{q}_1$ which satisfy Eq. (4.17); there are, however, complex values of $\bar{q}_1$ which do so - provided of course that one can analytically continue the function $n_2(\bar{q}_1)$ to find them.

To evaluate $n_2(\bar{q}_1)$ for complex values of $\bar{q}_1$ one must integrate the classical equations of motion with complex-valued initial conditions. During the course of such a trajectory, all coordinates and momenta become complex-valued,[61] but this causes no difficulties since the objects of physical meaning, the quantum numbers in the asymptotic regions, are real-valued for the trajectories which satisfy the appropriate double-ended boundary conditions; Section IV B of reference 9 discusses these points in some detail. The classical S-matrix is still given by Eq. (3.25), but there is now typically just one complex root of Eq. (4.17) for which $\text{Im}\,\Phi > 0$ so that the vibrational transition probability is

$$P_{n_2,n_1}(E) = [2\pi\,|n_2'(\bar{q}_1)|]^{-1} \exp[-2\text{Im}\Phi(n_2,n_1;E)/\hbar] \tag{4.18}$$

where Φ is the action integral of Eq. (3.6). The exponential damping factor which multiplies the "classical" probability factor (the reciprocal Jacobian) is the multidimensional generalization of the tunneling probability for one-dimensional barrier penetration, i.e., classically forbidden processes are essentially a generalized kind of tunneling.

The first calculations of the type outlined above were carried out by Miller and George;[62] similar calculations were carried out independently by Stine and Marcus.[63] These results are in excellent agreement (a few %) with the accurate quantum mechanical values obtained by Secrest and Johnson[24] even for extremely weak transitions with a probability as small as 10^{-11}. It is thus encouraging that the semiclassical model is able to describe such quantum-like phenomena for which ordinary (i.e., real-valued) classical trajectory methods would clearly be inapplicable.

It should be noted in passing that for this non-reactive collinear system a completely quantum mechanical (i.e., coupled channel) calculation may actually be no more difficult - i.e. require no more computer time - than these semiclassical calculations. Whether this is true or not is beside the point, of course, for the obvious interest in the semiclassical model is that it can be applied to physically realistic three-dimensional systems (see Section IV C) for which coupled channel calculations are usually unreasonable unless simplifying approximations are introduced. The purpose for carrying out semiclassical calculations for collinear systems is to obtain definitive comparisons with reliable quantum mechanical values (which exist only for collinear systems).

Doll[64] has applied classical S-matrix theory to the collinear A + BC collision where atom A and B interact via a hard sphere collision; this is the model studied quantum mechanically by Shuler and Zwanzig.[65] Doll treats classically allowed and forbidden processes and finds good agreement between semiclassical and quantum mechanical transition probabilities. This is a remarkable achievement for the semiclassical theory, for the hard sphere interaction is far from the "smooth" potential that one normally assumes to be necessary for the dynamics to be classical-like.

George and Miller[34] have also treated classically forbidden transitions in the collinear reactive system $H + H_2(n_1 = 0) \rightarrow H_2(n_2 = 0) + H$ at collision energies below the classical threshold for reaction. The reaction probability is given by Eq. (4.18) for this case also, and the only new feature of the calculation is that the complex time path must be chosen to insure that the reaction does occur; choice of a purely real time path would of course lead to a non-reactive trajectory at these energies. Section IV D discusses some of these aspects of the calculation in more detail.

Since this calculation by George and Miller[34] there have been several extensive quantum mechanical calculations of the reaction probability in this energy region on the Porter-Karplus[66] potential surface; the results of Schatz and Kuppermann[67] and Duff and Truhlar[68] are in excellent agreement and can be considered to be the numerically exact quantum mechanical values. Figure 11 shows the comparison of the semiclassical[34] and quantum mechanical[67,68] values from an energy just below the classical threshold down to where the transition probability has dropped to below 10^{-10}. The agreement over the entire range of ten orders of magnitude, for this process which should be as highly quantum-like as any encountered in molecular dynamics, is impressive. The relative error in the semiclassical values, 35-50%, however, is greater than that for the non-reactive collinear examples discussed above (typically a few % relative error). Whether this is due to inherent limitations of the semiclassical model or to some semiclassical effect which has been overlooked, is not clear at present. The direction of the error is mystifying since arguments based on the analogy to one-dimensional tunneling imply that the semiclassical result should err by being too large, the opposite of what is seen in Figure 11.

With regard to three dimensional A + BC collision systems, Doll and Miller[69] have calculated a few specific S-matrix elements for classically forbidden vibrational excitation in $He + H_2$ collisions. Agreement with quantum mechanical values is good, within the uncertainty of the correct quantum mechanical values. A number of S-matrix elements have also been calculated by Doll, George, and Miller[35] for reactive collisions of

$$H + H_2(n_1,j_1 = 0,0) \rightarrow H_2(n_2,j_2 = 0,1) + H \quad ,$$

in three dimensions on the Porter-Karplus[66] potential surface, again in the tunneling region. Agreement with the quantum mechanical calculations of Wolken and Karplus[70] is quite reasonable (within a factor of 2), but here again the quantum mechanical values, although the most serious treatment thus far, are probably not the numerically exact quantum results for this potential surface.

In the three dimensional A + BC examples discussed above the S-matrix elements

$$S_{n_2j_2\ell_2,n_1j_1\ell_1}{}^{(J,E)} \tag{4.19}$$

were calculated semiclassically. Thus with the initial quantum numbers n_1,j_1,ℓ_1 - and the total angular momentum J and total energy E - held fixed, the conjugate angle variables $\bar{q}_{n_1}$, $\bar{q}_{j_1}$, $\bar{q}_{\ell_1}$ must be chosen iteratively so that the final quantum numbers take on their desired integer values; i.e., one must solve the three equations

$$\begin{aligned} n_2(\bar{q}_{n_1},\bar{q}_{j_1},\bar{q}_{\ell_1}) &= n_2 \\ j_2(\bar{q}_{n_1},\bar{q}_{j_1},\bar{q}_{\ell_1}) &= j_2 \\ \ell_2(\bar{q}_{n_1},\bar{q}_{j_1},\bar{q}_{\ell_1}) &= \ell_2 \end{aligned} \tag{4.20}$$

simultaneously. (See Section III E of reference 9 for more discussion of the semiclassical description of three dimensional A + BC collision systems.) Because of the difficulty of finding the roots of Eq. (4.20), a multi-dimensional root-search problem, it is not practical to calculate the large number of individual S-matrix elements that would be necessary in order to construct actual cross sections. (Although Tyson, Saxon, and Light[33] have, with considerable effort, carried out such calculations for coplanar H + H_2 collisions.) The value of these three dimensional calculations has been to show that the semiclassical model, to the extent that it can be applied, provides a reasonably accurate description of the quantum effects in molecular collision dynamics. As a practical means for carrying out calculations for three dimensional A + BC collision processes the "partial averaging" approach described in the following section is fortunately much more useful.

C. Partial Averaging.

When considering three dimensional collision systems one is of course not interested in individual S-matrix elements, but rather cross sections that involve sums over many of them. Under realistic conditions, too, the cross sections of interest are a sum and average over some of the final and initial quantum states. For the still quite idealized process

$$\begin{aligned} A + BC(n_1 j_1) &\rightarrow A + BC(n_2 j_2) \\ &\rightarrow AB(n_2 j_2) + C \quad , \end{aligned}$$

for example, where the m-components of the rotational states are not observed, the integral cross section is a sum over three quantum numbers:

$$\sigma_{n_2j_2 \leftarrow n_1j_1}(E_1) = \frac{\pi}{k_1{}^2(2j_1+1)} \sum_{J,\ell_1,\ell_2} (2J+1)$$

$$|S_{n_2j_2\ell_2,n_1j_1\ell_1}(J,E)|^2 \tag{4.21}$$

As discussed in Section III B, quantum interference structure tends to be quenched by these sums, and if the transition is classically allowed, the semiclassical theory then effectively degenerates to a completely classical result.

To see explicitly how the Monte Carlo classical procedure emerges, note that if interference terms are discarded the square modulus of the classical S-matrix [Eq. (3.5)] for a classically allowed transition is given by (setting $\hbar = 1$)

$$S_{n_2j_2\ell_2,n_1j_1\ell_1}(J,E) = \left[(2\pi)^3 \left|\frac{\partial(n_2j_2\ell_2)}{\partial(\bar{q}_{n_1}\bar{q}_{j_1}\bar{q}_{\ell_1})}\right|\right]^{-1} , \tag{4.22}$$

so that Eq. (4.21) becomes

$$\sigma_{n_2j_2 \leftarrow n_1j_1}(E_1) = \frac{\pi}{k_1{}^2(2j_1+1)} \int dJ \int d\ell_1 \int d\ell_2 \cdot$$

$$\times \frac{2J+1}{(2\pi)^3} \left|\frac{\partial(n_2j_2\ell_2)}{\partial(\bar{q}_{n_1}\bar{q}_{j_1}\bar{q}_{\ell_1})}\right|^{-1} , \tag{4.23}$$

where it has been assumed that enough quantum numbers contribute to the sums in Eq. (4.21) to justify replacing them by integrals. If there are at least a few values of n_2 and j_2 that are classically allowed transitions from the initial values (n_1, j_1), then it is permissible to average Eq. (4.23) over a quantum number width[71] about the integer values of n_2 and j_2:

$$\sigma_{n_2j_2 \leftarrow n_1j_1}(E_1) \simeq \int_{n_2-\frac{1}{2}}^{n_2+\frac{1}{2}} dn_2 \int_{j_2-\frac{1}{2}}^{j_2+\frac{1}{2}} dj_2 \quad \sigma_{n_2j_2 \leftarrow n_1j_1}(E_1), \quad (4.24)$$

and with Eq. (4.23) this becomes

$$\sigma_{n_2j_2 \leftarrow n_1j_1}(E_1) = \frac{\pi}{k_1{}^2(2j_1+1)} \int dJ \int d\ell_1 \int dn_2 \int dj_2 \int d\ell_2 \; \frac{2J+1}{(2\pi)^3} \left| \frac{\partial(n_2 j_2 \ell_2)}{\partial(\bar{q}_{n_1} \bar{q}_{j_1} \bar{q}_{\ell_1})} \right|^{-1} . \qquad (4.25)$$

The advantageous feature of this averaging process is that Eq. (4.25) now involves an integral over all the final quantum numbers n_2, j_2 and ℓ_2, so that a change of variables of integration from (n_2, j_2, ℓ_2) to their conjugate initial values $(\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1})$ - i.e.,

$$\int dn_2 \int dj_2 \int d\ell_2 = \int d\bar{q}_{n_1} \int d\bar{q}_{j_1} \int d\bar{q}_{\ell_1} \left| \frac{\partial(n_2 j_2 \ell_2)}{\partial(\bar{q}_{n_1} \bar{q}_{j_1} \bar{q}_{\ell_1})} \right|$$

- introduces a Jacobian factor which <u>exactly</u> <u>cancels</u> the one in Eq. (4.25). The resulting expression for the cross section is considerably simplified:

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) = \frac{\pi}{k_1{}^2(2j_1+1)} \int d\ell_1 \int dJ \int d\bar{q}_{n_1} \int d\bar{q}_{j_1} \int d\bar{q}_{\ell_1} \frac{2J+1}{(2\pi)^3}$$

$$\times\, h[\tfrac{1}{2} - |n_2(\bar{q}_{n_1},\bar{q}_{j_1},\bar{q}_{\ell_1}) - n_2|]\, h[\tfrac{1}{2} - |j_2(\bar{q}_{n_1},\bar{q}_{j_1},\bar{q}_{\ell_1}) - j_2|],$$

(4.26)

where h(x) is the unit step function,

$$h(x) = 1 \;, \; x \geq 0$$
$$0 \;, \; x < 0 \quad ;$$

i.e., the product of the two step functions is 1 if

$$n_2 - \frac{1}{2} \leq n_2(\bar{q}_{n_1},\bar{q}_{j_1},\bar{q}_{\ell_1}) \leq n_2 + \frac{1}{2}$$

$$j_2 - \frac{1}{2} \leq j_2(\bar{q}_{n_1},\bar{q}_{j_1},\bar{q}_{\ell_1}) \leq j_2 + \frac{1}{2} \quad ,$$

and zero otherwise. To carry out such an integral in practice one simply sweeps the integration variables - now all initial conditions - through their complete ranges and assigns the final values $n_2(\bar{q}_{n_1},\bar{q}_{j_1},\bar{q}_{\ell_1})$ and $j_2(\bar{q}_{n_1},\bar{q}_{j_1},\bar{q}_{\ell_1})$ to the appropriate quantum number "boxes", thereby generating in one calculation the cross sections from (n_1,j_1) to all classically allowed final states.

The limits of integration are $\ell = 0 \to \infty$ and $J = |j_1 - \ell_1| \to (j_1 + \ell_1)$ but Eq. (4.26) is cast in a more obvious Monte Carlo form by replacing ℓ_1 by the impact parameter b,

$$b = (\ell_1 + \tfrac{1}{2})/k_1 \quad , \tag{4.27}$$

and replacing J by the variable z,

$$J + \tfrac{1}{2} = [(\ell_1 - j_1)^2 + (2\ell_1 + 1)\ (2j_1 + 1) z]^{1/2} \tag{4.28}$$

for which the integration limits are $z = 0 \rightarrow 1$. It is also customary to cut the impact parameter integration off at some value B beyond which there are no trajectories which lead to the transition of interest; since

$$\pi \int_0^B db\ 2b = \pi B^2 \int_0^1 d\xi \quad ,$$

where

$$\xi = (b/B)^2 \quad , \tag{4.29}$$

the changes of variables implied by Eqs. (4.27), (4.28), and (4.29) lead to the desired result:

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) = \pi B^2 \int_0^1 d\xi \int_0^1 dz \int_0^1 d\ (\bar{q}_{n_1}/2\pi) \int_0^1 d\ (\bar{q}_{j_1}/2\pi) \int_0^1 d(\bar{q}_{\ell_1}/2\pi)$$

$$\times\ h[\tfrac{1}{2} - |n_2(\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1}) - n_2|]\ h[\tfrac{1}{2} - |j_2(\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1}) - j_2|] \quad , \tag{4.30}$$

where

$$\ell_1 + \frac{1}{2} = k_1 B\sqrt{\xi}$$

$$J + \frac{1}{2} = [(\ell_1 - j_1)^2 + (2\ell_1 + 1)\ (2j_1 + 1) z]^{1/2} \quad .$$

The cross section which is summed over find rotational states,

$$\sigma_{n_2 \leftarrow n_1 j_1}(E_1) \equiv \sum_{j_2} \sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1)$$

$$\simeq \int dj_2\ \sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) \quad ,$$

is given by a similar expression:

$$\sigma_{n_2 \leftarrow n_1 j_1}(E_1) = \pi B^2 \int_0^1 d\xi \int_0^1 dz \int_0^1 d(\bar{q}_{n_1}/2\pi) \int_0^1 d(\bar{q}_{j_1}/2\pi) \int_0^1 d(\bar{q}_{\ell_1}/2\pi)$$

$$\times\ h[\frac{1}{2} - |n_2(\bar{q}_{n_1}, \bar{q}_{j_1}, \bar{q}_{\ell_1}) - n_2|] \quad . \qquad (4.31)$$

Since all five integrals in Eqs. (4.30) and (4.31) have limits 0 → 1, implementation of Monte Carlo integration procedures is straight-forward.

If the $n_1 j_1 \rightarrow n_2 j_2$ transition is classically forbidden, then although the above development is obviously inapplicable as it stands, it is still possible to follow it to some extent. Thus it is still a good approximation to neglect interference between various trajectories which contribute to the same S-matrix element-since they will be quenched by the sums - so that Eq. (4.22) is modified only by the addition of the exponential damping factor:

$$|S_{n_2 j_2 \ell_2, n_1 j_1 \ell_1}(J,E)|^2 = \left[(2\pi)^3 \left|\frac{\partial(n_2 j_2 \ell_2)}{\partial(\bar{q}_{n_1} \bar{q}_{j_1} \bar{q}_{\ell_1})}\right|\right]^{-1} \times \exp(-2\,\mathrm{Im}\Phi) \quad . \tag{4.32}$$

Since only a very few vibrational states are involved- because the transition is weak - it is not possible to average over the vibrational quantum number as was done above. However there will still typically be a reasonable number of final rotational states that have comparable transition probabilities. For the H + H_2 ($n_1 = 0$, $j_1 = 0$) reaction in three dimensions, for example, the classical trajectory results of Karplus, Porter, and Sharma[72] show that final rotational states $j_2 = 0 \to 5$ all have comparable probability for energies just above the classical threshold even though $n_2 = 0$ is the only energetically open vibrational state.

The "partial averaging" procedure is thus to average over the final rotational state but not the final vibrational state. (The reason one wishes to average over as many final quantum numbers as possible is that boundary conditions for those degrees of freedom can be replaced by <u>initial conditions</u>, thereby eliminating the root-search problem.) Since

$$\int d\ell_2 \int dj_2 = \int d\bar{q}_{j_1} \int d\bar{q}_{\ell_1} \left|\frac{\partial(j_2 \ell_2)}{\partial(\bar{q}_{j_1} \bar{q}_{\ell_1})}\right|_{n_2, n_1}$$

$$= \int d\bar{q}_{j_1} \int d\bar{q}_{\ell_1} \left|\frac{\partial(n_2 j_2 \ell_2)}{\partial(\bar{q}_{n_1}\bar{q}_{j_1}\bar{q}_{\ell_1})}\right|_{\bar{q}_{n_1},n_1} \left|\frac{\partial n_2}{\partial \bar{q}_{n_1}}\right|^{-1}_{n_1} ,$$

the partially averaged expression is

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1}(E_1) = \frac{\pi}{k_1^{2}(2j_1+1)} \int dJ \int d\ell_1 \int d(\bar{q}_{j_1}/2\pi) \int d(\bar{q}_{\ell_1}/2\pi)$$

$$\times\, h[\tfrac{1}{2} - |j_2(\bar{q}_{n_1},\bar{q}_{j_1},\bar{q}_{\ell_1}) - j_2|]\ [2\pi|\frac{\partial n_2}{\partial \bar{q}_{n_1}}|]^{-1} \exp(-2\mathrm{Im}\Phi), \quad (4.33)$$

where $\bar{q}_{n_1}$ is not integrated over in Eq. (4.30) but rather must be chosen to be that specific (complex) value for which

$$n_2(\bar{q}_{n_1};\bar{q}_{j_1},\bar{q}_{\ell_1},\ell_1,j_1,J,E_1) = n_2 \quad . \qquad (4.34)$$

The root-search problem has not been eliminated, but has been reduced to a one dimensional one which must be carried out many times.[73]

The same changes of variables as introduced above in Eqs. (4.30) and (4.31) can also be made in Eq. (4.33); so that the more useful expression for the cross section, summed over j_2, is

$$\sigma_{n_2 \leftarrow n_1 j_1}(E_1) = \pi B^2 \int_0^1 d\xi \int_0^1 dz \int_0^1 d(\bar{q}_{j_1}/2\pi) \int_0^1 d(\bar{q}_{\ell_1}/2\pi)$$

$$\times\, P_{n_2,n_1}(j_1\ell_1\bar{q}_{j_1}\bar{q}_{\ell_1};JE_1) \quad , \qquad (4.35)$$

where

$$P_{n_2,n_1}(j_1\ell_1\bar{q}_{j_1}\bar{q}_{\ell_1};JE_1) = [2\pi|\frac{\partial n_2}{\partial \bar{q}_{n_1}}|]^{-1} \exp\,(-2\mathrm{Im}\Phi) \qquad (4.36)$$

Dimensionally, P_{n_2,n_1} defined by Eq. (4.36) is a collinear-like vibrational transition probability [cf. Eq. (4.18)] which depends parametrically on the initial conditions of the other degrees of freedom. The analogy to a collinear collision is purely formal, however, for there are no dynamical approximations which have been introduced; the only approximations involved, beyond that of classical S-matrix theory itself, are the neglect of interference terms between different trajectories that contribute to the same S-matrix element and the assumption that enough j_2-values have comparable probability for a sum over them to be replaced by an integral.

The classically allowed version of Eq. (4.35), namely Eq. (4.31), can also be written in the form of Eq. (4.35) by defining the classically allowed vibrational transition probability as

$$P_{n_2,n_1}(j_1\ell_1\bar{q}_{j_1}\bar{q}_{\ell_1};JE_1) = (2\pi)^{-1}\int d\bar{q}_{n_1}\ h[\tfrac{1}{2} - |n_2(\bar{q}_{n_1};\bar{q}_{j_1}\bar{q}_{\ell_1}j_1\ell_1JE_1) - n_2|] \tag{4.37}$$

$$= \Delta q_{n_1}/2\pi \quad ,$$

which is also recognized as the form of the averaged vibrational transition probability for a collinear model [cf. Eq. (3.39)]. (For truly collinear systems it is a poor approximation, of course, to ignore the interference terms, however, since there are no averages over other variables to quench them.) In both the allowed and forbidden cases the cross section can be written in the phenomenological form often used in energy transfer theory,[74]

$$\sigma_{n_2 \leftarrow n_1 j_1}(E_1) = \pi B^2 \left\langle P_{n_2 \leftarrow n_1 j_1}(E_1) \right\rangle , \qquad (4.38)$$

where the "average transition probability" is the average over the four initial conditions as in Eq. (4.35), with the integrand given by Eq. (4.37) and Eq. (4.36) for the classically allowed and forbidden cases, respectively.

Although only integral cross sections have been discussed, it should be clear that differential cross sections, i.e., angular distributions, can also be generated within the Monte Carlo framework; these are defined by

$$\sigma_{n_2 \leftarrow n_1 j_1}(E_1) = \int d\,(\cos\theta)\ \ \sigma_{n_2 \leftarrow n_1 j_1}(\cos\theta, E_1) \qquad (4.39a)$$

$$= \int dj_2 \int d(\cos\theta)\ \sigma_{n_2 j_2 \leftarrow n_1 j_1}(\cos\theta, E_1). \qquad (4.39b)$$

To obtain the $n_1 j_1 \rightarrow n_2$ cross section differential in final rotational state and in scattering angle - i.e., $\sigma_{n_2 j_2 \leftarrow n_1 j_1}(\cos\theta)$ - therefore, one simply defines a set of "j_2-boxes" and "cos θ - boxes", and with the integration variables in Eq. (4.35) chosen by Monte Carlo the numerical value of the integrand, i.e., the vibrational transition probability, is assigned to the j_2 - and cos θ - box which corresponds to the final vaues of j_2 and cos θ for the trajectory which satisfies Eq. (4.34), i.e., the one from which the transition probability in Eq. (3.46) is constructed. The distributions in j_2 and cos θ are thus obtained simultaneously with the computation of the integral cross section $\sigma_{n_2 \leftarrow n_1 j_1}$, the only limitations being the usual Monte Carlo ones - that is, the more differential the quantities desired, the more Monte Carlo points required. Thus it might require only 50 Monte Carlo points, for example, to evaluate the integral cross section $\sigma_{n_2 \leftarrow n_1 j_1}$ to within 10% statistical error, but a larger number of points would be required to obtain the distribution of final rotational states, $\sigma_{n_2 j_2 \leftarrow n_1 j_1}$, and a still larger number of points to obtain the "doubly differential" cross section, $\sigma_{n_2 j_2 \leftarrow n_1 j_1}(\cos\theta)$, differential in j_2 and cos θ, to within 10% statistical error. It sounds very much like the experimental situation: The more detailed the information desired, more is the effort which is required.

Preliminary results of calculations such as these have been reported by Miller and Raczkowski[75] for the 0 → 1 vibrational excitation of H_2 and He. Preliminary calculations have also been made[76] for vibrational excitation of H_2 by Li^+, and comparison with the coupled channel calculations of Lester[77] are quite encouraging. Figure 12 shows the cross sections $\sigma_{n_2 j_2 \leftarrow n_1 j_1}$, for $(n_1, j_1) = (1,0)$ and $n_2 = 0$, as a function of the final rotational state, for an initial translational energy of 0.684 eV. Since there is a 10-20% uncertainty in these preliminary semiclassical results, and probably a similar level of uncertainty in the quantum mechanical values,[78] the agreement is essentially exact at this stage. Also shown in Figure 12 is a phase space distribution

$$(2j_2 + 1)\ [E_{tot} - \varepsilon(0,j_2]\qquad , \tag{4.40}$$

$\varepsilon(n_2,j_2)$ being the vibrational-rotational energy levels of H_2, which has been normalized to the total cross section of the quantum and semiclassical calculations. Thus although there is considerable rotational excitation in the 1 → 0 vibrational deactivation, it is not nearly so much as a completely random redistribution of the rotational energy.

D. Numerical Integration of Complex-Valued Trajectories.

Although the formalism of classical S-matrix theory deals with initial and final values of action-angle variables, it is actually most convenient to carry out the numerical integration of Hamilton's equations in cartesian coordinates and momenta. The procedure is that one specifies initial conditions in terms of action-angle variables (e.g., n_1,q_{n_1}, j_1,q_{j_1}, ℓ_1,q_{ℓ_1}. . .), transforms these into initial conditions for the cartesian variables, carries out the numerical integration of the trajectory in cartesian variables, and at the end of the trajectory transfroms the final values of the cartesian variables into final values of the action-angle variables (e.g., n_2,j_2,ℓ_2. . .). Appendix C of reference 27 gives the expressions for the initial values of the cartesian variables in terms of the action-angle variables (see also Section II B of reference 69). With regard to the transformation at the end of the trajectory, the final angular momentum variables j_2 and ℓ_2 are easily determined from the cartesian variables by using the classical relations

$$j_2 = [(\mathbf{r}_2 \times \mathbf{p}_2) \cdot (\mathbf{r}_2 \times \mathbf{p}_2)]^{1/2}$$

$$\ell_2 = [(\mathbf{R}_2 \times \mathbf{P}_2) \cdot (\mathbf{R}_2 \times \mathbf{P}_2]^{1/2} \quad ,$$

where $(\mathbf{r}_2, \mathbf{p}_2)$ are the cartesian variables of the diatom and $(\mathbf{R}, \mathbf{P})$ the cartesian variables for the atom-diatom separation. The final vibrational quantum number is determined from the cartesian variables by first computing the total energy of the diatom

$$\varepsilon_2 = (\mathbf{p}_2 \cdot \mathbf{p}_2)/2m + v(r_2) \quad , \tag{4.41}$$

$v(r)$ being the vibrational potential of the diatom, and then solving the equation

$$\varepsilon(n_2, j_2) = \varepsilon_2 \tag{4.42}$$

for n_2 (since j_2 is known), where $\varepsilon(n,j)$ is the WKB energy level formula for the diatom; it is usually known as a Dunham expansion. Alternatively, with ε_2 known from Eq. (4.41) n_2 can be computed directly from the WKB quantum condition:

$$(n_2 + \tfrac{1}{2})\pi = \int_{r_<}^{r_>} dr\ \{2m[\varepsilon_2 - v(r)] - j_2{}^2/r^2\}^{1/2} \quad . \tag{4.43}$$

To a large extent the actual numerical integration of complex-valued trajectories is the same as for ordinary real-valued ones; this is possible by taking advantage of the complex arithmetic capabilities of FORTRAN IV. Thus it is only necessary to declare all the coordinates and momenta, and the time increment, to be COMPLEX variables and use essentially the same numerical integration algorithm[79] - e.g., Runge-Kutta, Adams-Moulton, etc. - as used for real-valued trajectories. Since it is often convenient, however, to vary the direction in the complex time plane of the complex time increment, Miller and George[62] developed a variable step-size predictor-corrector algorithm; it has the variable step-size and self-starting advantages of Runge-Kutta routines with the efficiency of a predictor-corrector (e.g., Adams-Moulton) method. Appendix C of reference 62 gives the predictor and corrector formulae for the fifth order [error $\sim O(h^6)$] version of the algorithm; used in the PECE mode,[79] the integrator has excellent stability characteristics.

The principal feature which distinguishes the numerical integration of complex-valued trajectories from real-valued ones lies in the flexibility one has in choosing the complex time path along which time is incremented. Although the quantities from which the classical S-matrix is constructed are <u>analytic</u> functions and thus independent of the particular time path,[9] there are practical considerations that restrict the choice. Thus although translational coordinates behave as low order polynomials in time, so that nothing drastic happens to them when t becomes complex, the vibrational coordinate is oscillatory -

$$r(t) - r_{eq} \sim \cos(\omega t + \eta)$$

- so that it can become exponentially large along a complex time path. The complex time path must be chosen, therefore, in order to stabilize the vibrational motion.

There are a variety of ways of stabilizing the vibrational motion, but the most satisfactory procedure we have found to date is to head the oscillation always toward its next equilibrium position. Thus at time t_n the values r_n, $\dot{r}_n$, $\ddot{r}_n$ [$r_n = r(t_n)$, etc.] are known, so that for t near t_n one has the approximation

$$r(t) = r_n + \dot{r}_n(t - t_n) + \frac{1}{2}\ddot{r}_n(t - t_n)^2 \quad , \tag{4.44}$$

and one wishes to choose the next time, t_{n+1}, so that

$$r(t_{n+1}) = r_{eq} \quad ; \tag{4.45}$$

solving Eqs. (4.44) and (4.45) gives

$$\begin{aligned}\Delta t &\equiv t_{n+1} - t_n \\ &= (\ddot{r}_n)^{-1}\{-\dot{r}_n \pm [\dot{r}_n^{\,2} + 2\ddot{r}_n(r_{eq} - r_n)]^{1/2}\} \quad , \qquad (4.46)\end{aligned}$$

with the ± sign chosen to insure $\mathrm{Re}(\Delta t) > 0$.[80] Actually one wishes only to cause $r(t)$ to head in the direction of r_{eq}; thus the new time increment is chosen to have the phase of that in Eq. (4.46) but the magnitude determined by the truncation error estimate of the integrater.[62] If Δt is given by Eq. (4.46), then the new time increment is chosen as

$$h(\Delta t)/|\Delta t| \quad ,$$

where $|\Delta t|$ is the complex absolute value of Δt and h is the magnitude of time increment allowed by the integrater.

The above algorithm for choosing the complex time path applies to non-reactive A + BC collisions, collinear or three-dimensional, throughout the entire trajectory. It is currently being used, for example, in the "partial averaging" calculations described in the previous section.

To describe tunneling in reactive systems,[34,35]

$$A + BC \rightarrow AB + C \quad ,$$

The above procedure must be modified somewhat. If r_a is the vibrational coordinate of diatom BC, then the above procedure for choosing the time path is followed with regard to the variable r_a until A and BC reach their distance of closest approach. At this point the complex time path is chosen to cause the reaction to occur; i.e., one wants $r_c(t)$, the vibrational coordinate of AB, to head toward its equilibrium value. Thus the same procedure is used to choose the time path but with regard to r_c, the vibrational coordinate of the new diatom.

The procedures described above for choosing the complex time path are the most generally satisfactory ones we have found thus far, but they should not be considered the final answer to the problem. Various different approaches are still being actively pursued, and it appears that there is still much to be learned about analytically continued classical mechanics.

V. CONCLUDING REMARKS

One has at hand, therefore, a completely general semiclassical mechanics which allows one to construct the classical-limit approximation to any quantum mechanical quantity, incorporating the complete classical dynamics with the quantum principle of superposition. As has been emphasized, and illustrated by a number of examples in this review, all quantum effects--interference, tunneling, resonances, selection rules, diffraction laws, even quantization itself--arise from the superposition of probability amplitudes and are thus contained at least qualitatively within the semiclassical prescription. The semiclassical picture thus affords a broad understanding and clear insight into the nature of quantum effects in molecular dynamics.

In many cases, too, the semiclassical model provides a quantitative description of the quantum effects in molecular systems, although there will surely be situations for which it fails quantitatively or is at best awkward to apply. From the numerical examples which have been carried out thus far--and more are needed before a definitive conclusion can be reached--it appears that the most practically useful contribution of classical S-matrix theory is the ability to describe classically forbidden processes; i.e., although completely classical (e.g. Monte Carlo) methods seem to be adequate for treating classically allowed processes, they are not meaningful for classically forbidden ones. (Purely classical treatments will not of course describe quantum interference effects which are present in classically allowed processes, but under most practical conditions these are quenched). The semiclassical approach thus widens the class of phenomena to which classical trajectory methods can be applied.

Two common examples of classically forbidden processes have been discussed in Section IV: vibrationally inelastic transitions in atom-diatom collisions (V - T energy transfer) and tunneling near the threshold of chemical reactions. Another important example, which has been discussed in detail previously,[9] is electronically non-adiabatic transtions, i.e., transitions from one potential energy surface to another.[81] Miller and George[82] have formulated this problem semiclassically in such a way that incorporates the exact classical dynamics of the heavy particle motion (i.e., classical trajectories) and the quantum principle of superposition; the electronic transition is accounted for within a Stueckelberg-like model, i.e., by considering complex-valued classical trajectories which change from one adiabatic surface to another at a complex point of intersection.[83] (Such processes are "classically forbidden", therefore, since only complex-valued classical trajectories can reach these complex intersection points in order to change adiabatic potential energy surfaces.) The principle physical requirement of the model is that the electronic transition be localized in space and time, but it is important to recognize that this does <u>not</u> require that the adiabatic potential curves or surfaces have an "avoided intersection" for real coordinates; see Section V of reference 9. Recent calculations based on this theory have been carried out by Lin, George, and Morokuma[84] (for $H^+ + D_2 \rightarrow HD^+ + D$) and by Preston, Sloane, and Miller[85] (for $F(^2P_{3/2}) + Xe \rightarrow F(^2P_{1/2}) + Xe$), and it seems clear that there will be much more activity in the following years regarding the general topic of non-adiabatic transitions in low energy molecular collisions.

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20. This restricts the treatment to collisions of diatomic molecules or to polyatomic molecules which are described initially by noninteracting normal modes.
21. The second term in the expression for $\mathbf{q}(t)$ subtracts out the asymptotic "free particle" time dependence of the angle variables; i.e., since asymptotically $\mathbf{n}$ and P are constant and

$$R(t) \sim (P/\mu)t + \text{constant}$$

$$\mathbf{q}(t) \sim \frac{\partial \varepsilon(\mathbf{n})}{\partial \mathbf{n}} t + \text{constant},$$

it is clear that the phase shift variables,

m $$\bar{\underset{\sim}{q}}(t) \equiv \underset{\sim}{q}(t) - \frac{\partial\varepsilon(\underset{\sim}{n})}{\partial\underset{\sim}{n}}\,\mu R(t)/P \quad ,$$

are asymptotically constant.

22. Eq. (3.5) takes a manifestly symmetrical form by noting that

$$\left[\frac{\partial \underset{\sim}{n}_2\,(\bar{\underset{\sim}{q}}_1,\underset{\sim}{n}_1;E)}{\partial\bar{\underset{\sim}{q}}_1}\right]^{-1} = \frac{\partial^2\Phi(\underset{\sim}{n}_2,\underset{\sim}{n}_1;E)}{\partial\underset{\sim}{n}_2\,\partial\underset{\sim}{n}_1} \quad ;$$

since $\Phi(\underset{\sim}{n}_2,\underset{\sim}{n}_1;E) \equiv \Phi(\underset{\sim}{n}_1,\underset{\sim}{n}_2;E)$, the classical S-matrix is thus identically symmetric, i.e., microscopically reversible. The form of the pre-exponential factor in Eq. (3.5), however, is usually easier to evaluate numerically.

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28. Sometimes the "proper inclusion" of interference terms means that an appropriate *uniform* semiclassical expression must be utilized rather than the "primitive" semiclassical expressions of Eqs. (3.5) and (3.25).

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$H + H_2$ reaction on the Porter-Karplus potential surface, for example, the classical threshold is ∿ 0.20-0.21eV collision energy; quantum mechanically, of course, there is no absolute energetic threshold for the 0 → 0 reaction.

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51. The asymptotic free particle time dependence of x(t) and $\underset{\sim}{y}(t)$ is subtracted out in the usual way; see reference 21.

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56. See, for example, reference 43, pp. 404-405.

57. $\underset{\sim}{\mu}(\underset{\sim}{r})$ is the electronic matrix element of the dipole operator between two Born-Oppenheimer electronic wavefunctions and depends on nuclear coordinates through the parametric dependence of the wavefunctions on nuclear coordinates.

58. See, for example, reference 13, pp. 273-284.

59. See reference 14, pp. 39-41; or reference 52, pp. 437-441.

60. M. L. Goldberger and K. M. Watson, *Collision Theory*, Wiley, N.Y., 1964, p. 431 *et seq.*

61. When dealing with one-dimensional systems it is often convenient to eliminate t in favor of x as the independent variable and then require x to be real. [cf. D. W. McLaughlin, *J. Math. Phys.* **13**, 1099 (1972)]. This is no restriction for one-dimensional systems because it is always possible to choose the time path to keep x(t) real; i.e., for any value of Ret one can choose Imt to satisfy the equation Im x(t) = 0. One sees, however, that this is possible only for one-dimensional systems, for as soon as there are two coordinates, say, one cannot in general choose Imt to make the imaginary parts of both coordinates vanish; i.e., one cannot satisfy more than one equation with only one variable.

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80. This prevents the possibility of the trajectory backing up to a prior time at which the equilibrium position was passed.

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FIGURE CAPTIONS

1. An example of the quantum number function $n_2(\bar{q}_1, n_1)$, here for a collision of He and H_2 at a total energy $E = 10\hbar\omega$ and with $n_1 = 1$. The ordinate is the final value of the vibrational quantum number as a function of the initial phase $\bar{q}_1$ of the oscillator, along a classical trajectory with the initial conditions in Eq. (3.2). The dashed line at $n_2 = 2$ indicates the graphical solution for the two roots of the equation $n_2(\bar{q}_1, 1) = 2$.

2. Vibrational transition probabilities for collinear He + H_2 at total energy $E = 10\hbar\omega$ for an initial vibrational state $n_1 = 0$ (top), 1, 2 (bottom). The dashed lines connect results of the completely classical approximation, Eq. (3.28), and the solid lines connect the uniform semiclassical values (which on the scale of the drawing are essentially the same as the exact quantum mechanical values of reference 24 .)

3. The same quantity as in Figure 1, except for the reactive process $H + H_2(n_1 = 0) \rightarrow H_2(n_2) + H$, for a total energy $E = 14.7$ kcal/mole, as computed by Wu and Levine (reference 32). There are two roots of the equation $n_2(\bar{q}_1, 0) = 0$.

4. The same as Figure 3, except for a total energy E = 13.7 kcal/mole. Here there are four roots to the equation $n_2(\bar{q}_1,0) = 0$.

5. A qualitative sketch of the classical (upper) and uniform semiclassical (lower) transition probability P_{n_2,n_1} as a continuous function of n_2 (with n_1 fixed). n_2^{max} and n_2^{min} indicate the extrema of the function $n_2(\bar{q}_1,n_1)$ as a function of $\bar{q}_1$ (as seen in Figure 1, for example).

6. A potential curve V(r) and collision energy E for which potential (i.e., single-particle) resonances exist.

7. A schematic representation of three of the trajectories which contribute to the elastic scattering from the potential shown in Figure 6. There are an infinite sequence of other trajectories which differ from (c) only in the number of oscillations made between r_1 and r_2.

8. The same quantity as in Figure 1, except for reactive (solid line and solid points) and non-reactive (open points) collisions of $H + Cl_2(n_1 = 0) \rightarrow H + Cl_2(n_2)$, $HCl(n_2) + Cl$ as calculated by Rankin and Miller (reference 47). The total energy (referred to the saddle point) is 0.3 eV. The dashed line at $n_2 = 5$

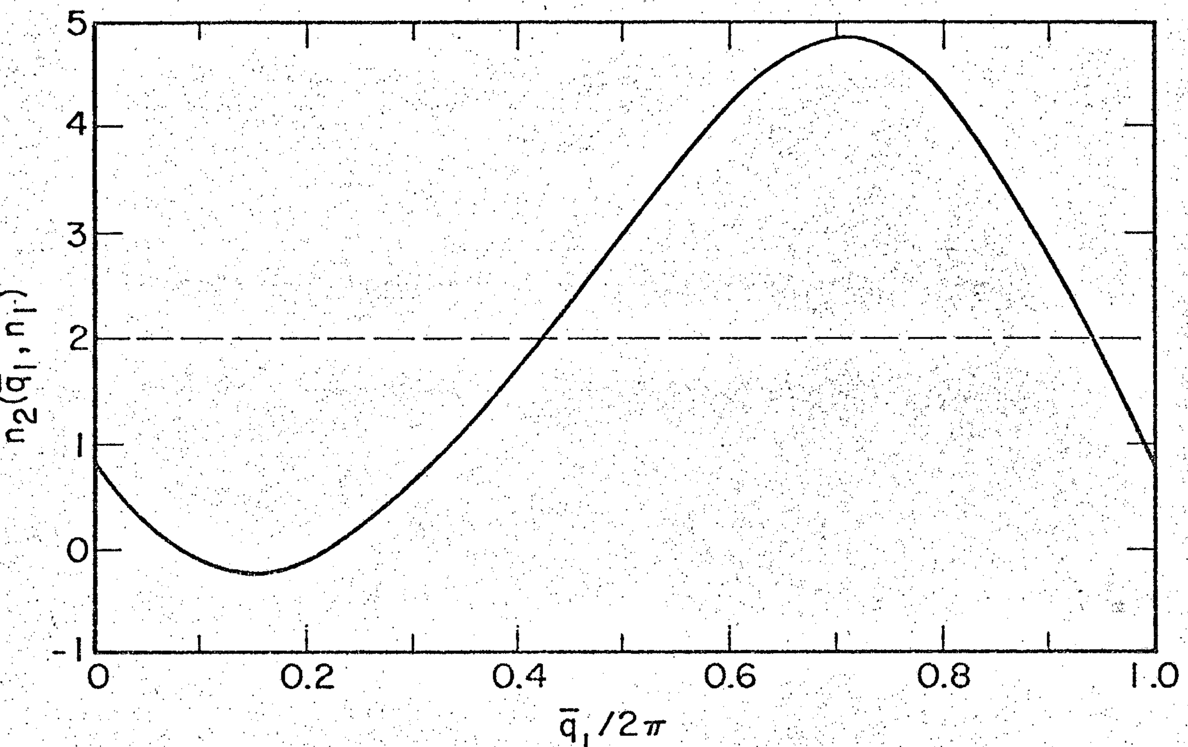
indicates that two "direct" trajectores and many "snarled" ones contribute to the 0 → 5 reactive transition.

9. A potential barrier and translational energy for which tunneling occurs.

10. The same quantity as in Figure 1, except for a total energy $E = 3\hbar\omega$. Here all inelastic transitions are classically forbidden.

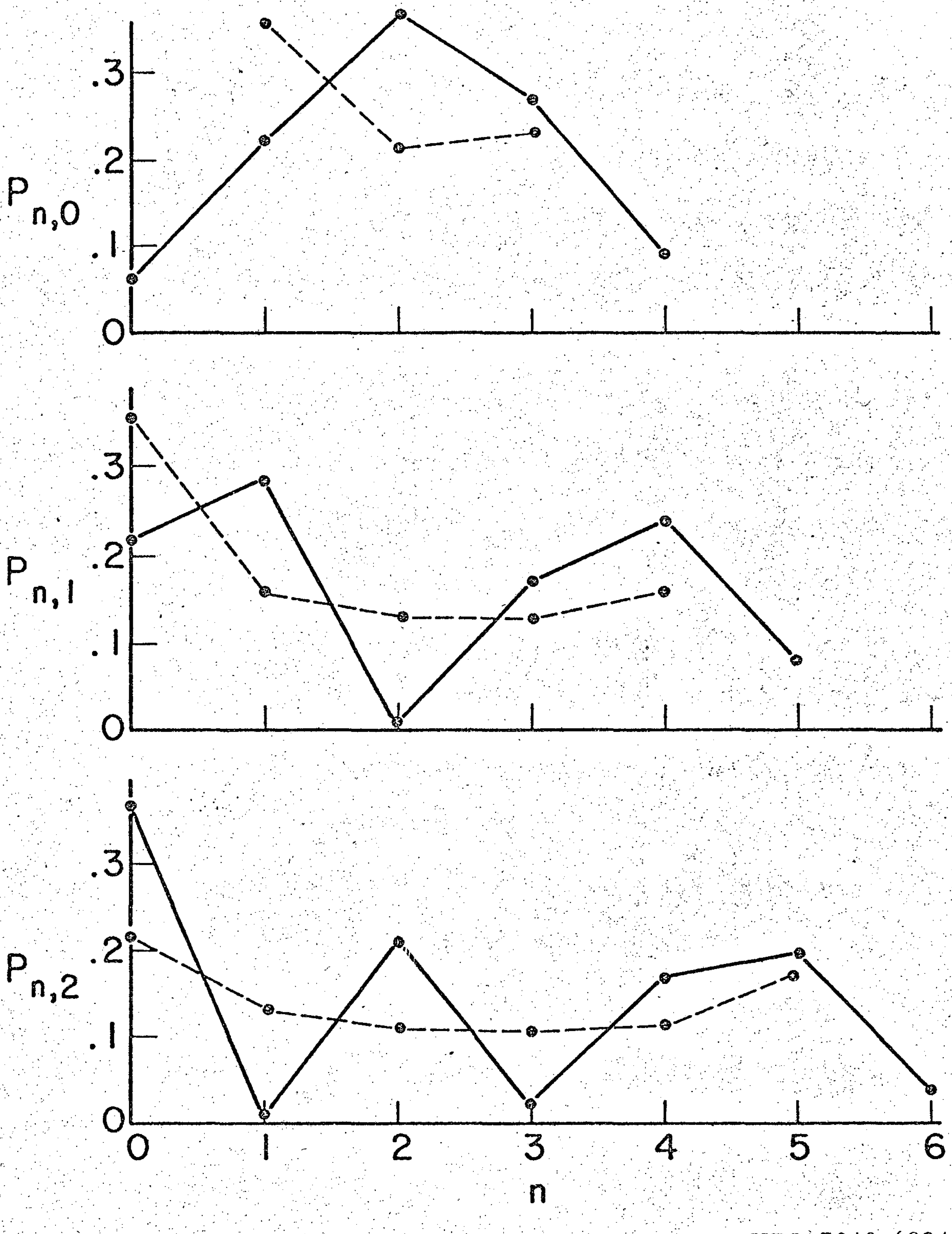
11. The reaction probability for $H + H_2(n_1 = 0) \rightarrow H_2(n_2 = 0) + H$ in the region below the classical threshold for reaction; E_o is the initial translational energy. The semiclassical (SC) results are those of George and Miller (reference 34) as given by Eq. (4.18), and the quantum mechanical (QM) values are the results of Schatz and Kuppermann (reference 67).

12. Cross sections for vibrational deactivation: $Li^+ + H_2 (n_1 = 1, j_1 = 0) \rightarrow Li^+ + H_2(n_2 = 0, j_2 = j)$, as a function of final rotational state, for an initial translational energy of 0.684 eV. The semiclassical and quantum mechanical values are those of Miller and Raczkowski (reference 76) and Schaefer and Lester (reference 77), respectively, and the "statistical" values are those given by Eq. (4.40) (normalized so that the cross section summed over j is equal to the semiclassical and quantum value).



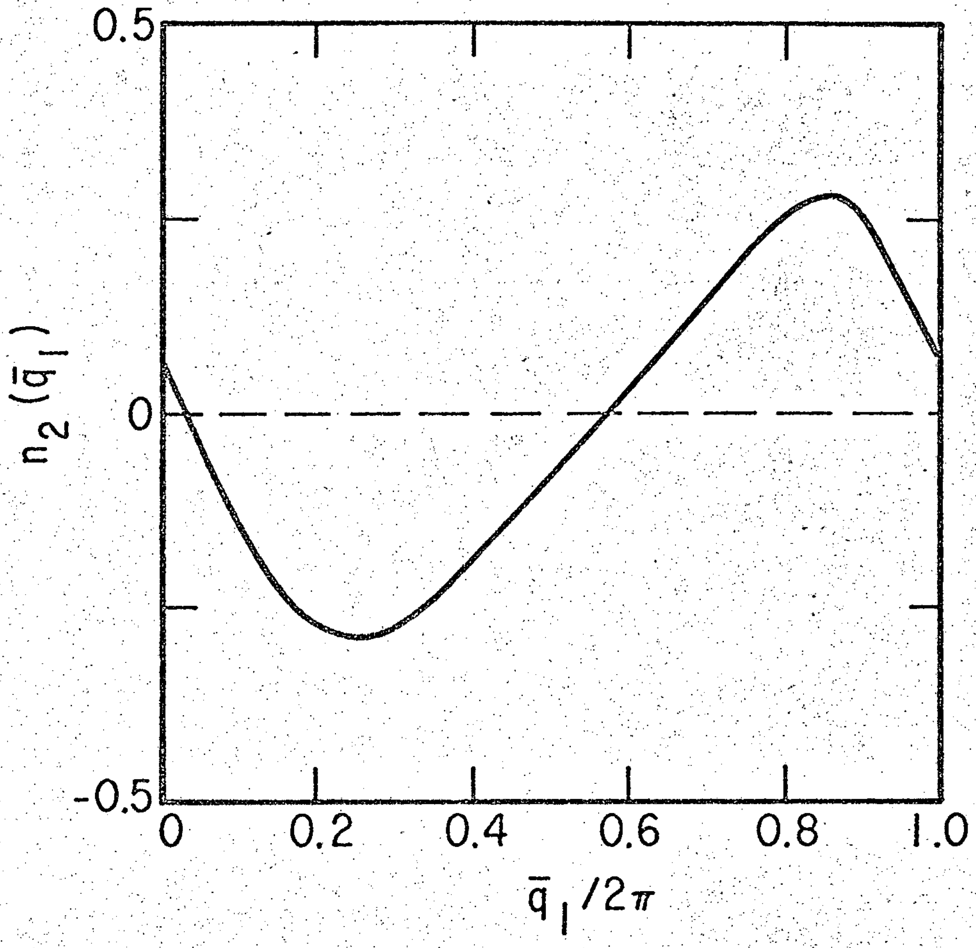
XBL 7010-6830

Fig. 1



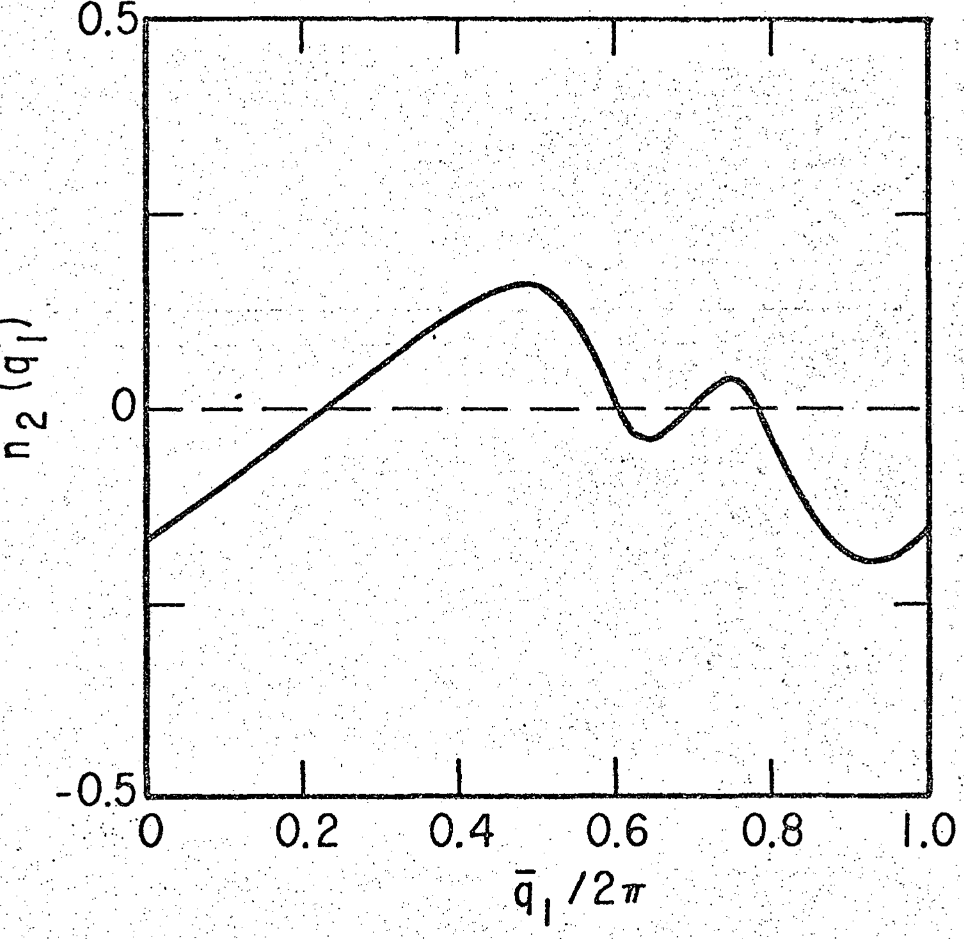
XBL 7010-6831

Fig. 2



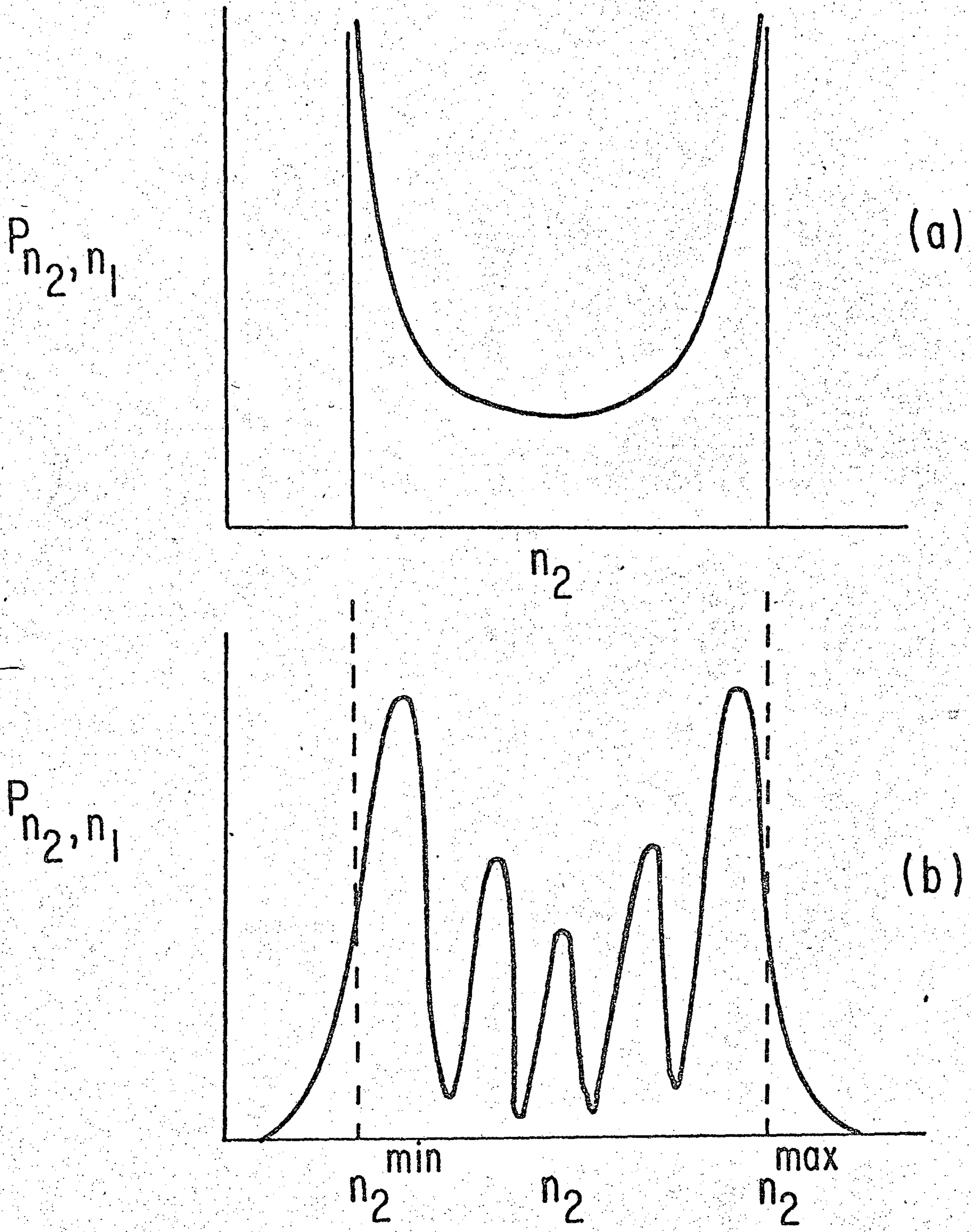
XBL 7312-7111

Fig. 3



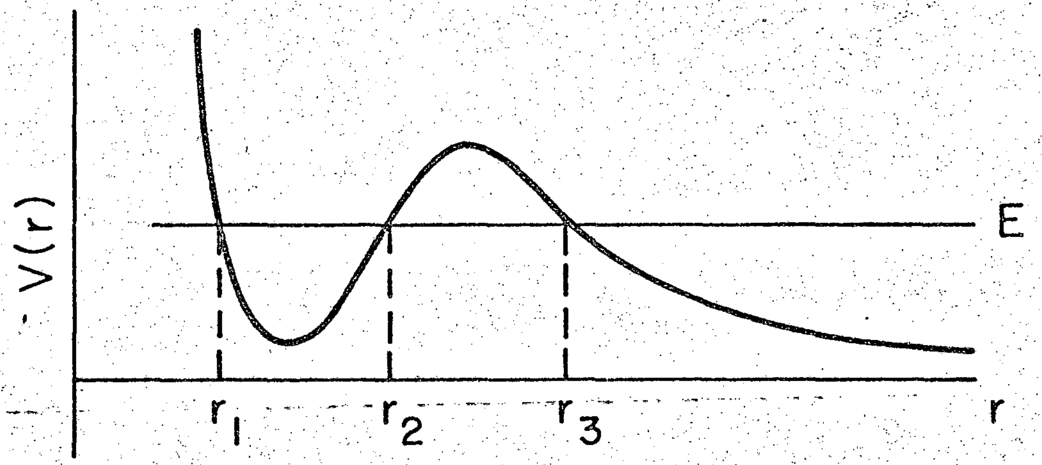
XBL 7312-7112

Fig. 4



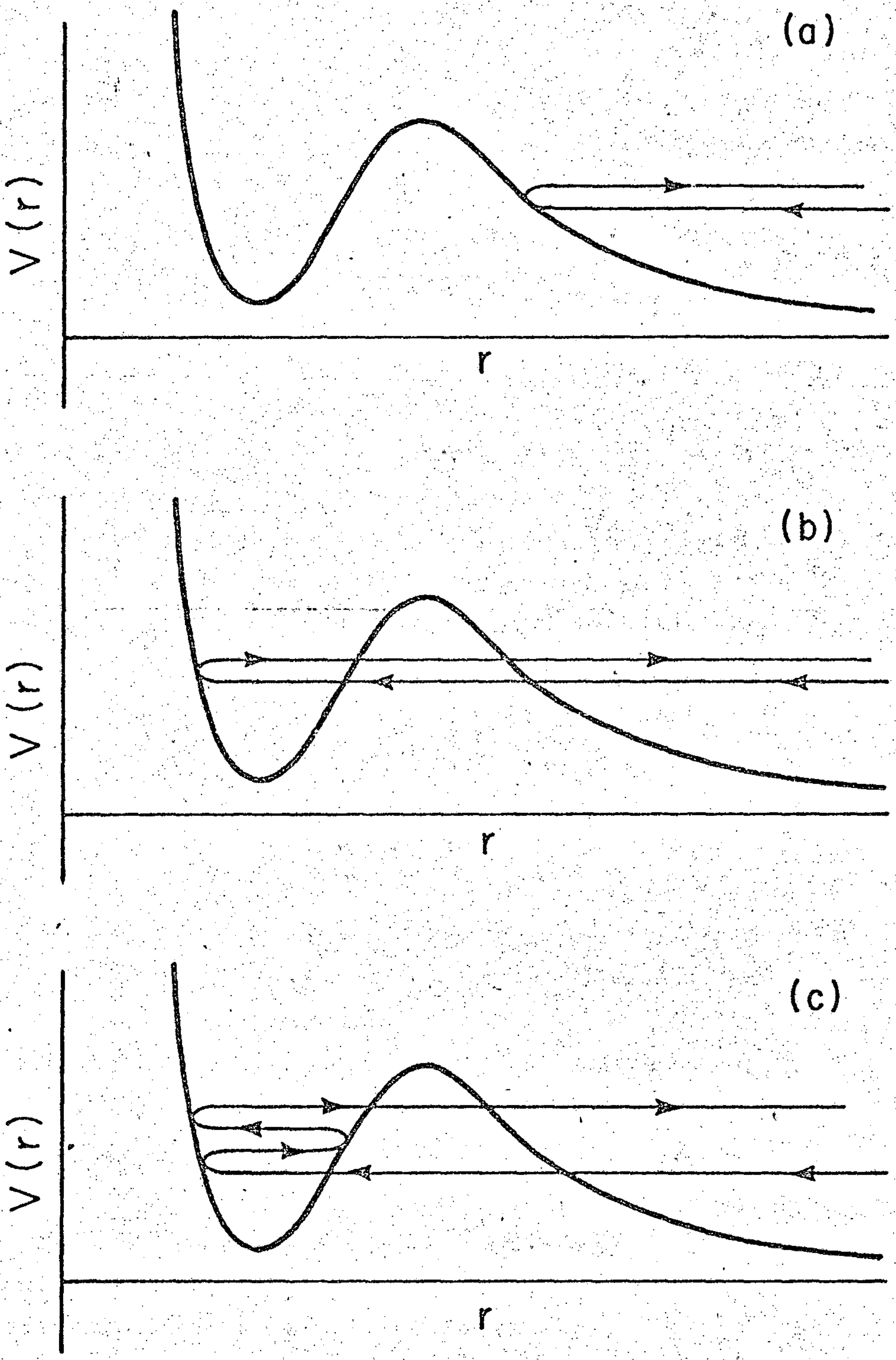
XBL 715-1022

Fig. 5



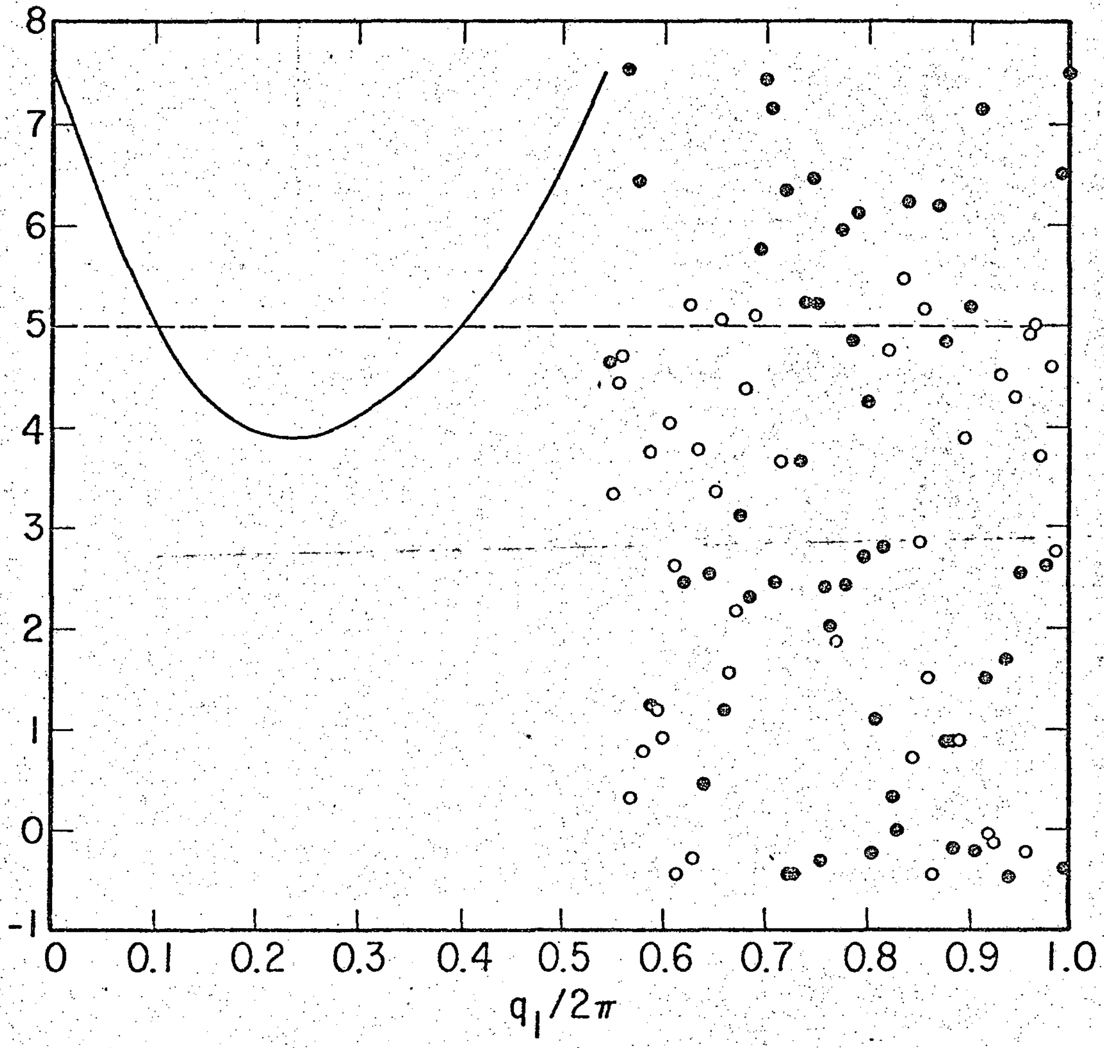
XBL 7311-6737

Fig. 6



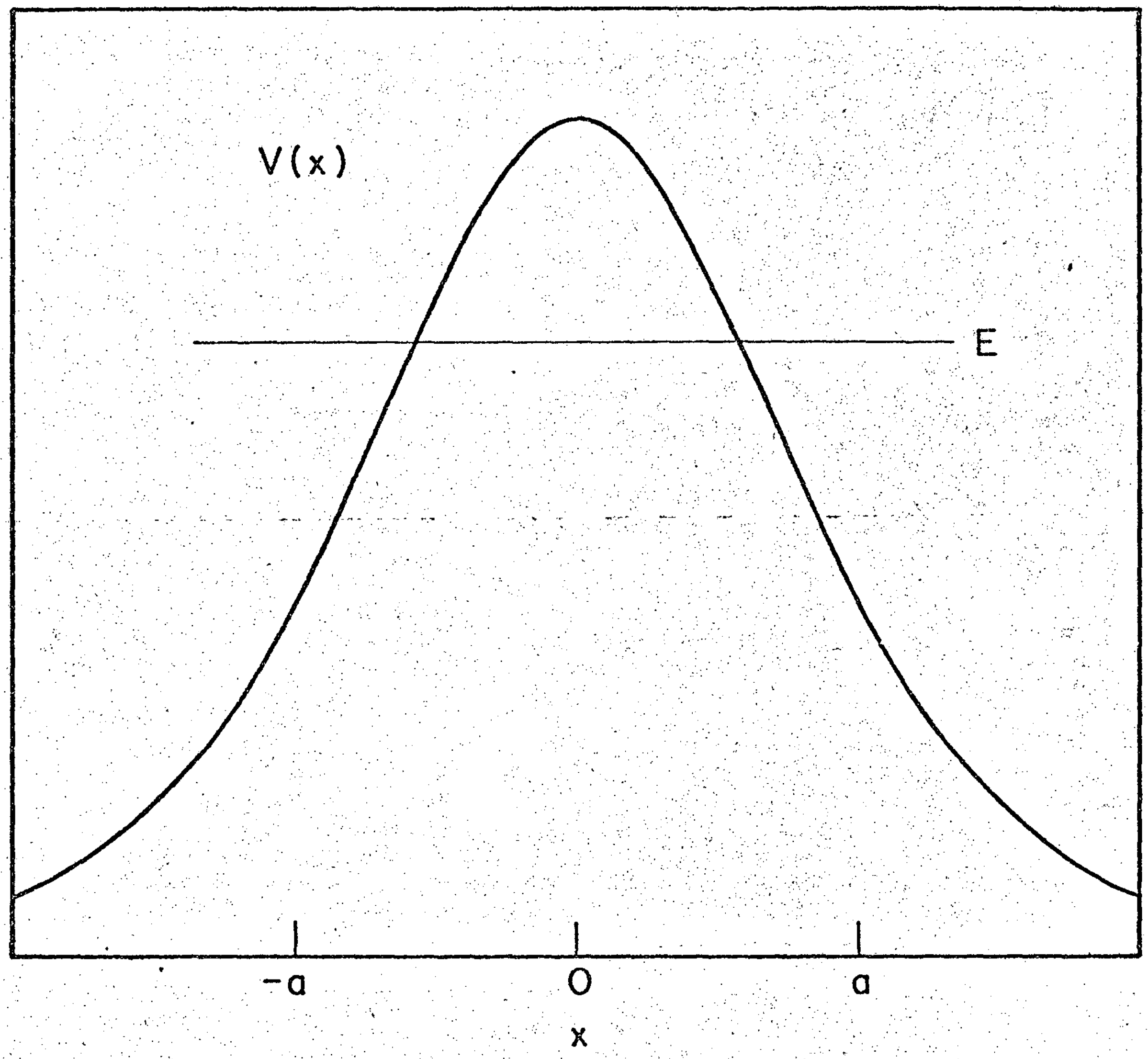
XBL 7311-6736

Fig. 7



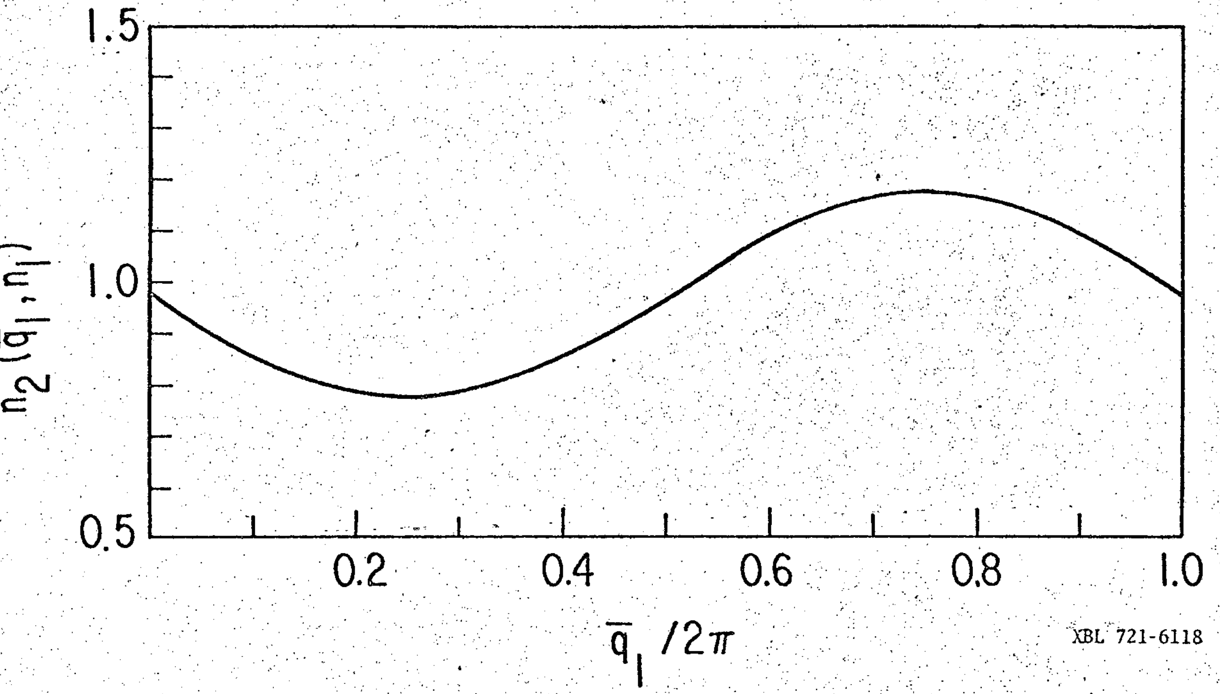
XBL 712-6501

Fig. 8



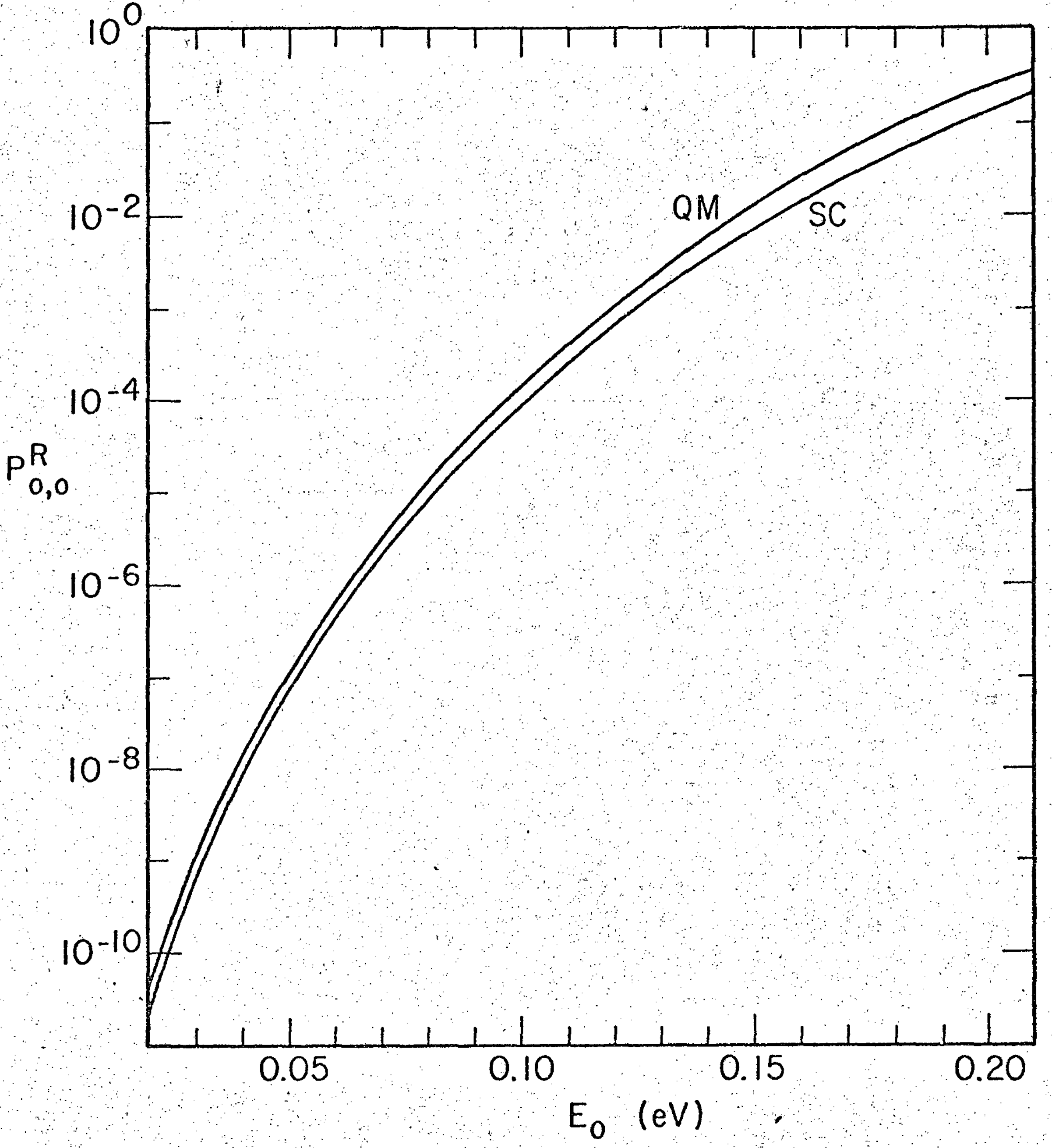
XBL 732-5749

Fig. 9



XBL 721-6118

Fig. 10



XBL 7310-5561

Fig. 11

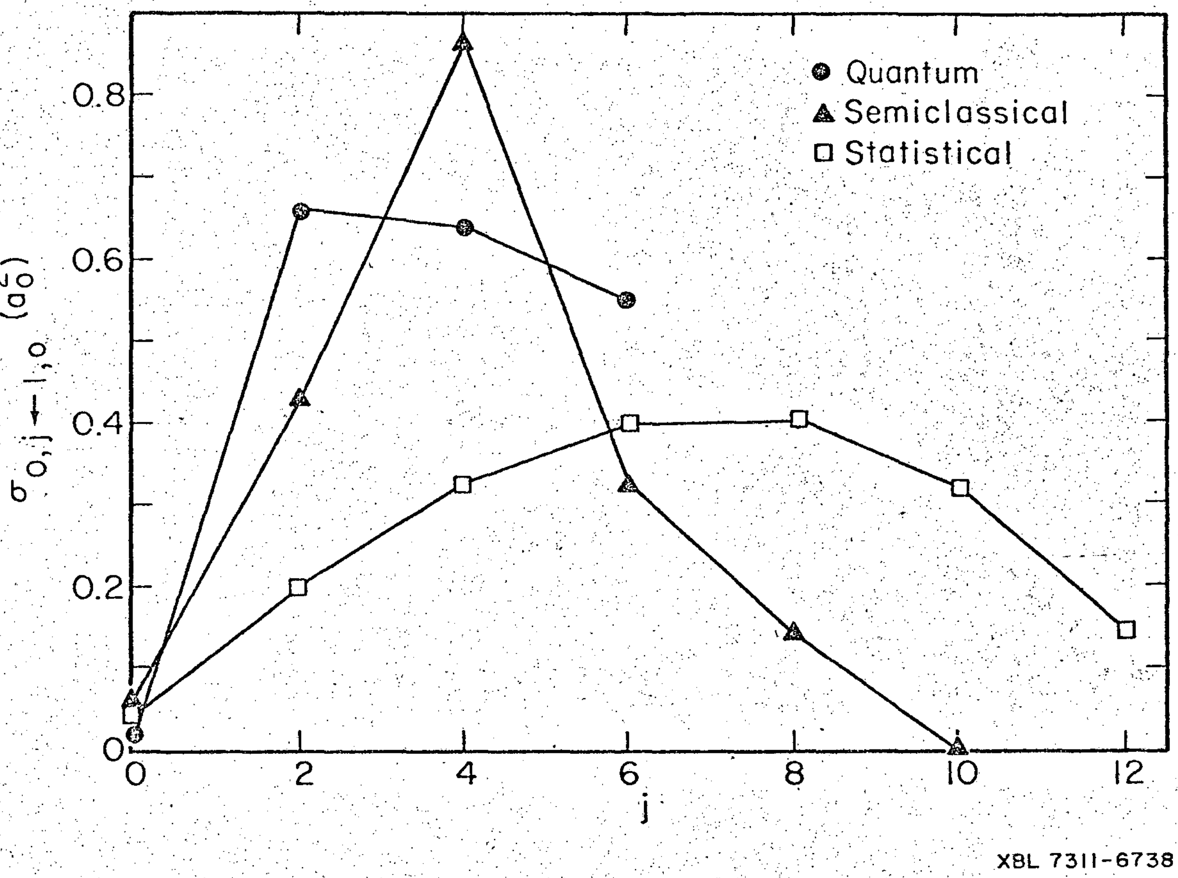

$\sigma_{0,j\rightarrow 1,0}$ (a_0^2)
0
0.2
0.4
0.6
0.8
0
2
4
6
8
10
12
j
● Quantum
▲ Semiclassical
□ Statistical
XBL 7311-6738

Fig. 12

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