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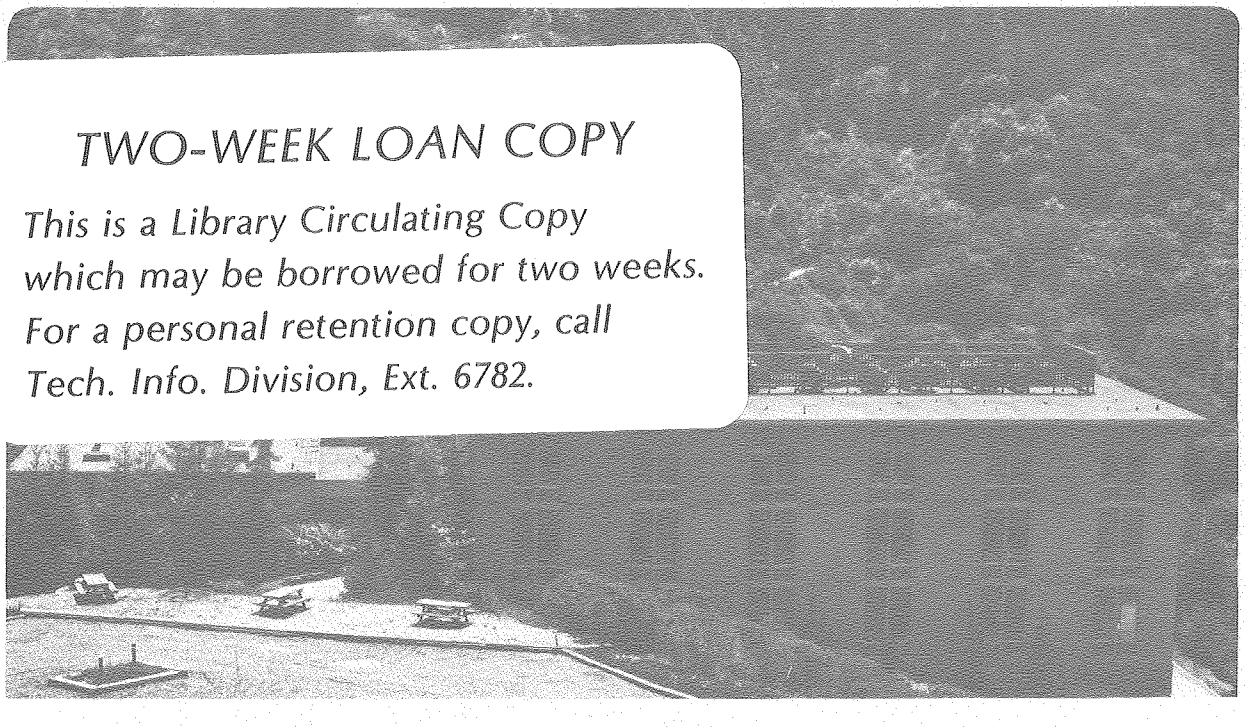

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Progress in the Application of Classical S-Matrix Theory to Inelastic Collision Processes

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Abstract

Methods are described which effectively solve two of the technical difficulties associated with applying classical S-matrix theory to inelastic/reactive scattering. Specifically, it is shown that rather standard numerical methods can be used to solve the "root search" problem (i.e., the non-linear boundary value problem necessary to impose semiclassical quantum conditions at the beginning and the end of the classical trajectories) and also how complex classical trajectories, which are necessary to describe classically forbidden (i.e., tunneling) processes, can be computed in a numerically stable way. Application is made to vibrational relaxation of H_2 by collision with He (within the helicity conserving approximation). The only remaining problem with regard to applying classical S-matrix theory to complex collision processes has to do with the availability of multidimensional uniform asymptotic formulae for interpolating the "primitive" semiclassical expressions between their various regions of validity.

I. Introduction.

The classical S-matrix description of molecular collisions has been developed and refined over the past decade and has been successfully applied to the calculation of a variety of collision processes.[1] Perhaps the most attractive feature of this approach is that it provides a clear physical understanding of various quantum effects which arise in inelastic/reactive scattering. One of its first predictions,[2] for example, was that interference effects, "rainbow" effects, etc., should appear in the distribution of final vibrational and/or rotational states of an inelastic collision process, quite analogous to such effects in the distribution of scattering angles (i.e., the differential cross section) in elastic scattering.[3] Furthermore, the origin of this interference structure is the same as that in elastic scattering, namely semiclassical interference between different classical trajectories which contribute to the process. Just as in elastic scattering, however, observation of this interference structure in final state distribution requires high resolution experiments, but recently rainbow effects have been seen by Beck, et al.[4] in rotational state distributions.

Numerical application of the classical S-matrix approach in its most rigorous version (i.e., using numerically computed classical trajectories) to systems with several internal degrees of freedom, however, encounters technical difficulties which has precluded its being employed routinely. The difficulty is not with computing classical trajectories, but with (1) finding, in a systematic and efficient manner, the particular trajectories that matter semiclassically,

(2) integrating the equations of motion along complex time contours[5] if the process of interest is classically forbidden (i.e., weak), and (3) having available an appropriate uniform semiclassical expression[2,6] if the system is too quantum-like for the "primitive" semiclassical expressions to be sufficiently accurate.

The purpose of this paper is to report methods that effectively solve problems (1) and (2) above; i.e., numerically stable ways have been developed for computing complex trajectories even for extremely weak transitions, and efficient ways have been found to find the particular trajectories (the "root search" problem) which satisfy the semiclassical boundary conditions. The test problem considered in this paper is vibrational relaxation of H_2 by collision with He, and it is treated within the helicity conserving approximation; the methods developed (and described in Section II), however, should be much more generally applicable than to just this example. Problem (3) above, however, is more fundamentally difficult to overcome, as is illustrated by the He + H_2 example treated: the known "uniform" methods are successful for most, but not all of the region of final rotational states j_f in the vibrational relaxation process (n = vibrational quantum number)

$$He + H_2(n=1;j=0) \rightarrow He + H_2(n=0;j=j_f) \quad . \qquad (1.1)$$

To make classical S-matrix theory more quantitatively useful it is thus concluded that the primary need is for more generally applicable multi-dimensional uniform formulae.

Section II first summarizes the basic aspects of classical S-matrix theory for an A + BC collision within the helicity conserving approximation, and then describes the methods for integrating trajectories along complex time contours and for finding the particular "root" trajectories, i.e., those satisfying semiclassical boundary conditions asymptotically. Results of the application to reaction (1.1) are given in Section III, along with a discussion of the possible "uniform" semiclassical formulae.

II. Computation of Complex Trajectories

a. The Classical Helicity Conserving Approximation

Earlier work[7] by us has described the classical version of the helicity conserved approximation (variously called the j_z-conserving coupled states approximation,[8] or the centrifugal sudden approximation[9]) as it applies to A + BC collisions when the diatom BC is restricted to be a rigid rotor, and it is a straight-forward extension to allow the molecule to vibrate. If (P,R) and (p,r) denote the coordinates and momenta for radial translation of A relative to BC and for relative B-C motion, respectively, and (j,q_j) are the action-angle variables for rotation of BC (i.e., j is the rotational angular momenta), then the same analysis as before[7] leads to the following classical helicity-conserving Hamiltonian,

$$H^{\ell,K}(P,R,p,r,j,q_j) = \frac{P^2}{2\mu} + \frac{p^2}{2m} + \frac{j^2}{2mr^2} + \frac{\ell^2}{2\mu R^2}$$

$$+ V(r,R,\gamma) \quad , \tag{2.1}$$

where ℓ, the orbital angular momentum for relative A-BC motion, has as before[7] been assumed to be conserved. The helicity K, which is conserved within this approximate Hamiltonian, appears in the relation between the angle γ ($\cos\gamma \equiv \hat{r}\cdot\hat{R}$) and the angle variable q_j,

$$\cos\gamma = \sqrt{1 + K^2/j^2}\ \cos q_j \quad . \tag{2.2}$$

For applications below, K is always 0 so that the simpler relation $\gamma = q_j$ holds.

In order to define vibrational quantum numbers semiclassically one must transform from the physical vibrational coordinate and momentum (r,p) to vibrational action-angle variables (n,q_n). This has been discussed in detail before;[1a,1b] specifically, the semiclassical vibrational-rotation eigenvalue function $\varepsilon(n,j)$ is defined implicitly by

$$(n + \tfrac{1}{2})\pi = \int_{r_<}^{r_>} dr \sqrt{2m[\varepsilon(n,j) - v(r) - j^2/r^2]} \quad , \tag{2.3a}$$

where $v(r)$ is the H_2 vibrational potential function, and the angle q_n is defined by

$$\cos^{-1}(\cos q_n) = m \frac{\partial \varepsilon(n,j)}{\partial n} \int_{r_<}^{r} dr' \{2m[\varepsilon(n,j)-v(r')-j^2/r'^2\}^{-1/2} \quad . \tag{2.3b}$$

As has also been noted before,[1b] it is most useful to carry out the actual numerical trajectory calculation using the cartesian vibration variables (p,r), transforming from the initial values of (n,q_n) at the beginning of the trajectory and to the final values of (n,q_n) at the end of the trajectory.

For $v(r)$ the 32-term polynomial representation of the Kolos-Wolneiwicz[10] function given by Waech and Bernstein[11] was used, and the interaction potential,

$$V_{int}(r,R,\gamma) \equiv V(r,R,\gamma) - v(r) \quad ,$$

was taken to be that of Gordon and Secrest.[12] The function $\varepsilon(n,j)$ was evaluated numerically for this choice of $v(r)$ and then fit to a

Dunham-like power series in $(n + \frac{1}{2})$ and j^2 up to third order terms, a sufficiently accurate representation for the range of n and j that are involved in the present application. Computing the function $\varepsilon(n,j)$ in classical S-matrix theory is analogous to finding the target eigenstates for a quantum mechanical coupled channel calculation, and we note that for very weak transitions, such as vibrational relaxation in H_2 + He, the cross sections are more sensitive to the description of the target than for processes with large cross sections.

b. Initial Conditions and Choice of the Complex Time Path

As discussed before,[1a,1b] it is most convenient to begin the actual numerical integration of each trajectory with r at an inner (or outer) classical turning point. If n_1 and j_1 are the initial vibrational and rotational quantum numbers and $\bar{q}_{n_1}$ and $\bar{q}_{j_1}$ the phase shift variables conjugate to them, then the specific initial conditions for a trajectory with orbital angular momentum ℓ are

$$r(t_1) = r_< \tag{2.4a}$$

$$R(t_1) = \left[\frac{2E_1}{\mu}\left(\frac{2\pi N - \bar{q}_{n_1}}{\partial\varepsilon(n,j)/\partial n}\right)^2 + \frac{\ell^2}{2\mu E_1}\right]^{1/2} \tag{2.4b}$$

$$q_j(t_1) = \bar{q}_{j_1} + \frac{\partial\varepsilon(n,j)}{\partial j}\,\frac{(2\pi N - \bar{q}_{n_1})}{\partial\varepsilon(n,j)/\partial n} \tag{2.4c}$$

$$p(t_1) = 0 \tag{2.4d}$$

$$P(t_1) = -\sqrt{2\mu E_1 - \ell^2/R(t_1)^2} \tag{2.4e}$$

$$j(t_1) = j_1 \tag{2.4f}$$

where E_1 is the initial translational energy, the derivatives of $\varepsilon(n,j)$ are evaluated at n_1 and j_1, and the integer N is chosen such that $R(t_1)$ is large enough to be in the asymptotic region.

The end of the trajectory at time t_2 is signaled by R becoming equal to a large final value chosen for all trajectories. To simplify the expression for the phase of the S-matrix contributions one integrates backwards to time $\bar{t}_2$ at which the most recent inner vibrational turning point occurred. In practice it is unnecessary to integrate backwards since by using the techniques described below one can integrate directly to $\bar{t}_2$. The final value of $j \equiv j_2$ is constant in this region and is given by the equations of motion directly and n_2 is determined by solving

$$\varepsilon(n_2,j_2) = v(r(\bar{t}_2)) + \frac{j_2^2}{2mr(\bar{t}_2)^2} \quad , \tag{2.5}$$

using the already determined form of the function $\varepsilon(n,j)$. Only the conditions at t_1 and $\bar{t}_2$ and a phase integral over the interval between t_1 and $\bar{t}_2$ are needed to compute the contribution of a root trajectory to the S-matrix.

The result of this trajectory calculation is to produce the functions $n_2(\bar{q}_{n_1},\bar{q}_{j_1})$ and $j_2(\bar{q}_{n_1},\bar{q}_{j_1})$, i.e., the final vibrational and rotational "quantum numbers" as a function of their conjugate initial angle variables, provided one can find an appropriate complex time path for the trajectory if the roots of the following equations are complex,

$$n_2(\bar{q}_{n_1}, \bar{q}_{j_1}) = n_2 \tag{2.6a}$$

$$j_2(\bar{q}_{n_1}, \bar{q}_{j_1}) = j_2 \quad , \tag{2.6b}$$

where n_2 and j_2 are specific integers. An appropriate complex time path must satisfy two criteria. First, it must produce final conditions which determine the correct branch of the (possibly) multivalued function $\underset{\sim}{n}_2(\bar{\underset{\sim}{q}}_1)$ ($\underset{\sim}{n}_2 \equiv (n_2, j_2)$, $\bar{\underset{\sim}{q}}_1 \equiv (\bar{q}_{n_1}, \bar{q}_{j_1})$). For inelastic collisions, such as the case we consider here, the correct branch is the original one, and this means that the trajectory must not encircle any branch points of the action-angle variables (or R) as functions of time. Secondly, the trajectory cannot be allowed to move outside the range of complex values of the coordinates for which we have accurate analytic continuations of the potentials v(r) and $V_{int}(r,R,\gamma)$.

The tendency of trajectories to "wander" unphysically far into the complex coordinate plane during numerical integration of the equations of motion is most pronounced for the vibrational degree of freedom. This behavior can be understood by considering trajectories in complex time for a harmonic oscillator description of vibration in which the time dependence of r(t) is given by

$$r(t) - r_0 = a \cos(\omega t + \delta) \quad . \tag{2.7}$$

For complex time the cosine function can become exponentially large, although for a fixed value of the imaginary part of t the trajectory

executes elliptical motion in the complex plane as the real part of t increases. However, the harmonic oscillator description is usually not adequate, and in any case during the collision the vibrational motion is coupled to other degrees of freedom. Thus it can be the case that $|r(t)|$ increases rapidly during the collision, even for fixed $Im(t)$.

To control this tendency we have employed three methods of stabilizing the vibrational motion through the choice of the complex time path. The first of these has been described elsewhere[13] and was found to be most useful in the portions of the trajectory before and after the collision. This approach assumes r(t) to be quadratic in t and solves at each step in the trajectory for the time step Δt which would bring the oscillator to r(t) at r_0; at step n this gives

$$\Delta t = \{- \dot{r}_n \pm [\dot{r}_n^2 + 2\ddot{r}_n(r_0 - r_n)]^{1/2}\}/\ddot{r}_n \quad , \tag{2.8}$$

where r_n, $\dot{r}_n$, $\ddot{r}_n$ are the current values of r_n and its time derivatives, and the $\pm$ sign is chosen to make $Re(\Delta t) > 0$. It is actually the phase of the time step which is chosen as that of Δt in Eq. (2.8); the magnitude of the time step is always determined by the truncation error criterion of the integrator.

When this method failed to stabilize the trajectory, as it invariably did in the region of closest approach of He to H_2, we switched to a second method which was found to stabilize the r(t) trajectory in the interaction region. In this procedure the phase of Δt is taken

to be the phase of $1/\omega$, where ω is the frequency of a local harmonic oscillator approximation to r(t). To obtain an expression for ω in terms of quantities which are available during the integration of a trajectory, we first find the (complex) equilibrium position r_0 for the potential U(r) defined by

$$U(r) = v(r) + \frac{j^2}{2mr^2} \tag{2.9}$$

for the current value of j. Simple analytic approximations for $r_0(j)$ can be used for this purpose. At any point in the trajectory $U(r_n)$ and $U'(r_n)$ are known from the equations of motion, and assuming that $U(r_n)$ is approximately quadratic,

$$U(r_n) \simeq U(r_0) + \frac{1}{2} m\omega^2 (r_n - r_0)^2 \quad , \tag{2.10}$$

one can find an expression for ω in terms of quantities available in r_n:

$$\omega = \left[\frac{U'(r_n)^2}{2m[U(r_n) - U(r_0)]} \right]^{1/2} \quad . \tag{2.11}$$

The sign of the square root is chosen so that $\mathrm{Re}(1/\omega) > 0$. Choosing the phase of Δt to be that of $1/\omega$ would keep the trajectory on a closed ellipse if the motion were purely harmonic, i.e., if r(t) satisfied Eq. (2.8) with a complex value of δ. In our calculations this procedure effectively stabilized the vibrational motion in the interaction region. It should be noted that in the interaction region

injudicious choice of the time path, for example choosing t such that r(t) remains real, can also lead to problematic motion of R(t). Our choice avoided this difficulty in most cases, and use of the rational fraction approach described below was able to avoid it in general.

A combination of these two procedures was sufficient to stabilize practically all of the trajectories which contributed to the S-matrix elements computed in this work. However, if very poor guesses are used for initial values of the angle variables in the root search to solve Eq. (2.6), the final values of the action variables can have such a large imaginary part that these simple methods of stabilizing the trajectories fail. For these extraordinary cases the following technique of choosing the complex time path was devised which, although more laborious, is much more reliable than the simpler methods.

At every point in the trajectory one has more information than the local values of the coordinates and momenta and their time derivatives; i.e., one also knows the values of those quantities at previous steps in the numerical integration of the trajectory. Using this information one can make use of standard techniques to form a rational fraction[14] approximation to, for example, r(t) which has the form

$$r(t) \simeq \frac{P_n(t)}{Q_m(t)} \quad , \tag{2.12}$$

where $P_n(t)$ and $Q_m(t)$ are polynomials of order n and m respectively. This approximation for r(t) allows one to "look ahead" in the t plane to find the direction of t in which to proceed to move r(t) to the next

turning point, r_{tp}, for example. Thus at time t_n one forms the rational fraction using the values of r(t) from previous integration steps and solves for the time t^* satisfying

$$r_{tp} = P_n(t^*)/Q_m(t^*) \tag{2.13}$$

with a simple numerical root search. Then for the next several steps in the integration time steps with the phase of (t^*-t_n) are taken. In practice we form the continued fraction representation of the rational fraction suggested by Schlessinger[14] from the values of r(t) from the previous twenty integration steps. This information was found to be sufficient to predict the motion of r(t) (or p(t)) over roughly half a vibrational period. Using this technique thus allows one to choose a time path to move from one vibrational turning point to the next.

Rational fraction analytic continuations can be used as a general tool for predicting the behavior of a trajectory for complex times. For example they can be used to help locate branch points in the time dependence of dynamical variables by exploiting the fact that the radius of convergence of the rational fraction decreases dramatically near a branch point. In these regions the difference between the predicted behavior and the results of integrating the trajectory becomes suddenly greater, particularly in the direction of the branch point.

Finally, we note that the continued fraction representation was always used in our calculations to find the complex time path which moved the trajectory to a turning point of vibrational motion at the final time $\bar{t}_2$ for each trajectory.

c. The Root Search

The difficulty of finding trajectories which satisfy Eq. (2.6) is probably the most awkward computational feature of classical S-matrix theory; it exists even when one is treating classically allowed processes, i.e., when the roots of Eq. (2.6) are real. However, this difficulty can be substantially overcome by the application of some standard numerical technology. With the methods described in the previous section we were able to stabilize, and therefore finish, trajectories beginning with arbitrary values of $\bar{\underset{\sim}{q}}_1$ and thus to construct the function $\underset{\sim}{n}_2(\bar{\underset{\sim}{q}}_1)$. To solve for the $\bar{\underset{\sim}{q}}_1$ satisfying Eq. (2.6) we used a method due to Powell,[15] which combines the virtues of the Newton and the steepest descent methods of finding roots of nonlinear algebraic equations.

Powell's method is a procedure for solving equations of the form

$$\underset{\sim}{f}(\underset{\sim}{q}) = \underset{\sim}{0} \tag{2.14}$$

and is based on the following equations for each step $\underset{\sim}{\delta}$ in the root search in the $\underset{\sim}{q}$ space,

$$(\underset{\approx}{J}^T \underset{\approx}{J} + \lambda \underset{\approx}{D}) \cdot \underset{\sim}{\delta} = -\underset{\approx}{J}^T \cdot \underset{\sim}{f}(\underset{\sim}{q}) \quad . \tag{2.15}$$

In this equation $\underset{\approx}{J}$ is the Jacobian matrix

$$J_{i,j} = f_i(\underset{\sim}{q})/\partial q_j \quad , \tag{2.16}$$

and $\underset{\approx}{J}^T$ is its transpose. $\underset{\approx}{D}$ is a diagonal matrix of constant weight factors which for the purpose of this discussion may be assumed to be the unit matrix.

If the parameter λ is zero, the method reduces to Newton iterations with steps given by

$$\underset{\sim}{\delta} = -\underset{\approx}{J}^{-1} \cdot \underset{\sim}{f}(\underset{\sim}{q}) \quad . \tag{2.17}$$

If on the other hand λ is very large (and $\underset{\approx}{D}$ is the unit matrix), steps are taken in the direction of steepest descent

$$\underset{\sim}{\delta} = -\lambda^{-1} \underset{\approx}{J}^{T} \cdot \underset{\sim}{f}(\underset{\sim}{q}) \quad . \tag{2.18}$$

Powell's method is effectively an algorithm for choosing λ at each step in the root search and at the same time solving Eq. (2.15) without explicit matrix inversion.

Equation (2.15) is only valid for real functions, but it can be shown that a generalization of Powell's method appropriate for complex functions can be obtained by replacing the matrix transposes by the Hermitian conjugate of $\underset{\approx}{J}$. In practice we found it more convenient to divide $\underset{\sim}{f}$ and $\underset{\sim}{q}$ [$\underset{\sim}{q} \equiv \underset{\sim}{\bar{q}}_1, \underset{\sim}{f}(\underset{\sim}{q}) = \underset{\sim}{n}_2(\underset{\sim}{\bar{q}}_1) - \underset{\sim}{n}_2$] into real and imaginary parts even though that appears to double the dimensions of the root search. The steps taken in this way are in fact the same as they would be in the complex generalization of Powell's method mentioned above; the only significant additional work arises because the Cauchy conditions are not used to simplify the computation of the Jacobian.

For given values of the total energy E and orbital angular momentum ℓ the method described above can be used to solve Eq. (2.6) for the initial angle values, $\underset{\sim}{\bar{q}}_1(E,\ell)$, for the root trajectories which contribute significantly to the classical S-matrix. It is important

to note that $\underset{\sim}{\bar{q}}_1(E,\ell)$ for each of these root trajectories is an analytic function of both E and ℓ. This observation allows us to simplify the search for root trajectories at different values of ℓ (or E) once they have been found at one value. For example, to perform the sum over ℓ in Eq. (3.1) we require $\underset{\sim}{\bar{q}}_1(E,\ell)$ for a range of ℓ at fixed E. To find these values we used linear or quadratic extrapolation to increasing values of ℓ from roots found at lower ℓ to give the first guess for each new root search. In our calculation this procedure never failed to give adequate values for beginning the root search. Clearly, rational fraction extrapolation would have been even more accurate.

III. Construction of the S-Matrix Elements and Cross Sections.

The cross section for the $(n_1,j_1) \rightarrow (n_2,j_2)$ transition, summed over final m-components of the rotational state and averaged over initial m-components, is given in the helicity conserving approximation by

$$\sigma_{n_2 j_2 \leftarrow n_1 j_1} = \frac{\pi}{k_1^2} \sum_{\ell=0}^{\infty} (2\ell+1) \frac{1}{2j_1+1} \sum_{K=-j_{min}}^{j_{min}} |S^{\ell,K}_{n_2 j_2, n_1 j_1}|^2 , \quad (3.1)$$

where j_{min} is the smaller of j_1 and j_2 and k_1 is the wave vector for the initial translational energy. For the calculations described below $j_1=0$, so that only the term K=0 appears in the sum over K. The task is to construct the S-matrix elements.

a. Primitive Semiclassical Model

The general expression for the classical S-matrix for an atom-diatom collision is well-known and has been given in several forms elsewhere.[1] Also, the simplifications which result from beginning and ending the trajectories at a vibrational turning point have been described previously,[1b] so to obtain the working equations for this calculation it only remains to specialize these results to the case of the helicity conserving approximation. Since the transitions considered begin with rotational angular momentum j_1 equal to zero, and therefore have helicity K equal to zero as well, the formulae below are specialized to this case.

Each S-matrix element is a sum over root trajectories (i.e., those which satisfy Eq. (2.6)),

$$S^{\ell}_{n_2 j_2, n_1 j_1} = \sum_{\text{roots}} \left[(-2\pi i\hbar)^2 \frac{\partial(n_2, j_2)}{\partial(\bar{q}_{n_1}, \bar{q}_{j_1})}\right]^{-1/2} e^{\frac{i}{\hbar}\Phi(n_2 j_2, n_1 j_1; \ell)} , \tag{3.2}$$

where the phase $\Phi(n_2 j_2, n_1 j_1; \ell)$ is given by

$$\Phi(n_2 j_2, n_1 j_1; \ell) = \int_{t_1}^{\bar{t}_2} dt\ (p\dot{r} + P\dot{R} + j\dot{q}_j)$$

$$+ \pi\ell - [jq_j + PR - \ell \tan^{-1}(PR/\ell)] \Big|_{t_1}^{\bar{t}_2} . \tag{3.3}$$

There is no contribution to Eq. (3.3) from the generator of the classical canonical transformation from the variables (p,r) to (n,q_n) because the trajectories are begun and ended at vibrational turning points. In Eqs. (3.3) $\partial(n_2,j_2)/\partial(\bar{q}_{n_1},\bar{q}_{j_1})$ is the determinant of the Jacobian of final quantum numbers with respect to initial values of the angle variables.

To construct the classical S-matrix for a particular transition it is useful to have a qualitative picture of the several classical trajectories which contribute to it. If rotation and vibration were separable in these collisions, Eq. (2.6) would separate into two equations involving the functions $n_2(\bar{q}_{n_1})$ and $j_2(\bar{q}_{j_1})$. For $n_1=1$ one would expect $n_2(\bar{q}_{n_1})$ to behave qualitatively as shown in Figure 1a. There is no solution of the equation $n_2(\bar{q}_{n_1})=0$ for real values of $\bar{q}_{n_1}$, but there are two solutions for complex $\bar{q}_{n_1}$ (complex conjugates of each other). Since the transition is strongly classically forbidden,

only one of these would contribute to the S-matrix, the other corresponding to the unphysical solution of the Schrödinger equation which would give an exponentially large contribution to the S-matrix.

The situation for the rotational degree of freedom is somewhat more complicated. For the collision of an atom with a homonuclear diatomic molecule the potential $V(R,r,\gamma)$ is periodic in γ so that $V(R,r,\gamma+\pi) = V(R,r,\gamma)$, and it is easy to show that $j_2(\bar{q}_{j_1} + \pi) = j_2(\bar{q}_{j_1})$. In the generic case there would thus be four real roots of the equation $j_2(\bar{q}_{j_1}) = j_2$, but the second two (at larger $\bar{q}_{j_1}$) are related by symmetry to the first pair and make identical contributions to the S-matrix. In the helicity conserving approximation for $j_1=0$ there will also be four roots of the equation $j_2(\bar{q}_{j_1}) = -j_2$--cf. Figure 1b and also reference 7--but these are symmetrically related to the roots for positive j_2 and make an identical contribution to the S-matrix. One thus expects two distinct roots of the rotational equation $j_2(\bar{q}_{j_1}) = \pm j_2$.

Combining one root in n with two unique roots in j, this separable reference thus suggests that there would be two unique (different) trajectories which contribute to the S-matrix. From symmetry considerations together with the inclusion of $-j_2$ roots, the S-matrix computed from the two unique roots with $j_2 > 0$ should be multiplied by four to obtain the S-matrix from all contributions.

In the actual calculations vibration and rotation are not separable, but the arguments leading to the expression for S-matrix as four times the contributions from the unique trajectories with

$j_2 > 0$ still applies. However, when the root search was performed four unique root trajectories were found which contribute significantly to the transitions $n_1 = 1$ and $j_1 = 0$ to $n_2 = 0$ and $j_2 = 0,2,4,6,8$. The locations of these roots in the complex $\bar{q}_{n_1}$ and $\bar{q}_{j_1}$ planes are shown in Figures 2 and 3 for $\ell = 23$. For each of the roots, denoted by I, II, III, and IV in the figures, $\bar{q}_{n_1}$ and $\bar{q}_{j_1}$ are continuous functions of j_2. The four curves in each figure connect the values of $\bar{q}_{n_1}$ or $\bar{q}_{j_1}$ in the complex plane at $j_2 = 0,2,4,6$ and 8 for the four distinct roots. If the separable situation sketched in Figure 1 had obtained, Figure 2 would consist of one point and Figure 3 would consist of only two curves which would be strictly on the real axis for small values of j_2. Thus rotation and vibration are very strongly coupled in this system.

The "primitive" semiclassical S-matrix elements of Eq. (3.2) thus involve four terms, and one only has to be careful to choose the proper phases of the square root pre-exponential factors. As has been discussed before,[1a,1b] this can be done in most cases from a knowledge of the relative signs of the Jacobians. In the present case there is an additional piece of information because roots I and II coalesce to cause "rainbow" behavior as ℓ is varied. This fact allows one to check the relative phases for these two roots by comparing it to that for two coalescing roots in the simpler case of elastic scattering rainbows.[3] These arguments lead to the following "primitive" formula for the classical S-matrix (including the above mentioned factor of 4 and setting $\hbar = 1$)

$$S^{\ell}_{n_2 j_2, n_1 j_1} = \frac{2}{\pi}\left[\frac{e^{i\frac{\pi}{4}}\, e^{i\Phi_I}}{\sqrt{-iD_I}} + \frac{e^{-i\frac{\pi}{4}}\, e^{i\Phi_{II}}}{\sqrt{iD_{II}}}\right.$$

$$\left. + \frac{e^{i\frac{\pi}{4}}\, e^{i\Phi_{III}}}{\sqrt{-iD_{III}}} + \frac{e^{-i\frac{\pi}{4}}\, e^{i\Phi_{IV}}}{\sqrt{iD_{IV}}}\right] \quad , \tag{3.4}$$

where D_I, D_{II}, D_{III}, and D_{IV} denote the Jacobians, $\partial(n_2, j_2)/\partial(\bar{q}_{n_1}, \bar{q}_{j_1})$, for each of the four roots and Φ_I, Φ_{II}, Φ_{III}, and Φ_{IV} denote the associated phases.

Figure 4 shows the cross sections obtained within the "primitive" semiclassical limit, i.e., Eq. (3.4) in Eq. (3.1), compared to the close coupling calculations of Raczkowski, Lester and Miller,[16] which are essentially the exact results for these potential functions. The semiclassical results agree reasonably well with the correct quantum values for all final rotational states except the highest, j_2=8, for which the semiclassical result is much too large. This behavior is analogous to the classical singularity at a rainbow in simple elastic scattering.[3] The coupling between rotation and vibration quenches the singularity to some extent in the present case, but an examination of the location of the roots in the complex $\bar{q}_{j_1}$ plane clearly shows the close approach of pairs of roots for j_2=8 and j_2=6 for some values of ℓ. Thus the maximum at j_2=6 in the quantum results corresponds to a classical rainbow in the classical S-matrix picture of the collision. In order to obtain more reliable

values near the rainbow one requires a uniform semiclassical approximation which is valid in the vicinity of the rainbow as well as the "primitive" region for $j_2 < 6$.

b. Uniform Approximation

Uniform semiclassical approximations for the scattering amplitude can be derived in the case of elastic scattering by abandoning the stationary phase approximation to an integral (over ℓ in the usual derivation) representation of the amplitude and instead employing more accurate approximations to the integral.[17] In more complicated cases, i.e., inelastic scattering, semiclassical theory provides only the "primitive" semiclassical expressions, and one can construct "uniform" approximations which only have the status of interpolations between regions for which valid "primitive" semiclassical approximations are available. In the present case it appears that the rainbow effect is primarily due to a near coalescence of roots I and II in the $\bar{q}_{j_1}$ plane. Thus we begin by finding a uniform formula for the contributions of these two roots. For small values of j_2 the primitive formula is applicable (the bright side of the rainbow), and the uniform formula for the contributions of roots I and II, should reduce to the first two terms of Eq. (3.4):

$$S = \frac{2}{\pi} \, e^{i(\Phi_I + \Phi_{II})/2} \left[\frac{e^{i(\frac{\pi}{4} - \Delta\Phi)}}{\sqrt{-iD_I}} + \frac{e^{-i(\frac{\pi}{4} - \Delta\Phi)}}{\sqrt{iD_{II}}} \right] , \qquad (3.5)$$

where $\Delta\Phi = (\Phi_{II}-\Phi_{I})/2$ and $\hbar$ has been set to 1. For values of j_2 beyond the rainbow singularity (on the dark side) only one of the roots, in our case Φ_{II}, should contribute because the other root becomes unphysically large. Thus in this limit the uniform formula should become

$$S = \frac{2}{\pi} \frac{e^{i(-\frac{\pi}{4}+\Phi_{II})}}{\sqrt{iD_{II}}} \quad . \tag{3.6}$$

The key quantity in the change from Eq. (3.5) to Eq. (3.6) is $\Delta\Phi$. For small j_2, $\Delta\Phi$ is approximately real, and for large j_2 it is almost pure imaginary, $\Delta\Phi \simeq i|\Delta\Phi|$, because $\mathrm{Im}(\Phi_{II}) >> \mathrm{Im}(\Phi_{I})$. The goal is to find a function of $\Delta\Phi$ which reduces to Eqs. (3.5) and (3.7) in the appropriate limits.

An approach which has been successful in other cases[2] of two coalescing roots is to use the asymptotic relationship for combinations of the two kinds of Airy functions[18]

$$\pi^{1/2}\, z^{1/4}[\mathrm{Ai}(-z) \pm i\, \mathrm{Bi}(-z)] \sim e^{\pm i(\frac{\pi}{4} - \Delta\Phi)} \quad , \tag{3.7}$$

where $z = \frac{3}{2}(\Delta\Phi)^{2/3}$. This substitution in Eq. (3.5), together with the assumption that $D_I \simeq -D_{II}$ in the regions on either side of the rainbow, produces the desired uniform formula provided that $\Delta\Phi$ is such that $0 < \arg(\Delta\Phi) < \pi/2$ as it changes from being large and real to large and imaginary, and also provided that the correct branch of the cube root is taken in the definition of z. In the present case, however, $\Delta\Phi$ does not remain in the first quadrant, but as it moves from near the real axis to near the imaginary axis the argument of $\Delta\Phi$ decreases

smoothly from zero to almost $-3\pi/2$. This case can be dealt with conveniently by using an asymptotic relation similar to Eq. (3.7), but in which Bi(-z) is replaced by $-Ai'(-z)/\sqrt{z}$ where Ai' is the derivative of Ai.[6] In this way one obtains a qualitatively correct uniform formula for the contributions of roots I and II:

$$S = \frac{2}{\pi} e^{i(\Phi_I+\Phi_{II})/2} \pi^{1/2} z^{1/4} \left[\frac{Ai(-z) - iAi'(-z)/\sqrt{z}}{\sqrt{-iD_I}}\right.$$

$$\left. + \frac{Ai(-z) + iAi'(-z)/\sqrt{z}}{\sqrt{iD_{II}}}\right] \quad . \tag{3.8}$$

This expression provides a smooth analytic continuation in $\Delta\Phi$ between the primitive semiclassical approximations in Eqs. (3.5) and (3.6) if the argument of $\Delta\Phi$ varies as described above and if the branch of the cube root in the definition of z is chosen such that $\arg(z) = \frac{2}{3}\arg(\frac{3}{2}\Delta\Phi)$. The branch of the square root in Eq. (3.8) is chosen such that $\arg(z^{1/2}) = \frac{1}{2}\arg(z)$.

In Figure 4 the cross sections obtained using this uniform formula for the contribution of roots I and II, but retaining the primitive semiclassical contribution of roots III and IV, are also shown. This approximate "uniformization" does indeed improve the semiclassical result for $j_2 = 8$, but still does not bring it into good agreement with the correct value. What seems to be needed is a "uniformization" also of the contribution from roots III and IV, but we have been unable to devise such a global "uniform" expression which deals with all four complex roots. That the problem at $j_2=8$ is due to the "primitive" treatment of roots III and IV is

also suggested by the fact that if the contribution from these roots is totally discarded, the cross section for $j_2=8$ is too small (the circle in Figure 4).

IV. Concluding Remarks.

Several of the computational difficulties associated with carrying out rigorous calculations based on classical S-matrix theory thus appear manageable; i.e., Powell's algorithm seems to deal with the root search problem quite efficiently, for real or complex roots, and the procedure described in Section IIb makes it possible to integrate trajectories along complex time contours in a numerically stable manner so as to be able to treat classically forbidden processes. The example treated in this paper is a very weak transition and thus a severe test of these methods.

A more fundamental difficulty, though, is the present lack of multi-dimensional uniform approximations which can deal with more general topologies of the pattern of roots to the trajectory relations $\underset{\sim}{n}_2(\bar{\underset{\sim}{q}}_1) = \underset{\sim}{n}_2$. This is a difficult problem but one clearly meriting further research effort.[19]

Acknowledgments

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Figure Captions

1. Qualitative sketch of the functions $n_2(\bar{q}_{n_1})$ and $j_2(\bar{q}_{j_1})$ in the separable limit. The actual situation is substantially more complicated. See text.

2. Locations of the roots of Eq. (2.6) in the complex $\bar{q}_{j_1}$ plane for ℓ=23. Roman numerals label the four distinct sets of roots. Integers label values of j_2.

3. Same as Figure 2 except for the location of roots in the $\bar{q}_{n_1}$ plane.

4. Calculated total cross sections at 1 eV initial translational energy, for $(n_1,j_1) = (1,0)$, n_2=0, as a function of final rotational quantum number j_2. The broken line connects the points of the "primitive" semiclassical model, the solid line those of the "uniform" semiclassical model, with the "exact" quantum results of reference 16 denoted by squares (□). The circle at j_2=8 is the "uniform" result including only the contribution from roots I and II; see text.

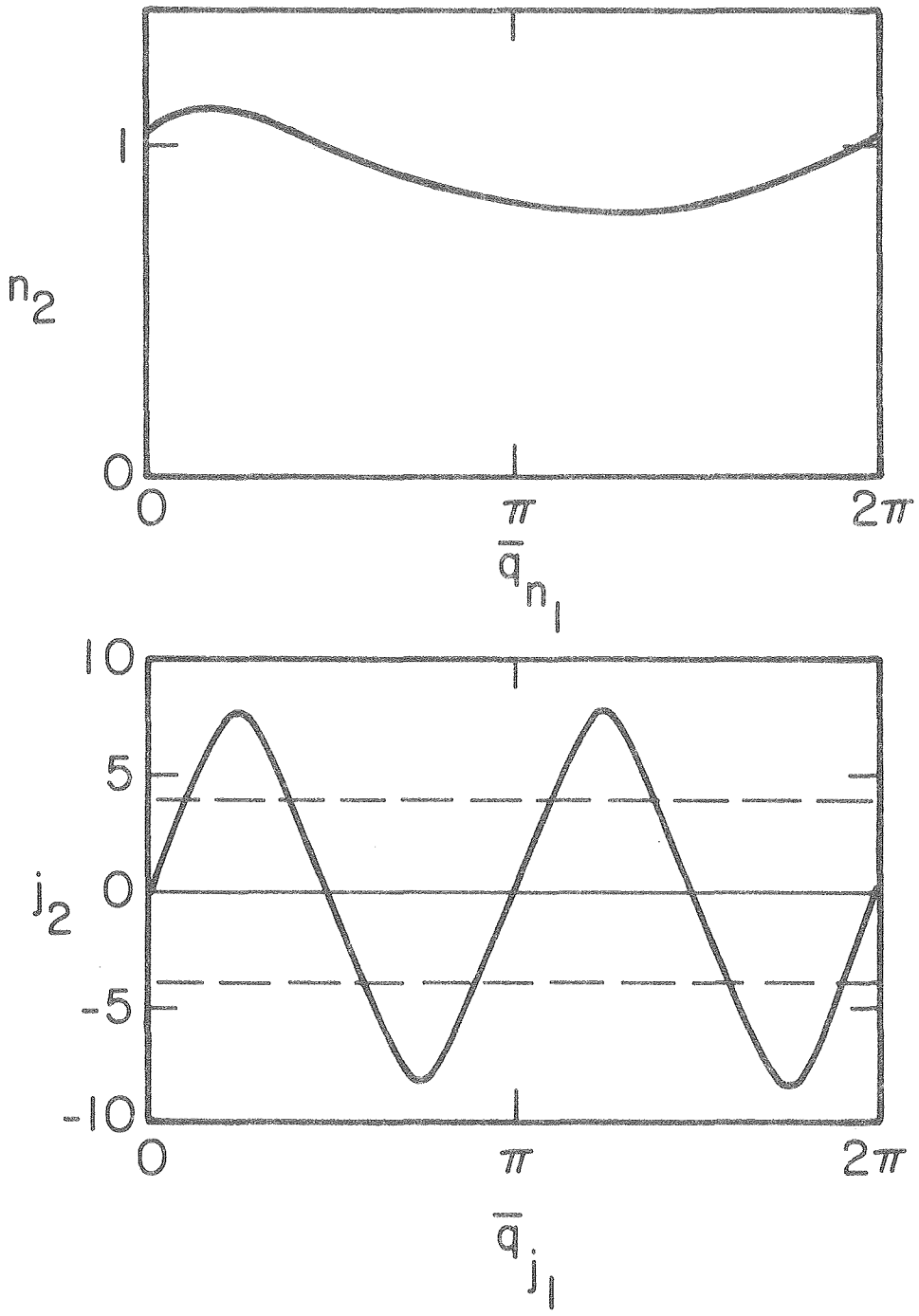
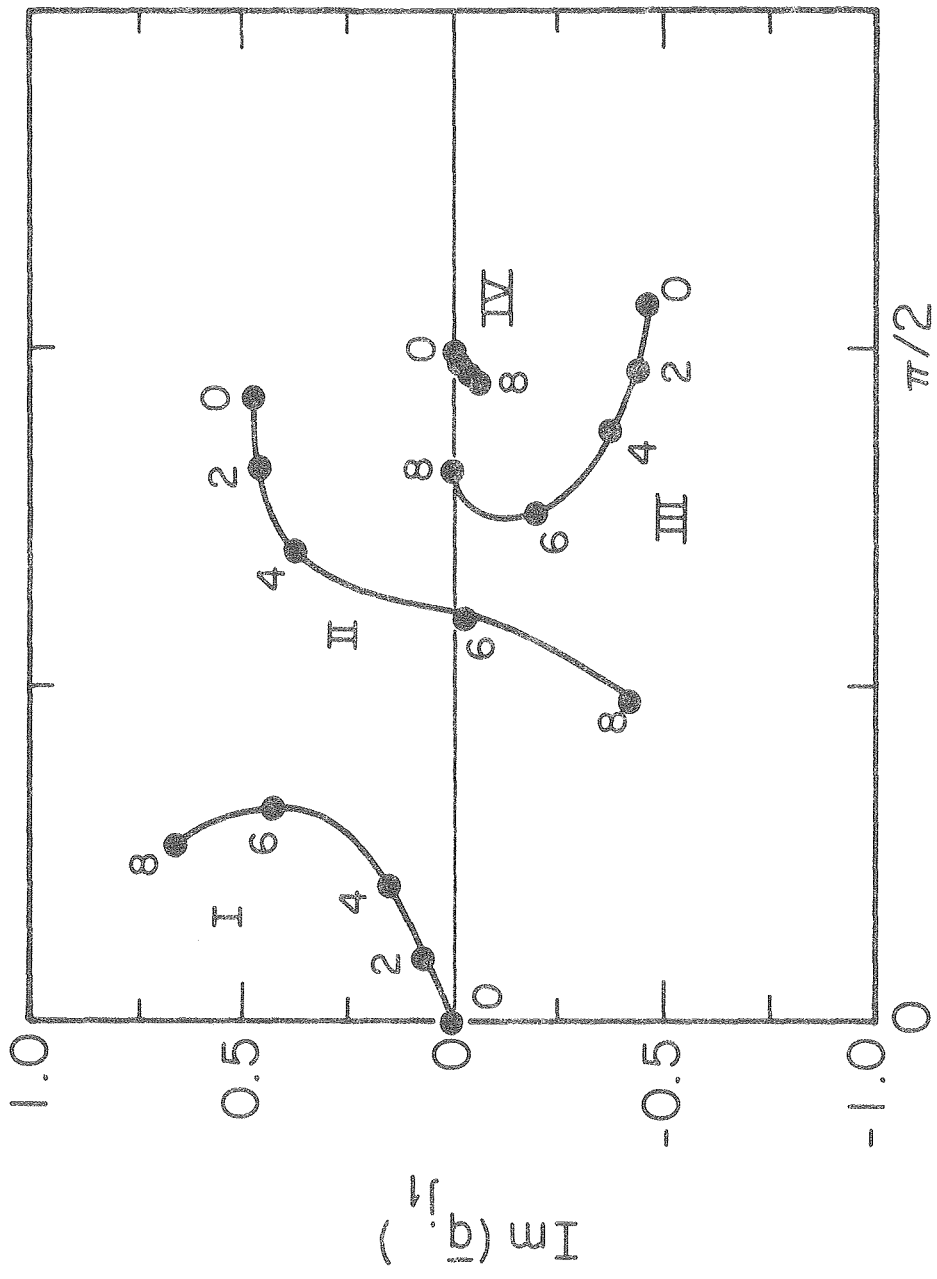


Figure 1

XBL 806-9982



XBL 806-9981

Figure 2

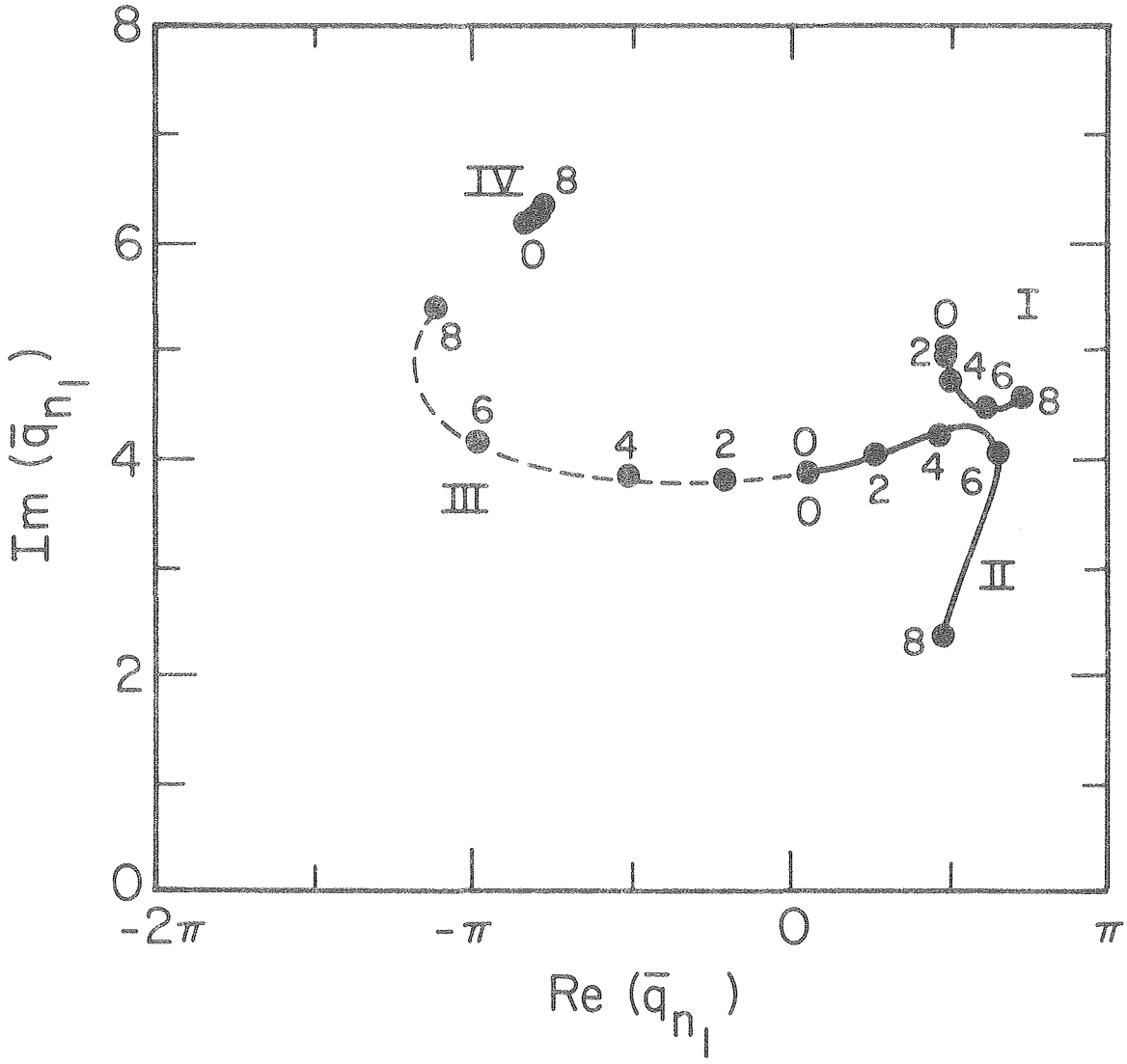


Figure 3

XBL 806-9980

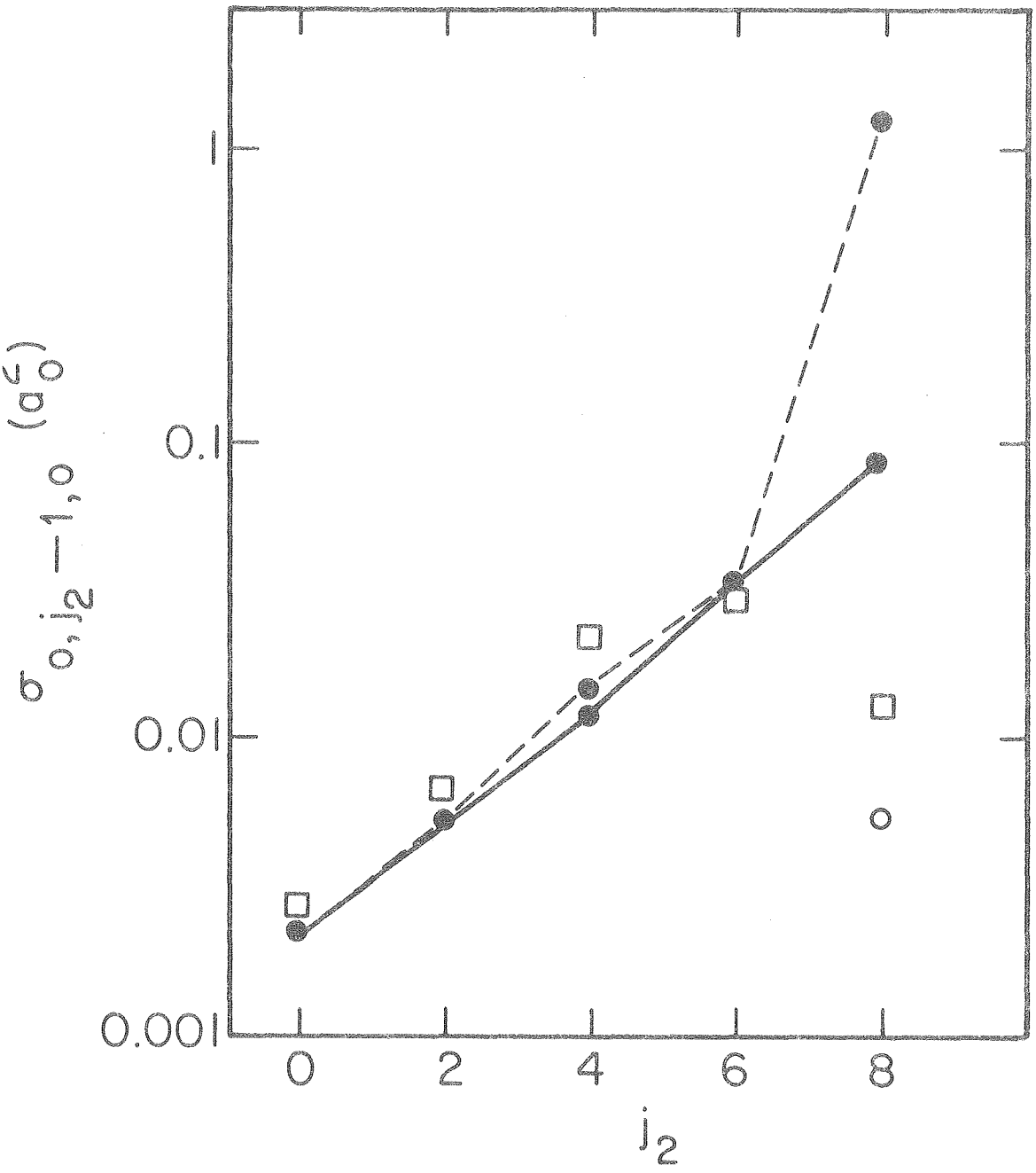


Figure 4

XBL 806-9983