THEORY OF SEMICLASSICAL TRANSITION PROBABILITIES FOR INELASTIC AND REACTIVE COLLISIONS. IV. CLASSICALLY-INACCESSIBLE TRANSITIONS CALCULATED BY INTEGRATION ALONG COMPLEX-VALUED TRAJECTORIES‡

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We calculate semiclassical S-matrix elements S_{mn} by numerical integration along complex-valued trajectories, by avoiding (simply) previously reported trajectory divergences. Now, one can numerically calculate even $|S_{mn}| \approx 10^{-11}$ for the Secrest–Johnson system (their lowest $|S_{mn}|^2$), instead of only $|S_{mn}|^2 > 10^{-3}$. Agreement is excellent.

1. Introduction

Recently, there has been a considerable interest in semiclassical theory for inelastic and reactive collisions [1–11]†. We describe in this letter a simple numerical solution to a formerly intractable problem in classically non-allowed transitions.

We first recall, for this discussion, that to any particular initial orbital–rotational–vibrational quantum state of a pair of collision partners at a given total energy E there corresponds, in semiclassical theory, (1) a particular value for each of the action variables J_i for the orbital, rotational, and vibrational degrees of freedom‡, and (2) all possible values of the phases (in more technical terms, the angle variables w_i) for these degrees of freedom. These w_i's are distributed uniformly over the interval (0, 1) in the correspondence [1].

We also recall, for this discussion, two classes of transitions $n \to m$ in a collision [1–11]. There are, firstly, transitions for which the final states m can be reached classically from the initial n, E and various initial phases, by trajectories satisfying Newton's laws of motion with *real* coordinates and momenta. The corresponding transitions $n \to m$ are termed "classically-accessible" [1–5].

There are, secondly, other final states m which are, in themselves, energetically allowed at the given E but which cannot be reached with classically-allowed (i.e., real valued) trajectories from the given initial n and E, for any *real* value of the initial coordinates w_i. Such transitions $n \to m$ are "classically-inaccessible" for these conditions [1–5]. They can be reached via a trajectory obeying Newton's equations of motion only when that trajectory is *complex-valued.*

We consider a simple treatment of the latter, one which avoids previously encountered [1–11] numerical difficulties (divergences), and calculate S-matrix elements S_{mn}.

2. Examples of classically accessible and inaccessible transitions

It is useful, first, to illustrate these classically accessible and inaccessible transitions with a simple example, a linear collision of an atom and a harmonic oscillator. We use a hamiltonian given by [13],

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† For other examples of recent semiclassical studies, see ref. [12].

‡ These variables are described in ref. [1]. J_i and the quantum number n_i are related by $J_i = (n_i + \delta_i)h$, where δ_i is frequently 0 or 1/2, depending on the degree of freedom [1]. If one sets $\hbar = 1$, as we later do in eq. (1b), J_i equals $2\pi(n_i + \delta_i)$.

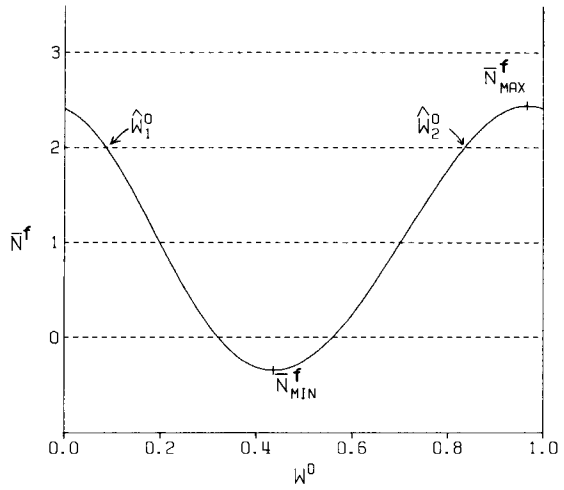

Fig. 1. Example of a plot of real $\bar{n}^f$ versus real w^0 for a linear collision of an atom with a harmonic oscillator (Secrest–Johnson parameters, α, μ and our E are 0.3, 2/3, 6 [13]).

$$H = \tfrac{1}{2}[(p_R^2/\mu) + p^2 + q^2] + \exp[-\alpha(R-q)] = E\,, \quad (1a)$$

which we have also expressed in

$$H = (p_R^2/2\mu) + (\bar{n}+\tfrac{1}{2}) + \exp\{-\alpha[R - (2\bar{n}+1)^{1/2} \sin 2\pi w]\}\,, \quad (1b)$$

in terms of action–angle variables for the oscillator†. q and p are the conventional oscillator coordinate and its momentum; R and p_R are the separation distance of collision partners and the conjugate momentum; μ, α and E are parameters given later in table 1; $2\pi(\bar{n}+\frac{1}{2})$ and w are the action and angle variables of the oscillator, repsectively, and we have set $\hbar = 1$. The quantum mechanics of this collision have been treated numerically by Secrest and Johnson [13].

Using actual classical mechanical trajectory data, the final value $\bar{n}^f$ of the vibrational "quantum number" $\bar{n}$ is plotted in fig. 1 as a function of the initial phase (the initial angle variable w^0) of the oscillator, for the cited values of $n(=1)$, α, μ and E. The trajectory data were obtained using real-valued w^0's and a large initial real value of the separation distance of the collision partners, R^0.

A transition $n \to m$ is classically accessible for the (α, μ, n, E) of the collision in fig. 1 when the $\bar{n}^f$ versus w^0 curve there intersects the (dotted) straight line $\bar{n}^f = m$ parallel to the abscissa. For a system with this (α, μ, n, E) the transitions $1 \to 1$, $1 \to 2$ and $1 \to 0$ in fig. 1 are thus classically-accessible, but the transition $1 \to 3$ is not, even though the state $n = 3$ can exist for the given total E: the straight line $n = 3$ intersects the $\bar{n}^f$ versus w^0 plot only at a complex value of w^0, found by solving the equation $\bar{n}^f(w^0) - 3 = 0$ for w^0. In semiclassical terms, the transition $1 \to 3$ occurs at this (α, μ, n, E) only as a result of some tunnelling from initial to final configurations, since tunnelling implies, semiclassically, complex-valued rather than purely real-valued dynamical quantities.

Efforts in the literature to evaluate S_{mn} for classically-inaccessible transitions with semiclassical theory in refs. [1–11], made indirectly via real-valued trajectories, have been successful only for transitions which are not too inaccessible, namely $|S_{mn}|^2 > 10^{-3}$ [5, 7, 9]. Efforts to use instead complex-valued trajectories for this purpose have almost entirely failed because of divergence of the trajectory [9, 14].

This letter is intended to accomplish the following: (1) locate the precise source of the earlier numerical divergences with complex-valued trajectories [9, 14]; (2) extend the previous semiclassical numerical work [4, 7, 9] for the system in eq. (1) from $|S_{mn}|^2$ available in ref. [13], namely 10^{-3}; and (3) note how the modified simple numerical method also applies to N-dimensional problems.

3. Source of divergence of complex-valued trajectories

To discover the source of the divergence of the above complex-valued trajectories and to describe the basic idea underlying our modification, we again consider first the linear atom–harmonic oscillator collision for which the hamiltonian is given by eq. (1). At an initial large separation distance R^0 between the collision partners before the collision, the time-behavior of the oscillator coordinate q is given by [15]

$$q = (2n+1)^{1/2} \sin 2\pi w = (2n+1)^{1/2} \sin 2\pi(w^0 + \nu^0 t)\,, \quad (2)$$

† To make this transformation one uses the standard generating function given by eq. (C4) of appendix C. It may be noted that the variables differ slightly from those used in ref. [5] and from those in ref. [7].

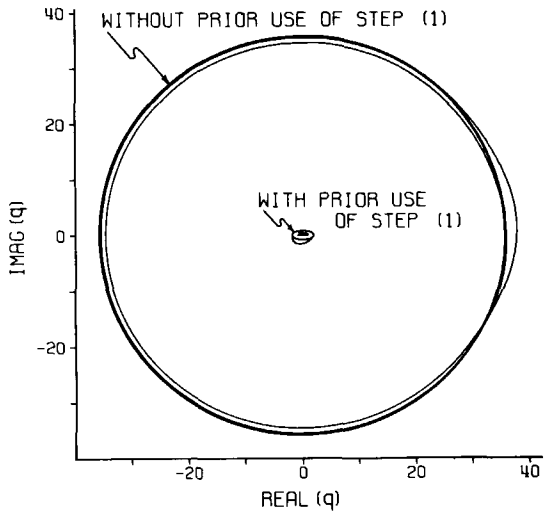

Fig. 2. Projection of trajectory onto complex q-plane, for system with α, μ and our E equal to 0.114, 0.5, 3.8 with and without the prior use of step (1).

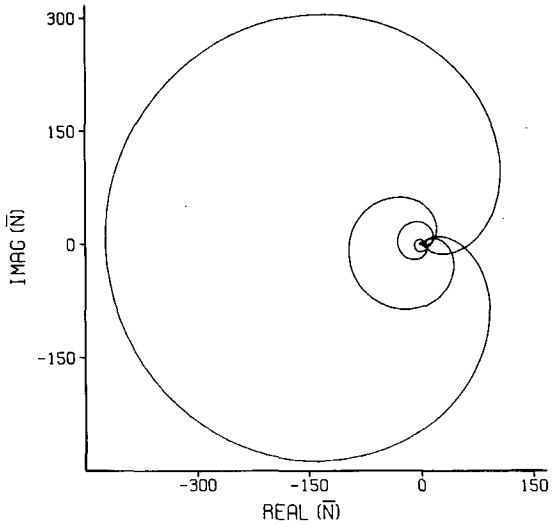

Fig. 3. Projection of trajectory onto complex $\bar{n}$-plane, for system in fig. 2, "without prior use of step (1)".

where w is the angle variable of the oscillator; w^0 is its initial value (value at time $t = 0$); ν^0 is the oscillator frequency at large R and, one can show from the equations of motion arising from eq. (1), equals $(1/2\pi)$ in the present case.

When a (dotted) line $\bar{n} = m$ in fig. 1 is greatly displaced from the curve $\bar{n}^f$ versus w^0 in fig. 1, the intersection of the two occurs in the complex w^0-plane at a point where the imaginary part of w^0 is large. Thus, if one begins a trajectory at this w^0 and at the given R^0, the oscillator q in eq. (2) will have a very large amplitude. In fact, if we write w^0 in terms of its real and imaginary parts,

$$w^0 = w' + \mathrm{i}w'' , \tag{3}$$

then for real n and t eq. (2) can be rewritten as

$$q = (2n+1)^{1/2} \cosh 2\pi w'' \sin 2\pi(w'+\nu^0 t) + \mathrm{i}(2n+1)^{1/2} \sinh 2\pi w'' \cos 2\pi(w'+\nu^0 t) . \tag{4}$$

When $2\pi|w''|$ is large, one sees from (4) that the magnitude of the amplitude of q in this complex-valued space is very large (namely ca. $\frac{1}{2}(2n+1)^{1/2} \exp 2\pi|w''|$).

Thus, during this complex-valued trajectory the oscillator undergoes, even initially, large oscillations in the complex q-plane, of the type indicated by the large circles in fig. 2 (and labelled there "without prior use of step 1"). During the collision with the atom, this oscillator therefore experiences extremely large oscillatory forces as a result of these large oscillations in q and of the exponential repulsion in eq. (1). Correspondingly, the oscillator "quantum number" $\bar{n}(t)$ also undergoes large fluctuations during the collision, as for example in fig. 3, which describes the motion in the complex $\bar{n}$-plane. Fig. 4 depicts the associated tortuous behavior of the R-motion in the complex R-plane. What is even worse, as noted earlier, is that for almost all trajectories, the trajectory data diverged. The trajectory in figs. 2 and 3 is an example of one which managed to converge. Those which did not showed even larger fluctuations in $\bar{n}(t)$.

4. Modified method for calculating complex-valued trajectories

The equations of motion deduced from the hamiltonian in eq. (1b) are

$$\frac{\mathrm{d}w}{\mathrm{d}t} = \frac{\partial H}{\partial(2\pi\bar{n})} = \frac{1}{2\pi}\left(1 + \frac{\partial H'}{\partial \bar{n}}\right), \qquad \frac{2\pi \mathrm{d}\bar{n}}{\mathrm{d}t} = -\frac{\partial H'}{\partial w} ,$$
$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{p_R}{\mu} , \qquad \frac{\mathrm{d}p_R}{\mathrm{d}t} = -\frac{\partial H'}{\partial R} , \tag{5}$$

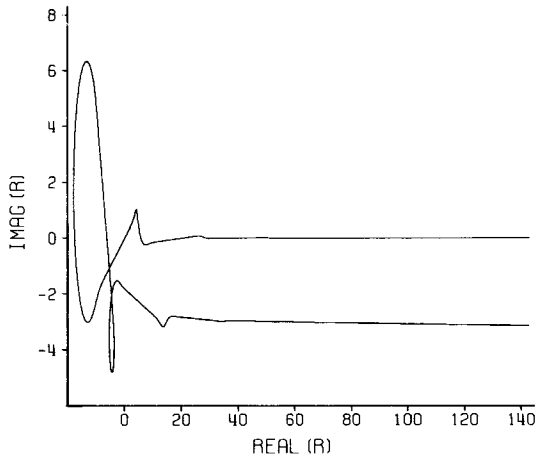

Fig. 4. Projection of trajectory onto complex R-plane, for system in fig. 2, "without prior use of step (1)".

where H' is the last term in eq. (1b). The initial conditions are

$$w = w^0 \ , \ R = R^0 \ , \qquad t = 0 \ . \quad (6)$$
$$\bar{n} = n \ , \ p_R = p_R^0 = -[2\mu(E - E_n^0)]^{1/2} \ ,$$

Here, E_n^0 is the initial vibrational energy.

Before describing the path which we use to integrate the equations of motion and to avoid the divergences of $\bar{n}(t)$ described in section 3, some general remarks on the path are in order: in a Feynman path integral description of wave mechanics [16], the system *tends* to follow a real classical dynamical path in classically-allowed regions and, when a classically-impassable potential barrier presents itself, the system tends to surmount the barrier by following a real but *non-dynamical* path (i.e., one *not* obeying the classical equations of motion). It can later resume its tendency to follow a classically dynamical path in any subsequent classically-allowed region. The semiclassical theory has a somewhat different point of view [1–5]: the theory is based on a short wavelength approximation for the wavefunction. The phase S of the wave is found to satisfy the Hamilton–Jacobi equation, which in turn we solve by the method of characteristics [1–5]. These characteristics, which propagate S, are the trajectories satisfying the classical equations of motion and are real-valued in classically-allowed regions and complex-valued in classically-non-allowed regions. (Complex-valued trajectories have also been used in elastic scattering, e.g., [17], and in propagation of electromagnetic waves, e.g., [18].) For the trajectory one may select any of an infinite number of paths, each obeying Hamilton's equations of motion, merely by choosing some path for the time-variable t in the complex t-plane. The final values of p_i and q_i should depend only on the initial and final t, and so be independent of the path of integration, because of the analyticity of $p_i(t)$ and $q_i(t)$ as functions of t†. We have tested numerically this path-independence property on various occasions and an example is given later.

We shall choose a path in the complex t-plane, and hence for $p_i(t)$ and $q_i(t)$, which removes completely the large oscillations in q described in section 3 and, thereby, the resulting divergences in $\bar{n}(t)$ and in the other quantities. This path is one whose initial step is an analytical integration over an imaginary time interval $\mathrm{i}\Delta t''$, such as to reduce the imaginary part of the initial w to zero. At large initial R, with H' in eq. (5) therefore being zero, we use (3), (5) and (6) and choose $\Delta t''$ so that

$$\nu^0 \mathrm{i}\Delta t'' = -\mathrm{i}w'' \ , \qquad (7)$$

where $\nu^0 = (1/2\pi)$. Then, the new w at the end of this interval is seen from eq. (3) to be simply w'. The change in R calculated from (5) and (7) is $-\mathrm{i}p_R^0 \, w''/\mu\nu^0$. There is no change in p_R^0 and n, as one sees from (5), since $H' = 0$ at large R.

Thus, denoting the new w and R by $\tilde{w}^0$ and $\tilde{R}^0$, we have at $t = \mathrm{i}\Delta t''$

$$w = \tilde{w}^0 = w' \ , \quad R = \tilde{R}^0 = R^0 - \mathrm{i}(p_R^0 \, w''/\mu\nu^0) \ , \qquad t = \mathrm{i}\Delta t''.$$
$$\bar{n} = n \ , \qquad p_R = p_R^0 \ , \qquad (8)$$

We call this initial analytical integration step, step (1).

Step 1 has served to transfer the complex value from the w^0, where it was harmful because of the oscillations of q, to R, where it is not harmful, since R

† This presumed analyticity is ensured, in typical cases, by the analytic nature of the hamiltonian as a function of the conventional p_i and q_i, and hence by that of the equations of motion themselves. One does not have, for example, $|p|$ and $|q|$ in H. When, as in eq. (1b), there is a chance of approaching the branch point at $(2\bar{n}+1)^{1/2} = 0$, one uses eq. (1a) for the actual integration instead of (1b). We used (1a) throughout.

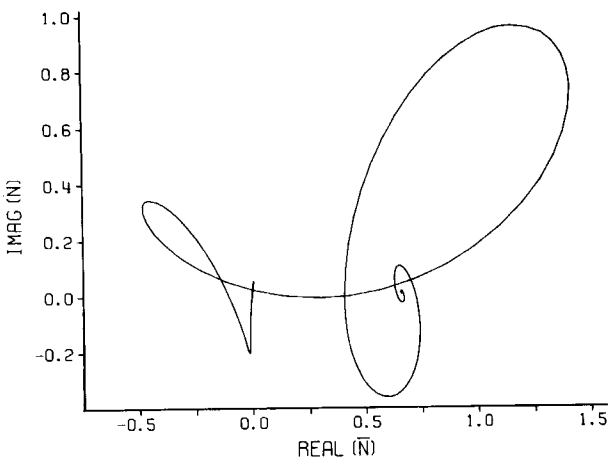

Fig. 5. Projection of trajectory onto complex $\bar{n}$-plane, for system in fig. 2, "with prior use of step (1)".

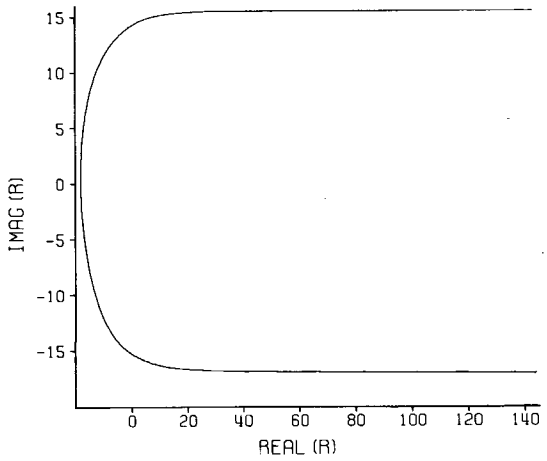

Fig. 6. Projection of trajectory onto complex R-plane, for system in fig. 2, "with prior use of step (1)".

undergoes at large R no intrinsic oscillatory motion. Using eq. (8) as the new initial conditions for the numerical integration and proceeding now to integrate with real time increments dt in the complex t-plane, q now executes during the collision only the small oscillations labelled "with prior use of step 1" in fig. 2. Correspondingly, $\bar{n}(t)$ also undergoes only small fluctuations (contrast the magnitudes in fig. 5 with those in fig. 3) and, because of the absence now of large oscillation forces, $R(t)$ now has a simple in- and out- behavior (fig. 6, which may be contrasted with fig. 4).

This numerical integration, with real dt and with eq. (8) providing the initial conditions, was performed using the equations of motion for q, p, R and p_R, rather than those for $w, \bar{n}, R$ and p_R‡. All quantities were allowed to become complex-valued. The integration was continued until the collision was over, i.e., until p_R reached a final constant value, its real component being positive. The numerical data were then inserted into the equations of Part II of this series for the S-matrix element S_{mn} for any transition $n \to m$.

There are a few technical details, given in appendices A to C: the method of making an initial guess for the w^0 in eq. (6) and hence for the w' and w'' in eq. (8), is described in appendix A, for any given transition $n \to m$. A few iterations from this initial choice served to obtain the desired $\bar{n}^f$ to six significant figures. Appendix B summarizes the equations for $|S_{mn}|^2$, taken from Part II. Appendix C gives details for converting appropriate phase integrals from conventional coordinate–momenta data to action–angle data, to have the data in a form appropriate for use in appendix B.

The semiclassical results for $|S_{mn}|^2$, calculated with initial conditions (8), followed by the numerical integration†, are given in table 1, for the hamiltonian in eq. (1) and for the values of the parameters α, μ, E and transitions $n \to m$ cited in the table. Also given there are the exact quantum mechanical results of Secrest and Johnson [13].

The agreement is seen to be excellent, even when the transition probability is as low as 10^{-11}.

‡ In this way one avoids the possibility of a singularity occurring if $(\bar{n}+\frac{1}{2})$ vanished during the collision. (The angle variable w would then be ill-defined, and the differential equations would contain a singularity.)

† The program was written in FORTRAN using double precision arithmetic and the University of Illinois IBM-360/75 was used for its execution. A standard fourth-order Runge–Kutta–Gill integration subroutine having variable step size was to integrate Hamilton's equations. A crude Newton–Raphson iteration procedure, was used to find $\hat{w}^0$, using eq. (A2) as initial guess. The calculation took on the average four iterations to obtain an $\bar{n}^f$ to 6 significant figures. The total computer time was roughly twice that for real-valued trajectories, there being twice as many differential equations.

Table 1
Transition probabilities for classically forbidden transitions for linear collision in eq. (1) [a,b]

α	μ	E	Transition	Quantum [b,c]	Uniform using complex trajectories [c,d]
0.114	1/5	3.0	0–2	9.03(−10)	9.14(−10)
0.114	1/5	3.0	1–0	7.06(−4)	7.59(−4)
0.114	1/5	3.0	1–2	5.11(−6)	5.79(−6)
0.114	1/5	7.0	1–0	1.32(−1)	1.33(−1)
0.114	1/5	7.0	1–2	1.27(−1)	1.32(−1)
0.114	1/5	9.0	1–3	4.08(−2)	4.12(−2)
0.114	1/2	3.8	0–1	4.30(−5)	4.69(−5)
0.114	1/2	3.8	0–2	1.28(−11)	1.40(−11)
0.114	1/2	4.4	0–2	1.13(−9)	1.14(−9)
0.114	1/2	4.4	1–2	2.23(−5)	2.52(−5)
0.114	1/2	5.0	0–2	2.51(−8)	2.53(−8)
0.114	1/2	6.0	0–1	2.85(−3)	3.03(−3)
0.114	1/2	6.0	0–2	9.43(−7)	9.46(−7)
0.114	1/2	8.0	0–2	8.12(−5)	8.08(−5)
0.1287	1/2	6.41825	0–2	3.21(−5)	3.20(−5)
0.1287	1/2	7.41825	1–3	9.50(−5)	9.84(−5)
0.2973	5/4	3.47275	0–2	1.69(−7)	1.70(−7)
0.2973	5/4	4.47275	1–3	5.29(−7)	5.52(−7)
0.2973	5/4	4.47275	2–0	2.31(−5)	2.30(−5)
0.2973	5/4	4.47275	2–1	5.97(−3)	6.50(−3)
0.2973	5/4	4.47275	2–3	3.52(−4)	3.95(−4)
0.3	2/3	4.0	0–1	1.08(−1)	1.08(−1)
0.3	2/3	4.0	0–2	1.22(−3)	1.20(−3)
0.3	2/3	4.0	1–2	4.18(−2)	4.41(−2)
0.3	2/3	4.0	1–3	1.46(−5)	1.51(−5)
0.3	2/3	4.0	2–3	1.33(−3)	1.48(−3)
0.3	2/3	4.0	3–1	1.46(−5)	1.51(−5)
0.3	2/3	5.0	1–2	1.82(−1)	1.87(−1)
0.3	2/3	5.0	1–3	3.31(−3)	3.36(−3)
0.3	2/3	6.0	1–3	3.70(−2)	3.73(−2)

a) α, μ and E are the dimensionless parameters in the model of Secrest and Johnson. (Our E is their $E/2$.)
b) Exact quantum mechanical results of Secrest and Johnson [13].
c) Number in parentheses is power of 10.
d) Results from using eq. (B1).

5. Discussion

There are few semiclassical data in the literature with which to compare the semiclassical results for classically-inaccessible transitions in table 1. The former include only values of $|S_{mn}|^2$ for slightly classically-inaccessible transitions, i.e., having probabilities not lower than ca. 10^{-3}, namely ones obtained by analytic continuation from real-valued trajectory data [9], and ones obtained by direct evaluation of the integral [5, 7]. The agreement of these values with the present ones, where they overlap, is good. As already noted, a few complex-valued trajectories had been calculated (results for S_{mn} not given) [9], but most diverged [9, 14]†. Thus, the present method

† A few values of $|S_{mn}|^2$ from trajectories which did not diverge are the following, corresponding to the conditions in rows 1, 2 and 25 of table 1: 9.14(−10); 7.59(−4); 1.51(−5). These values agree exactly with the corresponding values in table 1.

is far superior to any of these‡.

It is perhaps worthwhile emphasizing that the only approximation used in the present work is the semiclassical approximation. In spite of the Airy integrals appearing in the uniform approximation for $|S_{mn}|^2$ (appendix A, or Part II) there is no linearity of any potential energy function assumed near any classical turning point. (Tacit use in Parts I to III of the method of Langer [20] avoids any such approximation.) Nor, when there are two turning points close together, do we assume any parabolic approximation. (The method of Chester et al., used in Part II avoids any such approximation.) Again, all coordinates and momenta are treated numerically in the integration on the same basis. The "disappearance" of one differential (dR) in an integral for S_{mn} is a result of a canonical transformation followed by an exact integration and is described in Part III. The reasons for prior conversion of all coordinates but R into angle variables is discussed in Part I.

The expression for S_{mn} in Part III involves an integral, with volume element $\prod_i dw_i^0$, over a unit volume $0 \leqslant w_i^0 \leqslant 1$ [1–5]. As shown in Part I only small neighborhoods of certain trajectories contribute significantly to this integral, when a stationary phase (or uniform) asymptotic approximation is used to evaluate the integral. Thus, regardless of whether this neighborhood is one beginning with a real w^0 or, in classical-inaccessible $n \to m$ transitions, a complex-valued w^0, one does not have to "average over w^0's".

Finally, we note that the method outlined in this letter for making possible the integration of these complex-valued trajectories is readily extended to higher number of dimensions†. In this connection, we also note the derivation of the uniform approximation of the integral for S_{mn} for N-dimensional systems [4].

‡ A procedure for calculating complex-valued trajectories, quite different from the present one, has also been developed by George and Miller [19]. After the present letter was submitted, we received a copy of this manuscript. There are certain similarities (e.g., use of a step which we have labelled step 1) and certain differences (e.g., we use the method of appendix A to locate the initial w^0 and then integrate the trajectories in a forward direction. They, instead integrate one set of trajectories forward from state n, integrate another set backward from state m, and match the two sets in the middle by an iterative process involving the solution of simultaneous equations). Their five results agree exactly with the corresponding five results in our table 1.

Acknowledgment

We should like to thank Professor J.O. Hirschfelder for his helpful criticisms, which served to clarify this presentation.

Appendix A. Procedure to obtain an initial guess for w^0

The real-valued data plotted in fig. 1 could, accurately enough for the present purpose, be fitted by the first three terms of a Fourier series

$$\bar{n}^{\mathrm{f}} = a_0 + a_1 \cos 2\pi w^0 + b_1 \sin 2\pi w^0 \,. \qquad \text{(A1)}$$

(Frequently, for example, the higher Fourier coefficients were smaller by a factor of at least 10^{-3}.)

When m was classically inaccessible, it was set equal to the $\bar{n}^{\mathrm{f}}$ given by (A1), and the resulting equation was solved, yielding a pair of complex conjugate solutions, $\hat{w}^0$

$$\hat{w}^0 = w^0_{\mathrm{max(min)}} \pm (2\pi \mathrm{i})^{-1} \cosh^{-1} [(m-a_0)/(\bar{n}^{\mathrm{f}}_{\mathrm{max(min)}}-a_0)] \,, \qquad \text{(A2)}$$

where $w^0_{\mathrm{max(min)}}$ is the w^0 at which $\bar{n}^{\mathrm{f}} = \bar{n}^{\mathrm{f}}_{\mathrm{max(min)}}$ in fig. 1. It so happened, for the cases in table 1, that $a_0 \approx n$, but this approximation is not needed. We observe that with $a_0 \approx n$, $\hat{w}^0 - w^0$ has a very large imaginary component when $|m-n| \gg |\bar{n}^{\mathrm{f}}_{\mathrm{max(min)}}-n|$.

Appendix B. Equations for $|S_{mn}|^2$

The transition probability P_{mn} for $n \to m$ is given by

† With a higher number of dimensions all w_i^0's would change during $\Delta t''$ and some compromise $\Delta t''$ might be used, one which would make only the highly oscillative w^0's be real or near-real. In a collisional translational–vibrational–rotational energy transfer, for example, the orbital frequency at large R is zero, so its Δw^0 is zero. The rotational frequency is also typically relatively small, and so its Δw^0 during $\mathrm{i}\Delta t''$ is also small.

$$P_{mn} = |S_{mn}|^2 = 2\pi\rho[(1+\sin\beta)|\zeta|^{1/2}\,\mathrm{Ai}^2(|\zeta|) + (1-\sin\beta)|\zeta|^{-1/2}\,\mathrm{Ai}'^2(|\zeta|)] \,, \tag{B1}$$

an expression derived in Part II of this series [2], where†

$$|\zeta| = \{\tfrac{3}{4}|\Delta(\hat{w}_2^0) - \Delta(\hat{w}_1^0)|\}^{2/3} = \{\tfrac{3}{2}|\mathrm{Im}\,\Delta|\}^{2/3} \tag{B2}$$

[since $\Delta(\hat{w}_2^0) = \Delta(\hat{w}_1^0)^*$]; $\hat{w}_1^0$ and $\hat{w}_2^0$ are the points of stationary phase (the solutions of the equation $\bar{n}^{\mathrm{f}} = m$) [1–5]; $\rho^{-1/2}$ and $\beta/2$ are the amplitude and the phase of $(\mathrm{d}\bar{n}/\mathrm{d}w^0)^{1/2}$ $[= \rho^{-1/2}\exp(\mathrm{i}\beta/2)]$; Ai and Ai′ are the Airy function and its derivative, and Δ is given by

$$\Delta = -2\pi\int_n^{\bar{n}^{\mathrm{f}}} w\,\mathrm{d}\bar{n} - \left(\int_{p_R^0}^{p_R} R\,\mathrm{d}p_R\right) + \tfrac{1}{2}\pi \tag{B3}$$

for a system with one internal coordinate.

Appendix C. Conversion of a phase integral to one in action–angle variables in the expression for S_{mn}

The Δ in eq. (B3) is in terms of action–angle variables but the trajectory data were in terms of q's and p's. To convert the final trajectory results from conventional coordinates to action–angle variables we use a standard generating function as follows.

The phase Δ appearing in eq. (B3) equals $\frac{1}{2}\pi$ plus a term denoted in this appendix by $F_4(P_2, P_1)/\hbar$, with $\hbar = 1$. P_1 and P_2 signify initial and final values of the totality of momentum variables, e.g., P_2 denotes the final values of the momenta $2\pi(\bar{n}^{\mathrm{f}}+\frac{1}{2})$ and p_R^{f}. We have

$$F_4(P_2, P_1) = -2\pi\int_n^{\bar{n}^{\mathrm{f}}} w\,\mathrm{d}\bar{n} - \int_{p_R^0}^{p_R^{\mathrm{f}}} R\,\mathrm{d}p_R \,. \tag{C1}$$

† Recalling eq. (3.12) of ref. [2], where ζ is negative in our case and where f is our Δ, $\hat{w}_1^0$ is that member of the complex conjugate roots $(\hat{w}_1^0, \hat{w}_2^0)$ which makes ζ negative, i.e., as shown below, makes $\mathrm{Im}\,\Delta(\hat{w}_i^0)$ positive.
Proof: $[\Delta(\hat{w}_2^0) - \Delta(\hat{w}_1^0)]^{2/3}$ equals, on selecting the appropriate branch, $[(-1)(\mathrm{i})\,\mathrm{Im}\,\Delta(\hat{w}_1^0)]^{3/2}$ when $\mathrm{Im}\,\Delta(\hat{w}_1^0)^{3/2}$ is positive, and so equals $-[\mathrm{Im}\,\Delta(\hat{w}_1^0)]^{3/2}$, thus making $\zeta < 0$. Typically, one finds $\beta \approx +\frac{1}{2}\pi$ [2].

$F_4(P_2, P_1)$, defined by (C1), is also a generating function for a canonical transformation from the P_1's to the P_2's [15]. When the conventional coordinate and momentum is used for the harmonic oscillator instead of these action–angle variables one first evaluates an integral which we shall call $f_4(p_2, p_1)$

$$f_4(p_2, p_1) = -\int_{p_1}^{p_2} q\,\mathrm{d}p - \int_{p_R^0}^{p_R^{\mathrm{f}}} R\,\mathrm{d}p_R \,. \tag{C2}$$

A generating function transforming (q,p) into (Q,P), will be written as $\varphi_4(p,P)$ and is given below. The oscillator Q is w and its P is the classical action, i.e., $2\pi(\bar{n}+\frac{1}{2})$. The R and p_R are not changed by our transformation, and so it is only necessary to consider in the φ_4 and φ_1 below the transformation from the oscillator (q,p) to the oscillator (Q,P).

We note that [15]

$$F_4(P_2, P_1) = f_4(p_2, p_1) + \varphi_4(p_1, P_1) - \varphi_4(p_2, P_2) \,. \tag{C3}$$

$\varphi_4(p,P)$ can in turn be expressed in terms of a well-known generating function $\varphi_1(q,Q)$ for transforming conventional to action–angle variables for the oscillator [21] ‡

$$\varphi_1(q,Q) = \tfrac{1}{2}q^2\cot 2\pi Q \,, \tag{C4}$$

with $p = \partial\varphi_1/\partial q$ and $P = -\partial\varphi_1/\partial Q$. Further [15],

$$\varphi_4(p,P) = \varphi_1(q,Q) + QP - qp \,. \tag{C5}$$

Since p equals $q\cot 2\pi Q$, the $\varphi_1(q,Q)$ given in (C4) is seen to equal $\frac{1}{2}pq$.

The above equations thus yield

$$F_4(P_2, P_1) = -\int_{p_1}^{p_2} q\,\mathrm{d}p + \tfrac{1}{2}(p_2 q_2 - p_1 q_1) + P_1 Q_1 - P_2 Q_2 - \int_{p_R^0}^{p_R^{\mathrm{f}}} R\,\mathrm{d}p_R \,. \tag{C6}$$

In these equations, we note that

$$Q_1 = w^0 \,, \qquad Q_2 = w^{\mathrm{f}} \,, \qquad P_1 = 2\pi(n+\tfrac{1}{2}) \,, \qquad P_2 = 2\pi(\bar{n}^{\mathrm{f}}+\tfrac{1}{2}) \,, \tag{C7}$$

‡ Note that the ω in ref. [20] is unity in our case.

where w^f is the final value of w.

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