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"The Classical S-Matrix for Rotational Excitation;
Quenching of Quantum Effects in Molecular Collisions"*

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Abstract

A previously developed theory in which exact solutions of the classical equations of motion for a complex collision system (i.e., numerically computed trajectories) can be used to generate the classical limit of the quantum mechanical S-matrix (the "classical S-matrix") for the scattering process is applied to rigid rotor-atom collisions (rotational excitation). Comparison with essentially exact quantum results shows that transition probabilities (the square modulus of an S-matrix element) between individual quantum states are given reasonably accurately by classical dynamics provided the interference terms are properly accounted for; a strictly classical

approach (neglect of interference) gives poor agreement with the quantum values. For averaged collision properties, however, it is found that interference and tunneling effects are rapidly quenched. The linear atom-diatom system (vibrational excitation) and the rigid rotor-atom system are both investigated with regard to this question--namely, how much averaging is necessary to quench these quantum effects. Results indicate that even summation over a few quantum states is often sufficient to make a completely classical treatment appropriate.

I. INTRODUCTION.

This paper continues investigations of the role played by classical and quantum mechanics in molecular collision dynamics. Previous work¹ has shown how the exact (i.e., numerical) solution of the classical equations of motion for a complex collision (e.g., an atom plus diatom) can be used to construct the classical limit of the quantum mechanical S-matrix (the "classical S-matrix") for the scattering process. The only vestige of quantum mechanics retained in the scheme is the quantum principle of superposition--that probability amplitudes associated with indistinguishable processes are added, rather than the probabilities themselves.

Application^{2,3} to the linear atom-diatom collision (vibrational excitation) has shown that classical mechanics, used in this manner, accurately describes individual vibrational transition probabilities, even when tunneling and interference effects are large; i.e., these effects are basically the consequence of quantum superposition, and not the quantum equation of motion (i.e., the Schrodinger equation). The strictly classical approximation (omission of tunneling and interference) for the transition probabilities appeared to be accurate "on the average", but quite inadequate in describing transitions between individual quantum states.

The present work reports results of the classical S-matrix approach applied to the collision of an atom and a rigid rotor (a diatomic molecule without the vibrational degree of freedom), i.e., rotational excitation. The specific system

chosen is that for which Johnson, Secrest, Lester, and Bernstein⁴ have performed an essentially exact quantum mechanical computation of the S-matrix elements; this is in keeping with the desire to compare exact quantum and exact classical mechanics, there then being no ambiguity about the comparison due to any approximations introduced in either.

Section II summarizes the general expressions of paper I which pertain to the rigid rotor-atom collision and presents numerical results (Figure 1 and Table I) for the strictly classical, primitive semiclassical, and uniform semiclassical approximations to the S-matrix. Comparing with the exact quantum values of ref. 4, the picture is essentially the same as for the linear atom-diatom system of paper II: to obtain accurate results for individual S-matrix elements it is necessary that interference between the several classical trajectories which contribute to an individual transition be properly included. For this particular system the phase differences between the interfering trajectories are so small that it is essential that one uses the uniform semiclassical expressions to achieve reasonably accurate results; i.e., this is a very quantum-like system, which of course makes the classical S-matrix treatment all the more interesting--for one is fairly certain that it will work in highly classical-like situations.

In most actual cases, however, one does not observe the results of completely state-selected experiments; almost always

one obtains cross sections which are a sum over a group of final quantum states and an average over a number of initial states (as well as an average over initial relative collision energy). In the rigid rotor-atom system, for example, it is usually the case that one is interested in cross sections from an initial rotational state to a final one, summed and averaged over the final and initial M-components of the molecular rotation, respectively. Any averaging of this type--i.e., anything less than a completely state-selected and detected observation--will tend to diminish the effect of interference and tunneling: interference terms will tend to average to zero and tunneling transitions will be negligible in comparison to non-tunneling ones.

Sections III and IV pursue this question of how much averaging is necessary to obliterate, or quench, these quantum effects of interference and tunneling; Section III considers the rigid rotor-atom system, and Section IV the linear atom-diatom. Although one must view any general conclusions at this stage with caution, it appears that one need average over only a very few quantum states to quench completely the interference features. The principal situation in which the strictly classical treatment for averaged quantities fails is the case that all transitions are classically forbidden (i.e., proceed via tunneling), although even here there are special conditions under which it succeeds (see Sec. IV).

Since there is currently a great deal of interest in the application of classical mechanics to collision problems,⁵⁻⁹

we would like to conclude this Introduction with some remarks about our view of the general relation between classical and quantum mechanics. Appendix I presents a more elaborate discussion of this correspondence, including a derivation of the relation (stated in paper I) between unitary transformation elements in quantum mechanics and the generators of canonical transformations in classical mechanics; it is also pointed out that the expressions for the classical S-matrix follow directly from these general transformation relations without the necessity of appealing to path integrals (as was done in I).

The point we would like to make here is that there is not any basic inconsistency between the deterministic nature of classical mechanics and the principles of quantum mechanics, provided classical mechanics is used appropriately; in fact, the Uncertainty Principle is an integral part of the way classical mechanics is employed. Consider, for example, the classical limit of the propagator (time evolution operator) in a coordinate representation

$$\langle r_2 | e^{-iH(t_2-t_1)/\hbar} | r_1 \rangle; \quad (1)$$

the square modulus of this transformation element is the probability that the particle is at position r_2 at time t_2 provided it was at position r_1 at time t_1 --i.e., with r_1 fixed,

$$\text{Prob}(r_2) = |\langle r_2 | e^{-iH(t_2-t_1)/\hbar} | r_1 \rangle|^2. \quad (2)$$

With r_1 fixed, however, a unique relation between r_2 and p_1 (the momentum at time t_1) is determined by the classical

equations of motion; i.e., considering r_1 fixed throughout, specifying p_1 determines r_2 , or specifying r_2 determines p_1 (this is classical determinism). The probability distributions in r_2 and p_1 are therefore related by

$$\text{Prob}(r_2) dr_2 = \text{Prob}(p_1) dp_1; \quad (3)$$

i.e., the probability that r_2 has a particular value in the interval (r_2, r_2+dr_2) is equal to the probability that p_1 has the corresponding particular value in the interval (p_1, p_1+dp_1) . The Uncertainty Principle, however, implies that, with r_1 fixed, p_1 can have any value--it is random, or in other words, its probability distribution is constant:

$$\text{Prob}(p_1) = \text{constant}. \quad (4)$$

Eqs.(3) and (4), thus, imply that

$$|\langle r_2 | e^{-iH(t_2-t_1)/\hbar} | r_1 \rangle|^2 = \text{constant} \left/ \left| \left(\frac{\partial r_2}{\partial p_1} \right)_{r_1} \right| \right., \quad (5)$$

which is the normalization derived by Pechukas⁸ and differently in I.

The fact that the classical limit of the quantum mechanical matrix element in Eq.(1) is associated with one unique¹⁰ classical trajectory, therefore, is in no way contradictory with the basic laws of quantum mechanics, but indeed incorporates them. The particular classical trajectory associated with the matrix element in Eq.(1) is determined by the "double ended" boundary conditions r_1 and r_2 , and this is a fundamental feature of the correspondence between classical and quantum mechanics; it is intimately related

to the fact that the generator of a canonical transformation in classical mechanics¹¹ has as independent variables "one old variable and one new variable" (see Appendix I).

II. RIGID ROTOR-ATOM COLLISIONS.

Application of the classical S-matrix scheme to rigid rotor-atom collisions¹² is a special case of the general formulation for the atom-diatom collision problem presented in I. The classical Hamiltonian governing the system is

$$H(P, \ell, j; R, q_\ell, q_j) = (P^2 + \ell^2/R^2)/2\mu + B j^2 + V(R, \gamma), \quad (6)$$

where R and P are the center of mass radial (translational) coordinate and momentum, ℓ is the orbital angular momentum of the atom relative to the diatom, j is the rotational angular momentum of the diatom, μ is the reduced mass of translation, B is the rotational constant of the diatom, $V(R, \gamma)$ is the interaction potential between the atom and diatom, and γ is the angle between the center of mass radial vector and the vector pointing along the diatom; in terms of the canonical variables one has¹³

$$\cos \gamma = -\cos q_\ell \cos q_j + \frac{\ell^2 + j^2 - J^2}{2\ell j} \sin q_\ell \sin q_j, \quad (7)$$

where q_ℓ and q_j are the coordinates conjugate to ℓ and j , and J is the (fixed) total angular momentum. Units with $\hbar = 1$ are used throughout so that ℓ , j , and J are the classical equivalent of the corresponding quantum numbers; ℓ , j , and J are actually replaced in Eqs. (6) and (7) by $\ell + \frac{1}{2}$, $j + \frac{1}{2}$, and $J + \frac{1}{2}$, for the usual semiclassical reasons,¹⁴ but we have not indicated this explicitly for simplicity of presentation.

For fixed values of J and E , there are two internal degrees of freedom, characterized by canonical variables (ℓ, q_ℓ) and (j, q_j) . The domain of q_ℓ and q_j is the interval $(0, 2\pi)$, but one can easily see that the substitution

$$q_\ell \rightarrow q_\ell + \pi$$

$$q_j \rightarrow q_j + \pi$$

leaves the Hamiltonian unchanged. Thus only half of the $2\pi \times 2\pi$ phase region is independent, and one may restrict attention, say, to $0 \leq q_\ell \leq \pi$ and $0 \leq q_j \leq 2\pi$. This symmetry is that of total parity, and the division of the $2\pi \times 2\pi$ phase region into two equivalent parts is the classical analog to the factorization of the coupled-channel Schrodinger equation into two non-interacting blocks that is possible because of total parity conservation in the quantum mechanical version of this problem.¹⁵ If the diatom is homonuclear (which we assume it to be), then the potential $V(R, \gamma)$ is a function only of $\cos^2 \gamma$, so that the substitution $q_\ell \rightarrow q_\ell + \pi$ and the substitution $q_j \rightarrow q_j + \pi$ separately leave the Hamiltonian unchanged; i.e., molecular parity and orbital parity are separately conserved (not just their sum). The $2\pi \times 2\pi$ phase regions thus divides into four equivalent blocks, so that one only need consider the region $0 \leq q_\ell \leq \pi$ and $0 \leq q_j \leq \pi$. The quantum mechanical version of this is that the coupled-channel Schrodinger equations factors into four non-interacting blocks.¹⁵

Marcus⁶ has discussed the selection rules which result from these symmetries, which of course are the same as the

quantum mechanical ones; Appendix II shows how the normalization of the classical S-matrix is modified when symmetries are present. With this modification the classical S-matrix is constructed according to the general prescription of I. For fixed values of total angular momentum J and total energy E , initial values for ℓ , j , q_ℓ , and q_j --denoted by ℓ_1 , j_1 , q_{ℓ_1} , q_{j_1} --determine the classical trajectory, for R_1 is required only to be large, and by energy conservation

$$P_1 = - \sqrt{2\mu[E - B j_1^2] - \ell_1^2 / R_1^2}. \quad (8)$$

With these initial conditions Hamilton's equations

$$\dot{R} = \frac{\partial H}{\partial P}, \quad \dot{P} = - \frac{\partial H}{\partial R} \quad (9a)$$

$$\dot{q}_\ell = \frac{\partial H}{\partial \ell}, \quad \dot{\ell} = - \frac{\partial H}{\partial q_\ell} \quad (9b)$$

$$\dot{q}_j = \frac{\partial H}{\partial j}, \quad \dot{j} = - \frac{\partial H}{\partial q_j} \quad (9c)$$

with the Hamiltonian of Eq.(6), are numerically integrated¹⁶ and final values of ℓ and j obtained; these final values, denoted by ℓ_2 and j_2 , are functions of the initial values: $\ell_2(q_{\ell_1}, q_{j_1}, \ell_1, j_1)$ and $j_2(q_{\ell_1}, q_{j_1}, \ell_1, j_1)$.

A particular S-matrix element $S_{j_2 \ell_2, \ell_1 j_1}^{(J)}$ is constructed by finding the classical trajectories for which ℓ and j are equal to the integers ℓ_1 and j_1 before collision and the integers ℓ_2 and j_2 after collision. This is accomplished by fixing ℓ_1 and j_1 at the particular initial integer values and solving the two transcendental equations (with the functional dependence of j_1 and ℓ_1 suppressed)

$$j_2(q_{\ell_1}, q_{j_1}) = j_2 \quad (10a)$$

$$\ell_2(q_{\ell_1}, q_{j_1}) = \ell_2 \quad (10b)$$

iteratively to find the appropriate values for q_{ℓ_1} and q_{j_1} .

The phase associated with this trajectory is

$$\phi_{j_2 \ell_2, j_1 \ell_1}(J) = \frac{\pi}{2} (\ell_1 + \ell_2) - \int_{-\infty}^{\infty} dt [R\dot{P} + q_{\ell} \dot{\ell} + q_j \dot{j}], \quad (11)$$

and the classical S-matrix is

$$S_{j_2 \ell_2, j_1 \ell_1}(J) = \sum D^{-\frac{1}{2}} \exp[i\phi_{j_2 \ell_2, j_1 \ell_1}(J)], \quad (12)$$

where

$$D = (i\frac{\pi}{2})^2 \det \begin{bmatrix} \frac{\partial \ell_2}{\partial q_{\ell_1}} & \frac{\partial \ell_2}{\partial q_{j_1}} \\ \frac{\partial j_2}{\partial q_{\ell_1}} & \frac{\partial j_2}{\partial q_{j_1}} \end{bmatrix}, \quad (13)$$

with q_{ℓ_1} and q_{j_1} evaluated at the root of Eq.(10). (Note the $\frac{\pi}{2}$ factor rather than 2π ; see Appendix II). The summation in Eq.(12) indicates a sum of terms of this form over all roots of Eq.(10)--i.e., a sum over all trajectories for which j and ℓ are (j_1, ℓ_1) initially and (j_2, ℓ_2) finally. For the results presented below there are either two or four such terms.

In cases that $j(t)$ and/or $\ell(t)$ become small during the course of the trajectory, there are numerical problems in carrying out the numerical integration directly in action-angle variables.¹⁷ The physical origin of the problem is that the variable q_j , for example, is the amount of rotation in the plane perpendicular to the instantaneous $\vec{j}$ vector; if $j(t)$ becomes zero, or small, however, during the trajectory, this instantaneous plane of rotation is ill-defined, and the expression for $\dot{q}_j$ has a corresponding singularity as $j \rightarrow 0$.

For small quantum numbers, therefore, the initial conditions are specified in terms of action-angle variables as above, but then transformed to ordinary cartesian coordinates and the numerical integration carried out in these variables.¹⁶ At the end of the trajectory one transforms back to action-angle variables so that the trajectory functions $j_2(q_{\ell_1}, q_{j_1})$ and $\ell_2(q_{\ell_1}, q_{j_1})$ are obtained and used to construct the classical S-matrix as discussed above. Appendix III gives some of the details of the canonical transformation between action-angle and cartesian variables.

For their quantum mechanical computation, Johnson, Secrest, Lester, and Bernstein⁴ chose the potential in Eq.(6) to be

$$V(R, \gamma) = V_0(R) [1 + aP_2(\cos \gamma)], \quad (14)$$

where $V_0(R)$ is a Lennard-Jones 6-12 potential

$$V_0(R) = \epsilon[(r_m/r)^{12} - 2(r_m/r)^6], \quad (15)$$

and a is a constant. For the results on pg. 397 of ref. 4, $a = .25$, and one may set $\epsilon = r_m = 1$; in units for which $\hbar = 1$, then, one has $\mu = 500$, $B = 0.0025$, $E = 1$, for the reduced mass, rotational constant, and total energy, respectively, and the total angular momentum $J = 6$.

Table I gives numerical values for the square modulus of S-matrix elements for all the classically allowed inelastic $(j_1, \ell_1 \neq j_2, \ell_2)$ transitions for which $j_1, j_2 = 0, 2, 4$; transitions involving $j = 6$ are not considered since these quantum values are not likely to be accurate.⁴ The terms "classical", "semiclassical", and "uniform" in Table I have the same meaning

as in paper II: omission of all interference terms which result when the square modulus of Eq.(12) is formed, inclusion of interference terms just as they arise in squaring Eq. (12), and use of uniform semiclassical expressions to modify the primitive treatment of the interferences, respectively. When there are two terms in the classical S-matrix, the uniform semiclassical expression is the same as in paper II; when four classical trajectories contribute to a particular transition, the uniform expression used is that devised in Appendix IV.

The uniform semiclassical results in Table I are seen to be in good agreement with the exact quantum values, although the level of accuracy is not as high as that in paper II; Fig. 1 shows the comparison pictorially. This somewhat lower degree of accuracy is presumably due to the fact that the trajectory functions $j_2(q_{\ell_1}, q_{j_1})$ and $\ell_2(q_{\ell_1}, q_{j_1})$ for this particular system are not simple, harmonic-like functions as in II, but are more structured; also there is more error because of our inability to deal as accurately with four coalescent terms in the classical S-matrix as with only two terms (see Appendix IV). The potential parameters and collision energy of this particular system are, too, quite quantum-like (or else exact quantum calculations would not be feasible) as evidenced by the absence of large changes in the rotational quantum number (only $\Delta j = \pm 2$ is classically allowed). The highly quantum-like nature of the system, however, is exactly what makes application of the classical S-matrix approach so

interesting--for one is fairly certain that it will be accurate under classical-like conditions (large quantum numbers, large changes in quantum numbers), and the interest is to see just how far toward the quantum direction it is applicable.

Another feature of the results in Table I which points out the quantum-like nature of the present system is that the "primitive" semiclassical treatment of the interference is completely inadequate, and one must use the uniform expressions. The relation between the "primitive" and "uniform" treatment of the interference is essentially the same as that of the Airy function to its asymptotic approximation; Figure 2 shows this comparison. The argument of the Airy function which pertains to treating the interference between two terms in the classical S-matrix is $x = (\frac{3}{4}\Delta\phi)^{\frac{2}{3}}$, $\Delta\phi$ being the phase difference of the two interfering terms (in units of $\hbar$). From Figure 2 it is clear that the primitive and uniform treatments will be roughly equivalent if $\Delta\phi \gtrsim 1$, but that the primitive expressions become inadequate (quite rapidly) for $\Delta\phi < 1$. The fact that the primitive and uniform semiclassical values in Table I differ so greatly, therefore, results because the phase differences between the several terms in the classical S-matrix are small.

Even for a relatively quantum-like system such as this, therefore, the individual transition probabilities are given reasonably accurately by classical dynamics employed in the framework of the classical S-matrix; i.e., the major influence of quantum mechanics is that which results through quantum superposition.

III. AVERAGED COLLISION PROPERTIES; RIGID ROTOR-ATOM.

For the rigid rotor-atom collision considered in the previous section, one is most often interested in cross sections which are a sum over final M-components of molecular rotation and an average over initial M-components.¹⁸ It is well-known¹⁹ that this is equivalent to summing and averaging over final and initial values of the orbital angular momenta

$$\sum_{\ell_2, \ell_1} |S_{j_2 \ell_2, j_1 \ell_1}(J)|^2. \quad (16)$$

In any sum over quantum numbers, such as in Eq.(16), one expects that interference terms in the individual transition probabilities will tend to cancel one another; this is a type of "random phase approximation". If this is the case, then it will suffice to use the strictly classical approximation for the individual transition probabilities in Eq.(16)--i.e., there is no point in making the effort to include interference terms if they are going to average to zero.

In this and the following section, we wish to explore this point more fully--the extent to which one can use a completely classical treatment for averaged quantities; or, in other words, how much averaging is necessary to quench the quantum effects of tunneling and interference.

Before discussing the rigid rotor-atom system with regard to this question, consider first the much simpler quantity, the probability distribution for a single particle in a harmonic potential; the probability of finding the particle in the interval $(x, x+dx)$ is the square modulus of the wave function

$$P_n(x) \equiv |\langle x|n \rangle|^2, \quad (17)$$

and the strictly classical approximation for this is proportional to the inverse velocity

$$P_n^{CL}(x) = \frac{1}{\pi} [(n+\frac{1}{2})\alpha - x^2]^{-\frac{1}{2}}, \quad (18)$$

where $\alpha = 2\hbar/m\omega$.

The classical probability distribution in Eq.(18) has singularities at the classical turning points, a phenomenon characteristic of all classical probabilities (which are reciprocal Jacobians). A more satisfactory classical-like approximation is obtained by averaging the quantity in Eq.(18) over n ,

$$\bar{P}_n^{CL}(x) \equiv \int_{n-\frac{1}{2}}^{n+\frac{1}{2}} dn P_n^{CL}(x), \quad (19)$$

and with Eq.(18) this gives

$$\bar{P}_n^{CL}(x) = \frac{2}{\pi} \frac{1}{\alpha} [\sqrt{\alpha(n+1)-x^2} - \sqrt{\alpha n-x^2}]. \quad (20)$$

Since the singularity in Eq.(18) is integrable, therefore, this averaging process removes the singularity. Figure 3 shows the typical behavior of Eq.(17) and Eq.(20); not only are the singularities in the classical probability removed, but the general character of $\bar{P}^{CL}$ is quite similar to the true quantum probability, lacking only the interference structure. It seems clear, therefore, that within a strictly classical treatment one obtains more reasonable results by averaging the exact classical probability somewhat, and using it in preference to the exact classical probability itself.

Now consider the analogous modification of the strictly classical expression for a transition probability. The exact classical value is a reciprocal Jacobian

$$P_{n_2, n_1} = \left[2\pi \left| \left(\frac{\partial n_2}{\partial q_1} \right)_{n_1} \right| \right]^{-1} \quad (21)$$

where (n, q) are the action-angle variables for the internal degrees of freedom, n_2 being a function of q_1 and n_1 in the usual sense. (For clarity multi-dimensional notation is not explicitly used, but it should be clear how the expressions would be written.) Averaging this over n_2

$$\bar{P}_{n_2, n_1} \equiv \int_{n_2 - \frac{1}{2}}^{n_2 + \frac{1}{2}} dn_2 P_{n_2, n_1}, \quad (22)$$

with n_1 fixed, the variable of integration can be changed from n_2 to q_1 , so that one obtains

$$\bar{P}_{n_2, n_1} = \frac{1}{2\pi} \int dq_1 = \Delta q_1 / 2\pi, \quad (23)$$

where Δq_1 is the interval of q_1 for which

$$n_2 - \frac{1}{2} \leq n_2(q_1, n_1) \leq n_2 + \frac{1}{2}. \quad (24)$$

This averaged classical transition probability in Eq.(23) has no classical infinities, as does the exact classical quantity in Eq.(21), and is therefore much more satisfactory when one is restricting attention to a purely classical treatment.

One will recognize that the "averaged classical transition probability" in Eqs.(23) and (24) is exactly that which would be obtained by the traditional Monte Carlo treatment²⁰ of

classical trajectories. In this approach one would choose (with n_1 fixed) the initial phase q_1 randomly in the interval $(0, 2\pi)$; the number of trajectories for which the final quantum number is in the interval $(n_2 - \frac{1}{2}, n_2 + \frac{1}{2})$, divided by the total of trajectories, is the $n_1 \rightarrow n_2$ transition probability; this is just the Monte Carlo way of evaluating $\Delta q_1 / 2\pi$ in Eq.(23).

The major point of these arguments, then, is that if one is interested only in averaged collision quantities for which interference and tunneling are probably quenched, then the most sensible quantity to calculate is the averaged classical transition probability of Eqs.(23) and (24); the Monte Carlo methods are one way of evaluating this quantity, a very convenient one for averaging over many variables (collision energy, initial quantum state, etc.). For some purposes it might actually be more efficient to vary the initial variable q_1 systematically to map out the boundaries of the interval Δq_1 contributing to the final states of interest.

The main question remaining is how much averaging is necessary before the averaged classical transition probability gives accurate averaged collision properties. As an example, the quantities

$$\bar{P}(j_2 \leftarrow j_1 \ell_1) = \sum_{\ell_2} |S_{j_2 \ell_2, j_1 \ell_1}(J)|^2 \quad (25)$$

have been computed for the rigid rotor-atom system of Section II. These quantities are "less averaged" than those in Eq.(16) [for ℓ_1 is not summed over in Eq.(25)], so that any unquenched quantum effects should appear more prominently in them. In

the spirit of "averaged classical transition probabilities" discussed above, the quantities in Eq.(25) were computed in the following manner: with ℓ_1 and j_1 (and J) fixed, q_j and q_ℓ were assigned initial values

$$q_{j_1} = n(\pi/N)$$

$$q_{\ell_1} = m(\pi/N),$$

with $n, m = 0, \dots, N-1$, and trajectories (N^2 of them) computed; then the quantity in Eq.(25) is given by

$$\begin{aligned} \bar{P}(j_2 + j_1 \ell_1) &\approx [\text{number of trajectories for which} \\ &\text{final value of } j \text{ is in the interval } (j_2 - 1, j_2 + 1)] \div \\ &[\text{total number of trajectories}]; \end{aligned} \quad (26)$$

the interval $(j_2 - 1, j_2 + 1)$ is used, rather than $(j_2 - \frac{1}{2}, j_2 + \frac{1}{2})$ because of the selection rule $\Delta j = 0, \pm 2, \pm 4, \dots$.

Table II shows results of the above procedure for $N = 20$, compared to the exact quantum values of ref. 4; on the basis some calculations performed with various N values we estimate these results with $N = 20$ to be within about .02 of the exact ($N \rightarrow \infty$) averaged classical values. Since the number of terms in the quantum mechanical sum in Eq.(25) is only $(2j_2 + 1)$, it is indeed remarkable how few terms one need sum over before the averaged classical values agree quite well with the quantum ones. The quantity in Eq.(16), which also involves a sum over ℓ_1 , should be even more classical-like.

The basic conclusion of this section, therefore, is that although interference terms appear quite prominently in individual transition probabilities (as seen in Sec. II), a

relatively small amount of averaging quenches them; except for completely state-selected and detected observations, then, the averaged classical approach will probably suffice.²¹

As the complexity of the collision partners increases, the number of internal degrees of freedom increases, the possibility of complete state selection diminishes, and thus the validity of an averaged classical treatment is even more strongly warranted. The principal situation for which a completely classical treatment of averaged collision properties will probably not be sufficient is the case that all transitions are classically forbidden; the next Section considers this point further.

IV. AVERAGE ENERGY TRANSFER; LINEAR ATOM-DIATOM.

The model system here is that for which Secrest and Johnson²² have performed exact quantum mechanical computations: the diatom is a harmonic oscillator, and the interaction is an exponential repulsion between the atom and the closest end of the diatom. Papers II and III have presented classical S-matrix type calculations for this system, the results of which were summarized in the Introduction.

Here the averaged quantity of interest is the average energy transfer ΔE , which for a harmonic oscillator is (in units of $\hbar\omega$)

$$\Delta E(n_1) = \sum_{n_2} (n_2 - n_1) P_{n_2, n_1}, \quad (27)$$

where P_{n_2, n_1} is the transition probability from vibrational state n_1 to n_2 . Within the classical S-matrix framework one has

$$P_{n_2, n_1} = P_{n_2, n_1}^{\text{CL}} + \text{interference}, \quad (28)$$

$$\text{where } P_{n_2, n_1}^{\text{CL}} = \left[2\pi \left| \left(\frac{\partial n_2}{\partial q_1} \right)_{n_1} \right| \right]^{-1}. \quad (29)$$

If many terms contribute to the sum in Eq.(27), then one may replace the sum by an integral and assume that the interference term in Eq.(28) averages to zero; this gives

$$\Delta E(n_1) = \frac{1}{2\pi} \int dn_2 \frac{1}{\left| \frac{\partial n_2}{\partial q_1} \right|} - n_1,$$

and with a change of variables in the integral one has

$$\Delta E(n_1) = \frac{1}{2\pi} \int dq_1 [n_2(q_1, n_1) - n_1]. \quad (30)$$

Eq.(30), which results from the strictly classical approximation for the transition probabilities, is the phase-averaged energy transfer which has recently been computed by Heidrich, Wilson, and Rapp²³; in most cases they found excellent agreement between the results of Eq.(30) and the exact quantum values of ref. 22 used in Eq.(27). From the above presentation one certainly expects this to be true when there are many classically allowed transitions which contribute to the sum. The somewhat remarkable feature is that only one or two classically allowed terms are necessary for there to be good agreement between Eqs.(30) and (27).

To explore the situation more fully, we consider for the remainder of this section that $n_1 = 0$ and that the collision energy and mass parameter are such that all transitions are classically forbidden; this is a situation in which one would not necessarily expect Eqs.(27) and (30) to agree. Eq.(27) becomes

$$\Delta E = P_{1,0}, \quad (27')$$

since all higher transitions have much smaller transition probabilities; i.e., the average energy transfer is the $0 \rightarrow 1$ transition probability in this case.

There are two prescriptions by which classical mechanics may be used to generate an approximation to the average energy transfer (i.e., $P_{1,0}$): (1) compute the phase-averaged energy transfer by Eq.(30); (2) use the classical trajectory functions to construct the classical S-matrix approximation to the classically forbidden $0 \rightarrow 1$ transition probability

(24)

(by the methods in paper III). To simplify the comparison of these two approaches, suppose the trajectory function $n_2(q_1)$ is given by

$$n_2(q_1) = a + A \cos(q_1 + b), \quad (31)$$

where

$$|a|, |A| \ll 1;$$

in II it was seen that this is often a good approximation to the exact function $n_2(q_1)$. The phase-averaged energy transfer of Eq.(30) is then easily found to be

$$\Delta E = P_{1,0} = a. \quad (32)$$

The classical S-matrix approximation to $P_{1,0}$ is³

$$P_{1,0} = [2\pi |n_2(q_1)|]^{-1} e^{-2|\text{Im}\phi|}, \quad (33)$$

where q_1 is one of the complex roots of

$$n_2(q_1) = 1, \quad (34)$$

and ϕ is the phase:

$$\phi = -\int dq_1 q_1 n_2'(q_1), \quad (35)$$

evaluated at the root of Eq.(34). Eq.(33) can thus be evaluated, and using the fact that $|a|, |A| \ll 1$, one obtains

$$P_{1,0} \approx \frac{1}{4} A^2. \quad (36)$$

The two prescriptions, therefore, give completely different results: prescription 1 gives [Eq.(32)] $P_{1,0} = a$, and prescription 2 [Eq.(36)] $P_{1,0} = \frac{1}{4} A^2$, and in general there is no relation between the constants a and A ; in fact, the constant a can be negative, as it sometimes is, so that prescription 1 may give nonsense.

Table III shows a few examples of the Heidrich, Wilson, and Rapp results which compare most poorly with the quantum results of Secrest and Johnson; it is seen that Eq.(32) (the phase-averaged energy transfer) does indeed give negative values of $P_{1,0}$ in some cases. Also shown is the result of the classical S-matrix approach, Eq.(36), which is clearly more satisfactory in these cases.

It is interesting, though perhaps coincidental, that prescription 1 (the phase-averaged energy transfer) agrees exactly with the quantum mechanical result in the limit of a high energy, impulsive collision (which means a small mass parameter for this model). This is easy to show by solving the Shuler-Zwanzig problem²⁴ to first order in the mass parameter m ; the result is

$$P_{1,0} = 4m[(E-\frac{1}{2})(E-\frac{3}{2})]^{\frac{1}{2}}. \quad (37)$$

The result from Eq.(30) in this case is

$$P_{1,0} = 4m(E-1), \quad (38)$$

which agrees with Eq.(37) for $E \gg 1$. The averaged energy transfer approach works even for $P_{0,1} \ll 1$, therefore, if the collision is impulsive; indeed, the cases of poorest agreement of Eq.(30) with the quantum values are those of low energy and large mass parameter.

In summary, one expects the strictly classical approximation for the average energy transfer to be accurate if more than one or two transitions are classically allowed. If the collision is of an impulsive nature (translational velocity much greater than internal velocities), then this procedure

may give accurate results even if all transitions are highly forbidden classically. The principal situation in which it is expected to be poor is the adiabatic limit (internal velocities much greater than the collision velocity).

V. SUMMARY.

From the results of the rigid rotor-atom problem presented in Section II, one concludes (just as in paper II) that the dynamics of heavy particle collisions is largely classical, quantum mechanics contributing principally through superposition; interference effects appear quite prominently in the magnitude of individual transition probabilities.

If the observed collision property involves the sum and/or average over several quantum states, however, the interference terms are rapidly quenched, so that a strictly classical approximation to the transition probability (averaged so as to remove infinities in the Jacobian) gives good agreement with exact quantum results; Sections III and IV show examples of this.

In the case of impulsive dynamics it appears that averaged classical quantities may be accurate even when all transitions are classically forbidden; there may be other limiting cases for which this is also true. The limit of an adiabatic collision is a case in which averaged classical quantities are not expected to be accurate.

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Table I. Rigid Rotor-Atom Transition Probabilities.^a

<u>Transition</u> ^b	<u>Classical</u> ^c	<u>Semiclassical</u> ^d	<u>Uniform</u> ^e	<u>Quantum</u> ^f
2,4-0,6	0.161	0.428	0.213	0.176
2,6-0,6	0.233	0.509	0.108	0.142
2,8-0,6	0.263	0.645	0.263	0.234
2,6-2,4	0.130	0.172	0.116	0.109
4,2-2,4	0.238	0.560	0.211	0.220
4,4-2,4	0.115	0.136	0.071	0.078
2,8-2,6	0.260	0.266	0.059	0.063
4,4-2,6	0.105	0.109	0.028	0.019
4,6-2,6	0.102	0.146	0.109	0.087
4,8-2,6	0.080	0.106	0.067	0.107
4,10-2,8	0.636	1.20	0.369	0.297
4,4-4,2	0.113	0.134	0.070	0.083
4,6-4,4	0.121	0.178	0.140	0.111
4,8-4,6	0.116	0.130	0.056	0.073

- a. The quantities in the table are $|S_{j_2 l_2, j_1 l_1}(J)|^2$ for the rigid rotor-atom system discussed in Section II, $J = 6$.
- b. The quantum numbers are $j_2, l_2 - j_1, l_1$; microscopic reversibility ($j_1 l_1 \rightarrow j_2 l_2 \equiv j_2 l_2 \rightarrow j_1 l_1$) is identically true for all four methods.
- c. Omission of all interference terms which arise in constructing the square modulus of Eq.(12).
- d. Inclusion of interference terms just as they result in constructing the square modulus of Eq.(12).
- e. Inclusion of interference terms by the uniform semiclassical expressions given in Appendix IV.
- f. Essentially exact quantum values of Johnson, Secrest, Lester, and Bernstein.⁴

Table II. Averaged Rigid Rotor-Atom Transition Probabilities.^a

$j_1 l_1$	<u>Classical</u> ^b				<u>Quantum</u> ^c			
	0	2	4	6	0	2	4	6
0,6	0.33	0.59	0.08	0	0.32	0.55	0.12	0.01
2,4	0.14	0.41	0.41	0.04	0.18	0.43	0.33	0.07
2,6	0.10	0.54	0.34	0.02	0.14	0.56	0.25	0.04
2,8	0.21	0.37	0.40	0.02	0.23	0.38	0.33	0.06
4,2	0.02	0.26	0.33	0.39	0.02	0.25	0.38	0.35
4,4	0.01	0.16	0.56	0.27	0.02	0.10	0.64	0.24
4,6	0.01	0.16	0.53	0.30	0.02	0.11	0.61	0.26
4,8	0.01	0.22	0.39	0.39	0.02	0.14	0.53	0.30
4,10	0.02	0.37	0.24	0.38	0.04	0.32	0.30	0.34

- a. The quantities in the table are $\sum_{l_2} |S_{j_2 l_2, j_1 l_1}(J)|^2$ for the rigid rotor-atom system discussed in Section II.
- b. Column headings are the values of j_2 ; the entries are the averaged classical transition probabilities computed by the procedure described in the paragraph following Eq.(25).
- c. Column headings are the values of j_2 ; the entries result from using the quantum values of Johnson, Secrest, Lester, and Bernstein⁴ in Eq.(25).

Table III. Average Energy Transfer for Linear Atom-Diatom Collisions.

<u>m, α, E^a</u>	<u>Classical^b</u>	<u>Semiclassical^c</u>	<u>Quantum^d</u>
$\frac{2}{3}, 0.3, 3.0$	1.39×10^{-2}	2.70×10^{-2}	2.21×10^{-2}
1.25, 0.2973, 2.47275	-4.14×10^{-4}	4.35×10^{-4}	1.12×10^{-4}
1.25, 0.2973, 3.47275	1.66×10^{-3}	3.78×10^{-3}	2.93×10^{-3}
0.2, 0.114, 3.0	-2.99×10^{-4}	1.46×10^{-3}	7.06×10^{-4}
0.5, 0.114, 3.8	-2.51×10^{-5}	9.05×10^{-5}	4.30×10^{-5}
0.5, 0.114, 4.4	5.55×10^{-5}	2.84×10^{-4}	2.03×10^{-4}
0.5, 0.114, 5.0	4.11×10^{-4}	7.31×10^{-4}	6.58×10^{-4}

- a. These are the parameters of the model as defined by Secrest and Johnson,²² except that E is the total energy in units of $\hbar\omega$ (rather than $\frac{1}{2}\hbar\omega$).
- b. These values are the phase-averaged energy transfer as defined by Eq.(30), with $n_1 = 0$, and computed by Heidrich, Wilson, and Rapp.²³
- c. These values result from the classical S-matrix approximation to $P_{1,0}$, as given by Eq.(36).
- d. These values are the exact quantum results for $P_{1,0}$ as computed by Secrest and Johnson.²²

Figure Captions

1. A visual comparison of the exact quantum results (points connected by the solid line) and uniform semiclassical results (points connected by the dotted line) which are tabulated in Table I. For clarity of the display the order of transitions along the abscissa was chosen so that the quantum values increase monotonically.
2. The solid line is the regular Airy function $\text{Ai}(-x)$; the dashed line its asymptotic approximations: $\pi^{-\frac{1}{2}} x^{-\frac{1}{4}} \sin(\frac{\pi}{4} + \frac{2}{3} x^{\frac{3}{2}})$ for $x > 0$, and $\frac{1}{2} \pi^{-\frac{1}{2}} |x|^{-\frac{1}{4}} \exp(-\frac{2}{3} |x|^{\frac{3}{2}})$ for $x < 0$; the dotted line is its "classical" approximation: $(2\pi)^{-\frac{1}{2}} x^{-\frac{1}{4}}$, $x > 0$. The variable $\Delta\phi$ on the upper abscissa is $\Delta\phi = \frac{4}{3} x^{\frac{3}{2}}$.
3. Comparison of the exact quantum probability distribution (the solid lines) with the averaged classical probability distribution given by Eq.(20) (the dashed lines) for a single particle in a harmonic potential; the parameter $\alpha = 2$ ($\hbar = m = \omega = 1$). The a figure is the case $n = 0$, and b is for $n = 2$; even for these small quantum numbers the averaged classical values are seem to be in rough agreement with the quantum distribution (except for omission of the interference).

Appendix I. The Correspondence between Classical and Quantum Mechanics.

As Dirac²⁵ emphasizes, quantum mechanics is a mechanics of transformations, usually unitary transformations. In constructing a semiclassical theory of heavy particle dynamics, our approach has been to retain the quantum mechanical transformation principles, but to evaluate the transformation elements within the classical limit. Here we would like to give more details of this correspondence between unitary transformations of quantum mechanics and canonical transformations of classical mechanics than were given in I.

In discussing unitary transformation elements within the classical limit, it is only necessary to consider the phase of the transformation element, since it was shown in I how the magnitude of any unitary transformation is determined from its phase alone.

The starting point is the basic transformation relation²⁶

$$\langle q | p \rangle = (2\pi i \hbar)^{-1/2} e^{ipq/\hbar}, \quad (11)$$

where p and q are any variables canonically conjugate to one another; as Dirac shows, Eq.(11) is equivalent to the fundamental commutation relation

$$[q, p] = i\hbar,$$

and is also a statement of the Uncertainty Principle. This latter point follows since $|\langle q | p \rangle|^2$ is the probability distribution in q for fixed p (or vice-versa), and the fact that $|\langle q | p \rangle|^2$ is constant means that if p is fixed, then q can have any value (or vice-versa).

Consider now a canonical transformation¹¹ from the variables (q,p) to a new canonical set (Q,P) . Q and P are functions of the old variables q and p , or one may consider p and q to be functions of the new variables Q and P ; or one may consider Q and p to be functions of q and P , etc.-- i.e., one may choose any two of the four variables q,p,P,Q to be the independent variables, the remaining two then being functions of these two. It is well known¹¹ how the canonical transformation is carried out in classical mechanics; it is specified by the generator of the transformation, which is a function of one old variable and one new variable, such as $F_2(q,P)$ (q and P are the independent variables in this case).

In quantum mechanics the canonical transformation is specified by the matrix elements of a complete set of "old states" with a complete set of "new states", such as $\langle q|P\rangle$; it is the relation between the unitary transformation $\langle q|P\rangle$ and the classical generator $F_2(q,P)$ which we seek. Working within the classical limit, let

$$\langle q|P\rangle \sim e^{if(q,P)/\hbar}, \quad (I2)$$

where f is the function to be determined. Using Eqs.(I1) and (I2) and the transformation laws of quantum mechanics (i.e., matrix multiplication), one has

$$\begin{aligned} \langle p|P\rangle &= \int dq \langle p|q\rangle \langle q|P\rangle \\ &\sim \int dq e^{i[-pq+f(q,P)]/\hbar}, \end{aligned} \quad (I3)$$

and in the classical limit ($\hbar \rightarrow 0$) the integral can be evaluated by the method of stationary phase²⁷, giving

$$\langle p|P\rangle \sim e^{i[-pq+f(q,P)]/\hbar}, \quad (I4)$$

where q is evaluated at the point of stationary phase, the solution of

$$p = \frac{\partial f(q, P)}{\partial q} ; \quad (I5)$$

i.e., Eq.(I5) is the stationary phase requirement. Using Eqs.(I1) and (I2) again, one also has

$$\begin{aligned} \langle q | Q \rangle &= \int dP \langle q | P \rangle \langle P | Q \rangle \\ &\sim \int dP e^{i[f(q, P) - PQ]/\hbar}, \end{aligned} \quad (I6)$$

which is also to be evaluated by stationary phase, yielding

$$\langle q | Q \rangle \sim e^{i[f(q, P) - PQ]/\hbar}, \quad (I7)$$

where P is evaluated at the point of stationary phase, the solution of

$$Q = \frac{\partial f(q, P)}{\partial P} \quad (I8)$$

We now consider the variables q and P in Eqs.(I5) and (I8) (the stationary phase relations) to be the independent variables; if one assumes that the values of p and Q in these equations are precisely those values which are determined classically by the independent variables q and P , then one recognizes the stationary phase relations, Eqs.(I5) and (I8), to be the equations of classical mechanics which determine the classical generator $F_2(q, P)$ --i.e., the function f must be F_2 , so that the desired relation

$$\langle q | P \rangle \sim e^{iF_2(q, P)/\hbar} \quad (I9)$$

is proved. From Eqs.(I4), (I6), and (I9), other analogous correspondence relations follow simply

$$\begin{aligned} \langle p | P \rangle &\sim e^{iF_4(p, P)/\hbar} \\ \langle q | Q \rangle &\sim e^{iF_1(q, Q)/\hbar}, \end{aligned}$$

where the F_1 and F_4 generators are related to F_2 by

$$F_4(p, P) = F_2(q, P) - pq$$

$$F_1(q, Q) = F_2(q, P) - PQ.$$

The basic physical content of the above argument is the idea involved in going from Eq.(I3), say, to Eq.(I4): quantum mechanically the transformation element $\langle p|P\rangle$ has contributions from all possible values of q (cf. a "sum over all paths" alá Feynman²⁸); in the classical limit (expressed mathematically by the stationary phase approximation), however, only one value of q contributes to the "sum", namely that value which is determined classically by the fixed values of p and P .

Dynamical transformation elements (e.g., the S-matrix) can also be expressed within the above framework by realizing that dynamical transformations are also canonical (unitary) transformations. If $H(p, q)$ is the time-independent Hamiltonian governing the system, then the unitary transformation from variables q_1 and p_1 (the values of q and p at time t_1) to variables q_2 and p_2 (the values of q and p at time t_2) is (in the classical limit)

$$\langle q_2 | e^{-iH(t_2-t_1)/\hbar} | q_1 \rangle \sim e^{iF_1(q_2, q_1)/\hbar}, \quad (\text{I10})$$

where the F_1 generator is related to an F_2 in the usual way

$$F_1(q_2, q_1) = F_2(q_2, p_1) - p_1 q_1, \quad (\text{I11})$$

and here F_2 is the solution of the Hamilton-Jacobi equation²⁹ for the Hamiltonian H . It is a standard result of Hamilton-Jacobi theory, however, that this generator is related to the time integral of the Lagrangian

$$\begin{aligned}
 F_1(q_2, q_1) &= \int_{t_1}^{t_2} dt L(t) \\
 &= \int_{t_1}^{t_2} dt [p(t)\dot{q}(t) - H(p, q)]. \quad (I12)
 \end{aligned}$$

Eqs.(I10) and (I12) were the starting point in paper I for deriving all of the general expressions for the classical S-matrix. In I they were taken from the classical limit of the Feynman path integral²⁸; here one sees that it is actually not necessary to introduce the path integral at all. It is possible to derive the expressions for the classical S-matrix from standard classical mechanics, plus the general transformation principles of quantum mechanics.

Finally, in considering the $(q_1, p_1) \rightarrow (q_2, p_2)$ transformation in time as a special type of canonical transformation, one sees clearly the origin of "doubled-ended" boundary conditions as the ones fundamental to the correspondence with quantum mechanics--for the independent variables of the classical generator specifying the transformation must be "one old variable and one new variable".

Appendix II. Normalization of the Classical S-Matrix when Symmetries Exist.

For simplicity we consider only one internal degree of freedom for the discussion and then state the final result for an arbitrary number. The degree of freedom (p, q) has m -fold symmetry if the trajectory function $p_2(q_1)$ is identical in the m subintervals $(0, \frac{2\pi}{m})$, $(\frac{2\pi}{m}, \frac{4\pi}{m})$, ..., $(2\pi\frac{(m-1)}{m}, 2\pi)$. The classical S-matrix is

$$S_{p_2, p_1} = m \left[2\pi i \frac{\partial p_2}{\partial q_1} \right]^{-\frac{1}{2}} e^{i\phi}, \quad (\text{II1})$$

where q_1 is in the first subinterval $(0, \frac{2\pi}{m})$; the factor m appears since there are m equal terms in the $(0, 2\pi)$ interval, and one must sum over them all. One now only needs to consider the subinterval $(0, \frac{2\pi}{m})$.

To see that the expression in Eq.(II1) is indeed normalized correctly, consider

$$\sum_{p_2} |S_{p_2, p_1}|^2 = \sum_{p_2} \frac{m^2}{2\pi} \left| \frac{\partial p_2}{\partial q_1} \right|^{-1}; \quad (\text{II2})$$

p_2 takes on integer values, but because of the symmetry, the selection rule⁶ $|p_2 - p_1| = m, 2m, 3m, \dots$ pertains. Thus

$$\sum_{p_2} \rightarrow \frac{1}{m} \int dp_2,$$

so that Eq.(II2) becomes

$$\begin{aligned} \sum_{p_2} |S_{p_2, p_1}|^2 &= \frac{1}{m} \int_0^{2\pi/m} dq_1 \frac{m^2}{2\pi} \\ &= 1. \end{aligned}$$

For N internal degrees of freedom, it is not hard to see that the correct expression is

$$S_{p_2, p_1} = m_1 m_2 \dots m_N D^{-\frac{1}{2}} e^{i\phi},$$

where m_i is the degree of symmetry of the i th internal degree of freedom, D being the usual normalization factor

$$D = (2\pi i)^N \det \left[\frac{\partial p_i(t_2)}{\partial q_j(t_1)} \right].$$

Appendix III. Transformation between Action-Angle Variables and Cartesian Coordinates.

These relations are derived from the classical generator given by Whittaker.¹³ Initial values of the action-angle variables are specified as discussed in the paragraph preceeding Eq.(8) of the text. The angle q_J , which is conjugate to the total angular momentum J , may be set initially to any arbitrary value. The cartesian variables $\vec{r} = (x,y,z)$, $\vec{p} = (p_x, p_y, p_z)$, $\vec{R} = (X,Y,Z)$, and $\vec{P} = (P_X, P_Y, P_Z)$ are given in terms of the action-angle variables by

$$\begin{aligned}\vec{r} &= r \hat{r} \\ \vec{p} &= p_r \hat{r} + (j/r) \hat{p}_\perp \\ \vec{R} &= R \hat{R} \\ \vec{P} &= P_R \hat{R} + (\ell/R) \hat{P}_\perp\end{aligned}$$

where P_R is the variable P of the text, and

$$\begin{aligned}\hat{R} &= \begin{pmatrix} \sin q_J \cos q_\ell + \lambda_1 \cos q_J \sin q_\ell \\ -\cos q_J \cos q_\ell + \lambda_1 \sin q_J \sin q_\ell \\ \sin q_\ell \sqrt{1-\lambda_1^2} \end{pmatrix} \\ \hat{r} &= \begin{pmatrix} -\sin q_J \cos q_j - \lambda_2 \cos q_J \sin q_j \\ \cos q_J \cos q_j - \lambda_2 \sin q_J \sin q_j \\ \sin q_j \sqrt{1-\lambda_2^2} \end{pmatrix} \\ \hat{P}_\perp &= \begin{pmatrix} -\sin q_J \sin q_\ell + \lambda_1 \cos q_J \cos q_\ell \\ \cos q_J \sin q_\ell + \lambda_1 \sin q_J \cos q_\ell \\ \cos q_\ell \sqrt{1-\lambda_2^2} \end{pmatrix}\end{aligned}$$

$$\hat{p}_\perp = \begin{pmatrix} \sin q_J \sin q_j - \lambda_2 \cos q_J \cos q_j \\ -\cos q_J \sin q_j - \lambda_2 \sin q_J \cos q_j \\ \cos q_j \sqrt{1-\lambda_2^2} \end{pmatrix},$$

where

$$\lambda_1 = (\ell^2 - j^2 + J^2)/2\ell J$$

$$\lambda_2 = (j^2 - \ell^2 + J^2)/2jJ ;$$

for the rigid rotor case, of course, one has $p_r = 0$ and $r = r_0$, a fixed value.

Since the numerical integration is not carried out in action-angle variables, there might be some question as to how the phase in Eq.(11) is calculated. If (p,q) denote the set of cartesian variables and (P,Q) the action-angle variables, then from the general transformation relations in I, one has

$$\phi(P_2, P_1) = \phi(q_2, q_1) - F_2(q, P) \Big|_{t_1}^{t_2}, \quad (\text{III1})$$

where

$$\phi(q_2, q_1) = \int_{t_1}^{t_2} dt \, p\dot{q}, \quad (\text{III2})$$

and F_2 is the generator of the $(p,q) \leftrightarrow (P,Q)$ transformation (i.e., F_2 is the solution of the Hamilton-Jacobi equation²⁹ for the unperturbed Hamiltonian). From Whittaker's generator (which is of the F_3 -type) one can show that

$$F_2(q, P) = PQ, \quad (\text{III3})$$

so that Eq.(III1) becomes

$$\begin{aligned} \phi(P_2, P_1) &= -P_2 Q_2 + P_1 Q_1 \\ &+ \int_{t_1}^{t_2} dt \, p\dot{q}, \end{aligned} \quad (\text{III4})$$

the desired expression.

This is also a convenient place to discuss some features of the relation between our work and that of Marcus.⁶ With (p, q) and (P, Q) again denoting cartesian variables and action-angle variables, respectively, Marcus uses an expression for the S-matrix which projects unperturbed components out of the total wavefunction

$$S_{P_2, P_1} \sim \int dq_2 \psi_{P_2}^o(q_2)^* \psi_{P_1}(q_2), \quad (\text{III5})$$

where $\psi_{P_2}^o(q_2)$ is the eigenfunction of H_0 with eigenvalues P_2 , and $\psi_{P_1}(q_2)$ is the eigenfunction of the total Hamiltonian H which has evolved from the initial asymptotic state $\psi_{P_1}^o(q_1)$. In terms of transformation elements one has

$$\begin{aligned} \psi_{P_2}^o(q_2) &\sim e^{iF_2(q_2, P_2)} \\ \psi_{P_1}(q_2) &\sim \int dq_1 < q_2 | e^{-iH(t_2 - t_1)} | q_1 > e^{iF_2(q_1, P_1)}, \end{aligned}$$

so that Eq.(III5) gives

$$S_{P_2, P_1} \sim \int dq_2 \int dq_1 e^{i[-F_2(q_2, P_2) + \phi(q_2, q_1) + F_2(q_1, P_1)]},$$

and evaluation of the integrals by stationary phase gives

$$S_{P_2, P_1} \sim e^{i\phi(P_2, P_1)},$$

where $\phi(P_2, P_1)$ is given by Eq.(III1); i.e., the two approaches are essentially equivalent.

Appendix IV. Uniform Semiclassical Expressions.

The particular rigid rotor-atom system treated in Section II is so quantum-like that interferences between the several terms contributing to the classical S-matrix must be treated uniformly. When there are two such terms, the expressions in paper II are applicable; thus, if

$$S = p_1 e^{i(\phi_1 + e_1)} + p_2 e^{i(\phi_2 + e_2)} \quad (\text{IV1})$$

is the primitive semiclassical result, the uniform expression is

$$S = e^{i(\phi_1 + \phi_2 + e_1 + e_2)/2} \pi^{\frac{1}{2}} z^{\frac{1}{4}} \left[p_1 (A \pm iB) + p_2 (A \mp iB) \right], \quad (\text{IV2})$$

where

$$A = A_1(-z), \quad B = B_1(-z)$$

$$z = \left[\frac{3}{4} |\phi_2 - \phi_1| \right]^{\frac{2}{3}}$$

$$\pm = \text{sign}(\phi_2 - \phi_1),$$

and e_i , $i = 1, 2$, are the "extra" phases which come from the square root of the Jacobian. For the general case of N internal degrees of freedom one has that $e_i = \frac{\pi}{4}(n_+ - n_-)$, where $n_+(n_-)$ is the number of positive (negative) eigenvalues of the $N \times N$ Jacobian matrix; for two internal degrees of freedom, therefore, $e_i = 0$ or $\pm \frac{\pi}{2}$. From the asymptotic relation

$$\pi^{\frac{1}{2}} z^{\frac{1}{4}} [A_1(-z) \pm iB_1(-z)] \simeq e^{\pm i(\frac{\pi}{4} - \frac{2}{3}z^{\frac{3}{2}})}, \quad (\text{IV3})$$

one can easily see that Eq.(IV2) reduces to Eq.(IV1) as $z \rightarrow \infty$.

For the case that there are four terms in the classical S-matrix,

$$S = \sum_{i=1}^4 p_i e^{i(\phi_i + e_i)}, \quad (\text{IV4})$$

the situation is considerably more complicated, and the following discussion is more the form of a plausibility argument than a proof. For definiteness, the four terms are numbered so that $e_1 = \frac{\pi}{2}$, $e_2 = e_3 = 0$, $e_4 = -\frac{\pi}{2}$; this also implies that ϕ_1 is the smallest phase, and ϕ_4 is the largest.

If the four trajectories were coalescent (i.e., had small phase differences) in pairs, then it is clear that one could use Eq.(IV2) to treat the pair-wise coalescence uniformly, and interference between the two pairs in the ordinary way; one would have, for example,

$$S = S_{1,2} + S_{3,4}, \quad (\text{IV5})$$

where $S_{1,2}$ and $S_{3,4}$ are each of the form as in Eq.(IV2); this treats the coalescence of terms 1 and 2, and 3 and 4, uniformly. Since one must have $|e_i - e_j| = \frac{\pi}{2}$ if terms i and j coalesce, the only other possible pair-wise coalescence is that of 1 with 3, and 2 with 4; this would give

$$S = S_{1,3} + S_{2,4}, \quad (\text{IV6})$$

with each term here of the form as in Eq.(IV2).

Since uniform asymptotic expressions of the type we seek are normally obtained by evaluation of an integral representation for the desired quantity (see the Appendix of paper II), in the present case of two internal degrees of freedom one needs to consider the following type of integral

$$I = \int dx \int dy g(x,y) e^{if(x,y)}. \quad (\text{IV7})$$

Although we have not yet succeeded in developing a generally

valid uniform approximation for this 2-dimensional integral, various limiting cases can be evaluated uniformly, for example, the case that the phase of the integrand is separable: $f(x,y) = f_1(x) + f_2(y)$. In all such special cases the resulting uniform expression for the 2-dimensional integral is of the form of a product of two 1-dimensional uniform expressions. The implications of this are that the appropriate uniform expression corresponding to Eq.(IV4) should be of the form

$$S = e^{i(\phi_1 + \phi_2 + \phi_3 + \phi_4 + e_1 + e_2 + e_3 + e_4)/4} \times \left\{ \begin{aligned} & p_1 \pi z_1^{\frac{1}{4}} z_2^{\frac{1}{4}} (A_1 + iB_1)(A_2 + iB_2) \\ & + p_2 \pi z_3^{\frac{1}{4}} z_4^{\frac{1}{4}} (A_3 + iB_3)(A_4 - iB_4) \\ & + p_3 \pi z_5^{\frac{1}{4}} z_6^{\frac{1}{4}} (A_5 - iB_5)(A_6 + iB_6) \\ & + p_4 \pi z_7^{\frac{1}{4}} z_8^{\frac{1}{4}} (A_7 - iB_7)(A_8 - iB_8) \end{aligned} \right\}, \quad (\text{IV8})$$

where

$$A_1 = Ai(-z_1), \quad B_1 = Bi(-z_1)$$

$$A_2 = Ai(-z_2), \quad B_2 = Bi(-z_2), \text{ etc.,}$$

and the z_i 's are as yet unspecified. To determine them we appeal to Eqs.(IV4), (IV5), and (IV6), to which Eq.(IV8) must reduce in the appropriate limits. Writing out all of these relations, one finds that they can all be satisfied simultaneously by only one, unique choice of the z_i 's, namely

$$z_2 = z_4 = [\frac{3}{4}(\phi_2 - \phi_1)]^{\frac{2}{3}} \quad (\text{IV9a})$$

$$z_6 = z_8 = [\frac{3}{4}(\phi_4 - \phi_3)]^{\frac{2}{3}} \quad (\text{IV9b})$$

$$z_1 = z_5 = [\frac{3}{4}(\phi_3 - \phi_1)]^{\frac{2}{3}} \quad (\text{IV9c})$$

$$z_3 = z_7 = [\frac{3}{4}(\phi_4 - \phi_2)]^{\frac{2}{3}}. \quad (\text{IV9d})$$

Eqs.(IV8) and (IV9) are thus taken as the uniform version of Eq.(IV4).

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Fig. 1.

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Fig. 2.

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Fig. 3a.

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Fig. 3b.

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