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CLASSICAL S-MATRIX FOR VIBRATIONAL EXCITATION OF H_2 BY COLLISION WITH He IN THREE DIMENSIONS*

by

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ABSTRACT

Complex-valued classical trajectories have been computed by direct numerical integration of the equations of motion for three-dimensional collisions of He and H_2, and from such trajectories classical S-matrix elements for transitions between specific rotational-vibrational states of H_2 have been constructed. At the collision energies employed (~ 1-2 electron-volts) all vibrationally inelastic transitions are classically forbidden, thus the need for analytically continued, complex-valued trajectories. Comparison with the quantum mechanical calculations of Eastes and Secrest shows excellent agreement between the quantum and uniform semiclassical transition probabilities. Since, however, for three-dimensional collision systems one is seldom concerned with individual S-matrix elements, but rather sums over many of them, an important practical feature is developed which shows how one can combine the usual Monte Carlo classical treatment of some of the internal degrees of freedom with a semiclassical state-by-state description of others;

i.e., one can 'quantize' only those degrees of freedom that are highly quantum-like (e.g., vibration). This 'partial averaging' approach also greatly simplifies the practical aspects of applying classical S-matrix theory to systems with several internal degrees of freedom.

I. INTRODUCTION.

In the last few years much progress has been made in learning how classical mechanics can be used semiclassically to describe molecular collision phenomena[1-3]. The basic semiclassical idea is that one combines classical dynamics with the quantum principle of superposition (i.e., that one adds probability amplitudes corresponding to different contributions to a specific quantum transition, rather than the probabilities themselves) and it appears that many, perhaps all of the quantum effects in molecular collision dynamics can be accurately described within this framework. Applications[1b-1g] of this 'classical S-matrix' theory to reactive and non-reactive collision processes suggest that even highly quantum-like systems, for which the quantum effects are pronounced, are correctly described.

One of the most intriguing and important aspects of this theory is the ability to analytically continue the expressions for the classical S-matrix and thus be able to treat classically forbidden collision phenomena. By 'classically forbidden' one does not mean that the transition is forbidden by any conservation law or selection rule, but simply that ordinary classical dynamics does not lead to the transition. Even though there are no ordinary classical trajectories that contribute to such transitions, however, one can find complex-valued trajectories that have the correct double-ended boundary conditions.

Along such a trajectory the classical action integral ϕ also becomes complex, so that the classical S-matrix element has the exponential damping factor $\exp(-Im\phi/\hbar)$. This exponential damping is simply the appropriate analytic continuation of the quantum interference structure resulting from the principle of superposition and is a generalization of the concept of one-dimensional tunneling to systems with internal degrees of freedom.

Recent applications[1f, 1g] to reactive and non-reactive collisions have shown that classical S-matrix theory describes these classically forbidden transitions as accurately as it does classically allowed ones. These are indeed encouraging results, for as has been emphacized before[1f, 1g], classically forbidden phenomena are ones for which classical S-matrix theory can make an important and unique contribution. Thus when the transitions of interest are all classically allowed and when one does not consider a completely state-selected situation (which is almost always the case for three-dimensional collision systems), the interference effects predicted by the semiclassical theory are often completely quenched[1d]; in such cases classical S-matrix theory will essentially be equivalent to the well-known Monte Carlo classical trajectory methods[4]. If, on the other hand, the transitions of interest are classically forbidden, the strictly classical methods cannot in general give meaningful results.

Three important processes which are classically forbidden are reactive collisions with significant activation barriers (i.e., reactive tunneling), vibrationally inelastic transitions, and electronic transitions between different adiabatic potential energy surfaces[5]. Examples of the first two of these have been studied for the co-linear A + BC

collision system[1f, 1g], and this paper presents the first application of classical S-matrix theory to vibrationally inelastic collisions for a fully three-dimensional A + BC collision system, He + H_2.

The He + H_2 collision is an ideal one to study in detail for several reasons. First, an excellent potential energy surface for this system has been calculated by Gordon and Secrest[6]; the only feature lacking in this potential is a van der Waals minimum, but this should be unimportant at collision energies relevant to vibrational excitation. Second, the quantum effects in this system should be maximal, making it an ideal one to test the limits of validity of a semiclassical theory; vibrational transitions are strongly forbidden classically even at collision energies of 2-3 eV. Third, preliminary but reasonably accurate quantum mechanical calculations have been carried out by Eastes and Secrest[7] for the $0 \rightarrow 1$ vibrational transition; and finally, shock tube measurements of the vibrational relaxation time of D_2 (infinitely dilute) in He have recently been reported[8] over a wide temperature range.

Section II first summarizes the general features of classical S-matrix theory and discusses some of the computational details. Results for transition probabilities between specific vibrational-rotational states are presented in Section III and compared to the corresponding quantum mechanical values of Eastes and Secrest[7]; agreement with these quantum mechanical results is excellent.

Although it is interesting and gratifying to see that the semiclassical theory agrees so well with quantum mechanics even down to the level of individual S-matrix elements, the actual cross sections of interest for a three-dimensional collision system involve sums over many

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such individual matrix elements. Furthermore, there are often many quantum states of certain degrees of freedom (i.e., rotation) that contribute and which can thus be treated in a classical-like manner, whereas only a few quantum states of other degrees of freedom (i.e., vibration) take part and thus are highly quantum-like. When many quantum states of all degrees of freedom participate, it has been argued previously[1d] that the usual Monte Carlo classical methods are quite adequate; if the vibrational degree of freedom is 'highly quantized' - e.g., if all vibrationally inelastic transitions are classically forbidden as they are for He + H_2 - however, these arguments are invalid.

A particularly important practical feature, therefore, is developed in Section IV where it is shown how one can, without introducing any dynamical approximations, combine a Monte Carlo averaging treatment of some degrees of freedom with a semiclassical state-for-state description of other dergees of freedom. If in an A + BC collision system, for example, only a few vibrational states are involved but many rotational states play a role, then it is possible to treat rotation in the usual Monte Carlo fashion but include vibration within the spirit of classical S-matrix theory; i.e., one can quantize only those degrees of freedom that actually require it. As discussed in Section IV, this procedure of 'partial averaging' also drastically simplifies the semiclassical calculation by eliminating the most difficult aspects of applying the general expressions, and it is this version of classical S-matrix theory that appears to have most promise for wide spread utility.

II. SUMMARY OF THE GENERAL THEORY AND METHOD OF CALCULATION.

A. General Formulae.

The general expressions for the classical S-matrix for a three-dimensional atom-diatom collision system have been given previously[1a]; for the non-vibrating case they have also been written out in considerable detail[1d]. The formulas pertinent to the present case are thus a simple extension of those in ref. 1d to include the vibrational degree of freedom. In part A we first briefly summarize the general theory, and parts B and C then discuss several points regarding its application.

A specific S-matrix element is given by

$$S_{n_2 j_2 \ell_2, n_1 j_1 \ell_1}(J,E) = \sum D^{-1/2} \exp[i\phi(n_2 j_2 \ell_2, n_1 j_1 \ell_1)], \qquad (2.1)$$

where D is proportional to the 3 × 3 Jacobian determinant[9]

$$D = \frac{(2\pi)^3}{16} \frac{\partial(n_2, j_2, \ell_2)}{\partial(q_{n_1}, q_{j_1}, q_{\ell_1})}, \qquad (2.2)$$

and ϕ is the classical action integral along the trajectory determined by the indicated double-ended boundary conditions; units are used such that $\hbar = 1$. The summation in Equation (2.1) is over all classical trajectories that satisfy the appropriate boundary conditions (see next paragraph); J and E are the conserved total angular momentum and total energy, and $n_1 j_1 \ell_1$ ($n_2 j_2 \ell_2$) are the initial (final) integer values of the vibrational, rotational and orbital angular momentum quantum numbers, respectively.

In order to find the classical trajectories appropriate to a specific transition one considers the final quantum numbers (for fixed values of

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J, E, n_1, j_1, and ℓ_1) as functions of the initial angle variables conjugate to n_1, j_1, ℓ_1: $n_2(q_{n_1},q_{j_1},q_{\ell_1})$, $j_2(q_{n_1},q_{j_1},q_{\ell_1})$, and $\ell_2(q_{n_1},q_{j_1},q_{\ell_1})$. Numerical integration of the classical equations of motion is the operational procedure by which one evaluates these 'quantum number functions'; Section IIB discusses this in more detail. Finding the appropriate classical trajectories thus means solving the following equations simultaneously:

$$\begin{aligned} n_2(q_{n_1},q_{j_1},q_{\ell_1}) &= n_2 \\ j_2(q_{n_1},q_{j_1},q_{\ell_1}) &= j_2 \\ \ell_2(q_{n_1},q_{j_1},q_{\ell_1}) &= \ell_2 \quad , \end{aligned} \tag{2.3}$$

where the RHS of these equations are specified integers. The Jacobian in Equation (2.2) is the determinant of the matrix of partial derivatives of these functions with respect to the initial angle variables, with the angle variables evaluated at the root of Equation (2.3).

At collision energies no greater than a few electron volts all vibrationally inelastic transitions in He + H_2 collisions are classically forbidden; i.e., there are no ordinary classical trajectories at these energies for which the vibrational quantum number is 0 initially, say, and 1 finally. Stated another way, there are no real values of the angle variables $(q_{n_1},q_{j_1},q_{\ell_1})$ that satisfy Equation (2.3) There are, however, complex roots to these equations, or in other words, there exists complex-valued classical trajectories which satisfy the correct double-ended boundary conditions. Along such a trajectory the action integral ϕ is complex, so that Equation (2.1) has the 'tunneling factor' $\exp(-\mathrm{Im}\phi/\hbar)$

which is characteristic of classically forbidden processes.

As has already been demonstrated[1f] for co-linear A + BC collisions, it is actually possible to find the complex roots of Equation (2.3) by directly integrating the equations of motion with complex initial conditions. The numerical integration proceeds very much as for ordinary real trajectories (but see Section IIC) except, of course, that all the coordinates and momenta must be declared COMPLEX in the computer routines. It is also necessary that the potential energy function be an algebraic function of the coordinates so that it can be evaluated for complex coordinates; i.e., one cannot use potential functions that are defined 'piece meal' in various regions of coordinate space.

The formal justification for analytically continuing Equations (2.1)-(2.3) into complex domains has been discussed before[1f, 1g]. The arguments are essentially identical to those[10] in the one-dimensional case where complex solutions to the Hamilton-Jacobi equation (i.e., the classical action) are used to construct an asymptotic approximation to the wavefunction in classically inaccessible regions.

B. Specification of Initial Conditions.

As before[1d], the initial conditions are specified in terms of the action-angle variables discussed in the previous section, but the actual numerical integration of the equations of motion is most conveniently carried out in Cartesian coordinates. One thus specifies initial values of the action-angle variables (see below), transforms these into initial conditions for all the Cartesian coordinates and momenta, integrates the equations of motion for the Cartesian variables, and after the collision is over transforms the final Cartesian variables into final values of the action-angle variables.

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To minimize the length of time for which the trajectory must be numerically integrated it is useful to eliminate the asymptotic unperturbed motion. The unperturbed Hamiltonian is given in action-angle variables by[1a]

$$H_o(P,\ell,n,j,R,q_\ell,q_n,q_j) = (P^2 + \ell^2/R^2)/2\mu + \varepsilon(n,j) \quad , \qquad (2.4)$$

where R and P are the center of mass translational coordinate and momentum, and $\varepsilon(n,j)$ is the semiclassical rotational-vibrational eigenvalue function for the isolated diatomic molecule; the notation is the same as in reference 1a. Integration of the equations of motion resulting from this Hamiltonian from the reference time t = 0 to t gives

$$n(t) = n_1 \qquad (2.5a)$$

$$j(t) = j_1 \qquad (2.5b)$$

$$\ell(t) = \ell_1 \qquad (2.5c)$$

$$R(t) = (b^2 + v_1^2 t^2)^{1/2} \qquad (2.5d)$$

$$P(t) = -\mu v_1 [1 - b^2/R(t)^2]^{1/2} \qquad (2.5e)$$

$$q_n(t) = \bar{q}_{n_1} + \frac{\partial \varepsilon(n_1,j_1)}{\partial n_1}\, t \qquad (2.5f)$$

$$q_j(t) = \bar{q}_{j_1} + \frac{\partial \varepsilon(n_1,j_1)}{\partial j_1}\, t \qquad (2.5g)$$

$$q_\ell(t) = \bar{q}_{\ell_1} + \tan^{-1}(v_1 t/b) \quad , \qquad (2.5h)$$

where b is the initial impact parameter and v_1 the magnitude of the initial velocity,

$$v_1 = \{2[E - \varepsilon(n_1,j_1)]/\mu\}^{1/2} \qquad (2.6)$$

$$b = \ell_1/(\mu v_1) \quad .$$

The angle variables ($\bar{q}_{n_1}$, $\bar{q}_{j_1}$, $\bar{q}_{\ell_1}$) are phase shifts for these respective degrees of freedom, and as before [1b], they are taken as the independent initial values that are actually used in the manner discussed in Section IIA; i.e., for consistency of notation the angle variables in Section IIA and elsewhere in the paper (except for this present section) should have a "bar" over them, but this has been omitted in order to keep the notation as uncluttered as possible. For a homo-nuclear molecule, such as H_2, $\bar{q}_{\ell_1}$ and $\bar{q}_{j_1}$ can be taken without restriction[1d] to lie in the internal $(0,\pi)$, and $\bar{q}_{n_1}$ takes on values in the $(0,2\pi)$ interval.

The time t_1 at which the numerical integration is actually begun can be any negative value large enough so that

$$R(t_1) \equiv R_1 \geq R_{max} \quad , \tag{2.7}$$

where $R(t_1)$ is given by Equation (2.5d) and R_{max} is a value large enough for the scattering interaction to be neglible. Matters are considerably simplified if one in addition chooses t_1 so that the vibrational angle variable $q_n(t_1)$ is initially an integer multiple of 2π. From Equation (2.5f) it is seen that this choice is

$$t_1 = -(2\pi N + \bar{q}_{n_1}) \Big/ \frac{\partial \varepsilon(n_1, j_1)}{\partial n_1} \quad , \tag{2.8}$$

where N is a positive integer large enough so that Equation (2.7) is satisfied. The initial values of all the action-angle variables are then given by Equations (2.5) with t equal to this value t_1.

Since $q_n(t_1) = -2\pi N$, the diatomic molecule is initially at its inner radial turning point, i.e., the radial coordinate and momentum r and p at time t_1 are

$$p = 0 \qquad (2.9)$$
$$r = r_< \quad ,$$

$r_<$ being the inner radial turning point for the diatom. This means that the vibrational phase integral and the centrifugal distortion terms in Equations (27), (39), and (40) of reference 1a all vanish identically at t_1, and this is the principal reason for choosing t_1 in the above manner. With the initial values of the action-angle variables given by Equation (2.5) (with $t = t_1$), it is then possible to use the transformation in Appendix C of reference 1d without modification to obtain the corresponding values of all the Cartesian coordinates and momenta.

It is interesting to note that the procedure described in this section for specifying the initial conditions is essentially a verbatim application of the formal expression for the scattering operator,

$$S = \lim_{\substack{t_2 \to +\infty \\ t_1 \to -\infty}} \exp[-iH_0(0-t_2)/\hbar] \exp[-iH(t_2-t_1)/\hbar] \exp[-iH_0(t_1-0)/\hbar] \quad . \qquad (2.10)$$

The first operator describes propagation from the reference time $t = 0$ backward in time to t_1 under the influence of the unperturbed Hamiltonian; the system then evolves from t_1 to t_2 under the influence of the total Hamiltonian; and finally, the unperturbed Hamiltonian acts from $t = t_2$ backward in time again to the reference time $t = 0$.

Beginning the trajectory in the manner described above [i.e., such that Equation (2.9) is satisfied] also simplifies calculation of the action integral ϕ. The simplification is even greater if one also

terminates the numerical integration in the final asymptotic region at a time which the vibrational coordinate r is again at its inner radial turning point. This is a easy thing to do, but it simplifies matters considerably, again because the vibrational phase integral

$$\int_{r_<}^{r} dr' \{2m[\varepsilon - v(r')] - j^2/r'^2\}^{1/2} \qquad (2.11)$$

is identically zero at such a time. This means that the generator of the canonical transformation from the variables (r,p) to (n,q_n) has the numerical value 0 at the initial and final times t_1 and t_2. Consequently, the action integral ϕ is given by precisely the same expression that was used before for the rigid rotor- atom system,[1d] i.e.,

$$\phi = \frac{\pi}{2}(\ell_2 + \ell_1) - [Jq_J + \ell q_\ell + jq_j + PR + \tfrac{\pi}{2}(j^2-\ell^2)/J] \Big|_{t_1}^{t_2} + \int_{t_1}^{t_2} dt\, 2T \quad , \qquad (2.12)$$

where T is the total kinetic energy. The term $pr \Big|_{t_1}^{t_2}$, as well as action integrals like that in Equation (2.11), which formally appear in the expression for ϕ, are absent in Equation (2.12) because of these special choices for t_1 and t_2.

C. Choice of the Complex Time Path.

As has been discussed before[1f, 1g], there is a certain degree of flexibility one has when dealing with complex-valued trajectories that is not available with ordinary real-valued trajectories: since the total time increment (t_2-t_1) is complex, there is the question of what curve in the complex t-plane one should integrate along in incrementing the time from t_1 to t_2. This causes no formal problems because the final values

of the quantum numbers and the action ϕ (and, therefore, the classical S-matrix elements), being analytic functions of t, are independent of the path chosen for the time integration. One can thus view this ambiguity of the time path as an advantage and chose it in any way that facilitates the calculation. (For ordinary real trajectories one also has the option of choosing any contour in the t-plane along which to increment time, but of course the real time axis is the uniquely obvious choice in this case.)

From our experience with complex-valued trajectories the most critical feature appears to be the oscillatory degrees of freedom, i.e., vibration. The coordinates of non-oscillatory degrees of freedom, such as translation, are well characterized by low order polynomials in t, so that no drastic change in their behaviour occurs when t becomes complex. The vibrational coordinate r, however, is sinusoidal in t, and when t becomes complex this oscillatory motion acquires exponential character. If one is not careful, therefore, the vibrational coordinate can "run away" and the trajectory diverge.

To make the trajectories as well-behaved as possible the complex time path is thus chosen to keep the vibrational coordinate under control. After experimenting with various approaches, the following procedure was adopted: every time Re(p) passes through zero the phase α of the next time increment Δt,

$$\Delta t = |\Delta t| e^{i\alpha} \quad ,$$

is chosen to cause $p \to 0$; i.e., every time the oscillator passes around [11] a turning point the direction of the time path is chosen to force it in

the direction of the turning point. This procedure has the effect of preventing the oscillator from making excursions too far outside its classical turning points. Because of the dimensionality of the non-linear equations to be solved (i.e., three), it was highly undesirable to integrate the trajectory from both the initial and final asymptotic regions and match in the intermediate region[1f], for this would have doubled the number of non-linear equations to be solved simultaneously.

Although the above procedure of integrating the complex trajectories "straight through" from the initial to final asymptotic region was well-behaved under most conditions and reasonably efficient (about one second per trajectory on a CDC 7600), it is not at all clear that there may not be better algorithms for choosing the complex time path. The technology of computing complex-valued classical trajectories is still very much in its infancy.

III. RESULTS FOR SPECIFIC QUANTUM TRANSITIONS.

The specific system to which the theory is applied in this paper is the three-dimensional He + H_2 collision with the interaction potential of Gordan and Secrest[6]. In order to compare with the quantum mechanical calculations of Eastes and Secrest[7] the H_2 vibrational potential was chosen to be harmonic

$$v(r) = (1/2)m\omega^2(r-r_0)^2 \quad ,$$

and to get an idea of the sensitivity to anharmonicities in the H_2 potential the calculations were repeated with a Morse potential

$$v(r) = D\{\exp[-\alpha(r-r_0)] - 1\}^2 \quad .$$

(Semiclassically it is no more or less difficult to use one H_2 potential than any other.)

Eastes and Secrest[7] were primarily interested in studying the effect on pure rotational transitions of properly including the vibrational degree of freedom. In the process, however, they obtained some at least approximate results for vibrationally inelastic transitions. Specifically, for total energies $E = 2\hbar\omega$ and $3\hbar\omega$ and total angular momentum $J = 0$ and 10, they reported S-matrix elements for the transitions $(n_1 j_1 \ell_1) = (0,0,J)$ to $(n_2 j_2 \ell_2)$ for $n_2 = 1$; $j_2 = 0,2$; $\ell_2 = |J-j_2|$.

The most difficult aspect of applying classical S-matrix theory to the calculation of S-matrix elements for specific quantum transitions is finding the trajectories which satisfy Equation (2.3). For the present applications we took a rather straight-forward approach: with the initial quantum numbers fixed at their initial integer values, q_{n_1}, q_{j_1}, and q_{ℓ_1} were first varied over a course grid (five points per variable) of real values in their respective intervals. For these ordinary real-valued trajectories the final rotational quantum number attained values from 0 up to ~ 5, but for no trajectory was n_2 greater than ~ 0.2; i.e., vibrationally inelastic transitions are classically forbidden. The values of $(q_{n_1}, q_{j_1}, q_{\ell_1})$ for which n_2 was a maximum, however, provided rough initial guesses for the real parts of the desired complex values of $(q_{n_1}, q_{j_1}, q_{\ell_1})$.

Using a multi-dimensional Newton iteration scheme with initial guesses obtained as above, the complex roots of Equation (2.3) were found for the cases $J = 10$, $n_2 = 1$, $j_2 = 2$, $\ell_2 = J-2$, at both values of the total energy. There are actually <u>four</u> roots to Equation (2.3), i.e.,

four complex trajectories that contribute comparably to each transition. It was easy to see that this would be the case even from the preliminary real trajectories, for the vibrational degree of freedom is qualitatively separable from the rotational and orbital degrees of freedom. That is to say, the values of q_{n_1} for the four roots of Equation (2.3) are approximately the same, while q_{j_1} and q_{ℓ_1} are substantially different for the four roots; i.e., the four roots correspond qualitatively to the uncoupled equations:

$$j_2(q_{j_1},q_{\ell_1}) = 2$$

$$\ell_2(q_{j_1},q_{\ell_1}) = 8$$

which have four roots for (q_{j_1},q_{ℓ_1}), and

$$n_2(q_{n_1}) = 1$$

which has a single root.

This qualitative separability of vibration from the other two internal degrees of freedom is also manifest in the fact that the classically forbidden aspect of the transition is highly concentrated in the vibrational degree of freedom: the imaginary parts of q_{j_1} and q_{ℓ_1} are small ($\sim 10^{-2}$), but the imaginary part of q_{n_1} quite large (~ 5). Therefore, although one can rigorously speak only of the complete transition $n_1 j_1 \ell_1 \rightarrow n_2 j_2 \ell_2$ being classically forbidden, it is qualitatively meaningful to say that the rotational part of the transition is classically allowed and that only the vibrational part is classically forbidden.

As in earlier applications[1d] of classical S-matrix theory, when

0 0 0 0 3 8 0 . 1 7 2

there are several trajectories contributing to a particular transition, it is usually necessary to employ uniform semiclassical expressions to obtain highly accurate results for individual S-matrix elements. With four trajectories contributing to the present transitions the four-term uniform expression obtained earlier[12] could be used. (Marcus[2g] has recently generalized this result to the case of N internal degrees of freedom with up to 2^N contributing trajectories.) The numerical results obtained for these transitions are given in Table I; the quantum mechanical values of Eastes and Secrest[7] are those resulting from the largest number of coupled channels used in their calculation. From the variation of the quantum mechanical results with increasing size of the basis set it is clear that these are not the 'final' quantum mechanical values; i.e., the transition probabilities are still changing (and non-monotonically) with the addition of further channels at the point the calculation is discontinued. It appears, however, that the quantum mechanical results are probably correct to within at least a factor of 2.

The agreement of the uniform semiclassical transition probabilities and the quantum mechanical values is seen to be excellent, suggesting that the quantum mechanical coupled channel expansion has almost 'converged'.

The identical calculations carried out with the Morse vibrational potential also resulted in four trajectories contributing to each transition. The uniform semiclassical transition probability for $E = 2\hbar\omega$, however, is 1.47×10^{-5}, compared to 1.57×10^{-7} for the harmonic potential, a factor of 100 larger! At the higher energy $E = 3\hbar\omega$ the effect of anharmonicity is less, the Morse case giving 4.30×10^{-4}, compared to 8.40×10^{-5} for the harmonic potential, a factor of 5 larger. This

sizeable effect of anharmonicity is similar to that wich has been noted in the co-linear collision system[13-14] and is presumably due to the fact that the oscillator can tunnel more easily into the softer outer wall of the Morse potential. The corresponding quantum mechanical picture of this effect is that the vibrational wavefunctions decrease less rapidly for large r with the Morse potential.

It was originally planned to calculate some of the S-matrix elements for J = 0, too, but the preliminary sweep of $(q_{n_1}, q_{j_1}, q_{\ell_1})$ through the coarse grid of real values indicated there to be many roots to Equation (2.3), at least eight and probably more. First of all, it is not clear how to treat so many contributions to the S-matrix uniformly (the roots did not appear to be in a simple configuration that would allow use of Marcus'[2g] result); but second, when there are so many contributions, and thus a large number of interference terms, it is doubtful that any of the interference structure survives. For these reasons, and because of the methods developed in the next section, the J = 0 case was not pursued.

IV. PARTIAL AVERAGING.

The detailed comparison of classical S-matrix theory with accurate quantum mechanical results for specific S-matrix elements, such as in the previous section and in earlier applications, is important in learning just how far this semiclassical theory can go in describing quantum effects in molecular collisions. For this reason, too, it is most interesting to consider highly quantum-like systems such as He + H_2. Now that these features of the theory have been fairly well established, however, one would like to avoid the explicit construction of all the individual S-matrix elements, for the various cross sections of interest invariably

0 0 0 0 3 8 0 . 1 7 3

average over many of the quantum number indices and thus obliterate much of the fine detail.

In earlier work[1d] it has actually been shown how the semiclassical approach 'degenerates' to the Monte Carlo classical procedure when all the transitions of interest are classically allowed and one considers any situation other than complete state selection initially and finally. Unless all the degrees of freedom participating in the transitions of interest are classically allowed, however, these arguments are invalid and the ususal Monte Carlo treatment not in general justifiable.

This section shows how one can combine a Monte Carlo-like description of the classically allowed degrees of freedom (i.e., rotation and orbital angular momentum for the present He + H_2 system) with a semiclassical quantum-like description of the highly quantized degrees of freedom (i.e., vibration in the present case). This is possible, too, without making any dynamical approximations regarding separability of the different degrees of freedom, and it greatly simplifies the practical aspects of applying the semiclassical theory to systems with several internal degrees of freedom.

Suppose, for example, one is interested in the rate coefficients for specific initial and final vibrational states, summed and averaged over all initial and final rotational states. This matrix of vibrational rate constants, which is what is required in order to compute vibrational relaxation times, is given by

$$k_{n_2 \leftarrow n_1}(T) = Q(n_1)^{-1}\left(\frac{8kT}{\pi\mu}\right)^{1/2} \frac{\pi\hbar^2}{2\mu kT} \sum_J (2J+1)$$

$$\times \int d(E/kT)\, \exp(-E/kT) A_{n_2,n_1}(J,E) \quad , \qquad (4.1)$$

with the definition

$$A_{n_2,n_1}(J,E) = \sum_{j_2 j_1 \ell_2 \ell_1} |S_{n_2 j_2 \ell_2, n_1 j_1 \ell_1}(J,E)|^2 \qquad (4.2)$$

where it is assumed that translation and rotation are both completely 'relaxed', i.e., in thermal equilibrium, and $Q(n_1)$ is the rotational partition function for vibrational state n_1,

$$Q(n_1) = \sum_{j_1} (2j_1 + 1) \exp[-\epsilon(n_1,j_1)/kT]. \qquad (4.3)$$

The quantity of interest, therefore, is the matrix A_{n_2,n_1}, the square modulus of the S-matrix, summed over all initial and final values of the rotational and orbital quantum numbers. If all vibrationally inelastic transitions (i.e., $n_1 \neq n_2$) are classically forbidden in the relevant energy range, then strictly classical Monte Carlo methods are not applicable.

With the S-matrix elements given by Equation (2.1) the matrix A_{n_2,n_1} of Equation (4.2) is given by

$$A_{n_2,n_1} = \int dj_1 \int d\ell_1 \int dj_2 \int d\ell_2 \, (2\pi)^{-3} \left[\frac{\partial(n_2 j_2 \ell_2)}{\partial(q_{n_1} q_{j_1} q_{\ell_1}}\right]^{-1} \times \exp(-2\mathrm{Im}\phi) \quad , \qquad (4.4)$$

where the labels E and J have been suppressed, the sums over orbital and rotational quantum numbers have been replaced by integrals, and the factor of 16 associated with the $\Delta\ell$ and Δj selection rule[9] has for simplicity been dropped for the present discussion. There may actually be several terms in the integrand of Equation (4.4), e.g. four, which

has not been indicated explicitly; the interference terms resulting from them have been discarded, however, since it is being assumed that they are quenched by the sums over quantum numbers. Holding j_1, ℓ_1, n_2, n_1 fixed, the integration variables j_2 and ℓ_2 can be changed to q_{j_1} and q_{ℓ_1}, giving

$$A_{n_2,n_1} = (2\pi)^{-3} \int dj_1 \int d\ell_1 \int dq_{j_1} \int dq_{\ell_1} \left[\frac{\partial(j_2\ell_2)}{\partial(q_{j_1}q_{\ell_1})}\right] j_1\ell_1 n_2 n_1 \times \left[\frac{\partial(n_2 j_2 \ell_2)}{\partial(q_{n_1}q_{j_1}q_{\ell_1})}\right]^{-1} n_1 j_1 \ell_1 \quad \exp(-2\mathrm{Im}\phi) \quad , \tag{4.5}$$

where the variables held constant in the two Jacobians have been indicated explicitly. The awkward feature of Equation (4.5) is that the two dimensional Jacobian that arises from the change of integration variables is with respect to n_2 held constant, rather than the conjugate initial variable q_{n_1}. It is a good exercise in the manipulation of partial derivatives to show how these derivatives can be changed to those that hold only initial conditions constant; in particular, one can show that the two-dimensional Jacobian in Equation (4.5) can be expressed as

$$\left[\frac{\partial(j_2\ell_2)}{\partial(q_{j_1}q_{\ell_1})}\right] j_1\ell_1 n_2 n_1 = \left[\frac{\partial(n_2 j_2 \ell_2)}{\partial(q_{n_1}q_{j_1}q_{\ell_1})}\right] n_1 j_1 \ell_1 \times \left[\frac{\partial n_2}{\partial q_{n_1}}\right]^{-1} n_1 j_1 \ell_1 q_{j_1} q_{\ell_1} \quad , \tag{4.6}$$

so that Equation (4.5) thus takes the form

$$A_{n_2,n_1} = \int dj_1 \int d\ell_1 \int d(q_{j_1}/2\pi) \int d(q_{\ell_1}/2\pi) \left[2\pi \left|\frac{\partial n_2}{\partial q_{n_1}}\right|\right]^{-1} \exp(-2\mathrm{Im}\phi/\hbar) \quad , \tag{4.7}$$

where the one dimensional vibrational Jacobian is with regard to all other initial conditions held constant.

Equation (4.7) is the remarkably simple form that has been sought. To obtain the $n_1 \to n_2$ transition probability, summed over all initial and final orbital and rotational quantum numbers, it is necessary simply to perform a phase space average of a one-dimensional-like vibrational transition probability. Since the integrand in Equation (4.7) is positive definite, the integrals over j_1, ℓ_1, q_{j_1}, and q_{ℓ_1} can be evaluated efficiently by Monte Carlo methods. Thus for given initial values $(j_1, \ell_1, q_{j_1}, q_{\ell_1})$ one must solve only the one-dimensional non-linear equation

$$n_2(q_{n_1}) = n_2 \tag{4.8}$$

to find the value of q_{n_1} that results in the correct integer value for the final vibrational quantum number; the root of Equation (4.8) having been found, one constructs the one-dimensional-like transition probability and then Monte Carlo averages it over $(j_1, \ell_1, q_{j_1}, q_{\ell_1})$. The general statement of the 'partial averaging' trick is that all those degrees of freedom which are not 'state selected' can be treated by a Monte Carlo average over their initial coordinates and momenta, and it is necessary to deal with double-ended boundary conditions only for the degrees of freedom that are state-selected.

Note also that there will typically be only one term in the integrand of Equation (4.7), so that there is no concern about having to deal with many-term uniform semiclassical formulas. In addition, the Monte Carlo integration over j_1, ℓ_1, q_{j_1}, and q_{ℓ_1} is expected to be easy

for, as discussed in Section III, the root of Equation (4.8) varies only slightly for different values of the orbital and rotational degrees of freedom, and the 'one-dimensional' vibrational transition probability is thus only weakly dependent on j_1, ℓ_1, q_{j_1}, and q_{ℓ_1}.

Moreover, it is not necessary to discard information about the distribution in final rotational quantum number or in scattering angle; i.e., in evaluating Equation (4.7) one still computes fully three-dimensional classical trajectories, so that all of the information concerning the trajectories is available. Thus it is possible within the spirit of the usual Monte Carlo procedure to obtain the distribution in j_2 and θ that go along with a specific vibrational quantum transition ($n_1 \rightarrow n_2$) simply by putting the results of each trajectory (in this case the numerical value of the one-dimensional vibrational transition probability) in the appropriate 'box'. If, too, one wishes results that correpsond to a specific initial rotational state, then the integral over j_1 in Equation (4.7) is simply omitted.

Finally, it is interesting to see that Equation (4.7) can also be obtained by a simple heuristic derivation analogous to that which leads to the normalization of classical S-matrix elements[15]. For fixed values of the initial quantum numbers n_1, j_1, ℓ_1, therefore, the probability distribution in the final quantum numbers is related by the equations of motion to the distribution in the initial conjugate angle variables:

$$dn_2\, dj_2\, d\ell_2\, P(n_2 j_2 \ell_2 \leftarrow n_1 j_1 \ell_1) = P(q_{n_1})\, dq_{n_1}\, P(q_{j_1})\, dq_{j_1} \times P(q_{\ell_1})\, dq_{\ell_1}\, P_{traj} \quad , \tag{4.9}$$

where P_{traj} is a probability factor related to the degree that the

trajectory is allowed classically; i.e.,

$$P_{traj} \equiv \exp(-2\mathrm{Im}\phi) \quad , \tag{4.10}$$

so that $P_{traj} = 1$ for a classically allowed trajectory, and $P_{traj} < 1$ if the trajectory is classically forbidden. Since the initial angle variables are all random in $(0,2\pi)$,

$$P(q_{n_1}) = P(q_{j_1}) = P(q_{\ell_1}) = (2\pi)^{-1} \quad ,$$

and integration of Equation (4.9) over j_2 and ℓ_2 gives the desired result:

$$\int dj_2 \int d\ell_2 \, P(n_2 j_2 \ell_2 \leftarrow n_1 j_1 \ell_1) = \int d(q_{j_1}/2\pi) \int d(q_{\ell_1}/2\pi) \times \left[2\pi \left|\frac{\partial n_2}{\partial q_{n_1}}\right|\right]^{-1} \exp(-2\mathrm{Im}\phi) \quad . \tag{4.11}$$

Preliminary application of these methods of 'partial averaging' indicate them to be quite accurate and considerably easier to apply than the general formulas for the classical S-matrix. More extensive calculations for the He + H_2 system using these averaging methods are planned.

V. CONCLUDING REMARKS.

Application of classical S-matrix theory to the calculation of S-matrix elements for specific vibrational-rotational transitions has been made to the fully three-dimensional He + H_2 collision system. Agreement with quantum mechanical results for the same system is seen to be excellent, showing that molecular systems even as quantum-like as this one are essentially semiclassical in nature.

Although it is impressive that the semiclassical theory can reproduce

such quantum features in detail, in most cases one wishes to by-pass the construction of individual S-matrix elements and construct actual cross sections directly. As was shown in Section IV, it is possible to do this within the framework of classical S-matrix theory - and this 'partial averaging' actually greatly simplifies the application of the theory. Thus it is necessary to quantize semiclassically only those degrees of freedom that are highly quantum-like (e.g., vibration) and treat others via the usual Monte Carlo classical procedure. When all the transitions of interest are strongly allowed classically, the partial averaging procedure becomes identical to the usual Monte Carlo methods.

With the ideas discussed in Section IV, therefore, it may be possible to treat classically forbidden transitions, such as vibrational excitation in He + H_2 collisions, with essentially the ease and accuracy that Monte Carlo classical methods describe processes that are classically allowed.

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9. The factor of 16 is due to the selection rules $\Delta\ell$, $\Delta j = 0, \pm 2, \pm 4, \ldots$; see the discussion in Appendix B of reference 1d.

10. See any quantum mechanics textbook.

11. When the phase of an oscillator is complex, it in general undergoes ellipsoidal-like motion encircling the two classical turning points.

12. The expression in Equation (D.8) of reference 1d is given incorrectly; using the same notation as there, the correct expression is

$$\begin{aligned} S = {} & p_1 \pi z_1^{1/4} z_2^{1/4} (A_1 + iB_1)(A_2 + iB_2) \exp[\tfrac{i}{2}(\phi_3 + \phi_2)] \\ & + p_2 \pi z_3^{1/4} z_4^{1/4} (A_3 + iB_3)(A_4 - iB_4) \exp[\tfrac{i}{2}(\phi_4 + \phi_1)] \\ & + p_3 \pi z_5^{1/4} z_6^{1/4} (A_5 - iB_5)(A_6 + iB_6) \exp[\tfrac{i}{2}(\phi_4 + \phi_1)] \\ & + p_4 \pi z_7^{1/4} z_8^{1/4} (A_7 - iB_7)(A_8 - iB_8) \exp[\tfrac{i}{2}(\phi_3 + \phi_2)] \quad . \end{aligned}$$

All of the remarks made in Appendix D of reference 1d concerning the uniform semiclassical result apply to this correct expression (and not to the incorrect one). For the case of complex-valued classical trajectories the factors $\{p_i\}$, which are related to the Jacobians, are in general complex.

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TABLE I

TRANSITION PROBABILITIES

Transition[a]	Classical[b]	Semiclassical[c]	Uniform[d]	Quantum[e]
$E = 2\hbar\omega$	5.79×10^{-7}	2.65×10^{-7}	1.57×10^{-7}	1.40×10^{-7}
$E = 3\hbar\omega$	1.44×10^{-4}	1.10×10^{-4}	8.40×10^{-5}	6.72×10^{-5}

[a] Both transitions are for $J = 10$, $(n_1, j_1, \ell_1) = (0, 0, 10)$, and $(n_2, j_2, \ell_2) = (1, 2, 8)$, at the indicated total energy E.

[b] The sum of the square moduli of the four terms that contribute to the S-matrix element in Equation (2.1); i.e., neglect of all interference terms.

[c] The square modulus of the S-matrix element given by Equation (2.1); there are four terms which contribute to the sum.

[d] The uniform semiclassical values obtained by use of the four term uniform formula in footnote 12.

[e] The quantum mechanical values of Eastes and Secrest, reference 7.

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