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Semiclassical Theory Applied to Vibrationally Inelastic

Scattering in Three Dimensions

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B. S. University of New Mexico, 1967

M. S. Yale University, 1968

A Dissertation Presented to the Faculty

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Abstract

A hierarchy of semiclassical approximations is derived for solving vibrationally inelastic scattering problems in three dimensions. By semiclassical, one means that translational motion is treated classically and the internal motions of the molecules are treated quantum mechanically. The approximations range from a multi-trajectory method valid for large relative energy changes to the sudden approximation valid only for very small relative energy changes. It is shown that any three dimensional problem may be simplified considerably by treating the orbital angular momentum in the classical limit and the molecular rotations in the sudden limit. The appropriate expressions for obtaining transition probabilities, cross sections, and angular distributions are derived for several of the approximations. A three dimensional calculation of vibrational transition probabilities and cross sections for the case of an atom striking a diatomic molecule is presented. These calculations are carried out in the sudden limit, a high energy approximation in which the internal states of the molecule are taken to be degenerate. The results are discussed in the light of presently available experimental data and as they bear on previously used models in vibrationally inelastic scattering. A comparison of cross sections averaged over internal molecular coordinates to cross sections calculated from a potential averaged over internal molecular coordinates is presented in order to determine the validity of treating high energy molecular scattering results in terms of averaged potentials.

To My Family,

They were always there.

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There are many people to whom I owe thanks; they helped make this thesis a reality in one way or another.

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Introduction

The transfer of energy from one atom or molecule to another is vital to all chemically important processes. Vibrationally inelastic scattering, as one of several paths through which intermolecular energy transfer can occur, plays an important role in a wide range of intermolecular phenomena.[1-3] In addition to affecting lasers, gas flows, upper atmosphere phenomena, and a variety of spectroscopic processes, vibrational energy transfer is crucial to the course of many chemical reactions. Yet, as important as these interactions are, surprisingly little is known about them. One cause of this ignorance is the inability to describe intermolecular potentials accurately even in the simplest systems.[1,4] A second reason is the fact that methods for treating inelastic scattering events theoretically are quite complex and related numerical calculations are extremely time consuming.[5] For both of these reasons, it is common to find very simple models described by equally simple potential functions used in most calculations. From an experimental point of view, molecular beam techniques are just now reaching a level of sophistication such that inelastic events can be studied on a single particle rather than an aggregate level.[1,6-10]

A detailed look at the models used is informative. This work will be limited to consideration of only the simplest system, that of an atom striking a diatomic molecule, although it can be generalized to more complicated cases. The system may be represented by

$$A(s_A) + BC\ (s_{BC}, v, j, m) \rightarrow A(s'_A) + BC\ (s'_{BC}, v', j', m') \quad (1)$$

where molecule BC in vibrational state, v, rotational state, (j, m), and translational energy determined by its velocity, s_{BC}, is struck by atom A with translational energy determined by its velocity, s_A. The collision

leaves molecule BC in state (v', j', m') and separation velocity, s'_{BC} and atom A with separation velocity, s'_A. The possibility of electronically inelastic events is neglected here. The system is shown diagrammatically in Figure 1.
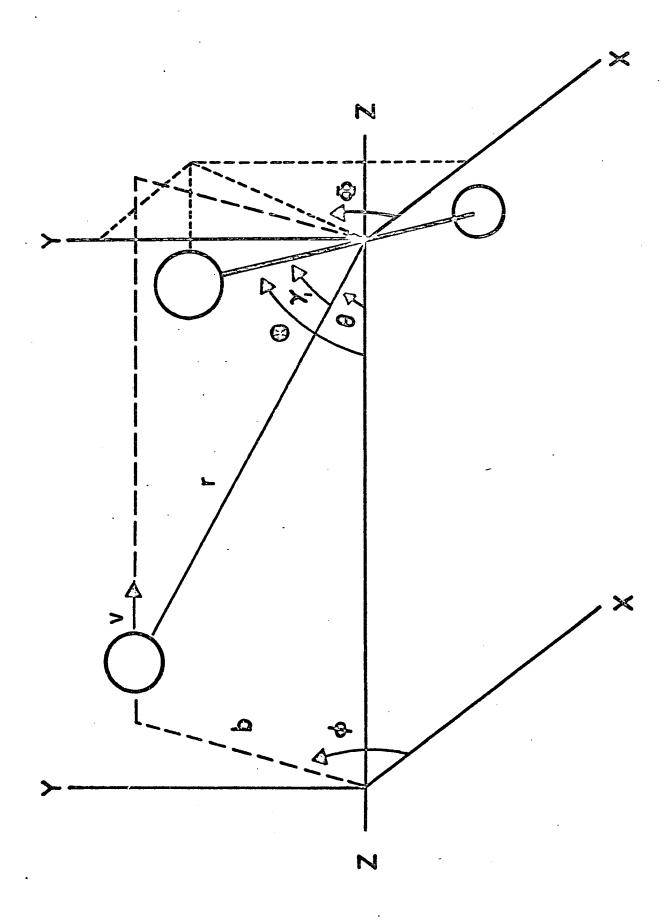
The traditional framework for treating this system theoretically is one dimensional, restricting the system to collinear collisions.[4] The assumptions involved are that the most efficient transfer of energy occurs for that collisional configuration in which all components of the velocity are directed along the molecular axis and that all other orientations and impact parameters make a rapidly and regularly decreasing contribution to the inelastic scattering. This leads to calculations being carried out at a single impact parameter $(b = 0)$ and orientation $(\Theta = 0, \Phi = 0)$ with the results being extrapolated across the whole range of impact parameters and orientations by use of an arbitrarily chosen, multiplicative "steric factor".[4] By ignoring all other orientations, one is forced to ignore the effects and complications of rotationally inelastic scattering which must be occurring at energies sufficient for vibrationally inelastic events to take place. By ignoring all other impact parameters, one is removing the more complicated aspects of the translational motion associated with the orbital angular momentum, since the orbital angular momentum is zero at zero impact parameter. Also, it is impossible to calculate cross sections in this model. Cross sections, Q, for a given molecular orientation are obtained by integrating the transition probabilities, P, over impact parameter according to

$$Q \propto \int P(b)\, b\, db. \tag{2}$$

Expression (2) cannot be solved knowing only the value of P at $b = 0$. Similarly, it is very difficult to calculate orientation averaged transition

Figure 1--Center of mass coordinate system used. R refers
to the change in the internuclear distance in the
diatomic molecule from its equilibrium value.

probabilities and cross sections having only the transition probability for $\Theta = 0$. In other words, only transition probabilities and not scattering properties such as angular distributions can be calculated using this model. So that while the collinear approximation removes much of the complexity of the problem, it also suffers in that it no longer describes real situations and is not generally useful for interpreting experiments. It is intuitively unacceptable to attempt to describe scattering resulting from a range of orientations and impact parameters by extrapolation, especially knowing that quantum mechanical systems can exhibit nonlinear behavior. In light of (2), it is impossible to calculate cross sections in this model. It is also unacceptable to simply ignore rotationally inelastic scattering when there is experimental evidence showing that it occurs to a greater extent when vibrationally inelastic events are occurring.[11]

The only extensive attempts to treat the system in three dimensions have been carried out using the "breathing sphere" model.[12-15] In this model, the vibrating molecule is treated as a sphere which undergoes changes in radius due to the vibration during the collision. This approximation entails the assumption that the molecule is rotating fast enough to appear as a sphere to the impinging atom, and the problem can then be solved using a spherical potential which varies during the duration of collision. The drawback to this approach is that at relative translational energies high enough for vibrationally inelastic scattering to occur, the diatomic molecule would have to be in an extremely high rotational state in order to appear as a sphere to the passing atom. Also, there can be no coupling of angular momenta when a spherical potential is used, so rotationally inelastic events cannot be treated concurrently with vibrationally inelastic events. Thus, the model is not generally applicable.

One purpose of this work will be to treat the vibrationally

inelastic scattering problem for the atom-diatom system in three dimensions, over the whole range of impact parameters and orientations.

Once the decision has been made to operate in three dimensions, the calculational formalism must be chosen. In spite of the many drawbacks to the collinear collision model, many calculations have been carried out using it, and the choice of a formalism can be made by looking at them. These calculations fall into three general categories: classical, semi-classical, and quantum mechanical. The most extensive classical calculations have been carried out by Kelly and Wolfsberg on this system. These were originally done for collinear collisions[16] and have lately been generalized to two dimensions.[17] Classical calculations are conceptually simple but difficult to bring into close agreement with nature. It is not a simple matter to impress the restriction of quantization on a classical framework, although Miller[18] seems to have accomplished it recently, at least for the collinear case. Classical mechanics is, however, an easily reconcilable limit for treating the translational motion of as heavy a particle as the impinging atom. At the opposite pole as far as calculations are concerned is an exact quantum mechanical treatment. Such an approach was taken by Secrest and Johnson[19] for the collinear case. In order to do a complete quantum mechanical treatment, one must solve the coupled equations resulting from the Schroedinger equation. Although the problem is difficult even in one dimension due to the rapidly oscillating nature of the wave functions, it is not impossible since the collinear restriction makes treatment of more than one angular momentum state and any rotational states unnecessary. So one must solve only as many coupled equations as there are vibrational states contributing to the problem. If, however, one tries to use this formalism in three dimensions, there are hundreds of orbital angular momentum states and rotational states which

would contribute, increasing the number of coupled equations by orders of magnitude. The approach, however, constitutes an exact solution to the problem. There exist several approximations to the exact quantum mechanical treatment such as the distorted wave approximation.[4] The distorted wave approximation is a perturbation approximation which takes the wave functions for the elastic problem as a first guess at the exact wave functions. It is usually only calculated to first order due to slow convergence of the perturbation equations and is thus valid only when the inelastic transition probabilities are small. It is therefore an approximation which is good only for small interactions between the colliding particles. Hence, it can only be applied to cases in which the change in vibrational energy is very small, and is not generally useful. It is, however, a relatively simple method and it is possible to generalize it to three dimensions.[20] Semiclassical methods make the solution slightly simpler. In this approach, one treats the translational motion of the collision partners classically and their internal motions quantum mechanically.[5] This method has been used by Rapp and Sharp to treat the collinear case in a first order perturbation approximation[21] and a slightly more accurate multistate solution.[22] Both of these solutions are valid only when the probability of inelastic transition is small in comparison to the elastic processes and when the relative change in energy is also small. Locker and Wilson[23] have treated the problem in a time-dependent semiclassical formalism which extends the treatable range of energies somewhat. Although it is necessary to change the formalism so that a wider range of relative energies can be handled, the semiclassical approach offers the most promise. It combines mathematical simplicity with a physically acceptable set of basic assumptions. It is calculationally simpler in that treating the translational motion classically allows one to transform the translational

part of the problem into a representation which has exchanged the orbital angular momentum quantum numbers for a s-: of angle variables which can be treated as continuous. Treating the translational part of the problem classically is certainly an acceptable notion where atoms are concerned and the quantization of internal molecular states is retained. For these reasons, semiclassical methods will be used here.

The second purpose of this work will be to extend the scope of the semiclassical formalism so as to be able to calculate the effects of vibrationally inelastic scattering in a three dimensional model for a large range of relative energies.

It is common practice to interpret the results of high energy molecular scattering experiments in terms of spherically symmetric potentials.[24-27] The third purpose of this work will be to determine whether this approach is valid. This is to be done by comparing differential cross sections averaged over molecular coordinates to those resulting from the same potential which has been previously averaged over molecular coordinates.

A formulation of the semiclassical theory of inelastic scattering is presented in the first section. Starting with the Schroedinger equation, a hierarchy of semiclassical approximations is derived for treating inelastic scattering over a wide range of energies. High and low energy limits are discussed and the appropriate expressions for obtaining angular distributions as well as transition probabilities are derived. The second section shows calculations of vibrational transition probabilities and cross sections for an atom striking a diatomic molecule. The calculation is done in the sudden limit, a high energy limit which treats the internal states of the diatomic molecule as being very closely spaced, and is three dimensional. In the final section, a comparison of molecular coordinate averaged cross sections to those obtained by averaging the potential over

molecular coordinates before calculating cross sections is shown.

Theory

The Schroedinger equation for the scattering of two atoms or molecules can be written[5]

$$[H_{INT}^{A} + H_{INT}^{B} - \frac{\hbar^2}{2\mu} \nabla^2 + V_o(r) - E] \, \Psi(r, \theta, \phi, \underset{\sim}{r}_A, \underset{\sim}{r}_B) = -\Delta V \, \Psi(r, \theta, \phi, \underset{\sim}{r}_A, \underset{\sim}{r}_B)$$

$$(3)$$

where H_{INT}^{A} and H_{INT}^{B} are the Hamiltonians for the free internal motions of the molecules, E is the total energy of the system, (r, θ, ϕ) is the vector joining the centers of mass of the scattering partners, and $\underset{\sim}{r}_A$ and $\underset{\sim}{r}_B$ are the internal coordinates for molecules A and B. The potential has been divided into two parts, a spherically symmetric part, $V_o(r)$, and a term, ΔV, representing the difference between the spherically symmetric portion and the total potential. The spherically symmetric part could be obtained in a number of different ways which might have an effect on the final result of any calculation. The most reasonable method of doing this is to average the total potential over internal molecular coordinates.

The wave function, Ψ, can be written as the product of wave functions for specific parts of the problem

$$\Psi(r, \theta, \phi, \underset{\sim}{r}_A, \underset{\sim}{r}_B) = \sum_{j \ell m} r^{-1} u_{j \ell m}(r) \, Y_{\ell m}(\theta, \phi) \, \phi_{Aj}(\underset{\sim}{r}_A) \, \phi_{Bj}(\underset{\sim}{r}_B) \qquad (4)$$

where $\phi_{Aj}(\underset{\sim}{r}_A)$ and $\phi_{Bj}(\underset{\sim}{r}_B)$ are the internal wave functions of the colliding molecules which satisfy $H_{INT}^{A} \phi_{Aj} = E_j^{A} \phi_{Aj}$ and a similar expression for molecule B, $Y_{\ell m}(\theta, \phi)$ are spherical harmonics which are the wave functions for the orbital angular momentum, ℓ and m are the orbital angular momentum quantum numbers associated with state j, and $u_{j \ell m}(r)$ are the unknown radial wave functions. j includes all of the internal quantum numbers of the molecules. Substitution of (4) into (3) yields

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k_j^2 - U_o(r)\right] \sum_{j\ell m} u_{j\ell m} Y_{\ell m} \phi_{Aj} \phi_{Bj} =$$

$$= \sum_{j\ell m} U_{j\ell m} Y_{\ell m} \phi_{Aj} \phi_{Bj} \quad (5)$$

where $U_o(r) = \frac{2\mu}{\hbar^2} V_o(r)$, $\Delta U = \frac{2\mu}{\hbar^2} \Delta V$, and $k_j^2 = \frac{2\mu}{\hbar^2}(E - E_j)$, E_j

being the internal energy associated with state j. μ is the reduced mass of

of the two molecules. If one now multiplies (5) by $Y_{\ell'm'}^*(\theta,\phi) \phi_{Ai}^*(r_A)$

$\phi_{Bi}^*(r_B)$ and integrates over r_A, r_B, θ and ϕ, one obtains the set of

coupled differential equations.

$$\left[\frac{d^2}{dr^2} - \frac{\ell'(\ell'+1)}{r^2} + k_i^2 - U_o(r)\right] u_{i\ell'm'}(r) = \sum_{j\ell m} U_{ij\ell'\ell m'm}(r) u_{j\ell m}(r)$$

$$(6)$$

where

$$U_{ij\ell'\ell m'm}(r) = \frac{2\mu}{\hbar^2} V_{ij\ell'\ell m'm}(r) = \frac{2\mu}{\hbar^2} \int \phi_{Ai}^*(r_A) \phi_{Bi}^*(r_B) Y_{\ell'm'}^*(\theta,\phi)$$

$$\Delta V(r,\theta,\phi,r_A,r_B) \phi_{Aj}(r_A) \phi_{Bj}(r_B) Y_{\ell m}(\theta,\phi)$$

$$d\Omega\, dr_A\, dr_B. \quad (7)$$

The quantum numbers i and j will now be expanded to include (ℓ',m') and

(ℓ,m) respectively. They will continue to include them until otherwise

stated. (6) can now be simplified to

$$u_i''(r) + p_i^2(r) u_i(r) = \sum_j U_{ij}(r) u_j(r) \quad (8)$$

with the definition

$$p_i^2(r) = k_i^2 - U_o(r) - \frac{\ell'(\ell'+1)}{r^2}. \quad (9)$$

Equation (8) reduces to the set of uncoupled equations for the elastic

scattering problem if ΔV goes to zero. The completely quantum mechanical

treatment consists in solving (8). This is practical only if there are a

small number of internal and orbital angular momentum states involved as

in the collinear model. There, the number of orbital angular momentum

states is reduced to one each in ℓ and m and rotational transitions are ignored completely. Hence, one needs to solve only as many coupled equations as there are vibrational states in the problem.[1,4,19] Even so, the u's are highly oscillatory functions in r and the solution of the problem is not trivial. Recently, Gordon has developed a more efficient numerical method for solving such equations.[28] If one wishes to generalize the treatment to three dimensions, inclusion of all of the orbital angular momentum and rotational states is necessary. Since the states number in the thousands, solution of the problem is nearly impossible.

The rest of this chapter is devoted to solving the problems caused by the highly oscillatory nature of the $\underset{\sim}{u}_i$ functions and the vast number of states involved in the calculation. This leads directly to a hierarchy of semiclassical approximations which can be used to treat the vibrationally inelastic scattering problem in three dimensions. In the section which follows, the elastic part of the problem is "filtered out" by expressing the $\underset{\sim}{u}_i$ functions as linear combinations of solutions to the elastic part of the problem according to a method used by Cross.[29] This leaves the solution in terms of new radial wave functions, $\underset{\sim}{X}_i$ and $\underset{\sim}{Y}_i$ which are much less oscillatory. The solutions which are chosen for the elastic problem are WKB wave functions. These are semiclassical in origin and define the scattering in terms of a classical trajectory. One treats the orbital angular momentum in the classical limit, that of large quantum numbers. By transferring from the space quantized in ℓ and m to one quantized in δ and γ, angle variables conjugate to ℓ and m, and realizing that δ and γ can be treated as continuous variables, one removes the necessity for treating the hundreds of ℓ and m states involved in the problem in favor of a single value for δ and γ. One is still left with the problem of treating the hundreds of rotational states involved in the calculation.

This problem is alleviated by treating the rotation in the sudden limit,[30-33] a high relative energy limit at which the rotational part of the problem can be transformed from the space quantized in j and m, the rotational quantum numbers, to one which is quantized in terms of Dirac delta functions of position (Θ, Φ) as shown in Figure 1, or equivalently that the rotation is slow compared to the duration of the collision. Justification for this is found in the work of Kramer and Bernstein.[31] This means that one has separated out both the orbital angular momentum and rotational parts of the problem and needs only to solve as many coupled differential equations as there are vibrational states contributing to the problem as functions of δ, γ, Θ, and Φ.

The hierarchy of semiclassical approximations developed in the rest of this chapter is derived according to the following plan. After the elastic part of the problem is filtered out, a series of approximations is derived to treat vibrationally inelastic processes ranging from a low relative energy multi-trajectory method to the high relative energy sudden limit. Each of these approximations results in a series of coupled differential equations which are quantized in the orbital angular momentum, rotation, and vibration. In each section, it is shown how the orbital angular momentum can be transformed in the classical limit and the removal of rotational quantization by use of the sudden limit is alluded to. When the section on the sudden limit is reached, the treatment of the rotational part of the problem is clarified. In the final section, angular distribution and transition probability expressions are derived for several of the approximations.

Filtering-out of the Elastic Part of the Problem

The semiclassical treatment begins by writing the wavefunctions, $u_i(r)$, in terms of solutions for the elastic scattering problem related to

V_0 (r). This substitution has the effect of "filtering out" the elastic part of the problem and thereby removing some of the oscillatory behavior from the radial wave functions which one is trying to obtain. One chooses two linearly independent solutions to the inelastic scattering problem, u_{1i} (r) and u_{2i} (r) corresponding to outgoing and incoming solutions. The total radial wave function is then expressed as

$$u_i (r) = X_i (r) u_{1i} (r) + Y_i (r) u_{2i} (r) \tag{10}$$

where X_i (r) and Y_i (r) represent the r dependent coefficients necessary to the definition. Since (20) does not uniquely define the coefficients, one adds a derivative restriction common to the solution of differential equations[29]

$$X_i' (r) u_{1i} (r) + Y_i' (r) u_{2i} (r) = 0 \tag{11}$$

Substituting (10) into (8) and simplifying the result using (11) yields

$$X_i' (r) = \sum_j [A_{ij} (r) X_j (r) + B_{ij} (r) Y_j (r)] \tag{12a}$$

$$Y_i' (r) = \sum_j [C_{ij} (r) X_j (r) + D_{ij} (r) Y_j (r)] \tag{12b}$$

where

$$A_{ij} (r) = W_i^{-1} (u_{2i} u_{1i}'' + p_i^2 u_{2i} u_{1i}) \delta_{ij} - W_i^{-1} u_{2i} U_{ij} u_{1j} \tag{13a}$$

$$B_{ij} (r) = W_i^{-1} (u_{2i} u_{2i}'' + p_i^2 u_{2i} u_{2i}) \delta_{ij} - W_i^{-1} u_{2i} U_{ij} u_{2j} \tag{13b}$$

$$C_{ij} (r) = -W_i^{-1} (u_{1i} u_{1i}'' + p_i^2 u_{1i} u_{1i}) \delta_{ij} + W_i^{-1} u_{1i} U_{ij} u_{1j} \tag{13c}$$

$$D_{ij} (r) = -W_i^{-1} (u_{1i} u_{2i}'' + p_i^2 u_{1i} u_{2i}) \delta_{ij} + W_i^{-1} u_{1i} U_{ij} u_{2j} \tag{13d}$$

and W is the Wronskian of u_1 and u_2,

$$W_i = u_{1i} \, u'_{2i} - u'_{1i} \, u_{2i} \tag{14}$$

The first terms of (13) are zero if u_1 and u_2 are exact solutions to the elastic part of the problem. They correct for the deviation of u_1 and u_2 from the exact elastic solutions.[29] They are usually small and will be neglected in the derivations which follow.

One set of solutions which one can use for u_1 and u_2 are the WKB wave functions, either the simple or uniform ones. These functions are semiclassical in origin and serve as a link between classical and quantum mechanics. The simple WKB wave functions may be written as[34]

$$u_{1i}(r) = p_i^{-\frac{1}{2}} \exp\left[i \, \xi_i - \frac{i\pi}{4}\right] \qquad (r > r_{ci}) \tag{15a}$$

$$u_{2i}(r) = p_i^{-\frac{1}{2}} \exp\left[-i \, \xi_i + \frac{i\pi}{4}\right] \qquad (r > r_{ci}) \tag{15b}$$

$$u_{1i} = u_{2i} = 0 \qquad (r < r_{ci}) \tag{15c}$$

where

$$\xi_i(r) = \left| \int_{r_{ci}}^{r} p_i(r') \, dr' \right|. \tag{16}$$

These wave functions lead to a classical trajectory which is related to the previously defined $p'_i(r)$. The relationships are $p_i = p_r/\hbar$ where p_r is the radial momentum for the classical trajectory, $\dfrac{dp_i}{dE}$ gives t, the time for the collision, and $\dfrac{dp_i}{d\ell}$ gives θ, the polar trajectory angle. The trajectory is defined for the time variable, t, which goes as follows: $-\infty < t \le t_c$ for the incoming half of the trajectory, t_c is the value at the timing point, r_c, and $t_c \le t < \infty$ for the outgoing half of the

trajectory. The turning point, r_c, may be subscripted r_{ci} or r_{cj} to indicate a given path. The simple WKB wave functions are not valid near the turning point since p_i goes to zero at r_{ci}, so they can be used only in those instances where the small area around the turning point does not contribute substantially to the scattering. This is the case when the ratio of energy transferred in collision to relative collision energy is not extremely large. When this restriction is not in force, the uniform WKB wave functions must be employed. The uniform functions consist of products of Airy functions such that the total wave function is finite at the turning point and falls off exponentially inside of the turning point. Not only are the uniform functions difficult to use in most calculations, but also it is hard to relate them to the physical aspects of any problem. The simple WKB functions lend themselves easily to physical interpretation and will be used in the derivations which follow.

Substitution of (15) into (13) ignoring the first terms of (13) yields the matrix elements

$$A_{ij} = -\tfrac{1}{2}i \, (p_i \, p_j)^{-\frac{1}{2}} \, U_{ij} \, \exp \, [-i \, \xi_i + i \, \xi_j] \tag{17a}$$

$$B_{ij} = \tfrac{1}{2} \, (p_i \, p_j)^{-\frac{1}{2}} \, U_{ij} \, \exp \, [-i \, \xi_i - i \, \xi_j] \tag{17b}$$

$$C_{ij} = \tfrac{1}{2} \, (p_i \, p_j)^{-\frac{1}{2}} \, U_{ij} \, \exp \, [i \, \xi_i + i \, \xi_j] \tag{17c}$$

$$D_{ij} = \tfrac{1}{2} \, i \, (p_i \, p_j)^{-\frac{1}{2}} \, U_{ij} \, \exp \, [i \, \xi_i - i \, \xi_j]. \tag{17d}$$

ξ is a large, rapidly varying function of r. Because of this, matrix elements which have sums of ξ's in the exponential, the B and C terms, will oscillate rapidly in r. Similarly, matrix elements which involve differences

of ξ's in the exponentials, the A and D terms, will oscillate slowly in r by comparison. Hence, the integrals over r which are necessary to the solution of (12) will consist mostly of contributions from the B and C terms. The B and C elements will therefore be neglected. Physically, this omission amounts to neglect of two sorts of contributions to the scattering. First, since there are two values of r contributing to the scattering for each trajectory, there are quantum interference terms present and these appear in B and C. Second, the B and C terms include deviations in the trajectory resulting from the inelastic scattering which are second order in $\triangle V$. These can be neglected except for cases where the relative energy change is very large. This omission leaves only the A and D matrix elements and (12), written in a more general form, becomes,

$$\underset{\sim}{X}{}' = \underset{\sim}{A}\,\underset{\sim}{X} \tag{18a}$$

$$\underset{\sim}{Y}{}' = \underset{\sim}{D}\,\underset{\sim}{Y}. \tag{18b}$$

Equations (18) are sets of coupled first order differential equations. Because of the way they were defined in (10), the X functions will refer to the outgoing half of the trajectory and the Y functions will refer to the incoming half. For the sake of continuity, X must equal Y at the turning point, r_c. Equations (18) can be solved with some effort as they stand. They are easier to solve than (8) since some of the oscillatory nature of the wave functions has been removed, but a large number of states is still present. The solution is sufficiently difficult that one would like to make further approximations.

Small Relative Angular Momentum Changes - the Multi-Trajectory Method

In most molecular collisions, one can assume that the relative change in angular momentum for a collision will be small.[8,35-37] Ordin-

arily, $\ell \approx 200$ and $\triangle \ell$ is on the order of 10 to 20. One would like to use this assumption to further simplify (18). Looking, then, only at the A matrix elements since the derivation for the D elements will follow exactly the same pattern, one has from (17)

$$A_{ij} (r) = - \frac{\mu i}{\hbar^2} (p_i \, p_j)^{-\frac{1}{2}} V_{ij} (r) \exp [i \, \xi_i - i \, \xi_j]. \qquad (19)$$

Since the relative change in angular momentum is assumed to be small, one expands $\xi_i - \xi_j$ in a Taylor series about an average ℓ_o which is presumed to be in the center of the range of ℓ values contributing significantly in the problem. Neglecting higher order terms, this gives

$$\xi_i (r, k_i, \ell') - \xi_j (r, k_j, \ell) = \xi_i (r, k_i, \ell_o) - \xi_j (r, k_j, \ell_o)$$

$$+ \tfrac{1}{2} [\int_{r_{ci}}^{r} p_i (r', k_i, \ell_o)^{-1} (\frac{2\ell_o + 1}{r'^2}) \, dr' (\ell_o - \ell')$$

$$- \int_{r_{cj}}^{r} p_j (r', k_j, \ell_o)^{-1} (\frac{2\ell_o + 1}{r'^2}) \, dr' (\ell_o - \ell)]. \qquad (20)$$

One can define

$$G_{ij}^{(\ell o)} (r) \equiv \pm [\xi_i (r, k_i, \ell_o) - \xi_j (r, k_j, \ell_o)] \qquad (21)$$

and

$$\frac{d\xi_i}{d\ell} = \mp [\theta_i(r) - \theta_{ci}] \equiv \int_{r_{ci}}^{r} p_i (r', k_i, \ell_o)^{-1} (\frac{\ell_o + \frac{1}{2}}{r'^2}) \, dr' \qquad (22)$$

where $\theta_i (r)$ is the polar trajectory angle defined for V_o at k_i and ℓ_o. θ_{ci} is the value of the scattering angle at $r = r_{ci}$. θ_i runs from π at $t = -\infty$ to χ_i, the final scattering angle, at $t = \infty$. A similar set of definitions exist for $[\theta_j (r) - \theta_{cj}]$. The upper sign in (21) and (22)

holds for the incoming half of the trajectory and the lower sign holds for the outgoing half. This will be the case in all ensuing discussion. Substituting (21) and (22) into (20) gives,

$$\xi_i - \xi_j = \pm \, G_{ij}^{(\ell_o)}(r) \pm \ell_o \, [(\theta_i - \theta_{ci}) - (\theta_j - \theta_{cj})] \mp [\ell'(\theta_i - \theta_{ci}) - \ell(\theta_j - \theta_{cj})]. \quad (23)$$

Expression (23) can be simplified by defining an average θ as

$$\theta_{oij}(r) - \theta_{cij} = \tfrac{1}{2} [(\theta_i - \theta_{ci}) - (\theta_j - \theta_{cj})]. \quad (24)$$

Also, it is reasonable that $\ell_o \approx \dfrac{\ell' + \ell}{2}$ or the center of the range of ℓ values contributing to the problem. Using this and substituting (24) into (23) gives

$$\xi_i - \xi_j \approx \pm \, G_{ij}^{(\ell_o)}(r) \mp (\ell' - \ell)(\theta_{oij} - \theta_{cij}). \quad (25)$$

Substituting (25) into (18a) gives

$$\frac{dX_i(r, \ell'. m')}{dr} = -\frac{\mu i}{\hbar^2} (p_i \, p_j)^{-\frac{1}{2}} \sum_{j \ell m} V_{ij}(r) \exp[i \, G_{ij}^{(\ell_o)}(r)]$$

$$\exp[-i(\ell' - \ell)(\theta_{oij} - \theta_{cij})] X_j(r, \ell, m)$$

$$(t \geq t_c) \quad (26a)$$

and by extension

$$\frac{dY_i(r, \ell', m')}{dr} = \frac{\mu i}{\hbar^2} (p_i \, p_j)^{-\frac{1}{2}} \sum_{j \ell m} V_{ij}(r) \exp[i \, G_{ij}^{(\ell_o)}(r)]$$

$$\exp[-i(\ell' - \ell)(\theta_{oij} - \theta_{cij})] Y_j(r, \ell, m) \quad (t \leq t_c) \quad (26b)$$

X_i (r, ℓ', m') and Y_i (r, ℓ', m') are equivalent to the $X_i(r)$ and $Y_i(r)$ defined previously. Although equations (26) are really not much simpler to solve than equations (18), the orbital angular momentum dependence in the exponential has been made clearer.

The fact that $(\xi_i - \xi_j)$ has been shown to depend only on $(\ell' - \ell)$ and not on each ℓ value individually will be important to the following diagonalization of this part of the problem.

The orbital angular momentum will be treated in the classical limit. This is the limit of large ℓ. Small relative changes in ℓ have already been assumed. The intention here is to use an action-angle transformation[35, 38, 39] valid in the classical limit to further simplify the problem. In the limit of large ℓ and $m \ll \ell$, one can write an asymptotic expansion for the spherical harmonics[40] which comes from the WKB approximation

$$Y_{\ell m}(\theta, \phi) = \pi^{-1}(\sin\theta)^{-\frac{1}{2}} \cos[(\ell + \tfrac{1}{2})\theta - \pi/4 + m\pi/2] \exp[im\phi] \quad (\theta \gg 1/\ell).$$

(27)

Using (27) in the expression for the potential matrix elements shown in (7) and allowing i and j to represent only the internal quantum states while expressing the orbital angular momentum quantum numbers explicitly, one gets

$$V_{ij\ell'\ell m'm}(r) = (4\pi^2)^{-1} \int_0^\pi d\theta' \int_0^{2\pi} d\phi' \; V_{ij}(r, \theta', \phi') \exp[-i\,\Delta m \phi']$$

$$\left\{ \exp[i\,\Delta\ell\,\theta' + i\,\Delta m\,\tfrac{\pi}{2}] + \exp[-i\,\Delta\ell\,\theta' - i\,\Delta m\,\tfrac{\pi}{2}] \right\}$$

(28)

where $\Delta\ell = \ell' - \ell$ and $\Delta m = m' - m$. Highly oscillating terms of the form $\exp[\pm i(\ell + \ell')\theta]$ have been neglected since they contribute only marginally to the integral. Since (θ', ϕ') and $(-\theta', \phi' + \pi)$ represent the same

point in space, (28) can be contracted to

$$V_{\underset{\sim}{ij}\ell'\ell m'm}(r) = (4\pi^2)^{-1} \int_o^\pi d\theta' \int_o^{2\pi} d\phi' \; V_{\underset{\sim}{ij}}(r,\theta',\phi') \exp\left[-i\,\Delta m(\phi'-\tfrac{\pi}{2})\right]$$

$$\exp\left[i\,\Delta\ell\,\theta'\right]. \qquad (29)$$

It is important that $V_{\underset{\sim}{ij}\ell'\ell m'm}(r)$ depends only upon $\Delta\ell$ and Δm and not on ℓ and m individually. The transformations which will be used to diagonalize the problem in the orbital angular momentum are

$$\underset{\sim}{X}_i (r,\delta,\gamma) = (N_\ell N_m)^{-\frac{1}{2}} \sum_{\ell'm'} \exp\left[i\,m'(\gamma - \tfrac{\pi}{2})\right]\exp[-i\ell'\delta] \; \underset{\sim}{X}_i(r,\ell',m') \quad (30a)$$

$$\underset{\sim}{Y}_i (r,\delta,\gamma) = (N_\ell N_m)^{-\frac{1}{2}} \sum_{\ell'm'} \exp\left[i\,m'(\gamma - \tfrac{\pi}{2})\right]\exp[-i\,\ell'\delta] \; \underset{\sim}{Y}_i(r,\ell',m'). \quad (30b)$$

These are similar to transformations which often appear in solid state physics. N_ℓ and N_m are the number of ℓ and m states used in the sum. δ and γ are defined by

$$\delta = \frac{2\pi\, n_\ell}{N_\ell} \qquad \text{and} \qquad \gamma = \frac{2\pi\, n_m}{N_m} \qquad (31)$$

This amounts to transforming from a space quantized in ℓ and m to one quantized in n_ℓ and n_m. However, as N_ℓ and N_m become large, δ and γ approach continuity. The reverse transforms corresponding to (30) are

$$X_i(r,\ell',m') = \frac{(N_\ell N_m)^{\frac{1}{2}}}{4\pi^2} \int_o^{2\pi} d\gamma \int_o^{2\pi} d\delta \exp\left[-i\,m'(\gamma - \tfrac{\pi}{2})\right]$$

$$\exp\left[i\,\ell'\delta\right] \underset{\sim}{X}_i(r,\delta,\gamma) \qquad (32a)$$

$$Y_i(r,\ell',m') = \frac{(N_\ell N_m)^{\frac{1}{2}}}{4\pi^2} \int_o^{2\pi} d\gamma \int_o^{2\pi} d\delta \exp\left[-i\,m'(\gamma - \tfrac{\pi}{2})\right]$$

$$\exp\left[i\,\ell'\delta\right] \underset{\sim}{Y}_i(r,\delta,\gamma). \qquad (32b)$$

Substituting (32) and (29) into (26) gives, after a bit of manipulation

$$\frac{d\underset{\sim}{X}_i(r,\delta,\gamma)}{dr} = -\frac{\mu i}{\hbar^2 P_o} \sum_j \underset{\sim\sim}{V}_{ij}(r,\delta+\theta_o-\theta_c,\gamma)\exp[i \underset{\sim\sim}{G}_{ij}^{(\ell_o)}(r)] \underset{\sim}{X}_j(r,\delta,\gamma)$$

$$(t \geq t_c) \qquad (33a)$$

$$\frac{d\underset{\sim}{Y}_i(r,\delta,\gamma)}{dr} = \frac{\mu i}{\hbar^2 P_o} \sum_j \underset{\sim\sim}{V}_{ij}(r,\delta+\theta_o-\theta_c,\gamma)\exp[i \underset{\sim\sim}{G}_{ij}^{(\ell_o)}(r)] \underset{\sim}{Y}_j(r,\delta,\gamma)$$

$$(t \leq t_c) \qquad (33b)$$

Equations (33) are a great simplification over (26). No longer must one be concerned with treating the vast number of ℓ and m states present since ℓ and m have been replaced by their conjugate variables, δ and γ and only one value of these contribute. These will be discussed more later. The approximation is called a multi-trajectory method since two trajectories must be calculated for every G value calculated, and then many G values must be calculated to solve the problem. As mentioned before, the approximation represented by (33) is not restricted as to quantity of energy transferred, but is confined to small changes in angular momentum. The approximation should be good for a broad range of collision processes. It reaches its limitation when behavior in the neighborhood of the turning point becomes critical and the uniform WKB wave functions must be used. This will occur as $\triangle E/E$ approaches unity. Although (33) are diagonal in δ and γ and thus much simpler than (26), they still depend on all of the rotational and vibrational states through $\underset{\sim}{i}$ and $\underset{\sim}{j}$, and are still difficult to solve. The rotational part of the problem will be removed by use of the sudden approximation and this will be discussed later.

Small Changes in Energy and Angular Momentum

By assuming that only small relative changes in energy and angular

momentum are possible as a result of the collision, a higher energy approximation may be derived. Expression (25) can be modified to treat this situation. The second term of (25) involving $(\theta_{oij} - \theta_{cij})$ remains the same, the $(\theta_i - \theta_{ci})$ and $(\theta_j - \theta_{cj})$ parts have simply become more nearly equal. A substitution will therefore be made for this term, omitting the ij subscript;

$$\theta_{oij} - \theta_{cij} \equiv \theta_o - \theta_c. \tag{34}$$

Again, θ_o goes from π to the final scattering angle χ and $\theta_c = \theta_o(r_c)$. The $G_{ij}^{(\ell_o)}(r)$ term must be expanded for the small relative changes in energy. Using a Taylor series to expand $G_{ij}^{(\ell_o)}(r)$ about some average k_o for the interaction·

$$G_{ij}^{(\ell_o)}(r) \approx k_o \int_{r_c}^{r} P_o(r, k_o, \ell_o)^{-1} \, dr \, (k_i - k_o)$$

$$- k_o \int_{r_c}^{r \cdot} P_o(r, k_o, \ell_o)^{-1} \, dr \, (k_j - k_o)$$

$$= k_o \, \Delta k \int_{r_c}^{r} P_o(r, k_o, \ell_o)^{-1} \, dr. \tag{35}$$

r_c is then defined for (k_o, ℓ_o). ℓ_o is defined as in the previous section and k_o is defined similarly. Here, since $\Delta k/k$ and $\Delta \ell/\ell$ are small, one can define a single trajectory by k_o and ℓ_o. By this definition,

$$dr = \frac{-}{+} \frac{P_o \hbar}{\mu} \, dt, \tag{36}$$

the upper sign holding for the incoming half of the trajectory and the lower sign holding for the outgoing half. Using (36) and the fact that $k_i^2 = \frac{2\mu E_i}{\hbar^2}$

in (35) gives

$$G_{ij}^{(\ell_o)} \approx \frac{\Delta E \text{ (translational)}}{\hbar} (t - t_c) \tag{37}$$

where t_c is the value of t at the turning point, r_c, t is defined by (36)

and $\Delta E = E_i(\text{translation}) - E_j(\text{translation})$. Substituting (37) and (34) into (26) then gives

$$\frac{d\, X_i(t, \ell', m')}{dt} = -\frac{i}{\hbar} \sum_{j\ell m} V_{ij\ell'\ell m'm}(t) \exp\left[i\, \omega_{ij}(t-t_c)\right.$$

$$\left. - i(\ell'-\ell)(\theta_o - \theta_c)\right] X_j(t, \ell, m)$$

$$(t \geq t_c) \qquad (38a)$$

$$\frac{d\, Y_i(t, \ell', m')}{dt} = -\frac{i}{\hbar} \sum_{j\ell m} V_{ij\ell'\ell m'm}(t) \exp\left[i\, \omega_{ij}(t-t_c)\right.$$

$$\left. - i(\ell'-\ell)(\theta_o - \theta_c)\right] Y_j(t, \ell, m)$$

$$(t \leq t_c) \qquad (38b)$$

where $\omega_{ij} = \dfrac{\Delta E\ (\text{internal})}{\hbar}$. As in the preceeding section, the equations

depend on the orbital angular momentum states. In exactly the same manner as previously, the orbital angular momentum may be treated in the classical limit and transformed so as to be more easily treatable. Using (29) and (32) in (38) one obtains

$$\frac{d\, X_i(t, \delta, \gamma)}{dt} = -\frac{i}{\hbar} \sum_j V_{ij}(t, \delta + \theta_o - \theta_c, \gamma) \exp\left[i\, \omega_{ij}(t-t_c)\right] X_j(t, \delta, \gamma)$$

$$(t \geq t_c) \qquad (39a)$$

$$\frac{d\, Y_i(t, \delta, \gamma)}{dt} = -\frac{i}{\hbar} \sum_j V_{ij}(t, \delta + \theta_o - \theta_c, \gamma) \exp\left[i\, \omega_{ij}(t-t_c)\right] Y_j(t, \delta, \gamma)$$

$$(t \leq t_c). \qquad (39b)$$

It is important to note that this expression could have been derived directly

from (33) by expansion of $G_{ij}^{(\ell_0)}$ (r) in a Taylor series about k_o. Since

this approximation is restricted to small energy changes, $\frac{\triangle E}{E}$ small, ap-

plication to vibrationally inelastic scattering problems will only be valid

at large E's on the order of several electron volts or higher as $\triangle E$ will

be 0.1 - 1.0eV ordinarily. It is interesting to note that equations of

the form of (38) can be derived from time dependent perturbation theory if

the spherical harmonics are included in the original wave function. Although

one can obtain transition probabilities using this formulation, the trans-

lational part of the problem has been neglected and one cannot obtain angu-

lar distributions or partial cross sections using it. Equations (38), on

the other hand, have retained the translational part of the problem and

all of the scattering data is latent in the equations. Equations similar

to (39) have been solved for atom-diatom vibrationally inelastic scatter-

ing in the collinear model.[21,22] The range of validity for this calculation

was restricted to those collisions for which the probability of a vibration-

ally inelastic event occurring was much less than unity by the fact that it

was done in a first order perturbation limit; thus, only small interactions

could be treated.

The rotational part of the problem has still not been removed

from the equations, and it is necessary to treat all of the rotational and

vibrational states if one wishes to solve (39) directly. The removal of

rotational states will be discussed in the next section.

Equations (39) can be solved in several different ways. If an

exact solution is desired, one can solve the coupled equations directly.

Alternatively, the Magnus expansion[41] presents a range of approximations

which can be made more or less exact depending upon the problem. The equa-

tions can also even be solved in the classical[29,35-37] or sudden

limits.[5,31-33,35-37,42-45] The classical limit is the limit of large quan-

tum numbers and is not generally applicable. The sudden limit will be discussed in the next section.

The Sudden Limit[5,31-33,35-37,42-45]

The coupled differential equations can be further simplified by use of the sudden limit. This is the limit at which the changes in energy and angular momentum are taken to be zero. This means that $\xi_i = \xi_j$ and the coupled equations (18) are

$$\frac{d\, X_i(r,\ell',m')}{dr} = -\frac{\mu i}{\hbar^2 p_o} \sum_{j\ell m} V_{ij\ell'\ell m'm}(r)\, X_j(r,\ell,m)$$

$$(t \geq t_c) \qquad (40a)$$

$$\frac{d\, Y_i(r,\ell',m')}{dr} = -\frac{\mu i}{\hbar^2 p_o} \sum_{j\ell m} V_{ij\ell'\ell m'm}(r)\, Y_j(r,\ell,m)$$

$$(t \leq t_c). \qquad (40b)$$

p_o has replaced $(p_i\, p_j)^{\frac{1}{2}}$ because there is now no difference in the trajectories. This is only true if all internal motions are treated in the sudden limit. These can be transformed to the (δ,γ) representation in exactly the same manner as previously. Using (29) and (32) and changing to the time dependent representation gives

$$\frac{d\, X_i(t,\delta,\gamma)}{dt} = -\frac{i}{\hbar} \sum_j V_{ij}(t,\delta + \theta_o - \theta_c,\gamma)\, X_j(t,\delta,\gamma)$$

$$(t \geq t_c) \qquad (41a)$$

$$\frac{d\, Y_i(t,\delta,\gamma)}{dt} = -\frac{i}{\hbar} \sum_j V_{ij}(t,\delta + \theta_o - \theta_c,\gamma)\, Y_j(t,\delta,\gamma)$$

$$(t \leq t_c). \qquad (41b)$$

(41) could have been derived directly from (39) by letting $\omega = 0$. It is now useful to look at the explicit expressions for the matrix elements, V_{ij}, in order to obtain a solution for this set of equations. The matrix elements have the form

$$V_{ij}(t) = \int \phi_{Ai}^*(\underset{\sim}{r}_A) \, \phi_{Bi}^*(\underset{\sim}{r}_B) \, \Delta V(t, \delta + \theta_o - \theta_c, \gamma, \underset{\sim}{r}_A, \underset{\sim}{r}_B) \, \phi_{Aj}(\underset{\sim}{r}_A) \, \phi_{Bj}(\underset{\sim}{r}_B)$$

$$d\Omega_A \, d\Omega_B. \qquad (42)$$

(42) represents a transformation from a basis set quantized in $\underset{\sim}{i}$ and $\underset{\sim}{j}$ to one quantized in Dirac delta functions in the internal coordinates of the molecules. The reverse transform is

$$\underset{ij}{\Sigma} \, \phi_{Ai}(\underset{\sim}{r}_A) \, \phi_{Bi}(\underset{\sim}{r}_B) < \phi_{Ai} \, \phi_{Bi} \mid \Delta V \mid \phi_{Aj} \, \phi_{Bj} > \phi_{Aj}^*(\underset{\sim}{r}'_A) \, \phi_{Bj}^*(\underset{\sim}{r}'_B)$$

$$= \Delta V(\underset{\sim}{r}_A, \underset{\sim}{r}_B) \, \delta(\underset{\sim}{r}_A - \underset{\sim}{r}'_A) \, \delta(\underset{\sim}{r}_B - \underset{\sim}{r}'_B). \qquad (43)$$

(43) results directly from the closure property of the internal wave functions. (43) can be used to diagonalize (41) leaving the decoupled equations,

$$\frac{d \, \underline{X}(r, \delta, \gamma, \underset{\sim}{r}_A, \underset{\sim}{r}_B)}{dt} = -\frac{i}{\hbar} \Delta V(r, \delta + \theta_o - \theta_c, \gamma, \underset{\sim}{r}_A, \underset{\sim}{r}_B) \, \underline{X}(r, \delta, \gamma, \underset{\sim}{r}_A, \underset{\sim}{r}_B)$$

$$(t \geq t_c) \qquad (44a)$$

$$\frac{d \, \underline{Y}(r, \delta, \gamma, \underset{\sim}{r}_A, \underset{\sim}{r}_B)}{dt} = -\frac{i}{\hbar} \Delta V(r, \delta + \theta_o - \theta_c, \gamma, \underset{\sim}{r}_A, \underset{\sim}{r}_B) \, \underline{X}(r, \delta, \gamma, \underset{\sim}{r}_A, \underset{\sim}{r}_B)$$

$$(t \leq t_c) \qquad (44b)$$

The solution of (44) consists of a simple integration in time over the trajectory. Since one is only interested in the behavior of X and Y as $r \sim \infty$, one can write the solution of (44) for this case as

$$X \ (t \sim \infty) = \exp \ [2 \ i\eta_1] \ Y \ (t \sim - \infty) \tag{45}$$

where

$$\eta_1 (\delta - \theta_c, \gamma, \underset{\sim}{r}_A, \underset{\sim}{r}_B) = -\frac{1}{2\hbar} \int_{-\infty}^{\infty} \Delta V \ (r, \delta + \theta_0 - \theta_c, \gamma, \underset{\sim}{r}_A, \underset{\sim}{r}_B) \ dt \tag{46}$$

and η_1 is the phase shift.

Here, the X and Y functions are no longer dependent upon the internal states of the colliding molecules, but are dependent upon their internal coordinates as is indicated in the arguments of the functions.

ΔV depends on time only through the trajectory variables. The internal molecular coordinates are independent of time. This is the physical interpretation of the sudden approximation. Since ΔE does not actually equal zero, but $\Delta E/E \approx 0$, the impinging atom energy is so large that the internal motions of the molecules are very slow relative to the collision duration. The sudden limit is the most restricted energetically of the approximations discussed. When it is necessary to look at specific transitions, the transformations represented by (43) can be reversed and applied to the solution of (44).

Application of the Sudden Approximation to the Rotational Portion of Atom-Diatom Collisions

The sudden approximation can be used on specific parts of problems. It is used here to uncouple the rotational part of the atom-diatom scattering problem. This is a reasonable limit in which to treat the rotational part of the problem, since if the collision energy is high enough for vibrational transitions to take place, the rotational motion will be slow compared to the collision time. The sudden approximation has been used successfully to treat the rotational problem alone.[31] One begins with equations of the form of (33) although (39) can be treated in exactly the same way. If the rotations are treated in the sudden limit, $G_{ij}^{(\ell_0)}$ is inde-

pendent of rotational energy differences and will be replaced by $G_{v'v}^{(\ell_o)}$ where

v and v′ are the initial and final vibrational states for the problem.

(33a) becomes

$$\frac{d\,\underline{X}_{v'}\,(r,\delta,\gamma)}{dr} = - \frac{\mu i}{\hbar^2}\,(P_{v'}P_v)^{-\frac{1}{2}}\,\sum_v\,V_{v'vj'jm'm}\,(r,\delta + \theta_{ov'v} - \theta_{cv'v},\gamma)$$

$$\exp\,[-i\,G_{v'v}^{(\ell_o)}\,(r)]\,\underline{X}_v\,(r,\delta,\gamma)$$

$$(t \geq t_c). \tag{47}$$

A similar expression can be written for (33b). All of the subscripts have

been replaced by v′ and v. (j,m) refer to the internal rotational states

of the diatomic molecule. Using the transformation represented by (44) for

the rotational states of one molecule

$$\sum_{\substack{jm \\ j'm'}}\,\phi_{j'm'}\,(\Theta,\Phi) < j'm' \mid \Delta V \mid jm > \phi_{jm}^{*}\,(\Theta',\Phi')$$

$$= V\,(\Theta,\Phi)\,\delta(\Theta - \Theta')\,\delta(\Phi - \Phi') \tag{48}$$

where Θ and Φ are the internal angles as defined in Figure 1. Using (48)

in (47) yields

$$\frac{d\,\underline{X}_{v'}(r,\delta,\gamma,\Theta,\Phi)}{dr} = - \frac{\mu i}{\hbar^2}\,(P_{v'}P_v)^{-\frac{1}{2}}\,\sum_v\,V_{v'v}\,(r,\delta + \theta_{ov'v} - \theta_{cv'v},\gamma,\Theta,\Phi)$$

$$\exp\,[-i\,G_{v'v}^{(\ell_o)}\,(r)]\,\underline{X}_v\,(r,\delta,\gamma,\Theta,\Phi). \tag{49}$$

A similar set of equations follow for the Y functions. Equation (49) and

the related Y equation or the equations resulting from a similar treatment

of (33) is the set which one would want to solve in order to treat the

vibrationally inelastic scattering problem in three dimensions. The vast

numbers of rotational and orbital angular momentum states have been trans-

formed out of the problem and one is left with only as many coupled equa-

tions as one has vibrational states.

The Scattering Matrix, Cross Sections, and Angular Distributions

Scattering properties such as angular distributions are determined by the asymptotic values of $\underset{\sim}{X}$ and $\underset{\sim}{Y}$ which are related through the scattering matrix.[5] In the (δ, γ) representation, this relationship is

$$\underset{\sim}{X}_i \ (t \rightarrow \infty, \delta, \gamma) = \underset{j}{\sum} S'_{1ij}(\delta, \gamma) \ \underset{\sim}{Y}_j (t \rightarrow \infty, \delta, \gamma). \tag{50}$$

Expression (50) can be transformed to the (ℓ, m) representation by (32), which gives

$$\underset{\sim}{X}_i \ (t \rightarrow \infty, \ \ell', m') = \underset{j \ell m}{\sum} S_{1ij\ell'\ell m'm} \ \underset{\sim}{Y}_j (t \rightarrow \infty, \ \ell, m). \tag{51}$$

The matrices are directly related by

$$S_{1ij\ell'\ell m'm} = \frac{1}{4\pi^2} \int_0^{2\pi} d\delta \int_0^{2\pi} d\gamma \ \exp \ [i \ (\ell' - \ell)\delta]$$

$$\exp \ [i(m' - m)(\gamma - \frac{\pi}{2})] \ S'_{1ij}(\delta, \gamma), \tag{52}$$

a transformation analogous to (29) and (32). It is interesting to note that the unprimed scattering matrix depends only upon changes in ℓ and m which follows from the same dependence found for ΔV in (29). The $\underset{\sim}{S}_1$ matrices refer only to the inelastic part of the total scattering problem. The complete scattering matrix, $\underset{\sim}{S}$, relates the behavior of the total wave function, u, as defined by (8) at its asymptotic limits. It is necessary to relate $\underset{\sim}{S}_1$ and $\underset{\sim}{S}$ in order to be able to describe the scattering. In the asymptotic limit, the complete wave function must be

$$\underset{\sim}{u}_i \sim \underset{\sim}{k}_i^{-\frac{1}{2}} [\ \underset{\sim}{a}_i \ \exp \ (-i \ \underset{\sim}{k}_i \ r + i\ell' \ \frac{\pi}{2}) - \underset{\sim}{b}_i \ \exp \ (i \ \underset{\sim}{k}_i \ r - i\ell' \ \frac{\pi}{2})]. \tag{53}$$

Here, an incoming and an outgoing solution are represented, and one can see that the total scattering matrix is defined by

$$b_i(\ell',m') = \sum_{j\ell m} S_{ij\ell'\ell m'm} \, a_j(\ell,m). \tag{54}$$

The asymptotic forms of u_{1i} and u_{2i} are[34]

$$u_{1i} \sim k_i^{-\frac{1}{2}} \exp[i\,\eta_{oi} + ik_i r - i\ell'\frac{\pi}{2} - i\frac{\pi}{2}] \tag{55a}$$

$$u_{2i} \sim k_i^{-\frac{1}{2}} \exp[-i\eta_{oi} - ik_i r + i\ell'\frac{\pi}{2} - i\frac{\pi}{2}] \tag{55b}$$

where η_{oi} is the WKB phase shift associated with the classical trajectory defined for state i. Using (10) to relate u to the X and Y functions, substituting (55) into (10) and equating terms with (53) yields

$$X_i \exp[i\,\eta_{oi} - i\frac{\pi}{2}] = -b_i \tag{56a}$$

$$Y_i \exp[-i\,\eta_{oi} + i\frac{\pi}{2}] = a_i. \tag{56b}$$

Substituting (56) into (54) and comparing with (51) gives

$$S_{ij\ell'\ell m'm} = S_{1ij\ell'\ell m'm} \exp[i\,\eta_{oi} + i\,\eta_{oj}]. \tag{57}$$

The two matrices are, then, rather simply related.

One important aspect of the scattering matrix is its unitarity. Both S and S_1 are unitary so that there exist a pair of phase shift matrices related to them by

$$S = \exp(2\,i\eta) \tag{58a}$$

$$S_1 = \exp(2\,i\eta_1). \tag{58b}$$

The transition probability for an inelastic event, P_{ij}, is related to the scattering matrix elements by[31]

$$P_{ij} = |S_{ij}|^2 = |S_{1ij}|^2. \tag{59}$$

Calculation of such phase shifts and associated transition probabilities takes on a very simple form in the sudden limit. This expression for η_1 is given by equation (46). Hence, in this limit, since η_1 has been diagonalized in the internal quantum numbers, so has the scattering matrix and it becomes

$$S_1'(\delta - \theta_c, \gamma, \underset{\sim}{r}_A, \underset{\sim}{r}_B) = \exp[2i\,\eta_1(\delta - \theta_c, \gamma, \underset{\sim}{r}_A, \underset{\sim}{r}_B)]. \qquad (60)$$

The reverse of (44) can then be used to obtain the scattering matrix elements

$$S_{1ij}'(\delta-\theta_c,\gamma) = \langle \overset{*}{\phi}_{Ai}(\underset{\sim}{r}_A)\,\overset{*}{\phi}_{Bi}(\underset{\sim}{r}_B) \mid S_1'(\delta-\theta_c,\gamma,\underset{\sim}{r}_A,\underset{\sim}{r}_B) \mid \phi_{Ai}(\underset{\sim}{r}_A)\,\phi_{Bi}(\underset{\sim}{r}_B)\rangle. \qquad (61)$$

The transition probabilities follow trivially. These are total transition probabilities for all scattering angles.

Another important aspect of the scattering matrix is its relation to the scattering amplitude and thus to angular distributions. For inelastic events, the scattering amplitude has the form[5,46]

$$f_{ij}(\theta',\phi') = \underset{\ell,\ell'm'}{\sum}[4\pi(2\ell+1)]^{\frac{1}{2}}\,i^{-(\ell'-\ell)}[2i\,(k_i k_j)^{\frac{1}{2}}]^{-1}$$

$$[S_{ij\ell'\ell m'm} - \delta_{ij}\,\delta_{\ell'\ell}\,\delta_{m'm}]\,Y_{\ell'm'}(\theta',\phi') \qquad (62)$$

where θ' and ϕ' are the final polar and azimuthal angles for the scattering event. In order to perform the sums in (62) one begins by substituting (52) and (57) into (62). This gives

$$f_{ij}(\theta',\phi') = \underset{\ell\ell'm'}{\sum}[4\pi(2\ell+1)]^{\frac{1}{2}}\,e^{-i(\ell'-\ell)\frac{\pi}{2}}\,[2i(k_i k_j)^{\frac{1}{2}}]^{-1}$$

$$\exp[i\eta_0(k_i,\ell') + i\eta_0(k_j,\ell)]\,Y_{\ell'm'}(\theta',\phi')$$

$$\frac{1}{4\pi^2}\int_0^{2\pi}d\delta\int_0^{2\pi}d\gamma\,\exp[i\Delta\ell\,\delta]\exp[-i\Delta m(\gamma-\frac{\pi}{2})]$$

$$S_{1ij}'(\delta,\gamma). \qquad (63)$$

Assuming now that $(2\ell + 1)$ varies slowly with ℓ and can therefore be replaced by $(2\ell' + 1)$ and that

$$\eta_0(k_j, \ell) \approx \eta_0(k_j, \ell') - \frac{d\eta_0}{d\ell} (\ell' - \ell) = \eta_0(k_j, \ell') - \tfrac{1}{2} \chi(k_j)(\ell' - \ell), \quad (64)$$

(63) can be written

$$f_{ij}(\theta', \phi') = \sum_{\ell' m} \frac{1}{2i} \left[\frac{4\pi(2\ell' + 1)}{k_i k_j} \right]^{\frac{1}{2}} \exp\left[i\eta_0(k_i) + i\eta_0(k_j)\right] Y_{\ell' m'}(\theta', \phi')$$

$$\frac{1}{4\pi^2} \sum_{(\ell' - \ell)} \int_0^{2\pi} \int_0^{2\pi} \exp\left[i(\ell' - \ell)(\delta - \frac{\pi}{2} - \frac{\chi(k_j)}{2})\right]$$

$$\exp\left[-i(m' - m)(\gamma - \frac{\pi}{2})\right] S'_{1ij}(\delta, \gamma) \, d\delta \, d\gamma. \quad (65)$$

If the sum over $(\ell' - \ell)$ is now carried out, one obtains

$$2\pi \, \delta(\delta - \frac{\pi}{2} - \frac{\chi(k_j)}{2}) \equiv 2\pi \, \delta(\delta - \theta_{cj}) \quad (66)$$

which identifies δ with θ_{cj}, the polar trajectory angle value at the turn-ing point, r_{cj}. For the small relative Δk, small relative $\Delta\ell$ approximation and in the sudden limit, $\theta_{cj} = \theta_c$, the value of the polar angle at the turning point, r_c, for the single trajectory used. For the multi-trajec-tory case, θ_{cj} is used. This slight difference arises from the fact that it was $\eta_0(k_j, \ell')$ used in (64).

To simplify (65) further, one rewrites the spherical harmonics in an asymptotic form valid in the classical limit of large ℓ' and $m' \ll \ell'$. The expression is[40]

$$Y_{\ell' m'}(\theta', \phi') = \frac{i^{-m'}}{2\pi} \left[\frac{\theta'(\ell' + \frac{1}{2})}{2\pi \sin\theta'} \right]^{\frac{1}{2}} \int_0^{2\pi} \exp\left[-i(\ell' + \tfrac{1}{2})\theta' \cos(\phi' - \phi) + im'\phi\right] d\phi$$

$$(67)$$

and is valid for all θ'. Substitution of (67) into (65) yields

$$f_{ij}(\theta',\phi') = \sum_{\ell' m'} \frac{(\ell'+\frac{1}{2})}{4\pi^2 i} [\frac{\theta'}{k_i k_j \sin\theta'}]^{\frac{1}{2}} \exp[i\,\eta_0(k_i) + i\,\eta_0(k_j)]$$

$$\int_0^{2\pi} \int_0^{2\pi} \exp[-i(m'-m)(\gamma - \frac{\pi}{2})]$$

$$\exp[im(\phi - \frac{\pi}{2})] S'_{1ij}(\theta'_c,\gamma) \exp[-i(\ell'+\frac{1}{2})\theta'\cos(\phi'-\phi)]\,d\phi\,d\gamma. \tag{68}$$

ϕ can be identified as the initial azimuthal angle. The sum over m' gives $\delta(\phi - \gamma)$ identifying γ with the initial azimuthal angle ϕ and making the integral in γ trivial. The sum in ℓ' can be converted into an integral in b', the final impact parameter, if one uses the definitions

$$b' = \frac{\ell'+\frac{1}{2}}{k_i} \qquad \text{and} \qquad d\ell' = k_i db'. \tag{69}$$

Substituting (69) into (68) and performing the integral in γ, one obtains

$$f_{ij}(\theta',\phi') = \frac{k_i}{2\pi i} [\frac{k_i \theta'}{k_j \sin\theta'}]^{\frac{1}{2}} \exp[i\eta_0(k_i) + i\eta_0(k_j)]\int_0^{\infty} \int_0^{2\pi} S'_{1ij}(\theta'_c,\phi')$$

$$\exp[-ik_i b'\theta'\cos(\phi'-\phi)]b'\,db'\,d\phi. \tag{70}$$

The initial azimuthal angle, ϕ, and final impact parameter, b', together define the direction of approach of the collision partners. The solution of (70) by stationary phase methods has been looked at previously.[47,48] The derivation of (70) is not restricted to any of the approximations treated in previous sections except as mentioned in connection with (66) above. Equation (70) can be made specific to the atom-diatomic molecule system, treating the rotation in the sudden limit and the vibration in any of the approximations discussed previously in exactly the same manner as was discussed at the end of the section on the sudden limit. If one had done this, the expression for the scattering amplitude would have taken the form

$$f_{v'v}(\theta', \phi', \Theta, \Phi) = \frac{k_{v'}}{2\pi i} \left[\frac{k_{v'}\theta'}{k_v \sin\Theta} \right]^{\frac{1}{2}} \exp\left[i\eta_0(k_v) + i\eta_0(k_{v'})\right]$$

$$\int_0^\infty \int_0^{2\pi} S'_{1v'v}(\theta'_c, \phi, \Theta, \Phi)$$

$$\exp[-ik_{v'}b'\theta'\cos(\phi'-\Phi)] \, b'db'd\phi. \tag{71}$$

v and v' are the initial and final vibrational quantum numbers. The reverse of transformation (44) can once again be used to obtain individual rotational transitions

$$f_{v'vj'jm'm}(\theta', \phi') = \langle j'm' | f_{v'v}(\theta', \phi', \Theta, \Phi) | jm \rangle. \tag{72}$$

If there is no m state selection and one is not interested in rotational transitions, the scattering amplitude can be summed over j and m states to obtain the partial differential cross sections for vibrationally inelastic scattering,

$$I_{v'v}(\theta', \phi') = \frac{k_{v'}}{k_v} (2j + 1)^{-1} \sum_{j'm'm} | \langle j'm' | f_{v'v}(\theta', \phi', \Theta, \Phi) | jm \rangle |^2$$

$$= \frac{k_{v'}}{k_v} (4\pi)^{-1} \int_0^\pi \sin\Theta \, d\Theta \int_0^{2\pi} d\Phi \, | f_{v'v}(\theta', \phi', \Theta, \Phi) |^2 \tag{73}$$

where the closure properties of the rotational wave functions have been used.

Finally, a semiclassical cross section, Q, averaged over scattering angles can be obtained by using the small $\Delta E/E$, small $\Delta\ell/\ell$ approximation to obtain the scattering matrix by substituting this into (70) and integrating over θ' and ϕ'. The result is[37]

$$Q_{ij}(E) = \int_0^{2\pi} d\phi \int_0^\infty P_{ij}(E, b', \phi) \, b' \, db'. \tag{74}$$

Discussion

A hierarchy of semiclassical approximations with which to treat the problem of vibrationally inelastic scattering in three dimensions has been derived in this section. These range from a multi-trajectory method which is expected to be valid for a spread of relative collision energies nearly as great as an exact quantum mechanical calculation to the sudden limit which is valid only for very high relative collision energies. Methods of treating individual parts of an inelastic scattering problem in different approximations have been discussed as a physically reasonable method of simplifying the three dimensional problem. It is shown that the translational motion can be treated in the sudden limit, and one has a choice, then, of treating the vibrational portion of the problem in approximations ranging from the multi-trajectory method to the sudden limit depending upon the relative energies of the collision partners. The scattering properties have been derived in general for all of these approximations.

Sudden Limit Transition Probabilities and Cross Sections

The sudden approximation[5,31-33,35-37,42-45] is used in the cal-
culations which follow to obtain basic trends in the vibrationally inelas-
tic transition probabilities and cross sections for atom-diatom scattering.
As discussed previously, the sudden limit is a high energy limit at which
the internal states of the colliding particles are assumed to be degener-
ate. This means that the scattering matrix is easily diagonalized in the
internal states of the diatomic molecule which makes calculations of the
scattering matrix elements much simpler. Since the expression for the
scattering matrix elements, transition probabilities, and cross sections
have been derived in the previous section, only an outline of the calcula-
tions will be given here. This will be followed by a discussion of the
potential function used and the results obtained.

Outline of the Sudden Limit Calculations

The calculations can best be described as being made up of several
sections, roughly following the flow of subroutines in the computer pro-
gram used. All calculations were done on an IBM 7040-7094 direct coupled
system. Simpson's rule was used for all numerical integrations.

1) A classical trajectory was calculated by integrating the classical
equations of motion using a spherical potential which was calculated by
averaging a calculated potential for the atom-diatom system over internal
molecular coordinates. The average over rotational coordinates was done
in the standard manner integrating over $\sin \Theta \, d \Theta \, d \Phi$. The average over
the vibrational coordinates was done using $\exp[-\alpha R^2]$ as a weighting fac-
tor where α was chosen according to the identity of the diatomic molecule.
This yielded a trajectory described by time, t, as a function of center of
mass distance, r, for a given initial energy and impact parameter. The
functionality was reversed to yield CM distance as a function of time. The

classical equations for the trajectory angle, θ, were then integrated. This gave a classical trajectory which could be described in terms of t, r(t), θ(t).

2) To use the sudden approximation, the original potential in terms of internal coordinates was integrated over the trajectory to obtain a phase shift, η, according to

$$\eta \ (E, \ b, \ R, \ \Theta, \ \Phi) = - \frac{1}{2\hbar} \int_{-\infty}^{\infty} V \ [r \ (t), \ \theta(t), \ \phi, \ R, \ \Theta, \ \Phi]dt \quad (75)$$

where E and b are the CM energy and impact parameter, R is the vibrational coordinate for the diatomic molecule, and Θ and Φ are the orientation angles for the diatomic molecule as shown in Figure 1. In (75), the total potential for the system is integrated over the trajectory rather than the difference from the spherical potential, ΔV, as shown in (46). This substitution has no effect on the scattering phenomena calculated since $V(r, \ R, \ \Theta, \ \Phi) = V_o(r) + \Delta V \ (r, \ R, \ \Theta, \ \Phi)$ and matrix elements consist of integrations over the internal molecular coordinates. This leads to a phase factor difference in the scattering matrix elements and no difference in the transition probabilities as can be seen from (59). The azimuthal angle, ϕ, was always taken to be zero since $V = V(\Phi - \phi)$.

3) Scattering matrix elements, $S_{v'v}$, were obtained by integrating the exponential phase shift over vibrational wave functions using the reverse of (43) according to

$$S_{v'v} \ (E, \ b, \ \Theta, \ \Phi) = \ < v' \ | \ exp \ [2i\eta \ (E, \ b, \ R, \ \Theta, \ \Phi) \ | v > \quad (76)$$

where v' and v are the final and initial states of the oscillator and are chosen to be harmonic oscillator wave functions and v is always the ground state, $v = 0$. The absolute squares of the scattering matrix elements yielded the transition probabilities, $P_{v'o}$, directly as

$$P_{v'o} (E, b, \Theta, \bar{\Phi}) = \left| S_{v'o} (E, b, \Theta, \bar{\Phi}) \right|^2. \tag{77}$$

4) Cross sections, $Q_{v'o}$, were calculated from transition probabilities using a form of (74). Since the azimuthal angle was always taken to be zero and one wants to look at cross sections as a function of orientation angle, a modified cross section was defined according to

$$Q_{v'o} (E, \Theta, \bar{\Phi}, \phi = 0) = 2\pi \int_o^\infty P_{v'o} (E, b, \Theta, \bar{\Phi}, \phi = 0) \, b \, db \tag{78}$$

This is done because an average over ϕ would average out the orientation dependence of the cross section due to the $\exp [i (\bar{\Phi} - \phi)]$ dependence of the potential.

5) Averaged cross sections, $Q'_{v'o} (E)$, were calculated according to

$$Q'_{v'o} (E) = \frac{1}{4\pi} \int_o^{2\pi} d\bar{\Phi} \int_o^\pi \sin \Theta \, d \, \Theta \, Q_{v'o} (E, \Theta, \bar{\Phi}) \tag{79}$$

which is equivalent to averaging (74) over internal angles.

All calculations were carried out at several CM energies, most commonly 1.7 eV, 4.8 eV, and 12.4 eV. Where figures give results for only one energy, it is because results at other energies were similar, as one would expect in the sudden limit.

Interaction Potential

A major problem in any scattering calculation is the choice of an interaction potential which will describe the problem reasonably. In the calculations presented here, a modification of the Krauss-Mies potential[49] for the He + H_2 system was used. The modifications are discussed below. The unmodified potential is

$$V (r, R, \gamma_1) = C \exp [-(\alpha_o - \alpha_1 R) \, r] [A (\gamma_1) + B (\gamma_1) R] \tag{80}$$

where r is the distance between the He and H_2 centers of charge, R is the

change in vibrational coordinate from equilibrium, γ_1 is the angle between the molecular axis and $\underset{\sim}{v}$, and

$$A(\gamma_1) = 1.10041 \, [\, 1 + 0.18250 \, P_2 \, (\cos \gamma_1)]$$

$$B(\gamma_1) = -0.52151 \, [\, 1 - 0.27506 \, P_2 \, (\cos \gamma_1)] \quad a.u.^{-1} \qquad (81)$$

$$C = 198.378 \text{ eV}$$

$$\alpha_o = 1.86176 \text{ a.u.}^{-1} \qquad \alpha_1 = 0.3206 \text{ a.u.}^{-2}$$

$P_2 (\cos \gamma_1)$ is the second Legendre polynomial. The coordinate system is shown in Figure 1. The potential is valid for $2.5 \leq r \leq 3.8$ a.u. and $-1.4 \leq R \leq .6$ a.u. Secrest and Gordon[50] have since calculated a potential function for the same system using more sophisticated methods. Although the constants differ slightly, the basic form of the potential is unchanged.

The potential has a limited range in both r and R. If R is greater than ≈ 6 a.u., the potential will become infinite as r becomes large. Two different modifications were made to take care of this. First, an extra exponential term was multiplied in to give the form

$$V_1 \, (r, R, \gamma_i) = C \exp \, [-(\alpha_o - \alpha_1 R)r - ar^2 R^4] \, [A(\gamma_1) + B(\gamma_1)R] \qquad (82)$$

where $a = 0.0001$ a.u.$^{-6}$. The extra term kept the potential finite even under the conditions stated above while having a negligible effect on V in its original range of validity. V_1 was used in all calculations of transition probabilities.

After the calculations of transition probabilities had been done, Professor R. E. Roberts pointed out[51] that the exponential term involving R in the original potential could be expanded to first order and that this had little effect on the transition probabilities. This treatment gives

the potential form

$$V_2(r, R, \gamma_1) = C \exp [-\alpha_o r] [1 + \alpha_1 r R] [A(\gamma_1) + B(\gamma_1) R]. \tag{83}$$

This form has the advantage that certain integrals used to obtain the phase shift which contain it can be done analytically. V_2 was used in the cross section calculations.

The angle γ_1 may be separated by use of the spherical harmonic addition theorem into a polar and azimuthal trajectory angle, θ and ϕ, and a polar and azimuthal orientation angle, Θ and Φ. γ_1 is the angle between (θ, ϕ) and (Θ, Φ) as shown in Figure 1.
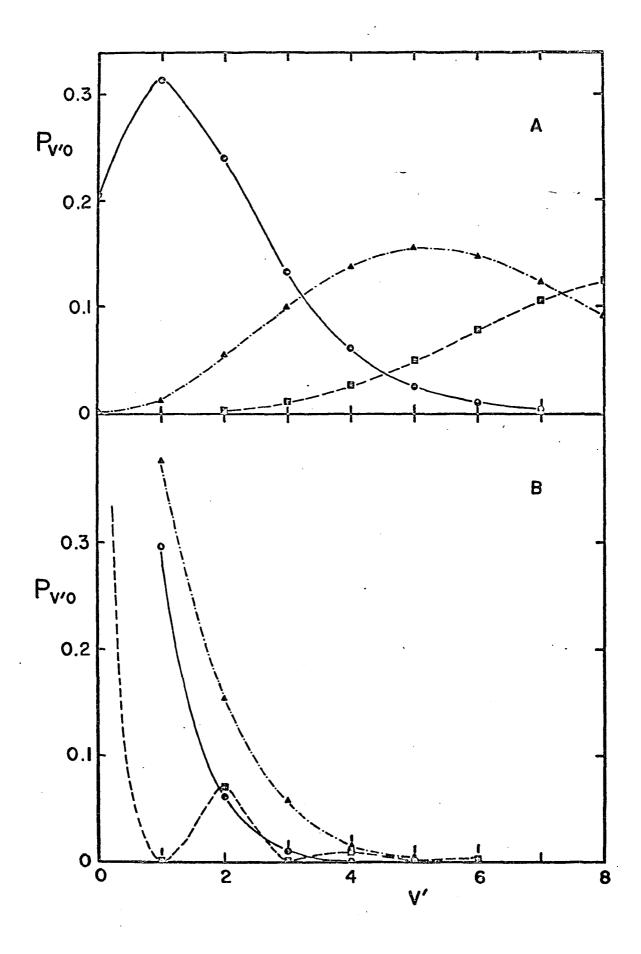
Results

Transition Probabilities

Transition probabilities, $P_{v'v}(E, b, \Theta, \Phi)$, were calculated in the sudden limit over a range of energies, impact parameters, and orientations. In all calculations, the initial state was assumed to be the ground vibrational state, $v = 0$, and the final state was varied.

Zero impact parameter collisions were studied for various orientations and collision energies. A comparison of transition probabilities for a range of final states and energies in the collinear orientation $(\Theta = 0, \Phi = 0)$ is shown in Figure (2A). In this case, as the energy is increased, the probability of transition to higher final states increases and more energy is transferred. Additionally, instead of simply shifting the maximum in the distribution of probabilities vs. final states, an increase in the collision energy spreads the distribution giving significant transition probabilities to more states. Changing the orientation of collision at zero impact parameter from collinear to perpendicular $(\Theta = 0, \Phi = 0$ to $\Theta = \frac{\pi}{2}, \Phi = \frac{\pi}{2})$ results in more complicated behavior. Figure (2B) shows a comparison of transition probabilities to various final states for three

Figure 2--Transition probability, $P_{v'o}$, plotted against

final state, v', for A: collinear collisions

($\Theta = 0$) and B: perpendicular collisions ($\Theta = \frac{\pi}{2}$)

at zero impact parameter. Energy: $\bigcirc = .19$ eV CM,

$\triangle = 1.7$ eV CM, $\square = 12.4$ eV CM.

different energies for this case. At higher energies, an oscillation in the transition probability vs. final state appears. The oscillation is due to the presence of a minimum in the phase shift vs. R approaching R = 0 at higher energies. A node in odd $< v'|$ at R = 0 at such energies causes the probability of transition to states of even $< v'|$ to be enhanced over those to the odd states. Varying Θ from 0 to $\frac{\pi}{2}$ with $\varphi = 0$ shows a smooth transition from the behavior exhibited in Figure (2A) to that shown in (2B). Figure (3) shows the variation of the (0-0) transition probabilities with initial relative velocity for the two extremes in orientation, collinear and perpendicular, at zero impact parameter. Intermediate orientations give curves in between. The collinear curve exhibits the expected smooth drop off with increasing energy. The perpendicular curve confirms the results discussed previously, since it drops off like the collinear one initially, but as the energy is raised and the minimum in the phase shift approaches R = 0, it begins to rise and approaches unity as the minimum reaches R = 0. It then begins to fall again as the minimum passes. Figure (3) confirms the interpretation given for (2B) and indicates the singificant inelastic transition probabilities for the perpendicular case.

For collisions where the impact parameter is not zero, the most efficient transfer of energy occurs not when the molecule is oriented parallel to the trajectory, but when one end of the molecule is closest to the atom's projected trajectory. This effect is best illustrated for a perpendicular collision as shown in Figure (4). Here, increasing the impact parameter from zero at constant energy gives a minimum in the elastic, (0 - 0), transition probability at $b \approx R_e/2$. For $b > R_e/2$, the probability of vibrational excitation drops off exponentially with increasing b. This indicates that the functional dependence of such scattering probabilities on b is more complicated than to lend itself to accurate description by

Figure 3--Natural log of the (0-0) transition probability, $\ln(P_{00})$, plotted against CM energy for zero impact parameter. E = 4.8 eV CM. Orientations- $\bigcirc$: $\Theta = \frac{\pi}{2}$, $\square$: $\Theta = 0$.
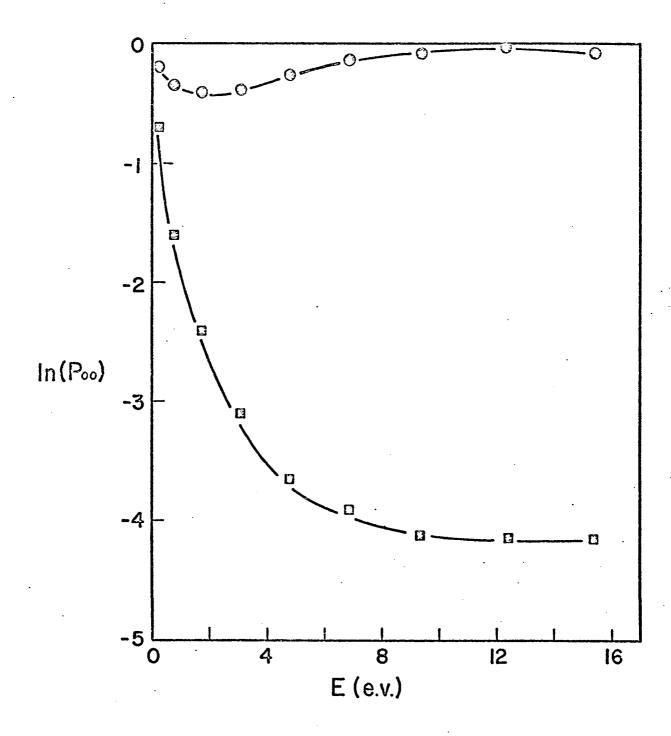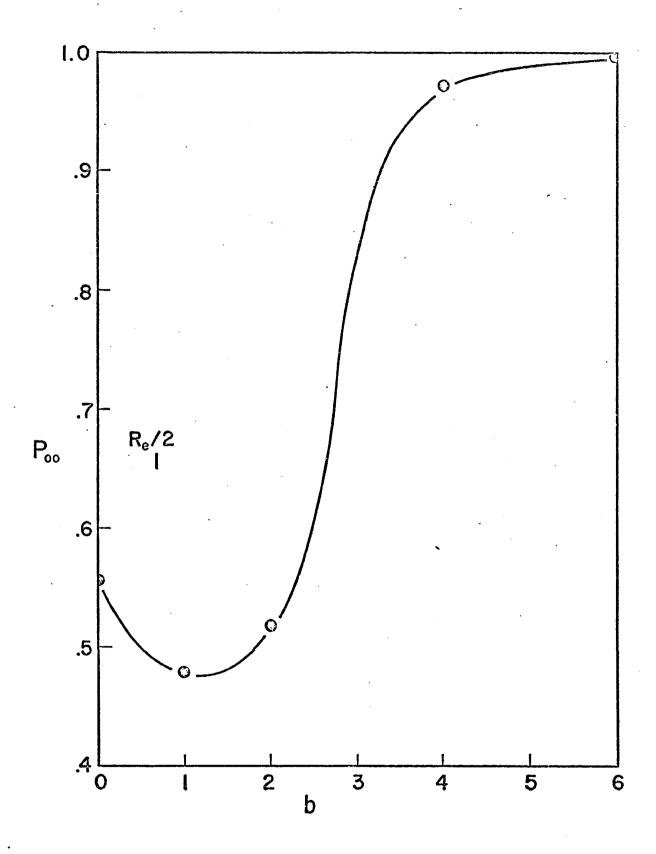
Figure 4--(0-0) transition probability, P_{oo}, plotted against

impact parameter, b. E = 4.8 eV CM, $\Theta = \frac{\pi}{2}$, $\Phi = 0$.
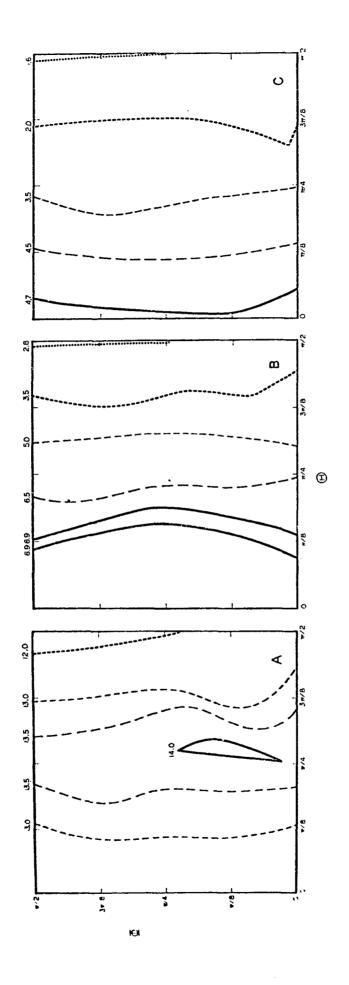
as simple a device as a steric factor. This is another indication along
with Figure (2) that the most efficient impact parameter for transfer
of energy occurs when the largest component of the translational motion
is along the molecular axis. Here, again, the distribution of energies
is broad rather than sharp.

It should be emphasized that there are significant transition
probabilities at all orientations for a given impact parameter and that it
is not always the zero impact parameter case which garners the highest
transition probability.

Cross Sections

Cross sections, $Q_{v'v}(E, \Theta, \Phi)$, were calculated in the sudden
limit for a range of energies and molecular orientations. The initial
state is once again the ground state of the oscillator, $v = 0$. The depen-
dence of cross sections on orientation is shown in Figure (5) where con-
tour type maps of the cross sections are given for the whole range of
orientations (Θ from 0 to $\frac{\pi}{2}$, Φ from 0 to $\frac{\pi}{2}$). Q_{10}, Q_{20}, and Q_{30} are
shown for $E \approx 1.7$ eV. The highest cross section for transition (0 - 1)
occurs at an orientation which is neither collinear nor perpendicular
($\Theta \approx \pi/4$, $\Phi \approx \pi/8$) as shown in Figure (5A). The highest cross section
for the (0 - 2) transition at the same energy comes at an orientation which
is closer to the collinear orientation as shown in Figure (5B). The high-
est cross section for the (0 - 3) transition is for the collinear orienta-
tion, Figure (5C). This behavior may be seen as another example of high-
er efficiency of energy transfer when larger components of the transla-
tional motion are directed along the molecular axis. The highest cross
section for the (0 - 1) transition occurs not where the most efficient
transfer of energy will take place in general, but where the correct quan-
tity for a (0 - 1) transition will exchange. This happens at the orienta-

Figure 5--Contours of constant $Q_{v',o}(\Theta, \bar{\Phi})$ as a function of Θ and $\bar{\Phi}$ at $E = 1.7$ eV CM. A: Q_{10}, B: Q_{20}, C: Q_{30}. Contour magnitudes are shown at the top of each graph.

tion of highest cross sections in Figure (5A). As the energy necessary for transition becomes larger, the (0-2) and (0-3) situations, the orientation of highest cross section moves toward one which will be more efficient for higher energy transfer, the collinear orientation, as can be seen to be happening in Figures (5B) and (5C). For all transitions higher than (0-3), the collinear orientation predominates. The same behavior is observed at higher energies, contour maps being similar for 4.8 eV and 12.4 eV.

An important aspect of the sudden approximation becomes evident in Figure (6). Here, the dependence of cross section on final state at several energies is shown for the collinear orientation. The cross sections decrease with increasing energy and more and more states become accessible. Since, in the sudden limit, it is assumed that all internal states are degenerate, the only difference bearing on given collisions at different energies is the time the atom spends in the neighborhood of the molecule. An increase in energy means that the collision duration will be shorter so that there will be a smaller cross section for a given inelastic event due to the shortened interaction time. This behavior is also seen in Figure (6). Regularity in this behavior exists as long as no outside factors influence the situation. An example of such factors is seen in comparison of Figure (6) to Figure (7). The latter shows cross sections for another orientation ($\Theta = 3\pi/8$, $\Phi = \pi/2$). Here, oscillatory behavior similar to that observed for the transition probabilities in Figure (2B) begins to appear at the same energy as previously. The explanation is the same as that given for Figure (2B). A minimum in the phase shift vs. R at R = 0 combines with nodes in the wave function to produce the oscillations. A damping of this behavior occurs as a result of the average over impact parameters.

A set of orientation averaged cross sections was also calculated.

Figure 6--Cross Section, $Q_{v\,'_0}$, plotted against v' for

$\Theta = 0$, $\bar{\Phi} = 0$. Energies: $\triangle$: 1.7 eV CM,
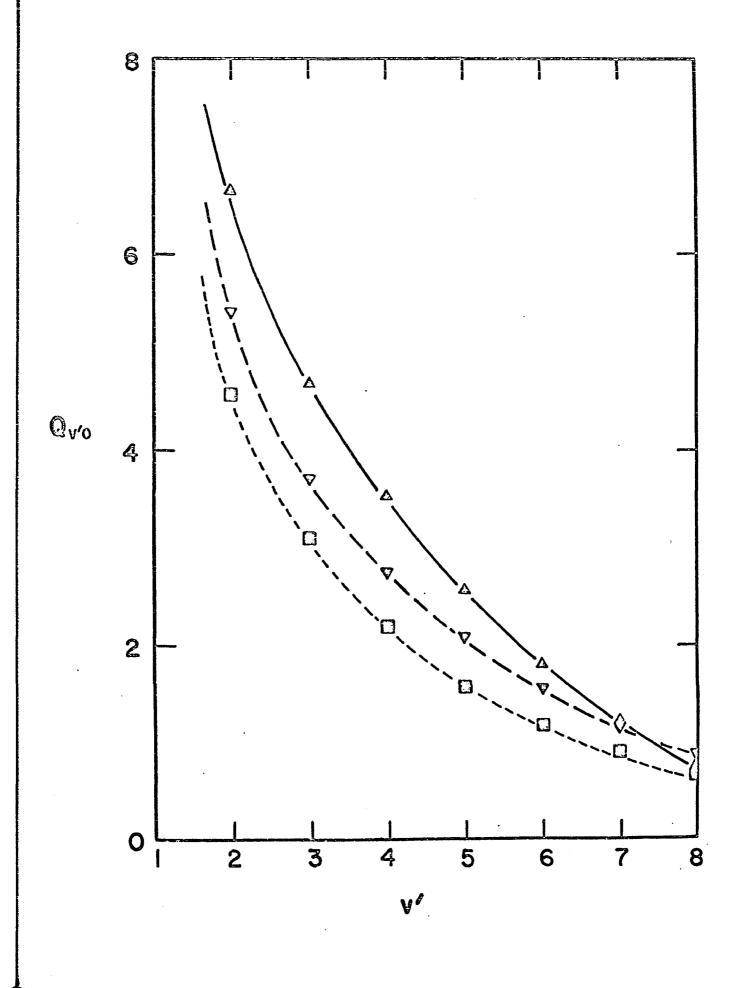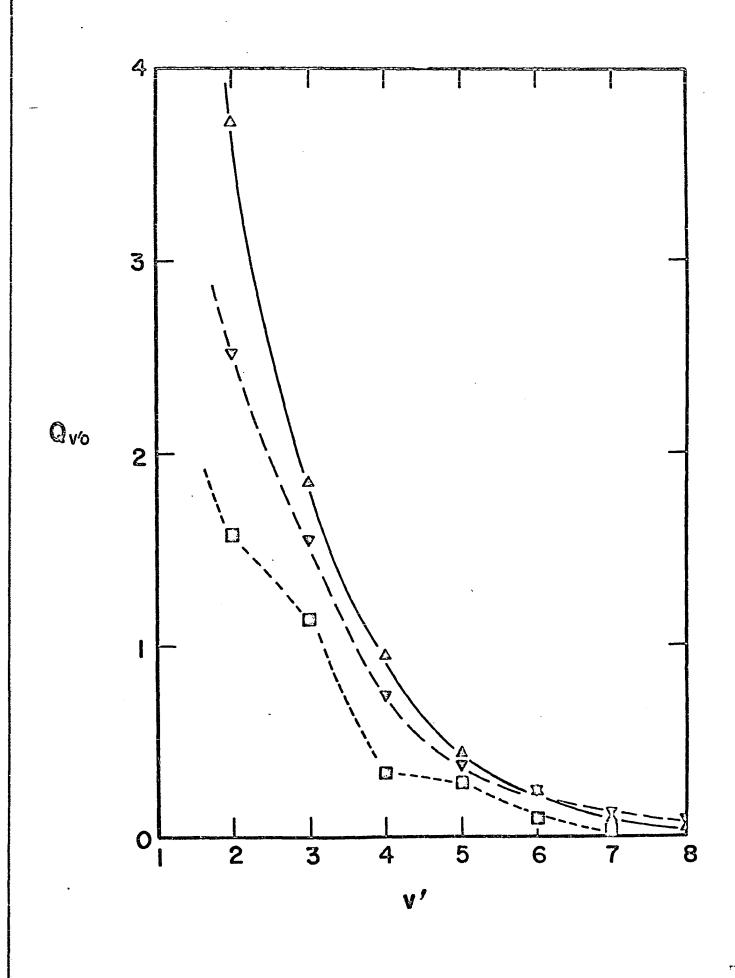
$\blacktriangledown$: 4.8 eV CM, $\square$: 12.4 eV CM.

Figure 7--Cross section, $Q_{v'o}$, plotted against v' for

$$\Theta = \frac{3\pi}{8} , \quad \bar{\varphi} = \frac{\pi}{2}.$$ Energies: $\triangle$:1.7 eV CM,

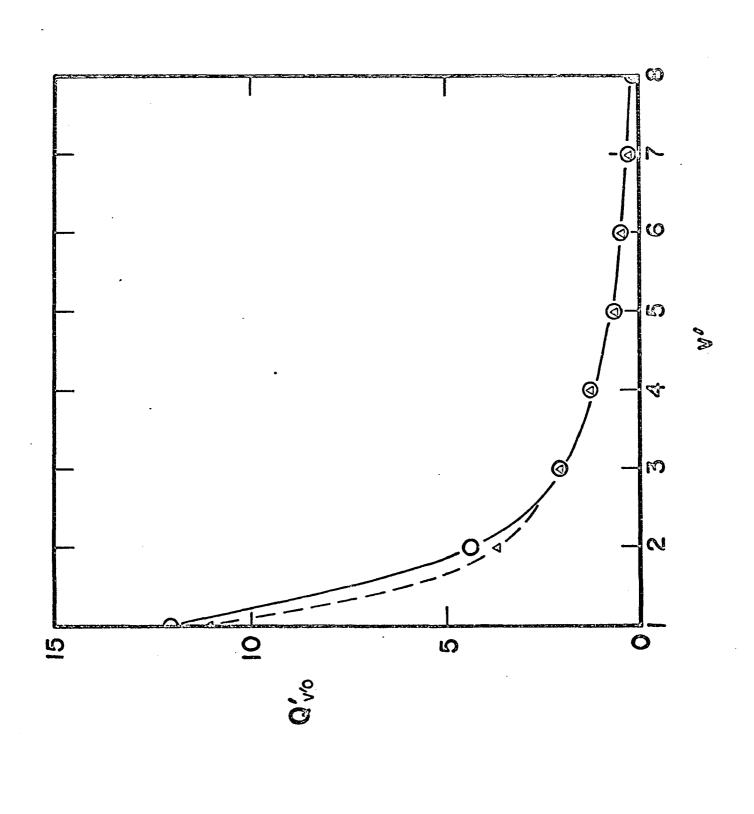∇ : 4.8 eV CM, $\square$: 12.4 eV CM.

These were compared with cross sections obtained by averaging $V_2(r, R, \gamma)$ over Θ and Φ before calculation. The results are shown in Figure (8) for $E \approx 4.8$ eV. Cross sections calculated via the two pathways agree closely. Similar results are obtained at 1.7 eV and 12.4 eV. Since the results agree so well and since the cross sections calculated from the averaged potential are much easier to calculate than a number of individual orientation cross sections, this may be the best way to obtain orientation averaged cross sections in cases like this where the potential is not too anisotropic.

Discussion

The sudden approximation represents a high energy limit as discussed previously. Results from calculations at this limit are therefore not expected to agree quantitatively with most other calculations or experiments, the majority of which have been done for low relative energy situations. They should give quantitative agreement with calculations and experiments only when the energies are of the order of several electron volts or higher since vibrational energies are on the order of .5 eV or lower. They are meant here to give a qualitative picture of the vibrationally inelastic scattering problem treated in three dimensions. As such, they give insights into the more commonly used assumptions in vibrationally inelastic scattering.

Figures (2) and (5) show orientation dependence of the transition probability and cross section, respectively. It is obvious from them that there is significant probability of an inelastic event occurring at almost any orientation and that it would be rather difficult to describe the details of the scattering given information from only the collinear orientation. Accordingly, it appears that use of a steric factor to generalize one dimensional results to three dimensions is invalid. This can be seen

Figure 8--$Q_v^{\prime},_v$ plotted against $v^{\prime}$ at 4.8 eV. $\bigcirc$:   cross

sections averaged over $\ominus$ and $\bar{\phi}$, $\triangle$: cross

sections for potentials averaged over $\ominus$ and $\bar{\phi}$.

from Table 1. The steric factor multiplies transition probabilities for the collinear case at b = 0, $P_{v'o}^{col}$, to give total cross section, $Q_{v'o}'$ for a given transition. It can therefore be defined as $Q_{v'o}'/ P_{v'o}^{col}$. Table 1 shows this ratio for various final states, v', at two different collision energies. The factor could also be defined as the ratio of the orientation averaged transition probability at b = 0, $P_{v'o}^{AVE}$, to $P_{v'o}^{col}$, also shown in Table 1. This steric factor gives transition probabilities for all orientations. The steric factors as defined here vary with energy and with transition. It would, therefore, be very hard to decide upon the proper steric factor to use in any given situation. Additionally, the behavior of the (0-0) transition probability as shown in Figure (4) indicates that it is insufficient to base assumptions concerning impact parameter dependence of transition probabilities on a breathing sphere model. Another often used model in vibrationally inelastic scattering is the envisioning of the vibrating molecule as two balls connected by a spring. This is one of the justifications for use of the steric factor since collinear collisions would be vastly more efficient for energy transfer in this model and other orientations would contribute uniformly and slightly. The model is partially valid as indicated in the discussion of Figures (4) and (5); however, the behavior exhibited in Figures (2B) and (7) indicates that the situation is not quite that simple. The markedly quantum mechanical interference behavior indicated by the oscillations points up the need for a more sophisticated model which includes the effects of the presence of the electron cloud as well as the behavior of the oscillator itself. Such a model was used in the calculation of the Krauss and Mies potential.

There are very few experimental results with which to compare calculations in this field. Held, Schüttler, and Toennies[9] have obtained

Table I.   Calculated Steric Factors

v$'$	$E_{cm} = 4.8$ eV		$E_{cm} = 12.4$ eV	
	$P^{AVE}_{v'o} / P^{COL}_{v'o}$	$Q'_{v'o} / P^{COL}_{v'o}$	$P^{AVE}_{v'o} / P^{COL}_{v'o}$	$Q'_{v'o} / P^{COL}_{v'o}$
1	$.111 \times 10^3$	$.604 \times 10^4$ a.u.^{2}	$.162 \times 10^3$	$.138 \times 10^4$ a.u.^{2}
2	$.127 \times 10^2$	$.479 \times 10^3$	$.355 \times 10^2$	$.840 \times 10^3$
3	$.490 \times 10$	$.105 \times 10^3$	$.581 \times 10$	$.154 \times 10^3$
4	$.164 \times 10$	$.286 \times 10^2$	$.247 \times 10$	$.336 \times 10^2$
5	$.856$	$.107 \times 10^2$	$.848$	$.113 \times 10^2$
6	$.480$	$.490 \times 10$	$.495$	$.426 \times 10$
7	$.318$	$.262 \times 10$	$.268$	$.211 \times 10$

results for direct backscattering of Li^+ from H_2. Their experiment consisted in scattering a beam of Li^+ atoms from H_2 and measuring only the scattering which occurred in the backwards direction in the center of mass system as a function of time. In this way, time lags could be associated with vibrational transitions. Their data takes the same form as that shown in Figure (2A). This behavior is similar to that found by Secrest and Johnson in their exact treatment of the collinear case.[19] The data is not expected to be in exact correspondence since the systems and potential forms used are different. The results here do not agree with the results obtained by Dittner and Datz for the backscattering of K^+ from H_2 and D_2.[7] Their results showed narrow distributions of vibrational states excited and indicates ·that perhaps there is a curve crossing affecting this system which makes the model used here invalid. Also, the mass ratio, K^+ to H_2, makes the sudden approximation invalid here. Cosby and Moran, however, found broad distributions of final states for Ar scattering from O_2^+ [6] which agrees with the results here.

The closeness of spherically averaged cross sections to those calculated by first averaging the potential over angles shown in Figure (8) is an indication that data from molecular scattering experiments is explicable in terms of a simple spherical potential rather than a complicated anisotropic one when rotational and vibrational transitions are summed over. This will be discussed further in the next section.

Semiclassical Differential Cross Sections for Molecular Scattering at High
Energies

The classical differential cross section for an elastic scatter-
ing event is well known and takes the form[46]

$$I(\chi) = b \left[\sin \chi \left| {}^{d\chi}/db \right| \right]^{-1} \tag{84}$$

where χ is the final deflection angle and b is the impact parameter. This
holds for spherical potentials where scattering out of the plane defined by
the center of mass distance, $\underset{\sim}{r}$, and the velocity, $\underset{\sim}{\dot{r}}$, does not occur. Here,
χ can be calculated rather simply as

$$\chi = \frac{2\hbar}{\mu v} \frac{\partial \eta}{\partial b} \tag{85}$$

where η is the phase shift, μ is the reduced mass of the system, and v is
the velocity. If the potential involved is not spherical, then scattering
out of the plane defined by $\underset{\sim}{r}$ and $\underset{\sim}{\dot{r}}$ can occur and (84) must be generalized
to

$$I(\chi, \phi') = b \left[\sin \chi \left| \partial (\chi, \phi') / \partial (b, \phi) \right| \right]^{-1} \tag{86}$$

where ϕ' is the final azimuthal angle and ϕ is the initial azimuthal angle.
(86) reduces to (84) for $V = V(r)$ which means that $\phi' = \phi, \phi + \pi$. χ and
ϕ' may be calculated semiclassically by use of expressions derived from (70).[48]
If one expresses (70) in a diagonal representation and evaluates the inte-
grals using the stationary phase approximation, one can make the following
identifications

$$\chi = \frac{2\hbar}{\mu v} \left[\left(\frac{\partial \eta}{\partial b}\right)^2 + b^{-2} \left(\frac{\partial \eta}{\partial \phi}\right)^2\right]^{\frac{1}{2}} \tag{87a}$$

$$\phi' = \phi + \arctan \left[\frac{(\partial \eta / \partial \phi)}{b(\partial \eta / \partial b)}\right]. \tag{87b}$$

Expressions (87) also reduce to the elastic ones for $V = V(r)$.

Expressions (86) and (87) will be used in the calculations which follow.

Calculations

The purpose of the following calculations is to compare differential cross sections at various final scattering angles calculated using (86) for a spherically symmetric potential with cross sections which are calculated by averaging cross sections obtained from a molecular coordinate dependent potential over molecular coordinates. In this way one can determine whether it is valid to interpret molecular scattering experiments in terms of spherical potentials.

Here, the He + H_2 system is studied at 4.8 eV CM energy. The sudden approximation, a high energy limit described in the previous section, was used to calculate phase shifts. The molecular coordinate dependent potential used is the unmodified Krauss and Mies potential. The spherical potential was obtained by spherically averaging the Krauss and Mies potential over molecular orientations and using the equilibrium oscillator position, R = 0. Straight line trajectories were used to calculate the phase shift and its derivatives, all of which could be calculated analytically. The calculation is limited to higher energies and small angles by the straight line trajectory assumption and the sudden approximation. The calculation can be outlined as follows:

Spherical Potential:

1) The desired final polar scattering angle was chosen and an initial guess at the correct impact parameter was made.

2) Phase shifts and derivatives were calculated for the impact parameter picked.

3) Newton's method was used to make closer and closer guesses at the correct impact parameter using (87).

4) When the correct value had been neared (within 10^{-3}), a differential cross section was calculated from (87).

Non-spherical Potential:

5) The final polar scattering angle, χ, is chosen to be the same as that for the spherical case and a final azimuthal angle, ϕ', is also chosen (usually $\phi' = 0$).

6) The impact parameter calculated as correct for the spherical case is used as an initial guess at the correct impact parameter here and a first guess is made at the initial azimuthal angle. The appropriate phase shifts and derivatives are then calculated.

7) A two dimensional Newton's method is used with (87) to iteratively calculate the correct impact parameter and initial azimuthal angle for the value of the initial internal molecular coordinates chosen. (86) is then used to calculate the cross section.

8) Steps 5) - 7) are repeated for the whole range of orientations and vibrational coordinates.

9) The cross sections obtained were averaged over orientation and vibrational coordinates using ground state harmonic oscillator wave functions to obtain values for comparison with the spherical results.
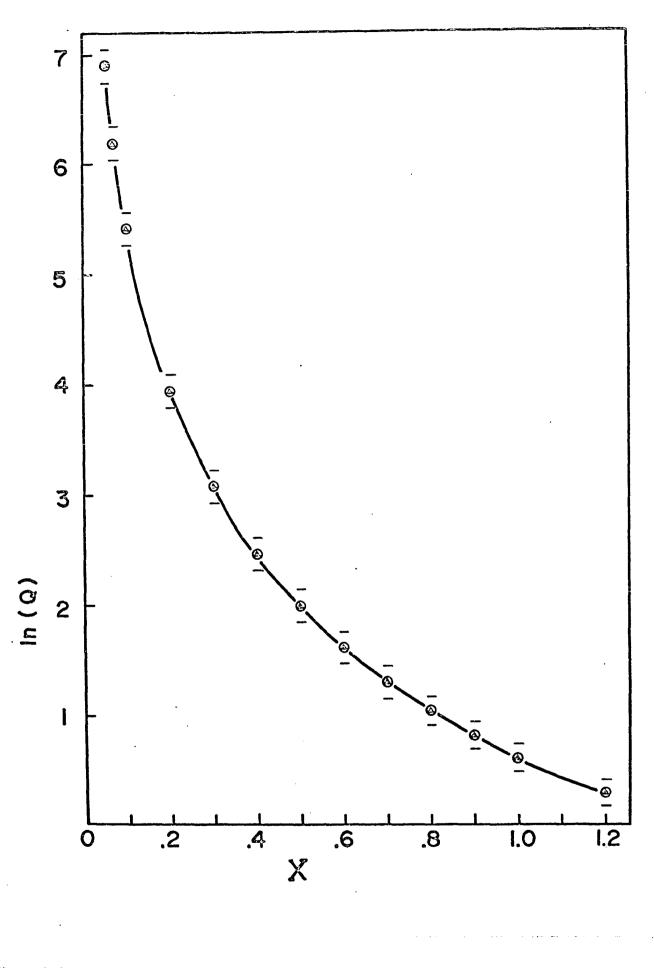
Results and Discussion

The results of the calculation are shown in Figure (9). The cross sections obtained from the spherical potential are compared with the averaged cross sections. They agree to within 0.1%. The bars represent the standard deviation in the cross sections involved in the average. In the sudden limit, this average is identical to summing over all inelastic

Figure 9--Differential cross section, $I(\chi)$, plotted against

scattering angle, χ, in radians at E = 4.8 eV CM.

$\triangle$: cross section for averaged potential,

$\bigcirc$: averaged cross sections. The bars are the

standard deviation in the cross sections compris-

ing the average.

transitions, so one must conclude that high energy scattering measurements may be interpreted in terms of a spherically symmetric potential which is just the average of the true potential over orientations and evaluated at the most probable vibrational coordinate. This conclusion is strengthened by the results given in the previous section, where orientation averages of cross sections for various transitions were compared with cross sections obtained from a spherically averaged potential as shown in Figure (8) for an energy of 4.8 eV. The agreement is not as close as that given for the differential cross sections, but it is sufficient so that the same conclusion may be drawn. These conclusions are not valid at low energies where the sudden approximation does not hold; however, at such energies, vibrationally inelastic scattering will not be important. The same results have, however, been shown previously for rotationally inelastic scattering.[47] The results will be valid for higher energies than the one given since the sudden approximation gives cross sections which bear a simple scaling factor relationship to each other at various energies.

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