WIS-ONR-5
9 October 1953

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WIS-ONR-5
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AN APPROXIMATE THEORY OF INELASTIC COLLISIONS**

by

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ABSTRACT

Approximate trajectories for describing the inelastic encounters between rigid diatomic molecules are described. These trajectories, together with quantum mechanical perturbation theory, are used to derive an approximate formulation of the inelastic differential scattering cross sections for such collisions. The quantum mechanical correspondence principle is used when necessary to bridge the gap between classical and quantum descriptions of the problem.

**This work was carried out at the University of Wisconsin Naval Research Laboratory under Contract N7onr-28511 with the Office of Naval Research. One of us (JFH) wishes to acknowledge the financial support which made this work possible. An Atomic Energy Commission Predoctoral Fellowship administered through the Oak Ridge Institute of Nuclear Studies provided support while most of this work and all of the preliminary work was being done. A General Electric Company Predoctoral Fellowship provided support while this work was being completed.

INTRODUCTION

A theoretical prediction of any of the non equilibrium properties of dilute gases depends on detailed information about the dynamics of a binary collision. One can, for example, calculate the transport coefficients of a rare gas if one knows the angle of deflection in an encounter as a function of the initial energy and angular momentum of the two body system. For more complex molecules, the probability of internal transitions accompanying the collision must also be known. Wang-Chang and Uhlenbeck[1] have derived a formal treatment of the kinetic theory of polyatomic molecules which is expressed in terms of a set of such differential scattering cross sections, one for every possible internal transition. Similarly, an exact theory of the pressure broadening of microwave spectral lines will require a knowledge of the probability of internal transitions accompanying collisions.

When molecules interact according to spherically symmetric laws of force and undergo only elastic collisions, the complete dynamics of a collision can readily by obtained. If one or both of these conditions are not satisfied, the problem becomes very much more difficult. Several investigations of transport phenomena of special molecular models with internal degrees of freedom have been carried out, but the two-fold difficulty of solving for the classical dynamics of an encounter, then of modifying the classical Boltzmann equation has usually led to inconclusive results. A brief summary of such work may be found in chapter seven of <u>The Molecular Theory of Gases and Liquids</u>

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[1] Wang-Chang-Chang, C. S., and Uhlenbeck, G. E. Univ. of Michigan publication CM-681 (1951)

by Hirschfelder, Curtiss, and Bird.

Rigorous quantum mechanical treatments of the problem are in progress and promise to yield the most fruitful results. The scattering of spherical molecules from slightly elongated ones has been worked out by Gioumousis and Curtiss[2] and is being used as the basis for a theory of the interaction of diatomic molecules. Buckingham and Delgarno[3] recently gave a remarkably successful solution for the diffusion and excitation transfer of metastable helium in normal gaseous helium. Although inelastic, this helium - metastable helium encounter is a case of exact resonance with a spherically symmetric potential, so that the theory is considerably simplified.

Unfortunately, the exact treatment of more complicated encounters may not be available for some time, so it would appear very desirable to develop an approximate theory of such inelastic encounters. We might expect that such an approximate theory, containing the essential features of inelastic collisions, would at least: 1) provide a basis for semi-empirical prediction of transport coefficients, and 2) indicate which features of the inelastic encounter cause important modifications in macroscopic phenomena.

In this report we describe such an approximate theory and apply it to the theory of transport properties. For convenience we will usually talk about the interaction of diatomic molecules, but wherever possible, we will proceed from the most general considerations so that the final result will at least suggest

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[2] Wis. ORD, OOR 8.

[3] Proc. Roy. Soc. A, 213, 506 (1952).

a treatment of more complicated situations. The purpose of the arguments will be two-fold: first to establish the validity of the overall procedure, to justify the use of the correspondence principle which makes the procedure possible, and secondly to indicate approximations which will make the method feasible for practical calculations. We will attempt to identify clearly the nature of all approximations as they are made, and to indicate their range of validity.

Beginning with the general quantum mechanical formulation of the problem, we will set up a solution in terms of a perturbation picture. It will be argued that the translational motion of the molecules can be treated classically, so that the zero order solution of this part of the problem will simply be classical elastic trajectories. For convenience, various approximations to the classical trajectories will be considered and compared. The nature of a trajectory in the vicinity of a sudden inelastic transfer will be discussed in general terms, giving certain restrictions or "selection rules" on the possible nature of the transfer at a point in space. Consistent with these selection rules, a method will be developed for treating an inelastic trajectory as a perturbation-induced transition between elastic trajectories. Finally, the formalism of a tentative procedure for determining the inelastic differential scattering cross sections will be developed.

A. QUANTUM MECHANICAL FORMULATION AND SEPARATION OF COORDINATES

Consider a system of two diatomic molecules "a" and "b", made up of atoms 1 and 2 in a, and 3 and 4 in b. For an arbitrary fixed set of coordinates, the Schroedinger equation of the system is

$$\sum_{i=1}^{4} \frac{1}{m_i} \nabla_i^2 \Psi - \frac{2}{\hbar^2}(V-E)\Psi = 0 \qquad (1)$$

Here ∇_i^2 is the Laplacian in the coordinates of the i'th atom. If we introduce relative coordinates:

$$\underline{r}_a = \underline{r}_1 - \underline{r}_2 \qquad\qquad \underline{r}_b = \underline{r}_3 - \underline{r}_4$$

$$\underline{R}_{ab} = \frac{m_1 \underline{r}_1 + m_2 \underline{r}_2}{m_1 m_2} - \frac{m_3 \underline{r}_3 + m_4 \underline{r}_4}{m_3 m_4} \qquad (2)$$

$$\underline{R} = \frac{(m_1+m_2)\left(\dfrac{m_1 \underline{r}_1 + m_2 \underline{r}_2}{m_1 m_2}\right) + (m_3+m_4)\left(\dfrac{m_3 \underline{r}_3 + m_4 \underline{r}_4}{m_3 m_4}\right)}{(m_1+m_2)(m_3+m_4)}$$

equation (1) becomes:

$$\frac{1}{M}\nabla_{\underline{R}}^2 \Psi + \frac{1}{\mu}\nabla_{\underline{R}ab}^2 \Psi + \frac{1}{\mu a}\nabla_{\underline{R}a}^2 \Psi \qquad (3)$$

$$+ \frac{1}{\mu b}\nabla_{\underline{R}b}^2 \Psi - \frac{2}{\hbar^2}(V-E)\Psi = 0$$

Here we have introduced reduced mass and total mass symbols

$$\mu_a = \frac{m_1 m_2}{m_1 + m_2} \qquad \mu = \frac{(m_1 + m_2)(m_3 + m_4)}{m_1 + m_2 + m_3 + m_4}$$

$$\mu_b = \frac{m_3 m_4}{m_3 + m_4} \qquad M = m_1 + m_2 + m_3 + m_4$$

This non singular, linear transformation amounts simply to using the well known separation of variables for two particle problem three times, once on each diatomic molecule, and once on the system of two molecules.

With the Schroedinger equation in this form it is quite easy to see the effects of various simple forms of the potential. Suppose the potential is the sum of separate terms:

$$V = V(r_a) + V(r_b) + V(R_{ab}) \tag{4}$$

Then there is a solution

$$\Psi(\underline{R}, \underline{R_{ab}}, \underline{r_a}\, \underline{r_b}) = X(\underline{R})\, \Phi(\underline{r_a})\, \Phi(\underline{r_b})\, \Theta(\underline{R_{ab}}) \tag{5}$$

where

$$\begin{aligned} &\frac{1}{M} \nabla^2_{\underline{R}} X + E_{trans} X = 0 \\ &\frac{1}{\mu_a} \nabla^2_{\underline{r_a}} \Phi_a - \frac{2}{\hbar^2}\left(V(\underline{r_a}) - E_a \right) \Phi_a = 0 \\ &\frac{1}{\mu_b} \nabla^2_{\underline{r_b}} \Phi_b - \frac{2}{\hbar^2}\left(V(\underline{r_b}) - E_b \right) \Phi_b = 0 \\ &\frac{1}{\mu} \nabla^2_{\underline{R_{ab}}} \Theta - \frac{2}{\hbar^2}\left(V(\underline{R_{ab}}) - E_{ab} \right) \Theta = 0 \end{aligned} \tag{6}$$

With this approximation, then we have separated the problem into four separate physically resonable parts. Equation 6.1 describes the motion of the center of mass of the whole system moving like a free particle of mass M.

The second and third equations describe internal motions of the molecules relative to their mass centers, and the last equation describes the relative motion of the two molecules relative to their joint center of mass. This motion can be described in terms of the equivalent one particle problem in which a particle of mass $M = \frac{M_a M_b}{M_a + M_b}$ moves under the influence of a potential $V(R_{ab})$. We will use this picture of the equivalent one particle problem in the rest of this report.

The influence of asymmetry in the potential field as far as modifying the trajectory and inducing internal transitions may now be treated as a perturbation problem. If the molecules had electric dipole moments, we would have such a potential of considerable physical interest. Before considering the effect of a perturbation, however, let us consider equations 6 in more detail.

The motion of the center of mass of the entire system will in general not enter into kinetic theory problems, so only the last three equations will be of interest. Equation 6.4, the relative motion of the molecules can frequently be replaced by its classical limit. The DeBroglie wave length of a molecule with energy kT is given, at room temperature, by $\lambda \doteq \frac{1.8}{\sqrt{M}}$ Å where M is the molecular weight. Or, from the point of view of the uncertainty principle, an uncertainty of 1 Å in the position leads to an uncertainty in the velocity such that $\frac{\Delta v}{v} \doteq \frac{0.3}{\sqrt{M}}$, again at room temperature. Thus, to a reasonable approximation, a classical trajectory may be used to describe the relative motion of the molecules. This approximation, of course, is the basis of the entire classical theory of transport properties; its validity over a rather wide range of conditions is shown by the success of that theory.

Clearly no such classical limit may be taken for equations 6.2 and 6.3. Solved with the usual approximations, these equations give the harmonic oscillator and rigid rotor wave functions. At ordinary temperatures only the lower vibrational and rotational levels will be populated, so that the quantum mechanical description of these coordinates of the system is necessary. In a great many special cases it will turn out that excitation of vibrational levels is very improbable in thermal collisions, so that only the rotational motion need be considered. For this reason we will concentrate on a treatment of the rotational motion, though the extension to include vibrational transitions would not be difficult.

B. APPROXIMATE TRAJECTORIES FOR ELASTIC COLLISIONS

Since the effect of a perturbation will in general be viewed as causing transitions among various unperturbed states of the system, it will first be necessary to investigate these unperturbed states. For the internal coordinates of a diatomic molecule, these are obviously the quantum mechanical wave functions for the harmonic oscillator and the rigid rotor. Since in the unperturbed state these do not change during a collision, the remainder of the zeroth order approximation is just the classical trajectory for the elastic collision of spherically symmetric molecules.

For the elastic classical trajectory we must first decide on some sort of effective spherical potential which will, in general, depend on the internal states of the two molecules. In the case of electric dipoles, this could be done by calculating the interaction energy of a pair of "clamped" rotating dipoles. This calculation has been done by London with his "Unscharfe Resonance", a modified second order perturbation technique. In any case, we will assume for the mement that we have such a potential $V_{ij}(R_{ab})$, where i and j denote the total quantum states of molecules a and b, and R_{ab} is the intermolecular distance. We also assume that this potential contains the necessary hard core or repulsive properties.

Elastic trajectories might now be calculated in the usual manner. Specification of g, the initial relative velocity, and b, the collision parameter or miss distance gives the energy and the absolute value of the angular mementum of the system. The distance of closest approach, r_m can now be calculated as the greatest positive root of the equation

$$1 - \frac{V_{ij}(r_m)}{\frac{1}{2} M g^2} - \frac{b}{r_m^2} = 0 \tag{7}$$

Then the angle of deflection χ is given by

$$\chi = \pi - 2 \int_{r_m}^{\infty} \left(\frac{r^4}{b^2} - r^2 - \frac{r^4 V_{ij}(r)}{b^2 \frac{1}{2} M g^2} \right)^{-\frac{1}{2}} dr$$

The resulting angles of deflection are rather complicated functions or r_m and b, so that it would be difficult to consider transitions among the elastic trajectories. Let us consider several approximate trajectories which would facilitate calculation. We observe that for certain rather simple trajectories the angle of deflection is uniquely determined by the ratio r_m/b. For $r_m > b$ the collision is repulsive, for $r_m < b$, it is attractive. To investigate the possibility of approximating the true trajectories by one of these simpler cases we will determine $\chi\left(\frac{r_m}{b}\right)$ for trajectories found when $V \propto \frac{1}{r}$ (Kepler orbits), $V \propto \frac{1}{r^4}$ (Maxwell molecules) and for a special trajectory of connected line segments. Then we will compare the functions $\chi\left(\frac{r_m}{b}\right)$ with values for the Lennard-Jones potential. For the Lennard-Jones potential χ is not a single valued function of r_m/b, but comparative numbers can be obtained over parts of the range by considering large b for attractive collisions and small b for repulsive ones.

a) Kepler trajectories

If $V = \frac{k}{r}$, the equation of the trajectory is easily shown to be the conic section

$$\frac{1}{r} = \frac{-k}{\mu g^2 b^2}(1 - e\cos\theta) \tag{8}$$

We are interested in the repulsive and attractive trajectories which are hyperbolae described by equation (8) if $e > 1$. If $k > 0$, the repulsive case, the center of force turns out to be an external focus of the hyperbola. $\chi\left(\frac{r_m}{b}\right)$ may be found as follows:

from equation (8)

$$r_m = \frac{\mu g^2 b^2}{k}\,\frac{1}{(e-1)} \tag{9}$$

from equation (7) for this potential

$$1 - \frac{2k}{\mu g^2 r_m} - \frac{b^2}{r_m^2} = 0$$

or

$$\frac{k}{\mu g^2} = \left[1 - \frac{b^2}{r_m^2}\right]\frac{r_m}{2} \tag{10}$$

solving for e ,

$$e = \frac{\left(\frac{r_m}{b}\right)^2 + 1}{\left(\frac{r_m}{b}\right)^2 - 1} \qquad r_m \geqslant b \tag{11}$$

If $\theta = \pm\psi$ are the directions of the assymptotes,

$$\cos\psi = \frac{1}{e} = \frac{\left(\frac{r_m}{b}\right)^2 - 1}{\left(\frac{r_m}{b}\right)^2 + 1} \tag{12}$$

Since the angle of deflection is given by

$$\chi = \pi - 2\psi \tag{13}$$

we have, finally,

$$\cos\chi = 1 - 2\left[\frac{\left(\frac{r_m}{b}\right)^2 - 1}{\left(\frac{r_m}{b}\right)^2 + 1}\right]^2 \tag{14}$$

For attractive collisions, $k < 0$ and $r_m \leqq b$, the center of force becomes an internal focus of the hyperbola. Letting $V = \frac{-k'}{r}$, and proceeding as above,

from equation (8)

$$r_m = \frac{\mu g^2 b^2}{k'(1+e)}$$

and from equation (7)

$$1 + \frac{2k'}{Mg^2 r_m} - \left(\frac{b}{r_m}\right)^2 = 0$$

we have

$$e = -\frac{\left(\frac{r_m}{b}\right)^2 + 1}{\left(\frac{r_m}{b}\right)^2 - 1}$$

so as before

$$\cos\chi = 1 - 2\left[\frac{\left(\frac{r_m}{b}\right)^2 - 1}{\left(\frac{r_m}{b}\right)^2 + 1}\right]^2$$

b) Repulsive potential proportional to $\frac{1}{r^4}$ (Maxwell molecules)

Let $V = \frac{k}{r^4}$, then the equation of the orbit is

$$\theta = \int_r^\infty \left[\frac{r^4}{b^2} - r^2 - \frac{k}{Eb^2}\right]^{-1/2} dr \tag{15}$$

where $E = \frac{1}{2}Mg^2$, b is the collision parameter or miss distance, and where $\theta = 0$ is parallel to the initial asymptote.

Let $x = \frac{b}{r}$ $\qquad x_0 = b\left(\frac{E}{k}\right)^4$

then

$$\theta = \int_0^{x_0} \left[1 - x^2 - \left(\frac{x}{x_0}\right)^4\right]^{-\frac{1}{2}} dx \tag{16}$$

The apse of the orbit, where $\frac{dr}{d\theta} = 0$, is given by the real positive root of

$$1 - x^2 - \left(\frac{x}{x_0}\right)^4 = 0 \tag{17}$$

Call this root $x_1 = \frac{b}{r_m}$. Then

$$\chi = \pi - 2\int_0^{x_1} \left[1 - x^2 - \left(\frac{x}{x_0}\right)^4\right] dx$$

The integral can be evaluated in terms of a complete elliptic integral of the first kind.

Let

$$a^2 = \frac{x_0^4}{2}\left[\sqrt{1+\frac{4}{x_0^4}} - 1\right]$$

$$b^2 = \frac{x_0^4}{2}\left[\sqrt{1+\frac{4}{x_0^4}} + 1\right] \qquad (18)$$

$$c^2 = a^2 + b^2 = x_0^4\sqrt{1+\frac{4}{x_0^4}}$$

then

$$\chi = \pi - 2x_0^2\int_0^{x_1}\left[(a^2-x^2)(b^2+x^2)\right]^{-1/2}dx \qquad (19)$$

This is a standard form of the incomplete elliptic integral of the first kind[4], so that

$$\chi = \pi - \frac{2}{\left(1+\frac{4}{x_0^4}\right)^{1/4}}F\left(\frac{a}{c}, \varphi\right) \qquad (20)$$

where

$$F(\kappa, \alpha) = \int_0^{\alpha}\frac{d\psi}{\sqrt{1-\kappa^2\sin^2\psi}}$$

and

$$\frac{\sin\varphi}{\sqrt{1-a^2/c^2\,\sin^2\varphi}} = \frac{cx_1}{ab}$$

Substituting from (17) and (18)

$$\chi = \pi - \frac{2x_1}{\sqrt{2-x_1^2}}K\left(\sqrt{\frac{1-x_1^2}{2-x_1^2}}\right) \qquad (21)$$

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[4] Jahnke and Emde Tables of Functions, Dover, 1945.

where

$$K(z) = \int_0^{\frac{\pi}{2}} \frac{d\psi}{\sqrt{1 - z^2 \sin^2\psi}} \,,$$

the complete elliptic integral of the first kind.

c) Attractive potential proportional to $\frac{-1}{r^4}$

Let $V = \frac{-k}{r^4}$, then proceeding as for Maswell molecules,

$$\Theta = \int_r^\infty \left[\frac{r^4}{b^2} - r^2 + \frac{k}{E b^2} \right]^{-1/2} dr \qquad (22)$$

Let

$$y = \frac{r}{b} \qquad\qquad A = \frac{k}{E b^4}$$

then

$$\Theta = \int_y^\infty \frac{dy}{\sqrt{y^4 - y^2 + A}}$$

Letting

$$\alpha^2 = \frac{1}{2}\left[1 - \sqrt{1-4A}\right]$$

$$\gamma^2 = \frac{1}{2}\left[1 + \sqrt{1-4A}\right]$$

gives

$$\chi = \pi - 2\int_{y_1}^\infty \frac{dy}{\sqrt{(y^2-\alpha^2)(y^2-\gamma^2)}} \qquad (23)$$

where y_1 is the largest positive real root of

$y^4 - y^2 + A = 0$

i.e. $y_1 = \gamma$. Again we have a standard form of the complete elliptic integral, giving, finally:

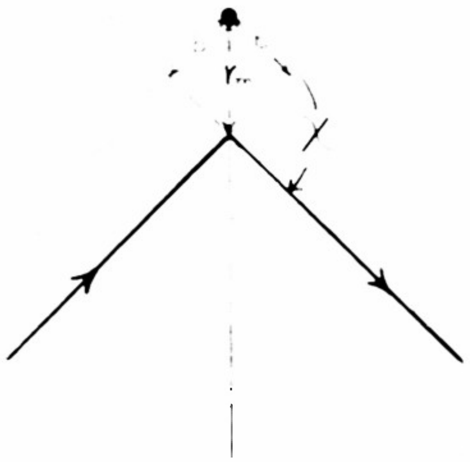
$$\chi = \pi - \frac{2}{y_1} K\left(\sqrt{\frac{1-y_1^2}{y_1^2}}\right) \qquad (24)$$

d) Straight line segments

Given r_m and b, we can specify an approximate trajectory such that the angle of deflection depends only on r_m/b by proceeding as follows:

For repulsive collisions ($r_m > b$) the molecule continues on its original straight line path until it reaches a distance r_m from the origin. At this point the molecule is deflected as though it were rebounding from a rigid sphere. (See Fig. 1).

Fig. 1



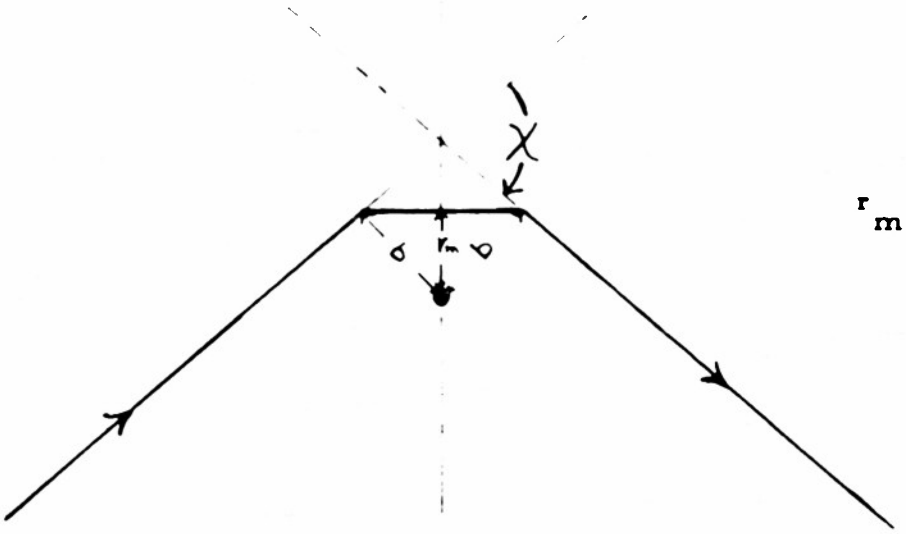
$r_m > b$

Simple geometry gives the angle of deflection

$$\cos \chi = 2\left(\frac{b}{r_m}\right)^2 - 1 \qquad (25)$$

For attractive collisions ($r_m < b$) the molecule continues on the straight line until it reaches a distance b from the origin. At this point it is deflected through an acute angle such that the new segment passes a distance r_m from the origin. The remainder of the trajectory is symmetric (See Fig. 2

Fig. 2



$r_m < b$

In this case

$$\cos\chi = 2\left(\frac{r_m}{b}\right)^2 - 1 \qquad (26)$$

In the following graph the functions $\cos\chi(r_m/b)$ are plotted against r_m/b for the various trajectories considered. For comparison, some Lannard-Jones values are given for several values of the reduced relative kinetic energy $g^* = \frac{\frac{1}{2}\mu g^2}{\epsilon}$ [5].

From the curves of Fig. 3, it is clear that the Kepler orbits are the poorest approximation to the trajectories produced by the more sharply varying intermolecular potentials.

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[5] The Molecular Theory of Gases and Liquids by Hirschfelder, Curtiss, and Bird (John Wiley & Sons, New York, 1954) (Appendix, Ch. 8 with Ellen L. Spotz).

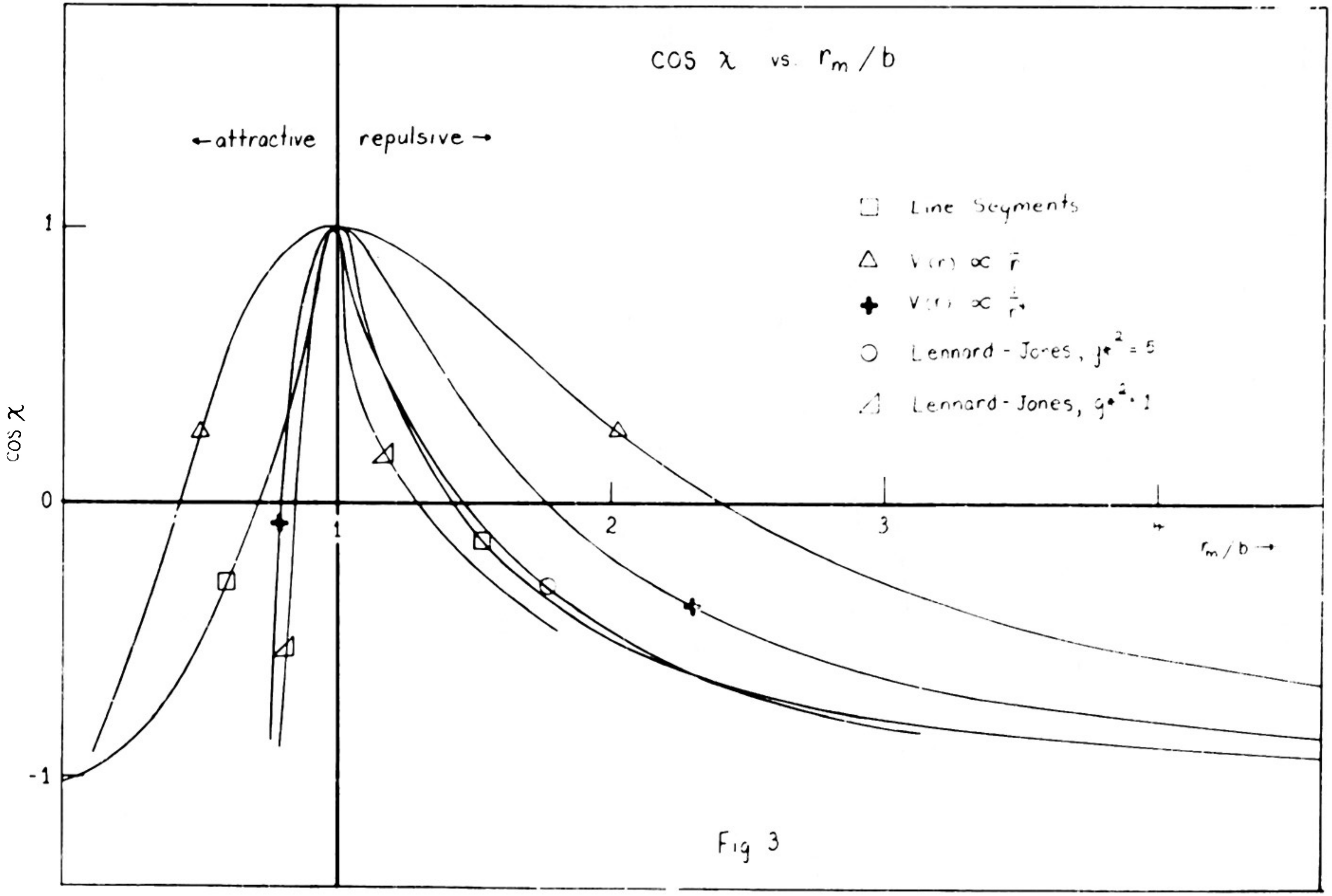
COS χ vs. r_m / b
←attractive
repulsive →
☐ Line Segments
△ $V(r) \propto \frac{1}{r}$
✚ $V(r) \propto \frac{1}{r^4}$
○ Lennard-Jones, $g^{*2} = 5$
◺ Lennard-Jones, $g^{*2} = 1$
cos χ
1
0
-1
1
2
3
4
r_m / b →

Fig 3

Choice between the line segments and the $1/r^4$ orbits would depend on ease of manipulation and success in giving the desired cross sections. For repulsive encounters the connected line segments give remarkably good answers. Since these line segment orbits would be expected to give the largest deflection of any purely repulsive trajectory characterized by a certain r_m, it must be that the attractive part of the Lennard-Jones potential tends to compensate for the softness of the repulsive part, resulting in a nearly hard sphere deflection.

In attractive encounters the line segments give good answers for r_m slightly less than b, but they do not reflect the orbiting tendency as r_m is decreased. The line segments, for example, give full 180° deflection only as r_m approaches zero.

To complete the specification of any of these approximate trajectories, we need only assign a speed to the particle at each point. Clearly this cannot, in general, be done so as to conserve both energy and angular momentum. Since we plan eventually to use the trajectories in a time dependent perturbation calculation of transition probabilities, we are most concerned with the time spent in each region of the potential. Now, the approximate trajectories have been adjusted so as to traverse the same region of the potential as the true trajectory. $r_m \leqslant r \leqslant \infty$, so it would appear reasonable to adjust the speed at each point so as to keep the total energy of the system constant. Angular momentum conservation would adjust the speed according to the direction of motion at the point in question, a feature of little interest to us as long as the total deflection of the path is nearly correct.

It is encouraging to note that at the distance of closest approach our attractive trajectories coincide with a point of a true trajectory with the correct energy and angular momentum parameters. It is from this region that we expect the greatest contribution to transition probabilities.

C. THE INELASTIC TRANSFER

Consistent with our perturbation picture we will want to consider transitions between elastic trajectories. Before investigating such transitions in terms of any of the approximate trajectories considered in the previous section, however, let us look at the limitations imposed by the conservation laws of classical mechanics on <u>any</u> trajectory at the moment of inelastic transfer.

The dynamic state of an encounter between linear rotating rigid molecules in conveniently specified, when the molecules are far separated, by the eight variables b, g, $\underline{\ell_a}$, and $\underline{\ell_b}$, where we have chosen a coordinate system such that the motion lies in the xy plane. $\underline{\ell_a}$ and $\underline{\ell_b}$ are the angular momenta due to the rotation of molecules a and b. The angular momentum due to translational motion relative to the center of mass is $\underline{\ell_T} = \mu g b\, i_z$. The internal energies ϵ_a and ϵ_b, and the translational energy ϵ_T are easily determined in terms of these variables.

Let us suppose that at some point along a trajectory determined by these initial conditions and the potential function $V_{(r)}$ there occurs an instantaneous change in the internal dynamic state such that $\underline{\ell_a} \rightarrow \underline{\ell_a'}$ and $\underline{\ell_b} \rightarrow \underline{\ell_b'}$ with the new potential $V'_{(r)}$. Applying the conservation laws of energy and angular mementum, we have

$$E = \epsilon_a + \epsilon_b + \epsilon_T(r) + V(r) = \epsilon_a' + \epsilon_b' + \epsilon_T'(r) + V'(r)$$

$$\underline{L} = \underline{\ell_a} + \underline{\ell_b} + \underline{\ell_T} = \underline{\ell_a'} + \underline{\ell_b'} + \underline{\ell_T'} \qquad (27)$$

To interpret the consequences of these equations, consider figure 4

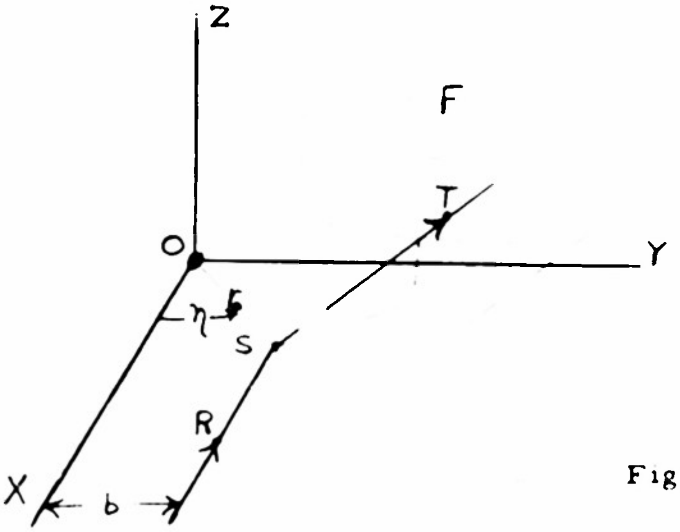

Fig 4

Here we picture the situation in terms of the equivalent one particle problem as usual. $\overline{RS}$, lying in the xy plane, is the segment of the trajectory just before the transition. The transition occurs at S, so $\overline{ST}$ is the trajectory immediately after transition. In general $\overline{ST}$ does not lie in the xy plane, but in a new plane determined by $\overline{ST}$ and point 0; we designate this as plane F. The xy plane and F intersect along $\overline{OS}$. The molecules are separated a distance r_o at the instant of transition.

Now, the total angular mementum is conserved, so in particular the component along $\overline{OS}$ must be constant. Thus:

$$(\underline{\ell}_a + \underline{\ell}_b + \underline{\ell}_T)_{OS} = (\underline{\ell}_a' + \underline{\ell}_b' + \underline{\ell}_T')_{OS}$$

But $\underline{\ell}_T$ and $\underline{\ell}_T'$ are clearly perpendicular to $\overline{OS}$ so that

$$\frac{(\underline{\ell}_a + \underline{\ell}_b)_x - (\underline{\ell}_a' + \underline{\ell}_b')_x}{(\underline{\ell}_a + \underline{\ell}_b)_y - (\underline{\ell}_a' + \underline{\ell}_b')_y} = \frac{\Delta(\underline{\ell})_x}{\Delta(\underline{\ell})_y} = \tan\eta \qquad (28)$$

or where $\underline{\ell}$ is the total internal angular mementum, and η is the angle in the xy plane as shown in Fig. 3. This result might be looked upon as a restriction on the possible redistribution of x and y components of the internal angular mementum for a given point on the trajectory. Alternatively, and more convenient for our purposes, it specifies the point or points (if any) on the trajectory at which a specified transition could take place. Let us see how this restriction might operate in practice for any purely attractive or repulsive trajectories. If $\theta = 0$ is the direction of the initial asymptote of a trajectory, as in Fig. 4, then for a repulsive collision the direction of the final asymptote θ_f will lie in the range $0 \leq \theta_f \leq \pi$. Since the tangent function is single valued on the interval $(0, \pi)$ a specified transition can lead to <u>at most one</u> allowable solution of equation 28. For attractive collisions, on the other hand, so that there will certainly be one solution η on the interval $(0, \pi)$ and it is quite possible that $\eta + \pi$ will also be acceptable. Qualitatively, however, it can already be observed that there will be a rather limited range of η such that the two points on the curve represented by η and $\eta + \pi$ will lie at about the same distance from the origin. Since we expect that the probability of transition will fall off rapidly with increasing separation of the molecules, it will frequently happen that only one of the allowed transition points is physically important.

From the energy equation:

$$\epsilon_T'(r_0) = \frac{1}{2} H g(r_0)^2 = E - \epsilon_a' - \epsilon_b' - V'(r_0). \qquad (29)$$

Solving for g' we have the speed of the particle after the transition. If this result is imaginary, we conclude that the transition is energetically forbidden. It is interesting to note at this point that if one were considering this problem in terms of curves on a multidimensional energy surfaces, this last result would simply be the Franck-Condon principle restricting transitions between such curves.

To complete our analysis of the transition we use the angular momentum equation again:

$$\underline{\ell_T'} = \underline{L} - \underline{\ell_a'} - \underline{\ell_b'}$$

The direction of $\underline{\ell_T'}$ determines the plane of the new trajectory. The selection rule on η has assured us that this plane will pass through $\overline{OS}$ (Fig. 4) so this last item of information gives us the angle between plane F and the xy plane. From the magnitude of $\underline{\ell_T'}$ we determine the new collision parameter

$$b' = \frac{|\ell_T'|}{g'} \qquad (30)$$

Apparently, if $b' > r_0$ no satisfactory trajectory can be constructed, so this result constitutes a third selection rule on the transition. If $b' < r_0$, surprisingly enough, there are two possible directions for the new trajectory, corresponding to the two tangents to a circle of radius b which pass through a point in the plane outside of the circle. Each of these directions is consistent with the total angular mementum of the system. The dual choice may also be seen directly from the expression for angular momentum, $\underline{L} = \underline{r} \times \underline{p}$. Working in the plane of r and p, $L = rp \sin\varphi$, where φ is the angle from $\underline{r}$ to $\underline{p}$. Apparently for a given $\underline{L}$, $\underline{r}$, and $\underline{p}$, both φ and $\pi - \varphi$ are acceptable solutions.

That the choice is really unique, however, may be argued as follows: Let us suppose that the inelastic transition specified by $\ell_a \rightarrow \ell_a'$ and $\ell_b \rightarrow \ell_b'$ approaches zero in such a way that $\frac{\Delta \ell_x}{\Delta \ell_y}$ as defined by equation (28) remains constant, thus keeping the transition at the same point on the trajectory. In the limit of no transition, the equations of motion say that the particle continues on the smooth course rather than taking the abrupt change in direction which would also be consistent with the energy and angular momentum of the system. Thus, if the particle is on the approaching branch of an elastic trajectory, it does not jump suddenly to the corresponding point on the receding branch. Now, a finite transition at the specified point on the trajectory may be considered as a series of small transitions with constant $\frac{\Delta \ell_x}{\Delta \ell_y}$. Then, by continuity of the whole process, the particle finds itself on that point of the new trajectory which corresponds to the starting point on the old trajectory, correspondence being interpreted in terms of the picture in which one trajectory is continuously transformed into the other by a progressively increased magnitude of the inelastic transfer. In practice this simply means that if the particle is on the approaching (receeding) part of one trajectory, it must appear on the approaching (receeding) part of the new trajectory.

Thus, in terms of a proposed transition, we have determined where the transfer could take place and what the speed and direction of motion of the particle must be after the transition. In the course of getting this information from the energy and angular momentum conservation laws, we have found three rather simple criteria or "selection rules" for determining whether the transition could take place at all:

1. η as given by equation 28 must lie on the initial trajectory.
2. g' as given by equation 29 must be real.
3. b' as given by equation 30 must be less than the separation of the molecules at the time of transition.

The second and third of these criteria simply tell whether or not the transition has taken place in a region compatable with the total energy and angular momentum of the system. The first is a restriction on the redistribution of angular momentum due to the fact that the trajectory must be continuous.

In the next section we will consider the application of these results to the problem of compounding our approximate elastic trajectories to represent inelastic encounters.

D. APPROXIMATE TRAJECTORIES FOR INELASTIC COLLISIONS

To be consistent with our approximations at this point, we must seek an inelastic trajectory such that energy is conserved at every point on it and such that the angular momentum is conserved when the molecules are far separated before and after the encounter. Such a trajectory may be constructed by the following procedure:

1. Given $\underline{\ell}_a$, $\underline{\ell}_b$, b, g and V(r) we have the approximate elastic trajectory $r = T(\theta)$. Specifying the transition by the new rotational angular momenta $\underline{\ell}_a'$ and $\underline{\ell}_b'$, we solve for an angle η as in the preceeding section. If the lines $\theta = \eta$ or $\theta = \eta - \pi$ do not interest T, the transition is impossible. If one or both of these intersections exist, we have possible points for the transition. Suppose $r_o = T(\eta)$ is an intersection.

2. At r_o we investigate equation 29, the energy equation, to determine the new relative speed g'. Since energy is to be conserved at every point, we apply the second selection rule rigorously and call the transition forbidden if g' is imaginary. Suppose g' is an acceptable solution of equation 29.

3. Strict application of the third selection rule on angular momentum at the transition point would now be inconsistent. Such a restriction would demand that this point on the new trajectory $r = T'(\theta')$ have correct energy and angular momentum, too stringent a condition for an approximate trajectory. Though certainly not undesirable in itself, such a restriction at this point would completely determine the rest of the path and would not leave us free to

adjust the asymtotic value of the angular momentum.

Instead, we simply use the direction of $\underline{\ell}_T' = \underline{L} - \underline{\ell}_a' - \underline{\ell}_b'$ to give us the orientation of the plane F in which the new trajectory $r = T'(\theta')$ must lie. Since the elastic trajectories lie in a plane, this will also be acceptable asymptotically. From E, $|L|$ and $V'(r)$ we can determine the shape of $T'(\theta')$ completely, lacking only its orientation in the plane F. Apparently if r_m' is greater than r_o, no orientation of T' will provide a continuous transition between T and T', so that the third selection rule appears here in a rather denatured form. If r_m' is less than r_o there will be two orientations of T' in F which will intersect T at r_o, but from the argument in the preceeding section the choice must be made so that the particle continues approaching or receeding from the apse of T' according to its motion on T.

Thus, we have a simple and unique method for construction of approximate inelastic trajectories.

E. THE INELASTIC DIFFERENTIAL SCATTERING CROSS SECTIONS

So far we have described a method for constructing approximate inelastic trajectories in terms of a combination of classical and quantum mechanical concepts. We have assumed a classically exact knowledge of all coordinates, but at the same time we considered a discontinuous change in the internal coordinates - a distinctly quantum mechanical idea. We now wish to use this information to solve the quantum mechanical scattering problem and determine the inelastic differential scattering cross sections $I_{ij}^{kl}(g,\alpha,\psi)$ in terms of which Uhlenbeck[1] has developed a theory of the transport phenomena.

$I_{ij}^{kl}(g,\alpha,\psi)$ may be defined as follows. Let α and ψ be the polar and azimuthal angles of the final relative velocity vector, measured from the initial relative velocity vector; let i and j signify all of the necessary quantum numbers to specify the initial internal quantum states of molecules a and b; and let k and l represent these quantum numbers after the encounter. Then $I_{ij}^{kl}(g,\alpha,\psi)\sin\alpha\, d\alpha\, d\psi$ is the probability that from a uniform beam (plane wave) of molecules in state i incident on a molecule in state j, with relative velocity g, a given molecule is scattered into the solid angle $\sin\alpha\, d\alpha\, d\psi$ about α, ψ while the internal quantum states go to k and l during the encounter.

If $\underline{\ell}_a$ and $\underline{\ell}_b$ are expressed in terms of the polar variables ℓ_a, θ_a, and φ_a, ℓ_b, θ_b and φ_b, the quantum numbers ij, kl are sufficient to specify the classical variables ℓ_a, θ_a, ℓ_b, θ_b, ℓ_a', θ_a', ℓ_b' and θ_b'. Thus the definition of the scattering cross section can be reformulated in terms of classical variables as follows: In the encounter specified by g, ℓ_a, θ_a, ℓ_b, and θ_b, what is the probability of scattering into $\sin\alpha\, d\alpha\, d\psi$ while the internal coordinates go to ℓ_a', θ_a', ℓ_b', and θ_b'?

In order to specify α and ψ, from our classical derivation, however, we need information about the extra variables φ_a, φ_b, φ_a', and φ_b' or their equivalent. If we can get the probability of the desired scattering event by assigning probabilities to these extra variables according to the quantum mechanical correspondence principle, then average over the extra variables, we ought to have an approximation of the differential cross sections, valid in the correspondence limit.

For a uniform beam of incident particles (the correspondence limit of a plane wave) the relative probability of a collision parameter in the range b, db is just $\pi b \, db$ Similarly in the correspondence limit the azimuthal angle of the angular momentum vector of a rigid rotor is completely uncertain, so that the probability density function for the unprimed φ's is just $\frac{1}{2\pi}$. For the primed φ's, however, the situation is a little different. If the transition occurs at a point r_o on the trajectory, all values of φ'_a and φ'_b are equally likely provided they are consistent with the first selection rule $\frac{\Delta \ell_x}{\Delta \ell_y} = \tan \eta$. Apparently this problem can be handled if we change variables from φ'_a and φ'_b to the arc length s, according to the first selection rule, and a variable z equal, say, to φ'_a. Now, if we can find a function $f(u)$ such that $f(s)\,ds$ is the probability of transition in the interval s, ds, then we know that all values of z will have probability consistent with all φ'_a and φ'_b equally likely. If $z = \varphi'_a$, for example, all z will be equally probable since the relation between φ'_a and φ'_b is satisfied automatically by the choice of s.

The function $f(s)\,ds$ is easily gotten from time dependent perturbation theory. Let us define the function $f'(ij, kl, b. g|t)$ so that $f'dt$ is the probability that the ij, kl tranasition takes place at t, dt when we are on the elastic trajectory determined by b, g, and ij. Let $\Phi_a^i(\underline{r_a})$ and $\Phi_b^j(\underline{r_b})$ be the wave functions of molecules a and b when they are in the i'th and j'th quantum states respectively, and let $V(\underline{r_a}, \underline{r_b}, t)$ be the interaction potential at time t . Then

$$a_{ij}^{kl}(t) = \frac{-i}{\hbar}\int_{t_0}^{t} e^{\frac{i}{\hbar}(E_{kl}-E_{ij})}\, V_{ij}^{kl}(t)\, dt \qquad (31)$$

where the probability of transition up to time t is

$$P_{ij}^{kl}(t) = \left| a_{ij}^{kl}(t) \right|^2$$

Here

$$a_{ij}^{kl}(t_0) = 0 \quad kl \neq ij$$

$$= i \quad kl = ij$$

and

$$V_{ij}^{kl}(t) = \int \Phi_a^{k*} \Phi_b^{l*} V(\underline{r}_a, \underline{r}_b, t)\, \Phi_a^i \Phi_b^j \, d\underline{r}_a \, d\underline{r}_b$$

Dropping the extra indices for a moment, let us expand $a(t)$ in a Taylor's series about some time $t_1 > t_0$

$$a(t) = a(t_1) + \left(\frac{d\,a(t)}{dt}\right)_{t=t_1} \Delta t + \cdots$$

so

$$P(t) = |a(t)|^2 = |a(t_1)|^2 + \left[a(t_1)\left(\frac{d\,a(t)}{dt}\right)^*_{t=t_1} + a^*(t_1)\left(\frac{d\,a(t)}{dt}\right)_{t=t_1} \right] \Delta t + \cdots$$

or

$$P(t) - P(t_1) = 2 \,\mathcal{R}e\; a(t_1)\left(\frac{d\,a(t)}{dt}\right)^*_{t=t_1} \Delta t$$

Apparently

$$f'(t) = \lim_{\Delta \to 0} \frac{P(t) - P(t_1)}{\Delta t} = 2 \,\mathcal{R}e\; a(t_1)\left(\frac{d\,a(t)}{dt}\right)^*_{t=t_1}$$

where $f'(t)$ is just the function we are seeking. Explicitly

$$f'(ij,k\ell,b,g|t) = \frac{2}{\hbar^2}\mathcal{R}e\, e^{-\frac{i}{\hbar}\Delta E t}\, V_{ij}^{*k\ell}(t)\int e^{\frac{i}{\hbar}\Delta E t}\, V_{ij}^{k\ell}(t)\, dt \qquad (32)$$

Here we assume that the encounter started at $t = -\infty$. Since the arc length s is a more convenient variable for us than the time, we write

$$\begin{aligned} f'(ij,k\ell,b\ g|t)\, dt &= f'(ij,k\ell,b\ g|t(s))\,\frac{dt}{ds}\, ds \\ &= f(ij,k\ell,b,g|s)\, ds \end{aligned} \qquad (33)$$

where $\frac{dt}{ds}$ is simply the reciprocal of the velocity at the point in question.

Before writing down a general formulation, let us introduce one new function $\xi(ij\ .\ k\ell\ ,\ b\ ,\ g\ ,\ \varphi_a\ ,\ \varphi_b\ ,\ \bar{z}\ ,\ s)$ which symbolically contains the last two selection rules. Thus, for a point s on the trajectory determined by b , g , ij , and $k\ell$, ξ is zero if the ij , kl transition is forbidden according to the last two selection rules and is unity if it is allowed.

We are now in a position to write down a formal procedure for determining $I_{ij}^{k\ell}(g,\alpha,\nu)$. In actual calculations a judicious choice of variables and sequence of calculation, as well as some approximations, will doubtless present themselves. The following formulation, therefore, is to be taken only as a formal presentation of the procedure.

The event of interest, a collision with definite scattering angles, is specified classically by the fourteen variables b , g , ij , kl , φ_a , φ_b , φ_a' , φ_b' . For a given g and ij , kl we wish to find the probability distribution function of the variables α and ψ. Let us use the first selection rule to introduce the arc length s as a new variable in place of, say, φ_b'.

For these variables we know all of the necessary probability functions. Let $P_{ij}^{kl}(g/b, \varphi_a, \varphi_b, \varphi_a', s)\, db\, d\varphi_a\, d\varphi_b\, d\varphi_a'\, ds$ be the probability of an inelastic collision in which the variables b, φ_a, φ_b, φ_a', and s lie in the specified ranges. From the preceeding discussion

$$P_{ij}^{kl}(g/b, \varphi_a, \varphi_b, \varphi_a', s) = (\cdot\ b)\left(\frac{1}{2\pi}\right)^3 f(ij, kl, b, g/s)\, \xi(ij, kl, b, g, \varphi_a, \varphi_b, \varphi_a', s) \qquad (34)$$

Now for a given g, ij, kl let us introduce new variables

$$\begin{aligned}
\alpha &= A(ij, kl, g/b, \varphi_a, \varphi_b, \varphi_a', s)\\
\psi &= \Psi(ij, kl, g/b, \varphi_a, \varphi_b, \varphi_a', s)\\
\chi_1 &= X_1(ij, kl, g/b, \varphi_a, \varphi_b, \varphi_a', s)\\
\chi_2 &= X_2(ij, kl, g/b, \varphi_a, \varphi_b, \varphi_a', s)\\
\chi_3 &= X_3(ij, kl, g/b, \varphi_a, \varphi_b, \varphi_a', s)
\end{aligned} \qquad (35)$$

Here χ_1, χ_2 and χ_3 are properly chosen combinations of the original variables which make the transformation convenient and non singular. Very likely the χ's will best be chosen in a simple manner such as $\chi_1 = b$, $\chi_2 = s$ and $\chi_3 = \varphi_a$.

Introducing these new variables in our probability function

$$P_{ij}^{kl}(g/b,\varphi_a,\varphi_0,\varphi_a',s)\,db\,d\varphi_a\,d\varphi_0\,d\varphi_a'\,ds$$

$$= P_{ij}^{kl}(g/b,\varphi_a,\varphi_0,\varphi_a',s)\,\frac{\partial(b,\varphi_a,\varphi_0,\varphi_a',s)}{\partial(\alpha,\psi,\chi_1,\chi_2,\chi_3)}\,d\alpha\,d\psi\,d\chi_1\,d\chi_2\,d\chi_3 \tag{36}$$

$$= P_{ij}'^{kl}(g/\alpha,\psi,\chi_1,\chi_2,\chi_3)\,d\alpha\,d\psi\,d\chi_1\,d\chi_2\,d\chi_3$$

If we now integrate over the appropriate ranges of χ_1, χ_2, and χ_3 we have

$$P_{ij}''^{kl}(g,\alpha,\psi) = \int_{\chi_1}\int_{\chi_2}\int_{\chi_3} P_{ij}'^{kl}(g,\alpha,\psi,\chi_1,\chi_2,\chi_3)\,d\chi_1\,d\chi_2\,d\chi_3 \tag{37}$$

Now $P_{ij}''^{kl}(g,\alpha,\psi)\,d\alpha\,d\psi$ is just the probability of scattering into $\alpha, d\alpha$ and $\psi, d\psi$ so that

$$P_{ij}''^{kl}(g,\alpha,\psi)\,d\alpha\,d\psi = I_{ij}^{kl}(g,\alpha,\psi)\sin\alpha\,d\alpha\,d\psi$$

or

$$I_{ij}^{kl}(g,\alpha,\psi) = \frac{1}{\sin\alpha}\,P_{ij}''^{kl}(g,\alpha,\psi)$$

Thus we finally have the desired result:

$$I_{ij}^{kl}(g,\alpha,\psi) =$$

$$\frac{1}{8\pi^2\sin\alpha}\iiint_{\chi_1\chi_2\chi_3} b\,f(ij,kl,b,g,s)\,\mathcal{G}(ij,kl,b,g,\varphi_a,\varphi_0,\varphi_a',s)\,\frac{\partial(b,\varphi_a,\varphi_0,\varphi_a',s)}{\partial(\alpha,\psi,\chi_1,\chi_2,\chi_3)}\,d\chi_1\,d\chi_2\,d\chi_3 \tag{38}$$