Study of the Statistical Model for Molecular Collisions

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I. INTRODUCTION

Unless one is prepared to integrate a large number of coupled radial equations numerically, there is no completely satisfactory manner of dealing with molecular collisions that involve strong coupling between the various possible channels. This strong coupling situation arises even in the simple one-channel case of potential scattering for small values of l (the orbital angular momentum), and the Massey–Mohr and Landau–Lifshitz approximations¹ made explicit use of the fact that the phase shift is large and essentially random. Bernstein, Dalgaro, Massey, and Percival² have used this same random phase idea to approximate the S matrix for a multichannel collision process [an atom plus a rigid rotor (diatomic molecule)], and Light³ and his co-workers have pursued and developed this approximation even further, applying it to more complicated systems and terming it the "statistical model." The statistical model has also found extensive use in nuclear theory.⁴a

In this paper, we wish to examine the statistical model from two points of view—formal derivation and application to simple examples. Section II presents a derivation of the statistical result from Feshbach's formal theory of resonant collisions.⁴b The statistical limit may also result from mechanisms other than the formation of a collision complex,²,⁸ but complex formation is one situation in which it is certainly expected to apply. By examining the structure of the formal expressions, one is able to see what restrictions must be imposed on any statistical-like parameterization and, therefore, what extensions are possible. Section III presents a detailed treatment of the rigid-rotor–atom collision in a simplified statistical approximation in order to see what general features one might expect from the model; total and differential cross sections are considered. Section IV considers another example, the Cs+RbCl reaction studied experimentally by Miller, Safron, and Herschbach.⁶

II. STATISTICAL APPROXIMATIONS FROM COMPLEX FORMATION

The collision system we have in mind throughout this paper is that of an atom and a diatomic molecule, although most of the results are by no means limited to this system. Application of Feshbach's⁴b theory of resonance scattering has been pursued in detail for the atom-diatom system by Michä,⁷ and here we wish to examine the structure of the S matrix that results from the Feshbach procedure. One should also see the work of Eu and Ross,⁸ who obtain the statistical model via a different procedure.

For a single, isolated resonance (see the Appendix for the more general case) the S matrix is given by

\[
S_{ij} = S_{ij}^{\Omega} - 2i(2\mu/k^2) \times \frac{\langle PS_i|V|PS_j\rangle \langle PS_i|V|PS_j^{(c)} \rangle}{E - E_r + i\frac{\Gamma}{2}},
\]

where

\[
\Gamma = (4\mu/k^2) \sum_k \langle PS_i|V|PS_k^{(c)}\rangle \langle PS_k^{(c)}|V|PS_i\rangle
\]

is the width of the resonance; \(E_r\) is the total energy; \(E_r\) is the energy of the metastable collision complex (including the "shift"); \(S_{ij}^{\Omega}\) is the S matrix resulting from the solution of the appropriate coupled equations for the open channels (the "direct" scattering matrix); \(PS_i^{(c)}\) is the open-channel wavefunction resulting from this set of coupled equations corresponding to initial channel \(i\), with the usual ± boundary condition; \(PS_i\) is the bound-state eigenfunction of the closed-channel Hamiltonian that describes the collision complex;
\( V \) is the interaction which couples the open and closed channels. The channel index "i" is a collective index denoting (for the atom-diatom system) orbital angular momentum and the vibrational-rotational state of the channel; diagonal indices, such as total angular momentum, have been suppressed. The open-channel wave-function is given explicitly by its coupled-channel expansion:

\[
P \Psi_F^{(oc)} = \sum_i \phi_i(r) u_{\mu_i}^{(oc)}(R),
\]

where \( \phi_i(r) \) is the internal wavefunction for channel \( j \) (\( r \) denotes all internal coordinates collectively), and \( u_{\mu_i}^{(oc)}(R) \) is the radial function with boundary condition

\[
u_j(R) \sim \{ -\exp[-i(k_j R-\frac{1}{2} \pi l_j)] \delta_{ij}
+ \exp[i(k_j R-\frac{1}{2} \pi l_j)] S_{ij}(\theta) (2ik_j R)^{-1};
\]

\( u_{\mu_i}^{(oc)}(R) \) is actually obtained by solving the coupled radial equations for the open channels. For convenience in parameterizing the \( S \) matrix, it is useful to convert the complex open-channel functions into real ones by employing the \( R \) matrix associated with \( S^0 \); these matrices are related by

\[
S^0 = (1 + iR^\theta) \cdot (1 - iR^\theta)^{-1},
\]

\( R^\theta = i(1 - S^0) \cdot (1 + S^0)^{-1},
\]

and \( R^\theta \) is real and symmetric. The procedure is reasonably straightforward, and one finds that Eq. (1) can be written as

\[
S = S^0 - iS^{0(1/2)} \cdot vv^t \cdot S^{0(1/2)} / (E-E_r + i\frac{1}{2} \Gamma),
\]

where \( v \) is the real vector defined by

\[
v = (\alpha \mu / R^\theta)^{1/2} \sum_j (1 + R^\theta) i^{j-1/2} \langle P \Psi_j| V | \Psi_r \rangle,
\]

\( P \Psi_j \) being the real function given by an expansion similar to Eq. (3) but with real radial functions whose boundary condition is

\[
u_j(R) \sim k_j^{-1/2} \{ \sin(k_j R-\frac{1}{2} \pi l_j) \delta_{ij} + \cos(k_j R-\frac{1}{2} \pi l_j) R_{ij} \}.
\]

The matrix \( S^{0(1/2)} \) is given by

\[
S^{0(1/2)} = (1 - iR^\theta)^{-1} \cdot (1 + R^\theta)^{1/2},
\]

which is well defined since \( 1 + R^\theta \) is positive definite; it can be easily shown that \( S^{0(1/2)} \) is unitary since \( S^0 \) is. The width \( \Gamma \) is given in terms of the vector \( v \) by

\[
\Gamma = v^t \cdot v = \sum_i v_i^2,
\]

and also

\[
\Gamma = v^t \cdot S^{0(1/2)} \cdot v^t \cdot S^{0(1/2)} \cdot v
= \sum_i \sum_j S_{ij}^{0(1/2)} v_j^2,
\]

since \( S^{0(1/2)} \) is unitary. \( S_{ij}^{0(1/2)} \) denotes the \( i-j \) element of \( S^{0(1/2)} \). Equations (5) and (7) are the most useful for introducing parameterizations of \( S \). We note that \( S \) given by Eq. (5), with \( \Gamma \) from Eq. (7), is unitary for any real vector \( v \); this can be easily proved by using the fact that

\[
(1 - cvv^t)^{-1} = 1 + v v^t c / (1 - c v^t \cdot v)
\]

for any constant \( c \) and vector \( v \).

With Eqs. (5) and (7) as the correct, formal result we now consider the quantity \( |S_{ij}|^2 \), the probability of the \( i \rightarrow j \) (or \( j \rightarrow i \)) transition. One obtains

\[
|S_{ij}|^2 = |S_{ij}^{0(1/2)}|^2 + \sum_k S_{ik}^{0(1/2)} S_{kj}^{0(1/2)} / (E-E_r)^2 + \Gamma^2,
\]

\[
-2 \text{Re} \left( \sum_k S_{ik}^{0(1/2)} S_{kj}^{0(1/2)} \right) \times (1-i)(E-E_r-\Gamma) / (E-E_r)^2 + \Gamma^2.
\]

We now average this quantity over a small energy range about \( E_r \), with weighting \( \rho(E) \); this averaging process may be thought to arise from experimental conditions, or may be considered to arise from a sum over a closely spaced set of metastable states with \( \rho(E) \) as the "density of states" (this latter idea is the same as that introduced in the usual derivation of the "golden rule"\(^9\)). Upon this averaging one has that

\[
\langle \Gamma/\Gamma \rangle \langle [E(E_r-\Gamma)^2 + \Gamma^2] \rangle \approx \pi \delta(E-E_r)
\]

so that

\[
\langle |S_{ij}|^2 \rangle = \rho_i \rho_j / \sum_k \rho_k,
\]

where

\[
\rho_i = 2\pi \sum_k S_{ik}^{0(1/2)} S_{jk}^{0(1/2)},
\]

and

\[
P_{ij}^{0(1/2)} = |S_{ij}^{0(1/2)}|^2
-2\pi \text{Re} \left[ \sum_k S_{ik}^{0(1/2)} S_{jk}^{0(1/2)} \right] \rho(E_r).
\]

It is clear from these expressions that the quantities \( P_{ij}^{0(1/2)} \) and \( \rho_i \) are not independent of one another; in fact, using the unitarity of \( S^0 \) and \( S^{0(1/2)} \), one can readily show that

\[
\rho_i + \sum_j P_{ij}^{0(1/2)} = 1,
\]

for all channels \( i \). Equations (9) and (12), therefore, lead to the following interpretation: \( P_{ij}^{0(1/2)} \) is the probability of a direct transition to channel \( j \) from initial channel \( i \) (or vice versa) without going through the intermediate complex, and \( \rho_i \) is the probability that a complex is formed from initial channel \( i \). Equation (12) is viewed in this light as a conservation of probability—either the system goes directly to some final channel or else to the complex. The over-all transition

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probability, given by Eq. (9), is seen to be the probability of a direct \(i\rightarrow j\) transition \((P_{ij})\), plus the probability of complex formation from channel \(i\) \((\rho_i)\) multiplied by the probability that the complex decomposes into channel \(j\) \((\rho_j/\sum_k \rho_k)\). It may at first seem disturbing that the direct transition probability \(P_{ij}\) depends in some way on the complex itself. If this were not the case, however, the only possible choice for it would be

\[
P_{ij} = |S_{ij}|^2,
\]

but the unitarity of \(S^0\) would demand that

\[
\sum_i P_{ij} = 1.
\]

From Eq. (12) we see that the true \(P_{ij}\) satisfies \(\sum_j P_{ij} < 1\); i.e., there is a “shadow” cast on the direct process by the possibility of complex formation—the second term in Eq. (11) is just this “shadow.” The most general parameterization of the over-all transition probability is given in terms of the direct transition probabilities by

\[
|S_{ij}|^2 = P_{ij} + (1 - \sum_k P_{ik})(1 - \sum_k P_{kj})/(N - \sum_k P_{kk}),
\]

(13)

\(N\) being the number of channels; it is trivially seen that unitarity has not been destroyed by the averaging process, nor has microscopic reversibility (the symmetry of \(|S_{ij}|^2\)).

It is doubtful, however, that Eq. (13) can prove useful, for the “input parameters” \((P_{ij})\) are just as numerous as the over-all transition probabilities themselves. Thus, one considers simplifying assumptions for \(P_{ij}\). The simplest possible case is that \(P_{ij} = 0\) (there is no possibility of a direct transition—all transitions proceed via complex formation), and one sees that \(\rho_i = 1\) for all \(i\), and

\[
|S_{ij}|^2 = 1/N,
\]

(14)

the usual form of the statistical model. A less drastic and more plausible assumption is that \(P_{ij} = \delta_{ij}\) is diagonal—that an elastic process may take place directly, but that all other processes proceed through complex formation. In this case, the over-all transition probability is conveniently parameterized in terms of the probabilities of complex formation, \(\rho_i\), as

\[
|S_{ij}|^2 = \delta_{ij}(1 - \rho_i) + \rho_i \rho_j / \sum_k \rho_k,
\]

(15)

with \(0 \leq \rho_i \leq 1\) being the only restriction. Equation (15) might indeed be a useful parameterization for extending the usual model \([\text{Eq. (14)}]\); instead of assuming the \(\rho_i\) is a step function \((0 \text{ or } 1)\) in the channel index, one could take \(\rho_i\) to be a more general function—allowing more dynamical structure to be built into the statistical model. Equation (15) is essentially equivalent to the expression obtained by Hauser and Feshbach.


from purely physical arguments. A still more elaborate, but perhaps useful, procedure would be to compute the direct \(S\) matrix \((S_{ij})\) in the distorted Born approximation (DWBA),+1 or by some other approximate method which applies to direct processes. Within the DWBA for \(S^0\) it is not difficult to show that,

\[
P_{ij} = |S_{ij}|^2 - \rho_i \delta_{ij},
\]

so that it would still only be necessary to specify the \(N\) parameters \((\rho_i)\) in order to use Eq. (9). The net expression for the over-all transition probability in this case is

\[
|S_{ij}|^2 = (1 - \rho_i) \delta_{ij} + (1 - \delta_{ij}) \left| \left( 4\mu/\hbar^2 \right) W_{ij} \right|^2 + \rho_i \rho_j \sum_k \rho_k
\]

where \(W_{ij}\) is the usual matrix element of the residual interaction in the distorted wave basis.

The matrix which actually arises in cross section formulas is \(|S_{ij}|^2\).

\[
|S_{ij} - \delta_{ij}|^2 = \delta_{ij} + |S_{ij}|^2 - 2\delta_{ij} \Re S_{ii}.
\]

The authors in Ref. 2 conclude that the assumption \(\Re S_{ii} = 0\) is consistent with the statistical approximation. One can easily show that this is the case for the two situations considered above, and we can think of no realistic case involving complex formation when this assumption should not be valid.

III. EXAMPLE: ROTATIONAL EXCITATION

In this section we apply the statistical model to rigid-rotor-atom collisions to see what general features one may expect from the model.

A. Total Cross Sections

The total (integrated) cross section for rotational excitation is given by

\[
\sigma_{J_a \rightarrow J_a} = (\pi/\hbar^2)(2J_a + 1)^{-1} \sum_J \left( 2J + 1 \right)
\]

\[
\times \sum_{l, l'} |S_{J_a l, J_a l'} - \delta_{J_a l, J_a l'}|^2,
\]

(16)

where the \(l, l'\) summations are restricted by conservation of total angular momentum:

\[
l = |J_a - J|, \ldots, J_a + J,
\]

\[
l' = |J_b - J|, \ldots, J_b + J;
\]

this cross section has been summed (averaged) over the final (initial) projections of molecular rotation. According to the statistical approximation,

\[
|S_{J_a l, J_a l'} - \delta_{J_a l, J_a l'}|^2 = |S_{J_a l, J_a l'}|^2 + \delta_{J_a l, J_a l'}
\]

\[
= \left( 2 - \rho(J_a l) \right) \delta_{J_a l, J_a l'} + \rho(J_a l) \rho(J_b l') \sum_{J, l''} \rho(J_a l''),
\]

(17)

Fig. 1. The function $f_{B-A}$, defined by Eq. (23) of the text, as a function of $B$ for values $A=0.1$ and $0.9$, $\alpha=0.5$.

where the dependence of $p(J_a, l)$ on $J$ and $E$ has been suppressed in the notation. For our example we take a simplified version of the statistical model, namely $p(J_a, l)$ is 0 or 1, depending on whether the impact parameter $l/k_o$ of the channel is greater than, or less than, some critical value $b_0$. If $E$ is the total energy and $B_r$ is the rotational constant of the molecule, then the precise choice for $p(J_a, l)$ is

$$p(J_a, l) = h[b_0(2\mu E/k^2 - 2\mu B_r J_a/k^2)^{1/2} - l],$$  \hspace{1cm} (18)

$h(x)$ being the usual step function:

$$h(x) = \begin{cases} 1, & x > 0, \\ 0, & x < 0. \end{cases}$$

Throughout this example we shall treat $J_a$, $J_b$, $l$, $l'$ as continuous variables, replace $(l+\frac{1}{2})$ by $l$, $(J_a+1)$ by $J_a$, etc., and replace sums over these indices by integrals.

The cross section may now be evaluated, the most difficult aspect being the evaluation of the sum over $p(J_a, l)$. One finds this sum (integral) to be

$$\sum_{J_a, l} p(J_a, l) = N(J) = \frac{1}{2} J_z^{2} W(x),$$  \hspace{1cm} (19)

where

$$W(x) = -x^2 + \alpha \sin \phi \left| \alpha \sin \phi - \cos \phi \right|$$

$$+ \sin \phi \left| \sin \phi - \alpha \cos \phi \right|$$

$$+ \alpha \sin^{-1} \left[ \min[2\alpha/(1+\alpha^2), \sin 2\phi]\right],$$  \hspace{1cm} (20)

$$x = J/J_z,$$

$$\sin \phi = x/(1+\alpha^2)^{1/2},$$

$$J_z = (E/B_r)^{1/2},$$

$$\alpha = b_0(2\mu B_r/k^2)^{1/2};$$

$J_z$ is the maximum allowed rotational state at energy $E$, and $\alpha$ is the only parameter in this simple model. If the atom is of mass $m_1$ and the rotor composed of atoms of mass $m_2$ and $m_3$ with internuclear separation $r_0$, then the dimensionless parameter $\alpha$ is given by

$$\alpha = (b_0/r_0) \left[ m_1(m_2+m_3)^2/m_2m_3(m_1+m_2+m_3) \right]^{1/2};$$  \hspace{1cm} (21)

$\alpha \ll 1$ applies to the situation of a light atom incident on a heavy rotor (e.g., He+Br), and $\alpha \gg 1$ corresponds to one of the atoms of the molecule being much lighter than the other two (e.g., Kr+HCl); thus one may envision physical systems in which $\alpha$ has any value between 0 and $\infty$. The cross section is given conveniently in reduced form by

$$\sigma_{J_a-J_a'} = \left( \frac{\pi b_0^2 J_z}{J_a + B (B-A)} \right),$$  \hspace{1cm} (22)

where

$$f_{B-A} = \frac{2}{\alpha^2 A (1-A^2)} \int_{x_1}^{x_2} dx \left| \min[x-A, \alpha(1-A^2)^{1/2}] - \right| x-A \left| \right. \right.$$}

$$\times \min[x+B, \alpha(1-B^2)^{1/2}] - \left| x-B \right|$$

$$W(x),$$  \hspace{1cm} (23)

where $x_1 = \max[0, A - \alpha(1-A^2)^{1/2}, B - \alpha(1-B^2)^{1/2}]$, $x_2 = \min[A + \alpha(1-A^2)^{1/2}, B + \alpha(1-B^2)^{1/2}]$.

$A$ and $B$ are the fractional rotational quantum numbers:

$$A = J_a/J_z,$$

$$B = J_b/J_z;$$

i.e., $A^2(B^2)$ is the fraction of the total energy initially (finally) in rotation. One may easily show that the function $f_{B-A}$ has the properties

$$\int_0^1 dB f_{B-A} = 1,$$  \hspace{1cm} (24)

$$A (1-A^2) f_{B-A} + B (1-B^2) f_{A-B}.$$  \hspace{1cm} (25)

It is the function $f_{B-A}$, therefore, which is of interest—it gives the partition of the total energy between rota-

Fig. 2. Same as Fig. 1 with $\alpha=1.5$. 
tion and translation after collision as a function of what it was before collision. The cross section summed over all final states is

$$\sigma_{J_a}^{\text{tot}} = \sum_{J_b} \sigma_{J_a-J_b} = 2\pi b^2,$$

and therefore uninteresting. Figures 1–3 show $f_{B-A}$ for the extreme case $A=0.1$ and 0.9, for several values of the parameter $\alpha$. As $\alpha \rightarrow 0$, $f_{B-A} \rightarrow 0(B-A)$; i.e., there is no transfer of energy between translation and rotation. As $\alpha \rightarrow \infty$ there is some exchange of energy, but the distribution tends to “remember” what it was before collision; i.e., if $A \ll 1(\approx 1)$, the peak of $f_{B-A}$ tends toward small (large) values of $B$. Only for the intermediate value of $\alpha \approx 1.5$ do we observe the truly statistical result that the distribution of energy after collision is essentially independent of what it was before collision. If $\alpha \approx 1.5$ is independent of $A$ (as this implies), then Eqs. (24) and (25) lead to the unique determination

$$f_{B-A} = 4B(1-B^2),$$

which fits the $\alpha = 1.5$ curves almost exactly.

We see, therefore, that the restrictions imposed by conservation of total angular momentum prevent complete loss of information about the initial state if one of the atoms is much lighter than the other two. Only in the roughly equal mass situation do we obtain completely statistical character. One expects this to be a reasonably general feature of such statistical models.

As indicated in Sec. II, a more realistic form for the probability function $p(J_a, l)$ could be obtained by replacing the step function in Eq. (18) by a “smooth” step function. In addition to the dependence on impact parameter, one could also include an explicit dependence on the internal energy of the molecule—e.g., that the probability of complex formation decreases (or increases) with increasing internal energy. These extensions have the undesirable feature of introducing more parameters into the model, but may be useful if more dynamical information about the system is available.

### B. Angular Distributions

The differential cross section, or angular distribution, for the rigid-rotor–atom system, summed and averaged over $M$ states, is

$$\sigma_{J_a-J_b}(\theta) = [4k_a^2(2J_a+1)^{-1}] \times \sum_{M_a, M_b} | \sum_J (2J+1) S_{J_b M_a J_a M_b} d_{M_a M_b}(\theta) |^2,$$

where the $S$ matrix in the $M$ representation is given in terms of that in the $l$ representation by

$$S_{J_b M_a J_a M_b} = \sum_{l, l'} C(J_l; M_b, -M_b) d_{M_a M_b}^{-1}(\theta),$$

from which the symmetry about $\theta = \frac{\pi}{2} (90^\circ)$ is immediately deduced,

$$\sigma_{J_a-J_b}(\pi-\theta) = \sigma_{J_a-J_b}(\theta).$$

Although this symmetry always results from a purely statistical model, it will most probably be true that the statistical approximation is valid for a certain range of $J$ (small $J$) and a direct process is dominant for another range (large $J$), so the resulting cross section will not display this symmetry.

Again neglecting cross terms, one has that

$$\sum_{J_a M_a, J_b M_b} | S_{J_a M_a J_b M_b} |^2 = \sum_{l, l'} C(J_l; M_b, -M_b)^2 \times | S_{J_b l, J_a l} |^2 C(J_a l; M_a, -M_a)^2.$$

With a statistical approximation for the $S$ matrix in the $l$ representation, namely

$$\sum_{J_b l, J_a l} | S_{J_b l, J_a l} |^2 = \rho(J_b, l') \rho(J_a, l)/N(J),$$

one finds the $S$ matrix in the $M$ representation to be of the same form,

$$\sum_{J_a M_a, J_b M_b} | S_{J_a M_a J_b M_b} |^2 = \rho(J_b, M_b) \rho(J_a, M_a)/N(J),$$

where

$$\rho(J_a, M_a) = \sum_l C(J_a l; M_a, -M_a)^2 \rho(J_a, l).$$

The important fact, we see, is that choosing the probability function which parameterizes $S$ in one representation determines the probability function which parameterizes $S$ in the other representation. With
\[ \phi(J_a, M_a) = \frac{1}{2} \pi^{-1} \sin^{-1} \left( \frac{\alpha^2 (J_a^2 - J^2_a) - J^2 - J_a^2 + 2M_a^2}{2[(J_a^2 - M_a^2)(J^2_a - M_a^2)]^{1/2}} \right), \]

where

\[ M_a^2 = \frac{\alpha^2 (J_a^2 - J^2_a) - (J - J_a)^2 [(J + J_a)^2 - \alpha^2 (J_a^2 - J^2_a)]}{4\alpha^2 (J_a^2 - J^2_a)}. \]

One observes that \( \phi(J_a, M_a) \) is a decreasing (increasing) function of \( M_a^2 \) if \( J \) is greater (less) than \( J_a^2 \) if \( J \) is greater than \( J_a^2 \). Miller et al.\(^{6}\) have discussed the possibility of parameterizing \( S \) in the \( M \) representation by using the model of Halpern\(^{13}\); they consider

\[ \phi(J_a, M_a) \sim \exp[\pm \text{constant} \times M_a^2], \]

and argue for the + or - sign depending on the structure of the complex intermediate—+ if an oblate rotor and - if a prolate rotor characterizes the intermediate. From \( \phi(J_a, M_a) \) in Eq. (33), obtained from \( \phi(J_a, I) \), we see that large (small) \( J \) corresponds to a prolate (oblate) rotor in the Halpern sense. This is certainly reasonable from a physical point of view. The point that we wish to emphasize, however, is that choosing the probability function to parameterize \( S \) in one representation determines what it must be in the other representation, and one must be careful not to introduce inconsistencies by mixing the two representations.

The angular distribution is given in terms of the \( \phi(J_a, M_a) \) function by

\[
\sigma_{J_a \rightarrow J_x}(\theta) = \frac{1}{2} b^2 \left[ (2J_a + 1) \right]^{-1} \sum_J (2J + 1)^2 N(J)^{-1} \times \sum_{M_a, M_b} \phi(J_b, M_b) \phi(J_a, M_a) \left| dM_{J_a J_b} \right|^2, \tag{35}
\]

or in reduced form by

\[
\sigma_{J_a \rightarrow J_x}(\theta) = \frac{1}{2} b^2 \phi(J_a, M_a) f_{B \rightarrow A}(\theta), \tag{36}
\]

where \( f_{B \rightarrow A}(\theta) \) is the differential form of \( f_{B \rightarrow A} \) above:

\[
f_{B \rightarrow A} = \int_0^\pi d\theta \sin \theta f_{B \rightarrow A}(\theta). \tag{37}
\]

In evaluating \( f_{B \rightarrow A}(\theta) \) we use the classical approximation for the square of the rotation matrix:

\[
\left| dM_{J_a J_b} \right|^2 = \pi^{-1} \left[ J^2 \sin^2 \theta - M_a^2 - M_b^2 + 2M_aM_b \cos \theta \right]^{-1/2},
\]

so that \( f_{B \rightarrow A}(\theta) \) is given by

\[
f_{B \rightarrow A}(\theta) = \frac{2}{\pi \alpha^2 A (1 - \alpha^2)} \int_{x_1}^{x_2} dx \int_{s_1}^{s_2} ds \int d\theta \left[ \left( x^2 \sin^2 \theta - r^2 - s^2 + 2rs \cos \theta \right)^{-1/2} g_x(A, r) g_x(B, s) \right], \tag{38}
\]

where \( W(x) \) is given by Eq. (20) and \( g_x(A, r) \) is given by \( \phi(J_a, M_a) \) of Eqs. (33) and (34) with \( J = xJ_a, J_a = AJ_a, M_a = rJ_a \), similarly for \( g_x(B, s) \); the limits of the \( r \) and \( s \) integration are the zeros of the radicand and the two \( g \) functions.

Rather than present a large number of figures displaying the results, we shall summarize the general features observed. For various values of \( A, B \), and the parameter \( \alpha, f_{B \rightarrow A}(\theta) \) varies from essentially const/\( \sin \theta \) to essentially isotopic (a constant); for no values of the quantities were we able to observe any but the very slightest peaking at \( \theta = \frac{\pi}{2} \). Thus, the results can all be characterized as to how strong is the forward-backward peaking. For fixed \( A \) and \( B \), increasing \( \alpha \) always increases the peaking. This is reasonable, since large \( \alpha \) corresponds to a heavy incident atom. For fixed \( \alpha \), the peaking diminishes as \( A \) and/or \( B \) is increased. This can also be understood, since large \( A \) (\( B \)) corresponds to small initial (final) translational energy which leads to a more nearly isotopic distribution. For example, with \( \alpha = 0.5 \) the distribution is essentially isotopic except for \( A \) and \( B \) both small, whereas with \( \alpha = 10 \) the distribution is strongly peaked except for \( A \) or \( B \) large.

Figure 4 shows the total angular distribution \( f_A(\theta) \),

\[
f_A(\theta) = \int_0^\pi d\theta \sin \theta f_{B \rightarrow A}(\theta), \tag{39}
\]

**FIG. 4.** The total angular distribution \( f_A(\theta) \), defined by Eqs. (38) and (39) of the text, for several values of \( A \) and \( \alpha \); for each value of \( \alpha \) the three curves correspond to \( A = 0.9, 0.5, \) and 0.1, the lower (higher) curve being \( A = 0.9 \) (0.1).
for several values of $A$ and $\alpha$. Since

$$\int_0^\pi d\theta \sin \theta f_A(\theta) = 1,$$

all the functions are scaled to be unity at $\theta = \frac{1}{2}\pi$ in order to display the variation in the peaking. The general conclusions of the previous paragraph can be seen in the figure. Figure 5 shows the distribution averaged over $A$ as well as summed over $B$,

$$f(\theta) = \int_0^1 dA A (1-A^2) f_A(\theta),$$

for several values of $\alpha$; these distributions are also scaled to be unity at $\theta = \frac{1}{2}\pi$.

Various thermal averages of these cross sections may also be carried out. For the case that one velocity selects the initial translational energy $E_a$, thermally averages over $J_a$, and sums over $J_b$, the cross section is

$$\sigma(\theta, T, E_a) = \frac{1}{2} b_0^2 f(\theta, E_a/kT),$$

and if the final translational energy $E_b$ is selected, with thermal averages over $J_a$ and $E_a$, the cross section is

$$\sigma(\theta, T, E_b) = \frac{1}{2} b_0^2 \exp(-E_b/kT) E_b(kT)^{-\frac{3}{2}} f(\theta, E_b/kT),$$

in both Eqs. (41) and (42). This function is shown in Fig. 6 for several values of $x$ and $\alpha$.

**IV. EXAMPLE: A CHEMICAL REACTION**

A beautiful example of complex formation that has been studied experimentally is the work by Miller, Safron, and Herschbach on the $\text{Cs}^+\text{RbCl} \rightarrow \text{Cs}^+\text{RbCl}$ reaction in crossed molecular beams. Here we would like to discuss this work in terms of the general results of Sec. II.

Within the simplest model the authors assume that there is a critical impact parameter $b_0$ such that collisions with $b < b_0$ lead to complex formation and collisions with $b > b_0$ do not; $b_0$ is determined by the criterion that the particles be able to surmount the maximum of the effective radial potential,

$$V(r)_{\text{eff}} = -C/r^6 + \frac{E_b^2}{2},$$

the attractive term being the long-range dipole-induced dipole interaction. The equation

$$E = \max V(r)_{\text{eff}}$$

leads to

$$b_0 = \left(\frac{27C}{4E}\right)^{1/6}.$$

For the particular system under consideration the authors use $C = 7973 \times 10^{-40}$ erg cm$^6$ and the average center-of-mass translational energy $E = 1.88 \times 10^{-13}$ erg, giving $b_0 = 8.11$ Å.

We wish to compute the reactive cross section $\sigma_r$ and nonreactive cross section $\sigma_{nr}$, summed and averaged over all final and initial channels, respectively, consistent with their being reactive or nonreactive. According to the statements in the preceding paragraph, one chooses the direct transition probability $P_\theta^0$ of
LL approximation implies that
\[ 2\pi B^2 \rightarrow 8.08(C/\hbar v)^{2/3}, \]
and for the specific example being considered, \(8.08(C/\hbar v)^{2/3} \approx 2230 \ A^2 = 10.8\pi b_0^2\).

From Eqs. (47) and (48) one sees that the cross section from direct processes (all of which appears in \(\sigma_{\text{nr}}\)) is \(2\pi B^2 - \pi b_0^2\); \(\pi b_0^2\) is the cross section for complex formation, and it is partitioned between reactive and nonreactive final channels. For an exothermic (endo-
thermic) reaction one expects \(N_r > N_{\text{nr}}(N_r < N_{\text{nr}})\), so that reactive (nonreactive) break up of the complex is favored. Since \(\pi b_0^2\) is an upper limit to the reactive cross section, regardless of the partitioning of the complex, one has that
\[ \sigma_{\text{nr}} / \sigma_r \geq (2\pi B^2 - \pi b_0^2) / \pi b_0^2 \geq 1.03(2\mu / \hbar v)^{1/3}(E^2C)^{1/3} - 1, \]
which is \(\approx 9.8\) for this case.

The angular distributions can also be discussed within this simplified model. Assuming a \(1/\sin \theta\) form for the distribution resulting from the complex (this is, of course, not valid too near 0 or \(\pi\), one has
\[ \sin \theta_{\sigma_r} = \left[ \frac{b_0^2 / 2\pi}{N_r + N_{\text{nr}}} \right]. \]
The nonreactive distribution \(\sigma_{\text{nr}}(\theta)\) has a contribution similar to that in Eq. (52) (with \(N_r \rightarrow N_{\text{nr}}\)) for the region \(0 < b < b_0\), but also has a contribution from \(b > b_0\). This nonresonant, or direct, contribution to \(\sigma_{\text{nr}}(\theta)\) can be obtained in the following manner. From the potential \(V(r) = -C/r^6\) one constructs the corresponding deflection function \(\Theta(b)\). This deflection function has an orbiting singularity at \(b = b_0\), but it is the outer branch, \(b > b_0\), which provides the direct contribution to \(\sigma_{\text{nr}}(\theta)\) because \(b < b_0\) leads to complex formation. The classical approximation to this contribution to \(\sin \theta_{\sigma_{\text{nr}}} = \left( b(\theta) / b_0 \right) \right|, \) where \(b(\theta)\) is defined by \(\Theta(b) = -\theta\). This contribution can be put in the form \(b_0^2 \sin \theta_{\sigma_{\text{nr}}}(\theta),\) where \(\sigma_{\theta}(\theta)\) is a dimensionless universal function of \(\theta,\) depending only on the power of the long-range potential (6 in this case); this function is given explicitly by
\[ \sin \theta_{\sigma_{\theta}} = \frac{1}{2} \sqrt{3} m(1 - m) \tan(\sec \alpha)\frac{1}{12}(1 - m^2 - m)^{-1/4} \]
\[ \times \left[ 2(1 + m^2 - m) E(m) - (1 - m)(2 - m) K(m) \right]^{-1}, \]
where
\[ -\theta = m - 2(1 + m^2 - m)^{1/2} K(m) \rightarrow m(\theta), \]
\[ m = \sin[\frac{1}{4}(\pi + \alpha)] / \sin[\frac{1}{4}(\pi - \alpha)] \rightarrow \kappa(m), \]
and \(K(m)\) and \(E(m)\) are the complete elliptic integrals of the first and second kind, respectively. Figure 7

---

shows \( \sin \theta \sigma_0(\theta) \). The limiting expressions are

\[
\sin \theta \sigma_0(\theta) = \begin{cases} 
\frac{1}{6}(5\pi/36)^{1/3}, & \text{\( \theta \) small} \\
144 \exp[-2(\pi+\theta)], & \text{\( \theta \) large.}
\end{cases}
\]

The nonreactive angular distribution, therefore, is given by

\[
\sin \theta \sigma_{nr}(\theta) = b_0^2 [N_{nr}/2\pi(N_r+N_{nr})] + \sin \theta \sigma_0(\theta); \quad (54)
\]

the positions of the constant \( (2\pi)^{-1}N_{nr}/(N_{nr}+N_r) \) are indicated in Fig. 7 for \( N_{nr}/(N_{nr}+N_r) = 1 \) (no reactive cross section) and \( \frac{1}{3} \) (equal reactive and nonreactive decomposition of the complex). The total angular distribution is

\[
\theta \sigma(\theta) = \sigma_{sr}(\theta) + \sigma_{r}(\theta) = b_0^2 \sin \theta \sigma_0(\theta) + (2\pi \sin \theta] .
\]

In concluding this section it should be pointed out how oversimplified has been this heuristic treatment. Proper account has not been taken of the fact that the critical impact parameter \( b_0 \) will be different for channels with different translational energy, nor has conservation of total angular momentum been imposed (as it was in Sec. III). Thus, the computation of the resonant contribution to the angular distribution is much more difficult than above, replacing the \( \text{const/} \sin \theta \) contribution to \( \sigma_{nr}(\theta) \) and \( \sigma_r(\theta) \) in Eqs. (52) and (54). Consistent with using the long-range potential \(-C/r^6\) to determine which collisions form complexes, however, one sees that all collisions not forming a complex must scatter elastically, with angular distribution \( \sin \theta \sigma_0(\theta) \) as above. Therefore, one expects the nonresonant contribution to \( \sigma_{nr}(\theta) \) to remain essentially unchanged from that above in a more detailed treatment.\textsuperscript{16} Averaging the nonresonant contribution over initial channels, including a thermal average over translation energy, simply averages the scale factor \( b_0^2 \),

\[
\langle b_0^2 \rangle = \int_0^{\infty} dE \frac{E}{kT} \exp \left( -\frac{E}{kT} \right) \frac{27C}{4E} \left( \frac{27C}{4kT} \right)^{1/3} = \Gamma(5/3) \left( \frac{27C}{4kT} \right)^{1/3}.
\]


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**APPENDIX**

For the case of several, possible overlapping resonances\textsuperscript{16} the \( S \) matrix can be written in the general form

\[
S_{ij} = S_{ij}^0 - i \sum_r \langle E_r \rangle (E - E_r + i\Gamma_r) \langle S_{ijr} \rangle \langle 1/L \rangle \langle \langle w_{ir} w_{jr} \rangle \rangle (A1)
\]

where the notation is analogous to that in Sec. II, and

\[
\langle w_{ir} w_{jr} \rangle = \sum_r S_{ijr} \langle w_{ir} \rangle \langle w_{jr} \rangle \langle 1/L \rangle (A2)
\]

Energy averaging \( |S_{ij}|^2 \) over some interval large compared to the widths (\( \Gamma_r \)) yields

\[
\langle |S_{ij}|^2 \rangle = \langle |S_{ij}^0|^2 \rangle - \text{Re} \langle S_{ij}^{0*} \sum_r 2\pi \rho w_{ir} w_{jr} \rangle + \sum_r \frac{\pi \rho (\Gamma_r + \Gamma_{r'}) w_{ir} w_{jr} w_{ir'} w_{jr'}}{E_r - E_{r'} + (\frac{1}{2}(\Gamma_r + \Gamma_{r'}))^2} (A3)
\]

The sum over resonances (index \( r \)) includes only those whose energy \( E_r \) is in the energy interval over which we average.

If the resonances do not overlap (i.e., \( |E_r - E_{r'}| \gg \Gamma_r \) for all \( r \neq r' \)), then only the \( r = r' \) terms contribute significantly in the last summation in Eq. (A3), and one immediately recovers a simple extension of Eqs. (9)–(11). For the case of truly overlapping resonances it is difficult to see how one can simplify Eq. (A3) any further. The fact that this case does not lend itself to a simple, intuitive parameterization should not cause worry, however, for the number of overlapping resonances in a complex system will usually be greatly outnumbered by narrow, isolated ones.