Inelastic Collisions of Slow Atoms

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A general approximate method for computing the cross sections for certain inelastic collision processes is developed. It is based on the possibility of obtaining, with the use of the impact-parameter method, an exact expression for the transition amplitude in a special case. The dependence of the cross section on the parameters of coupling constant, velocity, and energy difference between states is discussed for a two-level model. Detailed calculations are made of cross section for collisions of the type $A(3P_{1/2}) + B \rightarrow A(3P_{3/2}) + B$, where $A$ is an excited atom of an alkali metal and $B$ is an atom of a noble gas. An Appendix contains a review of the effective long-range interaction of atoms.

I. INTRODUCTION

The study of inelastic collisions of slowly moving atomic or molecular systems has been of considerable interest for many years. One problem of this sort which has received attention is that of sensitized fluorescence of alkali metals induced by collisions with rare-gas atoms.1-4 In such a process, an alkali-metal atom (denoted by $A$) in an excited state collides with a rare-gas atom (denoted by $B$) in its ground state, and makes a transition to another excited state of different $j$. The energy difference involved comes from (or goes into) the kinetic energy of relative motion.

$$A(3P_{1/2}) + B \rightarrow A(3P_{3/2}) + B.$$ 

Our object here is to develop a general method for the theoretical study of inelastic collisions of heavy particles, which can be applied to the problem of sensitized fluorescence as a special case. Our procedure is founded on the possibility of obtaining a complete solution to the equations of time-dependent perturbation theory in a special case, and offers considerable advantages of simplicity and generality over previous treatments.

Let us consider two general colliding objects, which we will call $A$ and $B$. They may be either individual atoms or molecules, although our specific considerations here will be devoted entirely to the former case. They are assumed to be distinguishable. We are particularly interested in the case in which $A$ undergoes an electronic transition, but $B$ does not. Moreover, we will ignore the possibilities of charge exchange, or excitation transfer, although similar techniques can be—and have been—applied in such processes.5-9

Our approach to the calculation of the cross section will be through the impact-parameter method.10 The relative motion of $A$ and $B$ is described classically. Two additional assumptions are also made at this point: (1) The energy change in the transition ($\hbar \omega$) is small enough so that the change in the speed of either particle can be ignored, and (2) the elastic scattering, or deflection, of the objects is neglected.

The reaction is considered in the coordinate system shown in Fig. 1. For purposes of illustration, $A$ is shown as having a single electron bound to a core. The origin of coordinates is taken at the center of mass of $A$, which is at rest, and the polar axis is chosen to be opposite to the velocity $v$ of $B$. The separation of $A$ and $B$ is $R(t)$, and the origin of time is chosen so that $R(0) = \rho$, where $\rho$ is the impact parameter.

The interaction of the atoms is described by means of an effective potential $V_{eff}$, which acts to produce transitions of atom $A$. This potential is considered only within a subspace of the Hilbert space of $A$ spanned by the states actually involved in the transition. (We are here considering the situation in which $B$ remains in its ground state.) Let $a_m(t)$ be the amplitude that at time $t$, $A$ will be in state $m$. This quantity obeys the differential equation:

$$\frac{da_m}{dt} = -i \frac{\hbar}{\omega_m} \sum_n (\langle n | V_{eff} | m \rangle a_n(t) \exp(-i \omega_{m,n} t)). \quad (1)$$

The sum over $m$ includes only those states involved in the transition. The quantity $\omega_{m,n}$ is given by

$$\hbar \omega_{m,n} = E_m - E_n. \quad (2)$$

The energies in (2) refer to the states of $A$ when $B$ is absent. They do not depend on $R$. The effective po-

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10 N. M. Mott, Proc. Cambridge Phil. Soc. 27, 531 (1931).
tential $V_{\text{eff}}$ depends on the electronic coordinates of $A$ and the $A-B$ separation $R$. We can expect that $V_{\text{eff}}$ will be a sum of terms involving the coordinates of each electron of $A$ separately. In this case, if the electronic wave function of $A$ is a Slater determinant, the matrix element will reduce to an integral involving a single electron coordinate. Thus, Eq. (1) can be regarded as applying to a one-electron problem.

We cannot solve Eq. (1) in a closed form. An iterative solution can, of course, be given but this is useful primarily for derivation of the perturbation expansion. An exact solution in closed form is known only in special cases. One such solution, for a two-level problem in which the matrix elements of the potential are independent of time, was obtained by Rabi. Another solution of a two-level problem with no diagonal elements of the potential and a special time dependence was found by Rosen and Zener. We want to propose an approximate solution of Eq. (1) which is not difficult to evaluate if the number of levels which must be included is not too large, and which becomes exact in an important special case. There are other advantages with respect to previous treatments of this problem which will be described below.

Let the matrix $Q(t)$ be defined as follows:

$$ hQ_{nm} = \langle n | V_{\text{eff}} | m \rangle e^{-i\omega_{nm} t}, $$

Further, let $a_n$ be regarded as the $n$th component of a vector $a$. Then Eq. (1) can be written as

$$ da/dt = -iQ(t) \cdot a(t). $$

Suppose the vector $a$ is known at $t = -\infty$. We propose the approximate solution of Eq. (4):

$$ a(t) = \exp \left[ -i \int_{-\infty}^{t} Q(t') dt' \right] \cdot a(-\infty). $$

Equation (5) is an exact solution of Eq. (4) if, and only if, the matrix

$$ T(t) = \int_{-\infty}^{t} Q(t') dt' $$

commutes with $Q$:

$$ [T(t), Q(t)] = 0. $$

To prove this, we observe that

$$ \exp(-iT) = \sum_{n} \frac{(-i)^{n}}{n!} [T(t)]^{n}. $$

Differentiate this with respect to time. Consider the $m$th term in the expansion:

$$ \frac{d}{dt} T_{nm}(t) = \left[ \frac{d}{dt} T(t) \right] \cdot T_{nm-1}(t) $$

$$ + T_{nm} \cdot \frac{dT}{dt} \cdot T_{nm-2} + \cdots + T_{nm} \cdot \frac{dT}{dt}. $$

But

$$ \frac{dT}{dt} = Q(i). $$

Then, using Eq. (6)

$$ \frac{dT_{nm}}{dt} = m Q \cdot T_{nm-1}(t) $$

so that

$$ (d/dt) \exp[-iT] = -iQ \cdot \exp[-iT]. $$

Thus

$$ da/dt = -i Q(t) \cdot \exp[-iT] \cdot a(-\infty) = -iQ(t) \cdot a(t). $$

From this, we see that if Eq. (6) is satisfied, Eq. (5) is a solution of the differential equation (4). Equation (5) also obviously satisfies the boundary condition that $a(t)$ must reduce to the known vector $a(-\infty)$ as $t \rightarrow -\infty$. Evidently, Eq. (6) is a sufficient condition. It is also easily seen to be necessary: If it is not satisfied, we cannot commute $Q$ through the factors of $T$, and so Eq. (7) will not hold.

One important situation in which Eq. (6) is satisfied is the following. Let all the elements of $Q$ be proportional to the same function of time (such that the integral for $T$ converges), then we have

$$ T_{nm}(t) = b_{nm} f(t), $$

where the quantities $b_{nm}$ are arbitrary complex numbers. Then $Q_{nm}(t) = b_{nm} f'(t)$, with $f' = df/dt$. Therefore, both $Q$ and $T$ are proportional to the same matrix, and thus must commute. We will see below that this situation occurs in an important case.

Now let us consider the utility of Eq. (5) as an approximation in cases in which Eq. (6) is not satisfied.

(1) The first term in the iterative solution of Eq. (4) coincides with the first term in the expansion of Eq. (5).

Therefore, whenever first-order perturbation theory is applicable, Eq. (5) gives a correct result.

(2) The exponential operator in Eq. (5) is unitary. Therefore the normalization of the state vector $a(t)$ is
preserved at all times. No transition probability can exceed unity. There are, of course, other methods of preserving the normalization of the state vector \(a(t)\); for instance one may take \(a\) as computed in first-order perturbation theory and divide this by the norm of \(a\), but this procedure does not yield an exact solution in the special case when (6) holds.

(3) For a two-level system, it is always possible to evaluate the exponential in (5) regardless of what the matrix elements of \(T\) are. If there are more than two levels, the exponential can frequently be evaluated using standard methods: one such example is discussed in Sec. III.

One further simplification is possible in Eq. (5). We define a matrix \(U\)

\[
U(t) = T(t) - (1/N)[\text{tr}T(t)]I
\]

(the dimension of \(T\) is \(N \times N\)). \(I\) is a unit matrix. We have

\[
\exp[-iT(t)] = \exp[-iU(t)]\exp[-(i/N)\text{tr}T(t)]. \quad (8)
\]

The second factor in Eq. (8) contributes only a change of phase to the amplitude, and therefore may be disregarded. Let us assume that the system was initially in the state \(j\). The probability that it will be in the state \(n\) finally is

\[
P = |a_n(\infty)|^2 = |(e^{-i0}a)_{nj}|^2. \quad (9)
\]

With the use of Eq. (9), the cross section for the process in which \(A\) goes from state \(j\) to state \(n\) is given by

\[
\sigma(j \rightarrow n) = \int_0^{2\pi} \int_0^{\infty} p|a_n(\infty)|^2 d\rho d\phi. \quad (10)
\]

The \(\phi\) dependence is usually trivial.

A particular advantage of the present approach is that the transition probability \(P\) can never be singular for any value of the impact parameter. Ordinarily, the use of interaction potentials proportional to negative powers of \(R\) leads to difficulty in the impact-parameter method when a perturbation expansion is employed. In that case, the integral (10) over the impact parameter will not converge. This makes the introduction of a lower cutoff necessary. Our method requires no arbitrary cutoff.

II. THE TWO-LEVEL MODEL

A. General Considerations

Before we investigate the alkali-metal–rare-gas collisions in detail, we shall examine a simple and general model in which only two levels are considered. Results similar to some of those we will present here have been obtained previously by Bates14 and by Vainshtein, Presnyakov, and Sobelman.15 Our analysis is, however, considerably more complete. It is, of course, based on the approximate Eq. (5). We can write

\[
U(t) = \begin{pmatrix} W(t) & S(t) \\ S^*(t) & -W(t) \end{pmatrix}. \quad (11)
\]

The diagonal elements are equal in magnitude but opposite in sign since the trace has been removed. The off-diagonal elements can be written as \(S\) and \(S^*\) since \(U\) is Hermitian. The square of this matrix is a multiple of the unit matrix. From this, it follows that if we define

\[
\xi^2 = W^2 + |S|^2,
\]

we have

\[
\exp \left[ -i \begin{pmatrix} W & S \\ S^* & -W \end{pmatrix} \right] = \begin{pmatrix} \cos \xi - iW(\sin \xi)/\xi & -iS(\sin \xi)/\xi \\ -iS^*(\sin \xi)/\xi & \cos \xi + iW(\sin \xi)/\xi \end{pmatrix}. \quad (12)
\]

If we assume that the system was initially in state 1 at \(t = -\infty\), the probability that it will be in state 2 at time \(t\) is

\[
|a_1(t)|^2 = \frac{|S|^2}{W^2 + |S|^2} \sin \xi. \quad (13)
\]

It is easily seen that for all times \(|a_1|^2 + |a_2|^2 = 1\). This must hold if the original vector \(a\) was normalized since the transformation of Eq. (5) is unitary.

To proceed further, it is necessary to introduce specific assumptions concerning the interaction \(V_{\text{eff}}\). In general, this may be a rather complicated function, particularly if it is necessary to consider close encounters. We shall restrict most of our analysis to distant collisions, by which we mean collisions in which the interaction is dominated by the smallest negative power of \(R\) appearing in \(V_{\text{eff}}\). It will be necessary to consider different powers of \(R\) in the diagonal and off-diagonal matrix elements of \(V_{\text{eff}}\) in the case of transitions between levels of different parity. After integration over the electronic coordinates, the matrix elements \(\langle n | V_{\text{eff}} | m \rangle\) will have the form

\[
\langle n | V_{\text{eff}} | m \rangle = q g_1(\Theta, \Phi)/R^n, \quad (n \neq m) \quad (14a)
\]

\[
\langle n | V_{\text{eff}} | n \rangle = q g_2(\Theta, \Phi)/R^1, \quad (14b)
\]

in which each \(q\) is an effective coupling constant containing, among other things, a radial integral over the electronic coordinates. The functions \(g_1\) and \(g_2\) depend on the angles specifying the orientation of \(R\). We must now find the integrals \(S\) and \(W\). To this end, consider the integral

\[
\int_{-\infty}^{\infty} e^{-i\Theta d} g(R, \Phi)/R^n dt. \quad (15a)
\]

This integral is not too difficult to evaluate. In all situa-
tions of interest to us, the function \( g(\theta, \phi) \) has the form

\[
g(\theta, \phi) = \sin \theta \cos^3 \theta f(\phi) \tag{15b}
\]
or is a sum of such terms. The function \( f(\phi) \) is of no concern at the present. The result can be expressed in terms of modified Bessel functions of the third kind and their derivatives. With \( g \) given by (15b), Eq. (15a) yields

\[
f(\phi) \frac{\pi^{1/2}}{\nu \beta^{n-1}} \Gamma[(n+j+k-1)/2] \Gamma[(n+j+k)/2] \times (-i)^k \frac{d^k}{dx^k} M_{j+k+n-1}(x) \tag{16a}
\]

in which

\[
M_s(x) = \frac{2}{\Gamma(s/2)} \left( \frac{x}{s/2} \right)^{s/2} K_{s/2}(x) \tag{16b}
\]

and \( x = \omega \beta/\nu \). The function \( K_{s/2} \) is the Bessel function referred to above. \( M_s \) is defined so that \( M_s(0) = 1 \). For small values of \( x \) we have

\[
M_s(x) = 1 - x^2/2(s-2) + \cdots (s > 2)
\]

while, for large values of \( x \), \( M_s \) decays exponentially:

\[
M_s(x) = 2/\Gamma(s/2)(x/2)^{s-3/2} e^{-x}
\]

It is evident that in the detailed analysis of a reaction cross section, the precise results will depend on the detailed form of \( g \). It is probable that many reactions of interest in which \( \omega \) is small are dominated by matrix elements in which \( k = 0 \). The alkali-metal–rare-gas collisions are of this type. We shall restrict ourselves to the case \( k = j = 0 \) from here on. Such restriction is consistent with the general idea of the two-level approximation. Moreover, we will ignore \( f(\phi) \). Thus we write

\[
W(\infty) = q_A / \hbar \nu \beta^{n-1}, \tag{17a}
\]

\[
S(\infty) = (q_B / \hbar \nu \beta^{n-1}) M_{n-1}(x), \tag{17b}
\]

in which \( A \) and \( B \) are numerical constants whose precise value does not concern us here.

We can now consider the calculation of the cross section. From Eqs. (17), (13), and (10) we have

\[
\sigma = 2 \pi \int_0^\infty \rho d \rho \int_0^\infty q^2 B^2 M_{n-1}^{-1} \left( \omega \nu / \beta \right) \times \sin^2 \left( \frac{1}{\hbar \nu \beta^{n-1}} \left( q_A A^2 \rho^2 (n-1) + q_B B^2 M_{n-1}^{-1} (\omega \nu / \beta) \right)^{1/2} \right), \tag{18}
\]

It is obvious that, in the general case, we cannot expect to evaluate this integral analytically. Before we discuss the formulation of approximate methods or the results of numerical computation, we shall examine the \( \omega = 0 \) limit in which the integration can be performed exactly if \( n = l \). In addition we set \( q_A = q_B \). Then we get

\[
\sigma = \frac{2 \pi^2}{A^2 + B^2} \int_0^\infty \rho d \rho \sin \left[ \frac{q^2}{\hbar \nu \beta^{n-1}} (A^2 + B^2)^{1/2} \right] \times \frac{1}{2(n-1) \Gamma[1+2/(n-1)] \sin[\pi/(n-1)]} \left( \frac{2q^2}{A^2 + B^2} \right)^{2/(n-1)} \times \frac{1}{\hbar \nu} \tag{19}
\]

This result is valid for values of \( n > 2 \). It is particularly to be noted that (for \( n > 2 \)) the integral is convergent without the introduction of any cutoff. This situation should be contrasted with that which would obtain if we used ordinary first-order perturbation theory, which requires retaining only the leading term in the expansion of \( \sin^2 \xi \). In that case, the integration over \( \rho \) always diverges at the lower limit. In the present situation, a natural cutoff is provided by the trigonometric function, which effectively enforces unitarity.

Equation (19) is exact for the two-level model with \( \omega = 0 \), \( n = l \), and no angular dependence. This follows from the fact that these conditions ensure that the elements of \( Q(t) \) are proportional to the same function of time. This guarantees that \( T(t) \) and \( Q(t) \) commute, so that Eqs. (5) holds exactly.

The dependence of the cross section on the coupling constant and velocity can be accounted for by the following very simple physical argument (due to M. H. Johnson).

1. The rate of change of the amplitude \( a_2 \) for finding atom \( A \) in state 2 is proportional to \( V_{\text{ett}} \). This interaction is proportional to \( q / \hbar \nu \beta^{n-1} \).

\[
\frac{da_2}{dt} = \frac{V_{\text{ett}}}{\hbar} \frac{q}{\nu \beta^{n-1}}.
\]

2. The interaction acts for a characteristic time \( \Delta t = \rho \nu / \hbar \). The change of \( a_2 \) in this time is

\[
\frac{da_2}{dt} \Delta t = \frac{q}{\hbar \nu \beta^{n-1}}.
\]

3. The cross section is proportional to \( \pi \rho_0^2 \), where \( \rho_0 \) is the value of \( \rho \) which gives \( \Delta a_2 = 1 \). Thus

\[
\rho_0 = (q / \hbar \nu \beta^{n-1})^{1/(n-1)}.
\]

These results may be contrasted with those obtained by Stuckelberg\[16\] in an earlier treatment of this problem. He obtained a result which, when expressed in our notation, has the following form for small energy differ-

ences \( (\hbar \omega) \).

\[ \sigma \propto q \delta n (\hbar \omega)^{n-3} n / h \nu . \]

It will be seen that his result is in agreement with ours only in the case \( n = 3 \). For higher values of \( n \), his expression for the cross section vanishes as \( \omega \to 0 \), in contrast to our result, Eq. (19), which remains finite in this limit.

### B. Relation to Perturbation Theory

It is important to understand clearly the circumstances in which Eq. (19) and similar results, to be obtained below, are applicable. The characteristic feature of the present treatment is the weak dependence of the cross section on the coupling constant. This appears at first sight to be in conflict with the expectation that if the coupling is weak, or the velocity is high, ordinary perturbation theory should apply. But first-order perturbation theory should give a cross section proportional to \( (q/\hbar \omega)^3 \) and Eq. (19) does not, no matter how small \( q \) is or how large \( v \) is. Thus, Eq. (19) does not agree in any limit with the Born approximation, which should hold when \( v \) is large.\(^{17}\)

The problem here arises from the assumptions made concerning the effective interaction. It is easily seen that the Born approximation does not exist for an effective potential proportional to \( R^{-n} \) if \( n \geq 2 \). However, Eq. (14) is only an approximation, and cannot hold for small \( R \).

A complete expression for the effective interaction will not resemble Eq. (14) as \( R \to 0 \). Let us therefore introduce a parameter \( b \) such that Eq. (17) is not a useful approximation if \( p > b \). For \( p < b \), Eq. (17) must be replaced by another expression whose dependence on \( p \) is quite different. Equations (10) and (13) are still valid, and we may write in general:

\[ \sigma = 2 \pi \int_{0}^{b} \int_{0}^{\infty} p d p \frac{S(P)^2}{W^2 + |S|^2} \sin^2 (W^2 + |S|^2)^{1/2} \]

in which \( W \) and \( S \) are determined from (11) as \( t \to \infty \).

Now define a value of \( p \) which we will call \( P \) by the condition

\[ W^2(P) + |S(P,\omega)|^2 = 1. \]

The arguments have been written in Eq. (21) to emphasize the fact that while \( S \) depends on the energy \( E \), it vanishes as \( \omega \to \infty \), \( W \) does not. Next, suppose that \( P > b \). In this case, the approximation in which the sine is replaced by its argument will not be valid near \( P \), in which case it will generally be a good approximation to set \( b = 0 \). Then Eq. (19) and similar results are obtained.

If Eq. (21) is not satisfied for \( P > b \) when the asymptotic expressions of Eq. (17) are substituted for \( S \) and \( W \), it may be that it is not satisfied for any value of \( p \) if the complete expression for the interaction is used. If this is so, that is, if \( S \) and \( W \) are actually nonsingular and small

\[ q \]

as \( \rho \to 0 \), then we have to a good approximation

\[ \sigma = 2 \pi \int_{0}^{b} \int_{0}^{\infty} p |S(P,\omega)|^2 d p. \]

We may use Eq. (17) in Eq. (22) for \( P > b \), but not for \( p < b \). A crude approximation is to set \( S = 0 \) for \( p < b \); \( b \) is then a cutoff for the simplest form of the impact-parameter method. If \( S \) and \( W \) are nonsingular, the conditions leading to Eq. (22) will be satisfied for fixed \( q \) for sufficiently large \( v \), and for fixed \( v \) for sufficiently small \( q \). In such cases, perturbation theory actually does apply, as would be expected, and the Born approximation is recovered in the appropriate limit. The situation with respect to the energy difference is, however, not the same. Because of the presence of \( W \) in Eq. (21), it may be possible to satisfy (21) with \( P > b \) for any value of \( \omega \) if \( q \) is large enough or \( v \) is small enough.

It is difficult to make a precise statement about the value of \( b \), but in general it should be of the order of an atomic radius. On the other hand, it is easily seen that \( P \) as defined by (21) is of the same order of magnitude as \( p_0 \). Thus, if \( a \) is the “radius” of the atom \( A \), a condition for the utility of the present analysis is that

\[ (q/\hbar \omega)^{n-3} > a. \]

It is possible to construct a simple model which shows explicitly the transition between perturbation theory and the regime of Eq. (19), as the parameters are varied.\(^{18}\) All we have to do is to replace the assumed matrix elements of \( V_{eff} \), given by Eq. (17), by expressions of the form

\[ (n|V_{eff}|m) = q/r_{\sigma}^n + R^n/2 \]

Then the analysis leading to the computation of the cross section may be repeated without difficulty. In the case \( \omega = 0 \), we find a cross section

\[ \sigma = \frac{\pi \rho^2}{2} \frac{B^2}{A^2 + B^2} \left[ 1 + \frac{1}{n-1} \Phi \left( -2, 1 - \frac{2}{n-1}, \frac{2i\xi_0}{n-1} \right) \right] \]

in which \( \Phi \) is a confluent hypergeometric function, and the parameter \( \xi_0 \) is

\[ \xi_0 = \frac{1}{r_0^{n-1}/\hbar \nu} q(A^2 + B^2). \]

If \( \xi_0 \) is small, the hypergeometric functions may be expanded in a power series, and the result of perturbation theory is recovered. If, however, \( \xi_0 \) is large, an asymptotic expansion leads back to Eq. (19); this condition will occur when Eq. (23) is satisfied.
C. Dependence of the Cross Section on the Parameters: \( l = n \)

Now we shall examine the consequences of the present method with respect to the dependence of the cross section on the parameters \( q, v, \omega \) in more detail, always supposing that Eq. (23) is satisfied, so that Eq. (17) may be employed without serious error. Although we cannot give an analytic expression for the cross section for general values of the parameters, we can still express Eq. (18) in a form suitable for numerical computation, and also describe a method for obtaining an approximate evaluation of Eq. (18) by elementary methods.

Let us first consider the case \( l = n \). We put \( C^2 = A^2 + B^2 \), \( K = \lambda / B \), \( q = q_1 = q_3 \), and define a dimensionless measure of the coupling:

\[
    x_0 = \frac{\omega}{v} \left( \frac{2q C}{\hbar v} \right)^{1/(n-1)}.
\]

(27)

Then Eq. (18) may be expressed as

\[
    \sigma = 2\pi \left( \frac{\omega}{v} \right)^2 \int_0^\infty \frac{x M^2(x)}{K^2 + M^2(x)} dx 
    \times \sin^2 \left[ \frac{1}{2} \frac{x_0}{x} \left( \frac{K^2 + M^2(x)}{K^2 + 1} \right)^{1/2} \right] dx,
\]

(28)

with \( x = \omega / v \). The subscript \( n - 1 \) on \( M \) has been dropped. The result previously obtained, Eq. (19), follows from Eq. (28) if \( M \) is set equal to unity. Except for the multiplicative factor of \( (n/\omega)^2 \), the cross section is expressed as a function of two parameters \( x_0 \) and \( K \). Equation (28) is reasonably convenient for the purposes of numerical calculation of the cross section, and some results based on such calculation will be presented below.

However, it is desirable to be able to obtain approximate results without the necessity for numerical integration. In order to do this, we observe that for \( x \ll x_0 \), the trigonometric function oscillates with great rapidity. For such values of \( x \), it is a good approximation to replace \( \sin^2 \frac{x}{2} \) by its average value, \( \frac{1}{2} \). For \( x > x_0 \) the argument of the trigonometric function becomes small, and we can replace \( \sin^2 \frac{x}{2} \) by \( \frac{x^2}{2} \). A similar approximation has been suggested by Seaton.\(^{18}\) Let us call the value of \( x \) at which we switch between these two approximations \( X \). We have

\[
    \sigma = \pi \left( \frac{\omega}{v} \right)^2 \int_0^X \frac{x M^2(x)}{K^2 + M^2(x)} dx 
    + \frac{x_0^{n/(n-1)}}{2(K^2 + 1)} \int_X^\infty x^{-2n+3} M^2(x) dx.
\]

(29)

In Eq. (29), \( X \) satisfies the condition

\[
    \frac{1}{2} \left( \frac{x_0}{X} \right)^{n-1} \left( \frac{K^2 + M^2(X)}{K^2 + 1} \right)^{1/2} = k
\]

(30)


In which \( k \) is a dimensionless constant of the order of unity.

We consider Eq. (29) in two limiting cases. If \( x_0 \) is small, \( X \) will also be small, and \( M^2(X) \) will be nearly unity. Then we can replace \( M^2 \) by the leading terms in its power-series expansion. The integrals are then elementary. Next, the expansion for \( M^2 \) is substituted into Eq. (30), and a solution for \( X(x_0) \) is determined by iteration. We shall not give the details of this calculation. Including terms of order \( (\omega/\nu)^3 \), we have for \( n > 3 \):

\[
    \sigma = \frac{\pi}{2} \left( \frac{qC}{\hbar v} \right)^{2/(n-1)} \frac{1}{n^2} \frac{1}{K^2 + 1} \frac{2k^2}{n-2} \left( \frac{qC}{\hbar v} \right)^{2/(n-1)} \frac{1}{x_0^{n-3}} \left( \frac{K^2}{(K^2 + 1)(n-1)} \right). \]

(31a)

We may abbreviate this result by lumping the dimensionless constants together into parameters \( \alpha \) and \( \beta \).

\[
    \sigma = \alpha \left( \frac{x_0}{\hbar v} \right)^{2/(n-1)} \frac{1 - \beta \left( \frac{x_0}{\hbar v} \right)^{2/(n-1)} \omega^2}{x_0^2} \frac{1}{v^4}.
\]

(31b)

Thus the leading corrections to the cross section are of order \( (\omega/\nu)^3 (\sigma(\omega = 0)) \).

Next we consider the case in which \( x_0 \) is large. In view of the exponentially decreasing nature of \( M(x) \) for large \( x \), it is legitimate (if \( K \neq 0 \)) to evaluate the cross section in this limit by allowing \( X \rightarrow \infty \). Then we see from Eq. (29) that

\[
    \sigma = \pi \left( \frac{\omega}{v} \right)^2 f(K),
\]

(32)

where

\[
    f(K) = \int_0^\infty \frac{x M^2(x)}{K^2 + M^2(x)} dx.
\]

(32)

In particular, the cross section is independent of the coupling constant (it depends, however, on the range of the force). The corrections to this result are obviously of order \( e^{-x} \).

Equations (31) and (32) assist us in constructing a general qualitative picture of the dependence of the cross section on the parameters describing the process.

(1) Energy difference between the states. If the cross section is regarded as a function of \( \omega \), for fixed velocity and coupling constant, and supposing the inequality (23) to be satisfied for all \( \omega \), it is seen that the cross section attains its maximum value when the energy difference is zero. For \( n > 3 \), it is flat as a function of \( \omega \), corrections being of the order \( \omega^2 \). As the energy difference increases, the cross section ultimately falls off as \( \omega^{-2} \). It should be noted, however, that the exact solution of Eq. (1) may contain terms of order \( \omega \) which Eq. (5) does not give.\(^{11}\)

(2) Velocity. Here, we consider the cross section as a function of velocity for fixed \( q, \omega \). We suppose that (23)
is satisfied for a substantial range of velocities above threshold. For small velocities, if $x_0$ is large, the cross section is proportional to $v^2$. It attains a rather flat maximum, and then decreases, proportional to $v^{-2/(n-1)}$. For very large velocities, (23) cannot be satisfied and the cross section ultimately decreases as $v^{-3}$, which is characteristic of the Born approximation.

(3) **Coupling Constant.** For values of the coupling constant sufficiently small so that Eq. (23) is not satisfied, the cross section is proportional to $q^2$. If $q$ is increased until Eq. (23) holds, the cross section then depends more weakly on $q$, being proportional to $q^{2/(n-1)}$. Finally, for very large $q$, the cross section approaches a limit independent of $q$.

Much of this information can be exhibited graphically if one plots the ratio of the cross section $\sigma$ [as computed numerically from Eq. (29)] to the limiting cross section for $\omega=0$, given by Eq. (19). This ratio is a function of the parameters $x_0$ and $K$. It is shown in Fig. 2 for $n=3$, 4, and 6 as a function of $x_0$ for $K=1$. The results for different values of $K$ are qualitatively quite similar to those that are shown.

A useful empirical representation of the dependence of the cross section on these parameters is the following (for $n>3$):

$$\sigma = \frac{\sigma_0}{1+\gamma(K^2)x_0^2}$$  \hspace{1cm} (33)

in which $\sigma_0$ is the limiting cross section given by Eq. (19), and $\gamma$ is an increasing function of $K^2$. For example, if $n = 6$, then $\gamma(\frac{1}{6}) = 0.12$, and $\gamma(1) = 0.15$. These representations are reasonably accurate for $x_0 < 10$.

The dependence of the cross section on velocity in this two-level model is shown in Fig. 3, which is based on the results of numerical computation for a transition between states with an energy difference of 0.007 eV. The behavior is in accord with the discussion above.

In order to be able to analyze experimental results based on measurements of reactions occurring in a gas at temperature $T$, it is necessary to average the cross section over a Maxwellian distribution of relative velocities. Since what is measured under these conditions is usually a reaction rate, we define an effective cross section at temperature $T$ by

$$\bar{\sigma}_{\text{eff}}(T) = \int P(v)\sigma(v)d\nu$$  \hspace{1cm} (34)

in which $P(v)$ is the probability of finding relative velocity $v$

$$P(v) = \frac{\mu}{2\pi kT} \frac{v^2}{2\pi kT} \exp(-\mu v^2/2kT).$$  \hspace{1cm} (35)

$\mu$ is the reduced mass of the $A$ and $B$ atoms in the gas, and $\nu$ is the average thermal velocity

$$\bar{v} = \left(\frac{8kT}{\mu}\right)^{1/2}.$$  \hspace{1cm} (36)

The averaging can be accomplished with the aid of Eq. (33), and the additional approximation, valid for large $n$, in which $v^{2n/(n-1)}$ is replaced by $v^2$. The result is

$$\sigma_{\text{eff}}(T) = \sigma_0 \left[1 - \gamma x_0^2 - (\gamma x_0^2)^2 \exp(\frac{1}{2}-\gamma x_0^2)\right].$$  \hspace{1cm} (37)

where $\sigma_0$ is the limiting cross section given by Eq. (19) evaluated at a velocity $v_0 = (2kT/\mu)^{1/2}$, and $x_0$ is also evaluated at this same velocity. When $x_0^2$ is large, Eq. (37) reduces to

$$\sigma_{\text{eff}}(T) = 2\sigma_0/\gamma x_0^2.$$  \hspace{1cm} (38)

**D. Dependence of the Cross Section on the Parameters: $l \neq n$**

We now return to a discussion of the behavior of the cross section as determined from Eq. (18) when $l \neq n$.  

![Graph showing the cross section as a function of velocity.](image)
This situation arises when the dominant powers of \( R \) in the diagonal and off-diagonal matrix elements are different. Let us first consider the case \( l = n + 1 \). Our description will not be as detailed as in the case \( n = l \) and we will consider only a few limiting situations. The rather important case of transitions induced by ions between states with an angular momentum difference of unity is included here. This situation is characterized by \( n = 2, \ l = 3 \). Other circumstances in which \( l = n + 1 \) applies can be determined from the Appendix. The dimensions of \( q_1 \) and \( q_2 \) must now be different. We can still define dimensionless parameters as follows:

\[
C^2 = B^2 + \left( \omega q_2 / q_1 q_1^2 \right) A^2, \quad K = \omega q_2 A / v q_1 B
\]

\[
x_0 = \omega \left( \frac{2q_2 C}{h v} \right)^{1/2} \left( n - 1 \right).
\]  

(39)

In place of Eq. (28), we have instead (with \( M = M_{n-1} \))

\[
\sigma = 2\pi \frac{\omega}{\omega_0} \int_0^\infty \frac{x^3 M^2(x)}{K^2 + x^2 M^2(x)} \times \sin^2 \left[ \frac{1}{2} \frac{x_0}{x} \left( \frac{x}{x_0} \right)^{n-1} \left( \frac{K^2 + x^2 M^2(x)}{K^2 + 1} \right)^{1/2} \right] \, dx.
\]

(40)

In order to understand the behavior of the cross section as \( \omega \to 0 \), we must compare two quantities which have dimensions of a length.

Let

\[
L_1 = (q_1 B / h_0)^{1/(n-1)}, \quad L_2 = q_2 A / q_1 B.
\]

If \( L_1 > L_2 \), the diagonal terms of \( U(l) \) can be neglected compared to the off-diagonal terms. Then the cross section is given by Eq. (19) with \( \lambda = 0 \).

On the other hand, we can consider the opposite case in which \( L_2 > L_1 \), which means that the diagonal terms dominate. In this case it does not appear to be possible to give an exact expression in the limit \( \omega = 0 \) as we did in Eq. (19) previously; however, an approximate analysis similar to that employed in Eq. (29) is still possible. Instead of Eq. (29) we have approximately

\[
\sigma = \pi \left[ \frac{\omega}{\omega_0} \right]^3 \int_0^\infty \frac{x^3 M^2(x)}{K^2 + x^2 M^2(x)} \, dx
\]

\[
+ \frac{x_0^2}{2(K^2 + 1)} \int_0^\infty x^{2+n-3} M^2(x) \, dx \right],
\]

(41)

where

\[
\frac{1}{2} \frac{x_0}{x} \left( \frac{x}{x_0} \right)^{n-1} \left( \frac{K^2 + x^2 M^2(x)}{K^2 + 1} \right)^{1/2} = k,
\]

\( k \) being, as before, a constant of order of magnitude unity.

The analysis is somewhat lengthy, and we will give only the result. In place of Eq. (31b) we have to order \( \omega / v \)^2

\[
\sigma = \pi \left( \frac{q_1 B}{4q_2 A} \right)^2 \left( \frac{q_2 A}{h_0} \right)^{4/n} \left\{ 1 + \frac{4k^3}{n-2} \right\}
\]

\[
- \alpha_1 \left( \frac{q_1 B}{q_2 A} \right) \left( \frac{q_2 A}{h_0} \right)^{2/n} \left[ 1 + \beta_1 \left( \frac{\omega q_2 A}{v q_1 B} \right)^2 \right],
\]

(42)

where

\[
\alpha_1 = \frac{2(n-3)}{n-3} \left( \frac{1+6k^2}{n-3} \right)
\]

\[
\beta_1 = n \left( \frac{(n-2)(n-3)}{n-3} \right)^{-1}.
\]

The stronger dependence of the cross section on the coupling constant will be noted.

Equation (42) applies only when \( n > 2 \). It will be seen that when \( n = 2 \), the second integral in Eq. (41) does not converge if we set \( M = 1 \). However, when \( n = 2 \), we have simply

\[
M_{n=1}(x) = e^{-x}.
\]

Then for small \( x_0 \) such that \( M_1(X) = 1 \), we have

\[
\sigma = \frac{\pi}{2} \left[ \frac{X^2 - K^2}{K^2} \ln(1+X^2/K^2) \right.
\]

\[
- \frac{x_0^2}{K^2+1} \left[ 1 + \frac{x_0}{K^2+1}\right].
\]

(43)
Then, after solving for $X$, we obtain

$$
\sigma = \frac{\pi}{2} \left( \frac{q_1 B}{\hbar v} \right)^2 \left[ 1 - \frac{\beta^2}{\alpha} \ln \left( 1 + \frac{\alpha}{\beta^2} \right) + \frac{4k^2}{\alpha} \frac{E \ln \left( \frac{2q_1 A c}{\hbar^2} \right)}{} \right] \tag{44}
$$

in which we have defined the following symbols

$$
\alpha = \frac{1}{2} \left[ 1 + (1 + 4\beta^2)^{1/2} \right]; \quad \beta = \frac{hq_1 A \pi}{q_1 B^2}.
$$

It is to be noted that, because of the presence of the exponential integral function in Eq. (44), the cross section in this case becomes logarithmically infinite as \(\omega \to 0\). Results of numerical calculation for this case are shown in Fig. 4.

Finally we should consider briefly the situation in which \(n = l + 1\). It is seen from the Appendix that this situation occurs in reactions between neutral atoms possessing no multipole moments if the states involved in the transition have opposite parity. The analysis is rather similar to that described above. In this case, however, the characteristic lengths are

$$
L_1 = \left( \frac{q_2 A}{\hbar v} \right)^{1/(n-2)},
$$

$$
L_2 = \frac{q_1 B}{q_2 A}.
$$

Now, if \(L_2 \gg L_1\), we can neglect the diagonal terms, and return to Eq. (19) with \(A = 0\). But, if \(L_2 \gg L_1\), the diagonal terms are important. We will present the result for this situation in the case \(\omega = 0\).

$$
\sigma = \frac{\pi}{2} \left( \frac{q_1 B}{q_2 A} \right)^2 \ln \left( \frac{q_2 A}{q_1 B} \right)^{1/(n-2)} + \frac{k^2}{n-2} \tag{45}
$$

in which \(k\) is again a constant of order of magnitude unity.

III. ALKALI-METAL–RARE-GAS COLLISIONS

We now turn to a quantitative description of reactions of the type

$$
A(^3P_{1/2}) + B \rightarrow A(^3P_{3/2}) + B
$$

mentioned in the Introduction.\(^{19}\) The leading term in the interaction is obtained from Eq. (A11) of the Appendix, and (since the states have the same parity)

$$
V_{\text{eff}} = -\frac{1}{4}(\alpha \rho^2/R^2)^2(3 \cos \theta^2 + 1) \tag{46}
$$

in which \(\alpha\) is the polarizability of the rare gas atom and \(\theta\) is the angle between \(r\) and \(R\). The basis states for the construction of the matrix \(Q\) are the six \(P\) levels,

four of which have \(j = \frac{3}{2}\) and two, \(j = \frac{1}{2}\). The wave functions for these states are products of radial functions and combinations of spin functions and spherical harmonics; these combinations are given by Schiff.\(^{20}\) It is a straightforward matter to perform the integration over the electronic coordinates, and then to calculate the integrals \(\int_{-\infty}^{\infty} Q(Q) dQ\) required by Eq. (7) with the use of Eq. (15). The matrix simplifies substantially in the limit that the energy difference between the states can be neglected (it is 0.002 eV for Na and 0.007 eV for K). With this assumption, and if the basis states are arranged properly, the matrix \(U\) defined in Eq. (7) consists of two identical diagonal blocks:

$$
U(\infty) = \begin{pmatrix} u_1 & 0 \\ 0 & u_1 \end{pmatrix}
$$

then the \(3 \times 3\) matrix \(u_1\) is given by

$$
u_1 = -a \begin{pmatrix} 1 & 5/\sqrt{3} & -5\sqrt{3} \\ 5/\sqrt{3} & -1 & -2 \\ -5\sqrt{3} & -2 & 0 \end{pmatrix}
$$

with

$$
a = \frac{3\pi K}{16 \hbar^6} \langle r^2 \rangle
$$

in which \(\langle r^2 \rangle\) represents the average value of \(r^2\) in the \(P\) state, computed with appropriate radial wave functions. The basis states may be characterized by giving the values of \((j, m_j)\). For the matrix of Eq. (47b) these are, in order \((\frac{3}{2}, \frac{3}{2}); (\frac{3}{2}, \frac{1}{2}); (\frac{3}{2}, -\frac{1}{2})\); and \((\frac{1}{2}, \frac{1}{2}); (\frac{1}{2}, -\frac{1}{2}); (\frac{1}{2}, -\frac{1}{2})\). An identical matrix connects the states \((\frac{3}{2}, -\frac{3}{2}); (\frac{3}{2}, \frac{1}{2}); (\frac{3}{2}, -\frac{1}{2})\); and \((\frac{1}{2}, \frac{1}{2}); (\frac{1}{2}, -\frac{1}{2}); (\frac{1}{2}, -\frac{1}{2})\). It will be observed that only states with \(\Delta m_j = \pm 2\) are coupled. This is a consequence of the assumption that \(\omega = 0\). The matrix elements connecting states with \(\Delta m_j = \pm 1\) are of order \(\omega/\gamma\). A nonessential dependence on \(\phi\) in Eq. (47b) has been discarded.

We must determine \(\exp(-iU)\). This is conveniently done by first obtaining a unitary transformation \(S\) which diagonalizes \(U\).

$$
US = SA, \tag{48}
$$

where \(A\) is the diagonal matrix of the eigenvalues of \(U\) and \(S\) is constructed from the normalized eigenvectors of \(U\). Then we have

$$
\exp(-iU) = S \exp(-iA) S^+, \tag{49}
$$

The matrix \(\exp(-iA)\) is diagonal. If the elements of \(A\) are \(\lambda_{nm}\), then the elements of \(\exp(-iA)\) are \(\exp(-i\lambda_{nm})\). The eigenvalues and eigenvectors of \(U\) as given in (47) can be determined without difficulty, since the secular equation factors. A straightforward computation gives

$$
\exp(-iU) = \begin{pmatrix} \exp(-i\lambda_1) & 0 \\ 0 & \exp(-i\lambda_2) \end{pmatrix}
$$

---


in which

\[
\exp(-i\eta_4) = \begin{cases} 
\frac{1}{2} \left[ e^{i\eta_4} + e^{-i\eta_4} \right] & \frac{-1}{\sqrt{12}} \left[ e^{i\eta_4} - e^{-i\eta_4} \right] \\
\frac{3}{2} e^{i\eta_4} + \frac{1}{2} e^{-i\eta_4} & \frac{1}{3} \sqrt{2} e^{i\eta_4} - \frac{e^{-i\eta_4}}{\sqrt{2}} \\
\frac{1}{3} \left[ e^{i\eta_4} - e^{-i\eta_4} \right] & \frac{1}{3} \sqrt{2} e^{i\eta_4} + \frac{e^{-i\eta_4}}{\sqrt{2}} 
\end{cases}
\]

(50b)

The cross sections are obtained from the appropriate matrix elements according to Eqs. (7) and (8). The integration over \( \rho \) is performed as in Eq. (19). We then sum over the final states and average over the initial states. We obtain for the transition \( \frac{1}{2} \rightarrow \frac{1}{2} \)

\[
\sigma_{\frac{1}{2} \rightarrow \frac{1}{2}} = C \left( \frac{3\pi \alpha e^2 (r^*)^2}{\hbar} \right)^{2/5}
\]

(51)

in which

\[
C = \frac{\pi^2 (1 + 4\pi^2 + 5\pi^2)}{45\pi^2(7/5) \sin(\pi/5)} \approx 1.95. \tag{52}
\]

The cross section for the \( \frac{1}{2} \rightarrow \frac{3}{2} \) transition is just twice that given in Eq. (51).

The cross sections given by Eq. (51) have been evaluated for collisions of sodium and potassium atoms with argon and helium. Self-consistent-field wave functions were used to evaluate the matrix element \( (r^*)^2 \). We give below the values of the cross section evaluated at a velocity

\[
v = \frac{2kT}{\mu} \tag{51/2}
\]

in which the temperature \( T \) is taken as 450°K, and \( \mu \) is the reduced mass of the interacting atoms. This temperature is close to that existing in the experiment of Lochte-Holtgreven.\(^5\) Since we have not computed the cross section for values of \( \omega/\nu \neq 0 \), we cannot perform the thermal averaging discussed in Sec. II. The results are given in Table I, where they are compared with the experimental measurements of Jordan,\(^2\) and Krause,\(^1\) and with Seiwert's deductions\(^4\) from the measurements of Lochte-Holtgreven.\(^8\) The results have been obtained with the use of the following numbers:

\[
\alpha_{Ar} = 16.3 \times 10^{-26} \text{ cm}^2, \quad \alpha_{He} = 2.1 \times 10^{-26} \text{ cm}^2
\]

\[
(r^*)_{Na} = 40.1 a_0^3, \quad (r^*)_{K} = 52.0 a_0^3.
\]

It is seen that the calculated values are in moderate agreement with the experimental results. Closer agreement is not to be expected since the computations are based on the assumption that \( \omega = 0 \), on the approximate solution of Eq. (5), and thermal averaging has not been performed.

Our result that the cross section for the \( \frac{1}{2} \rightarrow \frac{3}{2} \) and the \( \frac{3}{2} \rightarrow \frac{1}{2} \) transitions are in the ratio of 1 to 2 is an exact consequence of the impact-parameter method, and is independent of all specific assumptions relating to the interaction and of the approximate nature of Eq. (5). This may be seen from the following argument.

The state vector at \( t = \infty \) can be obtained from that existing at \( t = -\infty \) by a unitary transformation, even though this will not generally be given by Eq. (5). The elements of any \( n \times n \) unitary matrix \( U \) satisfy

\[
\sum_{j=1}^{n} |U_{ij}|^2 = \sum_{j=1}^{n} |U_{ji}|^2 = 1.
\]

The desired result follows from this statement when the cross sections for the two processes in question are written out in terms of the matrix elements of the transformation.

It follows that, in order to obtain a value of the cross-section ratio different from 2, we must go beyond the impact-parameter method; that is, we must treat the relative motion of \( A \) and \( B \) by quantum mechanics. A rough estimate of this effect indicates that the ratio of 2 will be reduced by a factor of the order of \( 1 - (\hbar \omega/kT) \).

**ACKNOWLEDGMENT**

We are indebted to Dr. F. W. Cummings for pointing out an error in an earlier version of this work.

**APPENDIX**

The principal objective of this paper is to describe a method for computing cross sections for inelastic collisions of atoms and to apply this method in a simple
Table II. The dependence of the matrix elements relating to an electronic transition of atom A interacting with an object B is given. The quantity $|\psi|^2$ is a matrix element of the $mth$ power of the electronic coordinate between the states. All angular factors and vector or tensor indices are omitted.

<table>
<thead>
<tr>
<th>Object B possesses</th>
<th>Matrix element same parity $\Delta l = 0, 2$</th>
<th>Matrix element opposite parity $\Delta l = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge $Q_B$</td>
<td>$e\psi_Q(r)/R^m$</td>
<td>$e\psi_Q(r)/R^m$</td>
</tr>
<tr>
<td>Permanent dipole moment $\mu_B$</td>
<td>$e\mu_B(r)/R^m$</td>
<td>$e\mu_B(r)/R^m$</td>
</tr>
<tr>
<td>Quadrupole moment $D_B$</td>
<td>$eD_B(r)/R^m$</td>
<td>$eD_B(r)/R^m$</td>
</tr>
<tr>
<td>Polarizability (B is spherically symmetric)</td>
<td>$\alpha_B(r^2)/R^m$</td>
<td>$\alpha_B(r^2)/R^m$</td>
</tr>
</tbody>
</table>

*The matrix element between two $n$ states falls off exponentially.*

The dominant interaction between two atoms A and B depends on whether the objects possess permanent multipole moments, and on whether the transition of interest occurs between states of the same or of opposite parity. In order to include the case in which $B$ is a molecule, we have also considered the case in which $B$ has a dipole moment. The results are presented in Table II; we will discuss the derivation below.

Let $A$ and $B$ be characterized by charges $Q_A$, $Q_B$; instantaneous dipole moments $\mathbf{p}_A$, $\mathbf{p}_B$; and quadrupole moment tensors $\mathbf{D}_{A,i}$ and $\mathbf{D}_{B,i}$. If the coordinates of the electrons on atom $A$ are denoted by $\xi_i$ (we do not write the electron number explicitly), then

$$P_{A,i} = \varepsilon \sum_j \xi_j,$$

$$D_{A,i} = \frac{1}{2} \varepsilon \sum_j (\xi_j \delta_{ij} - \frac{1}{2} \xi_i \delta_{ij}).$$

The sum includes all electrons of $A$. Similar expressions are valid for $B$. Octupole and higher moments are neglected.

The interaction potential $V$ between $A$ and $B$ can be expressed as a series of interactions between the various instantaneous multipole moments. The coordinate system is shown in Fig. 1, and the components of the vector $\mathbf{R}$ are denoted by $x_j$. It is assumed that $A$ and $B$ do not overlap. We include interactions up to quadrupole-quadrupole. Then we have

$$V = \frac{Q_A Q_B}{R} + \frac{(Q_A \mathbf{p}_B \cdot - Q_B \mathbf{p}_A \cdot \mathbf{x}_i)}{R^3} + \frac{(Q_A D_{B,i,j} + Q_B D_{A,i,j}) \mathbf{x}_i \mathbf{x}_j}{R^5}$$

$$+ \left[ \frac{(\mathbf{p}_A \cdot \mathbf{p}_B) - \mathbf{p}_A \cdot \mathbf{p}_B \cdot \mathbf{x}_i \mathbf{x}_j}{R^3} + \frac{2}{5} \frac{(\mathbf{p}_A \cdot \mathbf{D}_{B,i,j} - \mathbf{p}_B \cdot \mathbf{D}_{A,i,j}) \mathbf{x}_i \mathbf{x}_j}{R^5} \right]$$

$$+ \frac{2 D_{A,i,j} D_{B,i}}{R^5} - \frac{20}{R^7} + \frac{35}{R^9} \left[ \cdots \right]. \tag{A1}$$

Since $R$ varies with time, this interaction is time-dependent, and may cause $A$ and $B$ to undergo transitions. To describe this process, we expand the wave function for the $A$-$B$ system in terms of product wave functions for $A$ and $B$ separately. Let $\psi_n(A)$ denote the time-independent wave function for state $n$ of atom $A$; similarly, $\psi_j(B)$ the wave function for state $j$ of object $B$. We neglect exchange effects and write a general wave function for the $A$-$B$ system as

$$\Psi(A,B) = \sum_{n,j} a_{n,j}(t) \psi_n(A) \psi_j(B) e^{-i\omega_{n,j}t}, \tag{A2}$$

where $\omega_{n,j} = \hbar^{-1} [E_{n,A} + E_{j,B}]$. By standard methods, the coefficients $a_{n,j}$ are found to satisfy the equation

$$\frac{da_{n,j}}{dt} = \frac{i}{\hbar} \sum_{n,k} \langle n|V|m\rangle a_{n,k}(t) e^{-i\omega_{n,k}t}, \tag{A3}$$

with $\omega_{n,k} = \omega_{n,k} - \omega_{n,j}$. The interaction potential $V$ is given by Eq. (A1).

We suppose that atom $A$ has some low-lying excited states, and we are concerned with transitions which occur among these. We shall assume that $B$ does not have any low-lying excited states, so that it will remain in its ground state. Therefore, we are interested in the matrix element $\langle n|V|m|0\rangle$.

If $B$ possesses a permanent dipole moment, the expectation value of $\mathbf{r}_j$ will not vanish. Hence, if the $m-n$ transition of $A$ is allowed, the dipole-dipole term of (1) will give the leading contribution to the matrix element. This is of order $R^{-4}$. However, if the $m-n$ transition of $A$ is optically forbidden, the leading contribution will come from the dipole-quadrupole interaction which is of order $R^{-4}$. If $B$ has a quadrupole moment, but not a dipole moment, the leading term is of order $R^{-4}$ for an allowed transition, and $R^{-5}$ for a forbidden one. We will not consider higher moments.

However, suppose $B$ has no multipole moment. This will be the case if, for instance, $B$ is a noble-gas atom. In
this case, we must work to second order in the perturbation as is customary in the theory of the Van der Waals force.\textsuperscript{22,23} In order to do this, we divide the levels of the two-particle system into two groups: Group 1 includes those levels of \( A \) between which real transitions occur, plus the ground state of \( B \), while group 2 includes all other levels of the system which are only virtually excited. It is necessary for the validity of the analysis that all levels in group 1 be well separated in energy from any of those in group 2. This requirement may be expressed somewhat more precisely by the statement that if \( m_{(A)} j_{(A)} \) are any states in group 2, while \( n_{(A)} 0_{(B)} \) are states of group 1, then \( \omega_{m_{(A)} n_{(B)}} \ll \varepsilon \) any frequency occurring with appreciable amplitude in \( V(R) \).

We shall assume that this requirement is satisfied, and that the amplitudes of states in group 2 can be determined by first-order perturbation theory. A standard calculation then shows that we may replace Eq. (A3) by

\[
\frac{da_n}{dt} = -\sum_{j} \frac{i}{\hbar} \sum_{j^i} \frac{n|V| j^i j | V|m0}{\hbar \omega_{m_{(A)} j^i}} \times e^{-i\omega_{m_{(A)} n_{(B)}} t} a_m(t) \quad (A4)
\]

in which the sum over \( m \) includes only states in group 1 and the sum over \( j^i j \) includes all states in group 2. This result is, of course, well known, but it is useful to understand the conditions under which it applies.

Inspection of Eqs. (A1) and (A4) leads to the observation that the leading terms in Eq. (A4) will be of order \( R^{-6} \) since they arise from second-order perturbation of the dipole-dipole interaction. This was to be expected since we are dealing here with the Van der Waals interaction between two atoms. The next term in the series is of order \( R^{-7} \), and arises from cross terms between the dipole-dipole and dipole-quadrupole interactions. The term of order \( R^{-6} \) may be expected to dominate if states \( m \) and \( n \) are of the same parity, whereas if they have opposite parity, the leading contribution will be of order \( R^{-7} \).

We can define an effective potential which acts on the states of atom \( A \) falling in group 1 by

\[
(n | V_{eff} | m) = \sum_{j^i} \frac{n|V| j^i j | V|m0}{\hbar \omega_{m_{(A)} j^i}} \quad (A5)
\]

in which the sum includes states in group 2. Substitution of (A5) into (A4) converts (A4) into an equation resembling (A3) except that only states of \( A \) in group 1 are included in the sum

\[
\frac{da_n}{dt} = -\sum_{m} \frac{i}{\hbar} \sum_{j} \frac{n|V|m}{\hbar \omega_{m_{(A)} j^i}} a_m(t) e^{-i\omega_{m_{(A)} n_{(B)}} t}. \quad (A6)
\]

Here \( a_n = a_{s_{(A)}}, \omega_{m_{(A)} n_{(B)}} = \omega_{m_{(A)} n_{(B)}} \) etc. This is Eq. (1) of the main text.

We can give an approximate evaluation of \( V_{eff} \) in terms of the polarizability of \( B \). For this purpose we suppose, following Margenau\textsuperscript{21} that the energy denominators which appear in Eq. (A5) can be replaced by a constant. This constant characterizes the energy spectra of the atoms in an approximate way. There are two interesting cases:

1. If the excited states of \( A \) which contribute to Eq. (A5) are of low energy compared to the excited states of \( B \), then we set \( \hbar \omega_{m_{(A)} j^i} = -\Delta E_B \), where \( \Delta E_B \) is a characteristic excitation energy of \( B \).

2. If the spectra of \( A \) and \( B \) are similar, with excited states spaced more or less equally, then \( \hbar \omega_{m_{(A)} j^i} = -2\Delta E_B \).

We will analyze case (1) here; the result for case (2) can be obtained at the end simply by multiplying Eq. (A11) by \( \frac{1}{2} \).

We can now write Eq. (A5) as

\[
(n | V_{eff} | m) = -\frac{1}{(1/\Delta E_B) (n|V|m0)} \frac{1}{|r B|^2}. \quad (A7)
\]

To obtain a more explicit result we take (here only) the \( s \) axis to lie along \( R \), and insert Eq. (A1). Only the two leading terms are retained. A straightforward, but somewhat lengthy calculation gives, if exchange terms are neglected

\[
(n | V_{eff} | m) = -\frac{\mathcal{F}}{3\Delta E_B R^6} \sum \left( \begin{array}{c} \xi^2(3 \cos^2 \theta + 1) \\ R^2 \cos^2 \theta \end{array} \right) m \quad (A8)
\]

in which

\[
\langle r B^2 \rangle = \int \frac{|u_i(\xi^{(B)})|^2 \xi^{(B)} z^2 d\tau_B}{R} \quad (A9)
\]

and the sum in (A9) includes all the occupied one-electron states of \( B \). The sum in Eq. (A8) includes all electrons of \( A \). These electrons have coordinates \( \xi, \theta, \phi \) in the system mentioned above.

The polarizability of \( B, a_B \), is determined by considering the change in energy of \( B \) in a uniform field of strength \( F \). Let the perturbation be

\[
V_F = \varepsilon \sum F \xi^{(B)}. \quad (A10)
\]

To second order in \( F \), the change in energy of \( B \) is given by

\[
\frac{1}{2} a_B F^2 = \sum \left| \left( \begin{array}{c} 0 | V_F | j \end{array} \right) \right|^2 \quad (A10)
\]

It is now assumed, and again, this is only an approximation, that the energy denominators can be replaced by the same constant \( -\Delta E_B \) which appears in Eq. (A7). Then we obtain

\[
-\frac{1}{2} a_B F^2 = -\left( \Delta E_B \right)^{-1} \langle 0 | V_F^2 | 0 \rangle = -\frac{1}{2} \mathcal{F} \langle r B^2 \rangle. \quad (A10)
\]
We solve this for $\langle r_p^3 \rangle$ and insert the result into (A8).

$$
(n|V_{at}|m) = -\frac{\alpha_0 \hbar^2}{8 R^4} \sum_n \left( n^2 (3 \cos^2 \theta + 1) + \frac{122 \hbar^2}{R} \cos \theta \right) m,
$$

(A11)

This result is used in the main text [Eq. (40)] in discussing the interaction of an excited atom of an alkali metal with one of a rare gas. Evidently, our assumptions about the energy spectra of the atoms should apply in that case. It is interesting to note that our expression for the effective potential acting on $A$ can be derived classically by determining the change in energy of $B$, regarded as a lump of polarizable material, in the presence of $A$, which possesses instantaneous dipole and quadrupole moments.

Finally, we observe that if $A$ is described by a determinantal wave function, nonzero matrix elements exist only between states which differ by the occupancy of a single electron state. Thus, we may use the symbols $m, n$ to refer to one-particle states of $A$ without ambiguity, and this is done in the main text.

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**X-Ray Yields from K-Shell Ionization by $\alpha$ Particles**

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(Received 7 May 1965; revised manuscript received 9 July 1965)

The characteristic $K$ x-ray yields are measured in Sn, Te, Ce, Sm$^{144}$, Sm$^{153}$, Sm$^{154}$, Gd$^{157}$, W$^{186}$, and Pb, by bombarding them with $\alpha$ particles of energy 4 and 3 MeV. No excess of x-ray yield has been observed in the atoms of deformed even-even nuclei, when the observed data were corrected for the x-ray contribution due to internal conversion by using the theoretical values of $K$-shell internal-conversion coefficients. The observed variation of the number of $K$-shell vacancies per microcoulomb with the atomic number indicates that the $E2$ internal-conversion coefficients and also the probability for $K$-shell ionization are unaffected by nuclear deformation.

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**I. INTRODUCTION**

In the earlier measurements$^1$ of $K$-shell ionization and Coulomb excitation by bombardment with $\alpha$ particles, a larger characteristic $K$ x-ray yield was observed in atoms of deformed even-even nuclei. It was concluded from these measurements that this larger $K$ x-ray yield was due to higher internal-conversion probability which was thought possible due to some unknown effect of nuclear structure on the internal-conversion process. Several measurements$^2-^4$ of the $K$-shell internal-conversion coefficients supported the above conclusion, and an anomaly between the experiments and the theory was reported to exist. As the transitions ($2^+ \rightarrow 0^+$) involved in these cases are pure $E2$ in character, it was difficult to explain the above discrepancy by taking into account the finite-nuclear-size effect$^5$ and the dynamic effects of nuclear structure.$^6$ The recent $\alpha_0$ measurements with improved techniques carried out by us$^7$ in eight deformed even-even nuclei do not seem to indicate any discrepancy between theory and experiment. This has been supported by several other recent measurements.$^8-^{10}$ However, Hamilton et al.$^{11}$ point out the possibility of some nuclear-structure effects in the $E2$ conversion process in deformed nuclei from their measurements of particle parameters for such transitions.

In view of the above situation regarding the $E2$ conversion process we have carried out the measurements of $K$-shell ionization by the impact of 4- and 3-MeV $\alpha$ particles in Sn, Te, Ce, Sm$^{144}$, Sm$^{153}$, Sm$^{154}$, Gd$^{157}$, W$^{186}$, and Pb. The measurements on the isotopes of Sm, viz., Sm$^{144}$, Sm$^{153}$, and Sm$^{154}$, have provided a good comparison of the characteristic $K$ x-ray yields in atoms of spherical and deformed nuclei.

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9. P. Ermans and Solve Hultberg, Arkiv Fysik (to be published).