probability for rotational excitation upon collision between a helium atom and a hydrogen molecule is computed using the calculated interaction energy.

ACKNOWLEDGMENTS

The author wishes to thank Professor George F. Koster for suggesting this problem and for acting as his thesis advisor. The author is also indebted to the National Science Foundation for a graduate fellowship held during the course of this research. Thanks are also due to Charles A. Christy and Donald E. Ellis for providing the necessary molecular integral subprograms. The computations were done at the MIT Cooperative Computing Laboratory.

Inelastic Scattering from a Diatomic Molecule: Rotational Excitation upon Collision between He and H_2 and H_2 and H_2[†*]

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(Received 25 January 1963)

The formalism developed by Arthurs and Dalgarno has been used in the distorted wave approximation to calculate the inelastic scattering cross section for rotational excitation from the $j=0$ to the $j=2$ rotational state in collisions between a helium atom and a hydrogen molecule or two hydrogen molecules. All necessary computations were done with a digital computer, thus, allowing the Arthurs-Dalgarno formalism to be applied with no added approximations. The interaction energy between He and H_2 obtained in the preceding paper was used for the He-H_2 calculation while the interaction energy given by Takayanagi was used for the H_2-H_2 problem. Values for the total inelastic cross sections are given as well as graphs for the He$-H_2$ differential scattering cross section. Incident kinetic energies up to only 0.25 eV in the center-of-mass system were considered; for these low energies, vibrational or electronic excitation is impossible so that change in rotational quantum number is the only inelastic process possible. The results obtained for the H_2-H_2 cross section do not agree with the rate of de-excitation from the $j=2$ rotational level in H_2 gas as measured by dispersion experiments with ultrasonic waves. The disagreement may be due to an incorrect H_2-H_2 interaction potential or failure to consider all important de-excitation mechanisms.

I. INTRODUCTION

WHEN a diatomic molecule collides with another particle, atom, or molecule, inelastic as well as elastic scattering may occur; the diatomic molecule may undergo changes in any of the quantum numbers describing the state of its internal coordinates. If initially the diatomic molecule is in its ground electronic, vibrational, and rotational state, and we confine ourselves to incident kinetic energies measured in the center-of-mass coordinate system that are below the energy necessary to excite the molecule to its first excited vibrational state, then the only energetically possible inelastic process is change in rotational quantum number. Under these conditions, fairly low-incident energies, and no other competing inelastic process, it is possible to compute the inelastic scattering cross section from a rigorous quantum mechanical formalism and only two approximations. The first approximation is to treat the problem in the Born-Oppenheimer or adiabatic approximation where the net effect of the electrons

is to provide a potential energy function of r, the distance measured along a line from the incoming particle to the center of mass of the diatomic molecule, and γ, the angle between this line and the line joining the two nuclei of the molecule. This approximation is surely justified for low-incident velocities where the electrons have plenty of time to readjust themselves as the colliding partners move towards their rendezvous. The second necessary approximation is to use the method of distorted waves[1,2] to solve the coupled differential equations which result from the Schrödinger equation of the problem. For low-incident energies, it turns out that the distorted-wave approximation is quite good. The low-incident kinetic energies also make feasible the use of a partial wave analysis of the problem. While this is not an approximation, its use reduces the computations to solving ordinary differential equations, an easy task for a digital computer.

In the present work, the general methods described above are used to calculate the inelastic cross section for rotational excitation of a hydrogen molecule from the $j=0$ to the $j=2$ state when it collides with either

[1] T. Wu and T. Ohmura, *Quantum Theory of Scattering* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962), p. 219.
[2] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Oxford University Press, New York, 1949), Chaps. VI and VIII.
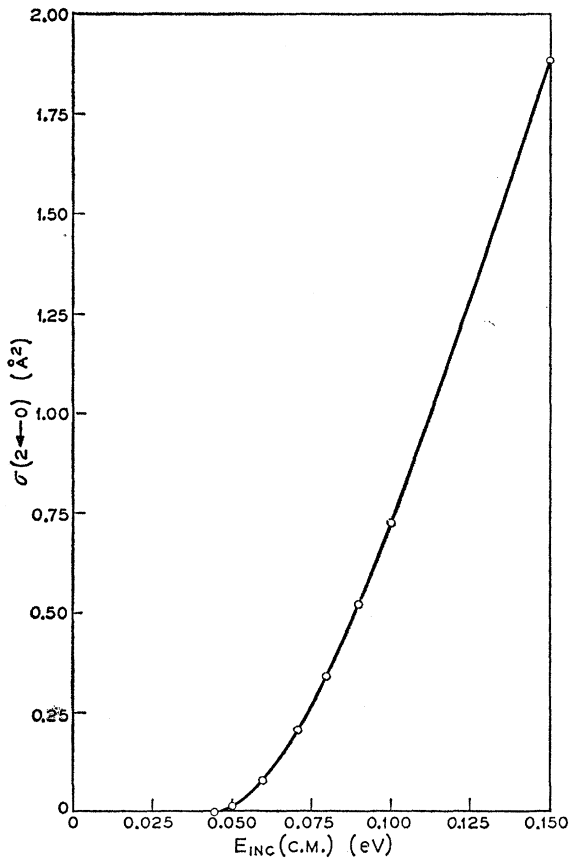
FIG. 1. Inelastic scattering of He by H_2. Potential of Eq. (5.2). Total inelastic cross section for the $j=0$ to $j=2$ transition vs incident kinetic energy.

a helium atom or another hydrogen molecule. The hydrogen molecule is treated as if it were a rigid rotor so that the theory developed by Arthurs and Dalgarno[3] may be used. This theory is based upon an earlier work on nuclear scattering theory given by Blatt and Biedenharn,[4] and it describes rigorously the scattering, both elastic and inelastic, of a particle from a rigid rotor. In treating rotational excitation from the state j to the state j', considerable simplification results if we do not distinguish between initial and final states of the magnetic quantum number m_j. This simplification is made in the Arthurs-Dalgarno treatment and, as a result, all cross sections calculated in this paper are for processes which do not distinguish between initial and final m_j states. For a formalism which includes m_j transitions, as well as for an alternative derivation of the Arthurs-Dalgarno formalism, one should see the paper by Gioumousis and Curtiss.[5]

The problem of rotational transition upon collision between two hydrogen molecules has been treated by

Takayanagi[6] and a few other authors. These treatments, while they profess to be distorted wave treatments, suffer from the fact that many other approximations were introduced in order to make computation easier.

II. ARTHURS-DALGARNO FORMALISM FOR SCATTERING FROM A RIGID ROTOR

The Arthurs-Dalgarno paper[3] forms the basis for the scattering computations performed in this research. We list here, for reference, only the equations which require computational consideration. To compute cross sections, the ordinary differential equations

$$\left[\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2}+k_{jj'}{}^2-\frac{l'(l'+1)}{r^2}\right)-\langle j'l';J|V|j'l';J\rangle\right]$$
$$\times w_{j'l'}{}^{Jjl}(r)=0 \quad (2.1)$$

must be solved subject to the boundary conditions

$$r\to 0:\quad w_{j'l'}{}^{Jjl}(r)=0, \quad (2.2a)$$

$$r\to\infty:\quad w_{j'l'}{}^{Jjl}(r)=\sin(k_{jj'}r-\tfrac{1}{2}l'\pi+\eta_{j'l'}{}^{Jj}). \quad (2.2b)$$

When this is accomplished, the scattering S matrix[7] is given by

$$S^J(jl;jl)=\exp[2i\eta_{jl}{}^{Jj}], \quad (2.3a)$$

$$S^J(jl;j'l')=-2i(k_{jj'}/k_{jj})^{1/2}\beta_{j'l'}{}^{Jjl}$$
$$\times\exp[i(\eta_{jl}{}^{Jj}+\eta_{j'l'}{}^{Jj})], \quad (2.3b)$$
$$\text{for}\quad j\neq j' \quad\text{or}\quad l\neq l'.$$

Here,

$$\beta_{j'l'}{}^{Jjl}=\frac{2\mu}{\hbar^2 k_{jj'}}\int_0^\infty dr w_{j'l'}{}^{Jjl}(r)$$
$$\times\langle j'l';J|V|jl;J\rangle w_{jl}{}^{Jjl}(r). \quad (2.4)$$

The total and differential scattering cross section may be obtained from the S matrix by use of the algebra of Clebsch-Gordan and Racah coefficients.[8] It should be noted that there is an error in the definition of $\beta_{j'l'}{}^{Jjl}$ in the Arthurs-Dalgarno paper. Our Eq. (2.4) differs from their Eq. (37) by a factor $2\mu/\hbar^2 k_{jj'}$. Equation (2.4) is correct.

III. EXPANSION OF THE POTENTIAL $V(r,\gamma)$

The interaction potential $V(r,\gamma)$ will be specified by giving the functions $v_\mu(r)$ in its expansion in a series of Legendre functions.

$$V(r,\gamma)=\sum_{\mu=0}^\infty v_\mu(r)P_\mu(\cos\gamma). \quad (3.1)$$

[3] A. M. Arthurs and A. Dalgarno, Proc. Roy. Soc. (London) A256, 540 (1960).
[4] J. M. Blatt and L. C. Biedenharn, Phys. Rev. 24, 258 (1952).
[5] G. Gioumousis and C. F. Curtiss, J. Math. Phys. 2, 96 (1961).

[6] K. Takayanagi, Sci. Rept. Saitama Univ. A3, 65 (1959); K. Takayanagi, Proc. Phys. Soc. (London) A70, 348 (1957).
[7] Reference 1, p. 412.
[8] L. C. Biedenharn, J. M. Blatt, and M. E. Rose, Rev. Mod. Phys. 24, 249 (1952).

The matrix elements $\langle j''l''; J | V | j'l'; J \rangle$ can then be expressed

$$\langle j''l''; J | V | j'l'; J \rangle = \sum_{\mu=0}^{\infty} f_\mu(j''l''; j'l'; J) v_\mu(r), \quad (3.2)$$

where

$$f_\mu(j''l''; j'l'; J) = \langle j''l''; J | P_\mu(\cos\gamma) | j'l'; J \rangle. \quad (3.3)$$

IV. COMPUTER PROGRAMMING METHODS

A package of programs was prepared for the IBM 709 digital computer to do the scattering computations in the distorted-wave approximation. The subprograms comprising the package were largely Fortran coded, although a few were done in FAP in order to save time and facilitate certain operations. The package considers all parameters to be center-of-mass system values and uses electron volts as the energy unit and angstroms as the unit of length. The potential $V(r,\gamma)$ is specified by giving the functions $v_\mu(r)$ in its expansion in $P_\mu(\cos\gamma)$, Eq. (3.1). A subprogram is supplied which tells the maximum value of μ occurring in the expansion and evaluates the different $v_\mu(r)$ functions. Although as many terms as desired may thus be taken, only a $v_0(r)$ and a $v_2(r)$ term were actually used in the calculations. The differential equations (2.1) were numerically integrated using the method of Runge-Kutta and Gill.[9] At the end of the numerical integration, the function was specified by a table of values in core storage. Each numerical integration was started by picking a value of r close enough to zero so that the interaction energy was very much greater than the incident kinetic energy. For this value of r, the value of the function was set equal to zero and the value of the slope was set equal to some arbitrary value. The initial value of the slope is unimportant since the entire function is normalized to conform to Eq. (2.2b) at the end of the process. The initial value of r is made small enough so that by decreasing it further we make no substantial change in the asymptotic behavior of the function. With these initial values of the function and its slope, the numerical integration process begins to compute the values of the function for larger values of r. A small integration interval is used at first, since in this region the potential varies quite rapidly and the solutions must be known accurately. As r passes the point where the potential has almost completely died out, the integration interval is increased to speed up the process. In this region the function is oscillatory and its phase shift is calculated every time it crosses the r axis by comparison with the corresponding values of the spherical Bessel and Neumann functions. When two successive evaluations of the phase shift agree to within a predetermined parameter, the numerical integration stops. This parameter is usually set equal to 0.0002 rad but was never larger than 0.002 rad. The function is now normalized to have the asymp-

[9] A. Ralston and H. S. Wilf, *Mathematical Methods for Digital Computers* (John Wiley & Sons, Inc., New York, 1960), p. 110.
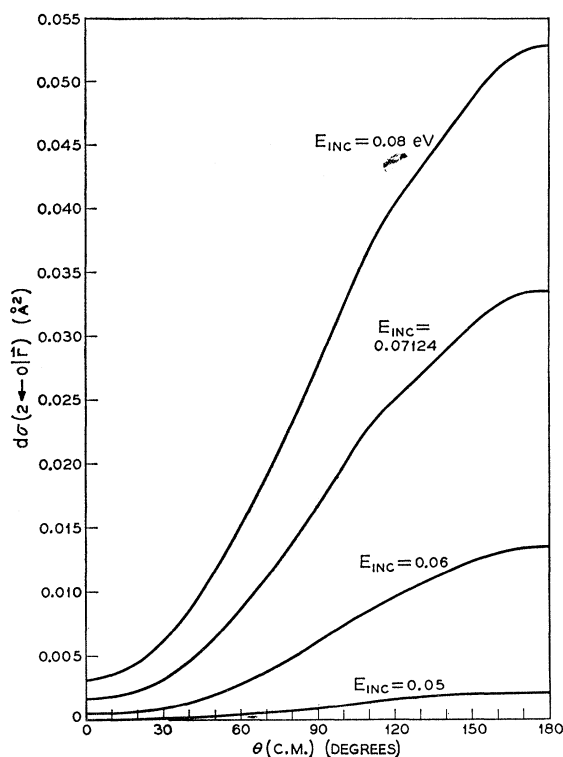

FIG. 2. Inelastic scattering of He by H_2. Potential of Eq. (5.2). Differential scattering cross section in the center-of-mass system for the $j=0$ to $j=2$ transition.

totic behavior (2.2b) by dividing through by an appropriately determined constant. After two such functions have been determined by the preceding method, the integrand of Eq. (2.4) is evaluated as a table of values, and the value of the $\beta_{j'l'}{}^{Jil}$ integral computed by Simpson's numerical quadrature rule. The magnitude and phase of the S-matrix element (2.3b) is now stored away for future use and the program continues on in its calculations of other S-matrix elements. After all S-matrix elements for the desired rotational transition have been evaluated up to some given value of $J = J_{max}$, the program computes the total cross section and the A_L coefficients in the expansion of the differential scattering cross section. Careful FAP coded subroutines were prepared for evaluating the Clebsch-Gordan, Racah, and Z coefficients needed. The value of J_{max} is chosen so that the absolute magnitude of the S-matrix elements has fallen off by a factor of 100 or 1000 when the final one is calculated.

While it was not possible to test the program by doing an actual molecular inelastic scattering problem since there have been no previous calculations of this type in the literature nor any simple case that could be solved analytically, the program was checked out in every possible way. The radial differential equation integration process was checked by putting in a zero potential function, whereupon the program produced spherical
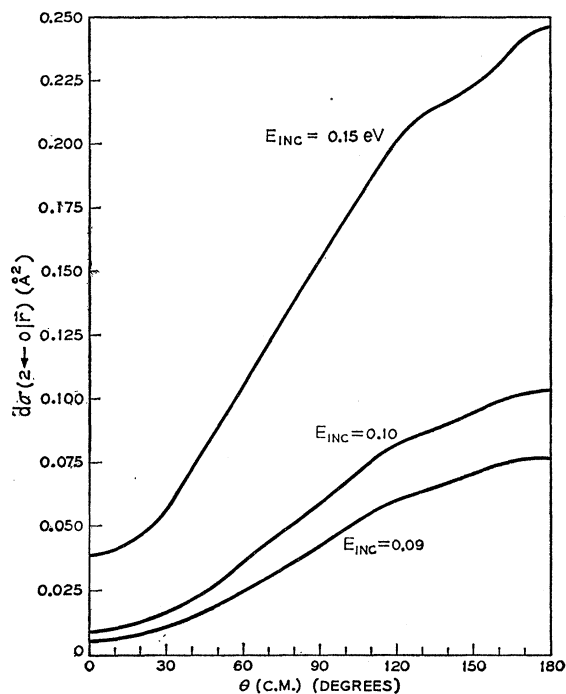
FIG. 3. Inelastic scattering of He by H_2. Potential of Eq. (5.2). Differential scattering cross section in the center-of-mass system for the $j=0$ to $j=2$ transition.

Bessel functions. The potentials used by Bernstein[10] in his elastic scattering calculations were inserted; his phase shift results were verified by the computer. The Simpson's rule subprogram used to evaluate the integrals (2.4) was tried on several known integrals; the results were always correct. The subprograms for the Racah, Clebsch-Gordon, and Z coefficients were checked against existing tables. The part of the program that generates the $f_\mu(j''l''; j'l'; J)$ coefficients, Eq. (3.3), was checked against the tables of Percival and Seaton.[11] In these checks, as in others, the programs checked out perfectly.

The time to compute a total inelastic cross section depends upon the value of J_{max} required and the number of differential equations which must be numerically integrated for each value of J. In general, it requires about 15 to 25 sec to solve a differential equation, depending upon how complicated the potential functions is to evaluate. For the transition $j=0 \rightarrow j=2$ where four differential equations must be solved for each J value, it, therefore, requires around 1 to $1\frac{1}{2}$ min per J value. Since a typical value of J_{max} is 20 or 25, it would take about 20 to 30 min to compute the total cross section. The time to compute each A_L coefficient depends upon the value of L as well as J_{max}. For $J_{max}=25$, the A_1 coefficient can be evaluated in approximately one minute, while ten to fifteen minutes is not an uncommon

time for an A_8 coefficient. For a total cross section and the A_L coefficients up to $L=8$, a typical time is 45 min to 1 h on the IBM 709 computer.

V. SCATTERING OF He BY H_2

The interaction energy between a helium atom and a hydrogen molecule computed in the preceding paper[12] may now be used with the foregoing formalism to compute the inelastic cross section for rotational transition when a helium atom and a hydrogen molecule collide. This potential is given by

$$V(r,\gamma) = Ce^{-\alpha r}[1+\beta P_2(\cos\gamma)] \qquad (5.1)$$

where

$$C = 17.283 \text{ double Ry} = 470.10 \text{ eV},$$

$$\alpha = 2.027 \text{ (au)}^{-1} = 3.830 \text{ Å}, \qquad (5.2)$$

$$\beta = 0.375.$$

Since this potential contains only a $v_0(r)$ and a $v_2(r)$ term,[13] the selection rule $\Delta j = 0, \pm 2$ will prevail.[14] The case $\Delta j = 0$, of course, corresponds to elastic scattering of the helium atom.

Before examining the results of the calculations, it is good to get an idea of the size of the energy parameters involved in the problem. From the $j=0$ to $j=2$ state of the hydrogen molecule, there is an energy difference of 0.0454 eV. The gap between the ground and first excited vibrational state is 0.3533 eV[15]; the first electronically excited state, of course, lies even higher. We must, therefore, restrict ourselves to energies lower than about 0.3 eV in order that our calculations have any meaning. Actually, we must restrict our incident kinetic energy to be even lower, since the partial wave analysis becomes too cumbersome and the distorted-wave approximation begins to fail at even lower energies. For these reasons, the author has chosen to study the transition $j=0$ to $j=2$ of parahydrogen. A similar calcula-

TABLE I. Inelastic scattering of He by H_2. Transition $j=0 \rightarrow j=2$. Potential of Eq. (5.2).

E_{inc} (eV)	J_{max}	$|S^0(20;00)|$	$|S^J(2,J-2;0J)|$	$\sigma(2 \leftarrow 0)$ (Å^2)
0.05	14	0.0596	0.00001	0.0117
0.06	17	0.1244	0.00033	0.0784
0.07124	22	0.1861	0.00015	0.2115
0.08	26	0.2294	0.00006	0.3479
0.09	30	0.2749	0.00002	0.5296
0.10	35	0.3169	0.00001	0.7314
0.15	35	0.4917	0.00098	1.8883

[10] R. B. Bernstein, J. Chem. Phys. 33, 795 (1960).

[11] I. C. Percival and M. J. Seaton, Proc. Cambridge Phil. Soc. 53, 654 (1957).

[12] C. S. Roberts, preceding paper, Phys. Rev. 131, 203 (1963).

[13] This terminology refers to the potential $V(r,\gamma)$ as expanded in Eq. (3.1).

[14] In reality, the potential $V(r,\gamma)$ will contain higher order terms than the $\mu=2$ term when expanded as in Eq. (3.1), but according to reference 12, these higher order terms should be much smaller. Therefore, the selection rule $\Delta j=0, \pm 2$ should be fairly well but not absolutely obeyed in experiment.

[15] W. Moore, Physical Chemistry (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1955), p. 341.

TABLE II. He–H$_2$ inelastic scattering. Transition $j=0 \to j=2$. Potential of Eq. (5.2). A_L coefficients in the expansion of the differential scattering cross section in the center-of-mass system.

E_{inc} (eV)	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8
0.05	0.1190	−0.1415	0.0252	0.0038	0.0026	−0.0024	−0.0004	0.0015	0.0012
0.06	0.9605	−1.0296	0.0887	0.0314	0.0237	−0.0251	0.0130	0.0223	−0.0036
0.07124	3.0759	−2.9547	0.0650	0.0610	0.0592	−0.0839	0.0782	0.0559	−0.0514
0.08	5.6817	−5.0822	−0.0608	0.0632	0.0777	−0.1475	0.1674	0.0702	−0.1144
0.09	9.7296	−8.1222	−0.3321	0.0461	0.0695	−0.2423	0.3188	0.0477	−0.1857
0.10	14.9305	−11.7501	−0.7466	0.0014	0.0503	−0.3728	0.5184	−0.0109	−0.2561
0.15	57.8182	−37.2990	−4.6690	−0.6847	−0.4638	−1.1769	1.8590	−0.8732	0.4761

tion could have been made for the $j=1$ to $j=3$ transition of orthohydrogen, but this was not attempted at the present juncture. These two transitions are the predominant rotational transitions that would occur at temperatures of several hundred degrees Kelvin.

The results of the scattering calculations with the potential (5.1) are shown in Table I. The incident energy given is measured in the center-of-mass system. The moment of inertia of the H$_2$ molecule was taken to be[15] 0.459×10^{-40} g cm^2. The number of J values that had to be taken before the values of the S-matrix elements had become small enough to neglect is listed under J_{max}. The absolute magnitude of the largest S-matrix element, $S^0(20;00)$, and the largest of the three matrix elements for $J=J_{max}$ are given so that one may see just how small the S-matrix elements have become for this value of J. The total cross section for the excitation $j=0$ to $j=2$ is listed in square angstroms and plotted versus incident kinetic energy in Fig. 1.

The value of the absolute magnitude of $S^0(20;00)$ can also furnish a check on how well the distorted-wave

TABLE III. Scattering results. Transition $j=0 \to j=2$. Potential of Eq. (5.7).

E_{inc} (eV)	J_{max}	$\|S^0(20;00)\|$	$\|S^J(2,J-2;0J)\|$	$\sigma(2 \leftarrow 0)$ (Å^2)
0.05	13	0.0654	0.00007	0.0148
0.06	17	0.1373	0.00041	0.1010
0.07124	22	0.2058	0.00019	0.2740
0.08	26	0.2539	0.00007	0.4519
0.09	30	0.3043	0.00003	0.6893
0.10	35	0.3509	0.00001	0.9530
0.15	35	0.5439	0.00130	2.4624

approximation is working.[16] Since the true S matrix is unitary, we must have

$$\sum_{j'l'} S^J(jl;j'l')S^J(j'l';jl)^\dagger = 1, \qquad (5.3)$$

and since the S matrix is also symmetric, we have

$$\sum_{j'l'} |S^J(jl;j'l')|^2 = 1. \qquad (5.3a)$$

Now, in the distorted-wave approximation the diagonal element $S^J(jl;jl)$ has an absolute magnitude of 1. Therefore, Eq. (5.3a) cannot be satisfied since the non-

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[16] A. Dalgarno (private communication).

diagonal elements are not all zero. In order to stay as close to the condition of Eq. (5.3a) as possible, we can set up a criterion that

$$\sum_{j'l'\neq jl} |S^J(jl;j'l')|^2 \ll 1, \qquad (5.4)$$

or the distorted-wave approximation is surely not valid. Just how much less than one Eq. (5.4) should be is a matter of judgment. The distorted wave approximation is better as the summation (5.4) gets smaller, but, of course, the nondiagonal S-matrix elements will get large if the probability of inelastic processes is appreciable. This all points out the well-known fact that the distorted-wave approximation works best when the nondiagonal matrix elements of the potential are small compared to the diagonal ones. One sees from Table I
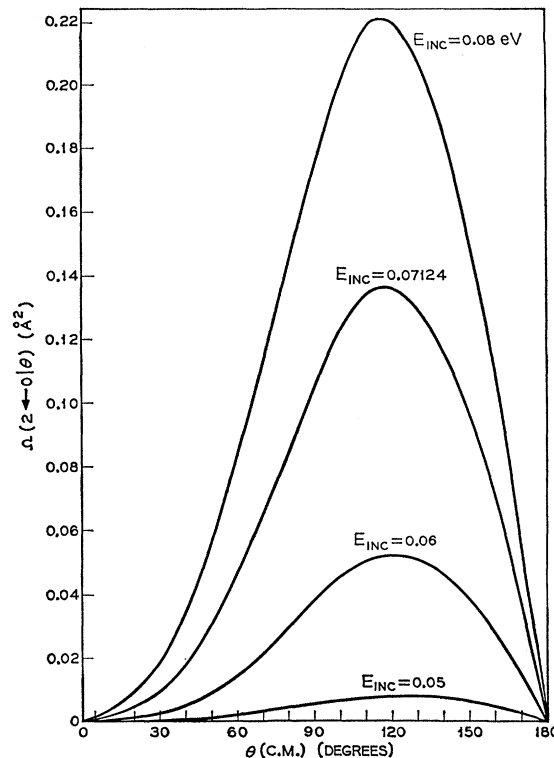

FIG. 4. Inelastic scattering of He by H$_2$. Potential of Eq. (5.2). Angular distribution of He atoms in the center-of-mass system after $j=0$ to $j=2$ transition.

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TABLE IV. Inelastic scattering results. Transition $j=0 \to j=2$. Potential of Eq. (5.7). A_L coefficients in the
expansion of the differential scattering cross section in the center-of-mass system.

E_{inc} (eV)	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8
0.05	0.1515	−0.1800	0.0313	0.0052	0.0037	−0.0038	−0.0007	0.0022	0.0017
0.06	1.2366	−1.3213	0.1056	0.0442	0.0332	−0.0391	0.0200	0.0322	−0.0074
0.07124	3.9846	−3.8019	0.0527	0.0893	0.0806	−0.1286	0.1182	0.0766	−0.0822
0.08	7.3803	−6.5393	−0.1384	0.0986	0.1026	−0.2246	0.2525	0.0894	−0.1782
0.09	12.6628	−10.4397	−0.5323	0.0846	0.0848	−0.3638	0.4773	0.0436	−0.2849
0.10	19.4542	−15.0787	−1.1199	0.0386	0.0463	−0.5503	0.7715	−0.0618	−0.3844
0.15	75.3969	−47.3717	−6.5255	−0.7182	−0.7719	−1.5928	2.7352	−1.4148	0.7808

that for incident energy equal to 0.15 eV $|S^0(20;00)|^2$
is already up to 0.242. This prevents us from going to
higher incident energies in our calculations.

Table II lists the values of the A_L coefficients up to
$L=8$ in the expansion of the differential scattering cross
section in the center-of-mass system. Although an ex-
amination of the expression for A_L will show that A_L
must approach zero as L gets larger, L must be of the
order of $2J_{max}$ before this condition is realized. If we
were, therefore, to calculate the next few higher A_L
coefficients, we would find that they had about the same
magnitude as A_7 or A_8. It is not necessary, though, to
calculate any of these higher A_L's if all one wants to
know is the shape of the differential scattering cross

section. The A_0, A_1, and perhaps the A_2 coefficients are
so much larger than the rest that the others make just
very small perturbations to the shape of the curve.
The differential scattering cross section versus angle of
scattering measured in the center-of-mass system is
plotted in Figs. 2 and 3. These curves were obtained by
evaluating the series for A_L up to $L=8$. Another graph
was tried taking L up to 11 and the two looked so much
alike that one would be hard pressed to distinguish be-
tween them. Since the differential scattering cross sec-
tion is independent of ϕ, the azimuthal angle about the
incident particle's direction, it is also useful to define the
function

$$\Omega(j';j|\theta) = 2\pi \sin\theta d\sigma(j';j|\mathbf{r}). \qquad (5.5)$$

It is obvious that

$$\int_0^\pi d\theta\, \Omega(j';j|\theta) = \sigma(j';j). \qquad (5.6)$$

The height of $\Omega(j';j|\theta)$ is proportional to the number
of helium atoms scattered between θ and $\theta+d\theta$. The
function $\Omega(2;0|\theta)$ is plotted for the various runs in
Figs. 4 and 5.

The curves in Figs. 1 through 5 show several interest-
ing features. The graph of the total cross section versus
energy goes to zero as it should at the threshold of the
excitation, 0.0454 eV. It begins to rise very slowly, and
then begins increasing in a rapid, almost linear manner.
The differential scattering cross sections all have about
the same shape except for a few wiggles here and there.
All have maxima at $\theta=180°$ corresponding to back scat-
tering in the center of mass or scattering at large angles
in the laboratory system. This property seems to be
characteristic of inelastic scattering processes in general,
while elastic differential cross sections generally have
their maxima at θ less than 90 deg. The graphs of
$\Omega(2;0|\theta)$ in Figs. 4 and 5 are peaked around 118° show-
ing again the high angle preference of the inelastic
process.

Calculations were also made for the scattering from
a hydrogen molecule with a slightly elongated bond
length of 1.486 a.u. The interaction energy at this bond
length is also calculated in reference 12; it is represented
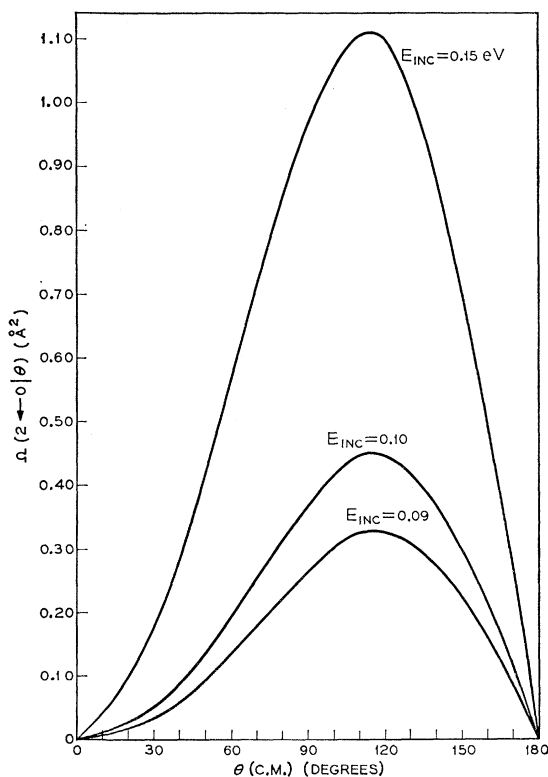by the function of Eq. (5.1) with the parameters

FIG. 5. Inelastic scattering of He by H_2. Potential of Eq. (5.2).
Angular distribution of He atoms in the center-of-mass system
after $j=0$ to $j=2$ transition.

TABLE V. H_2-H_2 inelastic scattering. Transition $j=0 \to j=2$. Potential of Eq. (6.1).

E_{out} (eV)	E_{inc} (eV)	J_{max}	$\|S^0(20;00)\|$[a]	$\|S^J(2,J-2;0J)\|$[b]	$\sigma(0 \leftarrow 2)$ (Å²)[c]	$\sigma(2 \leftarrow 0)$ (Å²)[d]
0.00462	0.05	12	0.0399	0.00005	0.0159	0.00735
0.0146	0.06	17	0.0561	0.00004	0.0163	0.0198
0.0259	0.07124	19	0.0713	0.00022	0.0200	0.0364
0.0346	0.08	20	0.0817	0.00056	0.0233	0.0503
0.0446	0.09	22	0.0923	0.00057	0.0269	0.0667
0.0546	0.10	22	0.1020	0.00181	0.0304	0.0831
0.1046	0.15	28	0.1413	0.00236	0.0466	0.1624
0.1546	0.20	30	0.1720	0.00681	0.0606	0.2343
0.2046	0.25	32	0.1979	0.01121	0.0733	0.2998

[a] Magnitude of largest S-matrix element calculated.
[b] Magnitude of last S-matrix element considered. All elements with $J > J_{max}$ were neglected.

[c] For incident kinetic energy in the center-of-mass system $= E_{out}$.
[d] For incident kinetic energy in the center-of-mass system $= E_{inc}$.

changed to

$$C = 16.666 \text{ double Ry} = 453.3 \text{ eV},$$
$$\alpha = 2.009 \text{ a.u.}^{-1} = 3.796 \text{ Å}^{-1}, \qquad (5.7)$$
$$\beta = 0.425.$$

While this potential has little relation to a physical situation, it will serve to show the behavior of the scattering results as the parameters are changed from those of (5.2). The results for the inelastic scattering using the above parameters are given in Tables III and IV.

The main difference in the potentials described by (5.2) and (5.7) is in the value of β. In one case $\beta = 0.375$ and in the other it is 0.425. It should be pointed out that the total cross sections in Table III are very nearly equal to $(0.425/0.375)^2 = 1.284$ times the corresponding total cross section in Table I. This demonstrates that the total cross section is approximately proportional to the square of the ratio $v_2(r)/v_0(r)$ when $v_0(r)$ is kept constant. One can see that this should be so by realizing that due to the selection rules for the $f_\mu(j''l''; j'l'; J)$ coefficients only the $v_2(r)$ term enters into the nondiagonal matrix elements of the potential $\langle j'l'; J | V | j''l''; J \rangle$. Since by Eqs. (2.3b) and (2.4) $S^J(2l'; 0l)$ is proportional to $\langle 0l; J | V | 2l'; J \rangle$ and the total cross section is proportional to the squares of these S-matrix elements the total cross section will be proportional to the square of the magnitude of $v_2(r)$, $v_0(r)$ kept constant. The only other place that $v_2(r)$ enters into the formalism is in the diagonal matrix elements of the potential. Such elements provide the distortion in the differential equations (2.1). The fact that the total cross section is so nearly proportional to the square of $v_2(r)$ means that its effect in providing distortion is overwhelmed by its role in the integral of Eq. (2.4).

At this point, one might well question the validity of using either of the potentials (5.2) or (5.7) to represent the potential between a helium atom and a hydrogen molecule. Due to the simplicity of the wave function that was set up to calculate the interaction potential,[12] the calculated interaction energy remained repulsive throughout the entire region of investigation. However, it is a well-known fact that at large separations the pair must exhibit a Van der Waals type attraction. Such

an attraction is provided by the $(1/r)^6$ term in the Amdur-Malinauskas experimental potential, Eq. (4.5) of reference 12. Despite this term, we can see from Fig. 3, reference 12, that all three potentials, the Amdur-Malinauskas experimental exp-6 and simple exp and the calculated $v_0(r)$, lie very close to one another in the region of 4 to 6 a.u. For the incident kinetic energies studied in this investigation, the classical turning point lies in this region. This is defined to be the point at which the interaction energy equals the incident kinetic energy. It is at this point that the two colliding partners would bounce off one another if they obeyed classical mechanics. In order to investigate how a change in the interaction energy outside of this region, especially the addition of a Van der Waals attraction term, would affect the scattering results, two new potentials were
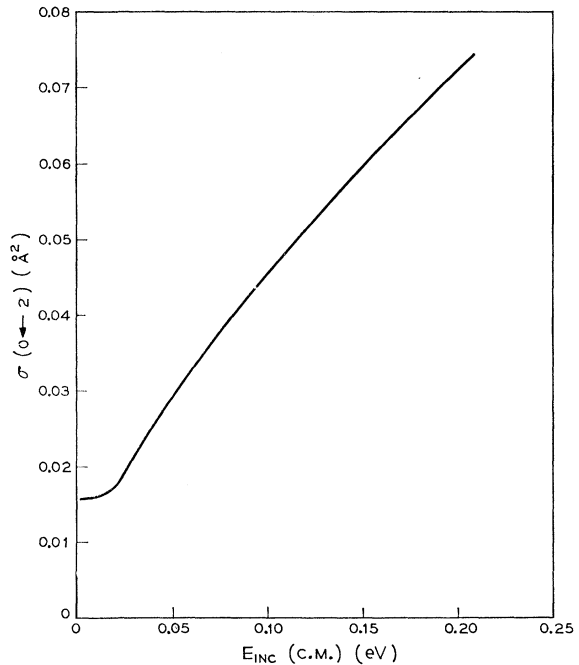
FIG. 6. Inelastic scattering of H_2 by H_2. Potential of Eq. (6.1). Total inelastic cross section for the de-excitation $j=2$ to $j=0$ vs incident kinetic energy.

TABLE VI. H_2-H_2 inelastic scattering. Transition $j=0 \to j=2$. Potential of Eq. (6.1). A_L coefficients in the expansion of the differential scattering cross section in the center-of-mass system.

E_{inc} (eV)	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8
0.05	0.0564	−0.0218	0.0065	0.0077	0.0079	0.0077	0.0059	0.0065	0.0040
0.06	0.1821	−0.1083	0.0014	0.0074	0.0104	0.0086	0.0091	0.0096	0.0081
0.07124	0.3982	−0.2322	−0.0052	0.0108	0.0179	0.0146	0.0183	0.0195	0.0153
0.08	0.6180	−0.3459	−0.0117	0.0147	0.0259	0.0214	0.0285	0.0292	0.0223
0.09	0.9211	−0.4919	−0.0202	0.0204	0.0378	0.0322	0.0447	0.0442	0.0333
0.10	1.2754	−0.6527	−0.0304	0.0257	0.0481	0.0400	0.0559	0.0514	0.0402
0.15	3.7396	−1.6628	−0.0978	0.0688	0.1327	0.1162	0.1727	0.1445	0.1246
0.20	7.1920	−2.9805	−0.2284	0.0758	0.1676	0.1243	0.1930	0.1012	0.1107
0.25	11.5004	−4.5795	−0.4585	0.0103	0.1044	0.0213	0.1016	−0.0648	0.0402

invented. It was decided to keep the value $\beta = 0.375$ so that

$$v_2(r) = 0.375 v_0(r), \qquad (5.8)$$

and to use the experimental exp-6 and simple exp potentials of Eqs. (4.5) and (4.6) of reference 12 for $v_0(r)$. The total cross section at 0.09 eV incident kinetic energy was then calculated for these two new potentials and the results compared with that obtained from potential (5.2). For the exp-6 taken as $v_0(r)$ a total inelastic cross section of 0.563 Å^2 was calculated, while for the simple exp potential the cross section was 0.449 Å^2. From Table I we see that the corresponding total cross section obtained with the theoretically calculated interaction energy was 0.530 Å^2. That these three values are so close together points up the fact that the scattering results are fairly insensitive to the behavior of the potential away from the region of the classical turning point. The mathematical manifestation of this comes through the $\beta_{j'l'}{}^{Jjl}$ integral defined in Eq. (2.4). When the integrands of several of these integrals were examined, it was found that they were peaked in the region of the classical turning point. When the integral is evaluated, little contribution comes from outside this region. In addition to this, the depth of the minimum of the Amdur-Malinauskas potential is only about 0.001 eV, while at least 0.045 eV of incident kinetic energy are needed to induce a rotational transition. Thus, the depth of the minimum is about fifty times smaller than the relevant energies in the problem and, therefore, can do little to effect any results.

It would be pleasing at this point to compare our results with some experimental evidence or a previous calculation. Unfortunately, there has never been, to the author's knowledge, any experimental measurement of the inelastic cross section for rotational excitation or de-excitation upon collision between a helium atom and a hydrogen molecule. Neither has there been, to the author's knowledge, any other theoretical treatment of the subject. Such comparisons will have to be delayed until other workers find it in their interest to examine this problem.

VI. SCATTERING OF H_2 BY H_2

The digital computer program already developed was used to compute the cross section for rotational de-

excitation from the $j=2$ to the $j=0$ state in a collision between two hydrogen molecules. Actually, the computer calculated the excitation cross section from $j=0$ to $j=2$, and then the law of detailed balance was used to obtain the cross section for the inverse process. While scattering of H_2 by H_2 is, in reality, scattering of a rotor by a rotor and not scattering of a particle by a rotor, it can be shown that the theory for the former process reduces to the theory of the latter if the distorted wave approximation is applied and both rotors are initially in the $j=0$ state.[16] Under these conditions, $V(r,\gamma)$ should be the potential between two hydrogen molecules averaged over all spacial orientations of one of the molecules. Takayanagi[6] has derived such an averaged potential from the work of Evett and Margenau[17] on the H_2–H_2 interaction. His result is

$$V(r,\gamma) = v_0(r) + v_2(r) P_2(\cos\gamma), \qquad (6.1a)$$

where

$$v_0(r) = D[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)}], \qquad (6.1b)$$

$$v_2(r) = \beta D e^{-2\alpha(r-r_0)}, \qquad (6.1c)$$

$D = 1.1 \times 10^{-4}$ double Ry $= 2.992 \times 10^{-3}$ eV,

$r_0 = 6.4$ a.u. $= 3.387$ Å,

$2\alpha = 1.87$ (a.u.)$^{-1} = 3.534$ Å^{-1},

$\beta = 0.075$.

There is some doubt in the author's mind concerning the accuracy of the above potential, especially the value of β given, but since an analysis of the existing knowledge of the H_2-H_2 interaction was not amenable to producing a more satisfactory result it was decided to compute cross sections using the above. The results for the total cross section are shown in Table V while Table VI lists the corresponding A_L coefficients in the expansion of the differential scattering cross section. Since the total de-excitation cross section from $j=2$ to $j=0$ is of interest in ultrasonic dispersion measurements in H_2 gas,[18] it was decided to graph it rather than the corresponding excitation cross section. The resulting curve is shown in Fig. 6. These results are in substantial agree-

[17] A. A. Evett and H. Margenau, Phys. Rev. **90**, 1021 (1953).
[18] K. F. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic Press Inc., New York, 1959).

ment with the distorted-wave calculation of Davison[19] who used the same potential as that given in Eq. (6.1). Davison, however, took proper account of the identity of the two hydrogen molecules while in the present research a distinction is made between the incident and target hydrogen molecules. For this reason, the cross sections could not be expected to agree exactly.

We can now compute the probability for rotational de-excitation from the $j=2$ state upon collision in H_2 gas and compare this with the value determined by ultrasonic dispersion measurements.[20] This probability for rotational de-excitation can be obtained from the following expression.

$$P_{20}=\sigma(0 \leftarrow 2)/\sigma_{\rm kin}(0 \leftarrow 0) \qquad (6.2)$$

where $\sigma_{\rm kin}(0 \leftarrow 0)$ is the elastic scattering cross section between H_2 molecules as measured in kinetic theory experiments. According to reference 20 $\sigma_{\rm kin}(0 \leftarrow 0)$ $=23.2$ $Å^2$ in H_2 gas. To be strictly correct, we should average the curve in Fig. 6 over a Maxwell-Boltzmann distribution of incident energies before dividing by $\sigma_{\rm kin}(0 \leftarrow 0)$, but to simplify matters we forego the averaging procedure and use the value of $\sigma(0 \leftarrow 2)$ at $E_{\rm inc}=kT$. For $T=300°K$, $kT=0.0259$ eV, and $\sigma(0 \leftarrow 2)$ at $E_{\rm inc}=0.0259$ eV is seen to have the value 0.020 from

[19] W. D. Davison, Discussions Faraday Soc. 33, 71 (1962).
[20] R. Brout, J. Chem. Phys. 22, 938 (1954).

Table V. Therefore,

$$\text{for } T=300°K, \quad P_{20} \approx 0.020/23.2, \\ \approx 0.86 \times 10^{-3}. \qquad (6.3)$$

The experimental value for P_{20} as given in reference 20 is

$$\text{for } T=300°K, \quad P_{20}=3.0 \times 10^{-3} \text{ (experimental)}. \quad (6.4)$$

The fact that the computed de-excitation probability is low may be due to the fact that we have not considered processes where both molecules come together in the $j=2$ state and one is de-excited to the $j=0$ state while the other is excited to the $j=4$ state, or to the fact that the value of β in the potential (6.1c) is too small. Since the inelastic cross section goes approximately as β^2, a value of $\beta=0.14$ will produce the correct answer. This is in exact agreement with the conclusion reached by Davison[19] in his calculation. Since it is not clear that Eq. (6.1) does indeed represent the correct potential to use for the averaged H_2-H_2 interaction potential, it is not unreasonable to surmise that perhaps β should actually be made larger.

ACKNOWLEDGMENTS

Čerenkov-Like Radiation by Plasma Oscillations*

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(Received 20 February 1963)

A coupling mechanism is shown to exist between electrostatic oscillations along a plasma cylinder and transverse electromagnetic waves outside, resulting in radiation by phase oscillations. Plasma oscillations along the cylinder can be decomposed into traveling waves with plasma velocity $v_p=\omega/k$. The macroscopic appearance of such a traveling wave is the same as if a series of alternating positive and negative charged bunches move with the phase velocity of the wave. For long wavelengths, where the phase velocity exceeds the speed of light in the surrounding medium, radiation takes place, having a pattern as expected from Čerenkov radiation of the charged bunches moving with v_p. Since for plasma oscillations $\omega/k>c$ modes exist (Dawson and Oberman), this radiation can also take place in vacuum.

A COLD electron plasma is known to exhibit electrostatic oscillations with the characteristic plasma frequency $\omega=\omega_p$. These oscillations are longitudinal, with the particle motion and electric field both parallel to the wave vector $\mathbf{k}$. The phase velocity $v_p=\omega_p/k$ can take on any value; in fact, it can exceed the speed of light in vacuum if the wave number is small enough: $k<\omega_p/c$.

This electrostatic plasma wave consists macroscopically of a sinusoidal spatial variation of space charge traveling with the velocity v_p. This is, of course, brought about by electrons exhibiting small oscillations about their equilibrium positions with their phases properly adjusted to give the above described macroscopic space charge wave.

In an infinite uniform plasma, longitudinal plasma oscillations have the interesting property that the conduction and displacement currents cancel exactly.