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Dissociation of Hydrogen Molecules by Vibrational Excitation and Three-Body Recombination Coefficient

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The recombination of two atoms in the presence of a third body is of importance in gas kinetics. The evaluation of its probability coefficient can be reduced to that of the reverse process, the dissociation of a molecule by collision, by means of the principle of detailed balance. Various mechanisms for dissociation are briefly discussed, and an attempt is made to estimate the general order of magnitude of the cross section for the excitation of a molecule into the vibrational continuum of its electronic ground state by carrying through a calculation for the dissociation of a hydrogen molecule by collision with an electron, proton, and hydrogen atom. The Born approximation is not satisfactory for the heavy particles at low energies, and a tentative method of correcting the cross section by means of the exact one-dimensional problem is given. The resulting value of the cross section for dissociation of a hydrogen molecule by a hydrogen atom is of the order 10^{-26} cm^2 at low energies; the three-body recombination coefficient for the reverse process, namely, the recombination of two hydrogen atoms in the presence of a third, is $\sim 10^{-43}$ cm^6/sec, which is very much smaller than the experimental value.

I. STATEMENT OF THE PROBLEM

REACTIONS in which two atoms A and B combine in the presence of a third body X to form a molecule AB, namely,

$$A+B+X\rightarrow AB+X^* \qquad (1)$$

are of great importance in many problems in the gas kinetics of chemistry and of the upper atmosphere. The problem is usually to understand the mechanism of the energy transfer (1) for given reactants A, B, X; and for this a knowledge of the probabilities of the various possible mechanisms of energy transfer is necessary. For any given mechanism, the probability of (1) taking place can best be measured by a cross section σ_3 for the three-body process defined in the following manner. Consider the reverse process of (1), namely, the dissociation of AB by the transfer of the energy of excitation of X^*, i.e.,

$$AB+X^*\rightarrow A+B+X \qquad (2)$$

and let $\sigma_2(v_0)$ be its cross section, v_0 being the relative velocity of AB and X^*. Let u be the relative velocity of A and B after the dissociation. The cross section $\sigma_3(u)$ may then be defined by the principle of detailed balancing, namely, that at equilibrium the number of processes (1) per unit volume and time is equal to that of (2) per unit volume and time

$$\sigma_3(u)u[A][B][X]=\sigma_2(v_0)v_0[AB][X^*], \qquad (3)$$

where $[A]$ is the concentration of A, etc. For any assumed mechanism for (1) and (2), statistical mechanical arguments enable one to obtain a relation between $\sigma_3(u)$ and $\sigma_2(v_0)$ in terms of the statistical weights and atomic and molecular constants of A, B, AB, and X alone. Thus, the three-body problem (1) can be reduced to the solution of its reverse, the two-body process (2), which is always simpler.

If X is an electron, two different modes of energy transfer (1) are possible, namely, (a) the electron may take up as kinetic energy the energy of the excited electronic state of AB arising from the close approach of A and B, or (b) it may take up the energy of the system $A+B$ in the vibrational continuum of the ground electronic state of AB. The cross section σ_2 for the reverse process (2) in the case (a), namely, the excitation of the electronic state of AB, is of the same general order of magnitude as that for the excitation of the electronic state of an atom by an electron, and hence $\sigma_2\sim 10^{-18}-10^{-16}$ cm^2. It can be shown that $C=\sigma_3 u$, which is usually called the coefficient of three-body recombination, is in this case $\sim 10^{-34}-10^{-32}$ cm^6/sec. For case (b), σ_2 for the excitation of the vibrational continuum by electronic impacts will be shown in the present work to be very small, leading to $\sigma_3 u\sim 10^{-40}$ cm^6/sec.

If X is a heavy particle such as an ion, atom, or molecule, there are other possible mechanisms in addition to (a) and (b). Thus, the system $A+B$ may transfer its electronic or vibrational energy to the electronic, vibrational, or rotational motion of X. In the case of the transfer of electronic energy of $A+B$ to electronic energy[1] of X, the cross sections σ_2 and σ_3 may be quite large if there is resonance. The exact treatment of any of these processes is difficult, but on general considerations they seem to be very improbable away from resonance. For the low energies occurring in the problems of interest, the velocities u, v_0 are small compared with the orbital velocities v_{orb} of the electronic processes, so that the collisions take place adiabatically because the collision time, which is inversely proportional to the velocity of approach, is large compared with the period of the electronic motion which is inversely proportional to v_{orb}. For such low velocities

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[1] H. E. Moses and T. Y. Wu, Phys. Rev. 83, 109 (1951), Appendix 5.

of approach, the cross section varies as $\exp(-v_{\mathrm{orb}}/v_0)$,[2] so that the cross sections σ_2 for typical electronic reactions are less than 10^{-36} cm^2.

Thus, apart from resonance phenomena, if X is a heavy particle, recombination will occur only by the transfer of the vibrational energy of the electronic ground state of $A+B$ into vibrational, rotational, or translational energy of X.[3] The excitation of vibrational motion is in general difficult, while translational and rotational energy are freely convertible into one another, so that one need only consider mechanism (b), namely, the transfer of vibrational to translational energy. The adiabatic effect of the previous paragraph is not of importance in these considerations because the periods of rotational and vibrational motion are much greater than those of electronic motion.

The object of the present work is to make a reasonable quantum-mechanical estimate of the probability of (1) when two atoms A and B, approaching each other in the vibrational continuum of the electronic ground state of AB, transfer this vibrational energy to an electron or heavy particle as kinetic energy. To make the calculation manageable, it has been carried out for the case of two hydrogen atoms combining in the presence of an electron, a proton, and another hydrogen atom. By using the principle of detailed balancing (3), the evaluation of the three-body recombination coefficient $C=\sigma_3\cdot u$ has been reduced to that of the cross section σ_2 of the reverse process, and we discuss the dissociation of hydrogen molecules by excitation into the vibrational continuum of the electronic ground state by collision with electrons, protons, and hydrogen atoms. The deexcitation of molecular vibrations in one-dimensional collisions has been investigated previously,[4] but it was supposed that van der Waals' forces provide the relevant interaction. These forces are now known to be satisfactory for distances greater than 5A;[5] however, the excitation of vibrational levels requires very close collisions as quite a large energy is transferred, and thus the use of van der Waals' forces in Margenau's sense is not satisfactory in the present problem.

Recently, Wu[6] has considered the excitation of vibrations in hydrogen molecules by collision with electrons, and in this case has obtained results which agree in their order of magnitude with the experimental cross sections.[7] Here this interaction is modified to account for the interaction of hydrogen atoms with hydrogen molecules.

The calculation has been carried out to Born's approximation. As the binding energy of the hydrogen molecule is about 4.4 ev, the coupling constant $\alpha_0 = Z'e^2/\hbar v_0$ is 2 and 69 for electrons and protons, respectively, at the threshold. Thus, while the Born approximation will be satisfactory for electrons fairly close to the threshold, this will not be so for the much more interesting case of heavy particles. For protons of 20-ev energy, the relation,

$$l_1\hbar \sim M_A v_0 b, \tag{4}$$

shows that for impact parameters $b\sim 0.5$A, $l_1\sim 30$, and thus at this energy perhaps 50 phases must be considered. It does not seem possible to find any convenient analytical expression for the phases, and thus it is not feasible to attempt an exact calculation. However, the one-dimensional problem can be evaluated numerically, and it is suggested that a comparison between the accurate treatment and the Born approximation for the same one-dimensional problem may furnish a basis for making a correction to the Born approximation in the three-dimensional case. In this way the cross section for the dissociation of hydrogen molecules by protons and hydrogen atoms by excitation into the vibrational continuum is estimated. The three-body coefficient $\sigma_3 u$ of the inverse process is calculated from this by means of (3).

II. THE INTERACTION

Wu[5] has considered the interaction of an electric charge distant r from the center of mass of a hydrogen molecule of nuclear separation ρ, in its normal $^1\Sigma$ state, described by Wang's variational eigenfunctions.[8] After integration over the electron coordinates, one term which is not important for the small angle elastic scattering of fast electrons is neglected; and as an approximation to integration over the polar angles (the molecule is not considered as rotating), the field is replaced by the central one

$$\begin{aligned} V_W(r,\rho) &= 2e^2(1+S)^{-1}\Lambda_\mu e^{-\mu r}/r,\\ \Lambda_\mu &= (1-\tfrac{1}{2}\mu\partial/\partial\mu),\\ S &= [1+\tfrac{1}{2}\mu\rho+(1/12)\mu^2\rho^2]^2 e^{-\mu\rho},\\ \mu &= 2Z/a_0;\quad Z=1.166,\quad a_0=\hbar^2/me^2. \end{aligned} \tag{5}$$

In its dependence on r, V_W is essentially the field due to a neutral atom, but in bringing out the dependence on the nuclear separation ρ through the overlap integral S, it furnishes the coupling between the translational coordinate r and the vibrational coordinate ρ without requiring any further assumptions for the interaction. Thus, V_W seems satisfactory for describing the vibrational excitation of a hydrogen molecule by an electron or proton; it will be satisfactory even for the dissociated

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[2] N. F. Mott and H. S. W. Massey, *Atomic Collisions* (Clarendon Press, Oxford, 1949), second edition, Chapter XII.

[3] There is one further possibility, namely, that the atoms A and B come together in a state of rotational energy greater than the binding energy, and transfer some or all of this rotational energy to X. This possibility has not been considered in the present work.

[4] C. Zener, Phys. Rev. **37**, 556 (1931); J. M. Jackson and N. F. Mott, Proc. Roy. Soc. (London) **A137**, 702 (1932).

[5] H. Margenau, Revs. Modern Phys. **11**, 1 (1939).

[6] T.-Y. Wu, Phys. Rev. **71**, 111 (1947).

[7] W. Harries, Z. Physik **42**, 26 (1927); H. Ramien, Z. Physik **70**, 353 (1931); Chao, Wang, and Shen, Science Record, Acad. Sinica **2** (4) 358 (1949).

[8] See H. Bethe, *Handbuch der Physik* **24/1** (Verlag. Julius. Springer, Berlin, 1933), second edition, Chapter III, Sec. 59.

molecule during the collision provided the constituent atoms do not move too fast and are in their normal electronic states.

In the case of a hydrogen atom, the effect of the orbital electron must be considered as well as that of the proton. At least at low velocities, the only effect of the electron will be to screen the proton, as the electron has not on the average sufficient kinetic energy to produce dissociation, even if its binding could be neglected.

For the nucleus at a point $\mathbf{r}$ and the electron, in the $(1s)$ state, at $\mathbf{s}$ relative to the proton, the interaction between the hydrogen atom and the molecule is

$$\left.\begin{aligned} V_M(r,\rho) &= \int d^3\mathbf{s}\,|\psi_{1s}(\mathbf{s})|^2\{V_W(r,\rho) \\ &\qquad - V_W(|\mathbf{r}+\mathbf{s}|,\rho)\} \\ &= V_W(r,\rho) - V_S(r,\rho), \end{aligned}\right\} \quad (6)$$

$$\left.\begin{aligned} V_S(r,\rho) &= \frac{4}{a_0^3}\frac{2e^2}{1+S(\rho)}\Lambda_\mu\left\{\frac{(e^{-\mu r}-e^{-2r/a_0})4}{ra_0(\mu^2-4/a_0^2)^2} + \frac{e^{-2r/a_0}}{\mu^2+4/a_0^2}\right\} \\ &\simeq [2e^2/(1+S)]V_S{}^0 e^{-gr}; \\ &\qquad V_S{}^0 = 0.619, \quad g = 1.44. \end{aligned}\right\} \quad (7)$$

The potential V_M has the correct qualitative form of an intermolecular potential, being strongly repulsive for $r<a_0$ and weakly attractive for $r>1.3a_0$; its minimum value is $-0.02e^2/a_0$.

Since we are interested in the probabilities of exciting the vibrational states, it is convenient to express V_W or V_M as a function of ρ in a more explicit manner. Following Wu,[6] only small displacements η of the nuclear separation ρ from its equilibrium value ρ_0 are considered; and thus we put

$$V_\lambda(r,\rho) = V_\lambda(r,\rho_0) + \eta\left[\frac{\partial}{\partial\rho}V_\lambda(r,\rho)\right]_{\rho_0} \quad (\lambda = W, M). \quad (8)$$

The ρ-dependence of V comes from the factor $S=S(\rho)$, and as $\rho_0 \simeq 1.5a_0$,

$$[(\partial/\partial\rho)V_\lambda(r,\rho)]_{\rho_0} = (0.42/\rho_0)V_\lambda(r,\rho_0). \quad (8')$$

Thus to this approximation only the matrix element of the nuclear separation is required.[9]

III. THE TOTAL CROSS SECTION σ_2: FORMULATION OF THE PROBLEM

We consider a collision in which the incident particle of reduced mass M_A changes its momentum from $\hbar\mathbf{k}_0$ to $\hbar\mathbf{k}_f$, and in so doing excites the molecule into the vibrational state p of energy $(\hbar^2/2M_0)P^2(p) = D + (\hbar^2p^2/2M_0)$ in the continuum; D is the binding energy of the molecule, and $M_0 = 1840m/2$ the reduced mass of its two atoms. Thus the condition of energy conservation is

$$(\hbar^2/2M_A)(k_0^2-k_f^2) = D + (\hbar^2p^2/2M_0) = \hbar^2P^2(p)/2M_0. \quad (9)$$

If the incident particle is scattered through an angle θ, and momentum $\hbar\mathbf{q}$ is transferred, conservation of momentum gives

$$qdq = -k_0k_fd(\cos\theta) \quad \text{at constant } k_0,\ k_f. \quad (10)$$

The differential cross section for scattering into an angle between θ and $\theta+d\theta$ is

$$2\hbar(k_f/k_0)\,|(M_A/2\pi\hbar^2)\langle\mathbf{k}_f,p|V_\lambda(r,\rho)|\mathbf{k}_0,0\rangle|^2\sin\theta d\theta. \quad (11)$$

For electrons and protons the interaction is V_W, while the screened interaction V_M must be taken for hydrogen atoms.

Now, from Eq. (8), $V_\lambda(r,\rho)$ is separable; and, in fact, $\hbar^2p^2/2M_0 \ll D$ for all values of p which contribute noticeably to the cross section. This brings about a further simplification in that the condition of energy conservation becomes

$$k_0^2-k_f^2 \simeq 2M_AD/\hbar^2, \quad (9')$$

so that the contributions of translational and nuclear motion to the cross section may be treated as independent. The vibrational state p lies in the continuous spectrum, and its wave function must be normalized per unit energy range if the standard expression for the probability of a transition per unit time, $P_{0p} = (2\pi/\hbar)|\langle 0|V|p\rangle|^2$, is to be used. In consequence of this, $\eta_{0p}{}^2$ has not the dimensions (length),^{2} and it is necessary to integrate over $E_p = \hbar^2p^2/2M_0$ to obtain a meaningful result for the total cross section. This means physically that we get σ_2 as a function of k_0, giving the total cross section for dissociation by vibrational excitation, integrated over all energies with which the dissociated hydrogen atoms move apart.

Thus, from Eqs. (8), (10), and (11), the cross section is given by

$$\sigma_2(k_0) = \chi(k_0)(0.42/\rho_0)^2\int_{p=0}^{p_{\max}}|\eta_{0p}|^2dE_p \quad (12)$$

where

$$\left.\begin{aligned} \chi(k_0) &= 2\pi(k_f/k_0)(M_A/2\pi\hbar^2)^2 \\ &\qquad\times\int_0^\pi |(f|V_\lambda(r,\rho_0)|0)|^2\sin\theta d\theta \\ &= 2\pi(M_A/2\pi\hbar^2k_0)^2 \\ &\qquad\times\int_{k_0-k_f}^{k_0+k_f}|(f|V_\lambda(r,\rho_0)|0)|^2\sin q dq. \end{aligned}\right\} \quad (13)$$

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[9] Equation (8) is very satisfactory because $2/\{1+S(\rho)\}$ is linear in ρ for $0.5a_0<\rho<3a_0$. In a width $\Delta\rho=0.5a_0$ on either side of the equilibrium position ρ_0, the wave function of the ground state, $\psi_0(\rho)$, has already fallen to $\frac{1}{5}$ of its maximum value, so that the linear approximation (8) is sufficient in the region where $\psi_0(\rho)$ is appreciable.

The value of $p_{\max}$ is not critical, because η_{0p}^2 falls off very rapidly with increasing p, so that the integration may be extended to infinity. The expression $(f|V|0)$ stands for a matrix element relative to the translational motion, and χ is a factor determined by the contribution of the translational motion to the cross section. The chief difficulty is the evaluation of χ, as an exact treatment is out of the question for heavy particles (see Sec. I). The Born approximation is given in Sec. V and a detailed one-dimensional analysis of $(f|V_W|0)$ in Sec. VI; the final results for σ_2 are given in Fig. 2 and discussed in Sec. VII.

IV. THE MATRIX ELEMENT OF THE NUCLEAR SEPARATION

It is required to find the matrix element η_{0p} for the transition from the ground state 0 to a state of momentum $\hbar p$. For a harmonic oscillator there is a selection rule $\Delta v=\pm 1$; but while the ground state may be represented by a harmonic oscillator wave function, transitions from it to states p in the vibrational continuum are no longer forbidden, as these are not harmonic oscillator states.

The wave function for a state p can be obtained readily from the WKB approximation by replacing the exact potential well (as a function of ρ) by a square well of the correct depth D and size, the potential becoming strongly repulsive for $\rho<\rho_1$. The wave function which has the correct (decreasing exponential) form for $\rho<\rho_1$ and is normalized per unit energy range is

$$\psi_p(\rho)=(1/\hbar)(2M_0/\pi P)^{\frac{1}{2}}\cos\{P(\rho-\rho_1)-\tfrac{1}{4}\pi\} \tag{14}$$

within the potential well; $P=P(p)$ is given by Eq. (9). The form of ψ_p outside the well is of little importance for the matrix element, as the ground-state wave function ψ_0 decreases very rapidly on either side of ρ_0.

For the $(0\rightarrow p)$ transition,

$$\left.\begin{aligned}\eta_{0p}&=(N_0/\hbar)(2M_0/\pi P)^{\frac{1}{2}}\int_{-\infty}^{\infty}d\eta\,\exp(-\tfrac{1}{2}\beta\eta^2)\\&\qquad\qquad\times\cos[P(\rho-\rho_1)-\tfrac{1}{4}\pi]\\&=-[2/(\beta^5\pi)^{\frac{1}{4}}\hbar](M_0P)^{\frac{1}{2}}\sin[P(\rho_0-\rho_1)-\tfrac{1}{4}\pi]\\&\qquad\qquad\times\exp(-P^2/2\beta)\\N_0^2&=(\beta/\pi)^{\frac{1}{2}};\quad \beta=M_0\omega_0/\hbar=18.4/a_0^2,\end{aligned}\right\}\tag{15}$$

where $\omega_0/2\pi$ is the oscillator frequency.

It is reasonable to choose ρ_1 so that at $\rho=\rho_1$ the energy of the hydrogen molecule is equal to $-2e^2/a_0$. Then it is found that the Hylleraas variational method,[8] gives $\rho_0-\rho_1=0.55a_0$; and, using this value, we find that $\eta_{0p}^2=7.6\times10^{-7}a_0^3/e^2$ at $p=0$, $1.3\times10^{-7}a_0^3/e^2$ at $p=3/a_0$, and 0 at $p=6.6/a_0$, $a_0=\hbar^2/me^2$ being[10] the first Bohr radius. $E_p=\hbar^2p^2/2M_0$ is the kinetic energy with which the two atoms of the molecule move apart after dissociation; for $E_p=\frac{1}{2}kT$ (at 300°K), $p=0.94a_0^{-1}$ and $\eta_{0p}^2=7.0\cdot10^{-7}a_0^3/e^2$, while for $E_p=kT$, $\eta_{0p}^2=6.3\times10^{-7}a_0^3/e^2$. Because of the normalization of ψ_p, we require $\int\eta_{0p}^2dE_p$. This is best evaluated numerically, and gives

$$\int_0\eta_{0p}^2dE_p=3.95\times10^{-9}a_0^2. \tag{16}$$

V. BORN APPROXIMATION FOR THE TRANSLATIONAL MOTION

Plane waves $\exp(i\mathbf{k}\cdot\mathbf{r})$ are used in the matrix element $(f|V|0)$ of Eq. (13), giving

$$\left.\begin{aligned}&(f|V_\lambda|0)=\int d^3\mathbf{r}e^{i\mathbf{q}\cdot\mathbf{r}}V_\lambda(r,\rho_0),\\&(f|V_W|0)=(4\pi/\mu^2)G(q^2/\mu^2);\\&\qquad\qquad G(x)=1/(1+x)+1/(1+x)^2,\\&(f|V_M|0)=(4\pi/\mu^2)\{G(q^2/\mu^2)-V_S^0H_g(q^2/\mu^2)\};\\&\qquad\qquad H_g(x)=2g/\mu^2(g^2/\mu^2+x)^2.\end{aligned}\right\}\tag{17}$$

Changing variables from q to $x=q^2/\mu^2$ in the integration, χ is given by

$$\left.\begin{aligned}&\chi=\pi\left(\frac{Z'e^2}{\hbar v_0}\right)^2\cdot\left(\frac{2}{\mu}\right)^2\\&\qquad\times\begin{cases}A & \text{for electrons and protons}\\A-B & \text{for hydrogen atoms,}\end{cases}\\&v_0=\hbar k_0/M_A;\quad Z'=2/1+S(\rho_0)=1.115,\\&A=\int_{x_{\min}}^{x_{\max}}G^2(x)dx,\\&B=\int_{x_{\min}}^{x_{\max}}\{2V_S^0G(x)H_g(x)-V_S^{02}H_g^2(x)\}dx,\\&x_{\max,\min}=[(k_0\pm k_f)/\mu]^2.\end{aligned}\right\}\tag{18}$$

VI. ONE-DIMENSIONAL TREATMENT OF THE TRANSLATIONAL MOTION

We shall consider the one-dimensional problem to estimate the error in Born's approximation for protons. The matrix element $(f|V_W|0)$ in the sine wave approximation, which is the one-dimensional analog of Born's approximation, is given first. With the normalization

$$\psi(x)=(\sin kx)/k^{\frac{1}{2}},$$

the matrix element for protons interacting with a

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[10] η_{0p} vanishes for $p=6.6/a_0$ because of the sine factor, which arises from the fact that the matrix element depends critically on the position of the nodes of ψ_p relative to the peak in ψ_0. The contributions due to states with $p>6.6/a_0$ need not be considered, because the matrix element η_{0p} falls off extremely fast.

hydrogen molecule is found to be

$$\left.\begin{aligned}(f|V_W|0)=\frac{Z'e^2}{4(k_0k_f)^{\frac{1}{2}}}\Bigg\{\log\left(\frac{\mu^2+k_+{}^2}{\mu^2+k_-{}^2}\right)&\\ +\mu^2\left(\frac{1}{\mu^2+k_-{}^2}-\frac{1}{\mu^2+k_+{}^2}\right)\Bigg\}&,\\ k_\pm=k_0\pm k_f.&\end{aligned}\right\}\tag{19}$$

Next we shall obtain the matrix element $(f|V_W|0)$ by two more accurate methods, namely, Langer's modification[11] of the WKB method, and also by approximating for the wave function by bessel functions of order chosen to fit the correct wave function at the turning point of the classical motion. The two methods agree quite well with one another.

(a) WKB Method

Langer's modification[11] is used to give the wave function for all x as the usual WKB approximation fails at x_1, the turning point of the classical motion. The results used here are the following. The wave equation

$$\{(d^2/dx^2)+k^2-(2M_A/\hbar^2)V(x)\}\psi=0 \tag{20a}$$

has a singular point at x_1, where

$$Q^2(x_1)=k^2-(2M_A/\hbar^2)V(x_1)=0, \tag{20b}$$

$V(x)$ being given by Eq. (5). The zero in $Q^2(x)$ at x_1 is a simple one, i.e., near x_1,

$$Q^2(x)=C'(x-x_1)\quad (C'>0) \tag{20c}$$

and the desired solution, which is oscillatory for large x and decreases rapidly for small x, is the following, if N is a normalizing constant:

$$\left.\begin{aligned}x>x_1:&\quad \psi(x)=N(2\pi\xi/3Q)^{\frac{1}{2}}[J_{\frac{1}{3}}(\xi)+J_{-\frac{1}{3}}(\xi)],\\ x<x_1:&\quad \psi(x)=N(2|\xi|/\pi|Q|)^{\frac{1}{2}}K_{\frac{1}{3}}(|\xi|),\\ &\quad \xi=\int_{x_1}^{x}Q(x)dx,\end{aligned}\right\}\tag{21}$$

with the following simplified forms:

$$\left.\begin{aligned}\psi((x-x_1)\rightarrow\infty)\sim 2NQ^{-\frac{1}{2}}\cos(\xi-\pi/4);&\\ \xi\sim k(x-x_1),&\\ Q\sim k&\\ \psi(x_1)=(N/C'^{1/6})\times 1.21&\\ \psi((x-x_1)\rightarrow-\infty)\sim N|Q|^{-\frac{1}{2}}e^{-|\xi|}.&\end{aligned}\right\}\tag{21'}$$

Especially at low energies, there is a considerable difference between x_1 for initial and final states. It is convenient to split the range of integration into three I: $0<x<\bar{x}_1$, where $\psi(x)$ decreases rapidly with decreasing x; II: $\bar{x}_1<x<x_2\sim 2\bar{x}_1$, $\psi(x)$ oscillates in a complicated way; III: $x>x_2$, where asymptotic values of $\psi(x)\sim\sin(kx-\text{const})$ may be used. In fact, the regions I and II contribute most to the matrix element (see Table II). The matrix elements are calculated in this way at two energies, 41.4 and 165 ev, and the results are given in Table I. It is seen that these matrix elements are much smaller than those using sine waves.

(b) Bessel Function Approximation

From Table II it is seen that the most important contribution to the matrix element comes from the region near x_1, and thus one is led to look for an analytic form of wave function which is satisfactory near x_1 and also has the correct behavior for very large and very small x. In fact, this can be done by replacing $V(x)$ by an inverse square interaction chosen to give the correct value of x_1. The result is a bessel function whose order depends on α (and x_1)—

Let

$$V(x_1)=Z'e^2\gamma_1/x_1. \tag{22a}$$

Then Eq. (20a) is approximated by

$$[(d^2/dx^2)+k^2-(2M_A/\hbar^2)Z'e^2\gamma_1x_1/x^2]\psi=0, \tag{22b}$$

which has a (suitably normalized) solution

$$\psi(x)=(\pi/2)^{\frac{1}{2}}x^{\frac{1}{2}}J_\nu(kx);\quad \nu^2=\tfrac{1}{4}+(2\alpha\gamma_1)^2. \tag{22c}$$

Unfortunately,

$$\int_0^\infty J_\nu(kx)J_{\nu'}(k'x)e^{-\mu x}dx$$

has no simple analytic form unless $\nu=\nu'$, when

$$\begin{aligned}\tfrac{1}{2}\pi\int_0^\infty J_\nu(k_0x)J_\nu(k_fx)e^{-\mu x}dx&\\ =[1/2(k_0k_f)^{\frac{1}{2}}]Q_{\nu-\frac{1}{2}}(\mu^2+k_0{}^2+k_f{}^2/2k_0k_f).&\end{aligned}\tag{23}$$

$Q_\nu(x)$ is a Legendre function of the second kind.[12]

However, bessel functions are well tabulated, and it is possible to evaluate the matrix element numerically with relatively little labor. This has been done at the two energies at which the WKB functions were evaluated, and the results agree quite well with the WKB method (see Tables I, II).

The difference $|\nu_f-\nu_0|$ decreases with decreasing coupling constant α_0, so that for $\pi_0<6$, say, we may put $\nu_0=\nu_f$ and use the result (23) to compare the "exact" matrix element obtained in this way with the sine wave matrix element (19). Now $(\mu^2+k_0{}^2+k_f{}^2)/2k_0k_f=1+\epsilon$, and $\epsilon=(\mu^2+k_-{}^2)/2k_0k_f\rightarrow\mu^2/2k^2$ as $E\rightarrow\infty$;

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[11] R. E. Langer, Phys. Rev. **51**, 669 (1937).

[12] G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge University Press, London, 1944), second edition, p. 390.

TABLE I. One-dimensional matrix elements.

		41.4	165
Energy (ev)		41.4	165
Coupling constants:	α_0	27.5	13.7
	α_f	30.0	14.0
Closest distance of approach (au)	x_1^0	0.522	0.212
	x_1^f	0.572	0.218
V_{0f} (au)	WKB:	1.41×10^{-3}	4.41×10^{-3}
	Bessel function:	1.25×10^{-3}	3.93×10^{-3}
	Sine waves:	36.2×10^{-3}	25.9×10^{-3}

a superficial difficulty arises from the fact that the $Q_\nu(1)$ diverge logarithmically. For integral order n[13] we have

$$\left.\begin{aligned} &Q_n(x)/P_n(x)=\tfrac{1}{2}\log[(x+1)/(x-1)]-L_n(x),\\ &L_n(x)=\frac{1}{x-}\,\frac{1^2}{3x-}\,\frac{2^2}{5x-}\cdots-\frac{(n-1)^2}{(2n-1)x},\\ &\qquad\text{a continued fraction.}\end{aligned}\right\}\quad(24)$$

In fact, $P_n(1)=1$ and the $L_n(1)$ are finite, so that ρ need only be retained in the logarithm;[14] and, in fact, the argument in the log term is the same as in Eq. (19).

The result (24) is quoted for integral n, but can clearly be extended to all real positive orders with appropriate modifications. Further, $V(x)$ is generated from $e^{-\mu x}/x$ by the operation $Ze^2(1-\frac{1}{2}\mu\partial/\partial_\mu)$, so that to the first order the contribution of the term $\frac{1}{2}\mu Ze^{-\mu x}$ to the matrix element is just the same as in the sine wave case. Thus the matrix element is

$$(f|V_W|0)=\frac{Z'e^2}{4(k_0k_f)^{\frac{1}{2}}}\left\{\log\frac{\mu^2+k_+^2}{\mu^2+k_-^2}\right.$$
$$\left.+\mu^2\left(\frac{1}{\mu^2+k_-^2}-\frac{1}{\mu^2+k_+^2}\right)-2L_{\nu-\frac{1}{2}}(1)\right\},\quad(25)$$

where $L_0(1)=0$; $L_1(1)=1$; $L_2(1)=1.5$; $L_5(1)=2.3$; $L_{10}(1)=2.9$; $L_{20}(1)=3.7$.

It is now possible to give an expression for ζ, the ratio of exact to sine wave matrix elements of $(f|V|0)$ in the one-dimensional case, as a function of the coupling constant α_0, and this is shown in Fig. 1. Equation (25) fails for large α_0 by giving too large a result for ζ, presumably because the difference $|\nu_f-\nu_0|$ becomes noticeable.

TABLE II. Comparison of the WKB and bessel function methods.

Energy (ev)		41.4		165	
Method:		WKB	Bessel function	WKB	Bessel function
ν_0		...	25.8	...	21.2
ν_f		...	26.2	...	21.5
$10^{-3}\times$au	V_{0f}^{I}	0.46	0.53	0.78	0.53
	V_{0f}^{II}	0.80	0.60	3.38	3.35
	V_{0f}^{III}	0.15	0.12	0.25	0.05
	V_{0f}	1.41	1.25	4.41	3.93

VII. RESULTS: THE CROSS SECTION σ_2

It seems plausible on physical grounds to suppose that the ratio of the exact value of $(f|V_W|0)$ to that calculated using plane waves for the 3-dimensional case will be of the same order of magnitude as this ratio for the one-dimensional case, and thus one may hope that for protons

$$\chi_{\text{corr}}=\zeta^2\chi_{\text{Born}}\quad(26)$$

will be a better approximation than χ_{Born}; ζ is given in Fig. 1. Since over an appreciable range of energies $\zeta^2\ll1$, this correction is hazardous; but the corrected results of Fig. 2 for the total cross section σ_2 seem reasonable, as the strong interaction represented by $\alpha\gg1$ means that the wave functions will differ considerably from plane waves, and the modification in general tends to reduce the probability of inelastic processes.[2]

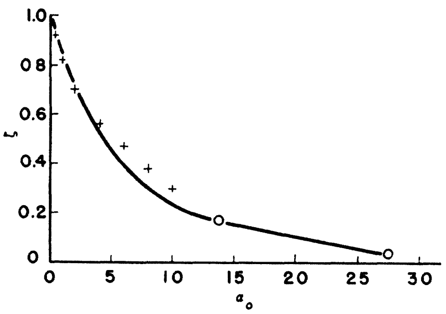

FIG. 1. ζ, the ratio of exact to sine wave translational matrix element of V_W in one dimension, as a function of the coupling constant $\alpha_0=Z'e^2/\hbar v_0$. Points ○ come from the WKB evaluation, + from the approximate bessel function method of Eq. (25).

If this reasoning is accepted tentatively, the results for ζ may be used to correct χ_{Born} for hydrogen atoms, as the effect of the screening field is small at low velocities. Naturally, the corrected cross sections for hydrogen atoms can be significant only in their order of magnitude.

The total cross section σ_2 is given in Fig. 2 as a function of energy for electrons, protons, and hydrogen atoms. The corrected cross section for hydrogen atoms is not shown: at low energies it is equal to that for protons, while at high energies it tends to 0.41 times that for protons, because of screening; at an energy of 15 ev it is $\sim6\times10^{-26}$ cm^2.

VIII. THE THREE-BODY COEFFICIENT $C=\sigma_3u$

The relative (3) holds in differential form, and must be integrated to give the three body recombination coefficient C as a function of $E_p=\hbar^2p^2/2M_0$ the mutual kinetic energy of approach of the two hydrogen atoms, and $E_f=\hbar^2k_f^2/2M_X$ the kinetic energy of the third-body

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[13] E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, London, 1927), fourth edition, p. 318.

[14] At $E_0=41.4$ ev, $\epsilon=5.1\times10^{-3}$.

X relative to the center of mass of the two hydrogen atoms. Following Moses and Wu,[1] Eq. (3) becomes

$$dC=\pi h\cdot\frac{G_{H_2}G_{X^*}}{G_H^2G_X}\cdot\frac{M_0\rho_0^2}{M_A^2}\cdot\frac{1}{k_f}\cdot\frac{d\sigma_2k_0^3dk_0}{p^2dp},\qquad(27)$$

where the G's are statistical weights of the individual systems. Now, from Eq. (12), we may write

$$\sigma_2(k_0,\,k_f)=B(k_0,\,k_f)\int_0 A(p)pdp,\qquad(12')$$

so that

$$C(E_{p_1}E_f)=\pi h\frac{G_{H_2}}{G_H^2}\,\frac{G_{X^*}}{G_X}\,\frac{M_0\rho_0^2}{M_A^2}\,\frac{1}{k_f}\,\frac{A(p)}{p}\times\int B(k_0,\,k_f)k_0^3dk_0.\qquad(28)$$

The limits of integration are $k_1<k_0<k_2$, where $k_1^2=2M_AD/\hbar^2$ is the threshold of the dissociation reaction, and $k_2=[k_f^2+k_1^2+(M_A/M_0)p^2]^{\frac{1}{2}}$ is the maximum possible value of k_0 subject to conservation of energy in the collision. One may take some suitable approximate form for $B=B(k_0)$ in the integration, such as $B_1(k_0^2-k_1^2)$ for heavy particles at low energies and $(B_2/k_0^2)\times[1-\exp(-\lambda(k_1-k_0))]$ for electrons; the resulting values of the three-body coefficient are the following—if $E_p=\frac{1}{2}kT$ and $E_f=5$ ev, then for electrons, $C\sim10^{-39}$ cm^6/sec and for a hydrogen atom as third body, $C\sim10^{-42}$ cm^6/sec; if $E_p=kT$, these values are reduced by a factor 1.6.[15] The values quoted increase roughly linearly with E_f up to 5 ev; but above this the coefficient C for electrons increases less rapidly, while that for hydrogen atoms increases faster.

Experimental values for the case of hydrogen as third body are of the order 3×10^{-32} cm^6/sec,[16] corresponding to $\sigma_2\sim10^{-14}$ cm^2. It is hard to understand such a large value for σ_2; but it is clear that a much closer study of both the experimental methods and their analysis, and also of the theoretical calculations,† is necessary to obtain a clear understanding of the recombination processes observed in the actual experiments.

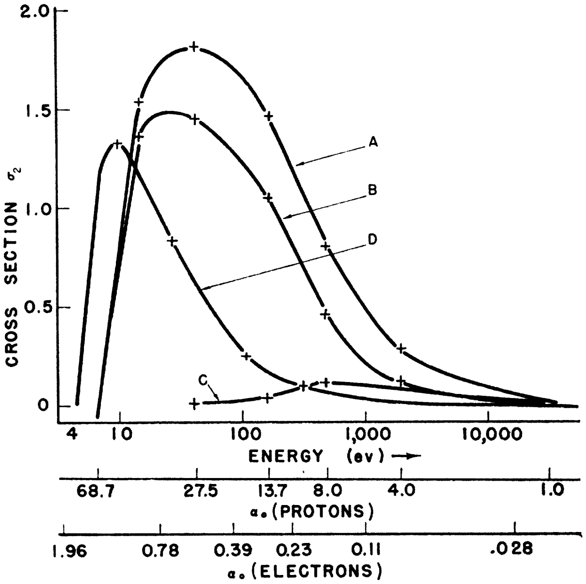

FIG. 2. The total cross section σ_2 as a function of the energy of the incident particle relative to the center of mass of the molecule. (A) Uncorrected cross section for protons. (B) Uncorrected cross section for hydrogen atoms. (C) Corrected cross section for protons. (D) Uncorrected cross section for electrons. The scale of σ_2 for (D) is 100 times larger than that for (A)-(C): for (A)-(C), the unit is 10^{-22} cm^2, while for (D) it is 10^{-24} cm^2. Thus, the cross section for electrons is greater than the corrected cross section (C) for protons only for energies less than 30 ev. The coupling constant α_0 is also shown on the abscissa for electrons and protons.

I should like to thank Dr. T.-Y. Wu, who suggested this problem, for many discussions.

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[15] At low energies (<50 ev) use of the uncorrected Born approximation cross sections increases σ_2 and C for hydrogen atoms and protons by a factor 10^3.

[16] H. J. Schumacher, *Chemische Gasreaktionen* (Theodor Steinkopff Verlag., Leipzig, 1938), p. 324.

† *Note added in proof:*—Further work has shown that if the molecule is formed by recombination in a highly excited vibrational state, the three-body coefficient C may be larger than the value calculated here by a factor of order 10^5. This work will be reported later.