

## The Quantum Mechanics of Chemical Kinetics of Homogeneous Gas Phase Reactions II. Approximations for Displacement Reaction between an Atom and a Diatomic Molecule

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Citation: [The Journal of Chemical Physics](#) **17**, 630 (1949); doi: 10.1063/1.1747349

View online: <http://dx.doi.org/10.1063/1.1747349>

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right side of Eq. (A-8) can be made to vanish. The last term will vanish only if the indicated matrix element is real.

Since  $\mathbf{H}$ ,  $\mathbf{H}^{(\alpha)}$ , and  $\mathbf{H}^{(\beta)}$  may be assumed real,  $\Psi_m^{(\alpha)}$  and  $\Psi_n^{(\beta)}$  as well as their complex conjugates are solutions of Eq. (A-4). For distinct energy levels these wave functions can differ from their complex conjugates only by an arbitrary phase factor, in which case the indicated matrix element is real. For degenerate levels the matrix element need not be real. However, since the set of wave functions corresponding to a degenerate level may always be arranged to consist of a linearly independent set of functions and their complex conjugates, the last term of Eq. (A-8) will vanish when summed over all degenerate states.

Hence, understanding that an integration with respect to the energy is to be carried out, as well as a summation over the degenerate states, one may take

$$P(\alpha, \beta) = 2 \left| \int d\tau \Psi_n^{(\beta)*} (\mathbf{H} - \mathbf{H}^{(\beta)}) \Psi_m^{(\alpha)} \right|^2 \times \left[ \frac{1 - \cos \{ (E_n^{(\beta)} - E_m^{(\alpha)}) / \hbar \} t}{(E_n^{(\beta)} - E_m^{(\alpha)})^2} \right]. \quad (\text{A-9})$$

Since

$$\begin{aligned} \int d\tau \Psi_n^{(\beta)*} (\mathbf{H}^{(\alpha)} - \mathbf{H}^{(\beta)}) \Psi_m^{(\alpha)} &= E_m^{(\alpha)} \int d\tau \Psi_n^{(\beta)*} \Psi_m^{(\alpha)} \\ &- \Sigma_k \left[ \int d\tau \Psi_n^{(\beta)*} \mathbf{H}^{(\beta)} \Psi_k^{(\beta)} \right] \left[ \int d\tau \Psi_k^{(\beta)} \Psi_m^{(\alpha)} \right] \\ &= (E_m^{(\alpha)} - E_n^{(\beta)}) \int d\tau \Psi_n^{(\beta)*} \Psi_m^{(\alpha)}, \quad (\text{A-10}) \end{aligned}$$

one can obtain, with the same understanding as in Eq. (A-9),

$$P(\alpha, \beta) = 2 \left| \int d\tau \Psi_n^{(\beta)*} (\mathbf{H} - \mathbf{H}^{(\alpha)}) \Psi_m^{(\alpha)} \right|^2 \times \left[ \frac{1 - \cos \{ (E_n^{(\beta)} - E_m^{(\alpha)}) / \hbar \} t}{(E_n^{(\beta)} - E_m^{(\alpha)})^2} \right]. \quad (\text{A-11})$$

Thus, in spite of the fact that  $(\mathbf{H} - \mathbf{H}^{(\beta)})$  and  $(\mathbf{H} - \mathbf{H}^{(\alpha)})$  represent entirely different perturbation functions, the transition probabilities which involve these perturbations (e.g., the forward and reverse perturbations in a chemical transition) are essentially equal.

## The Quantum Mechanics of Chemical Kinetics of Homogeneous Gas Phase Reactions\*

### II. Approximations for Displacement Reaction between an Atom and a Diatomic Molecule

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(Received November 17, 1948)

The quantum mechanics of a displacement reaction:  $AB + C \rightarrow A + BC$ , has been considered and the results have been applied to the reaction:  $\text{H}_2 + \text{Br} \rightarrow \text{H} + \text{HBr}$  at 500°K. The potential energy of the reacting system is based upon the London approximation as modified by Eyring and Polanyi. The absolute rate has been found to be a sensitive function of the coulombic energy fraction; when this fraction is taken to be 30 percent, the absolute rate is in essential agreement with the observed value. This agreement can only be regarded as fortuitous, however.

Several results have been derived which are not sensitive to the fraction of coulombic energy and furnish, therefore, a more stringent test of the present formulation. It has been found that the variation of the absolute rate with temperature, as calculated at 500°K, compares favorably with the observed variation. Approximately 95 percent of the rate comes from hydrogen molecules in the first excited vibrational state. The contribution from hydrogen molecules in various rotational states is given. The distribution of the initially formed hydrogen bromide molecules has been found to be representable by a pseudo-canonical distribution function of the rotational quantum number, in which the "rotational temperature" is approximately one-half the initial temperature.

### I. INTRODUCTION

A QUANTUM mechanical formulation for the rate of a chemical reaction has been presented in the first paper of this series.<sup>1</sup> In order to apply the results of (I) to a particular chemical reaction, one needs to know the potential energy (electronic energy) of the reacting system and the wave functions of both reactants and products. For reactions involving large numbers of molecules it is difficult

to obtain accurately the potential energy and the wave functions. Even in fairly simple cases, approximations must be made to all of these quantities.

In the present paper, we consider the simple example of a *displacement reaction*:  $AB + C \rightarrow A + BC$ . The perturbation energy is constructed from the Eyring and Polanyi<sup>2</sup> modification of the potential energy of a triatomic system as given by London.<sup>3</sup>

\* This paper represents one of the results of the research program on chemical kinetics being carried out at Hydrocarbon Research, Inc.

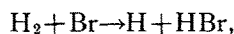
<sup>1</sup> Sidney Golden, "The quantum mechanics of chemical kinetics of homogeneous gas phase reactions, I. General considerations," *J. Chem. Phys.* **17**, 620 (1949). This paper will be referred to as (I).

<sup>2</sup> H. Eyring and M. Polanyi, *Zeits. f. physik. Chemie.* **B12**, 279 (1931); see also, for example, S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), pp. 85-152.

<sup>3</sup> F. London, *Probleme der modernen Physik (Sommerfeld Festschrift)* (S. Herzl, Leipzig, 1928), p. 104; *Zeits. f. Elektrochemie.* **35**, 552 (1929).

The admittedly crude assumption is made that the  $A-B$  and  $B-C$  potentials can be approximated by harmonic oscillator potentials, and that the  $A-C$  potential can be taken as some constant value.

The results are applied to the reaction:



at 500°K. The calculated value of the absolute rate is found to be sensitive to the exact value taken for the coulombic energy fraction in the Eyring—Polanyi approximation. Hence no value is given for the rate. Instead, the dependence of the calculated rate upon the coulombic energy fraction is given graphically in Fig. 1. When this fraction is between 25–30 percent, good agreement is obtained with experiment.

Several results have been derived which are not sensitive to the choice of the coulombic energy fraction. The variation of the absolute rate with temperature, as calculated at 500°K, compares favorably with the observed variation. The contribution to the rate made by each of the discrete states of the hydrogen molecule is obtained. It is found, for example, that by far the greatest contribution to the rate comes from hydrogen molecules in the first excited vibrational state. Of perhaps greater interest is the distribution among the rotational states of hydrogen bromide molecules formed. This distribution may be represented by a Gibbsian canonical form in which, however, the “rotational temperature” is significantly different from the temperature of the reactants.

## II. THE WAVE FUNCTIONS

Following the model of the reacting system discussed in (I) we assume that at the initial instant of time a diatomic molecule of mass  $(m_1 + m_2)$  and an atom of mass  $m_3$  enter a region of volume  $V$ . The momentum of the initial molecule is  $\mathbf{P}_{12}$ , while that of the initial atom is  $\mathbf{P}_3$ . Subsequent to the displacement reaction, the final molecule has mass  $(m_2 + m_3)$  and momentum  $\mathbf{P}_{23}$ , while the atom has mass  $m_1$  and momentum  $\mathbf{P}_1$ .

To the approximation that interactions between translational, rotational and vibrational motion may be neglected, and with the assumption of harmonic vibrations of the molecule, the initial wave function for the reacting system may be taken as<sup>4</sup>

$$\psi_i = \frac{N_n}{V} \exp\left(\frac{i}{\hbar} \mathbf{P}_{12} \cdot \mathbf{r}_{12}\right) \frac{H_n(\xi) \exp(-\xi^2/2)}{[\xi/(a_1)^{1/2} + \rho_1]} \times P_K^{LM}(\cos\theta) e^{iM\varphi} \exp\left(\frac{i}{\hbar} \mathbf{P}_3 \cdot \mathbf{r}_3\right). \quad (1)$$

<sup>4</sup> See, for example, L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), pp. 259–271.

Here  $N_n H_n(\xi) e^{-\xi^2/2}$  is a normalized hermite orthogonal function.  $P_K^{LM}(\cos\theta) e^{iM\varphi}$  is a normalized spherical harmonic, representing the rotational part of the wave function. The translational wave functions have been taken as plane waves, each normalized to the volume  $V$ ;

$$N_n = [(a_1/\pi)^{1/2} (1/2^n n!)]^{1/2}, \\ a_1 = (4\pi^2 \mu_1 \nu_1 / h);$$

$\mu_1 = m_1 m_2 / (m_1 + m_2)$ , the reduced mass of the initial molecule;  $\nu_1$  is the fundamental vibration frequency of the initial molecule;

$$\mathbf{r}_{12} = (m_1 / (m_1 + m_2)) \mathbf{r}_1 + (m_2 / (m_1 + m_2)) \mathbf{r}_2,$$

the (vector) coordinate of the center of mass of the initial molecule;  $(\xi/(a_1)^{1/2} + \rho_1)$  is the distance between atoms of the initial molecule, where  $\rho_1$  is the equilibrium distance between the atoms of the initial molecule;  $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3$ , are the (vector) coordinates of the respective atoms;  $\theta, \varphi$  refer to the polar and azimuthal angles in spherical polar coordinates which fix the orientation of the initial molecule in space;  $n, K$  and  $M$  are quantum numbers corresponding respectively to vibration, total angular momentum, and the component of the latter along a space fixed axis.

The volume element for this wave function is

$$d\tau_i = d\mathbf{r}_{12} d\mathbf{r}_3 \left( \frac{\xi}{(a_1)^{1/2}} + \rho_1 \right)^2 d\left( \frac{\xi}{(a_1)^{1/2}} \right) d(\cos\theta) d\varphi, \quad (2)$$

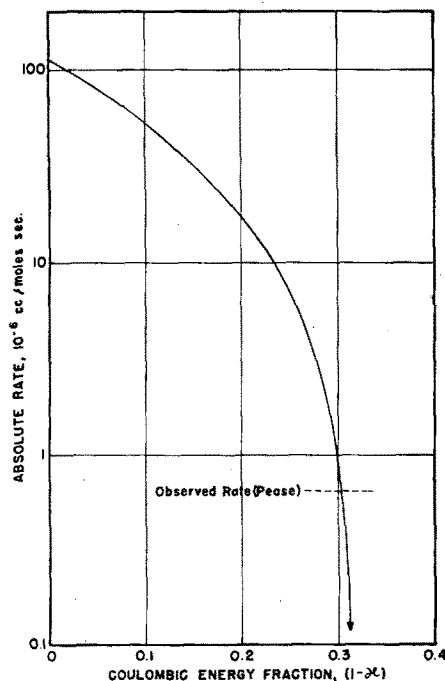


FIG. 1. Calculated variation of the absolute rate with fraction of coulombic energy.

where  $d\mathbf{r}=dxdydz$  and  $x, y, z$  are the cartesian coordinates of  $\mathbf{r}$ . The final wave function for the reacting system may be taken as

$$\psi_f = \frac{N_m}{V} \exp\left(\frac{i}{\hbar} \mathbf{P}_{23} \cdot \mathbf{r}_{23}\right) \frac{H_m(\eta) \exp(-\eta^2/2)}{[(\eta/(a_2)^{1/2}) + \rho_2]} \times P_L^{|N|}(\cos\theta') e^{iN\varphi'} \exp\left(\frac{i}{\hbar} \mathbf{P}_1 \cdot \mathbf{r}_1\right), \quad (3)$$

where

$$\mathbf{r}_{23} = (m_2/(m_2+m_3))\mathbf{r}_2 + (m_3/(m_2+m_3))\mathbf{r}_3,$$

and other quantities are defined analogous to the previous definitions.

The volume element for this wave function is

$$d\tau_f = d\mathbf{r}_1 d\mathbf{r}_{23} \left(\frac{\eta}{(a_2)^{1/2}} + \rho_2\right)^2 d\left(\frac{\eta}{(a_2)^{1/2}}\right) d(\cos\theta') d\varphi'. \quad (4)$$

It is convenient to make a change of variables at this point. Noticing that

$$\mathbf{r}_1 = \mathbf{r}_2 + \left(\frac{\xi}{(a_1)^{1/2}} + \rho_1\right) \hat{i}(\theta, \varphi),$$

where  $\hat{i}(\theta, \varphi)$  is a unit vector along the internuclear axis of the initial molecule, viz.

$$\begin{aligned} \hat{i}_x &= \sin\theta \cos\varphi, \\ \hat{i}_y &= \sin\theta \sin\varphi, \\ \hat{i}_z &= \cos\theta, \end{aligned}$$

and  $\mathbf{r}_3 = \mathbf{r}_2 + (\eta/(a_2)^{1/2} + \rho_2) \hat{j}(\theta', \varphi')$ , where  $\hat{j}(\theta', \varphi')$  is a unit vector along the internuclear axis of the final molecule, viz.

$$\begin{aligned} \hat{j}_x &= \sin\theta' \cos\varphi', \\ \hat{j}_y &= \sin\theta' \sin\varphi', \\ \hat{j}_z &= \cos\theta', \end{aligned}$$

one may show that

$$\begin{aligned} &\mathbf{P}_{12} \cdot \mathbf{r}_{12} + \mathbf{P}_3 \cdot \mathbf{r}_3 - \mathbf{P}_1 \cdot \mathbf{r}_1 - \mathbf{P}_{23} \cdot \mathbf{r}_{23} \\ &= (\mathbf{P}_{12} + \mathbf{P}_3 - \mathbf{P}_1 - \mathbf{P}_{23}) \cdot \mathbf{r}_2 \\ &+ \left(\frac{\xi}{(a_1)^{1/2}} + \rho_1\right) \left[\left(\frac{m_1}{m_1+m_2}\right) \mathbf{P}_{12} - \mathbf{P}_1\right] \cdot \hat{i}(\theta, \varphi) \\ &+ \left(\frac{\eta}{(a_2)^{1/2}} + \rho_2\right) \left[\left(\frac{m_3}{m_2+m_3}\right) \mathbf{P}_{23} - \mathbf{P}_3\right] \cdot \hat{j}(\theta', \varphi'). \quad (5) \end{aligned}$$

This facilitates a change to variables:  $\mathbf{r}_2, \xi, \eta, \theta, \theta', \varphi, \varphi'$  which gives

$$\begin{aligned} \psi_f^* \psi_i &= N_n N_m \frac{H_n(\xi) \exp(-\xi^2/2) H_m(\eta) \exp(-\eta^2/2)}{\left(\frac{\xi}{(a_1)^{1/2}} + \rho_1\right) \left(\frac{\eta}{(a_2)^{1/2}} + \rho_2\right)} \\ &\times P_K^{|M|}(\cos\theta) P_L^{|N|}(\cos\theta') \exp(iM\varphi - iN\varphi') \\ &\times \frac{1}{V^2} \exp\left\{\frac{i}{\hbar} \left[ \Delta\mathbf{P} \cdot \mathbf{r}_2 + \left(\frac{\xi}{(a_1)^{1/2}} + \rho_1\right) \boldsymbol{\alpha} \cdot \hat{i} \right. \right. \\ &\quad \left. \left. + \left(\frac{\eta}{(a_2)^{1/2}} + \rho_2\right) \boldsymbol{\beta} \cdot \hat{j} \right] \right\}, \quad (6) \end{aligned}$$

where

$$\begin{aligned} \Delta\mathbf{P} &= \mathbf{P}_{12} + \mathbf{P}_3 - \mathbf{P}_1 - \mathbf{P}_{23}, \\ \boldsymbol{\alpha} &= \left(\frac{m_1}{m_1+m_2}\right) \mathbf{P}_{12} - \mathbf{P}_1, \\ \boldsymbol{\beta} &= \left(\frac{m_3}{m_2+m_3}\right) \mathbf{P}_{23} - \mathbf{P}_3. \end{aligned} \quad (7)$$

In terms of the new coordinates the volume element is

$$\begin{aligned} d\tau &= \left(\frac{\xi}{(a_1)^{1/2}} + \rho_1\right)^2 \left(\frac{\eta}{(a_2)^{1/2}} + \rho_2\right)^2 d\mathbf{r}_2 d\left(\frac{\xi}{(a_1)^{1/2}}\right) \\ &\times d\left(\frac{\eta}{(a_2)^{1/2}}\right) d(\cos\theta) d(\cos\theta') d\varphi d\varphi'. \quad (8) \end{aligned}$$

### III. THE PERTURBATION ENERGY

Although the wave functions for the reactants and the products are approximate, one can have a degree of confidence in their reliability, which is based upon their successful application in molecular spectroscopy. The perturbation, however, is an entirely different matter. Since the potential energy of an interacting system has not been subjected to direct experimental verification, there is correspondingly greater uncertainty regarding the perturbation than there is regarding the wave functions.

In order to approximate the potential energy of the reacting system, we shall employ the results of London,<sup>3</sup> and the particular modification of his results by Eyring and Polanyi.<sup>2</sup>

London's expression for the potential energy of the system  $ABC$  is given by

$$V_{ABC} = Q_{AB} + Q_{BC} + Q_{AC} - (V_{AB}^2 + V_{BC}^2 + V_{AC}^2 - V_{AB}V_{BC} - V_{AB}V_{AC} - V_{BC}V_{AC})^{1/2}, \quad (9)$$

where  $Q$  and  $V$  represent the coulombic and exchange energies, respectively, of the various pairs of atoms.

The modification of Eyring and Polanyi consists

of noting that, in the London approximation,

$$\mathcal{V}_{AB} = Q_{AB} - |V_{AB}|,$$

and similarly, for the remaining pairs, and of setting

$$Q_{AB} = (1 - \kappa_{AB})\mathcal{V}_{AB}, \quad 0 < \kappa_{AB} < 1,$$

so that

$$|V_{AB}| = -\kappa_{AB}\mathcal{V}_{AB},$$

where  $(1 - \kappa_{AB})$  is the coulombic energy fraction. Substituting these expressions (as well as similar ones for the remaining pairs of atoms) into Eq. (9), one obtains

$$\mathcal{V}_{ABC} = (1 - \kappa)(\mathcal{V}_{AB} + \mathcal{V}_{BC} + \mathcal{V}_{AC}) - \kappa(\mathcal{V}_{AB}^2 + \mathcal{V}_{BC}^2 + \mathcal{V}_{AC}^2 - \mathcal{V}_{AB}\mathcal{V}_{BC} - \mathcal{V}_{AB}\mathcal{V}_{AC} - \mathcal{V}_{BC}\mathcal{V}_{AC})^{\frac{1}{2}},$$

where, for simplicity, we have taken all the  $\kappa$ 's equal.

For the reaction  $(AB + C \rightarrow A + BC)$  the perturbation is, according to (I),

$$\mathcal{H}' = \mathcal{V}_{ABC} - \mathcal{V}_{AB}.$$

Observe that the assumed harmonic oscillator wave functions for the initial and final states effectively restrict transitions to those configurations for which the  $A$ - $B$  and  $B$ - $C$  distances are in the neighborhood of their equilibrium values. One may, therefore, expand  $\mathcal{H}'$  in terms of  $\xi$  and  $\eta$  and neglect terms of higher order than the second. Assuming

$$\mathcal{V}_{AB} = \mathcal{V}_{AB}^0 + \frac{h\nu_1}{2}\xi^2 + 0(\xi^3),$$

$$\mathcal{V}_{BC} = \mathcal{V}_{BC}^0 + \frac{h\nu_2}{2}\eta^2 + 0(\eta^3),$$

one obtains

$$\begin{aligned} \mathcal{H}' = & \mathcal{V}_{BC}^0 + \mathcal{V}_{AC} - \kappa(\mathcal{V}_{AB}^0 + \mathcal{V}_{BC}^0 + \mathcal{V}_{AC} + \mathcal{V}^*) \\ & - \kappa \frac{h\nu_1}{2} \xi^2 \left[ 1 + \frac{1}{2\mathcal{V}^*} (2\mathcal{V}_{AB}^0 - \mathcal{V}_{BC}^0 - \mathcal{V}_{AC}) \right] \\ & + \frac{h\nu_2}{2} \eta^2 \left[ 1 - \kappa - \frac{\kappa}{2\mathcal{V}^*} (2\mathcal{V}_{BC}^0 - \mathcal{V}_{AB}^0 - \mathcal{V}_{AC}) \right], \end{aligned} \quad (10)$$

where

$$\mathcal{V}^* = [(\mathcal{V}_{AB}^0)^2 + (\mathcal{V}_{BC}^0)^2 + \mathcal{V}_{AC}^2 - \mathcal{V}_{AB}^0\mathcal{V}_{BC}^0 - \mathcal{V}_{AB}^0\mathcal{V}_{AC} - \mathcal{V}_{BC}^0\mathcal{V}_{AC}]^{\frac{1}{2}}.$$

Now if the  $A$ - $B$  and  $B$ - $C$  distances are essentially the equilibrium values,  $\mathcal{V}_{AC}$  will depend essentially upon the angle  $\angle ABC$ . Because we have been unable to evaluate the integrals which involve this angular dependence in any closed form, we shall crudely approximate  $\mathcal{V}^*$  by some constant value in which we assign  $\mathcal{V}_{AC}$  the value  $\mathcal{V}_{AC}^*$ . In particular we shall take values for  $\mathcal{V}_{AC}^*$  in the range

between that corresponding to a linear configuration, and that for which  $\mathcal{V}_{AC}$  is a minimum. Since the final results for the rate are dependent upon the actual value used for  $\mathcal{V}_{AC}^*$ , they must be regarded as only approximate.<sup>4a</sup>

Now Eq. (10) for the perturbation may be simplified by making use of certain results of (I). It was shown there that for those transitions which have large probability the matrix elements of  $(\mathcal{V}_f - \mathcal{V}_i)$  vanish. This permits us to eliminate the term in  $\xi^2$  from Eq. (10). The result is that the perturbation may be taken as

$$\mathcal{H}' = Y_0 + Y_1\eta^2, \quad (11)$$

where

$$Y_0 = (\mathcal{V}_{BC}^0 + \mathcal{V}_{AC}^*) - \kappa \left[ 2\mathcal{V}_{BC}^0 + \mathcal{V}_{AC}^* + \mathcal{V}^* - \frac{(\mathcal{V}_{AB}^0 - \mathcal{V}_{BC}^0)(2\mathcal{V}_{AB}^0 - \mathcal{V}_{BC}^0 - \mathcal{V}_{AC}^*)}{2\mathcal{V}^*} \right], \quad (12a)$$

and

$$Y_1 = \frac{h\nu_2}{2} \left[ 1 - 2\kappa - \frac{\kappa}{2\mathcal{V}^*} (\mathcal{V}_{BC}^0 + \mathcal{V}_{AB}^0 - 2\mathcal{V}_{AC}^*) \right]. \quad (12b)$$

For  $\mathcal{V}_{AB}^0$  and  $\mathcal{V}_{BC}^0$  nearly equal and  $\mathcal{V}_{AC}^*$  small,  $Y_1$  is very small compared to  $Y_0$ .

Inasmuch as the quantity  $Y_0$  is a sensitive function of  $\kappa$  and  $\mathcal{V}_{AC}^*$ , it is impossible to obtain a value for the rate that is not subject to a degree of arbitrariness. However, this is inherent in the approximation for the potential energy of the reacting system. This unsatisfactory feature makes any agreement that is obtained between calculated and observed values of the absolute rate of questionable validity in confirming the theory.

#### IV. THE TRANSITION PROBABILITY

The calculation of transition probabilities requires evaluation of integrals of the sort

$$I = \int \psi_f^* \psi_i (Y_0 + Y_1\eta^2) d\tau. \quad (13)$$

The probability of a transition from a particular initial to final state occurring within a time interval

<sup>4a</sup> Inasmuch as the actual dependence of the integrals upon the rotational state is not taken fully into account, the conclusions of sections VIII-C, D are subject to some modification. However, since the perturbation used in the present case appeared to be not very sensitive to the choices of  $\mathcal{V}_{AC}^*$  the conclusions reached there are probably not subject to marked change.

$(t_1 - t_0) = t$  is given<sup>5</sup> by

$$P(t) = 2|I|^2 \left[ \frac{1 - \cos(\Delta E t / \hbar)}{(\Delta E)^2} \right]. \quad (14)$$

$\Delta E$  is the difference between the final and initial energies. Now, from Eqs. (6) and (13) it is readily seen that the portion of the integral  $I$  depending only upon  $\mathbf{r}_2$  may be factored so that

$$I = \left[ \frac{1}{V^2} \int \cdots \int \exp[(i/\hbar) \Delta \mathbf{P} \cdot \mathbf{r}_2] d\mathbf{r}_2 \right] I_{int}. \quad (15)$$

Here  $I_{int}$  represents that portion of (13) integrated over the internal coordinates  $\xi, \eta, \theta, \theta', \varphi$ , and  $\varphi'$ . Carrying out the integrations in Eq. (15) and substituting in Eq. (14), we obtain

$$P(t) = \frac{16}{V^4} \left[ \frac{1 - \cos(\Delta E t / \hbar)}{(\Delta E)^2} \right] \times \prod_{i=x,y,z} \left[ \frac{1 - \cos(\Delta P_i t / \hbar)}{(\Delta P_i / \hbar)^2} \right] \times |I_{int}|^2, \quad (16)$$

where, for simplicity, we have taken  $V = l^3$ .

Since the assumed perturbation energy is independent of the angle variables  $\theta, \theta', \varphi, \varphi'$ , the quantity  $I_{int}$  can be simplified by integrating with respect to these variables. Combining (6), (8), and (13), we see that

$$I_{int} = \frac{N_n N_m}{(a_1 a_2)^{\frac{1}{2}}} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \mathcal{H}' H_n(\xi) \times \exp(-\xi^2/2) H_m(\eta) \exp(-\eta^2/2) \times Q_{KM} Q_{LN} \left( \frac{\xi}{(a_1)^{\frac{1}{2}}} + \rho_1 \right) \left( \frac{\eta}{(a_2)^{\frac{1}{2}}} + \rho_2 \right) d\xi d\eta,$$

where

$$Q_{KM} = \int_0^{2\pi} d\varphi \int_{-1}^{+1} d(\cos\theta) \times \exp\{(i/\hbar)(\xi/(a_1)^{\frac{1}{2}} + \rho_1)\alpha \cdot \hat{i}(\theta, \varphi)\} \times P_K^{1M}(\cos\theta) e^{iM\varphi}, \quad (17)$$

with a similar meaning for  $Q_{LN}$ . Using the value of  $Q_{KM}$  obtained in Appendix I, we have

$$|I_{int}| = \frac{16\pi^2 N_n N_m \rho_1 \rho_2}{(a_1 a_2)^{\frac{1}{2}}} \times |P_K^{1M}(\cos\omega_\alpha) P_L^{1N}(\cos\omega_\beta)| \cdot |R(\alpha, \beta)|, \quad (18)$$

<sup>5</sup> See, for example, P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press, London, 1947), pp. 178-181. See also reference (8) of (I).

where  $\omega_\alpha, \tau_\alpha$  are the angle coordinates of  $\alpha$ , and

$$R(\alpha, \beta) = \frac{\hbar}{8\pi \rho_1 \rho_2 (|\alpha| \cdot |\beta|)^{\frac{1}{2}}} \times \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \mathcal{H}' H_n(\xi) \exp(-\xi^2/2) H_m(\eta) \times \exp(-\eta^2/2) \left( \frac{\xi}{(a_1)^{\frac{1}{2}}} + \rho_1 \right)^{\frac{1}{2}} \left( \frac{\eta}{(a_2)^{\frac{1}{2}}} + \rho_2 \right)^{\frac{1}{2}} \times J_{K+\frac{1}{2}} \left( \frac{|\alpha|}{\hbar} \left( \frac{\xi}{(a_1)^{\frac{1}{2}}} + \rho_1 \right) \right) \times J_{L+\frac{1}{2}} \left( \frac{|\beta|}{\hbar} \left( \frac{\eta}{(a_2)^{\frac{1}{2}}} + \rho_2 \right) \right) d\xi d\eta. \quad (19)$$

The expression (16) must be integrated over all final translational states. It will be shown below that the number of final states having their energy and momentum in the range of specified values of these quantities and appearing in a certain element of solid angle is proportional to that element of solid angle,  $d\Omega_f$ , viz.,

$$d(\text{no. of final states}) = \rho_{\Omega_f}(E_f, \mathbf{P}_f) dE_f dP_{f,x} dP_{f,y} dP_{f,z} d\Omega_f. \quad (20)$$

Following the procedure used in (I), one obtains for the probability of a chemical transition

$$\bar{P} = \int P(t) d(\text{no. of final states}) = \int d\Omega_f (16\pi^4 \hbar^2 / V^3) \sum_{K,M,n,\mathbf{P}_i} \exp(-E_i/kT) \times \sum_{L,N,m} \rho_{\Omega_f}(E_i, \mathbf{P}_i) |I_{int}|^2 / \sum_{K,M,n,\mathbf{P}_i} \exp(-E_i/kT). \quad (21)$$

The summations indicated in Eq. (21) are purely formal and are to be understood as summation over the discrete variables (i.e.,  $K, M$ , etc.) and integration over the continuous variables (i.e.,  $\mathbf{P}_i$ ), for all accessible states.

## V. THE DENSITY OF TRANSLATIONAL STATES

Before evaluating  $\rho_{\Omega_f}(E_f, \mathbf{P}_f)$  of Eq. (20) we recall from (I) that Eq. (16) implies the conservation of energy and linear momentum. It is readily seen that the former leads to

$$\frac{|\mathbf{P}_{12}|^2}{2(m_1 + m_2)} + \frac{|\mathbf{P}_3|^2}{2m_3} + \frac{\hbar^2}{2I_i} K(K+1) + (n + \frac{1}{2})\hbar\nu_1 + E_1 = \frac{|\mathbf{P}_1|^2}{2m_1} + \frac{|\mathbf{P}_{23}|^2}{2(m_2 + m_3)} + \frac{\hbar^2}{2I_f} L(L+1) + (m + \frac{1}{2})\hbar\nu_2 + E_2. \quad (22)$$

$E_1$  and  $E_2$  fix the origin of vibrational energy so that zero energy corresponds to the molecule dissociated into atoms.  $-(E_1 + h\nu_1/2)$  is the dissociation energy of the initial molecule; similarly,  $-(E_2 + h\nu_2/2)$  is the dissociation energy of the final molecule.  $I_i$  and  $I_f$  are the moments of inertia of the initial and final molecule, respectively.

The conservation of linear momentum gives

$$\mathbf{P}_{12} + \mathbf{P}_3 = \mathbf{P}_1 + \mathbf{P}_{23}. \quad (23)$$

Equations (22) and (23), when combined, reduce to

$$\left| \mathbf{P}_1 - \frac{m_1}{M}(\mathbf{P}_{12} + \mathbf{P}_3) \right|^2 = \frac{m_1(m_2 + m_3)}{M^2} \left\{ \left| \left( \frac{m_3}{m_1 + m_2} \right) \mathbf{P}_{12} - \left( \frac{m_1 + m_2}{m_3} \right) \mathbf{P}_3 \right|^2 - 2\gamma M \right\},$$

where

$$M = m_1 + m_2 + m_3,$$

$$\gamma = (m + \frac{1}{2})h\nu_2 - (n + \frac{1}{2})h\nu_1 + (\hbar^2/2I_f)L(L+1) - (\hbar^2/2I_i)K(K+1) + (E_2 - E_1). \quad (24)$$

This equation may be converted to

$$\left| \left( \frac{m_2 + m_3}{m_1} \right) \mathbf{P}_1 - \left( \frac{m_1}{m_2 + m_3} \right) \mathbf{P}_{23} \right|^2 = \left| \left( \frac{m_3}{m_1 + m_2} \right) \mathbf{P}_{12} - \left( \frac{m_3}{m_1 + m_2} \right) \mathbf{P}_3 \right|^2 - 2\gamma M. \quad (25)$$

It may be concluded from Eq. (25) that unless the initial momenta are such as to make the right side of Eq. (25) non-negative, complex values for the final momenta result. We have defined the final states by *real* values for the momenta; hence transitions for which the momenta are complex will be assigned a zero probability.

For the density of final states, we need to consider only the translational states of the system. The total number of such states may be obtained from the volume of phase space,

no. of final states

$$= (1/h^6) \int \cdots \int dp_1 \cdots dp_6 dq_1 \cdots dq_6,$$

where  $p_i, q_i$  are conjugate variables. The  $p_i$ 's represent the components of  $\mathbf{P}_1$  and  $\mathbf{P}_{23}$ .

The integration over the position coordinates may be carried out, and the volume element in momentum space may be transformed to a new

set of variables, *viz.*  $(\mathbf{P}_1 + \mathbf{P}_{23})$  and

$$\left[ \left( \frac{m_2 + m_3}{m_1} \right) \mathbf{P}_1 - \left( \frac{m_1}{m_2 + m_3} \right) \mathbf{P}_{23} \right]$$

instead of  $\mathbf{P}_1$  and  $\mathbf{P}_{23}$ . One obtains

$$dp_1 \cdots dp_6 = d\mathbf{P}_1 d\mathbf{P}_{23} = -\frac{[m_1(m_2 + m_3)]^{\frac{1}{2}}}{M^3} d(\mathbf{P}_1 + \mathbf{P}_{23}) \times d \left[ \left( \frac{m_2 + m_3}{m_1} \right) \mathbf{P}_1 - \left( \frac{m_1}{m_2 + m_3} \right) \mathbf{P}_{23} \right].$$

Now we may write

$$d \left[ \left( \frac{m_2 + m_3}{m_1} \right) \mathbf{P}_1 - \left( \frac{m_1}{m_2 + m_3} \right) \mathbf{P}_{23} \right] = \frac{1}{2} \left| \left( \frac{m_2 + m_3}{m_1} \right) \mathbf{P}_1 - \left( \frac{m_1}{m_2 + m_3} \right) \mathbf{P}_{23} \right| \times d \left[ \left| \left( \frac{m_2 + m_3}{m_1} \right) \mathbf{P}_1 - \left( \frac{m_1}{m_2 + m_3} \right) \mathbf{P}_{23} \right|^2 \right] \sin u' du' dv',$$

where  $u', v'$  are the polar angles of the vector, measured with respect to some arbitrary set of space-fixed axes.

Since the integrations are to be carried out under conditions of essential conservation of momentum, we observe that the translational part of the final energy is very nearly

$$E = \frac{|\mathbf{P}_1|^2}{2m_1} + \frac{|\mathbf{P}_{23}|^2}{2(m_2 + m_3)} - \frac{|\mathbf{P}_1 + \mathbf{P}_{23}|^2}{2M} + \frac{|\mathbf{P}_{12} + \mathbf{P}_3|^2}{2M} = \frac{1}{2M} \left| \left( \frac{m_2 + m_3}{m_1} \right) \mathbf{P}_1 - \left( \frac{m_1}{m_2 + m_3} \right) \mathbf{P}_{23} \right|^2 + \frac{|\mathbf{P}_{12} + \mathbf{P}_3|^2}{2M},$$

so that

$$\frac{1}{2} d \left\{ \left| \left( \frac{m_2 + m_3}{m_1} \right) \mathbf{P}_1 - \left( \frac{m_1}{m_2 + m_3} \right) \mathbf{P}_{23} \right|^2 \right\} = MdE.$$

Combining these results, we obtain

$$d(\text{no. of final states}) = \left\{ \frac{V^2 [m_1(m_2 + m_3)]^{\frac{1}{2}}}{h^6 M^2} \left( \left| \left( \frac{m_3}{m_1 + m_2} \right) \mathbf{P}_{12} - \left( \frac{m_1 + m_2}{m_3} \right) \mathbf{P}_3 \right|^2 - 2\gamma M \right)^{\frac{1}{2}} \right\} \times d(\cos u') dv' d(\mathbf{P}_1 + \mathbf{P}_{23}) dE. \quad (26)$$

The terms in braces constitute the  $\rho_{\Omega_f}(E_f, \mathbf{P}_f)$  of Eq. (20).

## VI. EVALUATION OF REACTION PROBABILITY

To evaluate the probability (21), it is convenient to sum first over the quantum numbers  $M$  and  $N$ . With the use of the addition formula for spherical harmonics,<sup>6</sup> it can be shown that

$$\sum_{M=-K}^K |P_K^{(M)}(\cos\omega)|^2 = K + \frac{1}{2},$$

so that, from (18)

$$\sum_{M,N} |I_{int}|^2 = \frac{256\pi^4 N_n^2 N_m^2 \rho_1^2 \rho_2^2}{a_1 a_2} (K + \frac{1}{2})(L + \frac{1}{2}) |R|^2.$$

Thus, (21) becomes

$$\bar{P} = \frac{1024\pi^6 \hbar^2 \rho_1^2 \rho_2^2 t \int d\Omega_f \sum_{K,n,\mathbf{P}_i} N_n^2 (K + \frac{1}{2}) \exp(-E_i/kT) \sum_{L,m} N_m^2 (L + \frac{1}{2}) \rho_{\Omega_f}(E_i, \mathbf{P}_i) |R|^2}{a_1 a_2 V^3 \sum_{K,n,\mathbf{P}_i} (2K+1) \exp(-E_i/kT)}.$$

We next carry out the integration over the initial momenta,  $\mathbf{P}_i$ . Since

$$E_i = \frac{|\mathbf{P}_{12}|^2}{2(m_1+m_2)} + \frac{|\mathbf{P}_3|^2}{2m_3} + \frac{\hbar^2}{2I_i} K(K+1) + (n + \frac{1}{2})\hbar\nu_1 + E_1,$$

it follows that the reaction probability can be written as

$$\bar{P} = \sum_{K,L,m,n} W_{Knm} (L + \frac{1}{2}) S, \quad (27)$$

where

$$W_{Knm} = \frac{1024\pi^6 \rho_1^2 \rho_2^2 t [m_1(m_2+m_3)]^{\frac{1}{2}} N_n^2 N_m^2 (K + \frac{1}{2}) \exp[-(1/kT)((\hbar^2/2I_i)K(K+1) + n\hbar\nu_1)]}{a_1 a_2 V \hbar^4 M^2 \left\{ \sum_{K,n} (2K+1) \exp[-(1/kT)((\hbar^2/2I_i)K(K+1) + n\hbar\nu_1)] \right\}}$$

and

$$S = \frac{\hbar^6 M^2}{V^2 [m_1(m_2+m_3)]^{\frac{1}{2}}} \times \frac{\int_{\Omega_f} \cdots \int_Z \rho_{\Omega_f}(E_i, \mathbf{P}_i) |R|^2 \exp\{-(1/2kT)[(|\mathbf{P}_{12}|^2/(m_1+m_2)) + (|\mathbf{P}_3|^2/m_3)]\} d\mathbf{P}_{12} d\mathbf{P}_3}{\int_{-\infty}^{\infty} \cdots \int \exp\{-(1/2kT)[(|\mathbf{P}_{12}|^2/(m_1+m_2)) + (|\mathbf{P}_3|^2/m_3)]\} d\mathbf{P}_{12} d\mathbf{P}_3}.$$

In view of the discussion of Section V, the region  $Z$  in the numerator of  $S$  must be restricted to those values of  $\mathbf{P}_{12}$  and  $\mathbf{P}_3$  for which the final momenta are real. According to Eq. (25),  $Z$  is defined as the set of  $\mathbf{P}_{12}$  and  $\mathbf{P}_3$  for which

$$\left| \left( \frac{m_3}{m_1+m_2} \right)^{\frac{1}{2}} \mathbf{P}_{12} - \left( \frac{m_1+m_2}{m_3} \right)^{\frac{1}{2}} \mathbf{P}_3 \right|^2 \geq 2\gamma M.$$

For the case  $\gamma \leq 0$ , of course,  $Z$  represents the entire space of initial momenta. To evaluate  $S$ , we introduce the following notation.

$$\mathbf{x} = \left( \frac{m_3}{m_1+m_2} \right)^{\frac{1}{2}} \mathbf{P}_{12} - \left( \frac{m_1+m_2}{m_3} \right)^{\frac{1}{2}} \mathbf{P}_3, \quad x = |\mathbf{x}|;$$

$$\mathbf{y} = \left( \frac{m_2+m_3}{m_1} \right)^{\frac{1}{2}} \mathbf{P}_1 - \left( \frac{m_1}{m_2+m_3} \right)^{\frac{1}{2}} \mathbf{P}_{23}, \quad y = |\mathbf{y}|;$$

$u', v'$  (defined in Section V) are the polar angles of  $\mathbf{y}$  with respect to some arbitrary space fixed axes;  $u, v$  are the polar angles of  $\mathbf{x}$  with respect to the same axes;

$\sigma$  is the angle between  $\mathbf{x}$  and  $\mathbf{y}$ :

$$d\Omega_i = d(\cos u) dv;$$

$$d\Omega_f = d(\cos u') dv'.$$

The following relations are easily established from (7) and (25).

$$y^2 = x^2 - 2\gamma M,$$

$$\alpha = \frac{m_1}{M} \left( \frac{m_3}{m_1+m_2} \right)^{\frac{1}{2}} \mathbf{x} - \frac{(m_1(m_2+m_3))^{\frac{1}{2}}}{M} \mathbf{y},$$

$$\beta = \frac{(m_3(m_1+m_2))^{\frac{1}{2}}}{M} \mathbf{x} - \frac{m_3}{M} \left( \frac{m_1}{m_2+m_3} \right)^{\frac{1}{2}} \mathbf{y},$$

$$\frac{|\mathbf{P}_{12}|^2}{m_1+m_2} + \frac{|\mathbf{P}_3|^2}{m_3} = \frac{1}{M} [x^2 + |\mathbf{P}_{12} + \mathbf{P}_3|^2]. \quad (28)$$

<sup>6</sup> E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, New York, 1945), p. 145.



These results, together with (26), suggest that the integration over initial momenta be carried out in terms of the variables  $(\mathbf{P}_{12} + \mathbf{P}_3)$ ,  $x$ , and  $\Omega_i$ . With this change of variables

$$S = \frac{h^6 M^2}{V^2 [m_1(m_2 + m_3)]^{\frac{1}{2}}} \frac{\int_{\Omega_f} d\Omega_f \int_{(2\gamma M)^{\frac{1}{2}}}^{\infty} x^2 \rho_{\Omega_f}(E_i, \mathbf{P}_i) |R|^2 \exp[-x^2/(2MkT)] dx}{\int_{\Omega_i} d\Omega_i \int_0^{\infty} x^2 \exp[-x^2/(2MkT)] dx},$$

where it is understood that, in the integration on  $x$ , the lower limit  $(2\gamma M)^{\frac{1}{2}}$  is to be replaced by 0 when  $\gamma \leq 0$ . Using (26), we find that

$$S = \frac{1}{(2\pi MkT)^{\frac{1}{2}}} \int_{\Omega_f} d\Omega_f \int_{\Omega_i} d\Omega_i \times \int_{(2\gamma M)^{\frac{1}{2}}}^{\infty} x^2 (x^2 - 2\gamma M)^{\frac{1}{2}} |R|^2 \exp[-x^2/(2MkT)] dx.$$

We see from (19) and (28) that the dependence of the integrand upon  $\Omega_i$  and  $\Omega_f$  is due only to the appearance of  $\cos\sigma$  in the quantities  $|\alpha|$  and  $|\beta|$ . Since

$$\cos\sigma = \cos u \cos u' + \sin u \sin u' \cos(v - v'),$$

it is not difficult to show that

$$\int_{\Omega_f} d\Omega_f \int_{\Omega_i} F(\cos\sigma) d\Omega_i = 8\pi^2 \int_{-1}^1 F(\cos\sigma) d(\cos\sigma).$$

Hence

$$S = \frac{8\pi^2}{(2\pi MkT)^{\frac{1}{2}}} \int_{-1}^1 d(\cos\sigma) \times \int_{(2\gamma M)^{\frac{1}{2}}}^{\infty} x^2 (x^2 - 2\gamma M)^{\frac{1}{2}} |R|^2 \exp[-x^2/(2MkT)] dx.$$

Now, writing  $\alpha = |\alpha|$  and  $\beta = |\beta|$ , it follows from (28) that

$$(\beta^2/\mu_2) - (\alpha^2/\mu_1) = 2\gamma \quad (29)$$

so that  $R = R(\alpha, \beta)$  can be regarded as a function of either  $\alpha$  or  $\beta$  alone.

It is convenient to distinguish now between the cases  $\gamma \leq 0$  and  $\gamma > 0$ . For  $S$ , we shall write  $S^{(-)}$  or  $S^{(+)}$  according as  $\gamma \leq 0$  or  $\gamma > 0$ . For  $\gamma \leq 0$ , we have

$$S^{(-)} = \frac{8\pi^2}{(2\pi MkT)^{\frac{1}{2}}} \int_{-1}^1 d(\cos\sigma) \times \int_0^{\infty} x^2 (x^2 - 2\gamma M)^{\frac{1}{2}} |R(\alpha, \beta)|^2 \times \exp[-x^2/(2MkT)] dx,$$

where, according to (28),

$$\alpha = [B_1^2 x^2 + A_1^2 (x^2 - 2\gamma M) - 2A_1 B_1 x (x^2 - 2\gamma M)^{\frac{1}{2}} \cos\sigma]^{\frac{1}{2}},$$

$$A_1 = \frac{(m_1(m_2 + m_3))^{\frac{1}{2}}}{M}, \quad B_1 = \frac{m_1}{M} \left( \frac{m_3}{m_1 + m_2} \right)^{\frac{1}{2}}.$$

We carry out the integration with respect to the variables  $x$  and  $\alpha$ . The new volume element is

$$\frac{\alpha d\alpha dx}{A_1 B_1 x (x^2 - 2\gamma M)^{\frac{1}{2}}},$$

and, noting that  $B_1 x \leq A_1 (x^2 - 2\gamma M)^{\frac{1}{2}}$ , we obtain

$$S^{(-)} = \frac{8\pi^2}{A_1 B_1 (2\pi MkT)^{\frac{1}{2}}} \int_0^{\infty} x \exp[-x^2/(2MkT)] dx \times \int_{A_1(x^2 - 2\gamma M)^{\frac{1}{2}} - B_1 x}^{A_1(x^2 - 2\gamma M)^{\frac{1}{2}} + B_1 x} \alpha |R(\alpha, \beta)|^2 d\alpha.$$

Integrating first with respect to  $x$ , and using (28), we find

$$S^{(-)} = \frac{8\pi}{A_1 B_1 (2\pi MkT)^{\frac{1}{2}}} \times \int_{(-2\gamma\mu_1)^{\frac{1}{2}}}^{\infty} \alpha |R(\alpha, \beta)|^2 \sinh \left\{ \frac{MA_1 B_1 \alpha \beta}{kT \mu_1^{\frac{1}{2}} \mu_2^{\frac{1}{2}}} \right\} \times \exp \left\{ -\frac{M}{2kT} \left( \frac{A_1^2 \beta^2}{\mu_1 \mu_2} + \frac{B_1^2 \alpha^2}{\mu_1^2} \right) \right\} d\alpha. \quad (30a)$$

If we let

$$A_2 = \frac{m_3}{M} \left( \frac{m_1}{m_2 + m_3} \right)^{\frac{1}{2}}, \quad B_2 = \frac{(m_3(m_1 + m_2))^{\frac{1}{2}}}{M},$$

we obtain, in an analogous fashion,

$$S^{(+)} = \frac{8\pi e^{-\gamma/kT}}{A_1 B_1 (2\pi MkT)^{\frac{1}{2}}} \times \int_0^{\infty} \alpha |R(\alpha, \beta)|^2 \sinh \left\{ \frac{MA_2 B_2 \alpha \beta}{kT \mu_1^{\frac{1}{2}} \mu_2^{\frac{1}{2}}} \right\} \times \exp \left\{ -\frac{M}{2kT} \left( \frac{A_2^2 \beta^2}{\mu_2^2} + \frac{B_2^2 \alpha^2}{\mu_1 \mu_2} \right) \right\} d\alpha. \quad (30b)$$

To evaluate  $R(\alpha, \beta)$ , let

$$\epsilon_1 = \frac{\alpha}{\hbar(a_1)^{\frac{1}{2}}}, \quad \epsilon_2 = \frac{\beta}{\hbar(a_2)^{\frac{1}{2}}},$$

$$\delta_1 = \rho_1(a_1)^{\frac{1}{2}}, \quad \delta_2 = \rho_2(a_2)^{\frac{1}{2}}. \quad (31)$$

Then, in accordance with (11) and (19),

$$R(\alpha, \beta) = R_1(\alpha)R_2(\beta)$$

where

$$R_1(\alpha) = \frac{1}{2(2\pi)^{\frac{1}{2}}\delta_1\epsilon_1^{\frac{1}{2}}} \int_{-\infty}^{\infty} H_n(\xi) \\ \times \exp(-\xi^2/2)(\xi + \delta_1)^{\frac{1}{2}} J_{K+\frac{1}{2}}(\epsilon_1(\xi + \delta_1)) d\xi,$$

and

$$R_2(\beta) = \frac{1}{2(2\pi)^{\frac{1}{2}}\delta_2\epsilon_2^{\frac{1}{2}}} \int_{-\infty}^{\infty} (Y_0 + Y_1\eta^2) H_m(\eta) \\ \times \exp(-\eta^2/2)(\eta + \delta_2)^{\frac{1}{2}} J_{L+\frac{1}{2}}(\epsilon_2(\eta + \delta_2)) d\eta.$$

It is clear that  $R(\alpha, \beta)$  can be expressed as a simple combination of integrals of the type

$$G_{K,p} = \frac{1}{2(2\pi)^{\frac{1}{2}}\delta\epsilon^{\frac{1}{2}}} \int_{-\infty}^{\infty} (x + \delta)^{\frac{1}{2}} J_{K+\frac{1}{2}}(\epsilon(x + \delta)) x^p \\ \times \exp(-x^2/2) dx. \quad (32)$$

Approximations to  $G_{K,p}$  are obtained in Appendix II. For future reference, we note from Appendix II, that in the case  $m=0$ ,

$$R_2(\beta) = \frac{1}{2} Y_0 \frac{J_{L+\frac{1}{2}}(\epsilon_2\delta_2)}{(\epsilon_2\delta_2)^{\frac{1}{2}}} \\ \times \exp(-\epsilon_2^2/2) \left[ 1 - \frac{Y_1}{Y_0}(\epsilon_2^2 - 1) \right]. \quad (33)$$

With these results, and Eqs. (30a) and (30b), we see that, for a fixed set of  $m, n, K, L$ , the value of  $S$  may be obtained by numerical integration. Thus, the probability of a transition from a given initial state  $(n, K)$  to a given final state  $(m, L)$  can be calculated directly. The over-all reaction probability is then determined, in accordance with (27), by summing over all initial and final states.

For a typical reaction, values of  $K$  and  $L$  up to 10 or more must be considered, and it is clear that calculation of the reaction probability in this manner would be extremely tedious. Considerable simplification could be achieved by summing over one of the parameters  $K$  or  $L$ , but because of the dependence of  $\gamma$ , and hence, of the arguments of the Bessel functions, upon  $K$  and  $L$ , one could not expect, in general, to obtain closed forms for these

sums. For typical reactions, however, the dependence of  $\gamma$  upon  $K$  and  $L$  is not very strong. Referring to Eq. (24), the quantities  $\hbar^2/2I_1kT$  and  $\hbar^2/2I_2kT$  are very much less than unity, and we shall be able to approximate the sum over one of the parameters, say  $L$ , by regarding  $\gamma$  as independent of  $L$ . We carry out this sum over the final rotational states in the next section.

## VII. APPROXIMATION TO SUM OVER FINAL ROTATIONAL STATES

In summing over the final rotational states, we must distinguish between values of  $L$  for which  $\gamma \leq 0$  and for which  $\gamma > 0$ . From (24), we see that if  $K, m, n$ , are chosen so that  $\gamma_{L=0} > 0$ , then  $\gamma > 0$  for all  $L$ . If  $K, m, n$ , are chosen so that  $\gamma_{L=0} \leq 0$ , then there is an integer  $L_K$  such that  $\gamma \leq 0$  for  $L \leq L_K$  and  $\gamma > 0$  for  $L > L_K$ . Accordingly, if  $\sum^{(+)}$  and  $\sum^{(-)}$  denote, respectively, summation over values of  $K, m, n$ , for which  $\gamma_{L=0} > 0$  and  $\gamma_{L=0} \leq 0$ , we see from (27) that

$$\bar{P} = \sum_{K,m,n}^{(+)} W_{Knm} \sum_{L=0}^{\infty} (L + \frac{1}{2}) S^{(+)} \\ + \sum_{K,m,n}^{(-)} W_{Knm} \left[ \sum_{L=0}^{L_K} (L + \frac{1}{2}) S^{(-)} \right. \\ \left. + \sum_{L=L_K+1}^{\infty} (L + \frac{1}{2}) S^{(+)} \right]. \quad (34)$$

If we assume that the dependence of  $\gamma$  upon  $L$  is not very strong, then  $L_K$  is usually sufficiently large so that the second term of the last series may be neglected, and the upper limit of the first term taken as  $+\infty$ . If, for a particular choice of  $K, m, n$ , the quantity  $L_K$  is not large, then perhaps the best procedure is to evaluate the series term by term. It is only necessary, therefore, to consider the two sums

$$\sum_{L=0}^{\infty} (L + \frac{1}{2}) S^{(+)}, \quad \sum_{L=0}^{\infty} (L + \frac{1}{2}) S^{(-)}. \quad (35)$$

In what follows, we shall suppose that  $m=0$ . It will be clear how the approximations can be modified for larger values of  $m$ .

From (29) and (31), it follows that

$$\epsilon_2^2 = (2\gamma\hbar\nu_2) + (\alpha^2/\mu_1\hbar\nu_2), \quad (36)$$

and, using (33), Eq. (30b) becomes

$$S^{(+)} = \frac{2\pi Y_0^2 \exp[-(\gamma/kT)(1 + (2kT/\hbar\nu_2))]}{A_1 B_1 (2\pi M k T)^{\frac{1}{2}}} \\ \times \int_0^{\infty} \frac{J_{L+\frac{1}{2}}^2(\epsilon_2\delta_2)}{\epsilon_2\delta_2} \Psi(\alpha, \beta) \Theta_2(\alpha, \beta) d\alpha,$$

where

$$\Psi(\alpha, \beta) = \alpha R_1^2(\alpha) \times \exp[-\alpha^2/(\mu_1 h \nu_2)] \left[ 1 - \frac{Y_1}{Y_0} (\epsilon_2^2 - 1) \right]^2,$$

and

$$\Theta_j(\alpha, \beta) = \sinh \left\{ \frac{MA_j B_j \alpha \beta}{kT \mu_1^{\frac{1}{2}} \mu_2^{\frac{1}{2}}} \right\} \times \exp \left\{ -\frac{M}{2kT} \left( \frac{A_j^2 \beta^2}{\mu_2^2} + \frac{B_j^2 \alpha^2}{\mu_1 \mu_2} \right) \right\}, \quad j=1, 2.$$

Let  $c = \hbar^2/2I_f$ , so that  $c/kT \ll 1$ . We write

$$\begin{aligned} \bar{\gamma} &= \gamma - cL(L+1), \\ \bar{\beta} &= [\beta^2 - 2\mu_2 cL(L+1)]^{\frac{1}{2}}, \\ \bar{\epsilon}_2 &= \frac{\bar{\beta}}{h(a_2)^{\frac{1}{2}}}, \end{aligned}$$

so that  $\bar{\gamma}$ ,  $\bar{\beta}$  and  $\bar{\epsilon}_2$  are independent of  $L$ . Then

$$\Theta_2(\alpha, \beta) \approx \Theta_2(\alpha, \bar{\beta}) \times \exp[-(m_1 m_3 / M m_2)(cL(L+1)/kT)],$$

and we have

$$\begin{aligned} S^{(+)} &\approx \frac{2\pi Y_0^2 \exp[-(\bar{\gamma}/kT)(1 + (2kT/h\nu_2))]}{A_1 B_1 (2\pi M kT)^{\frac{1}{2}}} \\ &\times \int_0^\infty \Psi(\alpha, \bar{\beta}) \Theta_2(\alpha, \bar{\beta}) \\ &\times \left\{ \frac{J_{L+\frac{1}{2}}^2(\bar{\epsilon}_2 \delta_2)}{\bar{\epsilon}_2 \delta_2} \exp[-\lambda L(L+1)] \right\} d\alpha, \quad (37a) \end{aligned}$$

where

$$\lambda = \frac{c}{kT} \left[ 1 + \frac{m_1 m_3}{M m_2} + \frac{2kT}{h\nu_2} \right].$$

Similarly, we find

$$\begin{aligned} S^{(-)} &\approx \frac{2\pi Y_0^2 \exp(-2\bar{\gamma}/h\nu_2)}{A_1 B_1 (2\pi M kT)^{\frac{1}{2}}} \\ &\times \int_{(-2\bar{\gamma}\mu_1)^{\frac{1}{2}}}^\infty \Psi(\alpha, \bar{\beta}) \Theta_1 \left( \alpha \left( \frac{\mu_2}{\mu_1} \right)^{\frac{1}{2}}, \beta \left( \frac{\mu_2}{\mu_1} \right)^{\frac{1}{2}} \right) \\ &\times \left\{ \frac{J_{L+\frac{1}{2}}^2(\bar{\epsilon}_2 \delta_2)}{\bar{\epsilon}_2 \delta_2} \exp[-\lambda L(L+1)] \right\} d\alpha. \quad (37b) \end{aligned}$$

We see from (37a) and (37b) that, in order to evaluate the series (35), it will suffice to consider

the series

$$\sum_{L=0}^\infty (L+\frac{1}{2}) \frac{J_{L+\frac{1}{2}}^2(x)}{x} \exp[-\lambda L(L+1)]. \quad (38)$$

(From the results of Section VI, it follows that, for  $m > 0$ , we would encounter a linear combination of series similar to (38).)

The range of values of  $\alpha$  which yields the bulk of the contribution to (37a) and (37b) may be estimated roughly by consideration of the maximum value of the function  $\Theta_j(\alpha, \beta)$ . Using (29), we find that  $\Theta_j$  attains its maximum at

$$\alpha = A_j(2\bar{\gamma}\mu_1/(B_j^2 - A_j^2))^{\frac{1}{2}}$$

and, from (36), that this corresponds to

$$\bar{\epsilon}_2 \delta_2 = B_j \delta_2 \left( \frac{2\bar{\gamma}}{h\nu_2(B_j^2 - A_j^2)} \right)^{\frac{1}{2}} \geq \delta_2 \left( \frac{2|\bar{\gamma}|}{h\nu_2} \cdot \frac{m_1 m_3}{M m_2} \right)^{\frac{1}{2}}.$$

For typical reactions, this last quantity is found to be  $\gg 1$ , except for unusual cases in which  $\bar{\gamma}$  is very near zero. This suggests that we attempt an expansion of (38) in powers of  $x^{-1}$ .

Such an expansion is obtained in Appendix III. It is shown that

$$\begin{aligned} \sum_{L=0}^\infty (L+\frac{1}{2}) \frac{J_{L+\frac{1}{2}}^2(x)}{x} \exp[-\lambda L(L+1)] \\ \approx \frac{1}{2\pi x^2 \lambda} \left[ 1 + \frac{1}{2x^2 \lambda} \right], \quad (39) \end{aligned}$$

provided  $x^2 \lambda > 1$  (as is usually the case). If we combine (34), (37a), (37b) and (39), we arrive at a form for the reaction probability  $\bar{P}$  that is suitable for computational purposes.

The absolute rate of reaction is then given by

$$k_f' = \bar{P}/t.$$

## VIII. RESULTS AND DISCUSSION

### A. The Absolute Rate

We have made use of the foregoing results to calculate the absolute rate of the reaction:  $\text{H}_2 + \text{Br} \rightarrow \text{H} + \text{HBr}$  at 500°K.

The calculations were carried through separately for the ortho- and para-hydrogen. In order to take into account the fact that the initial molecule in this case is homonuclear, we have multiplied the calculated rate by two. The average rate was then obtained by treating hydrogen as a mixture of 25 percent para- and 75 percent ortho-hydrogen, although no substantial differences were obtained for the absolute rates of pure ortho- and pure para-hydrogen. Molecular constants used in the calculations were taken from the paper by Hulbert and

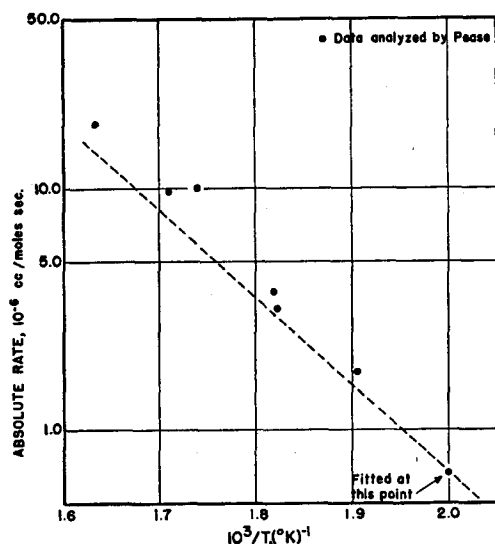


FIG. 2. Comparison of observed rates with extrapolation formula for the rate, calculated at 500°K.

Hirschfelder<sup>7</sup> and the compilation by Mayer and Mayer.<sup>8</sup>

In order to estimate the perturbation energy the quantity  $\mathcal{V}_{AC}^*$  was taken between the values corresponding to a linear configuration of  $A-B-C$  and that for which  $\mathcal{V}_{AC}$  is a minimum. The values for  $\mathcal{V}_{AC}^*$  were calculated from the paper by Hulbert and Hirschfelder. It was found that with  $\mathcal{V}_{AC}^*$  in this range of values, for a given value of  $\kappa$ , the absolute rate could change only by a factor of two.

The perturbation for which  $\mathcal{V}_{AC}^*$  was assigned the minimum value of  $\mathcal{V}_{AC}$  gave the largest value of the absolute rate, and was used in the detailed computations. The numerical value used for the perturbation was (see Eqs. (12a) and (12b)).

$$\mathcal{V}'(\text{kcal.}) = 270(\kappa - 0.67) + 3.81(1 - 1.5\kappa)\eta^2.$$

Because of the extreme sensitivity of the perturbation to the choice of  $\kappa$ , no value is given for the rate. Instead, Fig. 1 gives the dependence of the latter upon  $\kappa$ . It is seen that, with  $(1 - \kappa)$  ranging between 25–30 percent, agreement with experiment is obtained.

The result which has been obtained for the absolute rate is unsatisfactory because of the sensitivity of the result to the choice of  $\kappa$ . However, this is inherent in the Eyring-Polanyi expression used for the perturbation energy and indicates that a more accurate expression must be obtained for the potential energy of the interacting system before one can rely upon calculations of the absolute rate.

It may be noted that when  $\kappa = 0.67$ ,  $\mathcal{V}'$  vanishes. This point represents the change over from re-

pulsive interaction between the atom and the molecule to attractive interaction. It would seem reasonable to conclude that the latter region is not attained for, otherwise one should expect to find stable molecular species ( $\text{H}_2\text{Br}$ ). This emphasizes the inadequacy of the present approximation for the potential energy.

We have examined the effect of taking all  $\kappa$  equal (see Section III) as follows. The expressions used above were modified so that there was a  $\kappa_{\text{H}_2}$  and a  $\kappa_{\text{HBr}}$ . When the same approximations were made as for the case of equal  $\kappa$ 's, the rate was found not to depend strongly upon  $\kappa_{\text{H}_2}$ . Indeed, it was found that, as  $\kappa_{\text{H}_2}$  varies between zero and unity, the value of  $\kappa_{\text{HBr}}$  needed to give agreement with experiment changes only by ten percent. Thus, the quantity  $\kappa$  in Fig. 1 may be identified with  $\kappa_{\text{HBr}}$ .

### B. The Variation of Rate with Temperature

We have evaluated the quantity  $RT\partial \ln k'/\partial T$  at 500° K. We find that in the neighborhood of this temperature the absolute rate is given by

$$k_f' = C(T)T^{-1} \exp(-17.0/RT).$$

The function  $C(T)$  increases slightly with temperature. As indicated by this expression the "activation energy" is 17 kcal./mole. This may be compared with the value of 18.8 kcal./mole obtained by Pease<sup>9</sup> from an analysis of the data of Bodenstein and Lind and Bach, Bonhoeffer and Moelwyn-Hughes. From the rates of reaction of halogen atoms with hydrogen molecules, Morris and Pease<sup>10</sup> obtained a value of 17.7 kcal./mole.

In Fig. 2 we have compared the extrapolation formula obtained above with the results given by Pease<sup>9</sup> for the absolute rate. It is to be noted that because  $C(T)$  increases with temperature, the extrapolation formula is expected to be low in the high temperature region. Nevertheless, the agreement appears to be acceptable.

### C. Dependence of the Rate Upon the Initial State

Approximately 95 percent of the contribution to the rate comes from hydrogen molecules in the first excited vibrational state. The remainder is due almost exclusively to the hydrogen molecules in the ground vibrational state. The contribution from hydrogen molecules in all other vibrational states was estimated to be less than one percent. The dependence upon the vibrational and rotational state of the hydrogen molecule is presented in Fig. 3. The relative contribution to the rate was

<sup>7</sup> H. M. Hulbert and J. O. Hirschfelder, *J. Chem. Phys.* **9**, 61 (1941).

<sup>8</sup> J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), pp. 468–469.

<sup>9</sup> R. N. Pease, *Equilibrium and Kinetics of Gas Reactions* (Princeton University Press, Princeton, 1942), pp. 112–121.

<sup>10</sup> J. C. Morris and R. N. Pease, *J. Chem. Phys.* **3**, 796 (1935).

calculated separately on the basis of pure ortho- or para-hydrogen, and the results are presented in a form so that the sum of the contributions for the ortho- and the para-hydrogen are each normalized to unity. For transcribing these results to the equilibrium mixture obtainable at 500°K, the values associated with para-states must be multiplied by 1/4, while the values associated with the ortho states must be multiplied by 3/4.

It is interesting to note that about 40 percent of the contribution to the rate comes from hydrogen molecules in the first excited vibrational states having rotational quantum number  $K=4$ . In this state, the vibrational-rotational energy of the hydrogen molecule is nearly equal to the zero-point energy of the product hydrogen bromide molecule, so that nearly all initial and final translational states are accessible. In other words, in this particular case the condition of conservation of energy puts only a slight restriction on the number of translational states that are capable of participating in transitions. It would seem, therefore, that the most important contribution to the rate is associated with those discrete states (both initial and final) which differ but slightly in energy. However, this cannot be generalized to other reactions and perturbations unless the dependence of the matrix elements on the discrete states is examined in detail.

#### D. Distribution of Initially Formed Products

The present formulation permits one to calculate the probability of forming hydrogen bromide in various rotational and vibrational states. It appears that much less than one percent of the hydrogen bromide is formed in any excited vibrational state. Thus we have calculated the relative probability of forming a hydrogen bromide molecule in the various rotational states, and in the ground vibrational state. Specifically, we have calculated the probabilities on the basis of hydrogen molecules having vibrational quantum number unity and rotational quantum numbers 2, 3, 4. These hydrogen molecules make up approximately 75 percent of the rate.

As indicated in Fig. 4, the distribution of hydrogen bromide among the rotational states appears to be of the form

$$\begin{aligned} &(\text{number in states } L) \\ &\propto (2L+1)\exp[-(cL(L+1)/kT^*)] \end{aligned}$$

where, however,  $T^*$  is approximately one-half the temperature of the reactants. (The distributions obtained from each of the initial rotational states gave practically the same value of  $T^*$ .) Thus it appears that if one could obtain a pure rotation spectrum of the hydrogen bromide initially formed

from the reaction ( $\text{H}_2 + \text{Br} \rightarrow \text{HBr} + \text{H}$ ), an analysis of the line intensities would indicate a "temperature" of the hydrogen bromide of about 250°K compared to 500°K for the reactants. As pointed out to us by Professor Bryce L. Crawford, Jr., this distribution of rotational states may have some relation to the anomalous flame temperatures obtained from rotational spectra in flames.<sup>11</sup>

It may be noted that these results are suggested by Eqs. (34) and (37), which, if the integrals involved do not vary strongly with  $L$ , give the distribution formula

$$\begin{aligned} &(\text{number in states } L) \\ &\sim \text{const. } (2L+1)\exp[-\lambda L(L+1)], \end{aligned}$$

where

$$\begin{aligned} \lambda &= \frac{c}{kT} \left( 1 + \frac{m_1 m_3}{M m_2} + \frac{2kT}{h\nu_2} \right) \\ &\doteq 2.24(c/kT) \quad \text{at } T = 500^\circ\text{K}. \end{aligned}$$

From this distribution one would expect a value of 222°K for  $T^*$ .

#### IX. REMARKS

The results of this study show that the London-Eyring-Polanyi expression taken for the potential energy is a sensitive function of the coulombic

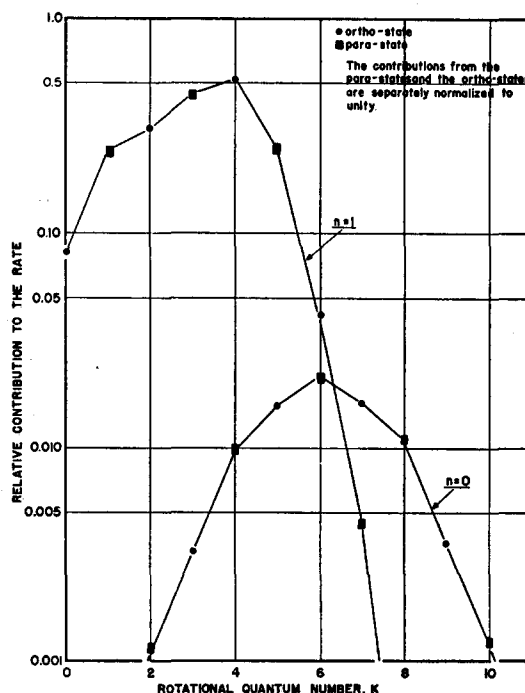


FIG. 3. Contribution to the rate by  $\text{H}_2$  molecules in various vibrational and rotational rates.

<sup>11</sup> See, for example, A. G. Gaydon and H. G. Wolfhard, Proc. Roy. Soc. A194, 169 (1948).

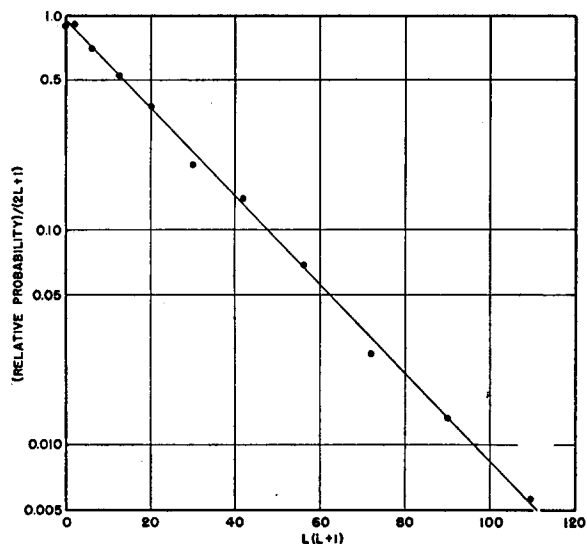


FIG. 4. Distribution of initially formed HBr among rotational states. The "temperature" calculated from the slope is 253°K.

energy fraction,  $(1-\kappa)$ . Consequently the absolute rate may not be calculated, from this approximation, without a great deal of uncertainty. Before any confidence can be had in computed values of the absolute rate, it seems clear that a more exact expression for the potential energy of interacting systems is needed.

However, the *relative* results given in Sections VIII-B, C, D are not affected appreciably by the value chosen for  $\kappa$ . This can be seen from Eqs. (11), (12a), and (12b); since  $Y_0 \gg Y_1$  (for the present case), the rate is essentially proportional to some function of  $\kappa$ . For the relative results mentioned, this function of  $\kappa$  no longer appears. It would seem, therefore, that to test the quantum mechanical formulation of chemical kinetics which has been given here, these relative results should be examined experimentally.

## X. ACKNOWLEDGMENTS

We wish to express our appreciation to Dr. M. Benedict for his encouragement and interest throughout this investigation. We are particularly indebted to Dr. A. M. Squires for the many stimulating suggestions which resulted from our discussions with him.

## APPENDIX I

### Evaluation of $Q_{KM}$

To evaluate  $Q_{KM}$  defined by Eq. (17), we note first that, by definition,  $\hat{i}$  is a unit vector along the internuclear axis of the initial molecule, so that  $\alpha \cdot \hat{i}$  represents the projection of  $\alpha$  upon that axis. Therefore

$$\exp[(i/\hbar)(\xi/(a_1)^{1/2} + \rho_1)\alpha \cdot \hat{i}(\theta, \varphi)] = \exp(i\delta_0 \cos \zeta),$$

where

$$\delta_0 = (|\alpha|/\hbar)(\xi/(a_1)^{1/2} + \rho_1),$$

and

$$\zeta \text{ is the angle between } \alpha \text{ and } \hat{i}.$$

From the addition theorem for Bessel functions,<sup>12</sup> we obtain

$$\exp(i\delta_0 \cos \zeta) = (2\pi/\delta_0)^{1/2} \sum_{n=0}^{\infty} (n + \frac{1}{2}) i^n J_{n+1/2}(\delta_0) P_n(\cos \zeta),$$

where  $J_n$  represents a Bessel function of the first kind and  $P_n$  a Legendre function of the first kind. From the addition theorem of spherical harmonics,<sup>6</sup> it can be shown that

$$P_n(\cos \zeta) = \frac{2}{2n+1} \sum_{m=-n}^n P_n^m(\cos \theta) P_n^m(\cos \omega_\alpha) \exp[im(\varphi - \tau_\alpha)],$$

where  $\theta, \varphi$  are the angle coordinates of  $\hat{i}$ ,  $\omega_\alpha, \tau_\alpha$  are the angle coordinates of  $\alpha$ , both referred to the same set of space fixed axes.

Substituting these results into Eq. (17) and carrying out the integrations, one obtains, by means of the orthogonality properties of the functions involved,

$$Q_{KM} = (2\pi/\delta_0)^{1/2} i^K J_{K+1/2}(\delta_0) P_K^{1/2}(\cos \omega_\alpha) \exp(iM\tau_\alpha).$$

## APPENDIX II

### Evaluation of $G_{K,p}$

In order to approximate  $G_{K,p}$  defined by Eq. (32), we note that, in the cases of interest,  $\delta \gg 1$ , so that, because of the factor  $\exp(-x^2/2)$ , the bulk of the contribution to the integrand comes from values of  $x$  considerably less than  $\delta$ . Writing<sup>13</sup>

$$(\epsilon(x+\delta))^{1/2} J_{K+1/2}(\epsilon(x+\delta)) = P(\epsilon(x+\delta)) \sin \epsilon(x+\delta) + Q(\epsilon(x+\delta)) \cos \epsilon(x+\delta),$$

where  $P(x)$  and  $Q(x)$  are polynomials in  $x^{-1}$ , we have, for these values of  $x$ ,

$$(\epsilon(x+\delta))^{1/2} J_{K+1/2}(\epsilon(x+\delta)) \approx P(\epsilon\delta) \sin \epsilon(x+\delta) + Q(\epsilon\delta) \cos \epsilon(x+\delta),$$

so that

$$G_{K,p} \approx \frac{1}{2(2\pi)^{1/2} \delta \epsilon} \left[ P(\epsilon\delta) \int_{-\infty}^{\infty} x^p \sin \epsilon(x+\delta) \exp(-x^2/2) dx + Q(\epsilon\delta) \int_{-\infty}^{\infty} x^p \cos \epsilon(x+\delta) \exp(-x^2/2) dx \right].$$

But, if we write

$$\Phi_1(x) = \frac{1}{(2\pi)^{1/2}} \exp(-x^2/2), \quad \Phi_p(x) = \frac{d^{p-1}}{dx^{p-1}} \Phi_1(x),$$

it is not difficult to show that

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\sin(\epsilon(x+\delta))}{\cos(\epsilon(x+\delta))} x^{2p} \exp(-x^2/2) dx = (-1)^p \Phi_{2p+1}(\epsilon) \frac{\sin(\epsilon\delta)}{\cos(\epsilon\delta)}.$$

Thus

$$G_{K,2p} \approx \frac{(-1)^p (\pi)^{1/2}}{\sqrt{2} \delta \epsilon} \Phi_{2p+1}(\epsilon) [P(\epsilon\delta) \sin \epsilon\delta + Q(\epsilon\delta) \cos \epsilon\delta] = (-1)^p \Phi_{2p+1}(\epsilon) \left( \frac{\pi}{2\epsilon\delta} \right)^{1/2} J_{K+1/2}(\epsilon\delta).$$

Estimates of  $G_{K,2p+1}$  may be obtained by integration by parts. For example, since

$$\frac{d}{dx} \{x^{1/2} J_{K+1/2}(x)\} = (K+1)x^{-1/2} J_{K+1/2}(x) - x^{1/2} J_{K+3/2}(x),$$

it follows that

$$G_{K,1} = \frac{K+1}{2(2\pi)^{1/2} \delta \epsilon} \int_{-\infty}^{\infty} \frac{J_{K+1/2}(\epsilon(x+\delta))}{(\epsilon(x+\delta))^{1/2}} \exp(-x^2/2) dx - \epsilon G_{K+1,0}.$$

<sup>12</sup> G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, London, 1945), p. 368.

<sup>13</sup> See reference 12, pp. 52-53.

The first integral here can be approximated by a procedure analogous to that used above, and we find

$$G_{K,1} \approx \Phi_1(\epsilon) \left[ \frac{K+1}{\delta} \left( \frac{\pi}{2\epsilon\delta} \right)^{\frac{1}{2}} J_{K+1}(\epsilon\delta) - \epsilon \left( \frac{\pi}{2\epsilon\delta} \right)^{\frac{1}{2}} J_{K+3/2}(\epsilon\delta) \right].$$

Approximations for  $G_{K,3}$ ,  $G_{K,5}$ ... are obtained in a similar manner.

### APPENDIX III

#### Evaluation of Series of Bessel Functions

We obtain here an asymptotic expansion of the series

$$\sum_{L=0}^{\infty} (L+\frac{1}{2}) \frac{J_{L+\frac{1}{2}}^2(x)}{x} \exp[-\lambda L(L+1)], \quad (38)$$

in powers of  $x^{-1}$ . We suppose  $x \gg 1$ ,  $\lambda \ll 1$  and  $x^2\lambda > 1$ . From the definition<sup>13</sup> of  $J_{L+\frac{1}{2}}(x)$ , it is easy to show that

$$\begin{aligned} J_{L+\frac{1}{2}}^2(x) &= \frac{2}{\pi x} \left[ \sin^2 \left( x - \frac{L\pi}{2} \right) \right. \\ &\quad + \frac{L(L+1)}{x} \sin(2x - L\pi) + \frac{L^2(L+1)^2}{4x^2} \cos^2 \left( x - \frac{L\pi}{2} \right) \\ &\quad \left. - \frac{(L+2)(L+1)L(L-1)}{4x^2} \sin^2 \left( x - \frac{L\pi}{2} \right) + O(x^{-3}) \right], \end{aligned}$$

so that, if we let

$$\begin{aligned} Q' &= \sum_{L \text{ even}} (L+\frac{1}{2}) \exp[-\lambda L(L+1)], \\ Q'' &= \sum_{L \text{ odd}} (L+\frac{1}{2}) \exp[-\lambda L(L+1)], \end{aligned}$$

we have

$$\begin{aligned} &\sum_{L=0}^{\infty} (L+\frac{1}{2}) \frac{J_{L+\frac{1}{2}}^2(x)}{x} \exp[-\lambda L(L+1)] \\ &= \frac{2}{\pi x^2} \left[ Q' \sin^2 x + Q'' \cos^2 x + \frac{\sin 2x}{x} \left( \frac{dQ'}{d\lambda} - \frac{dQ''}{d\lambda} \right) \right. \\ &\quad + \frac{1}{4x^2} \left\{ \left( \frac{d^2 Q'}{d\lambda^2} - \frac{d^2 Q''}{d\lambda^2} \right) \cos 2x - 2 \sin^2 x \frac{dQ'}{d\lambda} \right. \\ &\quad \left. \left. - 2 \cos^2 x \frac{dQ''}{d\lambda} \right\} + O(x^{-3}) \right]. \end{aligned}$$

Now, for small  $\lambda$

$$Q' \approx Q'' \approx \frac{1}{2} \sum_{L=0}^{\infty} (L+\frac{1}{2}) \exp[-\lambda L(L+1)] \approx \frac{1}{4\lambda},$$

and

$$\frac{dQ'}{d\lambda} \approx \frac{dQ''}{d\lambda} \approx -\frac{1}{4\lambda^2}, \quad \frac{d^2 Q'}{d\lambda^2} \approx \frac{d^2 Q''}{d\lambda^2} \approx \frac{1}{2\lambda^3},$$

so that

$$\sum_{L=0}^{\infty} (L+\frac{1}{2}) \frac{J_{L+\frac{1}{2}}^2(x)}{x} \exp[-\lambda L(L+1)] \approx \frac{1}{2\pi x^2 \lambda} \left[ 1 + \frac{1}{2x^2 \lambda} \right].$$

Higher order terms may be obtained, if necessary, by the same procedure.