Quantum-Mechanical Considerations of Chemical Reaction Rates. II. The Transmission through Curved Reaction Path

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Previous quantum-mechanical treatments[1-5] of chemical reaction rates deal principally with the behavior of the wave which represents the reacting system, passing from the region of the reactant to that of the resultant on the potential energy surface of reaction. These treatments also may be classed in two ways according to whether their objects are the transmission of the wave through the potential energy barrier[1-4] or through the curve or bend of the reaction path[5], for both the barrier and the bend are the important characteristics of the reaction path on the potential energy surface. Much knowledge of the microscopic feature of reaction rates, was obtained from these studies, but all these results were derived by the use of highly idealized models of potential, for example, one-dimensional square barrier or a path with a perpendicular turn, etc., to avoid mathematical difficulties.

Therefore, it is necessary to examine which of the conclusions correspond to the real behavior of reaction or are due merely to the used model itself.

For the purpose of considering the problem by the use of the more plausible potential models than those used before, Fueki and the present author have recently treated the transmission through the two-dimensional smooth barrier with a parabolic section and have made clear the properties of the quantum-mechanical correction which is necessary for the ordinary estimation of rate by the absolute reaction rate theory[6].

In this paper, another important problem, the transmission through the smoothly curved path with reasonable vibrational potential section is discussed in general and the extent of reflection and transmission is computed for some reaction examples. Then the inspection stated above is made comparing the present results with that of Hulburt and Hirschfelder's work[5] which was previously the first and only detailed one for the effect of the curved path. Also a consideration is made for their predictions of null transmission for the system with particular values of energy and of the availability of this effect for the isotopic separation.

Theoretical

Now we take, as a typical example of reaction, an elementary displacement reaction between atom A and molecule BC, A+BC→AB+C. The general feature of the potential energy surface for linear configuration is as shown in Fig. 1.

In order to discuss the transmission through the bend, we do not take the potential barrier into consideration and use a simplified surface and coordinate system shown in Fig. 2 hereafter.

We assume, as shown in Fig. 2, that the equi-potential lines are parallel with y and y' axes in regions I and II respectvely and that their radii at the bending part are constant. The dotted line shows the reaction path of radius r_e in region II, which traces minima in the direction of x, r or x' in the respective region.

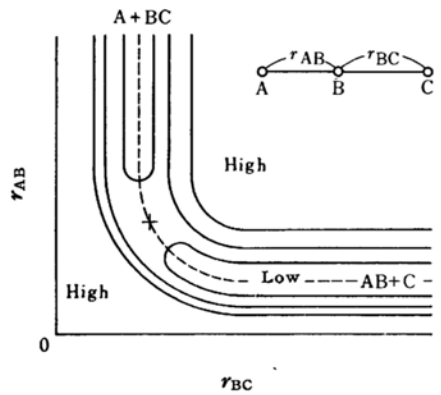

Fig. 1. Potential energy surface of reaction A+BC→AB+C.

1) J. O. Hirschfelder and E. Wigner, *J. Chem. Phys.*, **7**, 616 (1939).
2) E. Wigner, *Z. physik. Chem.*, **B19**, 203 (1932).
3) R. P. Bell, *Proc. Roy. Soc.*, **A139**, 466 (1933).
4) F. A. Matsen, *J. Chem. Phys.*, **22**, 165 (1954).
5) H. M. Hulburt and J. O. Hirschfelder, ibid., **11**, 276 (1943).
6) Paper I of this series: I. Yasumori and K. Fueki, This Bulletin, **29**, 1 (1956).

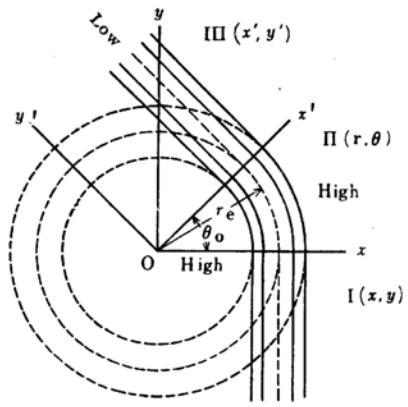

Fig. 2. Coordinate system of curved reaction path.

The wave equation to be satisfied by the system is

$$\nabla^2\Psi+\frac{8\pi^2\mu}{h^2}(E-V)\Psi=0 \tag{1}$$

where μ is the reduced mass of the system. According to the assumed form of potential V, the wave equation is separable with respect to the variables (x,y), (r,θ) and (x',y') in the regions I, II and III, respectively.

Now let us consider an incident wave of unit amplitude in region I, which expresses the state of reactant and comes from $y<0$ to the boundary $y=0$, being partly reflected at the boundary and partly transmitted through the bend.

Now, the wave functions which express the states of the system in each region are given as follows: In region I,

$$\Psi^{\mathrm{I}}=\phi_\kappa{}^{\mathrm{I}}(x)\cdot\exp\left(\frac{2\pi i}{h}p_\kappa\cdot y\right)+\sum_\lambda B_{\kappa\lambda}\phi_\lambda{}^{\mathrm{I}}(x)\cdot\exp\left(-\frac{2\pi i}{h}p_\lambda\cdot y\right) \tag{2}$$

where the first term represents the incident wave and the second the reflected waves. $\phi_\kappa{}^{\mathrm{I}}(x)$ is the eigenfunction of vibrational motion of the system in κ-th state and $\exp[(2\pi i/h)\cdot p_\kappa\cdot y]$ represents the eigenfunction of translational motion with the momentum p_κ. The total energy of the system, E, is equal to the sum of those of each motion, E_{vib} and E_{trans}. $B_{\kappa\lambda}$ is the coefficient of reflected wave referring to the transition between states, κ and λ.

In a similar way, the wave functions in regions II and III are expressed as

$$\Psi^{\mathrm{II}}=\sum_k[C_{\kappa k}\cdot\phi_k{}^{\mathrm{II}}(r)\cdot\exp(im_k\theta)+D_{\kappa k}\cdot\phi_k{}^{\mathrm{II}}(r)\cdot\exp(-im_k\theta)] \tag{3}$$

and

$$\Psi^{\mathrm{III}}=\sum_{\kappa'}F_{\kappa\kappa'}\phi_{\kappa'}{}^{\mathrm{III}}(x')\cdot\exp\left(\frac{2\pi i}{h}p_{\kappa'}\cdot y'\right) \tag{4}$$

where m_k is a constant and we may define a new constant q_k by the equation

$$m_k=\frac{2\pi}{h}\cdot q_k\cdot r_e \tag{5}$$

The coefficients of the transmitted waves, $C_{\kappa k}$ or $D_{\kappa k}$, are defined corresponding to the forward or backward translational motion in k-th state of region II and that of the transmitted wave, $F_{\kappa\kappa'}$ referring to κ'-th state in region III. We assume that all the wave functions for the vibrational motion, $\phi_\kappa{}^{\mathrm{I}}(x)$, $\phi_{\kappa'}{}^{\mathrm{III}}(x')$ and $\phi_k{}^{\mathrm{II}}(r)$ are normalized to unity.

Thus the following equations are readily obtained by the usual procedure of substituting the wave functions into the boundary conditions,

$$\Psi^{\mathrm{I}}=\Psi^{\mathrm{II}}\ \text{and}\ \frac{\partial\Psi^{\mathrm{I}}}{\partial y}=\frac{\partial\Psi^{\mathrm{II}}}{\partial y}=\frac{1}{r}\left(\frac{\partial\Psi^{\mathrm{II}}}{\partial\theta}\right)_{\theta=0} \tag{a), (b)}$$

at $y=0$ and

$$\Psi^{\mathrm{II}}=\Psi^{\mathrm{III}}\ \text{and}\ \frac{\partial\Psi^{\mathrm{III}}}{\partial y'}=\frac{\partial\Psi^{\mathrm{II}}}{\partial y'}=\frac{1}{r}\left(\frac{\partial\Psi^{\mathrm{II}}}{\partial\theta}\right)_{\theta=\theta_0} \tag{c), (d)}$$

at $y'=0$; we have

$$\delta_{\kappa\lambda}+B_{\kappa\lambda}=\sum_k(C_{\kappa k}+D_{\kappa k})u_{k\lambda} \tag{6}$$

$$\delta_{\kappa\lambda}p_\kappa-B_{\kappa\lambda}p_\lambda=\sum_k(C_{\kappa k}-D_{\kappa k})\cdot q_k\cdot v_{k\lambda} \tag{7}$$

$$\sum_k[C_{\kappa k}\cdot\exp(im_k\theta_0)+D_{\kappa k}\times\exp(-im_k\theta_0)]u'_{k\kappa'}=F_{\kappa\kappa'} \tag{8}$$

and

$$\sum[C_{\kappa k}\cdot\exp(im_k\theta_0)-D_{\kappa k}\times\exp(-im_k\theta_0)]\cdot q_k\cdot v'_{k\kappa'}=F_{\kappa\kappa'}\cdot p'_{\kappa'} \tag{9}$$

The expansion coefficients $u_{k\lambda}$'s and $v_{k\lambda}$'s are defined by the equations

$$[\phi_k{}^{\mathrm{II}}(r)]_{\theta=0}=\phi_k{}^{\mathrm{II}}(x)=\sum_\lambda u_{k\lambda}\cdot\phi_\lambda{}^{\mathrm{I}}(x) \tag{10}$$

and

$$\left[\frac{r_e}{r}\cdot\phi_k{}^{\mathrm{II}}(r)\right]_{\theta=0}=\frac{r_e}{x}\cdot\phi_k{}^{\mathrm{II}}(x)=\sum_\lambda v_{\kappa\lambda}\cdot\phi_\lambda{}^{\mathrm{I}}(x) \tag{11}$$

Similarly the coefficients $u'_{k\lambda'}$'s and $v'_{k\lambda'}$'s are also defined by the equations

$$[\phi_k{}^{\mathrm{II}}(r)]_{\theta=\theta_0}=\phi_k{}^{\mathrm{II}}(x')=\sum_{\lambda'}u'_{k\kappa'}\cdot\phi_{\lambda'}{}^{\mathrm{III}}(x') \tag{12}$$

and

$$\left[\frac{r_e}{r}\cdot\phi_k{}^{\mathrm{II}}(r)\right]_{\theta=\theta_0}=\frac{r_e}{x'}\cdot\phi_k{}^{\mathrm{II}}(x')$$

$$=\sum_{\lambda'} v'_{k\lambda'} \cdot \phi_{\lambda'}^{\mathrm{III}}(x') \qquad (13)$$

Eqs. 6—9 are expressed by the use of the matrix form as

$$1+B=(C+D)u \qquad (6')$$

$$p-Bp=(C-D)qv \qquad (7')$$

$$(CW+DW^*)u'=F \qquad (8')$$

and $$(CW-DW^*)qv'=Fp' \qquad (9')$$

where W and its complex conjugate W^* are diagonal matrices whose elements are $\exp(im_k\theta_0)$'s and $\exp(-im_k\theta_0)$'s, respectively. Accordingly the coefficient matrix of the reflected waves, B, and that of the transmitted waves, F, are formally derived as follows: We have

$$B=-(NWM'+MW^*N') \times (MWM'+NW^*N')^{-1} \qquad (14)$$

and $$F=1/2\cdot[B(MW+NW^*)+(NW+MW^*)]\cdot u' \qquad (15)$$

where

$$M=u^{-1}-pv^{-1}q^{-1} \qquad (16)$$

$$N=u^{-1}+pv^{-1}q^{-1} \qquad (17)$$

$$M'=u'-qv'p'^{-1} \qquad (18)$$

and $$N'=u'+qv'p'^{-1} \qquad (19)$$

By the use of the expressions of B and F, the reflection and transmission coefficients $\rho_{\kappa\lambda}$ and $\kappa_{\kappa\kappa'}$ are given by

$$\rho_{\kappa\lambda}=|B_{\kappa\lambda}|^2\cdot p_\lambda/p_\kappa \qquad (20)$$

and $$\kappa_{\kappa\kappa'}=|F_{\kappa\kappa'}|^2\cdot p_{\kappa'}/p_\kappa \qquad (21)$$

Furthermore, the total reflection and transmission coefficients from a definite initial κ-th state, ρ_κ, and κ_κ, are defined as

$$\rho_\kappa=\sum_\lambda \rho_{\kappa\lambda} \text{ and } \kappa_\kappa=\sum_{\kappa'}\kappa_{\kappa\kappa'} \qquad (22),\ (23)$$

κ_κ may be estimated from the value of ρ_κ by the use of the following equation,

$$\kappa_\kappa=1-\rho_\kappa \qquad (24)$$

For the simple case with a single boundary $y=0$, taking

$$D_{\kappa k}=0 \text{ and } F_{\kappa\kappa'}=0$$

the equations to be solved become

$$1+B=Cu \text{ and } p-Bp=Cqv. \qquad (25),\ (26)$$

Then the formal solutions of B and C are

$$B=(S-1)\cdot(S+1)^{-1} \qquad (27)$$

and $$C=2S(S+1)^{-1}\cdot u^{-1} \qquad (28)$$

where the matrix S has the form of

$$S=pv^{-1}q^{-1}u \qquad (29)$$

Therefore, the transmission coefficient, $\kappa_{\kappa k}$ is given by

$$\kappa_{\kappa k}=|C_{\kappa k}|^2\cdot q_k/p_\kappa \qquad (30)$$

in this case.

It is very difficult to obtain explicitly the rigorous form of the coefficients $B_{\kappa\lambda}$, $F_{\kappa\kappa'}$ and $C_{\kappa k}$ for general cases. We, therefore, confine ourselves to the simple case where the radius of the path, r_e, is much larger than the classical amplitude of vibration, $\rho_{\max}$,

$$r_e \ll \rho_{\max}$$

The approximate expressions of the coefficients in this case are given in Appendix I.

Vibrational Wave Function and Computation of the Coefficients

Now we treat the case in which the section of the channel is parabolic and the vibrational motion is simple harmonic. When we put, as the explicit form of vibrational potential,

$$V=2\pi^2\mu\nu_0^2x^2 \qquad (31)$$

the normalized vibrational eigenfunction with the quantum number κ in region I is

$$\phi_\kappa^{\mathrm{I}}(x)=N_\kappa\cdot\exp\left(-\frac{\alpha}{2}\rho^2\right)H_\kappa(\sqrt{\alpha}\cdot\rho) \qquad (32)$$

where

$$\rho=x-r_e \quad \text{and} \quad \alpha=4\pi^2\mu\nu_0/h \qquad (33)$$

$N_\kappa=[(\alpha/\pi)^{1/2}/2^\kappa\cdot\kappa!]^{1/2}$ is a normalization factor, $H_\kappa(\sqrt{\alpha}\cdot\rho)$ the κ-th Hermite polynomial and ν_0 the fundamental frequency of vibration. The total energy of the system in region I is

$$E=E_{\mathrm{vib}}+E_{\mathrm{trans}}=h\nu_0(\kappa+1/2)+(1/2\mu)p_\kappa^2 \qquad (34)$$

The eigenfunction of κ'-th state in region III is readily obtained by replacing κ and x in the above expressions with κ' and x' respectively.

The radial function $\phi_k^{\mathrm{II}}(r)$ in region II is obtained in the same way as the well-known treatment of the vibrational and rotational motions of diatomic molecule[7], since it is related to the circular potential shown in Fig. 2.

Therefore, under the condition $r_e \gg \rho_{\max}$, an approximate form of $\phi_k^{\mathrm{II}}(r)$ is given by

$$\phi_k^{\mathrm{II}}(r)=\frac{n}{r^{1/2}}\cdot N_k\cdot\exp\left(-\frac{\alpha'}{2}\zeta^2\right)\cdot H_k(\sqrt{\alpha'}\cdot\zeta) \qquad (35)$$

where

$$n\simeq[r_e(1+\beta)]^{1/2}\Big/\left[1+\frac{(2k+1)}{2\alpha r_e^2(1+\beta)^2}\right]^{1/2} \qquad (36)$$

7) L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics", McGraw-Hill Book Co., Inc., New York (1935), p. 298.

$$\zeta = \rho - \beta r_e \tag{37}$$

$$\beta = \xi^2/(1+3\xi^2) \tag{38}$$

$$\nu' = \nu_0(1+3\xi^2)^{1/2} \tag{39}$$

$$\xi = q_k/2\pi\mu r_e\nu_0 \tag{40}$$

α' is obtained by replacing ν_0 in α, Eq. 33, with ν' and N_k by replacing κ and α in N_κ with k and α', respectively.

The total energy in this region is described as

$$E \simeq \hbar\nu'(k+1/2) + (1/2\mu)(1-\beta)q_k^2 \tag{41}$$

The matrix elements of u and v are calculated by Eqs. 32 and 35 as shown in Appendix II.

The above consideration is also applicable, in principle, to the potential with Morse function-type section, but the formulation will be quite tedious.

Few potential energy surfaces with considerable accuracy have been constructed except for the ortho-para hydrogen conversion reaction, $H+H_2 \rightarrow H_2+H$[8,9]. Therefore, we performed the computation of the reflection and transmission coefficients for the potential surfaces which have a similar fearture to that of this reaction except that the barrier is neglected.

The constants used in the computation are

$$\hbar\nu_0 = 12.56 \text{ kcal./mol.}$$

$$\mu = (2/3)\cdot m_H = 1.1156\times10^{-24} \text{ g.}$$

$$\theta_0 = 2\pi/3$$

and $r_e = 1.0$ and 0.5 Å

These values of r_e scarcely satisfy the condition $r_e \gg \rho_{max}$, since the classical amplitudes of vibrational motion for the ground and the first excited levels are 0.09 and 0.15Å, respectively. Calculations were performed for the range of the total energy $E < \hbar\nu_0(2+1/2) = 31.4$ kcal./mol. The obtained values of coefficients are shown in Figs. 3 and 4.

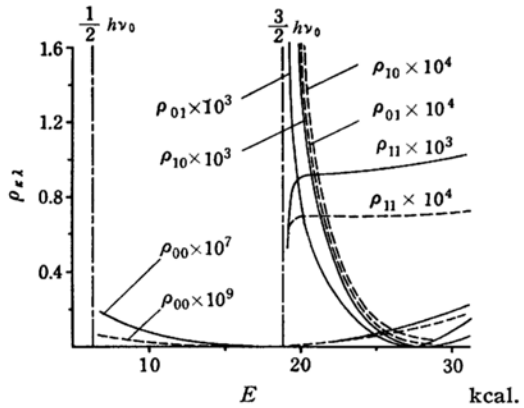

Fig. 3. Reflection coefficients for single boundary.
—— $r_e = 0.5$Å, ---- $r_e = 1.0$Å

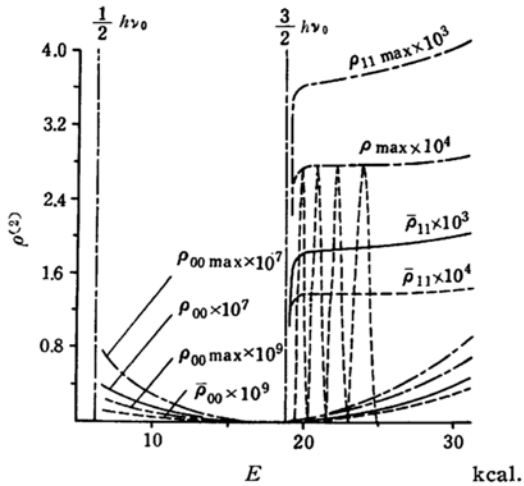

Fig. 4. Reflection coefficients for two boundaries.
—— $r_e = 0.5$Å, ---- $r_e = 1.0$Å, $\theta_0 = 2/3\cdot\pi$

Discussion

The present results agree, in many points, with those of Hulburt and Hirschfelder's in which the potential surface of square-well channel with 90° turn is used, but there are some noticeable differences between them.

That the reflection and transmission coefficients $\rho_{\kappa\lambda}$ and $\kappa_{\kappa\lambda}$ are not zero for $\kappa \neq \lambda$, shows the occurrence of the cross transition between the different vibrational states and also verifies their prediction about this occurrence obtained from the consideration of the classical motion of a particle in smoothly curved channel[10].

Apart from their absolute magnitude, the general properties of the coefficients resemble the results of Hulburt et al. for the case with vibrational transition.

In our case of single boundary with which their results include nothing to be compared, $\rho_{\kappa\kappa}$'s vary slightly with the increase of the translational energy, while $\rho_{\kappa\lambda}$'s, which rise where the translational energy is just equal to $\kappa\hbar\nu_0$ $(\kappa > \lambda)$ or $\lambda\hbar\nu_0$ $(\lambda > \kappa)$, fall rapidly and then increase

8) J. O. Hirschfelder, N. Rosen and H. Eyring, *J. Chem. Phys.*, 4, 121 (1936).
9) J. O. Hirschfelder, H. Eyring and B. Topley, ibid., 4, 173 (1936).
10) Ref. 5, p. 280.

gradually as the energy increases. In general, $\rho_{\varepsilon\lambda}$'s are much larger than $\rho_{\varepsilon\varepsilon}$'s in the available range of energy. For the case of two boundaries, the reflection coefficients are oscillating function of energy as shown in Fig. 4. This property is readily seen from the expressions of $B_{\varepsilon\lambda}$'s in Appendix I and those of ρ's, Eq. 20: By the introduction of such approximations as $(v_0^{-1}\cdot u_0)p \simeq q$, etc., the resultant forms are

$$\rho_{\varepsilon\varepsilon} \simeq 4\rho^{(1)}_{\varepsilon\varepsilon} \sin^2 m_\varepsilon\theta_0 \quad (42)$$

and $$\rho_{\varepsilon\lambda} \simeq 4\rho^{(1)}_{\varepsilon\lambda} \sin^2\{(m_\varepsilon + m_\lambda)/2\cdot\theta_0\} \quad (43)$$

where $\rho^{(1)}$'s represent those of single boundary under the same condition. The angle of bending, θ_0, which is related to the masses of component species, m_A, m_B and m_C, by the equation[11]

$$\sin(\theta_0 - \pi/2) = [m_A m_C/(m_A+m_B)(m_B+m_C)]^{1/2}$$

takes value which is between $\pi/2$ and π. A larger value of θ_0 makes the period of oscillation shorter (Fig. 5).

They also found such an oscillating property of coefficient as stated above and regarded it as an essential one for the transmission of waves through a bend. The present author presumes, however, that the property is partly of artificial nature being due to the form of potential models which have two discontinuous boundaries and is partly of real nature relating to the efficiency of energy transfer between the translational and vibrational motions, by the considerations given below.

The reasons why the form of potential model is responsible are as follows:

(a) Whatever the transmission to be estimated is for a bend or a barrier, all the reflection and transmission coefficients obtained change monotonously with energy in the case of smooth potential without any boundary[3,6], or even in those of single boundary[1], while they always oscillate in the cases of two boundaries[1,5].

(b) From the present result with two boundaries as shown in Fig. 4, it is found that the coefficients which are averaged over each period of oscillation[12] are about twice as large as those of a single boundary under the same condition. This property is based, perhaps, on the fact that the coefficients are the functions of amplitude of the standing waves which exist between boundaries and the amplitude of a wave with a definite phase varies periodically with respect to the momentum q and θ_0 at one of the boundaries. Therefore, when we take the average for each period of oscillation, which corresponds to superposition of all waves with any phase, the results seem to give good approximation for the actual behavior[13]. It goes without saying that such a property as stated above can not be expected in a real case, since the potential energy surface of reaction would be continuous everywhere considering the nature of valence force.

In the next place, their result that the oscillating transmission coefficients get zero values when the energy of translation is just equal to several energy units of quantized motion which is perpendicular to the direction of the above motion, is explained as the complete transfer of translational energy to the vibrational one. This property is also seen from the present result that the value of ρ_{01} rises steeply as the translational energy approaches to $h\nu_0$.

It seems that the speciality of the square-well channel with 90° turn used by them comprises incidentally these effects of real and of virtual: The wave functions which express the translational and vibrational motions are of similar form and their eigenvalues in the bending part are identical to each other.

From these considerations, it will be concluded that the total transmission coefficients κ_ε's decrease stepwise with the increase of energy on account of the entry of reflections in which the higher vibrational states are concerned. This tendency also agrees with that which Hulburt et al. pointed out previously.

Subsequently, the effect of the curvature is examined. A larger curvature (smaller radius) brings about the increase of reflection in both the cases with and without the vibrational transition (Figs. 3 and 4). Because of the smallness of net reflection, however, almost all systems pass through the bend, preserving initial vibration quanta. This persistency of vibrational state was also found for the transmission through the barrier which was treated in

11) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill Book Co., Inc., New York (1941), p. 102.

12) Since $\frac{1}{\pi}\int_0^\pi \sin^2 x dx = 1/2$, the averaged value of $\rho_{\varepsilon\varepsilon}$ in Eq. 43, $\bar{\rho}_{\varepsilon\varepsilon}$, is expressed by $\bar{\rho}_{\varepsilon\varepsilon} \simeq 2\rho_{\varepsilon\varepsilon}^{(1)}$, where $\rho_{\varepsilon\varepsilon}^{(1)}$ is assumed to be nearly constant in each period. Other coefficients are also treated analogously.

13) A similar situation is held in the case of Ref. 1, p. 621, in which the transmission through an energy barrier was treated.

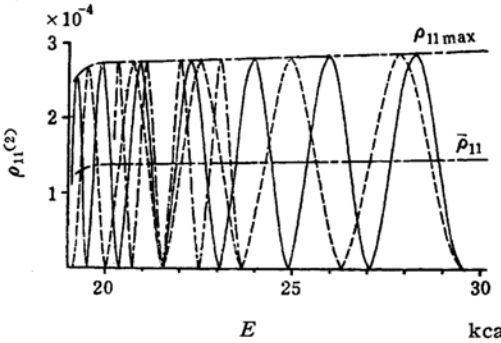

Fig. 5. Variation of $\rho_{11}^{(2)}$ with increase of bending angle θ_0.
r_e=1.0Å,
---- $\theta_0=\pi/2$, —— $\theta_0=2\pi/3$, —·—· $\theta_0=\pi$

Paper I of this series[14]. The case of Hulburt and Hirschfelder's, in which rather large decrease of transmission was estimated, corresponds to that of extremely small radius $r_e=\rho_{max}$ in our case.

It is expected that the transmission coefficient becomes different for the system including isotopes, since the resultant μ changes its magnitude for the same value of energy. This effect was also pointed out by them and their result of oscillating coefficient with perfect reflection made them expect its availability for the isotopic separation. Since, however, the difference between reflections for isotopic reactions is also very small, the transmission through the bend seems not to be effective for the process.

As a quantum-mechanical correction necessary for the rate-estimation by the usual method, the overall transmission coefficient κ_{bend} is defined by[6]

$$\kappa_{bend}=\sum_{\varepsilon} e^{-\frac{E_{vib}}{kT}}\cdot\int_0^{\infty}\kappa_{\varepsilon}\cdot e^{-\frac{p_{\varepsilon}^2}{2\mu kT}}\cdot p_{\varepsilon}\,dp_{\varepsilon}$$
$$\times\left[\sum_{\varepsilon} e^{-\frac{E_{vib}}{kT}}\cdot\int_0^{\infty} e^{-\frac{p_{\varepsilon}^2}{2\mu kT}}\cdot p_{\varepsilon}\,dp\right]^{-1}$$
$$=1-(\mu kT)^{-1}\cdot(1-e^{-\frac{h\nu_0}{kT}})$$
$$\times\left[\sum_{\varepsilon=0} e^{-\frac{\varepsilon h\nu_0}{kT}}\cdot\int_0^{\infty}\rho_{\varepsilon}e^{-\frac{p_{\varepsilon}^2}{2\mu kT}}\cdot p_{\varepsilon}\,dp_{\varepsilon}\right] \quad (44)$$

Since the individual κ_{ε}'s are nearly equal to unity, the resultant κ_{bend} is also close to unity and gradually decreases as the temperature becomes higher. The values,

TABLE I. VALUES OF $(1-\kappa_{bend})$[15]

Temp. °K	300	500	1000	2000
r_e=0.5 Å	3.0×10^{-8}	1.3×10^{-6}	3.8×10^{-4}	3.4×10^{-3}
r_e=1.0 Å	2.0×10^{-11}	7.3×10^{-7}	2.3×10^{-4}	2.8×10^{-3}

$1-\kappa_{bend}$, for the hydrogen atom-molecule reaction, for example, are shown in Table I.

Finally, as concerns the reacting system which includes heavier species than hydrogen, it is very difficult to presume the exact behavior of the transmitting waves, because the factors μ, r_e, ν_0 and θ_0 change markedly for respective cases. In general, increased μ and lowered ν_0 provide an increase of the reflection which is canceled to some extent by an increased r_e. However, the deviation of the total transmission from unity will be very small after all, since the fact that the de Broglie wavelength corresponding to the translational motion becomes shorter than that of hydrogen atom-molecule reaction (1.8Å at 300°K) makes the classical consideration of motion more valid.

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Appendix I. Approximate Formulae of the Coefficients $B_{\varepsilon\lambda}$, $C_{\varepsilon k}$ and $F_{\varepsilon\varepsilon'}$

Under the condition $r_e \gg \rho_{max}$, it is expected that the vibrational eigenfunction in region II, $\psi_k^{II}(r)$ becomes close to the function $\psi_{\varepsilon}^{I}(x)$ with $\varepsilon=k$ in its form at the boundary between regions I and II and that the matrix v is nearly equal to u. Accordingly, when we divide u into the two parts, u_0, the diagonal part of u, and u_1, the offdiagonal part,

$$u=u_0+u_1 \quad (A1)$$

and also
$$v=v_0+v_1 \quad (A2)$$

in a similar manner, it may be assumed that the elements of u_1 (or v_1) are small compared with those of u_0 (or v_0).

(a) The Case of Single Boundary.—We have the matrix S, Eq. 29, of the following approximate form,

$$S=pv_0^{-1}(1-v_1\cdot v_0^{-1})q^{-1}(u_0+u_1) \quad (A3)$$

or neglecting the term including $u_1\cdot v_1$,

14) This effect means that the perturbation at the bend should be very small compared with the total energy of the system. The present condition, $r_e\gg\rho_{max}$, which is equivalent to that in Ref. 6, p. 2, $a_0\gg aV_r(r)$, satisfies this restriction.

15) In the estimation, the values of ρ_{10} and ρ_{01} at $E=3/2\cdot h\nu_0$ were assumed for convenience to be unity.

$$S=S_0+S_1 \tag{A4}$$

where $S_0=pv_0^{-1}q^{-1}u_0$ (A5)

and $S_1\simeq pv_0^{-1}q^{-1}u_1-pv_0^{-1}v_1v_0^{-1}u_0q^{-1}$ (A6)

Since the matrix B of Eq. 27 is expressed by the use of the above equations, as

$$B=(S_0-1)(S_0+1)^{-1}+2(S_0+1)^{-1}S_1(S_0+1)^{-1} \tag{A7}$$

we can finally get the expressions of the coefficients of reflected waves $B_{\kappa\lambda}$'s and those of transmitted waves $C_{\kappa k}$'s,

$$B_{\kappa\lambda}=\frac{p_\kappa(v_0^{-1}\cdot u_0)_\kappa-q_\kappa}{p_\kappa(v_0^{-1}\cdot u_0)_\kappa+q_\kappa}\delta_{\kappa\lambda}+\frac{2p_\kappa(v_0^{-1})_\kappa[u_{1,\kappa\lambda}q_\lambda-q_\kappa v_{1,\kappa\lambda}(v_0^{-1}\cdot v_0)_\lambda]}{[p_\kappa(v_0^{-1}\cdot u_0)_\kappa+q_\kappa]\cdot[p_\lambda(v_0^{-1}\cdot u_0)_\lambda+q_\lambda]} \tag{A8}$$

and

$$C_{\kappa k}=\frac{2p_\kappa(v_0^{-1}\cdot u_0)_\kappa u^{-1}{}_{\kappa k}}{p_\kappa(v_0^{-1}\cdot u_0)_\kappa+q_\kappa}+\sum_\lambda\frac{2p_\kappa(v_0^{-1})_\kappa[u_{1,\kappa\lambda}q_\lambda-q_\kappa\cdot v_{1,\kappa\lambda}(v_0^{-1}\cdot u_0)_\lambda]u^{-1}{}_{\lambda\kappa}}{[p_\kappa(v_0^{-1}\cdot u_0)_\kappa+q_\kappa]\cdot[p_\lambda(v_0^{-1}\cdot u_0)_\lambda+q_\lambda]} \tag{A9}$$

(b) The Case of Two Boundaries.—By the introduction of the same approximations for u' and v' as those for u and v, the coefficients $B_{\kappa\lambda}$'s are expressed as follows:

$$B_{\kappa\kappa}=L_\kappa[(v_0^{-1}\cdot u_0)_\kappa p_\kappa{}^2-(u_0^{-1}\cdot v_0)_\kappa q_\kappa{}^2]\cdot(Q_\kappa)^{-1} \tag{A10}$$

and

$$\begin{aligned}B_{\kappa\lambda}=&2p_\kappa(Q_\kappa\cdot Q_\lambda)^{-1}\\&\times[(4-G_\kappa\cdot G_\lambda)q_\lambda q_\kappa\{(v_0^{-1})_\kappa v_{1,\kappa\lambda}p_\kappa\\&-(u_0^{-1})_\kappa u_{1,\kappa\lambda}p_\lambda\}\\&-L_\kappa L_\lambda\{(u_0^{-1})_\kappa v_{1,\kappa\lambda}(v_0^{-1}\cdot u_0)_\lambda p_\lambda q_\kappa{}^2\\&-(v_0^{-1})_\kappa\cdot u_{1,\kappa\lambda}(u_0^{-1}\cdot v_0)_\lambda\cdot p_\kappa\cdot q_\lambda{}^2\}\\&+G_\kappa L_\lambda q_\kappa\{(v_0^{-1})_\kappa\cdot v_{1,\kappa\lambda}(v_0^{-1}\cdot u_0)_\lambda p_\kappa p_\lambda\\&-(u_0^{-1})_\kappa\cdot u_{1,\kappa\lambda}(u_0^{-1}\cdot v_0)_\lambda q_\lambda{}^2\}\\&+G_\lambda L_\kappa\{(u_0^{-1})_\kappa\cdot v_{1,\kappa\lambda}q_\kappa{}^2\\&-(v_0^{-1})_\kappa\cdot u_{1,\kappa\lambda}p_\kappa p_\lambda\}]\end{aligned} \tag{A11}$$

where

$$\begin{aligned}Q_\kappa=&L_\kappa\{(v_0^{-1}\cdot u_0)_\kappa\cdot p_\kappa{}^2+(u_0^{-1}\cdot v_0)_\kappa\cdot q_\kappa{}^2\}\\&-2G_\kappa p_\kappa\cdot q_\kappa\end{aligned} \tag{A12}$$

$$G_\kappa=(W+W^*)_\kappa=2\cos m_\kappa\theta_0 \tag{A13}$$

and $$L_\kappa=(W-W^*)_\kappa=2i\sin m_\kappa\theta_0 \tag{A14}$$

The $F_{\kappa\kappa'}$'s is obtained by substituting the above expressions of $B_{\kappa\lambda}$'s into Eq. 15.

Appendix II. Calculations of $u_{k\lambda}$ and $v_{k\lambda}$

The matrix element $u_{k\lambda}$ is defined by

$$\psi_k{}^{\mathrm{II}}(x)\sum_\lambda u_{k\lambda}\cdot\psi_\lambda{}^{\mathrm{I}}(x) \tag{A15}$$

Making use of the property of ψ^{I}, we obtain

$$u_{k\lambda}=\int_{-\infty}^{+\infty}\psi_\lambda{}^{\mathrm{I}*}\cdot\psi_k{}^{\mathrm{II}}\mathrm{d}\rho \tag{A16}$$

where the lower limit of integration with respect to ρ can be practically extended to minus infinity instead of $\rho=-r_e$ because of the rapid diminution of $\psi_\lambda{}^{\mathrm{I}}$ and $\psi_k{}^{\mathrm{II}}$ where ρ is smaller than $-\rho_{\max}$.

From the condition $r_e\gg\rho_{\max}$, $\psi_k{}^{\mathrm{II}}(x)$, Eq. 35, is described approximately by

$$\psi_\kappa{}^{\mathrm{II}}(x)\simeq\frac{n}{r_e{}^{1/2}}\cdot\left(1-\frac{\rho}{2r_e}+\frac{3\rho^2}{8r_e{}^2}\right)\cdot N_k\times\exp\left(-\frac{\alpha'}{2}\zeta^2\right)\cdot H_k(\sqrt{\alpha'}\zeta) \tag{A17}$$

Accordingly, $u_{k\lambda}$ which is given by Eq. A16 consists of the sum of the general term,

$$\text{const.}\times\int_{-\infty}^{+\infty}\rho^n\cdot N_kN_\lambda\cdot\exp\left(-\frac{\alpha'}{2}\zeta^2-\frac{\alpha}{2}\rho^2\right)\times H_k(\sqrt{\alpha'}\cdot\zeta)\cdot H_\lambda(\sqrt{\alpha}\cdot\rho)\,\mathrm{d}\rho$$

which is resolved, furthermore, into the sum of the following integrals with some coefficients[16],

$$I_{\kappa\lambda}=N_kN_\lambda\cdot\int_{-\infty}^{+\infty}\exp\left(-\frac{\alpha'}{2}\zeta^2-\frac{\alpha}{2}\rho^2\right)\times H_k(\sqrt{\alpha'}\cdot\zeta)\cdot H_\lambda(\sqrt{\alpha}\cdot\rho)\cdot\mathrm{d}\rho \tag{A18}$$

Since

$$\alpha'\zeta^2+\alpha\rho^2=(\alpha+\alpha')\left[\rho-\left(\frac{\alpha'}{\alpha+\alpha'}\right)\beta r_e\right]^2=at^2 \tag{A19}$$

where a and t are defined by

$$a=\alpha+\alpha' \quad\text{and}\quad t=\rho-\left(\frac{\alpha'}{\alpha+\alpha'}\right)\beta r_e \tag{A20), (A21}$$

Eq. A18 is also written as

$$I_{k\lambda}=N_kN_\lambda\cdot\exp\left[-\frac{1}{2}\left(\frac{\alpha\alpha'}{\alpha+\alpha'}\right)(\beta r_e)^2\right]\times\int_{-\infty}^{+\infty}\exp\left(-\frac{a}{2}t^2\right)H_kH_\lambda\mathrm{d}\rho \tag{A22}$$

Transforming the variables, $\sqrt{\alpha}\cdot\rho$ in H_λ and $\sqrt{\alpha'}\cdot\zeta$ in H_k, into a new variable,

$$s=\sqrt{a}\cdot t \tag{A23}$$

we can write

$$H_\lambda(\sqrt{\alpha}\cdot\rho)=\sum_l g_{\lambda l}H_l(\sqrt{a}\cdot t) \tag{A24}$$

and $$H_k(\sqrt{\alpha'}\cdot\zeta)=\sum_l h_{kl}H_l(\sqrt{a}\cdot t) \tag{A25}$$

where $g_{\lambda l}$ and h_{kl} are coefficients of expansion.

Substituting Eqs. A24 and A25 into Eq. A22, we can get the final expression of $I_{k\lambda}$,

$$I_{k\lambda}=N_kN_\lambda\cdot\exp\left[-\frac{1}{2}\left(\frac{\alpha\alpha'}{\alpha+\alpha'}\right)(\beta r_e)^2\right]\times\sum_l g_{\lambda l}\cdot h_{kl}(N_l)^{-2} \tag{A26}$$

where N_l is obtained by replacing α and λ in N_λ with a and l respectively. In a similar way, the matrix element $v_{k\lambda}$

$$v_{k\lambda}=\int_{-\infty}^{+\infty}\left(\frac{r_e}{r_e+\rho}\right)\cdot\psi_\lambda{}^{\mathrm{I}*}\cdot\psi_k{}^{\mathrm{II}}\mathrm{d}\rho \tag{A27}$$

is computed, since the function $r_e/(r_e+\rho)\cdot\psi_k{}^{\mathrm{II}}(x)$ has the following approximate form,

16) See, for example, H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry", John Wiley & Sons, Inc., New York (1949), p. 60.

$$\left(\frac{r_e}{r_e+\rho}\right)\cdot\psi_k^{II}(x)\simeq\frac{n}{r_e^{1/2}}\cdot\left(1-\frac{3\rho}{2r_e}+\frac{15\rho^2}{8r_e^2}\right)\cdot N_k \times\exp\left(-\frac{\alpha'}{2}\zeta^2\right)\cdot H_k(\sqrt{\alpha'}\cdot\zeta) \quad (A28)$$

and can also be resolved into the sum of $I_{k\lambda}$ with reasonable coefficient as well as in the case of $u_{k\lambda}$.

The obtained expressions of $u_{k\lambda}$ and $v_{k\lambda}$ for $k,\lambda=0,1$ are shown as follows:

$$u_{00}=A_{00}\cdot\left[\left(1-\frac{1}{2}\varepsilon+\frac{3}{8}\varepsilon^2\right)+\frac{3}{8}\eta\right] \quad (A29)$$

$$u_{10}=2A_{10}\sqrt{\alpha'}r_e\cdot\left[\left(1-\frac{1}{2}\varepsilon+\frac{3}{8}\varepsilon^2\right)(\varepsilon-\beta)+\frac{1}{8}\{9\varepsilon-(4+3\beta)\eta\}\right]$$

$$u_{01}=2A_{01}\sqrt{\alpha}\cdot r_e\cdot\left[\left(1-\frac{1}{2}\varepsilon+\frac{3}{8}\varepsilon^2\right)\varepsilon+\frac{1}{8}(9\varepsilon-4)\eta\right]$$

$$u_{11}=4A_{11}\sqrt{\alpha\alpha'}\cdot r_e^2\cdot\left[\left(1-\frac{1}{2}\varepsilon+\frac{3}{8}\varepsilon^2\right)(\varepsilon-\beta)\varepsilon+\frac{3}{8}\eta^2+\left\{\left(1-\frac{1}{2}\varepsilon+\frac{3}{8}\varepsilon^2\right)+\left(\frac{3}{4}\varepsilon-\frac{1}{2}\right)(2\varepsilon-\beta)+\frac{3}{8}(\varepsilon-\beta)\varepsilon\right\}\eta\right]$$

and

$$v_{00}=A_{00}\cdot\left[\left(1-\frac{3}{2}\varepsilon+\frac{15}{8}\varepsilon^2\right)+\frac{15}{8}\eta\right] \quad (A30)$$

$$v_{10}=2A_{10}\sqrt{\alpha'}r_e\cdot\left[\left(1-\frac{3}{2}\varepsilon+\frac{15}{8}\varepsilon^2\right)(\varepsilon-\beta)+\frac{1}{8}\{45\varepsilon-(12+15\beta)\}\eta\right]$$

$$v_{01}=2A_{01}\sqrt{\alpha}\cdot r_e\cdot\left[\left(1-\frac{3}{2}\varepsilon+\frac{15}{8}\varepsilon^2\right)\varepsilon+\frac{1}{8}(45\varepsilon-12)\eta\right]$$

$$v_{11}=4A_{11}\sqrt{\alpha\alpha'}\cdot r_e^2\cdot\left[\left(1-\frac{3}{2}\varepsilon+\frac{15}{8}\varepsilon^2\right)(\varepsilon-\beta)\varepsilon+\frac{15}{8}\eta^2+\left\{\left(1-\frac{3}{2}\varepsilon+\frac{15}{8}\varepsilon^2\right)+\left(\frac{15}{4}\varepsilon-\frac{3}{2}\right)(2\varepsilon-\beta)+\frac{15}{8}(\varepsilon-\beta)\varepsilon\right\}\eta\right]$$

where,

$$A_{k\lambda}=(n_k/r_e^{1/2})\,(N_kN_\lambda/\bar{N}_0^2)\times\exp\left[-\frac{1}{2}\left(\frac{\alpha\alpha'}{\alpha+\alpha'}\right)\cdot(\beta r_e)^2\right] \quad (A31)$$

$$\bar{\alpha}=(\alpha+\alpha')/2 \quad (A32)$$

$$\varepsilon=\{\alpha/(\alpha+\alpha')\}\beta \quad (A33)$$

$$\eta=(2\bar{\alpha}r_e^2)^{-1} \quad (A34)$$

and $\bar{N}_0$ is obtained from the normalization factor N_κ of vibrational eigenfunction by replacing α and κ with $\bar{\alpha}$ and zero.

The expressions of $u'_{k\lambda'}$ and $v'_{k\lambda'}$ are identical with the above, because the form of the potential channel is symmetrical at the two boundaries.