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The Theory of Collisions between Two Diatomic Molecules

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The general features of the elastic and the inelastic collisions have been investigated in this paper. The inelastic collisions are confined to the rotational and the vibrational ones, and the electronic degrees of freedom are disregarded throughout. Starting from the fundamental set of equations for the collision problem, the effects of the non-spherical character of the intermolecular potential are discussed. For the rotational transitions where the level spacings are rather small, the semi-classical method is employed and for the vibrational transitions, the distorted wave method is developed and some simple methods to estimate the cross sections are also discussed. Special considerations are also given for the cases in which the two colliding molecules are identical.

§ 1. Introduction

As is well known, the knowledge of molecular collision processes, in general, together with that of the stationary states of molecules form the fundamental part of the chemical physics. And these molecular collisions which may be accompanied with the rotational and/or the vibrational transitions can be treated, in principle, by solving the well-established Schroedinger wave equation for that system. The straightforward solution, however, impels us to carry out the extremely laborious calculations. It may be said that it is almost impossible to do so unless some specially designed calculating machines are invented. For this reason, the calculations for the elastic molecular collisions are usually done by assuming the spherically symmetric potential without taking the internal degrees of freedom into account, while the calculations of the probabilities of the vibrational or the rotational transitions have been made for the special orientations of the two colliding molecules (e.g. collinear collision or collision in a plane).[1)-3)] Thus, it is desirable to investigate more fully the general feature of the collision processes and to seek for some approximation methods of treatment. In this paper, some detailed investigations for the collisions between two diatomic molecules in the unrestricted space are reported.

First thing we have to do is to set up the fundamental equations for our problem. Then we must determine the intermolecular force for particular case and calculate its matrix elements which appear in the fundamental equations. The pure theoretical determination of the intermolecular potential presents one of the outstanding difficulties for the collision problem, and the semi-empirical determination is preferable if it is possible. These problems are investigated in the first part (§ 2, § 3). Special considerations are also given for the case in which the two colliding molecules are identical. (§ 4) In the next part

of this paper, the cross section for the elastic scattering is defined in relation to the asymptotic behaviour of the wave function (§ 5), and some considerations, especially on the effects of the non-spherical nature of the potential, are given for the elastic scattering. (§ 6) The inelastic transitions, especially the vibrational one, in the thermal collisions may be treated by the distorted wave method. (§ 7) The general formulation on this line and some attempts to estimate the cross sections in simple ways are explained in § 9. For the rotational transitions, however, the transition probabilities are rather large so that the distorted wave method can no longer be employed. Instead, the semi-classical method, in which the translational motion is described classically, is proposed for this case. (§ 8) Finally, we must consider the statistical problems, such as the viscosity, the diffusion, the ultrasonic dispersion and so forth, in order to combine the theory of elementary processes with the experimental data. In particular, we are interested in the effects due to the existence of the internal degrees of freedom. Some brief discussions are given for these effects. (§ 10)

The numerical examples are not shown in this paper. It is also desirable to investigate the other types of collision, such as the collisions between the larger molecules and the multiple collisions in which more than two molecules collide simultaneously. These problems are postponed to another chance.

§ 2. Derivation of the fundamental set of equations*)

We shall first consider the wave function of a free diatomic molecule. As is well-known, it has the following form

$$u_{nl}(\xi)\,Y_{lm}(\theta,\varphi)/\xi\,,$$

where ξ is the internuclear distance, and θ, φ define the direction of the molecular axis with respect to the fixed coordinate axes in the space. u_{nl} is the vibrational wave function which satisfies the equation of the form**)

$$\{d^2/d\xi^2-l(l+1)/\xi^2-2\mu V(\xi)+2\mu W_{nl}\}u_{ln}(\xi)=0,$$

together with the boundary conditions ($u(0)=0$ and $u(\xi)\to 0$ for $\xi\to\infty$), and is normalized according to

$$\int_0^\infty u_{nl}^*(\xi)\,u_{n'l}(\xi)\,d\xi=\delta_{nn'}\,.$$

Y_{lm} is the ordinary spherical harmonic function:

$$\left.\begin{aligned} &Y_{lm}(\theta,\varphi)=\Theta_{lm}(\theta)\,\Phi_m(\varphi),\\ &\Theta_{lm}(\theta)=(-1)^m\left\{\frac{2l+1}{2}\frac{(l-m)!}{(l+m)!}\right\}^{1/2}\sin^m\theta\frac{d^m}{(d\cos\theta)^m}P_l(\cos\theta),\\ &\Theta_{l-m}(\theta)=(-1)^m\cdot\Theta_{lm}(\theta), \end{aligned}\right\}\quad(m>0)$$

* Essential part of §§ 1–3 was reported in the international symposium on molecular physics at Nikko, Japan (September, 1953).

** Atomic units are used throughout this paper.

$$\Phi_m(\varphi) = (1/\sqrt{2\pi})\exp(im\varphi).$$

$V(\xi)$ in the above equation is the vibrational potential, and μ means the reduced mass of the two atoms. W_{nl} is the internal energy of the molecule, disregarding the electronic one. The electronic wave function does not appear explicitly in this work.

Now we shall proceed to the system consisting of the two diatomic molecules. If the two molecules are far apart, the potential energy of the system is simply the sum of the intramolecular potentials of both molecules

$$V = V_1(\xi_1) + V_2(\xi_2),$$

and when these two molecules approach to each other, the mutual interaction starts to act and the potential energy function may be written as

$$V = V_1(\xi_1) + V_2(\xi_2) + V'(R, \Theta, \Phi, \xi_1, \theta_1, \varphi_1, \xi_2, \theta_2, \varphi_2). \qquad (2\cdot1)$$

(See Fig. 1) Since the third term, intermolecular potential, depends on the internal coordinates of the two molecules, the rotational transition (change of l, m) and the vibrational transition (change of n) can take place. The separation of the potential into three parts as in the expression $(2\cdot1)$ is useful only in the distant collision such as the thermal collision in the room temperature, and may become meaningless in the extremely close collision, especially in the case of the rearrangement chemical reaction such as the double decomposition: AB + CD = AC + BD, which is beyond the scope of our present considerations.

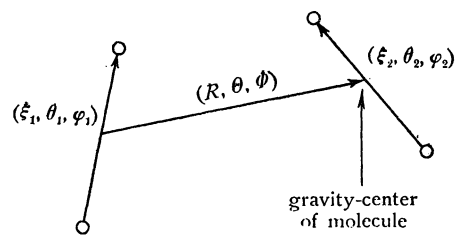

Fig. 1

On the other hand, the kinetic energy of this system may be expressed as

$$T = -(1/2\mu_1)\nabla_1^2 - (1/2\mu_2)\nabla_2^2 - (1/2M)\nabla_R^2, \qquad (2\cdot2)$$

where M means the reduced mass of the two-molecule-system. The first and the second terms in the right hand side correspond to the internal motions of two molecules and the third term corresponds to the relative motion of them. The translational energy of the system as a whole has been separated out, which is always possible without loss of generality.

Then the Schroedinger wave equation is given by

$$(T + V - E)\Psi = 0 \qquad (2\cdot3)$$

where Ψ is the wave function representing the whole system.

Now if the intermolecular potential is small, or if, at least, the dependence of the intermolecular potential on the internal coordinates of two molecules is assumed to be little, it is convenient to expand the total wave function as follows:

$$\Psi = \sum_\alpha (1/R) f_\alpha(R) A_\alpha(\Theta, \Phi, \xi_1, \theta_1, \varphi_1, \xi_2, \theta_2, \varphi_2) \qquad (2\cdot4)$$

$$A_\alpha \equiv Y_{jv}(\Theta\Phi)\frac{1}{\xi_1}u_{nl}(\xi_1)Y_{lm}(\theta_1\varphi_1)\frac{1}{\xi_2}u_{n'l'}(\xi_2)Y_{l'm'}(\theta_2\varphi_2),$$

where α stands for $(j, \nu, n, l, m, n', l', m')$. By substituting this expansion into (2·3), we have a set of equations for $f(R)$:

$$\frac{1}{2M}\left\{\frac{d^2}{dR^2}-\frac{j(j+1)}{R^2}+k_\alpha^2\right\}f_\alpha(R)=\sum_{\alpha'}(\alpha|V'|\alpha')f_{\alpha'}(R), \tag{2·5}$$

where

$$k_\alpha^2/2M=E-W_{nl}^{(1)}-W_{n'l'}^{(2)}, \tag{2·6}$$

$$(\alpha|V'|\alpha')=\int\int\int\int\int d\Omega\, d\Omega_1 d\Omega_2 \xi_1^2 d\xi_1 \xi_2^2 d\xi_2 A_\alpha \cdot V' \cdot A_{\alpha'}, \tag{2·7}$$

$$d\Omega=\sin\theta\, d\theta d\Phi, \quad d\Omega_i=\sin\theta_i d\theta_i d\varphi_i .$$

In the above treatment, the total angular momentum of the system is not definite. However, since the total angular momentum quantum numbers J, μ (μ corresponds to the z-component of the angular momentum) are the good quantum numbers, it is desirable to use the representation in which the values of these quantum numbers appear explicitly. For this sake, the following linear combinations of the single products of the spherical harmonics must be employed as the basic functions of the expansion :

$$\mathbf{Y}_{jLll'}^{J\mu}=\sum_{m,m'} s_{J\mu-mm}^{jl}\, s_{Lm'm-m'}^{ll'}\, Y_{j\mu-m}(\Theta\Phi)\, Y_{lm}(\theta_1\varphi_1)\, Y_{l'm-m'}(\theta_2\varphi_2). \tag{2·8}$$*)

Then the equations (2·4), (2·5) and (2·7) are respectively replaced by

$$\Psi=\sum_\beta (1/R)F_\beta(R)\cdot B_\beta(\Theta, \Phi, \xi_1, \theta_1, \varphi_1, \xi_2, \theta_2, \varphi_2) \tag{2·9}$$

$$B_\beta\equiv(1/\xi_1)u_{nl}(\xi_1)\,(1/\xi_2)u_{n'l'}(\xi_2)\,\mathbf{Y}_{jLll'}^{J\mu},$$

$$\frac{1}{2M}\left\{\frac{d^2}{dR^2}-\frac{j(j+1)}{R^2}+k_\beta^2\right\}F_\beta(R)=\sum_{\beta'}(\beta|V'|\beta')F_{\beta'}(R), \tag{2·10}$$

$$\beta\equiv(J, \mu, n, n', j, L, l, l'),$$

$$(\beta|V'|\beta')=\delta_{JJ'}\delta_{\mu\mu'}\int\int\int\int\int d\Omega\, d\Omega_1 d\Omega_2 \xi_1^2 d\xi_1 \xi_2^2 d\xi_2 B_\beta \cdot V' \cdot B_{\beta'}. \tag{2·11}$$

Sometimes, the nuclear and/or electronic spin may exist which have not been taken into account in the above equations. But the spin does not couple with the orbital angular momenta strongly, J and μ are still good quantum numbers even if we don't include the spin in this resultant angular momentum.

The equations (2·10) are our fundamental set of equations to be solved. The next step is the determination of the matrix elements in these equations (§ 3), and then comes the investigation of the general features of the solution (§§ 6–9).

If we can neglect the vibrational motion of the molecules, $u(\xi)$ is replaced by

$$\sqrt{\delta(\xi-\xi_0)}$$

where ξ_0 means the equilibrium value of the internuclear distance.

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* The so-called Clebsch-Gordan's coefficients $s_{lmm'}^{ll'}$ is the same with that defined by Wigner in his text book.[7] See also Appendix II.

Recently, Hirschfelder, Curtiss and Adler in Wisconsin University have also investigated the general formulation of the collision problem for the polyatomic molecules.[4)-6)] They have separated the rotational coordinates from the N-particle Schroedinger equation by making use of the group theoretical method and have obtained[6)] a similar set of equations to our equations (2·10).

§ 3. Intermolecular force potential and its matrix elements

All kinds of collision process have its origin in the intermolecular potential V', and usually the cross sections of various processes depend rather sensitively on this potential function. But, unfortunately, the calculation of the intermolecular force potential is a very difficult thing, and no theoretical calculations of V' have been made for diatomic molecules, except for H_2–H_2 force.[8)-10)] For this reason, it is preferable to use the semi-empirical formula as far as possible. For instance, we may determine the potential function from the equation of state of the gas or from some transport phenomena such as viscosity and then employ the so-determined function to calculate the cross sections of some inelastic processes.

The intermolecular force is usually divided into two parts. The one is the strong repulsive force (V_r) in the closest distances which arises from the overlapping of the electron clouds of the two molecules. The other is the so-called Van der Waals force (V_a) which is usually attractive and have a long range of action. The former may be expressed approximately by the sum of the interatomic repulsive potentials between the atoms belonging to the different molecules, i.e.

$$V_r = v_{13}(r_{13}) + v_{14}(r_{14}) + v_{23}(r_{23}) + v_{24}(r_{24}), \qquad (3\cdot1)$$

where r_{ij} is the distance between i-th and j-th atoms.[9) 11)] (See Fig. 2.) The interatomic potential v_{ij} may be determined empirically, by assuming a simple form containing some parameters which should be adjusted by comparing with some experimental data.

If the internuclear distances ξ_1, ξ_2 are both small compared with the intermolecular distance R (this is roughly true for the thermal collisions at ordinary temperatures), it is convenient to expand the function (3·1) into the following series

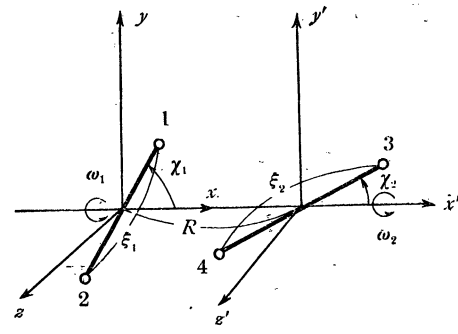

Fig. 2

$$V_r = \sum_{a=1,2}\sum_{b=3,4}\sum_{i,j,k}^{\infty}\sum_{l,m,n}^{\infty} \frac{x_a^i y_a^j z_a^k}{i!\,j!\,k!}\frac{x_b'^l y_b'^m z_b'^n}{l!\,m!\,n!}\left[\frac{\partial^{i+j+k+l+m+n} v_{ab}(r)}{\partial X^i \partial Y^j \partial Z^k \partial X'^l \partial Y'^m \partial Z'^n}\right]_{\substack{X=Y=Z=0 \\ X'=Y'=Z'=0}}$$

$$(r^2=(X'-X-R)^2+(Y'-Y)^2+(Z'-Z)^2)$$

$$=\{v_{13}(R)+v_{14}(R)+v_{23}(R)+v_{24}(R)\}$$

$$
\begin{aligned}
&+\{(x_1-x_3')(\partial v_{13}/\partial X)_0+(x_1-x_4')(\partial v_{14}/\partial X)_0\\
&\quad+(x_2-x_3')(\partial v_{23}/\partial X)_0+(x_2-x_4')(\partial v_{24}/\partial X)_0\}\\
&+[\tfrac{1}{2}\{(x_1^2+x_3'^2)(\partial^2 v_{13}/\partial X^2)_0+(x_1^2+x_4'^2)(\partial^2 v_{14}/\partial X^2)_0\\
&\quad+(x_2^2+x_3'^2)(\partial^2 v_{23}/\partial X^2)_0+(x_2^2+x_4'^2)(\partial^2 v_{24}/\partial X^2)_0\\
&\quad+(y_1^2+y_3'^2+z_1^2+z_3'^2)(\partial^2 v_{13}/\partial Y^2)_0+(y_1^2+y_4'^2+z_1^2+z_4'^2)(\partial^2 v_{14}/\partial Y^2)_0\\
&\quad+(y_2^2+y_3'^2+z_2^2+z_3'^2)(\partial^2 v_{23}/\partial Y^2)_0+(y_2^2+y_4'^2+z_2^2+z_4'^2)(\partial^2 v_{24}/\partial Y^2)_0\}\\
&\quad+\{x_1x_3'(\partial^2 v_{13}/\partial X\partial X')_0+x_1x_4'(\partial^2 v_{14}/\partial X\partial X')_0\\
&\qquad+x_2x_3'(\partial^2 v_{23}/\partial X\partial X')_0+x_2x_4'(\partial^2 v_{24}/\partial X\partial X')_0\\
&\quad+(y_1y_3'+z_1z_3')(\partial^2 v_{13}/\partial Y\partial Y')_0+(y_1y_4'+z_1z_4')(\partial^2 v_{14}/\partial Y\partial Y')_0\\
&\quad+(y_2y_3'+z_2z_3')(\partial^2 v_{23}/\partial Y\partial Y')_0+(y_2y_4'+z_2z_4')(\partial^2 v_{24}/\partial Y\partial Y')_0\}]\\
&+3rd\ and\ higher\ order\ terms. \qquad (3\cdot2)
\end{aligned}
$$

It is easy to see that this expression is a function of three cosines $\cos\chi_1$, $\cos\chi_2$ and $\cos\chi'$ (See Fig. 3) and ξ_1, ξ_2, R. This can be proved either by substituting the relations

$$
\begin{aligned}
&x_1=\xi_1(m_2/m_1+m_2)\cos\chi_1,\\
&\qquad(m_i\ is\ the\ mass\ of\ the\ i\text{-}th\ atom.)\\
&y_1^2+z_1^2=\xi_1^2(m_2/m_1+m_2)^2(1-\cos^2\chi_1),\\
&y_1y_3'+z_1z_3'=\xi_1\xi_2(m_2/m_1+m_2)\\
&\quad\times(m_4/m_3+m_4)\sin\chi_1\sin\chi_2\cos(\omega_1-\omega_2)\\
&\quad=\xi_1\xi_2(m_2/m_1+m_2)(m_4/m_3+m_4)\\
&\quad\times(\cos\chi'-\cos\chi_1\cos\chi_2)\ \text{etc.},
\end{aligned}
$$

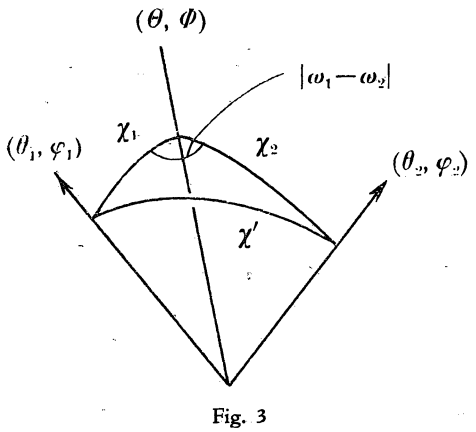

Fig. 3

into the above expression directly, or by noticing that these three cosines together with ξ_1, ξ_2 and R determine the distances of each atom from three other atoms uniquely. Thus, after all, the repulsive potential V_r must have the form

$$V_r=\sum_{\alpha,\beta,\gamma} v_{\alpha\beta\gamma}^{(r)}(\xi_1,\xi_2,R)\,P_\alpha(\cos\chi_1)\,P_\beta(\cos\chi_2)\,P_\gamma(\cos\chi') \qquad (3\cdot3)$$

and, if the anisotropy of this potential is not so large, only the first few terms have to be employed.

Now it is easy to calculate the matrix elements of V_r. By remembering the addition theorem

$$P_\alpha(\cos\chi_1)=(4\pi/2\alpha+1)\sum_{\rho=-\alpha}^{\alpha} Y_{\alpha\rho}^*(\theta\Phi)\,Y_{\alpha\rho}(\theta_1\varphi_1)$$

$$P_\beta(\cos\chi_2)=(4\pi/2\beta+1)\sum_{\sigma=-\beta}^{\beta}Y_{\beta\sigma}^*(\Theta\Phi)\,Y_{\beta\sigma}(\theta_2\varphi_2)$$

$$P_\tau(\cos\chi')=(4\pi/2\gamma+1)\sum_{\tau=-\tau}^{\tau}Y_{\tau\tau}^*(\theta_1\varphi_1)\,Y_{\tau\tau}(\theta_2\varphi_2), \qquad (3\cdot4)$$

it is clear that the matrix elements of the function (3·3) can be expressed in terms of

$$c^L(l'm';lm)=(2/2L+1)^{1/2}\int\int Y_{lm'}^*(\theta\varphi)\,Y_{L,m'-m}(\theta\varphi)\,Y_{lm}(\theta\varphi)\sin\theta\,d\theta\,d\varphi\,.$$

The values of these integrals have been calculated for not too large values of l and l'.[12) 13)] For the larger values of l and l', we have to calculate by making use of the general formula for these integrals.[12) 14)]

The matrix elements of the Van der Waals force V_a can be derived similarly if this potential has been expressed in a similar form to (3·3).

If two molecules are homonuclear, we have $x_1=-x_2$, $y_1=-y_2$ *etc.*, and furthermore the four interatomic potentials v_{13}, v_{14}, v_{23}, v_{24} become same functions and, therefore, the repulsive potential can be expressed in a much simpler form:

$$V_r=4v(R)+2\left[(x_1^2+x_3'^2)(\partial^2v/\partial X^2)_0+(y_1^2+y_3'^2+z_1^2+z_3'^2)(\partial^2v/\partial Y^2)_0\right], \qquad (3\cdot5)$$

higher terms being neglected for simplicity. In this case, we can determine the intermolecular potential semi-empirically. The empirical interaction potential, which is derived from the observed data on the transport phenomena etc., is usually spherically symmetric one such as Lennard-Jones type

$$\nu R^{-n}-\mu R^{-6}, \qquad (3\cdot6)$$

or a little more reasonable form[15)]

$$P\exp(-R/\rho)-\mu R^{-6}. \qquad (3\cdot7)$$

Then by assuming $v(r)=a/r^n$ or $a\exp(-br)$ and by comparing the expressions (3·5), after averaging over the orientation of the two molecules, with (3·6) or (3·7), we can easily determine the best values of the parameters. The van der Waals force potential, on the other hand, can be estimated employing the empirical or the theoretical values of the permanent quadrupole moment (the dipole moment is zero for homonuclear case), the polarizability and its anisotropy etc., for both molecules, and this potential is given by

(*interactions between permanent multipoles*)
+ (*interactions between permanent multipoles and induced multipoles*)
+ (*interactions between induced multipoles*). (3·8)

The last term, e.g., is usually given in a form: const. $\alpha_1\alpha_2/R^6$, α_1, α_2 being the polarizabilities of two molecules. But the constant coefficient is not certain from the simple theoretical calculations, and thus it will be better to adjust such coefficient by comparing (3·8) with the attractive part of the empirical potential (3·6) or (3·7).

In this way, the dependence of $V'=V_r+V_a$ on the orientations of the two molecules will be obtained. But for the calculation of the vibrational transition probability it

is also required to determine the dependence on the internuclear distances ξ_1, ξ_2. For this sake, we must know the dependence of permanent multipoles and polarizabilities on ξ_1 and ξ_2. For the polarizabilities, the intensity of the Raman spectra will serve for getting the required knowledge. For the permanent multipoles, however, the theoretical estimations are needed. Of course, the rigorous calculations of the multipoles of the molecule are very hard to do and the results are not reliable enough in the absolute scale. But it may be said that the ratio of the variation of the multipole to the multipole itself is reliable, though there is no authentic foundation for this expectation, at present.

For the heteronuclear molecules, the situation becomes more complex, because of the presence of the dipole moment and many undetermined parameters in V_r. But even in this case, the experimental value will serve to renormalize the uncertain results of the pure theoretical calculations.

Finally, we shall consider briefly the symmetry property of the intermolecular potential V' for the pair of the identical molecules. For this sake, it is convenient to adopt the expression of V' in the same form as (3·3), i.e.

$$V'=\sum_{\alpha\beta\gamma} v_{\alpha\beta\gamma}'(\xi_1, \xi_2, R)P_\alpha(\cos\chi_1)P_\beta(\cos\chi_2)P_\gamma(\cos\chi'). \tag{3·9}$$

First, we shall neglect the vibration and put $\xi_1=\xi_2$. Then the potential becomes symmetric for the exchange of χ_1 and $\pi-\chi_2$ for the fixed value of $|\omega_1-\omega_2|$. (Atoms 1 and 3, 2 and 4 are assumed to be identical, resp.) Then it can be shown (Appendix I) that there are the following relations between the coefficients in the expression (3·9)

$$v_{\alpha\beta\gamma}'=(-1)^{\alpha+\beta}v_{\beta\alpha\gamma}'. \tag{3·10}$$

Therefore, if we divide the potential V' into two parts:

$$V'=V^+ + V^- \ ; \ V^+=\sum_{\alpha+\beta=\text{even}}\cdots, \ V^-=\sum_{\alpha+\beta=\text{odd}}\cdots, \tag{3·11}$$

it is easy to see that V^+ is a symmetric function for the interchange of the pairs of coordinates, (θ_1, φ_1) and (θ_2, φ_2), and V^- is an antisymmetric one. Especially, for homonuclear cases the simultaneous substitutions

$$(\chi_1, \omega_1)\rightarrow(\pi-\chi_1, \pi+\omega_1), \quad (\chi_2, \omega_2)\rightarrow(\pi-\chi_2, \pi+\omega_2)$$

do not change the potential function, because by these substitutions the geometrical configuration is unaltered. From this fact, it results that there is no antisymmetric part V^- in these cases. Thus the potential between two identical homonuclear diatomic molecules is symmetric for the interchange of (θ_1, φ_1) and (θ_2, φ_2).

If we take the vibrational degrees of freedom into account, we have

$$v_{\alpha\beta\gamma}'(\xi_1, \xi_2, R)=(-1)^{\alpha+\beta}v_{\beta\alpha\gamma}'(\xi_2, \xi_1, R). \tag{3·12}$$

For the case of homonuclear molecules, we have $V^-=0$ again.

§ 4. Effect of statistics for the identical pair of molecules

For the collision between the identical molecules, we must use the properly symmetrized

wave function. Thus, instead of

$$\zeta_N(X_1)\zeta_{N'}(X_2)\varphi(\boldsymbol{R}),$$

we must employ

$$\begin{aligned}&(1/\sqrt{2})[\zeta_N(X_1)\zeta_{N'}(X_2)\varphi(\boldsymbol{R})\pm\zeta_N(X_2)\zeta_{N'}(X_1)\varphi(-\boldsymbol{R})]\\&=(1/\sqrt{2})[\zeta_N(X_1)\zeta_{N'}(X_2)\pm\zeta_N(X_2)\zeta_{N'}(X_1)]\cdot(1/2)[\varphi(\boldsymbol{R})+\varphi(-\boldsymbol{R})]\\&+(1/\sqrt{2})[\zeta_N(X_1)\zeta_{N'}(X_2)\mp\zeta_N(X_2)\zeta_{N'}(X_1)]\cdot(1/2)[\varphi(\boldsymbol{R})-\varphi(-\boldsymbol{R})],\end{aligned}$$

where $\zeta_N(X)$ means the internal wave function of a molecule, i.e., abbreviation of $u_{nl}(\xi)Y_{lm}(\theta,\varphi)/\xi$ and N, X stand for (n, l, m) and (ξ, θ, φ) respectively. The upper of the double sign corresponds to the Bose statistics and the lower to the Fermi statistics. In the following, however we shall confine ourselves to the Bose statistics only. Of course, the treatment for the Fermi statistics can be obtained similary.

Now we shall define the symmetrized basis

$$\begin{aligned}&Z_{NN'}^{\pm}=(1/\sqrt{2})[\zeta_N(X_1)\zeta_{N'}(X_2)\pm\zeta_N(X_2)\zeta_{N'}(X_1)],\quad(N\neq N')\qquad(4\cdot1)\\&Z_{NN}^{+}=\zeta_N(X)\zeta_N(X),\qquad Z_{NN}^{-}=0,\end{aligned}$$

then the wave function of the system may be written as follows

$$\Psi=\sum_{NN'}[Z_{NN'}^{+}\varphi_{NN'}^{+}(\boldsymbol{R})+Z_{NN'}^{-}\varphi_{NN'}^{-}(\boldsymbol{R})],\qquad(4\cdot2)$$

where φ^+ and φ^- mean the functions which are symmetric and antisymmetric for the substitution $\boldsymbol{R}\rightarrow-\boldsymbol{R}$ respectively. Inserting this expression into the Schroedinger equation, we have the following set of equations

$$\begin{aligned}(\nabla^2+k_{NN'}^2)\varphi_{NN'}^{+}(\boldsymbol{R})&=2M\sum_{PP'}(Z_{NN'}^{+}|V^{+}|Z_{PP'}^{+})\varphi_{PP'}^{+}(\boldsymbol{R})\\&\quad+2M\sum_{PP'}(Z_{NN'}^{+}|V^{-}|Z_{PP'}^{-})\varphi_{PP'}^{-}(\boldsymbol{R}),\\(\nabla^2+k_{NN'}^2)\varphi_{NN'}^{-}(\boldsymbol{R})&=2M\sum_{PP'}(Z_{NN'}^{-}|V^{+}|Z_{PP'}^{-})\varphi_{PP'}^{-}(\boldsymbol{R})\\&\quad+2M\sum_{PP'}(Z_{NN'}^{-}|V^{-}|Z_{PP'}^{+})\varphi_{PP'}^{+}(\boldsymbol{R}),\end{aligned}\qquad(4\cdot3)$$

where V^+ and V^- are the parts of the potential V' which are symmetric and antisymmetric for the exchange of X_1 and X_2 as defined in the last section.

φ^+ and φ^- can further be expanded as follows

$$\begin{aligned}\varphi_{NN'}^{+}(\boldsymbol{R})&=\sum_{j=\text{even}}\sum_{\nu}(2j+1)^{1/2}\{G_{NN'}^{j\nu}(R)/R\}\,Y_{j\nu}(\theta\Phi)\\\varphi_{NN'}^{-}(\boldsymbol{R})&=\sum_{j=\text{odd}}\sum_{\nu}(2j+1)^{1/2}\{G_{NN'}^{j\nu}(R)/R\}\,Y_{j\nu}(\theta\Phi),\end{aligned}\qquad(4\cdot4)$$

and inserting these expansions into the equation (4·3), we get

$$\begin{aligned}&\{d^2/dR^2+k_{NN'}^2-j(j+1)/R^2\}\,G_{NN'}^{j\nu}\\&=2M\sum_{j'=\text{even}}\sum_{\nu'PP'}(2j'+1/2j+1)^{1/2}(Y_{j\nu},Z_{NN'}^{+}|V^{+}|Y_{j'\nu'},Z_{PP'}^{+})G_{PP'}^{j'\nu'}\\&+2M\sum_{j'=\text{odd}}\sum_{\nu'PP'}(2j'+1/2j+1)^{1/2}(Y_{j\nu},Z_{NN'}^{+}|V^{-}|Y_{j'\nu'},Z_{PP'}^{-})G_{PP'}^{j'\nu'}.\end{aligned}\qquad(4\cdot5)$$

for even j, and similar set of equations can be written down easily for odd values of j.

If the non-diagonal elements of the potential function are assumed to be small, we can neglect them in the treatment of the elastic scattering. Then, for the case $N=N'$, we have

$$\Psi = Z^{+}_{NN}\varphi^{+}_{NN}$$

and

$$(\nabla^2 + k^2_{NN})\varphi^{+}_{NN} = 2M(Z^{+}_{NN}|V^{+}|Z^{+}_{NN})\varphi^{+}_{NN},$$

thus the orbital angular momentum j is restricted to be even integer. For $N \neq N'$, the total wave function becomes

$$\Psi = Z^{+}_{NN'}\varphi^{+}_{NN'} + Z^{-}_{NN'}\varphi^{-}_{NN'},$$

and the set of equations becomes

$$(\nabla^2 + k^2_{NN'})\varphi^{+}_{NN'} = 2M(Z^{+}_{NN'}|V^{+}|Z^{+}_{NN'})\varphi^{+}_{NN'} + 2M(Z^{+}_{NN'}|V^{-}|Z^{-}_{NN'})\varphi^{-}_{NN'}$$
$$(\nabla^2 + k^2_{NN'})\varphi^{-}_{NN'} = 2M(Z^{-}_{NN'}|V^{+}|Z^{-}_{NN'})\varphi^{-}_{NN'} + 2M(Z^{-}_{NN'}|V^{-}|Z^{+}_{NN'})\varphi^{+}_{NN'}.$$

For the homonuclear diatomic molecules, these equations are separated as

$$(\nabla^2 + k^2_{NN'})\varphi^{+}_{NN'} = 2M\{(NN'|V^{+}|NN') + (NN'|V^{+}|N'N)\}\varphi^{+}_{NN'}$$
$$(\nabla^2 + k^2_{NN'})\varphi^{-}_{NN'} = 2M\{(NN'|V^{+}|NN') - (NN'|V^{+}|N'N)\}\varphi^{-}_{NN'},$$

where

$$(NN'|V^{+}|PP') \equiv \int \zeta_N^*(X_1)\zeta_{N'}^*(X_2)\, V^{+}\zeta_P(X_1)\zeta_{P'}(X_2)\, dX_1 dX_2 .$$

It may be noted that the exchange potential $(NN'|V^{+}|N'N)$ appears in this case which does not appear in the unsymmetrized treatment. But, these exchange potential may be as small as the other non-diagonal terms which have been neglected in our treatment.

Next, we shall consider the inelastic collision. Here again we shall assume $V^{-}=0$ for simplicity, and compare the two processes

$$(N) + (N) \rightleftarrows (N) + (N') \qquad \begin{matrix}(4\cdot6a)\\(4\cdot6b)\end{matrix}$$

$$(N'') + (N) \rightleftarrows (N'') + (N'), \qquad \begin{matrix}(4\cdot7a)\\(4\cdot7b)\end{matrix}$$

where (N) stands for the molecule in the N-state. In the unsymmetrized theory, the cross sections of these processes will be proportional to the following square of matrix elements

$$Q_{(4\cdot6a)} \propto |(NN'|V^{+}|NN)|^2$$
$$Q_{(4\cdot7a)} \propto |(N''N'|V^{+}|N''N)|^2$$

and $Q_{(4\cdot6a)} \simeq Q_{(4\cdot7a)}$ in the first approximation. Here and in the following, the equality $\simeq$ corresponds to the linear approximation of the perturbation potential, i.e.

$$(NN'|V^{+}|PP')$$
$$\simeq a\,\delta(N,P)\,\delta(N',P') + b\,\delta(N,P)\cdot(N'|v'|P') + c\,\delta(N',P')\,(N|v|P).$$

According to the Bose statistics, on the other hand, we have

$$Q_{(4\cdot 6a)} \propto |(Z^{+}_{NN'}|V^{+}|Z^{+}_{NN'})|^2 = 2|(NN'|V^{+}|NN)|^2$$
$$Q_{(4\cdot 7a)} \propto |(Z^{\pm}_{N''N'}|V^{+}|Z^{\pm}_{N''N'})|^2 \simeq |(N''N'|V^{+}|N''N)|^2,$$

and in the first approximation $Q_{(6a)} \simeq 2Q_{(7a)}$.

Now, in the unsymmetrized treatment of (4·6a), we must take into account the possibility that both molecule can suffer the transition. Thus the effective cross section of inelastic collision is obtained from the above value by multiplying 2. It is not the case in the Bose statistics, because the only one final state $Z^{+}_{NN'}$ is permissible for this case. As a result, approximate relation $Q_{(6a)} \simeq 2Q_{(7a)}$ is valid for both unsymmetrized theory and the symmetrized treatment. Furthermore, the collision number in gas phase is reduced to half for the identical pair of molecules. Thus the reaction rates of (4·6a) and (4·7a) are approximately the same. From the principle of detailed balance, this equality must hold for the inverse processes (4·6b) and (4·7b) too. It can be confirmed easily. For the unsymmetrized theory, we have

$$Q_{(4\cdot 6b)} \propto |(NN|V^{+}|NN')|^2$$
$$Q_{(4\cdot 7b)} \propto |(N''N|V^{+}|N''N')|^2,$$

and in the first approximation $Q_{(6b)} \simeq Q_{(7b)}$. In the symmetrized treatment, on the other hand, we have

$$Q_{(4\cdot 6b)} \propto \tfrac{1}{2}|(Z^{+}_{NN}|V^{+}|Z^{+}_{NN'})|^2 = |(NN|V^{+}|NN')|^2$$
$$Q_{(4\cdot 7b)} \propto |(Z^{\pm}_{N''N}|V^{+}|Z^{\pm}_{N''N'})|^2 \simeq |(N''N|V^{+}|N''N')|^2,$$

where the factor $\frac{1}{2}$ corresponds to the fact that only the partial waves with even orbital angular momenta j can be combined with the final state. Thus we have $Q_{(6b)} \simeq Q_{(7b)}$. Now this time the collision numbers are equal and, therefore, the reaction rates are equal for (4·6b) and (4·7b) as expected. (On these effects of the statistics, our previous considerations have been mistaken, in which we concluded $Q_{(6b)} \simeq \frac{1}{2}Q_{(7b)}$.[14])

In this section we have employed the (j, ν, l, m, l', m')-representation. However, this can be transformed easily into the (J, j, L, l, l', μ)-representation.

§ 5. General discussions on the cross section

In this section, the general asymptotic form of the scattered wave function is considered and then, in relation to this asymptotic form, we proceed to the definition of the cross sections of the elastic and inelastic scatterings. As is well known the plane wave is expanded as follows

$$\exp(ikR\cos\theta) = \sum_{j=0}^{\infty}{}'(2j+1)i^j P_j(\cos\theta)\bar{f}_j(R),$$

where $\bar{f}$ behaves asymptotically as

$$\bar{f}_j(R) \sim \sin(kR - \tfrac{1}{2}j\pi)/kR \quad \text{for } R\to\infty.$$

Thus the incident wave for our problem can be written, except for the vibrational part, as follows

$$\begin{aligned}\Psi_0 &= Y_{lm}(\theta_1\varphi_1)\,Y_{l'm'}(\theta_2\varphi_2)\exp(ikR\cos\Theta)\\ &=\sum_{j=0}^{\infty}(2j+1)i^j\bar{f}_j(R)\,(4\pi/2j+1)^{1/2}\,Y_{j0}(\Theta\Phi)\,Y_{lm}(\theta_1\varphi_1)\,Y_{l'm'}(\theta_2\varphi_2) \qquad (5\cdot1)\\ &=(1/R)\sum_{j=0}^{\infty}\sum_{J,L}\bar{F}^{lml'm'}_{Jj L}\,\boldsymbol{Y}^{J\,m+m'}_{jLl'},\end{aligned}$$

where $\bar{F}$ behaves asymptotically as

$$\begin{aligned}\bar{F}^{lml'm'}_{Jj L} &\sim S^{jL}_{J0\,m+m'}\,S^{ll'}_{Lmm'}\,[4\pi(2j+1)]^{1/2}i^j\sin(kR-\tfrac{1}{2}j\pi)/k\\ &=S^{jL}_{J0\,m+m'}\,S^{ll'}_{Lmm'}\,[\pi(2j+1)]^{1/2}\,\{\exp(ikR)-(-1)^j\exp(-ikR)\}/ki, \quad (R\to\infty).\end{aligned}$$

The vibrational part can be taken into account easily. But in the thermal collisions between diatomic molecules, the vibrational transition takes place with very small probability and its influence on the elastic scattering or the rotational transition is negligible. For this reason, we shall neglect the vibrational degrees of freedom in this section. Now we can assume the following form for the elastically scattered wave

$$\begin{aligned}&\Psi_{el}=(1/R)\sum_{j=0}^{\infty}\sum_{J,L}E^{lml'm'}_{Jj L}\,\boldsymbol{Y}^{J\,m+m'}_{jLl'} \qquad (5\cdot2)\\ &E^{lml'm'}_{Jj L}\sim S^{jL}_{J0\,m+m'}\,S^{ll'}_{Lmm'}\,[\pi(2j+1)]^{1/2}(S^{lml'm'}_{Jj L}-1)\exp(ikR)/ki\,, \quad (R\to\infty).\end{aligned}$$

The inelastically scattered wave, on the other hand, may be written as

$$\begin{aligned}&\Psi_{in}=(1/R)\sum_{\lambda\lambda'}\sum_{j=0}^{\infty}\sum_{J,L}G^{lml'm'}_{Jj L\lambda\lambda'}\,\boldsymbol{Y}^{J\,m+m'}_{jL\lambda'} \qquad (\lambda,\lambda')\neq(l,l') \qquad (5\cdot3)\\ &G^{lml'm'}_{Jj L\lambda\lambda'}\sim S^{jL}_{J0\,m+m'}\,S^{ll'}_{Lmm'}\,[\pi(2j+1)]^{1/2}\,T^{lml'm'}_{Jj L\lambda\lambda'}\exp(ik_fR)/k_fi\,, \quad (R\to\infty).\end{aligned}$$

k_f is the wave number corresponding to the final state, which is defined by (2·6). In the asymptotic form (5·3) the factors before T can be, of course, included in the undetermined factor T. But the above form is adopted to make equal its form with the case of elastic scattering.

Now the cross section can be expressed easily by making use of the scattering matrix S. By imagining a large spherical surface (SS) with the radius R_0, the outgoing flux of the wave Ψ_{el} across this SS is easily calculated as

$$\begin{aligned}I_{el}&=(1/2iM)\int_{SS}R_0^2d\Omega\iint d\Omega_1\,d\Omega_2(\Psi_{el}^*\cdot\partial\Psi_{el}/\partial R-\partial\Psi_{el}^*/\partial R\cdot\Psi_{el})\\ &=(k/M)\,(\pi/k^2)\sum_j\sum_{J,L}(2j+1)\,(s^{jL}_{J0\,m+m'}\,S^{ll'}_{Lmm'})^2|S^{lml'm'}_{Jj L}-1|^2,\end{aligned}$$

where we have used the orthonormality of $\boldsymbol{Y}$. The flux of the incident plane wave, on the other hand, is clearly

$$I_0=v=k/M \quad \text{per unit area.}$$

Thus the cross section for the elastic scattering can be defined as usual

$$Q_{el}\equiv I_{el}/I_0=(\pi/k^2)\sum_j(2j+1)\sum_{J,L}(s^{jL}_{J0\,m+m'}s^{ll'}_{Lmm'})^2|S^{lml'm'}_{jjL}-1|^2. \qquad (5\cdot4)$$

Now the continuity equation must hold for the total wave function $\Psi=\Psi_0+\Psi_{el}+\Psi_{in}$, which means that the net incoming flux of $\Psi_0+\Psi_{el}$ must be equal to the flux of the outgoing wave Ψ_{in}. (Remember that $\Psi_0+\Psi_{el}$ and Ψ_{in} are orthogonal to each other because of different internal wave functions.) From this fact, the cross section for the inelastic scattering can be given formally by the integral

$$Q_{in}=-\frac{1}{2iM}\int_{ss}R_0^2\,d\Omega\iint d\Omega_1\,d\Omega_2\Big\{(\Psi_0^*+\Psi_{el}^*)\frac{\partial}{\partial R}(\Psi_0+\Psi_{el})$$
$$-\frac{\partial}{\partial R}(\Psi_0^*+\Psi_{el}^*)\cdot(\Psi_0+\Psi_{el})\Big\}\Big/I_0\,.$$

In calculating the integral, the terms which contain Ψ_0 and Ψ_0^* only cancel with each other, and the terms which contain Ψ_{el} and Ψ_{el}^* only become $-Q_{el}$. Thus we have

$$Q_{in}=-Q_{el}+\frac{1}{2ik}\int_{ss}R_0^2\,d\Omega\iint d\Omega_1\,d\Omega_2\Big(\frac{\partial\Psi_0^*}{\partial R}\Psi_{el}+\frac{\partial\Psi_{el}^*}{\partial R}\Psi_0-\Psi_0^*\frac{\partial\Psi_{el}}{\partial R}-\Psi_{el}^*\frac{\partial\Psi_0}{\partial R}\Big)$$
$$=(\pi/k^2)\sum_j(2j+1)\sum_{J,L}(s^{jL}_{J0\,m+m'}s^{ll'}_{Lmm'})^2\{1-|S^{lml'm'}_{jjL}|^2\}. \qquad (5\cdot5)$$

It can be seen from this, that the cross section for the inelastic scattering is determined by the scattering matrix S which determines the elastic scattering. Properly speaking, however, matrix S itself can be determined by taking not only the elastic but also the inelastic processes into account. Of course, the item of the inelastic processes can not be expressed by S, but by T. Using the matrix T, the particular inelastic collision cross section $l\to\lambda$, $l'\to\lambda'$ can be given by

$$Q_{in}=(\pi/kk_f)\sum_j(2j+1)\sum_{J,L}(s^{jL}_{J0\,m+m'}s^{ll'}_{Lmm'})^2|T^{lml'm'}_{jjL\lambda\lambda'}|^2.$$

Summing up such cross sections over all possible inelastic processes and equating the result with (5·5), we have the following relation between S and T,

$$\sum_j(2j+1)\sum_{J,L}(s^{jL}_{J0\,m+m'}s^{ll'}_{Lmm'})^2\Big\{1-|S^{lml'm'}_{jjL}|^2-\sum_{\lambda\lambda'}\frac{k}{k_f}|T^{lml'm'}_{jjL\lambda\lambda'}|^2\Big\}=0\,.$$

Even if the inelastic processes are forbidden energetically or take place with very small probabilities, the absolute value of the elements of matrix S are not equal to unity in general. That is, even if the expression (5·5) vanishes, some of the $|S^{lml'm'}_{jjL}|$ may be larger and some others smaller than unity, corresponding to the possibility of the change of j and L during the collision. Such redistribution in j and L can take place easily for the non-spherical scattering potential. For this reason, it is impossible to express the elastic scattering by the phase shifts only, as in the spherical fields. However, if we can assume in the first approximation that the quantum numbers j, l, l', L are good quantum numbers (J, $m+m'$ are good quantum numbers, rigorously.), the absolute values of matrix elements of S become unity and, therefore, by putting

$$S^{lml'm'}_{JjL}=\exp(2i\delta^{JL}_{jll'})$$

we have immediately that

$$Q_{el}=(4\pi/k^2)\sum_j(2j+1)\sum_{J,L}(s^{jL}_{J0\,m+m'}s^{ll'}_{Lmm'})^2\sin^2\delta^{JL}_{jll'}, \qquad (5\cdot6)$$

which is also obtained directly by replacing the $\sin^2\delta_j$ in the well-known formula

$$Q_{el}=(4\pi/k^2)\sum_j(2j+1)\sin^2\delta_j \quad (\textit{central field})$$

by its weighted mean

$$\sum_{J,L}(s^{jL}_{J0\,m+m'}s^{ll'}_{Lmm'})^2\sin^2\delta^{JL}_{jll'}.$$

The cross sections which are effective for the viscosity or the diffusion can be obtained straightforwardly, but these have not such simple forms. For instance, for the case of negligible inelastic scattering, the cross section for the viscosity is given formally by

$$Q_{vis}=\int\int\int d\Omega\,d\Omega_1 d\Omega_2\sin^2\Theta\Big|\sum_{jJL}F^{lml'm'}_{JjL}\,Y^{J\,m+m'}_{jLll'}\Big|^2.$$

But this integral does not become simple, even if we assume that the absolute value of the matrix elements of S are unity. (See Appendix II.)

§ 6. More detailed discussions on the elastic scattering

As in the previous section, we shall neglect the vibrational degrees of freedom in this section too. It is easy to see by analyzing the experimental data of ultrasonic dispersion that the probabilities of the vibrational transitions are very small under the ordinary conditions.[16] For instance, the deactivating transition of an excited O_2 molecule takes place only once in 160000 collisions in the O_2 gas for the room temperature. For an excited Cl_2 molecule in Cl_2 gas, transition takes place once in 34000 collisions. For Cl_2 in HCl gas, which is one of the most favorable cases, once in 120 collisions. The probabilities of exciting processes to the upper vibrational states are much smaller than these figures. Thus we may safely neglect the vibrational transitions in the first approximation.

Now the most simple method of treatment of the elastic scattering is to reduce the problem to the scattering under the spherically symmetric potential field which is obtained from the non-spherical potential by averaging over the orientations of two molecules. In fact, even if the two colliding molecules have the definite rotational angular momenta l, l' respectively, the z-components of these angular momenta will change from one particular collision to another and, therefore, the effective scattering process must be obtained by averaging over the quantum numbers m, m' which define the z-components of the angular momenta. The average of V' over m and m' leads, indeed, to the spherical potential which is independent of l and l'. Property speaking, however, the averaging must be made not for the potential, but for the cross section, and now we shall investigate the difference of these two averaging procedures, by assuming that l, l', L j (and of course J) are good quantum numbers.

We denote the averaged potential field by V_0, and the phase shifts of the scattered

wave from this field V_0 by δ_j. Then the scattering cross section for this potential is given by

$$Q_{el}^0=(4\pi/k^2)\sum_j(2j+1)\sin^2\delta_j\,, \tag{6·1}$$

k being the wave number. Next, we shall denote the phase shifts for the actual potential field*)

$$(J, j, L, l, l'\,|V'|\,J, j, L, l, l')$$

by

$$\delta_{jll'}^{JL}=\delta_j+\Delta\delta_{jll'}^{JL}\,,$$

and the cross section calculated by these phase shifts by

$$Q_{el}=Q_{el}^0+\Delta Q_{el}\,.$$

Q_{el}^0 is a function of the wave number k only, but Q_{el} depends on l, l', m, m' too. If $\Delta\delta$'s are assumed to be small, we can get from the equation (5·6) that

$$\Delta Q_{el}=(4\pi/k^2)\sum_j(2j+1)\sin 2\delta_j\sum_{J,L}(s_{J0\,m+m'}^{JL}\,s_{Lmm'}^{ll'})^2\,\Delta\delta_{jll'}^{JL} \tag{6·2}$$

in the first approximation. The change of the phase shifts appeared in this formula can be given by the integral

$$\Delta\delta_{jll'}^{JL}\fallingdotseq(1/k)\int_0^\infty dR|F_j(R)|^2\Delta V_{jll'}^{JL} \tag{6·3}$$

in the first approximation, where $\Delta V_{jll'}^{JL}$ means the potential change

$$\Delta V_{jll'}^{JL}=(J, j, L, l, l'\,|V'|\,J, j, L, l, l')-V_0$$

and $F_j(R)$ is the solution of the radial equation

$$\{d^2/dR^2+k^2-j(j+1)/R^2-2MV_0(R)\}F_j(R)=0, \tag{6·4}$$

which vanishes at the origin and is normalized as $\sin(kR-\frac{1}{2}j\pi+\delta_j)$ asymptotically. The formula (6·3) can be derived as follows. Let F_j' be the solution of the radial equation for a potential $V_0+\Delta V$, which is normalized as $\sin(kR-\frac{1}{2}j\pi+\delta_j+\Delta\delta_j)$ asymptotically. Multiplying F_j' from the left to (6·4) and multiplying F_j to

$$\{d^2/dR^2+k^2-j(j+1)/R^2-2M(V_0+\Delta V)\}F_j'(R)=0$$

and subtracting one from the other, we obtain

$$d/dR(F_j'\cdot kF_j/dR-F_j\cdot dF_j'/dR)=F_j\Delta VF_j'.$$

By noting that both F_j and F_j' vanish at the origin, we get by integration

$$(F_j'\cdot dF_j/dR-F_j\cdot dF_j'/dR)_{R=\infty}=\int_0^\infty dR\,F_j\,\Delta VF_j'$$

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* Matrix elements of V' do not depend on the sixth quantum number μ, because the latter quantity define the z-component of the total angular momentum, i.e., the orientation of the system as a whole, while V' depends only on the relative configuration of the two molecules. (See also Appendix III.)

the left hand side of which can be calculated easily, resulting $k \sin \Delta\delta_j$. This is yet a rigorous equation. Since $\Delta\delta_j$ have been assumed to be small we may put $\sin \Delta\delta_j \fallingdotseq \Delta\delta_j$, and also $F_j' \fallingdotseq F_j$ which results the above equation (6·3).

As is shown in the Appendix III, we can prove that

$$\sum_{mm'JL} (S^{JL}_{J0\,m+m'} S^{ll'}_{Lmm'})^2 \Delta V^{JL}_{jll'} = 0, \tag{6·5}$$

Thus, from (6·2), (6·3) and (6·5), we get immediately that

$$\sum_{mm'} \Delta Q_{el} \fallingdotseq 0 \tag{6·6}$$

in the first approximation. Therefore, we may calculate the cross section for the spherical potential V_0, instead of the non-spherical potential V' in the first approximation.

On the other hand, if $\Delta V^{JL}_{jll'}$ are assumed to be small, m and m' may be considered as the good quantum numbers. Then we may calculate the cross section from the equations

$$\{d^2/dR^2 + k^2 - j(j+1)/R^2\} f_{j0lml'm'} = 2M (j0lml'm'|V'|j0lml'm') f_{j0lml'm'}$$

corresponding to (2·5). In this approximation, the cross section is given by

$$Q_{el} = (4\pi/k^2) \sum_j (2j+1) \sin^2 \delta_j^{lml'm'}$$

and we can easily verify the same conclusion as before, i.e., $\sum_{mm'} \Delta Q_{el} \fallingdotseq 0$ by employing the relation

$$\sum_{mm'} \Delta V_j^{lml'm'} = 0$$

$$\Delta V_j^{lml'm'} \equiv (j0lml'm'|V'|j0lml'm') - V_0 .$$

In any case, if the anisotropic part of the intermolecular potential is small, the calculation of the scattering cross section, taking the anisotropy into account in the first approximation, leads to the same result as that obtained by using the averaged potential V_0.

In this connection, it must be noted that K. Ohno and the present author have investigated recently the thermal elastic collision between H_2 molecules at low temperatures.[17] They compared the cross section of para-para collision with that of para-ortho collision and found that the difference (6·2) of the total cross sections and also the corresponding difference in the cross sections for viscosity were very small indeed, though their calculations were based on direct evaluation of the phase shifts, without employing the approximate relation (6·3).

Of course, these conclusions will be broken if the anisotropy of the intermolecular potential is large. First of all, in such a case, the quantum numbers j, L etc. can not be considered as good quantum numbers. This makes the treatment of the scattering process very difficult because we have to solve a coupled set of differential equations. Now we shall proceed to discuss such more general cases.

First, we shall consider the special case in which j is yet a good quantum number, but L is not so. Then the wave equations have the form

$$\{d^2/dR^2+k^2-j(j+1)/R^2\}F_L=2M\sum_{L'}(L|V'|L')F_{L'}\,. \qquad (6\cdot7)$$

Furthermore, if V' has the property that the matrix elements of it can be written in a form

$$(L|V'(R)|L')=(L|u|L')v(R),$$

in which the first factor is independent of R, then the first factor must be hermitian and can be diagonalized by suitable unitary transformation. In this case, the equations (6·7) become a set of separated equations, and, therefore, become much easier to treat. But this is a special case. In the general case, we are not in such a fortunate situation, and also j is not good quantum number.

The change of j is, of course, a kind of elastic scattering for the observer. But it is rather close to the inelastic collision processes. Probably the jump of j will take place in the neighborhood of the classically closest distance R_0 and in this region the change of j means the apparent change of the kinetic energy by an amount $j(j+1)/2MR_0^2$ in the radial equation. Thus, in order to change the j-value, the wave length of the radial wave function must change suddenly in this region, which is just the feature of the inelastic processes. Therefore, j can be a good quantum number, only if the condition

$$\textit{change of } j(j+1)/2MR_0^2 \gg \textit{initial kinetic energy} \qquad (6\cdot8)$$

is valid or the anisotropy of the intermolecular potential, which causes the change of j, is extremely small. Unfortunately, the condition (6·8) is not insured to be valid in the thermal collisions at room temperature, even for the most favourable case, i.e., for the hydrogen.

Now the equations to be solved are

$$\{d^2/dR^2+k^2-j(j+1)/R^2\}F_{jL}(R)=2M\sum_{sN}(jL\cdots|V'|sN\cdots)F_{sN}(R). \qquad (6\cdot9)$$

Since this set of equations are linear, we can obtain the required solution by superposing the particular solutions with proper amplitudes and phases. Thus, we shall first consider the problem in which the incoming wave has the definite values of j and L. In the following, the solution of the equation

$$\{d^2/dR^2+k^2-j(j+1)/R^2\}F_{jL}(R)=2M(jL\cdots|V'|jL\cdots)F_{jL}(R) \qquad (6\cdot10)$$

satisfying the boundary conditions

$$F_{jL}(0)=0, \quad F_{jL}(R)\sim\sin(kR-\tfrac{1}{2}j\pi+\delta_j) \quad (R\to\infty) \qquad (6\cdot11)$$

will be denoted by F_{jL}^0, and the deviations due to the non-diagonal matrix elements of V' by δF_{jL}. Then we have

$$\begin{aligned}&\{d^2/dR^2+k^2-j(j+1)/R^2-2M(jL|V'|jL)\}\delta F_{jL}=2M\sum_{sN\neq jL}(jL|V'|sN)\delta F_{sN},\\&\{d^2/dR^2+k^2-s(s+1)/R^2-2M(sN|V'|sN)\}\delta F_{sN}\\&\qquad=2M\sum_{pQ\neq sN}(sN|V'|pQ)\delta F_{pQ}+2M(sN|V'|jL)F_{jL}^0.\end{aligned} \qquad (6\cdot12)$$

Assuming that F_{jL}^0 is a quantity of zeroth order and V' is a small quantity of the first

order, we can see that δF_{sN} $(sN \neq jL)$ are of the first order and δF_{jL} is a second order small quantity. Thus in the first approximation, (6·12) become

$$\begin{aligned} &\delta F_{jL}=0\,, \\ &\{d^2/dR^2+k^2-s(s+1)/R^2-2M(sN|V'|sN)\}\delta F_{sN}=2M(sN|V'|jL)F_{jL}^0\,. \end{aligned} \tag{6·13}$$

The first of these equations means that the damping effect is not taken into account in this approximation, while the second equation can be solved formally and its solution which represents the outgoing wave asymptotically is given by[18]

$$\delta F_{sN}=-G_{sN}(R)\int_0^R F_{sN}^0(R)(sN|V'|jL)F_{jL}^0(R)\,dR \tag{6·14}$$

where G_{jL} is the solution of the equation (6·10) which is normalized asymptotically as $(1/k)\exp\{i(kR-\frac{1}{2}j\pi+\delta_j)\}$. Thus the asymptotic form of δF_{sN} is

$$\delta F_{sN}\sim(1/k)\exp\{i(kR-\tfrac{1}{2}j\pi+\delta_s)\}\int_0^\infty F_{sN}^0(sN|V'|jL)F_{jL}^0 dR\,. \tag{6·15}$$

Now we shall return to our problem in which the plane wave is incoming. In this case the solution in the zeroth approximation is given by the linear combination of F_{jL}^0 with the coefficients

$$s_{J0\,m+m'}^{jL}\,s_{Lmm'}^{ll'}\,[4\pi(2j+1)]^{1/2}i^j\exp(i\delta_j)/k\,.$$

(See the asymptotic form of $\bar{F}$ in the previous section.) Thus the asymptotic form of the solution in the first approximation is given by

$$\begin{aligned} F_{jL}^{(J)}\sim(\sqrt{4\pi}/k)\Big[&s_{J0\,m+m'}^{jL}\,s_{Lmm'}^{ll'}(2j+1)^{1/2}i^j\exp(i\delta_j)F_{jL}^0 \\ &+\sum_{sN}s_{J0\,m+m'}^{sN}\,s_{Nmm'}^{ll'}(2s+1)^{1/2}i^s\exp(i\delta_s)\,(1/k)\exp\{i(kR-\tfrac{1}{2}j\pi+\delta_j)\} \\ &\times\int_0^\infty F_{jL}^0(jL|V'|sN)F_{sN}^0 dR\Big]\,. \end{aligned}$$

This solution being equated with $\bar{F}_{jjL}^{lml'm'}+E_{jjL}^{lml'm'}$ in the previous section, we have the scattering matrix

$$\begin{aligned} S_{jjL}^{lml'm'}=\exp(2i\delta_j)+(2/k)\sum_{sN}&(s_{J0\,m+m'}^{sN}\,s_{Nmm'}^{ll'}/s_{J0\,m+m'}^{jL}\,s_{Lmm'}^{ll'})\times \\ &(2s+1/2j+1)^{1/2}i^{s-j+1}\exp(i\delta_j+i\delta_s)\times \\ &\int_0^\infty F_{jL(ll')}^{(J)0}(JjLll'|V'|JsNll')F_{sN(ll')}^{(J)0}dR\,. \end{aligned} \tag{6·16}$$

Substitution of this expression into (5·4) yields the formula for Q_{el}.

The approximate solution thus obtained may be substituted in the right hand side of (6·12), giving the equation for the second approximation, though the solution will become more complex. If the second order correction terms thus calculated are not small enough compared with the first order correction δF_{jL}, this successive approximation method may be impracticable, because we must investigate whether the next, i.e. the third, approximation terms are small or not. Unfortunately, however, we have no general method to solve a set of differential equations in other way. Stueckelberg[19] reduced the coupled pair of

differential equations to a higher order equation and solve the latter by means of WKB approximation method, while Massey and Mohr[20] solved directly the coupled pair of differential equations for a simplified case. But these methods are hard to extend to the set of a number of coupled equations.

Finally, it must be noted that the non-diagonal elements which cause the inelastic collision processes may also affect the elastic collision cross section, even if the inelastic processes are forbidden energetically. In other words, some excited states may appear virtually in the intermediate stage of collision. This effect also force us to solve the set of equations in the general case, but, if this effect is not so large, we may employ the second order perturbation method. On the other hand, if this effect is large enough, the two molecules can no longer continue their free rotations and a particular relative orientation becomes favourable during the collision, which means the temporary excitation of the upper rotational states. In such a case, the method of p.s.s. (perturbed stationary state), which is familiar in the theory of atomic collisions,[21] may be more reasonable procedure of solution than the ordinary perturbation method. The essential point of this p.s.s. method is very simple. In this method, the total wave function is expanded in terms of the proper functions of

$$\left\{-\frac{1}{2\mu_1}\nabla_1^2-\frac{1}{2\mu_2}\nabla_2^2+V_1(\xi_1)+V_2(\xi_2)+V'-E(R,\,\theta,\,\Phi)\right\}\Psi=0,$$

while according to the method in the previous sections the proper functions of

$$\left\{-\frac{1}{2M}\nabla_R^2-\frac{1}{2\mu_1}\nabla_1^2-\frac{1}{2\mu_2}\nabla_2^2+V_1(\xi_1)+V_2(\xi_2)-E\right\}\Psi=0$$

are employed. In the former of these equations, the values of $(R,\,\theta,\,\Phi)$ are fixed, and the kinetic energy of the relative motion of two molecules is treated as the perturbation, while in the latter method the intermolecular potential is considered as the perturbation. The general formulation of the problem according to the p.s.s. method can be given straightforwardly, but we shall not enter this problem further.

§ 7. General discussions on the inelastic collisions

The problem of the inelastic collisions is the most interesting part of our collision problem, because the inelastic processes depend essentially on the internal structures of the colliding molecules, while the main features of the elastic collisions have been obtained already from the rigid sphere model or from other spherical fields. Unfortunately, however, the straightforward calculations of the cross sections for the inelastic processes impel us to carry out the overwhelmingly hard work. Thus the simplifying assumptions must be introduced before the practical calculations.

Now the cross sections for the inelastic collisions are influenced remarkably by the following two factors. The first is the overlaping between the initial and the final translational wave functions. Applying the Born approximation for simplicity, the transition probability will proportional to the absolute square of the matrix element

$$V_{if}=\int \exp\{-i(\boldsymbol{k}_f-\boldsymbol{k}_i)\boldsymbol{R}\}\cdot(\alpha_f|V'(\boldsymbol{R})|\alpha_i)d\boldsymbol{R}$$

where α_i, α_f indicate the internal state of the molecules; $\boldsymbol{k}_i$, $\boldsymbol{k}_f$ the wave numbers in the initial and the final states respectively. In the thermal collisions, the wave length of the relative motion of the two molecules is usually less than 1 A.U., while the matrix element $(\alpha_f|V'|\alpha_i)$ changes more slowly as a function of R. Thus, V_{if} will be small in absolute value, unless $\Delta\boldsymbol{k}=\boldsymbol{k}_f-\boldsymbol{k}_i$ is small. Of course, the Born approximation is not adequate for the molecular collisions in the thermal energy region, but the essential feature must not be changed when the plane wave $\exp(i\boldsymbol{kR})$ is replaced by the suitable distorted wave. Thus, we may conclude that if the difference between the wave number of the initial translational motion and that of the final one is very large, the transition probability will be very small.

It is easy to see that the inelastic collision can hardly occur in the low energy collisions. For endothermic reactions, transition can not take place, of course, if the initial energy is less than the threshold energy. If the initial energy is just above the threshold one, the change in the wave number will be large. And even for the exothermic reactions, the wave number will change appreciably if the initial kinetic energy is not large enough. In another words, in order to get the large probability for transition, the initial kinetic energy must be large enough compared with the energy change in the inelastic process. On the other hand, if the initial velocity is extremely large, there will be no time for the transition to take place during the collision and, therefore, the cross section will be small. The cross section may become large for a intermediate region between these two extreme cases.

The second factor which influences the inelastic collision cross section is the dependence of the intermolecular force potential on the coordinate in which the transition takes place. Thus in order that the vibrational transition takes place with an appreciable probability, a small change in the internuclear distance of a molecule must bring the considerable change in the intermolecular force and in order to have the rotational transition it is necessary that the molecular potential deviates very much from the spherical symmetry. Now the intermolecular potential which is effective for the thermal collisions is determined by the electron distributions in the outermost shells of both molecules. It is clear that in a molecule the force field, under which the outermost electron moves, is something like the Coulomb field of the hydrogen nucleus which is placed in the center of the molecule, especially when the electron considered is far apart from the center. It means that the molecular orbital for the outermost electron will become something like hydrogen-atomic-orbital asymptotically and does not depend very much on the nuclear distance and on the orientation of the molecular axes. For this reason, the intermolecular force becomes rapidly spherically symmetric for the larger values of the intermolecular separation, and also becomes independent of the internuclear distances in the two molecules. Therefore, in order that the inelastic process takes place, two molecules must approach closely to each other and also for this sake the incident energy must be large.

Now the vibrational level spacings in the ordinary diatomic molecules are much larger

than the energy of the thermal motion in the room temperature. Thus, it is expected from the above considerations, that the transition probability is very small under the ordinary thermal condition. This expectation has been confirmed by the experimental data mentioned in the beginning of the last section. The rotational transition in the hydrogen molecule also takes place with very small probability because of its rather large level spacing.*) Thus for the vibrational transitions in the ordinary diatomic molecules and for the rotational transitions in some special molecules such as H_2, the first order approximation in the perturbation method i.e. the method of distorted wave may be applied to calculate the cross sections, while for the rotational transitions in the other molecules we must solve a coupled set of equations because the transition probabilities are rather large for these cases. Of course, the straightforward solution of such set of differential equations is very difficult as was seen in the elastic scattering problem and we must simplify the problem as far as possible before solving it. For these cases with small level spacings, the translational energy does not change appreciably in the transition process. Furthermore, the motion of a molecule as a whole is very similar to that of the classical particle, having a rather definite orbit with a definite velocity, because of its large mass. Therefore, the translational motion may be treated approximately in the classical manner, i.e., we may determine the translational motion by solving the classical equation of motion under the averaged potential field. Then the relative distance of the two molecules is given by a function of the time. The transition will be caused by the time-dependent perturbation. Such semi-classical treatments of the inelastic collision processes have been reported frequently by many authors.[24] These authors have investigated only the first order perturbation problem by this method. But the strong coupling case may also be treated in this way, if the kinetic energy does not change appreciably during the collision.

§ 8. Rotational transitions

Now we shall consider the rotational transitions disregarding the vibrational degrees of freedom. The special case of H_2 can be treated by the distorted wave approximation in exactly the same way as in the vibrational transitions which are discussed in the next section. In this paper, therefore, we shall confine ourselves to mention that the problem of H_2 has been investigated by Roy and Rose previously[11] and a little more thorough calculations have also been made recently by the present author.[14]

In the following we shall consider the rotational transition in which the energy exchange between the translation and the rotation is rather small. We shall employ the semi-classical method, as discussed above. For this sake, we must start from the time-dependent Schroedinger equation:

$$i\,\partial\Psi/\partial t=\{(-1/2M)\nabla_R^2+H_0+V'\}\Psi\,, \qquad (8\cdot1)$$

* It is well known that the transition between para- and ortho-hydrogens is usually forbidden. Thus the rotational transition between the neighboring levels is forbidden in the hydrogen molecule. This fact, together with the small moment of intertia, makes the effective level spacings very large. The experimental evidence for the small transition probability in H_2 have been given by Stewart[22] and Rhodes.[23]

where H_0 means the Hamiltonian operator for the internal degrees of freedom of the two colliding molecules. The wave function Ψ may be expanded as

$$\Psi(\boldsymbol{R}, X_1, X_2, t) = \sum_{\alpha'\alpha''} \zeta_{\alpha'}(X_1)\zeta_{\alpha''}(X_2)(2\pi)^{-3/2}$$

$$\times \int f_{\alpha'\alpha''}(\boldsymbol{k}, t)\exp\{i\boldsymbol{k}\boldsymbol{R} - i(E_k + E_{\alpha'} + E_{\alpha''})t\}\, d\boldsymbol{k} \qquad (8\cdot2)$$

or

$$= \sum_{\alpha} \zeta_{\alpha}(X)(2\pi)^{-3/2}\int f_{\alpha}(\boldsymbol{k}, t)\exp\{i\boldsymbol{k}\boldsymbol{R} - i(E_k + E_{\alpha})t\}\, d\boldsymbol{k} \qquad (8\cdot2\text{a})$$

for brevity, where $\zeta_{\alpha'}(X_1)\zeta_{\alpha''}(X_2)$ (or $\zeta_{\alpha}(X)$) stand for the orthonormalized internal wave functions and

$$E_k = k^2/2M, \quad E_{\alpha} = \textit{internal energy in the state } \alpha.$$

By inserting (8·2a) into (8·1), and taking the equation

$$\{(-1/2M)\nabla_R^2 + H_0\}\exp(i\boldsymbol{k}\boldsymbol{R})\zeta_{\alpha}(X) = (E_k + E_{\alpha})\exp(i\boldsymbol{k}\boldsymbol{R})\zeta_{\alpha}(X) \qquad (8\cdot3)$$

into account, we get

$$i\sum_{\alpha}\zeta_{\alpha}(X)\int\frac{\partial f_{\alpha}}{\partial t}\exp\{i\boldsymbol{k}\boldsymbol{R} - i(E_k + E_{\alpha})t\}\, d\boldsymbol{k}$$

$$= V'\sum_{\alpha'}\zeta_{\alpha'}(X)\int f_{\alpha'}\exp\{i\boldsymbol{k}'\boldsymbol{R} - i(E_{k'} + E_{\alpha'})t\}\, d\boldsymbol{k}'$$

which gives, by the orthonormality of $\zeta_{\alpha}(X)$,

$$i\int\frac{\partial f_{\alpha}}{\partial t}\exp(i\boldsymbol{k}\boldsymbol{R} - iE_k t)\, d\boldsymbol{k} = \sum_{\alpha'}(\alpha|V'|\alpha')\int f_{\alpha'}\exp\{i\boldsymbol{k}'\boldsymbol{R} - iE_k t + i\Delta E_{\alpha\alpha'}t\}\, d\boldsymbol{k}' \qquad (8\cdot4)$$

where

$$(\alpha|V'|\alpha') = \int\zeta_{\alpha}^*(X)\, V'\zeta_{\alpha'}(X)\, dX, \quad \Delta E_{\alpha\alpha'} = E_{\alpha} - E_{\alpha'}.$$

Now the function

$$\varphi_{\alpha}(\boldsymbol{R}, t) = (2\pi)^{-3/2}\int f_{\alpha}(\boldsymbol{k}, t)\exp(i\boldsymbol{k}\boldsymbol{R} - iE_k t)\, d\boldsymbol{k} \qquad (8\cdot5)$$

represents the wave packet and we may assume that this function takes the appreciable values only in the limited region in space for each time t.

Here we shall factorize the function f_{α} in the following way:

$$f_{\alpha} = C_{\alpha}\cdot f_{\alpha}^0, \qquad (8\cdot6)$$

$$\int|f_{\alpha}^0|^2\, d\boldsymbol{k} = 1, \qquad (8\cdot6\text{a})$$

$$i\int\frac{\partial f_{\alpha}^0}{\partial t}\exp(i\boldsymbol{k}\boldsymbol{R} - iE_k t)\, d\boldsymbol{k} = (\alpha|V'|\alpha)\int f_{\alpha}^0\exp(i\boldsymbol{k}'\boldsymbol{R} - iE_{k'}t)\, d\boldsymbol{k}' \qquad (8\cdot7\text{b})$$

i.e., f_{α}^0 is a solution representing the elastic scattering. Generally speaking, $C_{\alpha}\cdot f_{\alpha}^0$ cannot be a solution of (8·4) if C_{α} is a function of the time t only. But since all important

contributions come from the small values of $\Delta E_{\alpha\alpha'}$, the velocity of the center of wave packet will not change appreciably when an inelastic transition takes place and, therefore, if we further assume that the potential $(\alpha|V'|\alpha)$ does not depend very much on the internal state α, we can conclude that the wave packet will not deviate appreciably from that for the elastic scattering. In such a case, we can assume that C_α is a function of the time t only and does not depend on $\boldsymbol{R}$. This is the essential assumption in our semi-classical treatment. Corresponding to (8·6), we have the normalized wave packet

$$\varphi_\alpha{}^0(\boldsymbol{R}, t)=(2\pi)^{-3/2}\int f_\alpha{}^0 \exp(i\boldsymbol{k}\boldsymbol{R}-iE_k t)d\boldsymbol{k}$$

and

$$\int|\varphi_\alpha{}^0|^2 d\boldsymbol{R}=\int|f_\alpha{}^0|^2 d\boldsymbol{k}=1.$$

Thus the equation (8·4) is transformed into

$$i\,\partial C_\alpha/\partial t=\sum_{\alpha'\neq\alpha} C_{\alpha'}\exp(i\Delta E_{\alpha\alpha'}t)\int\varphi_\alpha{}^{0*}(\boldsymbol{R}, t)\cdot(\alpha|V'|\alpha')\varphi_{\alpha'}{}^0(\boldsymbol{R}, t)d\boldsymbol{R}\,. \quad (8\cdot7)$$

Strictly speaking, $\varphi_\alpha{}^0$ and $\varphi_{\alpha'}{}^0$ do not completely coincide with each other for any finite time interval, but owing to our assumptions, these wave packets will not shift appreciably from each other during the collision time, so that we can replace them by an averaged wave packet $\varphi^0(\boldsymbol{R}, t)$. Finally, in the semi-classical treatment, $|\varphi^0(\boldsymbol{R}, t)|^2$ must be replaced by

$$\delta(\boldsymbol{R}-\boldsymbol{R}(t)).$$

$\boldsymbol{R}=\boldsymbol{R}(t)$ describes a classical orbit under the averaged potential $(\alpha|V'|\alpha)_{\mathrm{AV}}$, averaging being taken over various internal states. Generally $(\alpha|V'|\alpha)$ depends on the direction of the vector $\boldsymbol{R}$ and this dependence causes the coupling between the orbital angular momentum and the rotational angular momenta. By averaging over the various states, however, $(\alpha|V'|\alpha)_{\mathrm{AV}}$ becomes spherically symmetric which depends only on $R=|\boldsymbol{R}|$. Of course the motion of the center of wave packet will not be affected considerably even if the orbital angular momentum quantum number j changes to some extent. But if the change in j helps or reduces the inelastic transition, we can not neglect this effect and we must employ the sum

$$\sum_{j'}(\alpha, j|V'|\alpha', j')\exp\{i(\eta_{j'}-\eta_j)\}$$

instead of $(\alpha|V'|\alpha')$ for each value of j (or corresponding impact parameter b, classically). Unfortunately, it is not easy to determine the phase shifts η_j for the present case, because of the strong coupling among many states. Therefore we must employ some averaged value of this summation, e.g.

$$\{\sum_{j'}(\alpha, j|V'|\alpha', j')^2\}^{1/2}.$$

In order to make the resulting expression hermitian, it is convenient to modify this furthermore as follows

$$\{\tfrac{1}{2}\sum_{j'}(\alpha, j|V'|\alpha', j')^2+\tfrac{1}{2}\sum_{j'}(\alpha, j'|V'|\alpha', j)^2\}^{1/2},$$

Finally, if we consider the definite transition $\alpha_0 \to \alpha$, the initial velocity of the classical motion may be equated with the averaged value of the true initial and the true final velocities. But if we consider the many processes, some of which are exciting and some others are deactivating processes, the true initial velocity may be taken conveniently as the asymptotic velocity of the classical motion.

After these discussions, the equation (8·7) takes the following final form

$$i\,\partial C_\alpha/\partial t = \sum_{\alpha' \neq \alpha} (\alpha|V'(\boldsymbol{R}_b(t))|\alpha')\, C_{\alpha'} \exp(i\Delta E_{\alpha\alpha'} t), \tag{8·8}$$

where the suffix b indicates the value of the impact parameter. We can confirm easily from this set of equations that the total probability $\sum_\alpha |C_\alpha|^2$ is independent of the time t (as is required), if the matrix $(\alpha|V'|\alpha')$ is hermitian.

For the weak coupling case, this set of equations is approximated by

$$i\,\partial C_\alpha/\partial t = (\alpha|V'|\alpha_0)\, C_{\alpha_0} \exp(i\Delta E_{\alpha\alpha_0} t) \quad \textit{for} \quad \alpha \neq \alpha_0,$$
$$C_{\alpha_0} = 1.$$

α_0 being the initial internal state. This gives

$$|C_\alpha(b)|^2_{t\to\infty} = \left|\int_{-\infty}^{\infty} (\alpha|V'(\boldsymbol{R}_b(t))|\alpha_0) \exp(i\Delta E_{\alpha\alpha_0} t)\, dt\right|^2 \tag{8·9}$$

and the cross section for the process $\alpha_0 \to \alpha$ is given by

$$Q(\alpha_0 \to \alpha) = 2\pi \int_0^\infty |C_\alpha(b)|^2_\infty\, b\, db. \tag{8·10}$$

The formula (8·9), (8·10) are employed previously by Zener and others and quite recently by Widom and Bauer.[24]

If there is a group of a few states $\alpha_1, \alpha_2, \cdots$ which couple with the initial state α_0 strongly, and if the probabilities of the second order processes of the type : $\alpha_0 \to$ a state α_t in this group $\to$ a state outside this group are small, we may first solve the equation (8·8) for the states $\alpha_0, \alpha_1, \alpha_2, \cdots$ only. This solution is performed, if necessary, by numerical calculation. Then the final probability amplitudes for the other states may be obtained by

$$|C_\alpha(b)|^2_\infty = \left|\int_{-\infty}^{\infty} \sum_G (\alpha|V'|G) \exp(i\Delta E_{\alpha G} t)\, C_G(t)\, dt\right|^2, \quad (G \equiv \alpha_0, \alpha_1, \cdots). \tag{8·11}$$

If there are many states which couple with each other considerably, we must solve a set of many coupled equations. For such a case, we shall propose here an approximate procedure of solution, which will serve to reduce the laborious calculations.

Before proceeding further, we shall write the equation (8·8) in the matrix form

$$i\,\partial \mathbf{C}(t)/\partial t = \mathbf{A}^b(t) \cdot \mathbf{C}(t), \tag{8·12}$$

where $\mathbf{C}$ is an one-column matrix and $\mathbf{A}^b$ is a square matrix,

$$A^b_{\alpha\alpha'} = (\alpha|V'(\boldsymbol{R}_b(t))|\alpha') \exp(i\Delta E_{\alpha\alpha'} t),$$

all diagonal elements being lacking. Clearly this is a hermitian matrix. Now if $\mathbf{A}(t)$

and $\int_{-\infty}^{t}\mathbf{A}(t')dt'$ commute, we can get the formal solution of the equation (8·12) as follows[25]

$$\mathbf{C}(t)=\exp\left[-i\int_{-\infty}^{t}\mathbf{A}(t')dt'\right]\cdot\mathbf{C}(-\infty). \tag{8·13}$$

Here $\exp[\mathbf{M}]\equiv\sum_{0}^{\infty}\mathbf{M}^{\nu}/\nu!$, $\mathbf{M}^{\nu}$ being defined by the ordinary matrix multiplication rule. In our present case,

$$\left[\mathbf{A}(t)\int_{-\infty}^{t}\mathbf{A}(t')dt'\right]_{\alpha\alpha'}=\sum_{\alpha''}(\alpha|V'(t)|\alpha'')\exp(i\Delta E_{\alpha\alpha''}t)\times\int_{-\infty}^{t}(\alpha''|V'(t')|\alpha')\exp(i\Delta E_{\alpha''\alpha'}t')dt', \tag{8·14a}$$

$$\left[\int_{-\infty}^{t}\mathbf{A}(t')dt'\cdot\mathbf{A}(t)\right]_{\alpha\alpha'}=\sum_{\alpha''}\int_{-\infty}^{t}(\alpha|V'(t')|\alpha'')\exp(i\Delta E_{\alpha\alpha''}t')dt'\times(\alpha''|V'(t)|\alpha')\exp(i\Delta E_{\alpha''\alpha'}t). \tag{8·14b}$$

Generally speaking, these are not equal with each other, and, therefore, (8·13) can not be an exact solution of our problem. But if these two expressions are nearly equal, we may adopt (8·13) as an approximate solution. Now in many calculations we may put approximately that

$$(\alpha|V'(t)|\alpha')=(\alpha|v|\alpha')\cdot f(t),$$

v being independent of t. In this case, (8·14a) and (8·14b) become

$$\sum_{\alpha''}(\alpha|v|\alpha'')(\alpha''|v|\alpha')\int_{-\infty}^{t}f(t)f(t')\exp(i\Delta E_{\alpha\alpha''}t+i\Delta E_{\alpha''\alpha'}t')dt', \tag{8·15a}$$

$$\sum_{\alpha''}(\alpha|v|\alpha'')(\alpha''|v|\alpha')\int_{-\infty}^{t}f(t)f(t')\exp(i\Delta E_{\alpha\alpha''}t'+i\Delta E_{\alpha''\alpha'}t)dt' \tag{8·15b}$$

respectively. Here we must take the following two effects into consideration. The first is the general tendency that if the two sets of quantum numbers α and α' are extremely different from each other, the matrix element $(\alpha|v|\alpha')$ is vanishingly small. This tendency is concluded from the reasonable expectation that in the expression (3·9) for the intermolecular force potential, the main contribution comes from the smaller values of α, β and γ. The second effect is due to the oscillating factor $\exp(i\Delta Et)$. If the two states α and α' being to the extremely different energy values, the integral of the form

$$\int_{-\infty}^{t}f(t')\exp(i\Delta E_{\alpha\alpha'}t')dt'$$

must be vanishingly small, because $f(t')$ is a rather gentle function usually. Now if the first effect dominates, the main contributions to the expressions (8·15a), (8·15b) come from the region:

$$\alpha''\simeq(\alpha+\alpha')/2$$

(this equality means, more or less symbolically, that α'' is a set of quantum numbers which is intermediate between α and α'). On the other hand, if the second effect predominates, main contribution to (8·15a) comes from $\alpha''\simeq\alpha'$ and for (8·15b), $\alpha''\simeq\alpha$.

In both extreme cases, the two expressions (8·15a) and (8·15b) are not completely coincide with each other, but, at the same time, we can not find out any essential difference between them. Thus we may conclude that (8·13) can not be an exact solution, but may be an approximate solution. In order to make sure, the validity of this formula must be examined for each special problem.

By employing (8·13), we can get the desired result

$$C_\alpha(t=+\infty)=\left[\exp\left[-i\int_{-\infty}^{\infty}\mathbf{A}(t)dt\right]\right]_{\alpha\alpha_0} \tag{8·16}$$

or

$$\mathbf{C}(\infty)=\mathbf{C}(-\infty)+\frac{1}{i}\int_{-\infty}^{\infty}\mathbf{A}(t')dt'\cdot\mathbf{C}(-\infty)-\frac{1}{2}\left\{\int_{-\infty}^{\infty}\mathbf{A}(t')dt'\right\}^2\cdot\mathbf{C}(-\infty)-\cdots, \tag{8·16a}$$

while the solution by the successive approximation is given by

$$\mathbf{C}(\infty)=\mathbf{C}(-\infty)+\frac{1}{i}\int_{-\infty}^{\infty}\mathbf{A}(t')dt'\cdot\mathbf{C}(-\infty)-\int_{-\infty}^{\infty}dt\int_{-\infty}^{t}dt'\mathbf{A}(t)\mathbf{A}(t')\cdot\mathbf{C}(-\infty)-\cdots. \tag{8·17}$$

The calculation of the series (8·16a) is much easier to do than that of (8·17).

Finally, even if our approximation leads to a rather good result, we must perform such calculation for many values of impact parameter b. We can reduce, however, the number of such calculations by the same device as we employ in the modified wave number method in the next section. In another words, we can reduce the collision problem from the three-dimensional space to the head-on collison problem (of course, one-dimensional) by replacing the effective kinetic energy

$$p_0^2/2M-p_0^2b^2/2MR^2$$

with

$$\tilde{p}_0^2/2M, \quad \tilde{p}_0^2=\{1-(b^2/R_0^2)\}p_0^2,$$

where p_0 is the initial momentum and R_0 is a suitable constant radius, the transition probabilities being neglected for $b\geqq R_0$.

§ 9. Vibrational transition

As mentioned above, the distorted wave method is appropriate for calculating the cross section for the vibrational transition. Thus we may proceed as follows: In the equation (2·10), i.e.,

$$\{d^2/dR^2-s(s+1)/R^2+k_\beta^2-2M(\beta|V'|\beta)\}F_\beta=\sum_{\beta'\neq\beta}2M(\beta|V'|\beta')F_{\beta'}, \tag{9·1}$$

we substitute in the right hand side the solution which is obtained by disregarding the vibrational transition. The resulting equation is for the unknown function F_β, for which the vibrational state is different from the initial state. Of course, it is desirable that the possibility of the rotational transition has already included in the zeroth order function which must be inserted in the right hand side. But to solve the problem of the rotational

transition is not easy matter as we have seen in the previous section. On the other hand, the distortion of the rotational wave functions will not considerably affect the vibrational transition, if the result is averaged over the initial rotational state. Thus it is convenient to employ the wave function corresponding to a pure rotational state, i.e., $F_{\beta'}$ are the solution of

$$\{d^2/dR^2-j(j+1)/R^2+k_{\beta'}{}^2-2M(\beta'|V'|\beta')\}F_{\beta'}=0 \qquad (9\cdot2)$$

$$\beta'\equiv(J,\ \mu,\ n,\ n',\ j,\ L,\ l,\ l')$$

and are normalized asymptotically as

$$F_{\beta'}\sim s^{jL}_{J0\ m+m'}\,s^{\mu l'}_{Lmm'}\,[4\pi(2j+1)]^{1/2}i^j k_{\beta'}^{-1}\sin(k_{\beta'}R-j\pi/2+\delta_{\beta'}). \qquad (9\cdot3)$$

(See § 5.)

In this way, the right hand side of (9·1) may be calculated and become a known function. Then the outgoing wave F_β can be determined as usual[18] and we have the asymptotic form of F_β as follows:

$$F_\beta\sim-2M\exp\{i(k_\beta R-s\pi/2+\delta_\beta)\}\int_0^\infty F_\beta{}^0(R)\sum_{\beta'}(\beta|V'|\beta')F_{\beta'}(R)dR\,, \qquad (9\cdot4)$$

where $F_\beta{}^0$ is the solution of the homogeneous equation which is derived from (9·1) by putting the right hand side zero, and is normalized asymptotically as

$$k_\beta^{-1}\sin(k_\beta R-s\pi/2+\delta_\beta). \qquad (9\cdot5)$$

Thus the cross section for the transition $(n,\ l,\ m\,;\ n',\ l',\ m')\to(p,\ q\,;\ p',\ q')$ is given by

$$(k_\beta/k_{\beta'})\iiint|\sum_{JsN}F^{J\mu pp'}_{sNqq'}(R\to\infty)\,\boldsymbol{Y}^{J\mu}_{sNqq'}|^2\,d\Omega\,d\Omega_1\,d\Omega_2$$

$$=(k_\beta/k_{\beta'})\sum_{JsN}|2M\int_0^\infty F_\beta{}^0(R)\sum_{\beta'}(\beta|V'|\beta')F_{\beta'}(R)\,dR|^2.$$

$$[\mu\equiv m+m',\ \beta\equiv(J,\ \mu,\ p,\ p',\ s,\ N,\ q,\ q')]$$

Then by averaging this over m, m', we get the cross section for the inelastic process $(n,\ l\,;\ n',\ l')\to(p,\ q\,;\ p',\ q')$:

$$Q(n,\ l,\ n',\ l'\to p,\ q,\ p',\ q')=(k_\beta/k_{\beta'})[4M^2/(2l+1)\,(2l'+1)]\times$$

$$\sum_{mm'}\sum_{JsN}|\int_0^\infty F^{0\,J\mu pp'}_{sNqq'}\sum(Jpp'sNqq'|V'|Jnn'jLll')F^{J\mu nn'}_{jLll'}\,dR|^2. \qquad (9\cdot6)$$

In principle, this formula can be applied without difficulty to any particular problem. The most difficult thing to do is the determination of the distorted waves, $F_\beta{}^0$, $F_{\beta'}$ and these functions can be obtained by solving the ordinary differential equations numerically. Nevertheless, here is a practical difficulty, because the number of differential equations to be solved is enormous. Such situation arises from the fact that a large number of the states which are defined by j, l, l' and L contribute appreciably to the collision process in the room temperature. If we know the rather exact potential V' and want to get the rigorous cross section as far as possible, we must not hesitate to find out these distorted

waves one by one. Otherwise, however, it is desirable to seek for some simplifying procedures.

In the first place, we may neglect the difference in the potential function V' for the different rotational states, i.e., we may employ the distorted waves which are distorted by the averaged potential V_0 defined in § 6. If we adopt this simplification, the distorted wave $F_{\beta'}$ does not depend on J, μ and L and depend on n, n', l, l' through the wave number $k_{\beta'}$ only. Similar situation is also obtained for F_{β}^{0}. Yet, there remain many states with different j-values. The best way in this stage of approximation is to carry out the integration $\int\cdots dR$ in the above formula for some j-values and to obtain the integrals for the other j-values by the interpolation procedure. This interpolation will be a good method of simplification, because it is unlikely that the integral $\int\cdots dR$ fluctuates very much when j changes, though some fluctuations may be expected.

If we want to make further simplifications, we must give up the desire to follow the formula (9·6). By making such simplifications, we must also give up, more or less, to obtain the quantitative results. Before proceeding to discuss some such simplifications we shall consider the general features of the vibrational transitions.

According to the kinetic theory of gases, the probability that the initial translational energy in the thermal collision is lying in the region E, $E+dE$, is independent of the reduced mass and the mean kinetic energy of the relative motion is $2\kappa T$ (κ is the Boltzmann constant; T, the absolute temperature), though the collision number depends on the reduced mass. Thus we may roughly consider that the initial kinetic energy is always $2\kappa T$. Then $k^2=2M\cdot E$ is proportional to the reduced mass M. Therefore, if we compare the equations of the form (9·2) for the two cases with different reduced masses M and M' providing that the intermolecular force and the excitation energy are same for both cases, we can get the similar wave functions $F(kR)$, $F(k'R)$ for the suitable pair of quantum numbers j, j' where $j:j'\fallingdotseq\sqrt{M}:\sqrt{M'}$. In this case, the wave function for the larger reduced mass oscillates more frequently than the other. If we take the same j-value, this contrast becomes more remarkable. Now in contrast to this rather rapid oscillation of the radial wave functions, the variation of the potential energy curve as the function of R is usually gentle, at least for the collisions in the room temperature. Therefore, the integral in (9·6) decreases if the reduced mass increases, providing that the radial wave functions are always normalized asymptotically to be sinusoidal functions of the amplitude unity, or a constant amplitude independent of the reduced mass. Of course, the wave functions in our formula (9·6) are normalized in such a way that they are inversely proportional to the wave number k asymptotically. But, on the other hand, these normalization factors are cancelled out by the factor M^2 outside the absolute square. Thus we may conclude that the cross section increases if the reduced mass decreases providing that the other quantities remain unchanged. We may also say that lighter molecules are more effective to deactivate the vibrational excitation of the particular collision partner.

We shall next consider the effect of the magnitude of ΔE, i.e., the energy change due to the transition and also the effect of the initial wave number, providing that the reduced mass is unchanged. For this sake, however, we shall confine ourselves to the one-

dimensional collision problem*), and furthermore to the intermolecular potential of the form $A\exp(-aR)$. Then the transition probability per collision is given by Jackson-Mott's formula[26]

$$P=\text{const.}\ (q_f^2-q_i^2)^2 \sinh \pi q_f \sinh \pi q_i/(\cosh \pi q_f-\cosh \pi q_i)^2, \qquad (9\cdot7)$$

$$i\cdots initial,\quad f\cdots final.$$

Here, $q=2k/a$ and $q\gg1$ in all cases of importance. Furthermore, in the usual cases $\exp(\pi q_f)\gg\exp(\pi q_i)$ for the deactivation process and $\exp(\pi q_f)\gg\exp(\pi q_i)$ for the excitation process, because the change of the energy ΔE is very large. Because of these situations, we have

$$\begin{aligned} P&=\text{const.}\ M^2a^{-4}(\Delta E)^2\exp(-2\pi|\Delta k|/a) \\ |\Delta k|&=2M|\Delta E|/(k_i+\sqrt{k_i^2\pm2M|\Delta E|}) \end{aligned} \qquad (9\cdot8)$$

where the upper of the double sign corresponds to the deactivation and the lower to the excitation. Usually the exponential factor is very small and the order of magnitude of the transition probability is mainly determined by this factor. Clearly the transition probability decreases rapidly if $|\Delta E|$ increases, while the transition probability increases if the initial wave number k_i increases. Furthermore, the transition probability increases if the quantity a increases. In many cases a is 1.5–2.5 A.U. Now, for $a=1$ and $a=3$, for example, we have extremely different transition probabilities unless $|\Delta E|$ is very small.[3] Therefore, the transition probability is found to be very sensitive to the intermolecular force and consequently, it is very hard to get the theoretical transition probability which agrees with the experimental one within factor 2 say.

On the other hand, since a large $|\Delta E|$ depresses the transition probability largely, it is possible that the two or even three quanta transitions may take place with larger probabilities than the one quantum transition, if $|\Delta E|$ of the former processes are smaller than that of the latter. Thus, it is probable that in the deactivation process of the vibration, the excess energy is not transferred to the translation entirely, but some part of it is transferred to the other internal degrees of freedom. Of course, the rotational degrees of freedom can not be an acceptor of the excess energy unless the rotational level spacings are large.**) Thus the main acceptors are the vibrational degrees of freedom, and such energy transfer between the vibrational degrees of freedom will occur appreciably if the frequencies of the two vibrations are comparable. By taking account this energy-transfer process or the coupling between the different vibrations, we can understand the fact that many of the polyatomic gases, for instance CO_2, which have many vibrational degrees of freedom, do not reveal many-relaxation-time phenomena, but behave as if these molecules have only one relaxation time.[3]

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* Four atoms in the two diatomic molecules are assumed to be on a straight line.

* It is expected that the molecules for which the rotational level spacings are rather large, such as H_2, HCl etc., can be good acceptors of the excess energy of another molecule. In fact, according to the ultrasonic dispersion data, these molecules are found to be rather effective to deactivate the vibrational excitation of many gases.

The above formula (9·7), (9·8) can hold in the head-on collision only. In general case, in which the impact parameter is not zero we can get the general tendencies of the radial wave functions by replacing $k^2-j(j+1)/R^2$ with $\tilde{k}^2\equiv k^2-j(j+1)/R_0^2$ in the wave equation, where R_0 is a suitable constant radius. (See the references (14) and also "the method of modified wave number" below.) Thus the effective wave number decreases rapidly with increasing j and, therefore, the transition probability decreases rapidly for the larger impact parameter.

For the vibrational transition of diatomic molecules in the room temperature, $|\Delta E|$ is usually larger than κT. Consequently, the semi-classical treatment in which the translation is described classically is not suitable. But for many of the vibrations in the polyatomic molecules $|\Delta E|$ becomes smaller than κT, and, at the same time, the mass of the molecule becomes large. For these larger molecules, we may apply the semi-classical method with greater and greater success.

Now we shall discuss some simplified methods to estimate the cross sections.

(i) *Utilization of the Born approximation.*

Born approximation gives usually too large cross section for the inelastic processes in the thermal collisions. This is because this method of approximation allows the approach of the two molecules without limitation. In reality, the wave function doesn't enter very much into the region inside the classical turning point, i.e., the distortion of the wave function is very important. But since the Born approximation is considerably easy to handle, it is convenient if some simple methods of correction can be found to improve the fault of Born approximation.

An interesting investigation has been done by E. Bauer.[27] According to his prescription, we must multiply a correction factor to the cross section which has been obtained by the ordinary Born approximation. This correction factor is determined by solving the corresponding one-dimensional problem for which both the plane-wave-type and the distorted-wave-type calculations of the transition matrix element can be done without difficulty. But we have no foundation that the correction factor for the three-dimensional and for the one-dimensional problems are same. In fact, the calculated cross section by Bauer was very much smaller than the experimental one. The reason for this can be understood to some extent as follows: If we decompose the wave function in the three-dimensional space into the partial waves, each of which corresponds to the definite value of the angular momentum (or impact parameter, classically), the partial wave with zero angular momentum, i.e., S-wave, will be distorted very much to the same extent as the

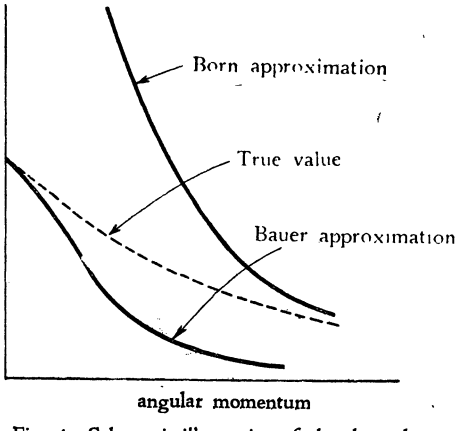

Fig. 4 Schematic illustration of the dependence of the cross section upon the angular momentum, incident energy being fixed.

distortion which we find in the one-dimensional problem. But for the other partial waves, the distortions are partially due to the centrifugal force, and for larger angular momenta, the distortions are mainly due to this virtual force. Such kind of distortion, however, has already been included in the Born approximation. Thus it is clear that the use of the one-dimensional correction factor in the three-dimensional problem is an overcorrection. (See the illustrating figure 4.) If we want to improve this situation, we must multiply the different correction factor for each angular momentum, or a suitable averaged correction factor to the cross section as a whole.

The other method of estimation of the cross section, utilizing the Born approximation, is the "cut-off" method. In this method, the potential is cut-off (i.e., replaced by zero) inside a suitable intermolecular distance, corresponding to the fact that the two colliding molecules can not approach without limitation. Then the calculation may be done according to the Born approximation method. As the cut-off radius, a value near the classical turning point will be adopted. But the potential curve is so steep in this region that the cross section depends rather sensitively on the cut-off radius. Therefore, the choice of the cut-off radius must be fixed empirically, from some typical examples.

(ii) *Method of the modified wave number.*

In the radial wave equations, the only difference between the S-wave case and the other cases is the appearance of the centrifugal force in the latter cases, and usually the S-wave case is much easy to treat than the others. Now if we replace $k^2-j(j+1)/R^2$ by $k^2-j(j+1)/R_0^2$ approximately, all equations to be solved become S-wave type, and, therefore, become easy to handle. Here R_0 is a suitable constant which may depends on k and j, in general. For larger values of j, the curve of $j(j+1)/R^2$ is rather steep and can not be replaced by a suitable constant $j(j+1)/R_0^2$ even in a narrow region near the classical turning point. But the above procedure is expected to give a rather satisfactory result, because the main contribution to the cross section comes from the smaller values of j. In fact, we have had the rather good agreement with the experimental evidences, when we have applied this method to the rotational transitions in H_2-gas.[14] Recent preliminary calculation on the vibrational transition of O_2-molecule, colliding with He-atom, has given a reasonable result too.[28]

As a concluding remark, we shall say again that for the diatomic molecules, the intermolecular force can be considered as spherical in the first approximation and then the non-spherical character may be taken into account as a perturbation, while for the polyatomic molecules, the deviation from the spherical field is essential and, therefore, the distorted wave function under the spherical potential can not be employed. For the latter case, instead, we may apply the semi-classical treatment.

§ 10. Discussions on the statistical problems. Conclusion.

In the above sections, we have treated the system consisting of two molecules only. But in almost all practical cases, we must treat an assembly of a number of molecules as a whole, and only the totality of a number of elementary processes is important. Thus some statistical procedures are required in order to connect the knowledge of the elementary

processes with the experimental data. Now in the usual theory of gases, the component molecules are assumed to be spherical particles, without internal degrees of freedom. Therefore, we must develop the theory of gases which are composed of the polyatomic molecules (including the diatomic molecules). In this paper, however, we shall confine ourselves to some brief discussions. More detailed discussions are postponed to another chance.

(1) In the pure gases, all molecules are identical except for the possibility that there may be a few kinds of isotope. Then we must apply the Bose or the Fermi statistics for these gases. When the number of the elementary particles (electrons and nucleons) in a molecule is even, the wave function of the whole system must be symmetric for an interchange of any two molecules, and for the odd number of constituent particles, the wave function must be antisymmetric. As is well known, the effect of these symmetrization is appreciable for the monatomic gases at low temperatures. For the diatomic molecules, on the other hand, we have already investigated some features of the symmetry effect in § 4. There, we could see that both even and odd values of the orbital angular momentum quantum number (j) appear in a collision process if the internal states of the two colliding molecules are different. If, however, the internal states of the two molecules are same, only the even values of j appear in the cross section formula for the Bose statistics and odd values of j for the Fermi statistics, as in the monatomic gases. We may, therefore, conclude that if the molecules in gas are distributed over many excited states, the symmetry effect will not be significant, because the probability of the encounter between the molecules with identical internal states is very small. Only one exceptional case is the hydrogen gas at low temperatures. In this case, almost all para-H_2 molecules are in the lowest rotational state while almost all ortho-H_2 molecules are in the first excited state. Of course, they are both in the lowest vibrational state. Therefore, there is a large probability of collision between the identical molecules, and thus the symmetry effect appear appreciably. We can expect a similar effect for the deuterium too. We do not enter into this problem further, but only notice that this special case has been investigated recently by K. Ohno and the present author.[17]

(2) Now the important feature of the polyatomic molecules is their non-spherical character. But, if the cross section is averaged over the initial orientations of the colliding molecules, this will not lead to an appreciable effect. When, on the other hand, the molecules are directed to some special direction to some extent by the external force, the averaged cross section becomes different according to the direction of the collision. A typical example is the *Senftleben effect*. This effect was investigated theoretically by Zernike and van Lier.[29] However, they employed a simplified geometrical consideration to estimate the collision cross section and, therefore, there remained some points which were not explained satisfactorily. The quantum mechanical method developed in the present paper will serve to improve their calculations.*)

(3) Next, we shall consider the effects due to the inelastic collision. Two kinds

* This possibility was pointed out by Prof. Gorter in the Symposium on Molecular Physics at Nikko, Japan (September, 1953).

of effect may be distinguished. The one is the modification of the phenomena which can be found already in the monatomic gases, e.g. (probably small) corrections to the viscosity coefficient, to the diffusion constant, and other properties of gases. Since we can not pick up separately the main term and the correction term of the viscosity coefficient and of other quantities from the experimental data and since the rigorous calculation of the scattering cross section is very difficult, the corrections to these quantities are not significant, unless these quantities are affected extraordinarily by the inelastic collisions. The other kind of effects are the phenomena which can not occur in the monatomic gases, such as ultrasonic absorption due to the finite rate of the rotational or the vibrational transitions. For the effects of this kind, we can compare directly the calculated cross section of the inelastic process with the experimental data and we can also predict the results before the observations. Therefore, the theoretical investigations for this kind of effect are very useful.

In this paper, we have discussed the various features of the collisions between two diatomic molecules. In this collision problem, we are faced with two kinds of difficulties. The one is the fact that we have had no satisfactory knowledge on the intermolecular force potential, on which the collision cross section depends rather sensitively. The other is the necessity of solving the coupled set of differential equations. We have investigated mainly the latter kind of difficulties. The most easy case to handle is the weak coupling case, for which the first order approximation method of perturbation can be applied. Even in such a fortunate case, we must perform a vast volume of calculations because there are many parameters to be specified for each set of equations. Therefore, it is desirable to investigate furthermore, the approximation methods such as proposed in the last part of § 9. The validity of these proposed approximation methods will become clear when we compared the matrix elements calculated by these methods with that calculated by employing the true distorted waves.

Strong coupling case is more difficult to treat. But for such a case, the change in the translational energy during a collision is usually rather small so that we can apply the semi-classical treatment. We have proposed an approximate procedure in this direction (§ 8).

The cross sections for the elastic scatterings are mainly determined by the geometrical extension of the molecules and even rough calculations give the result of the right order of magnitude. Therefore, new calculations of these cross sections are useful, only if the reliability of the results is very high. Of course, such rigorous calculations are very difficult. Furthermore, the intermolecular potential must be determined usually from the experimental data for which only the averaged intermolecular force is responsible. Accordingly, the pure theoretical, and accurate, calculations of the elastic scattering processes may be of no significance.

The author wishes to express his sincere thanks to Prof. M. Katani for his continual encouragement and valuable discussions.

Appendix I

By geometrical consideration, it is easy to see that the intermolecular potential V' must be unchanged for the substitution operation Λ:

$$\Lambda : \quad \xi_1=\xi_2, \quad \chi_1\to\pi-\chi_2, \quad \chi_2\to\pi-\chi_1 .$$

Thus

$$\begin{aligned} V_{\alpha\beta\gamma}'\equiv v_{\alpha\beta\gamma}'(\xi_1=\xi_2, R)P_\alpha(\cos\chi_1)P_\beta(\cos\chi_2)P_\gamma(\cos\chi') \\ +v_{\beta\alpha\gamma}'(\xi_1=\xi_2, R)P_\beta(\cos\chi_1)P_\alpha(\cos\chi_2)P_\gamma(\cos\chi') \end{aligned}$$

must be equal to

$$\begin{aligned} \Lambda V_{\alpha\beta\gamma}'\equiv v_{\alpha\beta\gamma}'(\xi_1=\xi_2, R)P_\alpha(\cos\chi_2)P_\beta(\cos\chi_1)P_\gamma(\cos\chi')(-1)^{\alpha+\beta} \\ +v_{\beta\alpha\gamma}'(\xi_1=\xi_2, R)P_\beta(\cos\chi_2)P_\alpha(\cos\chi_1)P_\gamma(\cos\chi')(-1)^{\alpha+\beta}. \end{aligned}$$

Other sets of (α, β, γ) don't mix with each other. By the linear independence of the Legendre polynomials, we get from the above equality

$$v_{\alpha\beta\gamma}'(\xi_1=\xi_2, R)=(-1)^{\alpha+\beta}v_{\beta\alpha\gamma}'(\xi_1=\xi_2, R). \qquad (3\cdot10)$$

Thus we have

$$V_{\alpha\beta\gamma}'=v_{\alpha\beta\gamma}(\xi_1=\xi_2, R)[P_\alpha(\cos\chi_1)P_\beta(\cos\chi_2)+(-1)^{\alpha+\beta}P_\beta(\cos\chi_1)P_\alpha(\cos\chi_2)]P_\gamma(\cos\chi')$$

and when $\alpha+\beta=$even (odd), the expression in the bracket is symmetric (antisymmetric) function of χ_1 and χ_2 and, therefore, symmetric (antisymmetric) function of (θ_1, φ_1) and (θ_2, φ_2).

Similarly, if we employ the equality $(3\cdot12)$, we have

$$\begin{aligned} V_{\alpha\beta\gamma}'&\equiv v_{\alpha\beta\gamma}'(\xi_1, \xi_2, R)P_\alpha(\cos\chi_1)P_\beta(\cos\chi_2)P_\gamma(\cos\chi') \\ &\quad +v_{\beta\alpha\gamma}'(\xi_1, \xi_2, R)P_\beta(\cos\chi_1)P_\alpha(\cos\chi_2)P_\gamma(\cos\chi') \\ &=[v_{\alpha\beta\gamma}'(\xi_1, \xi_2, R)P_\alpha(\cos\chi_1)P_\beta(\cos\chi_2) \\ &\quad +(-1)^{\alpha+\beta}v_{\alpha\beta\gamma}'(\xi_2, \xi_1, R)P_\beta(\cos\chi_1)P_\alpha(\cos\chi_2)]P_\gamma(\cos\chi') \end{aligned}$$

from which we can see that for $\alpha+\beta=$even (odd), this expression is symmetric (antisymmetric) function of $(\xi_1, \theta_1, \varphi_1)$ and $(\xi_2, \theta_2, \varphi_2)$, and, therefore, such expression belongs to $V^+(V^-)$.

Appendix II

The coefficients $s_{Lmm'}^{ll'}$.

When ψ_{lm} and $\psi_{l'm'}$ form the bases of the irreducible representation $D^{(l)}$, $D^{(l')}$ of the rotation group respectively, the coefficients are defined so that the linear combinations

$$\Psi_{L,m}=\sum_{m'} s_{Lm'm-m'}^{ll'}\psi_{lm'}\psi_{l'm-m'}$$

transform among themselves according to the representation $D^{(L)}$. Undetermined factor can

be chosen so that all these coefficients are real and positive. The coefficients $s^{ll'}_{Lmm'}$ are the elements of the matrix representing an unitary transformation and, therefore, have the following properties

$$\sum_{\mu} s^{ll'}_{L\mu\, m-\mu}\, s^{ll'}_{L'\mu\, m-\mu} = \delta_{LL'}\,, \tag{A2·1}$$

$$\sum_{L} s^{ll'}_{L\mu\, m-\mu}\, s^{ll'}_{L\,\mu'\, m-\mu'} = \delta_{\mu\mu'}\,. \tag{A2·2}$$

Sometimes the notation $(ll'\,m\,m'|ll'\,L\,m+m')$ is used instead of $s^{ll'}_{Lmm'}$.

The cross section for viscosity.

The cross section which is effective for the viscosity, is given by the formula

$$Q_{vis} = \sum_{jj'JJ'LL'} (E^{lml'm'*}_{JjL} E^{lml'm'}_{J'j'L'})_{R\to\infty} \iiint \boldsymbol{Y}^{J\,m+m'*}_{jLl'} \boldsymbol{Y}^{J'\,m+m'}_{j'L'l'} \sin^2\Theta\, d\Omega\, d\Omega_1 d\Omega_2\,. \tag{A2·3}$$

(As to the notations, see (5·2).) Since, by definition,

$$\boldsymbol{Y}^{J\mu}_{jLl'} \equiv \sum_{\nu} s^{jL}_{J\,\mu-\nu\,\nu}\, Y_{j\,\mu-\nu}(\Theta\Phi) \sum_{\nu'} s^{ll'}_{L\,\nu'\,\nu-\nu'}\, Y_{l\nu}(\theta_1\varphi_1)\, Y_{l'\,\nu-\nu'}(\theta_2\varphi_2),$$

we can easily integrate over $d\Omega_1 d\Omega_2$ and have

$$\begin{aligned}\iiint \cdots &= \delta_{LL'} \sum_{\nu} s^{jL}_{J\,\mu-\nu\,\nu}\, s^{j'L}_{J'\,\mu-\nu\,\nu} \int Y_{j\,\mu-\nu}{}^*(\Theta\Phi)\, Y_{j'\,\mu-\nu}(\Theta\Phi) \sin^2\Theta\, d\Omega \\ &= \delta_{LL'} \sum_{\nu} s^{jL}_{J\nu\,\mu-\nu}\, s^{j'L}_{J'\,\nu\,\mu-\nu} \int Y_{j\nu}{}^*(\Theta\Phi)\, Y_{j'\nu}(\Theta\Phi) \sin^2\Theta\, d\Omega\end{aligned} \tag{A2·4}$$

where we have used the orthonormality of the spherical harmonics and (A2·1). Next, by making use of the well-known formula

$$\begin{aligned}\iint Y_{j\nu}{}^*(\theta,\varphi)\, Y_{j'\nu}(\theta,\varphi) \sin^3\theta\, d\theta\, d\varphi &= \frac{2(j^2+j-1+\nu^2)}{(2j-1)(2j+3)}\,\delta_{jj'} \\ &- \frac{1}{2j+3}\sqrt{\frac{(j+1+\nu)(j+1-\nu)(j+2+\nu)(j+2-\nu)}{(2j+1)(2j+5)}}\,\delta_{j+2,j'} \\ &- \frac{1}{2j-1}\sqrt{\frac{(j-1+\nu)(j-1-\nu)(j+\nu)(j-\nu)}{(2j+1)(2j-3)}}\,\delta_{j-2,j'}\,.\end{aligned} \tag{A2·5}$$

and by remembering the asymptotic form of $E^{lml'm'}_{JjL}$ (see (5·2).) the cross section Q_{vis} becomes: $(\mu \equiv m+m')$

$$\begin{aligned}Q_{vis} = \frac{\pi}{k^2} \sum_{jJJ'L\nu} s^{jL}_{J\nu\,\mu-\nu}\, s^{jL}_{J0\mu} (s^{ll'}_{Lmm'})^2 \Bigg[& s^{jL}_{J'\,\nu\,\mu-\nu}\, s^{jL}_{J'0\mu} \frac{2(2j+1)(j^2+j-1+\nu^2)}{(2j-1)(2j+3)} |S^{lml'm'}_{JjL} - 1|^2 \\ & - s^{j+2,L}_{J'\,\nu\,\mu-\nu}\, s^{j+2,L}_{J'0\mu} \frac{\sqrt{(j+1+\nu)(j+1-\nu)(j+2+\nu)(j+2-\nu)}}{2j+3} \\ & \qquad \times (S^{lml'm'*}_{JjL} - 1)(S^{lml'm'}_{J'\,j+2,L} - 1) \\ & - s^{j-2,L}_{J'\,\nu\,\mu-\nu}\, s^{j-2,L}_{J'0\mu} \frac{\sqrt{(j-1+\nu)(j-1-\nu)(j+\nu)(j-\nu)}}{2j-1} (S^{lml'm'*}_{JjL} - 1)(S^{lml'm'}_{J'\,j-2,L} - 1) \Bigg].\end{aligned}$$

When we sum up over J and J', the second and the third terms become complex conjugate with each other. Therefore, we have

$$Q_{vis}=\frac{2\pi}{k^2}\sum_{jJJ'L\nu}\frac{1}{2j+3}S^{jL}_{J\nu\,\mu-\nu}S^{jL}_{J'0\mu}\left(S^{ll'}_{l-mm'}\right)^2\Bigg[S^{jL}_{J'\nu\,\mu-\nu}S^{jL}_{J'0\mu}\times\frac{(2j+1)(j^2+j-1+\nu^2)}{2j-1}|S^{lml'm'}_{JjL}-1|^2$$
$$-S^{j+2,L}_{J'\nu\,\mu-\nu}S^{j+2,L}_{J'0\mu}\sqrt{(j+1+\nu)(j+1-\nu)(j+2+\nu)(j+2-\nu)}\times\mathrm{Re}\{(S^{lml'm'*}_{JjL}-1)(S^{lml'm'}_{Jj+2,L}-1)\}\Bigg]. \qquad (A2\cdot6)$$

Appendix III

Here, we shall prove the two relations which have been used in § 6.

(i) *Independence of the matrix elements of the intermolecular potential V' upon the quantum number μ* which defines the z-component of the total angular momentum of the whole system.

Since our system consists of four atoms, the configuration can be expressed completely by 12 coordinates, which may be classified as follows:

I: three coordinates which define the position of the center-of-gravity of the system,
II: three coordinates R, ξ_1, ξ_2, (See Fig. 2.)
III: three coordinates χ_1, χ_2, $\omega_1-\omega_2$, which define the relative orientation of the two molecules,
IV: three coordinates which define the orientation of the system as a whole.

Now we are considering the matrix elements $(J\mu jLl l'|V'|J'\mu' j'L'\lambda\lambda')$ in the subspace (III) + (IV) and wave function can be written in this subspace as [4) 6)]

$$\phi^{jLll'}_{J\mu}=\sum_s D^J(\mathcal{R})_{s\mu}\chi^{jLll'}_{Js}(\chi_1,\chi_2,\omega_1-\omega_2)$$

where $\mathcal{R}$ is the rotation of coordinate system which bring the system into a standard configuration.[6)] Thus we have

$$(J\mu jLl l'|V'|J'\mu' j'L'\lambda\lambda')$$
$$=\sum_{ss'}\int dv_{\mathrm{III}}\int dv_{\mathrm{IV}}D^{J*}(\mathcal{R})_{s\mu}D^{J'}(\mathcal{R})_{s'\mu'}\chi^{jLll'*}_{Js}\chi^{j'L'\lambda\lambda'}_{J's'}V'$$
$$=\sum_{ss'}\int dv_{\mathrm{III}}\chi^{jLll'*}_{Js}V'\chi^{j'L'\lambda\lambda'}_{J's'}\int dv_{\mathrm{IV}}D^{J*}(\mathcal{R})_{s\mu}D^{J'}(\mathcal{R})_{s'\mu'}.$$

The first integral is independent of $\mathcal{R}$ while the second integral becomes $(1/2J+1)\times\delta_{JJ'}\delta_{ss'}\delta_{\mu\mu'}\int dv_{\mathrm{IV}}$ by the property of the representation of rotation group. Thus we obtain that the above matrix element is

$$(2J+1)^{-1}\delta_{JJ'}\delta_{\mu\mu'}\sum_s\int dv_{\mathrm{III}}\chi^{jLll'*}_{Js}V'\chi^{j'L'\lambda\lambda'}_{Js}\int dv_{\mathrm{IV}}$$

the value of which is independent of μ, so long as $\mu=\mu'$.

(ii) *Proof of* $\sum_{mm'}\sum_{JL}(s^{jL}_{J0\,m+m'}s^{ll'}_{Lmm'})^2\Delta V^{JL}_{jll'}=0$ $\cdots(6\cdot5)$

From the definition, we get

$$V_0=(1/2l+1)(1/2l'+1)\sum_{mm'}(j0lml'm'|V'|j0lml'm')$$
$$=(1/2l+1)(1/2l'+1)\sum_{mm'}\sum_{JJ'LL'}s^{jL}_{J0\,m+m'}s^{jL'}_{J'0\,m+m'}s^{ll'}_{Lmm'}s^{ll'}_{L'mm'}(J\mu jLll'|V'|J'\mu jL'll').$$

Since the elements in the summation do not depend on $\mu\equiv m+m'$ and vanish for $J\neq J'$ as just proved in (i), the summation on m and m' can be carried out as

$$\sum_{mm'}s^{jL}_{J0\,m+m'}s^{jL'}_{J0\,m+m'}s^{ll'}_{Lmm'}s^{ll'}_{L'mm'}$$
$$=\sum_{\mu}s^{jL}_{J0\mu}s^{jL'}_{J0\mu}\sum_{\nu}s^{ll'}_{L\nu\,\mu-\nu}s^{ll'}_{L'\nu\,\mu-\nu}$$
$$=\sum_{\mu}(s^{jL}_{J0\mu})^2\cdot\delta_{LL'},$$

where we have used (A2·1). Thus we have

$$V_0=(1/2l+1)(1/2l'+1)\sum_{JL\mu}(s^{jL}_{J0\mu})^2(JjLll'|V'|JjLll'). \qquad (A3\cdot1)$$

Now, from the definition,

$$\Delta V^{JL}_{jll'}=(JjLll'|V'|JjLll')-V_0$$

and, therefore, we get

$$\sum_{mm'}\sum_{JL}(s^{jL}_{J0\,m+m'}s^{ll'}_{Lmm'})^2\Delta V^{JL}_{jll'}$$
$$=\sum_{JL}\{\sum_{\mu\nu}(s^{jL}_{J0\mu}s^{ll'}_{L\nu\,\mu-\nu})^2\}(JjLll'|V'|JjLll')-V_0\sum_{mm'}\sum_{JL}(s^{jL}_{J0\,m+m'}s^{ll'}_{Lmm'})^2$$
$$=\sum_{JL\mu}(s^{jL}_{J0\mu})^2(JjLll'|V'|JjLll')-V_0(2l+1)(2l'+1) \quad \text{by (A2·1), (A2·2)}$$
$$=0 \quad \text{by (A3·1).}$$

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Note added in proof: Detailed report on our work in the reference (28) will be published soon in the Science Reports of the Saitama University.