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## Collisional Excitation Transfer of *S-P* Type Between Identical Atoms\*

TSUTOMU WATANABE

*Department of Applied Physics, University of Tokyo, Bunkyo-Ku, Tokyo, Japan*

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The electronic excitation transfer cross section between identical atoms in *S* and *P* states in the gas phase was investigated theoretically in the low-incident-energy range by means of the impact-parameter method. With respect to the *P* states of an atom, all three degenerate *P* states of mutually orthogonal polarizations were taken into account. The direction of *P* polarization was taken into account using two different methods. These methods were the "fixed-atom approximation" and the "rotating-atom approximation," respectively. The difference between the solution from coupled equations with respect to the direction of *P*-state polarization and those from the respective approximations mentioned above was studied. The fixed-atom approximation was found to be better than the rotating-atom approximation for the computation of the over-all cross section of *S-P*-type excitation transfer. The cross section obtained from the coupled equations was nearly one-half of that from the rotating-atom approximation and nearly 1.5 times as much as that from the fixed-atom approximation. It is shown that the total cross section can be written as  $\sigma = 3.36\pi e^2 \mu^2 / \hbar v$ , where  $v$  represents the relative velocity of an incident atom,  $e$  the electronic charge, and  $\mu$  the transition dipole matrix element between the *S* and *P* states under consideration.

### INTRODUCTION

THE collisional charge transfer problem  $H^+ + H \rightarrow H + H^+$  has been investigated theoretically and experimentally by many authors.<sup>1-3</sup> On the other hand, the electronic excitation transfer problem has not yet been so actively investigated because the direct measurement of the cross section is rather difficult.<sup>4</sup> However, the process of the collisional excitation transfer has recently been studied with respect to the basic mechanism of the effect of radiation on matter. Mori, Watanabe, and Katsuura<sup>5</sup> investigated the problem of the electronic excitation transfer between identical atoms in *S* and *P* states through dipole-dipole-type interaction with two simple approximations concerning the direction of *P*-state polarization during collision. The "fixed-atom approximation" is that in which the direction of *P*-state polarization is assumed to be fixed in

space as it is initially. The "rotating-atom approximation" is that in which the direction of the *P* state is assumed to point toward the *S*-state atom during collision. In the present paper we have treated the problem in which a *P*-state atom is incident to an identical atom in an *S* state with an arbitrary direction of polarization. All three degenerate *P* states of mutually orthogonal polarization were taken into account at all times during the collision process. Either the *S* or *P* state may be considered the ground state. The opposite state will then be the excited state. We also restrict ourselves to the case where the relative kinetic energy of atoms is so low that we can apply the impact parameter method extended by Gurnee and Magee<sup>1</sup> with high accuracy. Since the problem can be treated by the use of a classical procedure, the probability of excitation transfer from one atom to the other during collision is determined by the impact parameter of the incident atom. The cross section of the excitation transfer is obtained from the probability by integrating it over the impact parameter.

When a *P*-state atom with a certain direction of polarization is incident and interacts or collides with an *S*-state atom, both of the following processes are possible: (1) the interchange of the excitation between the *S*- and *P*-state atoms and (2) the change in the direction of the polarization of the *P*-state atom with

\* The author is indebted to IBM Japan Ltd. (Tokyo) for the use of an IBM 7090 computer in carrying out numerical calculations from matrix elements to transition probabilities and cross sections.

<sup>1</sup> H. F. Gurnee and J. L. Magee, *J. Chem. Phys.* **26**, 1237 (1957).

<sup>2</sup> J. B. Hasted, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., London, 1962), Chap. 18.

<sup>3</sup> J. B. Hasted, *Physics of Atomic Collisions* (Butterworths Scientific Publications Ltd., London, 1964), Chap. 12.

<sup>4</sup> J. B. Hasted, Ref. 3, Chap. 13, Sec. 13.1.

<sup>5</sup> M. Mori, T. Watanabe, and K. Katsuura, *J. Phys. Soc. Japan* **19**, 380 (1964); **19**, 1504(E) (1964).

the  $S$ -state atom still in the same  $S$  state. The transition probabilities of all the conversion and transfer processes as well as the total cross section of excitation transfer were obtained.

The comparison was made of calculated results without any approximation with respect to the direction of the  $P$ -state polarization (the results from coupled equations) with the values obtained using the two approximate methods. The relationship between the calculation from the coupled equations and that with the rotating or the fixed-atom approximation was also discussed. Some remarks concerning  $W$  value measurements in gas-phase experiments and gas-laser experiments have been given.

### FORMULATION

Consider the case where an  $S$ -state atom ( $A$ ) with a nucleus  $A$  and  $N$  electrons  $\mu=1, 2, \dots, N$ , exists at rest at the origin of the coordinate system, and a  $P$ -state atom ( $B$ ) with a nucleus  $B$  and  $N$  electrons  $\nu=N+1, N+2, \dots, 2N$ , is incident along one axis of the Cartesian coordinate system, the  $\zeta$  axis, with impact parameter  $R_0$  as shown in Fig. 1. The  $\eta$  axis is taken to be orthogonal to the  $\zeta$  axis in the plane of the two nuclei and the  $\xi$  axis is orthogonal to the other two axes. In this treatment only the cases where the cross section of the excitation transfer is so large that the classical trajectories of the incident atom are straight lines will be considered. The direction of the  $P$ -state polarization can be expressed by each axis component denoted by  $P_\xi$ ,  $P_\eta$  or  $P_\zeta$  according to the vector model of the electronic angular momentum. Then, the problem under consideration is that of transition among the six states, i.e.,  $P_\xi$  state of  $A$  atom and  $S$  state of  $B$  atom,  $S$  state of  $A$  atom and  $P_\xi$  state of  $B$  atom, and so on. These six

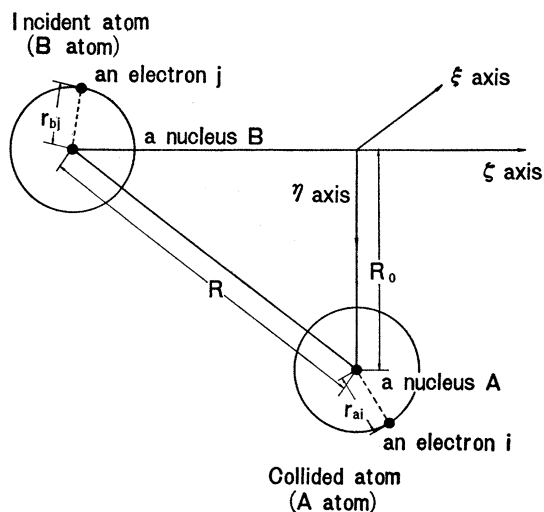


FIG. 1. Two identical atoms in an excitation transfer process. Atom  $A$  is located at rest at the point  $R_0$  distant from  $\zeta$  axis. Atom  $B$  moves along the  $\zeta$  axis with a constant relative velocity  $v$  from  $\zeta = -\infty$  to  $\zeta = +\infty$ .

TABLE I. Six states of the system of two identical atoms under consideration.

State	Wave function	Incident atom ( $B$ atom)	Collided atom ( $A$ atom)
1	$\psi_1$	$P_\xi$	$S$
2	$\psi_2$	$S$	$P_\xi$
3	$\psi_3$	$P_\eta$	$S$
4	$\psi_4$	$S$	$P_\eta$
5	$\psi_5$	$P_\zeta$	$S$
6	$\psi_6$	$S$	$P_\zeta$

states may be denoted as states 1, 2,  $\dots$ , and 6 as shown in Table I.

The electronic state  $\Psi$  of the two-atomic system can be assumed to be expressed by the linear combination of the above six states  $\psi_1, \psi_2, \dots, \psi_6$ , as

$$\Psi = e^{(iE/\hbar)t} \sum_i C_i(t) \psi_i, \quad i=1, 2, \dots, 6, \quad (1)$$

where  $E$  is the total energy of the system, and  $C_i$  is the coefficient of each state eigenfunction and the function of time  $t$  or internuclear distance  $R$ . Let  $\mathcal{H}$  be the total Hamiltonian,  $\mathcal{H}_0$  that of two atoms at an infinite distance, and  $\mathcal{H}'$  that of their interaction, i.e.,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'. \quad (2)$$

Since the electronic interaction at large internuclear distance will be important in the excitation transfer process, the exchange between an electron  $\mu$  in  $A$  atom and an electron  $\nu$  in  $B$  atom can be ignored. Accordingly, every state  $\psi_i$  is assumed to be a single product of the respective self-consistent field (SCF) wave function of an atom  $A$  and an atom  $B$  as expressed by

$$\begin{aligned} \psi_1 &= \psi_{aS}(\mathbf{r}_1, \dots, \mathbf{r}_\mu, \dots, \mathbf{r}_N) \psi_{bP\xi}(\mathbf{r}_{N+1}, \dots, \mathbf{r}_\nu, \dots, \mathbf{r}_{2N}) \\ &\vdots \\ \psi_6 &= \psi_{aP\xi}(\mathbf{r}_1, \dots, \mathbf{r}_\mu, \dots, \mathbf{r}_N) \psi_{bS}(\mathbf{r}_{N+1}, \dots, \mathbf{r}_\nu, \dots, \mathbf{r}_{2N}). \end{aligned} \quad (3)$$

The function  $\Psi$  should satisfy the Schrödinger equation

$$i\hbar(\partial\Psi/\partial t) = \mathcal{H}\Psi.$$

A solution of  $\Psi$  can be obtained, if all the  $C_i(t)$  are known for each value of  $t$  or  $R$ . Out of all possible solutions of  $\Psi$ , it is necessary to obtain the final value of every  $|C_i|^2$  at  $t = \infty$  under the various initial conditions:  $|C_1|^2 = 1$ ,  $|C_i|^2 = 0$  for  $i \neq 1$  at  $t = -\infty$ ;  $|C_3|^2 = 1$ ,  $|C_i|^2 = 0$  for  $i \neq 3$  at  $t = -\infty$ ; or  $|C_5|^2 = 1$ ,  $|C_i|^2 = 0$  for  $i \neq 5$  at  $t = -\infty$ . The cross section for each transition  $\sigma_{i \rightarrow j}$  can be evaluated from the expression

$$\sigma_{i \rightarrow j} = 2\pi \int_0^\infty |C_j(\infty)|^2 R_0 dR_0, \quad (4)$$

where  $C_j(\infty)$  is the solution under the initial condition  $|C_i|^2 = 1$ ,  $|C_j|^2 = 0$  for  $i \neq j$ .

The method of Gurnee and Magee<sup>1</sup> can be extended by analogy to the case of six states of the system

$\mathcal{H}C_0\psi_i = E\psi_i$  ( $i=1, \dots, 6$ ), where the solution of the Schrödinger equation for  $\Psi$  leads to the equation for  $C_j$ :

$$\sum_j H_{ij}C_j = i\hbar \sum_j S_{ij}\dot{C}_j \quad \text{for } i, j=1, 2, \dots, 6. \quad (5)$$

In Eq. (5)  $H_{ij}$  and  $S_{ij}$  are given as

$$H_{ij} = \int \psi_j^*(\mathbf{r}_1, \dots, \mathbf{r}_{2N}) \mathcal{H}' \psi_i(\mathbf{r}_1, \dots, \mathbf{r}_{2N}) \prod_{\mu, \nu}^{2N} d\tau_\mu d\tau_\nu$$

and

$$S_{ij} = \int \psi_j^*(\mathbf{r}_1, \dots, \mathbf{r}_{2N}) \psi_i(\mathbf{r}_1, \dots, \mathbf{r}_{2N}) \prod_{\mu, \nu}^{2N} d\tau_\mu d\tau_\nu,$$

where  $\psi_i$  is expressed by the product of the SCF electronic wave functions of atom  $A$  and atom  $B$  as shown by (3).

$\mathcal{H}'$  can be expanded by using two-center expansions at the positions of nuclei  $A$  and  $B$  with Legendre polynomials. Note that the displacement vectors from the nuclei  $A$  and  $B$  to the electrons  $\mu$  and  $\nu$  are  $\mathbf{r}_{\mu a}$  and  $\mathbf{r}_{\nu b}$ , respectively. Since  $R \gg r_{\mu a}, r_{\nu b}$  in the above case,  $\mathcal{H}'$  is expressed as a dipole-dipole-type interaction in terms of  $\mathbf{r}_{\mu a}, \mathbf{r}_{\nu b}, R, \cos\theta_{\mu a}, \cos\theta_{\nu b}$  (the direction cosines of  $\mathbf{r}_{\mu a}$  or  $\mathbf{r}_{\nu b}$  with respect to the  $\zeta$  axis, respectively):

$$\mathcal{H}' = (e^2/R^3) \left\{ \sum_{\mu, \nu} (\mathbf{r}_{\mu a} \cdot \mathbf{r}_{\nu b}) - 3 \sum_{\mu, \nu} r_{\mu a} \cos\theta_{\mu a} r_{\nu b} \cos\theta_{\nu b} \right\}. \quad (7)$$

Neglecting the exchange between electrons  $\mu$  and  $\nu$  from the orthogonality relation, Eq. (5) can be reduced to

$$\begin{pmatrix} 0 & H_{12} & 0 & 0 & 0 & 0 \\ H_{21} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & H_{34} & 0 & H_{36} \\ 0 & 0 & H_{43} & 0 & H_{45} & 0 \\ 0 & 0 & 0 & H_{54} & 0 & H_{56} \\ 0 & 0 & H_{63} & 0 & H_{65} & 0 \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \\ C_5 \\ C_6 \end{pmatrix} = i\hbar \begin{pmatrix} \dot{C}_1 \\ \dot{C}_2 \\ \dot{C}_3 \\ \dot{C}_4 \\ \dot{C}_5 \\ \dot{C}_6 \end{pmatrix}. \quad (8)$$

Using  $u_1, \dots, u_4$  for  $C_3, \dots, C_6$  which are defined by the relations

$$\begin{aligned} u_1 &= C_3 + C_4, \\ u_2 &= C_5 + C_6, \\ u_3 &= C_3 - C_4, \\ u_4 &= C_5 - C_6, \end{aligned} \quad (9)$$

Eq. (8) can be reduced to three sets of simultaneous equations for  $C_1$  and  $C_2$ ,  $u_1$  and  $u_2$ , and  $u_3$  and  $u_4$ . Introducing the axes  $\sigma, \pi, \bar{\pi}$  instead of the axes  $\xi, \eta, \zeta$  as shown in Fig. 2,  $\psi_{P\xi}, \psi_{P\eta}, \psi_{P\zeta}$  can be expressed by the angle between  $\eta$  and  $\sigma$ ,  $\theta$ , and the usual  $P$ -state eigenfunctions  $\psi_{P\sigma}, \psi_{P\pi}, \psi_{P\bar{\pi}}$  characterized by the directions of  $\sigma, \pi, \bar{\pi}$ . Accordingly, every matrix element of the equations can be expressed in terms of the internuclear distance  $R$ , the angle  $\theta$ , and transition-dipole matrix elements  $\mu$ , with

$$\mu = \int \psi_{\alpha S} \sum_{\nu} r_{\lambda\nu} \psi_{\beta P\lambda} \prod_{\nu} d\tau_{\nu}, \quad (10)$$

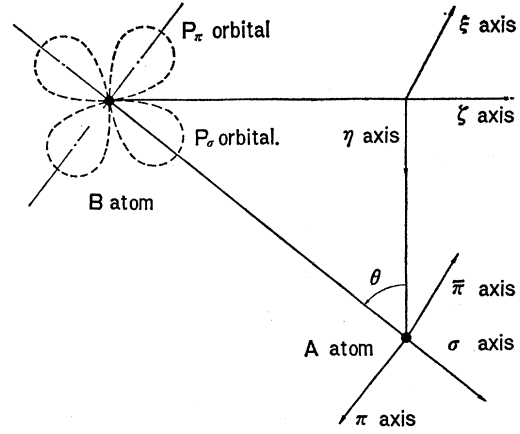


FIG. 2. Coordinate systems of  $\sigma, \pi, \bar{\pi}$ , and  $\xi, \eta, \zeta$ .

where  $\alpha, \beta = a$  or  $b$ ;  $\lambda = \sigma, \pi$ , or  $\bar{\pi}$ ; and  $r_{\lambda\nu}$  means  $\lambda$  component of  $\mathbf{r}_{\nu}$ . Then the following equations can be obtained:

$$k \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} = \frac{d}{dx} \begin{bmatrix} C_1 \\ C_2 \end{bmatrix}, \quad (11)$$

$$k \begin{bmatrix} 3x^2 - 2 & -3x(1-x^2)^{1/2} \\ -3x(1-x^2)^{1/2} & 1 - 3x^2 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \frac{d}{dx} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix}, \quad (12)$$

$$-k \begin{bmatrix} 3x^2 - 2 & -3x(1-x^2)^{1/2} \\ -3x(1-x^2)^{1/2} & 1 - 3x^2 \end{bmatrix} \begin{bmatrix} u_3 \\ u_4 \end{bmatrix} = \frac{d}{dx} \begin{bmatrix} u_3 \\ u_4 \end{bmatrix}, \quad (13)$$

with  $k = e\mu^2 / i\hbar R_0^2 v$  and  $x = \sin\theta$ . In the above equation, the initial and the final states correspond to the states at  $x = -1$  and  $+1$ , respectively. When an incident atom has an arbitrary direction of  $P$ -state polarization, the final probability can be obtained from appropriate linear combination of the final values of  $C_i$  using the three initial conditions  $|C_i|^2 = 1$  for  $i = 1, 3$ , and  $5$ .

From the Hermitian property of  $H_{ij}$  and orthogonal property of  $\psi_i$ , the conservation rule that  $\sum_i |C_i|^2 = \text{const}$  can be derived. In Eq. (5),

$$H_{ij} = H_{ji}^* \quad \text{and} \quad S_{ij} = \delta_{ij}$$

so that

$$\sum_j H_{ij} C_j = i\hbar \dot{C}_i, \quad (14)$$

$$\sum_j H_{ji} C_j^* = -i\hbar \dot{C}_i^*.$$

The inner product of  $(C_1^*, C_2^*, \dots, C_6^*)$  or  $(C_1, C_2, \dots, C_6)$  and each Eqs. (14) in matrix form can be written as

$$\sum_i \sum_j H_{ij} C_i^* C_j = i\hbar \sum_i (C_i^* \dot{C}_i)$$

and

$$\sum_i \sum_j H_{ji} C_i C_j^* = -i\hbar \sum_i (\dot{C}_i C_i^*). \quad (15)$$

These equations reduce to

$$\frac{d}{dt} \sum_j |C_j|^2 = 0. \quad (16)$$

From the unitary property of  $|\Psi|^2$  and Eq. (16),

$$\sum_j |C_j|^2 = 1. \quad (17)$$

In the approximation with which Eq. (8) was derived, the following relations hold:

$$\begin{aligned} |C_1|^2 + |C_2|^2 &= M_1, \\ \sum_i |C_i|^2 &= M_2 \quad \text{for } i=3, 4, 5, 6, \end{aligned} \quad (18)$$

and

$$M_1 + M_2 = 1. \quad (19)$$

From the relations between the equations which are satisfied for  $u_1, u_2$  and  $u_3, u_4$  [Eqs. (12) and (13)],  $u_3(x)$  and  $u_4(x)$  are obtained by replacing  $k$  by  $-k$ . Since  $k$  is pure imaginary,

$$u_1(x)^* = u_3(x), \quad \text{and} \quad u_2(x)^* = u_4(x).$$

Using these relations and Eq. (9), it can be shown that

$$\begin{aligned} C_3(x) &= \text{Re}u_1(x), \\ C_4(x) &= \text{Im}u_1(x), \\ C_5(x) &= \text{Re}u_2(x), \\ C_6(x) &= \text{Im}u_2(x). \end{aligned} \quad (20)$$

#### SOLUTION OF THE COUPLED EQUATION

From Eq. (8) it can be seen that states 1 and 2 do not interact with any other state in the case of dipole-dipole type interaction. Thus, the case of initial condition  $|C_1|^2 = 1$  or  $|C_2|^2 = 1$  can be treated separately from other cases. When  $|C_1|^2 = 1$  at  $x = -1$ , we obtain from Eq. (11) and

$$\begin{aligned} k(C_1 + C_2) &= d(C_1 + C_2)/dx, \\ k(C_1 - C_2) &= d(C_1 - C_2)/dx, \end{aligned}$$

the same results as Grunne and Magee<sup>1</sup> at  $x = 1$ :

$$\begin{aligned} C_1 &= \cos(2k_0), \\ C_2 &= \sin(2k_0), \\ C_i &= 0 \quad \text{for } i \neq 1, 2 \quad \text{with } k_0 = -ik. \end{aligned} \quad (21)$$

Because of the simultaneous property of the equations for  $C_3$  through  $C_6$  in Eq. (8),  $C_3$  through  $C_6$  can not be solved by the same procedure. It will be convenient to start with Eqs. (12) and (13) instead of Eq. (8). Since one can easily find that Eq. (13) is the same as Eq. (12) if  $k$  is replaced by  $-k$ , it will be enough to consider only Eq. (12) under the initial condition of  $|u_1|^2 = 1$  and  $|u_2|^2 = 0$ , or of  $|u_2|^2 = 1$  and  $|u_1|^2 = 0$  at  $x = -1$ .

Denote a matrix  $\mathbf{L}$  as

$$\mathbf{L} = \begin{bmatrix} 3x^2 - 2 & -3x(1-x^2)^{1/2} \\ -3x(1-x^2)^{1/2} & 1 - 3x^2 \end{bmatrix} \quad (22)$$

and matrices  $\mathbf{L}_n$  as

$$\begin{aligned} \mathbf{L}_n &= \int_{-1}^x \mathbf{L}(x') dx' \int_{-1}^{x'} \mathbf{L}(x'') dx'' \int_{-1}^{x''} \mathbf{L}(x''') dx''' \dots \\ &\times \int_{-1}^{x^{n-1}} \mathbf{L}(x^{(n)}) dx^{(n)}, \quad n=0, 1, 2, 3, \dots, \end{aligned} \quad (23)$$

where  $\mathbf{L}_0$  means the unit matrix. Then, the solution of Eq. (13) is obtained in the following form with above notations:

$$\begin{bmatrix} u_1(x) \\ u_2(x) \end{bmatrix} = \left[ \sum_{n=0}^{\infty} k^n \mathbf{L}_n(x) \right] \begin{bmatrix} u_1(-1) \\ u_2(-1) \end{bmatrix} \quad (24)$$

as shown in the Appendix.

When  $u_1(x)$  and  $u_2(x)$  can be obtained, the relation (20) gives the excitation transfer probability from a state  $i$  to a state  $j$   $P_{i \rightarrow j}$  [under the initial condition  $\text{Re}u_1(-1) = 1$ ] as

$$\begin{aligned} P_{3 \rightarrow 3} &= |\text{Re}u_1(1)|^2, \\ P_{3 \rightarrow 4} &= |\text{Im}u_1(1)|^2, \\ P_{3 \rightarrow 5} &= |\text{Re}u_2(1)|^2, \\ P_{3 \rightarrow 6} &= |\text{Im}u_2(1)|^2, \end{aligned} \quad (25)$$

and so on. The excitation transfer cross section from a state  $i$  to a state  $j$   $\sigma_{i \rightarrow j}$  can be estimated from Eq. (4).

The fixed-atom approximation corresponds to the approximation  $H_{36} = H_{45} = 0$  in Eq. (8). In this approximation Eq. (12) has solutions

$$\begin{aligned} u_1(x) &= \exp[+k(x^3 - 2x - 1)]u_1(-1) \\ \text{and} \\ u_2(x) &= \exp[+k(x - x^3)]u_2(-1). \end{aligned} \quad (26)$$

Since  $u_1$  and  $u_2$  do not mix in the approximation, we find

$$\begin{aligned} |\text{Re}u_1(x)|^2 &= \cos^2[+k(x^3 - 2x - 1)], \\ |\text{Im}u_1(x)|^2 &= \sin^2[+k(x^3 - 2x - 1)], \\ |\text{Re}u_2(x)|^2 &= 0, \\ |\text{Im}u_2(x)|^2 &= 0, \end{aligned} \quad (27)$$

as in the case of initial condition  $u_1(-1) = 1, u_2(-1) = 0$ . In the case of initial condition  $u_1(-1) = 0, u_2(-1) = 1$ ,

$$\begin{aligned} |\text{Re}u_1(x)|^2 &= 0, \\ |\text{Im}u_1(x)|^2 &= 0, \\ |\text{Re}u_2(x)|^2 &= \cos^2[+k(x - x^3)], \\ |\text{Im}u_2(x)|^2 &= \sin^2[+k(x - x^3)], \end{aligned} \quad (28)$$

can be obtained in a similar way. Thus, we can obtain

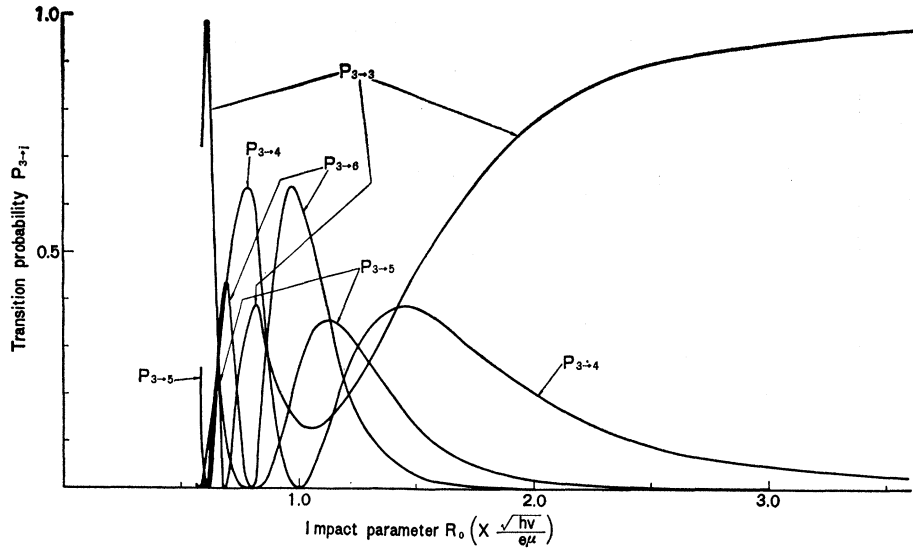


FIG. 3. Probabilities of the excitation transfer  $P_{3 \rightarrow j}$  versus impact parameter  $R_0$  under the initial condition of  $|C_3|^2 = 1$  (an incident atom is initially in  $P_7$  state).

the solutions of (12) in different forms:

$$\begin{bmatrix} u_1(x) \\ u_2(x) \end{bmatrix} = \exp(+k(x^2 - 2x - 1)) \left[ \sum_{n=0}^{\infty} k^n \mathbf{M}_n(x) \right] \begin{bmatrix} u_1(-1) \\ u_2(-1) \end{bmatrix} \quad (29)$$

and

$$\begin{bmatrix} u_1(x) \\ u_2(x) \end{bmatrix} = \exp(-k(x - x^3)) \left[ \sum_{n=0}^{\infty} k^n \mathbf{N}_n(x) \right] \begin{bmatrix} u_1(-1) \\ u_2(-1) \end{bmatrix}, \quad (30)$$

where  $\mathbf{M}_n(x)$  and  $\mathbf{N}_n(x)$  are similar  $n$ -fold iteration integrals of matrixes

$$\mathbf{M}(x) = \begin{bmatrix} 0 & -3x(1-x^2)^{1/2} \\ -3x(1-x^2)^{1/2} & 3(1-2x^2) \end{bmatrix}$$

and

$$\mathbf{N}(x) = \begin{bmatrix} 3(x^2-1) & -3x(1-x^2)^{1/2} \\ -3x(1-x^2)^{1/2} & 0 \end{bmatrix},$$

as is  $\mathbf{L}_n(x)$ . Comparing these forms with Eqs. (26) and (28), one easily finds the factors  $\sum_n k^n \mathbf{M}_n(x)$  and  $\sum_n k^n \mathbf{N}_n(x)$  give corrections to the fixed-atom approximation in the cases of the initial conditions  $u_1(-1) = 1$ ,  $u_2(-1) = 0$ , and  $u_1(-1) = 0$ ,  $u_2(-1) = 1$ , respectively.

In the rotating atom approximation, the excitation of an atom  $A$  transfers to an atom  $B$  by the equation

$$\begin{bmatrix} 0 & b \\ b & 0 \end{bmatrix} \begin{bmatrix} r_1(t) \\ r_2(t) \end{bmatrix} = i\hbar \begin{bmatrix} \dot{r}_1(t) \\ \dot{r}_2(t) \end{bmatrix}, \quad (31)$$

where  $b = -2e^2\mu^2/R^3$ ,  $r_1(t)$  are the coefficients of  $A$  atom in  $S$  state and  $B$  atom in  $P$  state and  $A$  atom in  $P$  state and  $B$  atom in  $S$  state, respectively. The coeffi-

cients  $r_1(x)$  and  $r_2(x)$  change with  $x$  in the form

$$\left. \begin{aligned} r_1(x) &= \cos[-2k(x+1)]r_1(-1) \\ r_2(x) &= \sin[-2k(x+1)]r_2(-1) \end{aligned} \right\} \quad (32)$$

Equation (12) can also be solved in terms of  $n$ -fold iteration integral  $\mathbf{O}_n(x)$  of matrix  $\mathbf{O}(x)$ :

$$\mathbf{O}(x) = \begin{bmatrix} 3x^2 & -3x(1-x^2)^{1/2} \\ -3x(1-x^2)^{1/2} & 3(1-x^2) \end{bmatrix}$$

as

$$\begin{bmatrix} u_1(x) \\ u_2(x) \end{bmatrix} = \exp[-2k(x+1)] \left[ \sum_n k^n \mathbf{O}_n(x) \right] \begin{bmatrix} u_1(-1) \\ u_2(-1) \end{bmatrix}. \quad (33)$$

The factor  $\sum_n k^n \mathbf{O}_n(x)$  similarly means correction from the rotating-atom approximation.

## RESULTS OF CALCULATION

The calculations for each matrix component of  $\mathbf{L}_n$ ,  $\mathbf{M}_n$ ,  $\mathbf{N}_n$ , and  $\mathbf{O}_n$  have been carried out with aid of an IBM 7090 computer. These calculations involve only numerical multiple integration (from single integration to 50-fold integration in this case). The numbers of intervals used in the integrations, using Simpson's method, were 64, 128, 256, 512, 1024, 2000. In the last two cases, the calculated values are the same to within the relative errors of  $0.5 \times 10^{-6}$  for  $n = 0 \sim 20$ ,  $0.5 \times 10^{-5}$  for  $n = 21 \sim 40$ , and  $0.5 \times 10^{-3}$  for  $n = 41 \sim 50$ .<sup>6</sup>

The transition probabilities and the cross sections have been also estimated with the computer by the four expressions, (24), (29), (30), and (33). The error was evaluated by the deviation from the conservation

<sup>6</sup> Tsutomu Watanabe, J. Fac. Eng., Univ. Tokyo (to be published). The tables for  $\mathbf{L}_n(1)$  through  $\mathbf{O}_n(1)$  may be obtained by writing the author.

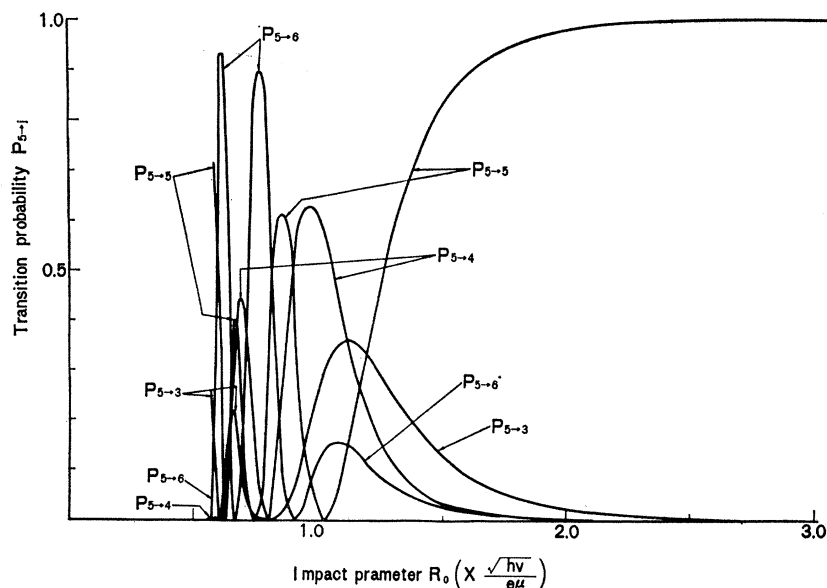


FIG. 4. Probabilities of the excitation transfer  $P_{5 \rightarrow j}$  versus the impact parameter  $R_0$  under the initial condition of  $|C_5|^2=1$  (an incident atom is initially in  $P_\xi$  state).

rule (18) and also by comparing the solutions obtained from the four expressions. The transition probabilities are shown in Figs. 3 through 6 as the functions of impact parameter  $R_0$ . The calculation is not so accurate in the region  $k_0 (= -ik) \geq 3.00$ , because the transition probabilities do not always obey the conservation condition (18) there. The transfer cross sections were estimated from the equation

$$\sigma_{i \rightarrow j} = 2\pi \int_{R_{0c}}^{\infty} P_{i \rightarrow j}(R_0) R_0 dR_0 + \sigma_{i \rightarrow j'}, \quad (34)$$

where

$$\sigma_{i \rightarrow j'} = \frac{2\pi}{4} \int_0^{R_{0c}} R_0 dR_0$$

$$R_{0c}^2 = (e^2 \mu^2 / \hbar k_{0c} v), \quad \text{and} \quad k_{0c} = 3.00,$$

because the excitation transfer may be equally distributed to every state, on an average, in the cases  $R_0 < R_{0c}$  (or  $k_0 > k_{0c}$ ). The respective cross sections were obtained as follows:

$$\begin{aligned} \sigma_{1 \rightarrow 2} &= 3.14\pi\mu^2 e^2 / \hbar v, & \sigma_{3 \rightarrow 6} &= 1.04\pi\mu^2 e^2 / \hbar v, \\ \sigma_{3 \rightarrow 4} &= 4.09\pi\mu^2 e^2 / \hbar v, & \sigma_{5 \rightarrow 3} &= 1.12\pi\mu^2 e^2 / \hbar v, \\ \sigma_{3 \rightarrow 5} &= 1.12\pi\mu^2 e^2 / \hbar v, & \sigma_{5 \rightarrow 4} &= 1.05\pi\mu^2 e^2 / \hbar v, \\ \sigma_{5 \rightarrow 6} &= 0.781\pi\mu^2 e^2 / \hbar v. \end{aligned} \quad (35)$$

The total excitation transfer cross sections to the other atom in the cases where the directions of  $P$ -state polarization are initially on  $\xi$ ,  $\eta$ ,  $\zeta$  axes are

$$\begin{aligned} \sigma_\xi &= \sigma_{1 \rightarrow 2} = 3.14\pi\mu^2 e^2 / \hbar v, \\ \sigma_\eta &= \sigma_{3 \rightarrow 4} + \sigma_{3 \rightarrow 6} = 5.13\pi\mu^2 e^2 / \hbar v, \end{aligned} \quad (36)$$

and

$$\sigma_\zeta = \sigma_{5 \rightarrow 4} + \sigma_{5 \rightarrow 6} = 1.83\pi\mu^2 e^2 / \hbar v,$$

respectively.

Thus, mean excitation transfer cross section  $\sigma$  can be written as

$$\begin{aligned} \sigma &= \frac{1}{3}(\sigma_\xi + \sigma_\eta + \sigma_\zeta) \\ &= 3.36\pi\mu^2 e^2 / \hbar v. \end{aligned} \quad (37)$$

This value can be compared with that obtained from the rotating-atom approximation  $(\frac{2}{3})\pi^2\mu^2 e^2 / \hbar v$  and that obtained from the fixed-atom approximation  $2\pi^2\mu^2 e^2 / \hbar v$ . The magnitude of mean excitation cross section is nearly one-half of that given in the rotating-atom case and nearly 1.5 times as much as that given in the fixed-atom case.

TABLE II. Some typical cross sections of the excitation transfer between identical atoms in thermal energy.

Atom ( $M$ =mass number)	Ground and <sup>a</sup> excited states (transition)	Cross section <sup>a</sup> of excitation transfer (in $\pi a_0^2$ )
H ( $M=1$ )	$1S-2P$	$1.32 \times 10^3$
	$1S-3P$	$2.12 \times 10^2$
	$1S-4P$	$7.37 \times 10$
He ( $M=4$ )	$1^1S-2^1P$	$1.06 \times 10^3$
	$1^1S-3^1P$	$(8.42 \times 10^2)^b$
Li ( $M=7$ )	$1^1S-3^1P$	$2.60 \times 10^2$
	$1^1S-4^1P$	$9.52 \times 10$
	$2^2S-2^2P$	$3.2 \times 10^4$
Ne ( $M=20$ )	$2^2S-3^2P$	$2.0 \times 10^2$
	$2^2S-4^2P$	$1.9 \times 10^2$
	$2p^6 1S_0-2p^5 ({}^2P_{1/2}) 3s^1 P_1$	$2 \times 10^4$
Na ( $M=23$ )	$3^2S_{1/2}-3^2P_{1/2}$	$2.4 \times 10^4$
	$3^2S_{1/2}-3^2P_{3/2}$	$4.9 \times 10^4$
Ar ( $M=40$ )	$3S-4^2P$	$5.8 \times 10^2$
	$3p^6 1S_0-3p^5 ({}^2P_{1/2}) 4s^1 P_1$	$4.3 \times 10^2$

<sup>a</sup> Oscillator strengths and transition wavelengths are obtained from *Landolt-Börnstein Zahlenwerte und Funktionen, 6 Auflage* (Springer-Verlag, Berlin, 1950), Vol. I, Chap. 1, p. 260.

<sup>b</sup> The value of oscillator strength is obtained from W. F. Miller and P. L. Platzman, Proc. Phys. Soc. (London) **A70**, 299 (1957).

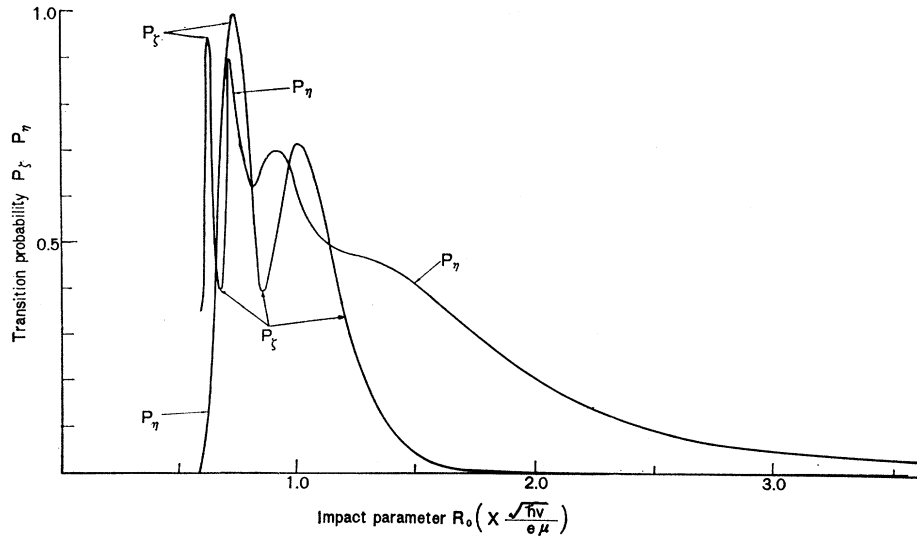


FIG. 5. Probabilities of the excitation transfer from an incident atom to a struck atom  $P_\eta$  and  $P_\zeta$  versus the impact parameter  $R_0$  under the initial conditions of  $|C_3|^2=1$  and  $|C_5|^2=1$ , respectively.

In order to obtain the excitation transfer cross sections in gas-phase experiments at room temperature, the relative velocity of the atoms in thermal motion is adopted to the value of  $v$  in Eq. (37). The mean excitation transfer cross section  $\sigma$  in a gaseous system at room temperature is given as

$$\sigma = 238\mu^2\sqrt{M}, \quad (38)$$

where  $M$  is the mass number of the atom.<sup>7</sup> The cross sections of the excitation transfer in some typical cases are tabulated in Table II.

### DISCUSSIONS

The impact-parameter method including the straight-line trajectory which was adopted in the present approach should be appropriate for the discussion of the problem concerning large transfer cross sections. The expressions (35) through (37) will be valid for the cases in which the cross sections are estimated above the order of  $10^2\pi a_0^2$ . The results (35) through (37) will be valid for  $\mu^2\sqrt{M} > 10^{-1}a_0^2$  in the cases of thermal motion. This condition may hold in almost all S-P-type transitions of atoms. The matrix elements in  $\mathbf{O}_n(1)$  for comparatively large  $n$  are larger than the corresponding elements in  $\mathbf{M}_n(1)$  and  $\mathbf{N}_n(1)$ .<sup>6</sup> This feature shows that the convergence of the series (33) is not as good as that of the series (24), (29), and (30). The conservation property (18) can be expressed as

$$\sum_{j=3}^6 P_{3 \rightarrow j} = 1, \quad \sum_{j=3}^6 P_{5 \rightarrow j} = 1. \quad (39)$$

<sup>7</sup> In the previous paper (Ref. 5), the mean excitation transfer cross section was estimated with the rotating- and the fixed-atom approximations for the case where an atom was incident with thermal velocity and the other atom at rest. The relative velocity of two identical atoms both in thermal energy is  $\sqrt{2}$  times as much as that of the incident atom in the former case. The cross section of the excitation transfer between two identical atoms in thermal motion is  $1/\sqrt{2}$  times as much as that in the former case.

The summations  $\sum_{j=3}^6 P_{3 \rightarrow j}$  and  $\sum_{j=3}^6 P_{5 \rightarrow j}$  are calculated for a given  $k_0(R)$  from  $k_0=0$  through  $k_0=10$  by the four methods of solution. From the largest magnitude for  $k_0$  for which the conservation condition (39) is fulfilled, one can select the most appropriate expression to use. The critical values of  $k_0$  are obtained as shown in Table III. From the magnitude of the matrix elements of  $\mathbf{M}_n(1)$ ,  $\mathbf{N}_n(1)$  and  $\mathbf{O}_n(1)$ , the excitation-transfer probability curves versus  $R_0$  in Figs. 5 and 6, and Table III, the method of expansion based on the rotating-atom approximation is considered

TABLE III. The value of maximum  $k_0$  for which the conservation properties  $\sum_{j=3}^6 P_{3 \rightarrow j} = 1$  and  $\sum_{j=3}^6 P_{5 \rightarrow j} = 1$  [Eq. (39)] obtain within the error of  $0.5 \times 10^{-3}$ .

Conservation property	Expansion used	Critical (maximum) $k_0$
$\sum_{j=3}^6 P_{3 \rightarrow j} = 1$	based on the initial state [Eq. (24)]	3.20
$\sum_{j=3}^6 P_{5 \rightarrow j} = 1$	based on the initial state [Eq. (24)]	3.30
$\sum_{j=3}^6 P_{3 \rightarrow j} = 1$	based on the $\eta$ -polarization fixed atom state [Eq. (29)]	3.00
$\sum_{j=3}^6 P_{5 \rightarrow j} = 1$	based on the $\eta$ -polarization fixed atom state [Eq. (29)]	3.10
$\sum_{j=3}^6 P_{3 \rightarrow j} = 1$	based on the $\zeta$ -polarization fixed atom state [Eq. (30)]	3.00
$\sum_{j=3}^6 P_{5 \rightarrow j} = 1$	based on the $\zeta$ -polarization fixed atom state [Eq. (30)]	3.10
$\sum_{j=3}^6 P_{3 \rightarrow j} = 1$	based on the rotating atom state [Eq. (33)]	2.70
$\sum_{j=3}^6 P_{5 \rightarrow j} = 1$	based on the rotating atom state [Eq. (33)]	2.30

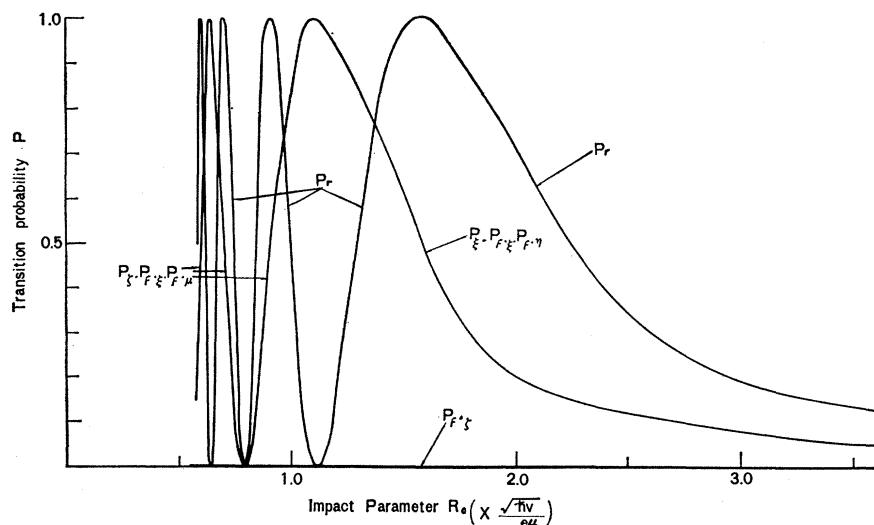


FIG. 6. Probabilities of the excitation transfer from an incident atom to a struck atom  $P_\xi$  versus the impact parameter  $R_0$  under the initial condition of  $|C_1|^2=1$  (an incident atom is initially in  $P_\xi$  state), and probabilities with the fixed-atom approximation under the respective initial conditions of  $|C_1|^2=1$ ,  $|C_3|^2=1$ , and  $|C_5|^2=1$ :  $P_{f\xi}$ ,  $P_{f\eta}$ ,  $P_{f\zeta}$  and that with the rotating-atom approximation  $P_r$ . (Probabilities  $P_\xi$  and those with the fixed-atom approximation under initial condition of  $|C_1|^2=1$  and  $|C_3|^2=1$  are identical with each other. Probabilities with the fixed-atom approximation under the initial condition of  $|C_5|^2=1$   $P_{f\zeta}$  is zero owing to the symmetrical property of electronic wave function with respect to incident atom path.)

to yield the largest amount of error among these methods. Thus, it may be concluded that the fixed-atom approximation may be better than the rotating-atom approximation.

Since the transfer cross section is extremely large compared with that of other collision processes, this excitation transfer process may play an important role in gas-phase experiments in which electronically excited atoms are involved, such as, measurements of  $W$  values in the radiation effect on gaseous systems, experiments with gas-lasers, gas-phase experiments in photochemistry, experiments on magnetohydrodynamic power generation, etc.

In these experiments, one can classify the gas pressure (in this case the ground state of the atom is restricted to  $S$  or  $P$  state) into three regions according to the process of  $S$ - $P$ -type excitation transfer. The first region is a low-pressure one in which the excitation transfer scarcely occurs during the life-time of the excitation under consideration (independent excitation region). The second is a middle-pressure region where the excitation transfer occurs during the life-time of the excitation, but not as frequently since the mean free path of the excitation transfer is smaller than the mean distance between identical atoms (excitation transfer region). The last is a high-pressure region where the excitation transfer occurs so frequently that the mean free path of the transfer exceeds the mean distance between atoms (collective-excitation region). In the last case, the excited state of an independent atom is not in a good eigenstate, and the "exciton state" or the "collectively excited state" should be taken into account.

The lower limit of the excitation transfer pressure region  $P_i$  can be obtained from the following relation: The mean free path of the excitation transfer  $l$  equals the excited-atom range  $r_e$  as  $l=r_e$ . Here  $l=N_0v$ ;  $N_0$  is

the concentration of the identical atoms and  $r_e=v\tau$ ,  $\tau$  being the life-time of the excitation. Since  $\tau$  is expressed in terms of  $\mu$  and the emission frequency of the excita-

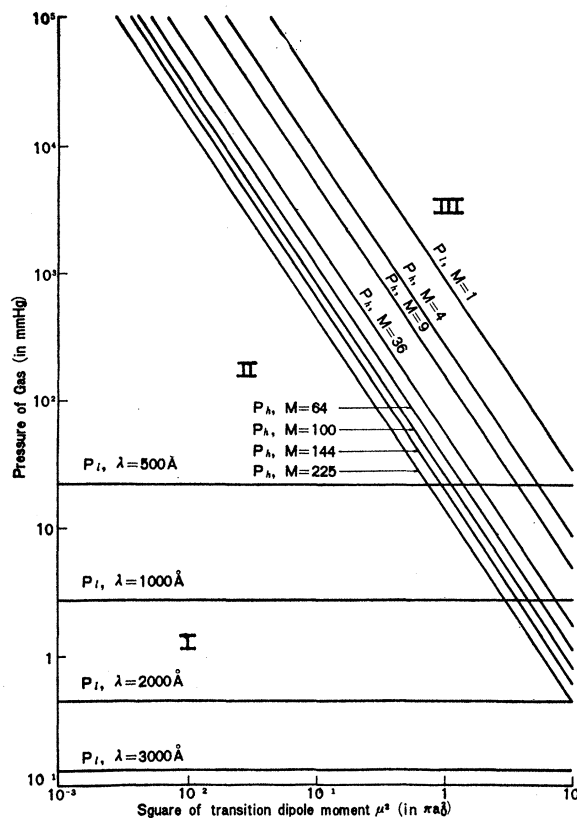


FIG. 7. Three pressure regions of the gaseous system of identical atoms with respect to their excitation transfer and their critical pressures versus the square of the transition dipole matrix elements. ( $M$  is the mass number of the atom and  $\lambda$  is the wave length of the excitation.) I. Independent excitation region; II. excitation transfer region; III. collective excitation region.



tion  $\omega_{0n}$  as<sup>8</sup>

$$\tau = (3/4)(\hbar c^3/e^2)\omega_{0n}^{-3}\mu^{-2},$$

$P_l$  is written as

$$P_l = \left( \frac{\text{molar volume}}{\text{Avogadro number}} \right) \times \frac{4}{3 \times 3.36} \left( \frac{\omega_{0n}}{c} \right)^3, \quad (40)$$

which is independent of both  $\mu$  and  $v$ , and dependent only on  $\omega_{0n}$ . The higher limit of the excitation transfer pressure region  $P_h$  can also be obtained from the condition that  $l$  equals the mean distance between the identical atoms  $L(=N_0^{-1/3})$ . Thus, one may have

$$P_h = \left( \frac{\text{molar volume}}{\text{Avogadro number}} \right) \times \frac{1}{\sigma^{3/2}}. \quad (41)$$

The critical pressures  $P_l$  and  $P_h$  versus the square of the transition dipole matrix element  $\mu^2$  are shown in Fig. 7.

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The author wishes to express his sincere thanks to Professor Ayao Amemiya and Professor Hiroshi Fujita of the University of Tokyo; the former for valuable suggestions and encouragement during the course of this work and the latter for useful remarks from a mathematical viewpoint. He is also grateful to Professor R. A. Bonham of Indiana University for useful discussions and for reading the manuscript.

#### APPENDIX

In order to solve Eq. (12), consider it in a general form:

$$d\mathbf{U}(x)/dx = k\mathbf{A}(x)\mathbf{U}(x), \quad (x_0 \leq x), \quad (A1)$$

where  $\mathbf{U} = \mathbf{U}(x)$  is the unknown  $m$ -vector function,

<sup>8</sup>L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., p. 261.

$\mathbf{A}(x)$  is a given  $m \times m$ -matrix function and  $k$  is a constant. Our objective is to obtain a solution  $\mathbf{U}$  of (A1) with a given  $\mathbf{U}(x_0)$ . Since (A1) is equivalent to

$$\mathbf{U}(x) = \mathbf{U}(x_0) + k \int_{x_0}^x \mathbf{A}(z)\mathbf{U}(z)dz,$$

one expects to have the solution in the form

$$\mathbf{U}(x) = \sum_{k=0}^{\infty} k^n \mathbf{A}_n(x) \mathbf{U}(x_0) \quad (A2)$$

with  $\mathbf{A}_0 = \mathbf{I}$ ,  $\mathbf{A}_n$  defined by

$$\mathbf{A}_n(x) = \int_{x_0}^x \mathbf{A}_{n-1}(z)dz, \quad (n=1, 2, \dots).$$

Actually, (A2) gives the solution if the series on the right side converges uniformly with respect to  $x$  in the interval in mind, say, on  $x_0 \leq x \leq x_1$ . Suppose that  $\|\mathbf{A}(x)\|$  is bounded by a constant  $N_A$  in the interval  $x_0 \leq x \leq x_1$ , where  $\|\mathbf{A}(x)\|$  means the norm of the matrix  $\mathbf{A}(x)$ , i.e.,  $\|\mathbf{A}(x)\| = \max_{i,j} \|A_{ij}(x)\|$ . Then it can be easily verified by induction that

$$\|\mathbf{A}_n(x)\| \leq (1/n!) (x-x_0)^n N_A^n = (1/n!) M_A^n, \quad (n=0, 1, \dots) \quad (A3)$$

for any  $x$  in  $x_0 \leq x \leq x_1$ ,  $M_A$  being  $(x_1-x_0)N_A$ . Noting  $\|k^n \mathbf{A}_n(x) \mathbf{U}(x_0)\| \leq |k|^n \|\mathbf{A}_n(x)\| \|\mathbf{U}(x_0)\|$ , it can be seen that the absolutely convergent numerical series with the  $n$ th term  $|k|^n M_A^n/n!$  majorizes the series in (A2). This implies the required uniform convergence and also the estimate

$$\|\mathbf{U}(x)\| \leq \exp(|k| M_A) \|\mathbf{U}(x_0)\|, \quad (x_0 \leq x \leq x_1).$$

Incidentally we see from (A3) that every matrix element of  $\mathbf{A}_n(x)$  at each point  $x$  is of the order  $(\text{const})^n/n!$  for large  $n$ . This is also the case with  $\mathbf{L}_n(x)$ ,  $\mathbf{M}_n(x)$ ,  $\mathbf{N}_n(x)$  and  $\mathbf{O}_n(x)$ .<sup>6</sup>