An application of the dynamical Lie algebraic method to energy transfer of the collinear scattering system AB + CD

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The dynamical Lie algebraic method has been applied to treat the V–V and T–V energy transfers in the collinear scattering system AB + CD. The expression for the vibrational transition probability, which contains the main dynamical parameters, is given analytically. By using this expression we probe into the V–V resonance and T–V resonance phenomena appearing in the process of energy transfer. We find that the transition probability of V–V resonance is in good agreement with that obtained using the resonant exchange hypothesis. Then the reliability of the resonant exchange hypothesis is confirmed.

1. Introduction

The dynamical Lie algebraic method developed by Alhassid and Levine has successfully been used to describe the topics of gas–surface scattering [2,4] and energy transfer in the collinear scattering system AB + BC [3]. Comparing with the usual perturbation theory, its advantage lies in the fact that the expression for the transition probability that contains the main dynamical parameters may be given analytically without being limited by the perturbation condition [2–4].

In our dealing with energy transfer, however, we treat the translational motion classically. This is the so-called semiclassical energy transfer theory [3,7]. In this paper, we will generalize the dynamical Lie algebraic method to the collinear collision of the AB+CD scattering system, in which the translational motion is also treated quantum mechanically, i.e., a purely quantum mechanical energy transfer theory [7]. It is obvious that the quantization of the translational motion may result in increasing of the dimension of the dynamical Lie algebra. In this way, the dimension of the dynamical Lie algebra of the system AB + CD increases from 15 (semiclassical treating) to 28 (pure quantum treating).

The interaction potential energy function of the system AB + CD is still the exponential type potential presented by Rapp and Golden [7]. Due to the existence of

vibration–translation and vibration–vibration couplings, there are T–V and V–V energy transfers in the system AB + CD.

On the basis of the method mentioned above we obtain the analytical expression for the transition probabilities containing the main dynamical parameters of the collinear system AB + CD. As an application we investigate the T–V resonance and V–V resonance appearing in the process of T–V and V–V energy transfer, respectively. The expression of the V–V resonant transition probability displays good agreement with that obtained by Rapp and Golden's resonant exchange hypothesis. This confirms the reliability of resonant exchange hypothesis.

This paper is organised as follows. In section 2 the Hamiltonian of the scattering system AB + CD is described, in section 3 we present the evolution operator and transition probability. The results are discussed in section 4.

2.   Hamiltonian of the scattering system AB + CD

According to scattering theory [7], the Hamiltonian operator of the collinear scattering system AB + CD can be expressed in the form

$$H = H_x + H_1 + H_2 + V(x_1, Y_1, Y_2), \tag{1}$$

$$H_x = \frac{1}{2\widetilde{M}} p_x^2, \tag{2}$$

$$H_j = \frac{1}{2\mu_j} p_j^2 + \frac{1}{2}\mu_j \omega_j^2 Y_j^2 \quad (j = 1, 2), \tag{3}$$

$$V(x, Y_1, Y_2) = A'' e^{-x/L} e^{\gamma_1 Y_1/L} e^{\gamma_2 Y_2/L}, \tag{4}$$

where H_x denotes the relative translation energy operator between AB and CD. x is the coordinate between the center of mass of AB, G_1, and that of CD, G_2 (see figure 1), p_x is the momentum operator corresponding to x, $\widetilde{M} = (m_A + m_B)(m_C + m_D)/(m_A + m_B + m_C + m_D)$. H_1 and H_2 represent vibrational energy operators of AB and CD,
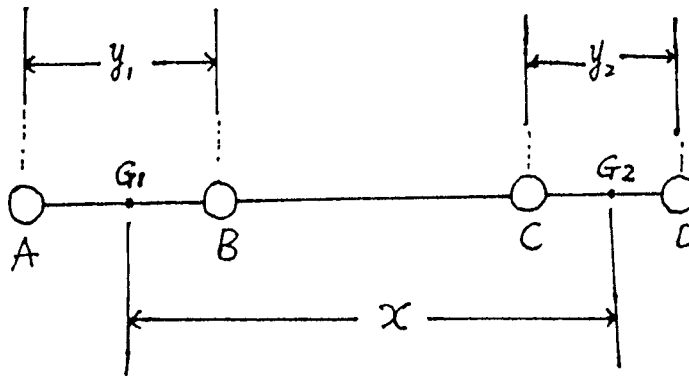

Figure 1. Coordinates for the collinear scattering system AB + CD.

respectively. ω_1 and ω_2 are vibrational angular frequencies of AB and CD, respectively, $\mu_1 = m_A m_B/(m_A + m_B)$, $\mu_2 = m_C m_D/(m_C + m_D)$. $Y_1 = y_1 - y_1^{(0)}$ and $Y_2 = y_2 - y_2^{(0)}$ stand for vibrational coordinates of AB and CD, respectively, $y_1^{(0)}$ and $y_2^{(0)}$ are the corresponding equilibrium vibrational coordinates. p_j $(j = 1, 2)$ are momentum operators corresponding to Y_j. $V(x, Y_1, Y_2)$ denotes the interaction potential of AB and CD. A'', L are potential parameters $(A'' = E_0$, $E_0 = \frac{1}{2}\widetilde{M}v_0^2$, v_0 is the initial translational velocity) [7], $\gamma_1 = m_A/(m_A + m_B)$, $\gamma_2 = m_D/(m_C + m_D)$.

In order to adopt the dynamical Lie algebraic method effectively, we need to make some approximations to the potential function $V(x, Y_1, Y_2)$ [1,3]. By using Taylor expansion we expand the potential V with respect to variables x, Y_1 and Y_2. It is necessary to consider at least terms of the second order in the expansion so that the couplings among x, Y_1 and Y_2 emerge and result in the effect of T–V and V–V energy transfer. Thus we obtain

$$
V(x, Y_1, Y_2) = A'' \left\{ -\frac{1}{L}x + \frac{\gamma_1}{L}Y_1 + \frac{\gamma_2}{L}Y_2 + \frac{1}{2L^2}x^2 + \frac{\gamma_1^2}{2L^2}Y_1^2 \right.
$$
$$
\left. + \frac{\gamma_2^2}{2L^2}Y_2^2 - \frac{\gamma_1}{L^2}xY_1 - \frac{\gamma_2}{L^2}xY_2 + \frac{\gamma_1\gamma_2}{L^2}Y_1Y_2 \right\}. \tag{5}
$$

In deriving equation (5) we have neglected those parameter terms (terms containing no coordinate operators) which make no contribution to the dynamics. As for the dynamical Lie algebraic method, it is convenient to use the particle number picture. So we introduce the following transformation formulas:

$$
x = \frac{\lambda}{2\pi\sqrt{2}}(b^+ + b),
$$
$$
p_x = i\frac{2\pi\hbar}{\lambda\sqrt{2}}(b^+ - b),
$$
$$
Y_j = \left(\frac{\hbar}{2\mu_j\omega_j}\right)^{1/2}(a_j^+ + a_j),
$$
$$
P_j = \left(\frac{\hbar\mu_j\omega_j}{2}\right)^{1/2}(a_j^+ - a_j) \quad (j = 1, 2), \tag{6}
$$

where λ is the de Broglie wave length corresponding to p_x; b^+, b are creation operators and annihilation operators corresponding to x, p_x; a_j^+, a are those corresponding to Y_j, P_j. By using the commutation relation $[x, p_x] = i\hbar$, $[Y_j, P_j] = i\hbar$ and equation (6) we have

$$
[a_j, a_k^+] = \delta_{jk} \quad (j, k = 1, 2),
$$
$$
[b, b^+] = 1. \tag{7}
$$

a_j^+, a_j and b^+, b commute each other. Equation (7) is the basic relations used to seek the dynamical Lie algebra of the scattering system. It follows by substituting equation (6) into equations (1)–(5), respectively, and using equation (7) that

$$H = H^{(0)} + V_s, \tag{8}$$

$$H^{(0)} = H_T + H_1 + H_2, \tag{9}$$

$$H_T = \frac{1}{2\widetilde{M}}\left(\frac{2\pi\hbar}{\lambda}\right)^2 b^+ b, \tag{10}$$

$$H_j = \hbar\omega_j\left(a_j^+ a_j + \frac{1}{2}\right) \quad (j = 1, 2), \tag{11}$$

$$
\begin{aligned}
V_s ={}& s_1 a_1^+ + s_2 a_1 + s_3 a_1^+ a_1 + s_4 a_1^{+2} + s_5 a_1^2 + s_6 a_2^+ + s_7 a_2 + s_8 a_2^+ a_2 + s_9 a_2^{+2} \\
&+ s_{10} a_2^2 + s_{11} b^+ + s_{12} b + s_{13} b^+ b + s_{14} b^{+2} + s_{15} b^2 + s_{16} a_1^+ a_2^+ + s_{17} a_1 a_2 \\
&+ s_{18} a_1^+ a_2 + s_{19} a_1 a_2^+ + s_{20} a_1^+ b^+ + s_{21} a_1 b + s_{22} a_1^+ b + s_{23} a_1 b^+ + s_{24} a_2^+ b^+ \\
&+ s_{25} a_2 b + s_{26} a_2^+ b + s_{27} a_2 b^+,
\end{aligned}
\tag{12}
$$

in which $H^{(0)}$ is the free Hamiltonian of the system. H_T denotes translational energy operators between molecules, H_j are vibrational energy operators of molecules. V_s is the interaction Hamiltonian between molecules. Seeing that we are free to divide the free Hamiltonian from the total Hamiltonian, we divide again the free Hamiltonian represented by equation (1) and the interaction Hamiltonian. The expressions of dynamical parameters s_l $(l = 1, 2, \ldots, 27)$ are listed in table 1.

Table 1
The expressions for dynamical parameters.

$s_1 = s_2 = A''\frac{\gamma_1}{L}(\frac{\hbar}{2\mu_1\omega_1})^{1/2}$, $s_4 = s_5 = A''\frac{\gamma_1^2\hbar}{4L^2\mu_1\omega_1}$, $s_3 = A''\frac{\gamma_1^2\hbar}{2L^2\mu_1\omega_1}$,

$s_6 = s_7 = A''\frac{\gamma_2}{L}(\frac{\hbar}{2\mu_2\omega_2})^{1/2}$, $s_9 = s_{10} = A''\frac{\gamma_2^2\hbar}{4L^2\mu_2\omega_2}$, $s_8 = A''\frac{\gamma_2^2\hbar}{2L^2\mu_2\omega_2}$,

$s_{11} = s_{12} = -A''\frac{\lambda}{2\pi L\sqrt{2}}$, $s_{14} = s_{15} = A''\frac{\lambda^2}{16\pi^2 L^2} - \frac{1}{4\widetilde{M}}(\frac{2\pi\hbar}{\lambda})^2$, $s_{13} = A''\frac{\lambda^2}{8\pi^2 L^2}$,

$s_{16} = s_{17} = s_{18} = s_{19} = A''\frac{\gamma_1\gamma_2}{L^2}(\frac{\hbar^2}{4\mu_1\mu_2\omega_1\omega_2})^{1/2}$,

$s_{20} = s_{21} = s_{22} = s_{23} = -A''\frac{\gamma_1\lambda}{2\pi L^2\sqrt{2}}(\frac{\hbar}{2\mu_1\omega_1})^{1/2}$,

$s_{24} = s_{25} = s_{26} = s_{27} = -A''\frac{\gamma_2\lambda}{2\pi L^2\sqrt{2}}(\frac{\hbar}{2\mu_2\omega_2})^{1/2}$,

$v_1 = s_1 e^{i\omega_1 t}$, $v_2 = v_1^*$, $v_4 = s_4 e^{2i\omega_1 t}$, $v_5 = v_1^*$, $v_3 = s_3$,

$v_6 = s_6 e^{i\omega_2 t}$, $v_7 = v_6^*$, $v_9 = s_9 e^{2i\omega_2 t}$, $v_{10} = v_9^*$, $v_8 = s_8$,

$v_{11} = s_{11} e^{iEt/\hbar}$, $v_{12} = v_{11}^*$, $v_{14} = s_{14} e^{2iEt/\hbar}$, $v_{15} = v_{14}^*$, $v_{13} = s_{13}$,

$v_{16} = s_{16} e^{i(\omega_1+\omega_2)t}$, $v_{17} = v_{16}^*$, $v_{18} = s_{18} e^{i(\omega_1-\omega_2)t}$, $v_{19} = v_{18}^*$,

$v_{20} = s_{20} e^{i(\hbar\omega_1+E)t/\hbar}$, $v_{21} = v_{20}^*$, $v_{22} = s_{22} e^{i(\hbar\omega_1-E)t/\hbar}$,

$v_{23} = s_{22}^*$, $v_{24} = v_{24} e^{i(\hbar\omega_2+E)t/\hbar}$, $v_{25} = s_{24}^*$,

$v_{26} = s_{26} e^{i(\hbar\omega-E)t/\hbar}$, $v_{27} = s_{26}^*$, $E = \frac{1}{2\widetilde{M}}(\frac{2\pi\hbar}{\lambda})^2$.

To seek the dynamical Lie algebra of the system one needs to transform V_s into the interaction picture:

$$
\begin{aligned}
V_I(t) &= \exp\left\{\frac{\mathrm{i}}{\hbar}H^{(0)}t\right\}V_s\exp\left\{-\frac{\mathrm{i}}{\hbar}H^{(0)}t\right\} \\
&= v_1 a_1^+ + v_2 a_1 + v_3 a_1^+ a_1 + v_4 a_1^{+2} + v_5 a_1^2 + v_6 a_2^+ + v_7 a_2 + v_8 a_2^+ a_2 \\
&\quad + v_9 a_2^{+2} + v_{10} a_2^2 + v_{11} b^+ + v_{12} b + v_{13} b^+ b + v_{14} b^{+2} + v_{15} b^2 + v_{16} a_1^+ a_2^+ \\
&\quad + v_{17} a_1 a_2 + v_{18} a_1^+ a_2 + v_{19} a_1 a_2^+ + v_{20} a_1^+ b^+ + v_{21} a_1 b + v_{22} a_1^+ b + v_{23} a_1 b^+ \\
&\quad + v_{24} a_2^+ b^+ + v_{25} a_2 b + v_{26} a_2^+ b + v_{27} a_2 b^+.
\end{aligned} \tag{13}
$$

The expressions of dynamical parameters v_l $(l = 1, 2, \ldots, 27)$ are listed in table 1. Subscript I stands for interaction picture. Under the commutation relations presented by table 2 the operators on the right-hand side of equation (13) are closed, so they form a 28-dimensional dynamical Lie algebra $h^{(28)}$, the algebra elements are: I, a_1^+, a_1, $a_1^+ a_1$, a_1^{+2}, a_1^2, a_2^+, a_2, $a_2 a_2^+$, a_2^{+2}, a_2^2, b^+, b, $b^+ b$, b^{+2}, b^2, $a_1^+ a_2^+$, $a_1 a_2$, $a_1^+ a_2$, $a_1 a_2^+$, $a_1^+ b^+$, $a_1 b$, $a_1^+ b$, $a_1 b^+$, $a_2^+ b^+$, $a_2 b$, a_2^+, $a_2 b^+$ (here the order of the algebra elements has been preordained).

Table 2
The commutation relations for the dynamical Lie algebra $h^{(28)}$. Other commutation relations can be obtained by taking the adjoint of those listed in this table.

$[a_j, a_j^+] = I$, $[a_j^+ a_j, a_j^+] = a_j^+$, $[a_j^2, a_j^+] = 2a_j$, $[a_j^+ a_j, a_j^{+2}] = 2a_j^{+2}$,

$[a_j^2, a_j^{+2}] = 2 + 4a_j^+ a_j$ $(j = 1, 2)$, $[b^+, b] = 1$, $[b^+ b, b^+] = b^+$, $[b^2, b^+] = 2b$,

$[b^+ b, b^{+2}] = 2b^{+2}$, $[b^2, b^{+2}] = 2 + 4b^+ b$, $[a_1 a_2, a_1^+ a_2^+] = 1 + a_1^+ a_1 + a_2^+ a_2$, $[a_1^+ a_2, a_1^+ a_2^+] = a_1^{+2}$,

$[a_1 a_2^+, a_1^+ a_2^+] = a_2^{+2}$, $[a_1^+ a_2, a_1 a_2^+] = a_1^+ a_1 - a_2^+ a_2$, $[a_j^+ b, a_j^+ b^+] = 1 + a_j^+ a_j + b^+ b$,

$[a_j^+ b, a_j^+ b^+] = a_j^{+2}$, $[a_j b^+, a_j^+ b^+] = b^{+2}$, $[a_j^+ b, a_j b^+] = a_j^+ a_j - b^+ b$ $(j = 1, 2)$,

$[a_1 a_2, a_1^+ b^+] = a_2 b^+$, $[a_1 a_2^+, a_1^+ b^+] = a_2^+ b^+$, $[a_1^+ b, a_2^+ b] = a_1^+ a_2^+$,

$[a_1 b, a_2^+ b^+] = a_1 a_2^+$, $[a_1 a_2, a_2^+ b] = a_1 b^+$, $[a_1^+ a_2, a_2^+ b^+] = a_1^+ b^+$,

$[a_1 a_2, a_1^+ b] = a_2 b$, $[a_1 a_2^+, a_1^+ b] = a_2^+ b$, $[a_1 b, a_2 b^+] = a_1 a_2$,

$[a_1^+ b, a_2 b^+] = a_1^+ a_2$, $[a_1 a_2, a_2^+ b] = a_1 b$, $[a_1^+ a_2, a_2^+ b] = a_1^+ b$,

$[a_1, a_1^+ a_2^+] = a_2^+$, $[a_1, a_1^+ a_2] = a_2$, $[a_1^+ a_1, a_1^+ a_2^+] = a_1^+ a_2^+$,

$[a_1^+ a_1, a_1^+ a_2] = a_1^+ a_2$, $[a_1^2, a_1^+ a_2^+] = 2a_1 a_2^+$, $[a_1^2, a_1^+ a_2] = 2a_1 a_2$,

$[a_2, a_1^+ a_2^+] = a_1^+$, $[a_2, a_1 a_2^+] = a_1$, $[a_2^+ a_2, a_1^+ a_2^+] = a_1^+ a_2^+$,

$[a_2^+ a_2, a_1 a_2^+] = a_1 a_2^+$, $[a_2^2, a_1^+ a_2^+] = 2a_1^+ a_2$, $[a_2^2, a_1 a_2^+] = 2a_1 a_2$,

$[a_j, a_j^+ b^+] = b^+$, $[a_j, a_j^+ b] = b$, $[a_j^+ a_j, a_j^+ b^+] = a_j^+ b^+$,

$[a_j^2, a_j^+ b^+] = 2a_j b^+$, $[a_j^2, a_j^+ b] = 2a_j b$, $[b, a_j^+ b^+] = a_j^+$, $[b, a_j b^+] = a_j$,

$[b^+ b, a_j^+ b^+] = a_j^+ b^+$, $[b^+ b, a_j b^+] = a_j b^+$, $[b^2, a_j^+ b^+] = 2a_j^+ b$,

$[b^2, a_j b^+] = 2a_j b$ $(j = 1, 2)$.

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3. Evolution operators and transition probability

In the light of the dynamical Lie algebra theory, the evolution operators of the system can be expressed as [1]

$$U(t, t_0) = e^T, \tag{14}$$

$$T = -\frac{i}{\hbar} \sum_{k=0}^{27} u_k(t, t_0) H^{(k)}, \tag{15}$$

where $H^{(k)}$ denote the algebra elements (according to the preordained order). $u_k(t, t_0)$ are group parameters, they are determined by the following equation (under the first order approximation of the group parameters) [1]:

$$\frac{\partial}{\partial t} \mathbf{u} = \left\{ \mathbf{I} - \frac{1}{2} \mathbf{d}(T) \right\} \mathbf{v}, \tag{16}$$

Table 3
Matrix elements $i\hbar d_{lk}$.

	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
0	0	u_2	$-u_2^*$	0	$2u_5$	$2u_5^*$	u_7	$-u_7^*$	0	$2u_{10}$	$-2u_{10}^*$	u_{12}	$-u_{12}^*$	0	$2u_{15}$
1	0	u_3	$-2u_5^*$	$-u_1$	$2u_2$	0	u_{18}	$-u_{17}^*$	0	0	0	u_{22}	$-u_{21}^*$	0	0
2	0	$2u_5$	$-u_3^*$	u_2	0	$-2u_2^*$	u_{17}	$-u_{18}^*$	0	0	0	u_{21}	$-u_{22}^*$	0	0
3	0	0	0	0	$4u_5$	$-4u_5^*$	0	0	0	0	0	0	0	0	0
4	0	0	0	$-2u_4$	$2u_3$	0	0	0	0	0	0	0	0	0	0
5	0	0	0	$2u_5$	0	$-2u_3^*$	0	0	0	0	0	0	0	0	0
6	0	u_{19}	$-u_{17}^*$	0	0	0	u_8	$-2u_{10}^*$	$-u_6$	$2u_7$	0	u_{26}	$-u_{25}^*$	0	0
7	0	u_{17}	$-u_{19}^*$	0	0	0	$2u_{10}$	$-u_8^*$	u_7	0	$-2u_7^*$	u_{25}	$-u_{26}^*$	0	0
8	0	0	0	0	0	0	0	0	0	$4u_{10}$	$-4u_{10}^*$	0	0	0	0
9	0	0	0	0	0	0	0	0	$-2u_9$	$2u_8$	0	0	0	0	0
10	0	0	0	0	0	0	0	0	$2u_{10}$	0	$-2u_8^*$	0	0	0	0
11	0	u_{23}	$-u_{21}^*$	0	0	0	u_{27}	$-u_{25}^*$	0	0	0	u_{13}	$-2u_{15}^*$	$-u_{11}$	$2u_{12}$
12	0	u_{21}	$-u_{23}^*$	0	0	0	u_{25}	$-u_{27}^*$	0	0	0	$2u_{15}$	$-u_{13}^*$	u_{13}	0
13	0	0	0	0	0	0	0	0	0	0	0	0	0	0	$4u_{15}$
14	0	0	0	0	0	0	0	0	0	0	0	0	0	$-2u_{14}$	$2u_{13}$
15	0	0	0	0	0	0	0	0	0	0	0	0	0	$2u_{15}$	0
16	0	0	0	$-u_{16}$	$2u_{19}$	0	0	0	$-u_{16}$	$2u_{18}$	0	0	0	0	0
17	0	0	0	u_{17}	0	$-2u_{19}^*$	0	0	u_{17}	0	$-2u_{18}^*$	0	0	0	0
18	0	0	0	$-u_{18}$	$2u_{17}$	0	0	0	u_{18}	0	$-2u_{17}^*$	0	0	0	0
19	0	0	0	$-u_{19}$	0	$-2u_{17}^*$	0	0	u_{19}	$2u_{17}$	0	0	0	0	0
20	0	0	0	$-u_{20}$	$2u_{23}$	0	0	0	0	0	0	0	0	$-u_{20}$	$2u_{22}$
21	0	0	0	u_{21}	0	$-2u_{23}^*$	0	0	0	0	0	0	0	u_{21}	0
22	0	0	0	$-u_{22}$	$2u_{21}$	0	0	0	0	0	0	0	0	u_{22}	0
23	0	0	0	u_{23}	0	$-2u_{21}^*$	0	0	0	0	0	0	0	$-u_{23}$	$2u_{21}$
24	0	0	0	0	0	0	0	0	$-u_{24}$	$2u_{27}$	0	0	0	$-u_{24}$	$2u_{26}$
25	0	0	0	0	0	0	0	0	u_{25}	0	$-2u_{27}^*$	0	0	u_{25}	0
26	0	0	0	0	0	0	0	0	$-u_{26}$	$2u_{25}$	0	0	0	u_{26}	0
27	0	0	0	0	0	0	0	0	u_{27}	0	$-2u_{25}^*$	0	0	$-u_{27}$	$2u_{25}$

in which column vectors **u** and **v** are

$$\mathbf{u} = \begin{bmatrix} u_0 \\ u_1 \\ \vdots \\ u_{27} \end{bmatrix}, \qquad \mathbf{v} = \begin{bmatrix} 0 \\ v_1 \\ \vdots \\ v_{27} \end{bmatrix},$$

I is a 28×28 identity matrix. The 28×28 matrix $\mathbf{d}(T)$ can be determined by the following operators equation [1]:

$$\left[T, H^{(k)}\right] = \sum_{l=0}^{27} d_{lk}(T) H^{(l)}, \quad k = 0, 1, 2, \ldots, 27. \tag{17}$$

Table 3
(Continued.)

	15	16	17	18	19	20	21	22	23	24	25	26	27
0	$-2u_{15}^*$	u_{17}	$-u_{17}^*$	0	0	u_{21}	$-u_{21}^*$	0	0	u_{25}	$-u_{25}^*$	0	0
1	0	u_7	0	$-u_6$	0	u_{12}	0	$-u_{11}$	0	0	0	0	0
2	0	0	$-u_7^*$	0	u_6^*	0	$-u_{12}^*$	0	u_{11}^*	0	0	0	0
3	0	u_{17}	$-u_{17}^*$	$-u_{19}$	u_{19}^*	u_{21}	$-u_{21}^*$	$-u_{23}$	u_{23}^*	0	0	0	0
4	0	u_{18}	0	$-u_{16}$	0	u_{22}	0	$-u_{20}$	0	0	0	0	0
5	0	0	$-u_{18}^*$	0	u_{16}^*	0	$-u_{22}^*$	0	u_{20}^*	0	0	0	0
6	0	u_2	0	0	$-u_2^*$	0	0	0	0	u_{12}	0	$-u_{11}$	0
7	0	0	$-u_2^*$	u_2	0	0	0	0	0	0	$-u_{12}^*$	0	$-u_{11}^*$
8	0	u_{17}	$-u_{17}^*$	u_{19}	$-u_{19}^*$	0	0	0	0	u_{25}	$-u_{25}^*$	$-u_{27}$	u_{27}^*
9	0	u_{19}	0	0	$-u_{17}^*$	0	0	0	0	u_{26}	0	$-u_{24}$	0
10	0	0	$-u_{19}^*$	u_{17}	0	0	0	0	0	0	$-u_{26}^*$	0	u_{24}^*
11	0	0	0	0	0	u_2	0	0	$-u_2^*$	u_7	0	0	$-u_7^*$
12	$-2u_{12}^*$	0	0	0	0	0	$-u_2^*$	u_2	0	0	$-u_7^*$	u_7	0
13	$-4u_{15}^*$	0	0	0	0	u_{21}	$-u_{21}^*$	u_{23}	$-u_{23}^*$	u_{25}	$-u_{25}^*$	u_{27}	$-u_{27}^*$
14	0	0	0	0	0	u_{23}	0	0	$-u_{21}^*$	u_{27}	0	0	$-u_{25}^*$
15	$-2u_{13}^*$	0	0	0	0	0	$-u_{23}^*$	u_{21}	0	0	$-u_{27}^*$	u_{25}	0
16	0	t_1	0	$-u_9$	$-2u_9$	$-2u_5^*$	0	$-u_{24}$	0	u_{22}	0	$-u_{20}$	0
17	0	0	t_2	$2u_5$	$2u_9^*$	0	$-u_{26}^*$	0	u_{24}^*	0	$-u_{22}^*$	0	u_{20}^*
18	0	$2u_{10}$	$-2u_5^*$	t_3	0	u_{25}	0	$-u_{27}$	0	0	$-u_{21}^*$	0	u_{23}^*
19	0	$2u_5$	$-2u_{10}^*$	0	t_4	0	$-u_{25}^*$	0	u_{27}^*	u_{21}	0	$-u_{23}$	0
20	0	u_{27}	0	$-u_{24}$	0	t_5	0	$-2u_{14}$	$-2u_5^*$	u_{18}	0	0	$-u_{17}^*$
21	$-2u_{22}^*$	0	$-u_{27}^*$	0	u_{24}^*	0	t_6	$2u_5$	$2u_{14}^*$	0	$-u_{18}^*$	u_{17}	0
22	$-2u_{21}^*$	u_{25}	0	$-u_{26}$	0	$2u_{15}$	$-2u_5^*$	t_7	0	0	$-u_{17}^*$	u_{18}	0
23	0	0	$-u_{25}^*$	0	u_{26}^*	$2u_5$	$-2u_{15}^*$	0	t_8	u_{17}	0	0	$-u_{18}^*$
24	0	u_{23}	0	0	$-u_{21}^*$	u_{19}	0	0	$-u_{17}^*$	t_9	0	$-2u_{14}$	$-2u_{10}^*$
25	$-2u_{26}^*$	0	$-u_{23}^*$	u_{21}	0	0	$-u_{19}^*$	u_{17}	0	0	t_{10}	$2u_{10}$	$2u_{14}^*$
26	$-2u_{25}^*$	u_{21}	0	0	$-u_{23}^*$	0	$-u_{17}^*$	u_{19}	0	$2u_{15}$	$-2u_{10}^*$	t_{11}	0
27	0	0	$-u_{21}^*$	u_{23}	0	u_{17}	0	0	$-u_{19}^*$	$2u_{10}$	$-2u_{15}^*$	0	t_{12}

Here, $t_1 = u_3 + u_8$, $t_2 = -u_3^* - u_8^*$, $t_3 = u_3 - u_8$, $t_4 = -u_3^* + u_8^*$, $t_5 = u_3 + u_{13}$, $t_6 = -u_3^* - u_{13}^*$, $t_7 = u_3 - u_{13}$, $t_8 = -u_3^* + u_{13}^*$, $t_9 = u_8 + u_{13}$, $t_{10} = -u_8^* - u_{13}^*$, $t_{11} = u_8 - u_{13}$, $t_{12} = -u_8^* + u_{13}^*$.

The expressions of matrix elements $d_{lk}(T)$ are listed in table 3. Equation (16) can be solved with the help of the progressive approach method. Table 4 presents the results obtained under the first order progressive approach.

In the particle number picture [1,3], the eigenstates of the particle number operators $a_j^+ a_j$ $(j = 1, 2)$ and $b^+ b$ are

$$|n_j\rangle = \frac{a_j^{+n_j}}{\sqrt{n_j!}}|0\rangle \quad \text{and} \quad |m\rangle = \frac{b^{+m}}{\sqrt{m!}}|0\rangle.$$

Since the three types of particle operators commute each other, they have the common eigenstate $|n_1\rangle|n_2\rangle|m\rangle$. Then we have

$$H^{(0)}|n_1\rangle|n_2\rangle|m\rangle = \left\{ mE + \hbar\omega_1\left(n_1 + \frac{1}{2}\right) + \hbar\omega_2\left(n_2 + \frac{1}{2}\right) \right\}|n_1\rangle|n_2\rangle|m\rangle, \quad (18)$$

in which $E_T = mE$ is the eigenvalue of the translational energy operators,

$$E = \frac{1}{2\widetilde{M}}\left(\frac{2\pi\hbar}{\lambda}\right)^2.$$

$\hbar\omega_j(n_j + 1/2)$ are eigenvalues of the vibrational energy operator of molecules. The transition matrix element (under the first order approximation of the group parameter) of the system transiting from quantum state m, n_1, n_2 to m', n_1', n_2' is

$$\lim_{\substack{t\to\infty \\ t_0\to-\infty}} \langle m'|\langle n_1'|\langle n_2'|U(t,t_0)|n_2\rangle|n_1\rangle|m\rangle$$

$$= \lim_{\substack{t\to t_e \\ t_0\to-t_e}} \langle m'|\langle n_1'|\langle n_2'|U(t,t_0)|n_2\rangle|n_1\rangle|m\rangle$$

$$= \langle m'|\langle n_1'|\langle n_2'|U(t_e,-t_e)|n_2\rangle|n_1\rangle|m\rangle$$

$$= \langle m'|\langle n_1'|\langle n_2'| \left\{ I - \frac{\mathrm{i}}{\hbar}\sum_{l=0}^{27} u_l(t_e,-t_e)H^{(l)} \right\}|n_2\rangle|n_1\rangle|m\rangle. \quad (19)$$

The expressions of equation (19) are listed in table 4. Here $2t_e$ is the effective collision time [5], that is,

$$\lim_{\substack{t\to\infty \\ \text{or } t_0\to-\infty}} V_I(t) = \lim_{\substack{t\to t_e \\ \text{or } t_0\to-t_e}} V_I(t) = 0.$$

Finally, the corresponding transiton probability is

$$P_{m,n_1,n_2\to m',n_1',n_2'} = \left| \langle m'|\langle n_1'|\langle n_2'|U(t_e,-t_e)|n_2\rangle|n_1\rangle|m\rangle \right|^2. \quad (20)$$

The expressions of the group parameters $u_l(t_e,-t_e)$ $(l = 1, 2, \ldots, 27)$ appearing in equation (19) or (20) are given in table 4.

Table 4
The expressions for group parameters $u_j(t_e, t_e)$ and transition probability.

$u_1 = \frac{2s_1}{\omega_1} e^{(i/2)\omega_1 t_e} \sin\frac{\omega_1 t_e}{2},$ $u_2 = u_1^*,$ $u_3 = 2s_3 t_e,$

$u_4 = \frac{s_4}{\omega_1} e^{i\omega_1 t_e} \sin(\omega_1 t_e),$ $u_5 = u_4^*,$

$u_6 = \frac{2s_6}{\omega_2} e^{(i/2)\omega_2 t_e} \sin\frac{\omega_2 t_e}{2},$ $u_7 = u_6^*,$ $u_9 = \frac{s_9}{\omega_2} e^{i\omega_2 t_e} \sin(\omega_2 t_e),$

$u_{10} = u_9^*,$ $u_8 = 2s_8 t_e,$

$u_{11} = \frac{2\hbar s_{11}}{E} e^{(i/(2\hbar))E t_e} \sin\frac{E t_e}{2\hbar},$ $u_{12} = u_{11}^*,$ $u_{13} = 2s_{13} t_e,$

$u_{14} = \frac{\hbar s_{14}}{E} e^{(i/\hbar)E t_e} \sin\frac{E t_e}{\hbar},$ $u_{15} = u_{14}^*,$

$u_{16} = \frac{2s_{16}}{\omega_1+\omega_2} e^{(i/2)(\omega_1+\omega_2)t_e} \sin\frac{(\omega_1+\omega_2)t_e}{2},$ $u_{17} = u_{16}^*,$

$u_{18} = \frac{2s_{18}}{\omega_1-\omega_2} e^{(i/2)(\omega_1-\omega_2)t_e} \sin\frac{(\omega_1-\omega_2)t_e}{2},$ $u_{19} = u_{18}^*,$

$u_{20} = \frac{2\hbar s_{20}}{\hbar\omega_1+E} e^{(i/2\hbar)(\hbar\omega_1+E)t_e} \sin\frac{(\hbar\omega_1+E)t_e}{2\hbar},$ $u_{21} = u_{20}^*,$

$u_{22} = \frac{2\hbar s_{22}}{\hbar\omega_1-E} e^{(i/2\hbar)(\hbar\omega_1-E)t_e} \sin\frac{(\hbar\omega_1-E)t_e}{2\hbar},$ $u_{23} = u_{22}^*,$

$u_{24} = \frac{2\hbar s_{24}}{\hbar\omega_2+E} e^{(i/2\hbar)(\hbar\omega_2+E)t_e} \sin\frac{(\hbar\omega_2+E)t_e}{2\hbar},$ $u_{25} = u_{24}^*,$

$u_{26} = \frac{2\hbar s_{26}}{\hbar\omega_2-E} e^{(i/2\hbar)(\hbar\omega_2-E)t_e} \sin\frac{(\hbar\omega_2-E)t_e}{\hbar},$ $u_{27} = u_{26}^*.$

$\langle m'|\langle n_1'|\langle n_2'|U(t_e, -t_e)|n_2\rangle n_1\rangle|m\rangle$

$$= \langle m'|\langle n_1'|\langle n_2'| \left\{ I - \frac{i}{\hbar} \sum_{l=0}^{27} u_l(t_e, -t_e) H^{(l)} \right\} |n_2\rangle n_1\rangle|m\rangle$$

$$= \delta_{m',m}\delta_{n_1',n_1}\delta_{n_2',n_2} - \frac{i}{\hbar}\{ u_0\delta_{m',m}\delta_{n_1',n_1}\delta_{n_2',n_2} + u_1\sqrt{n_1+1}\delta_{m',m}\delta_{n_1',n_1}\delta_{n_2',n_2}$$

$$+ u_2\sqrt{n_1}\delta_{m',m}\delta_{n_1',n_1-1}\delta_{n_2',n_2} + u_3 n_1\delta_{m',m}\delta_{n_1',n_1}\delta_{n_2',n_2}$$

$$+ u_4\sqrt{(n_1+1)(n_1+2)}\delta_{m',m}\delta_{n_1',n_1+2}\delta_{n_2',n_2} + u_5\sqrt{n_1(n_1-1)}\delta_{m',m}\delta_{n_1',n_1-2}\delta_{n_2',n_2}$$

$$+ u_6\sqrt{n_2+1}\delta_{m',m}\delta_{n_1',n_1}\delta_{n_2',n_2+1} + u_7\sqrt{n_2}\delta_{m',m}\delta_{n_1',n_1}\delta_{n_2',n_2-1}$$

$$+ u_8 n_2\delta_{m',m}\delta_{n_1',n_1}\delta_{n_2',n_2} + u_9\sqrt{(n_2+1)(n_2+2)}\delta_{m',m}\delta_{n_1',n_1}\delta_{n_2',n_2+2}$$

$$+ u_{10}\sqrt{n_2(n_2-1)}\delta_{m',m}\delta_{n_1',n_1}\delta_{n_2',n_2-2} + u_{11}\sqrt{m+1}\delta_{m',m+1}\delta_{n_1',n_1}\delta_{n_2',n_2}$$

$$+ u_{12}\sqrt{m}\delta_{m',m-1}\delta_{n_1',n_1}\delta_{n_2',n_2} + u_{13}m\delta_{m',m}\delta_{n_1',n_1}\delta_{n_2',n_2}$$

$$+ u_{14}\sqrt{(m+1)(m+2)}\delta_{m',m+2}\delta_{n_1',n_1}\delta_{n_2',n_2} + u_{15}\sqrt{m(m-1)}\delta_{m',m-2}\delta_{n_1',n_1}\delta_{n_2',n_2}$$

$$+ u_{16}\sqrt{(n_1+1)(n_2+1)}\delta_{m',m}\delta_{n_1',n_1+1}\delta_{n_2',n_2+1} + u_{17}\sqrt{n_1 n_2}\delta_{m',m}\delta_{n_1',n_1-1}\delta_{n_2',n_2-1}$$

$$+ u_{18}\sqrt{(n_1+1)n_2}\delta_{m',m}\delta_{n_1',n_1+1}\delta_{n_2',n_2-1} + u_{19}\sqrt{n_1(n_2+1)}\delta_{m',m}\delta_{n_1',n_1-1}\delta_{n_2',n_2+1}$$

$$+ u_{20}\sqrt{(n_1+1)(m+1)}\delta_{m',m+1}\delta_{n_1',n_1+1}\delta_{n_2',n_2} + u_{21}\sqrt{n_1 m}\delta_{m',m-1}\delta_{n_1',n_1-1}\delta_{n_2',n_2}$$

$$+ u_{22}\sqrt{(n_1+1)m}\delta_{m',m-1}\delta_{n_1',n_1+1}\delta_{n_2',n_2} + u_{23}\sqrt{n_1(m+1)}\delta_{m',m+1}\delta_{n_1',n_1-1}\delta_{n_2',n_2}$$

$$+ u_{24}\sqrt{(n_2+1)(m+1)}\delta_{m',m+1}\delta_{n_1',n_1}\delta_{n_2',n_2+1} + u_{25}\sqrt{n_2 m}\delta_{m',m-1}\delta_{n_1',n_1}\delta_{n_2',n_2-1}$$

$$+ u_{26}\sqrt{(n_2+1)m}\delta_{m',m-1}\delta_{n_1',n_1}\delta_{n_2',n_2+1} + u_{27}\sqrt{n_2(m+1)}\delta_{m',m+1}\delta_{n_1',n_1}\delta_{n_2',n_2-1}.$$

4. Results and discussion

(I) In the transition matrix elements (see table 4), the terms containing group parameters $u_{16}, u_{17}, \ldots, u_{27}$ are the ones describing energy transfer. In detail, the terms containing u_{16}, u_{17}, u_{18} and u_{19} describe the energy transfer between vibrations of

AB and CD, while the terms containing u_{20}, u_{21}, u_{22}, u_{23} describe the energy transfer between the vibration and translation of AB and the terms containing u_{24}, u_{25}, u_{26}, and u_{27} correspond to that of CD. As an application of equation (20), we will calculate the following two kinds of transition probabilities.

(i) Transition $m = m'$; $n_1 = 1$, $n_2 = 0 \rightarrow n_1' = 0$, $n_2' = 1$. In this case the translational energy is not changed [7], the vibrational quantum numbers satisfy $n_1 + n_2 = n_1' + n_2'$. The corresponding transition probability is

$$P_{m,1,0 \rightarrow m,0,1} = \frac{A''^2 \gamma_1^2 \gamma_2^2}{L^4 \mu_1 \mu_2 \omega_1 \omega_2 (\omega_1 - \omega_2)^2} \sin^2 \left(\frac{(\omega_1 - \omega_2)t_e}{2} \right). \tag{21}$$

Equation (20) indicates that the transition probability increases with ω_1 approaching ω_2. When $\omega_1 = \omega_2$, it reaches the maximum value

$$P_{m,1,0 \rightarrow m,0,1}^{(\text{max})} = \frac{A''^2 \gamma_1^2 \gamma_2^2 t_e^2}{4L^4 \mu_1 \mu_2 \omega_1^2}. \tag{22}$$

That is to say that the effect of V–V energy transfer is optimum when the angular frequencies of two molecules are equal. This phenomenon may be called V–V resonance. It is easy to see that the results mentioned above are very similar to those obtained using usual time-dependent periodic perturbation theory. But it should be pointed out that the resonance of the latter results from the periodic perturbation out side, while that of the former from the interaction between molecules. For this reason the physical mechanisms are different.

(ii) Transition $n_2 = n_2'$; $m = 1$, $n_1 = 0 \rightarrow m' = 0$, $n_1' = 1$. It represents the energy transfer between vibration of AB and translation under the condition that the vibrational quantum number of CD is not changed. The corresponding transition probability is

$$P_{1,0,n_2 \rightarrow 0,1,n_2} = \frac{A''^2 \hbar \gamma_1 \lambda^2}{4\pi^2 \mu_1 \omega_1 (\hbar \omega_1 - E)^2} \sin^2 \frac{(\hbar \omega_1 - E)t_e}{2\hbar}. \tag{23}$$

Equation (23) indicates that the transition probability increases with E approaching $\hbar \omega_1$, when $E = \hbar \omega_1$ it reaches the maximum value

$$P_{1,0,n_2 \rightarrow 0,1,n_2}^{(\text{max})} = \frac{A''^2 \gamma_1^2 \lambda^2 t_e^2}{16\pi^2 \hbar \mu_1 \omega_1}. \tag{24}$$

That is to say that the effect of T–V energy transfer is optimum when the translational energy difference E is equal to the vibrational energy difference $\hbar \omega_1$. This phenomenon is called T–V resonance. Obviously, the results mentioned above are still similar to those obtained by using time-dependent periodic perturbation theory. But the former results from the interaction of vibration of AB and translation. So two mechanisms of them are different.

(II) Rapp and Golden had delt with the so-called resonant exchange process [6,7]

$$AB(n_1 = 1) + BA(n_2 = 0) \rightarrow AB(n'_1 = 0) + BA(n'_2 = 1). \tag{25}$$

The transition of such a process can be obtained by solving the following equation [7]:

$$\frac{d}{dt}c_{rs}(t) = -\frac{i}{\hbar}E_0 A(t) \sum_{j=0}^{\infty} \sum_{n=0}^{\infty} B_{rs,jn} e^{(\omega_{rj} - \omega_{sn})t} c_{jn}(t), \tag{26}$$

where $E_0 = \frac{1}{2}\widetilde{M}v_0^2$ is the initial translational energy, $A(t)$ denotes the classical trajectory. ω is the angular frequency of AB (or CD). $\gamma_1 = \gamma_2 = m_A/(m_A + m_B)$, $\mu_1 = \mu_2 = \mu = m_A m_B/(m_A + m_B)$, $\widetilde{M} = \frac{1}{2}(m_A + m_B)$. The transition probability from the quantum state n_1, n_2 to n'_1, n'_2 is

$$P_{n_1,n_2 \rightarrow n'_1,n'_2} = |c_{n'_1,n'_2}|^2. \tag{27}$$

Due to that equation (26) contains infinite variables $c_{rs}(t)$, it cannot be solved by usual method [8]. To solve equation (26) we should introduce some hypothesis. We assume that there exists a certain resonant mechanism between the initial state $n_1 = 1$, $n_2 = 0$ and the final state $n'_1 = 0$, $n'_2 = 1$ of the process (25), i.e., the so-called resonant exchange mechanism [6,7]. Therefore, we can retain the terms containing c_{10} and c_{01}. Thereby (26) can be simplified to be a set of equations containing only two variables c_{10} and c_{01}, they can be solved by using usual method. Then we can obtain

$$P_{1,0 \rightarrow 0,1} = |c_{01}|^2 \cong \sin^2\left(5 \cdot 10^{-7} v_0\right), \tag{28}$$

here v_0 is the initial translational velocity.

However, why is there resonant exchange mechanism between the initial state and final state of process (25)? What is the theoretical basis? In view of the fact that this resonant mechanism is not similar to that in classical mechanics or quantum mechanics, the reliability of the expression of transition probability, equation (28), remains to be confirmed.

It is easy to see that the resonant exchange process (25) is just the case of (i) discussed above. Here we still adopt the method presented by Rapp and Golden. For the process (25), under the condition of near resonance there is interconversion between translational energy and vibrational energy [7] $\Delta E = \hbar(\omega_1 - \omega_2)$. On the other hand, since this process concerns translational energy, we have $\Delta E = fE_0$ (f is proportion parameter). If we set $t_e = R_e/\overline{v}_0$, $\overline{v}_0 = v_0/2$, R_e may be approximately regarded as effective collision distance. Thus we get $\omega_1 - \omega_2 = fE_0/\hbar$, $(\omega_1 - \omega_2)t_e = (f\widetilde{M}R_e/\hbar)v_0$. Substituting those expressions into equation (21) yields

$$P_{m,1,0 \rightarrow m,0,1} \equiv P_{1,0 \rightarrow 0,1} = \frac{\gamma^4 \hbar^2}{L^4 \mu^2 \omega^2 f^2} \sin^2 \frac{f\widetilde{M}R_e}{\hbar} v_0. \tag{29}$$

In deriving equation (29) we have used $A'' = E_0$. With the aids of the data presented by table 5 we can obtain $R_e = 4.8 \cdot 10^{-10} m_B/m_A = 0.9 \cdot 10^{-8}$ cm,

Table 5
Dynamical parameters in process (25).

Dynamical parameters	Reference
$\widetilde{M} = \frac{1}{2}(m_A + m_B) = 10$ amu	[6,7]
$m_A = 1$ amu, $m_B = 19$ amu	[6,7]
$L = 0.2 \cdot 10^{-8}$ cm	[7]
$\omega = 1.2 \cdot 10^{14}$ sec^{-1}	[5]
$t_e \cong 10 \cdot 10^{-13}$ sec	[5]

$f = 12.55 \cdot 10^{-2} m_A/m_B = 3.3 \cdot 10^{-3}$. Substituting these results into equation (20), we obtain equation (28) again. The results above show that the reliability of expression (28) obtained by resonant exchange hypothesis can be confirmed by using the dynamical Lie algebraic method. But it should be noted that the resonance stems from V–V resonance between not the initial state and final state of process (25) but two molecules. Such a resonance depends not on whether two molecules are the same, but on whether the vibrational frequencies of the two molecules are identical approximately ($\omega_1 \cong \omega_2$).

Acknowledgements

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