Application of dynamical Lie algebraic method to atom–diatomic molecule scattering

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The dynamical Lie algebraic approach developed by Alhassid and Levine combined with intermediate picture is applied to the study of translational–vibrational energy transfer in the collinear collision between an atom and an anharmonic oscillator. We find that the presence of the anharmonic terms indeed has an effect on the vibrational probabilities of the oscillator. The computed probabilities are in good agreement with those obtained using exact quantum method. It is shown that the approach of dynamical Lie algebra combining with intermediate picture is reasonable in the treating of atom–anharmonic oscillator scattering.

KEY WORDS: scattering, anharmonic oscillator, Lie algebra, translational–vibrational energy transfer

1. Introduction

The study of translational–vibrational energy transfer in atom–molecule and molecule–molecule collision has been the subject of theoretical investigations [1–12]. Alhassid and Levine have developed the dynamical Lie algebraic method [13], which, at first, was used to the linearly driven harmonic oscillator. The dynamical Lie algebraic method was recently used to describe a number of topics in both gas phase and gas–surface scattering [14–17]. A much greater advantage, which is observed in the calculation, is that the evolution operator for a given Hamiltonian can be expressed analytically in terms of the group parameters, which can be determined by solving coupled nonlinear differential equations. The transition probability that contained main dynamical parameters may be given analytically. Thus, the method can provide more insight into the relation between the potential function and the transition probability. Because of quite small numerical effort required in the calculation, it is also possible to carry out extensive parameter variation in an assumed potential function in order to fit calculations to experiments. Application of the dynamical Lie algebraic mehtod to problems in inelastic and reactive scattering has shown that it is well suited to the description of these phenomena.

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In this paper we focus our attention on the dynamical Lie algebraic approach combining with intermediate picture and applying it to atom–diatom collisions. As known, any problem of quantum mechanics essentially consists of a more or less complete and more or less precise determination of the properties of the unitary operator $U(t, t_0)$. When one sets $U(t, t_0) = U^{(0)}U'$, here $U^{(0)}(t, t_0)$ is approximate solution of the equation

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}U(t, t_0) = HU(t, t_0),$$

U' is an operator changing slowly as a function of time. The Hamiltonian H is, thus, the sum of two Hermitian operators $H = H^{(0)} + H'$, where H' may be considered as a small perturbation, $H^{(0)}$ is the Hamiltonian of the Schrödinger equation whose solution is known, then U' satisfies the equation

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}U' = H'_I U',$$

in which H'_I is deduced from H' by the time-dependent unitary transformation $H'_I = U^{(0)+}H'U^{(0)}$. In this way, it is then convenient to adopt a "picture" intermediate between that of Schrödinger and of Heisenberg, intermediate picture [18]. When the collison energy is not high, it is reasonable to regard the diatomic molecule as a harmonic oscillator. But for higher collision energies the oscillator may be brought to a highly-excited vibrational state, the harmonic oscillator model no longer holds, for this reason we will consider the diatomic molecule as an anharmonic oscillator with cubic and quartic terms present. The total Hamiltonian of the colliding system can be adequately approximated by the linear combination of a finite number of simple operators and divided into two parts H_1 and H_2, where H_1 is constituted by the operators which form a dynamical Lie algebra and treated by using dynamical Lie algebraic approach. While H_2 contains operators in which the order of parts of the operators is greater than two and cannot construct a dynamical Lie algebra, then H_2 is dealt with in intermediate picture. As examples, the collinear collision systems of $H_2 + He$, $H_2 + H$ are explicitly treated using this method to illustrate its general procedure.

2.   Hamiltonian of the scattering system

The Hamiltonian of the isolated diatomic molecule, which is considered as an anharmonic oscillator, is expressed as

$$H_{\mathrm{an}} = \frac{P^2}{2\mu} + \frac{1}{2}\mu\omega^2 Y^2 + k_1 Y^3 + k_2 Y^4, \tag{1}$$

in which μ is the reduced mass of diatomic molecule, k_1, k_2 are force constants. $Y = y - y_0$, y_0 is the equilibrium position of vibrational coordinate y. P is momentum operator corresponding to momentum p, ω denotes the vibrational angular freqency of diatomic molecule.

For the collinear collision of a diatomic molecule with an atom, the interaction potential in the semiclassical approximation is given by [1]

$$V = E(t)\exp\left(\frac{\gamma}{L}Y\right),\tag{2}$$

where $E(t) = E_0\text{sech}^2(v_0 t/(2L))$, v_0 the initial relative velocity, $E_0 = mv_0^2/2$ is the initial kinetic energy, m is the reduced mass of the collison system, γ and L are potential constants.

The total Hamiltonian of the scattering system is

$$\begin{aligned}H &= H_{\text{an}} + V \\ &= \frac{P^2}{2\mu} + \frac{1}{2}\mu\omega^2 Y^2 + k_1 Y^3 + k_2 Y^4 + E(t)\exp\left(\frac{\gamma}{L}Y\right).\end{aligned}\tag{3}$$

Making a Taylor series expansion of the fifth term in equation (3) with respect to Y to the fourth order we can transform equation (3) into

$$H = \frac{P^2}{2\mu} + \frac{1}{2}\mu\omega^2 Y^2 + B_0 + B_1 Y^2 + (k_1 + B_3)Y^3 + (k_2 + B_4)Y^4.\tag{4}$$

where

$$B_0 = E(t) = E_0\text{sech}^2\left(\frac{v_0 t}{2L}\right), \qquad B_1 = B_0\left(\frac{\gamma}{L}\right),$$

$$B_2 = B_0\left(\frac{\gamma}{L}\right)^2, \qquad B_3 = B_0\left(\frac{\gamma}{L}\right)^3, \qquad B_4 = B_0\left(\frac{\gamma}{L}\right)^4.$$

Let $H = H_1 + H_2$,

$$H_1 = \frac{P^2}{2\mu} + \frac{1}{2}\mu\omega^2 Y^2 + B_1 Y + B_2 Y^2 + B_0,\tag{5}$$

$$H_2 = (k_1 + B_3)Y^3 + (k_2 + B_4)Y^4.\tag{6}$$

In order to adopt dynamical Lie algebraic approach, it is convenient to make use of particle number picture, the transformation formulas are

$$\begin{aligned}a^+ &= \frac{1}{\sqrt{2}}\left(\sqrt{\frac{\mu\omega}{\hbar}}Y - i\sqrt{\frac{1}{\mu\hbar\omega}}P\right), \\ a &= \frac{1}{\sqrt{2}}\left(\sqrt{\frac{\mu\omega}{\hbar}}Y + i\sqrt{\frac{1}{\mu\hbar\omega}}P\right).\end{aligned}\tag{7}$$

Substituting equation (7) into equations (5) and (6) we can obtain

$$H_1 = H_0 + V',\tag{8}$$

$$H_0 = \hbar\omega'\left(a^+ a + \frac{1}{2}\right),\tag{9}$$

$$V' = D_1(a^+ + a) + D_2(a^2 + a^{+2}), \tag{10}$$

$$H_2 = D_3(a^3 + 3a^+a^2 + 3a^{+2}a + 3a + 3a^+ + a^{+3})$$
$$+ D_4(a^4 + 4a^+a^3 + 6a^{+2}a^2 + 4a^{+3}a + a^{+4} + 6a^{+2} + 6a^2 + 12a^+a + 3), \tag{11}$$

where

$$D_1 = B_1\left(\frac{\hbar}{2\mu\omega}\right)^{1/2}, \qquad\qquad D_2 = B_2\frac{\hbar}{2\mu\omega},$$

$$D_3 = (k_1 + B_3)\left(\frac{\hbar}{2\mu\omega}\right)^{3/2}, \qquad D_4 = (k_2 + B_4)\left(\frac{\hbar}{2\mu\omega}\right)^2.$$

In deriving equations (8)–(11) we have neglected several constant terms (those terms not containing operators) which make no contribution to dynamics. Here $\omega' = \omega + 2D_2/\hbar$, $2D_2/\hbar$ denotes the revised term to angular frequency ω of harmonic oscillator from the potential V. It can be found from equation (11) that the order of most of the operators is greater than two, thus, these operators in equation (11) cannot construct a dynamical Lie algebra, we will treat them using intermediate picture in section 4.

To obtain the transition probability it is convenient to make a transformation to the interaction picture where the free motion of the system has been seperated from the motion of the total system [18]. In the interaction picture V' can be transformed to

$$V_I(t) = e^{(i/\hbar)H_0 t} V' e^{-(i/\hbar)H_0 t} = v_1^* a^+ + v_1 a + v_2^* a^{+2} + v_2 a^2, \tag{12}$$

where $v_1 = D_1 e^{-i\omega' t}$, $v_2 = D_2 e^{-i2\omega' t}$. The dynamical algebra corresponding to equation (12) is a six-dimensional Lie algebra h_6: I, a^+, a, a^+a, a^{+2}, a^2, where the order of the algebra elements has been preordained and the commutation relations between the algebra elements are

$$[a, a^+] = 1, \qquad [a, a^+a] = a, \qquad [a^+, a^+a] = -a^+,$$
$$[a, a^{+2}] = 2a^+, \qquad [a^+, a^2] = -2a, \qquad [a^{+2}, a^+a] = -2a^{+2}, \tag{13}$$
$$[a^2, a^+a] = 2a^2, \qquad [a^2, a^{+2}] = 2I + 4a^+a.$$

3. Time evolution operator

The time evolution operator $U(t, t_0)$, which is equivalent to the scattering wave function, in the interaction picture is defined by [13]

$$U_I(t, t_0) = \exp\{T\},$$
$$T = -\frac{i}{\hbar}(u_1 I + u_2^* a^+ + u_2 a + u_4 a^+ a + u_3^* a^{+2} + u_3 a^2), \tag{14}$$

where the group parameters u_1, u_4 are real, u_2, u_3 are complex, they are determined by the following equation [13]:

$$\frac{\partial \mathbf{u}}{\partial t} = \sum_{j=0} \frac{B_j}{j!} \mathbf{d}^j(T)\mathbf{v}, \tag{15}$$

in which B_j ($j = 0, 1, 2, \ldots$) are Bernoulli numbers and j is positive integer, the matrix $\mathbf{d}$ is [10]

$$\mathbf{d} = -\frac{i}{\hbar} \begin{bmatrix} 0 & u_2 & -u_2^* & 0 & 2u_3 & -2u_3^* \\ 0 & u_4 & -2u_3^* & -u_2^* & 2u_2 & 0 \\ 0 & 2u_3 & -u_4 & u_2 & 0 & -2u_2^* \\ 0 & 0 & 0 & 0 & 4u_3 & -4u_3^* \\ 0 & 0 & 0 & -2u_3^* & 2u_4 & 0 \\ 0 & 0 & 0 & -2u_3 & 0 & -2u_4 \end{bmatrix}.$$

Matrices $\mathbf{u}$ and $\mathbf{v}$ are column matrices

$$\mathbf{u} = \begin{bmatrix} u_1 \\ u_2^* \\ u_2 \\ u_4 \\ u_3^* \\ u_3 \end{bmatrix}, \qquad \mathbf{v} = \begin{bmatrix} 0 \\ v_1^* \\ v_1 \\ 0 \\ v_2^* \\ v_2 \end{bmatrix}.$$

The first-order approximation to equation (15) is

$$\frac{\partial \mathbf{u}}{\partial t} \simeq \left\{ 1 - \frac{1}{2}\mathbf{d} \right\}\mathbf{v} \tag{16}$$

with the initial condition

$$\mathbf{u}|_{t=t_0} = \mathbf{0}.$$

Solving equation (16) enables us to determine time evolution operator $U(t, t_0)$.

4. Transition probability

The state $|\Psi(t)\rangle$ of the system at time t is obtained from the state $|\Psi_i\rangle$ at t_0 as

$$\big|\Psi(t)\big\rangle = U(t, t_0)|\Psi_i\rangle, \tag{17}$$

where the time-dependent operator $U(t, t_0)$ is a solution of

$$i\hbar \frac{dU(t, t_0)}{dt} = HU(t, t_0), \qquad U(t_0, t_0) = \hat{I}. \tag{18}$$

Here H is the Hamiltonian of the scattering system and $\hat{I}$ is the identity operator. In the intermediate picture we write

$$\big|\Psi(t)\big\rangle = U'\big|\Phi(t)\big\rangle. \tag{19}$$

U' is called effective evolution operator. U' and $|\Phi(t)\rangle$ satisfy the following equations respectively [18]:

$$i\hbar \frac{dU'(t, t_0)}{dt} = H'U'(t, t_0), \qquad U'(t_0, t_0) = \hat{I}, \tag{20}$$

and

$$i\hbar \frac{d}{dt}|\Phi(t)\rangle = H_I|\Phi(t)\rangle, \qquad |\Phi(t_0)\rangle = |\Psi_i\rangle, \tag{21}$$

in which H' is an effective Hamiltonian, and

$$H_I = U'^{+}(H - H')U' \tag{22}$$

is the Hamiltonian of the system in the intermediate picture, $+$ stands for adjoint. To solve equation (21) we should expand $\Phi(t)$ in a basis set $\{|\chi_k\rangle\}$. In our calculations $\{|\chi_k\rangle\}$ are set to be the basis functions of harmonic oscillator:

$$|\Phi(t)\rangle = \sum_k c_k|\chi_k\rangle. \tag{23}$$

Expansion coefficients $\{c_k\}$ satisfy

$$i\hbar \frac{d\mathbf{c}}{dt} = \mathbf{H}_I\mathbf{c}. \tag{24}$$

The elements of matrix $\mathbf{H}_I$ are

$$H_{ij}^I = \langle\chi_i|H_I|\chi_j\rangle, \tag{25}$$

and those of matrix $\mathbf{c}$ are $\{c_k\}$, then matrix $\mathbf{c}$ may be expressed as

$$\mathbf{c} = \begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix}. \tag{26}$$

To determine the coefficients $c_0, c_1, \ldots, c_n$, we need to give out the expression of matrix elements H_{ij}^I ($i, j = 0, 1, 2, \ldots, c_n$). Here, $U' \equiv U_I(t, t_0)$ and $H' \equiv H_1$, then from equations (22) and (11) we obtain

$$\begin{aligned}
H_I &= U_I^{+}(t, t_0)(H - H_1)U_I(t, t_0) = U_I^{+}(t, t_0)H_2U_I(t, t_0) \\
&= A_1a^4 + A_2a^{+4}a + A_3a^{+3}a + A_4a^{+}a^3 + A_5a^{+2}a^2 + A_6a^3 \\
&\quad + A_7a^{+3} + A_8a^{+2}a + A_9a^{+}a^2 + A_{10}a^{+}a + A_{11}a^{+2} \\
&\quad + A_{12}a^2 + A_{13}a^{+} + A_{14}a + A_{15},
\end{aligned} \tag{27}$$

where $A_1, A_2, \ldots, A_{15}$ are functions of group parameters, the expressions of them are listed in table 1. Substituting equation (27) into equation (25), we have

$$
\begin{aligned}
H^I_{ij} = {} & A_1\sqrt{j(j-1)(j-2)(j-3)}\delta_{i,j-4} + A_6\sqrt{j(j-1)(j-2)}\delta_{i,j-3} \\
& + \left[A_4(j-2)\sqrt{j(j-1)} + A_{12}\sqrt{j(j-1)}\right]\delta_{i,j-2} + \left[A_9(j-1) + A_{14}\right]\sqrt{j}\delta_{i,j-1} \\
& + [A_5 j(j-1) + A_{10}j + A_{15}]\delta_{i,j} + [A_8 j + A_{13}]\sqrt{j+1}\delta_{i,j+1} \\
& + [A_3 j + A_{11}]\sqrt{(j+1)(j+2)}\delta_{i,j+2} + A_7\sqrt{(j+1)(j+2)(j+3)}\delta_{i,j+3} \\
& + A_2\sqrt{(j+1)(j+2)(j+3)(j+4)}\delta_{i,j+4}.
\end{aligned}
\tag{28}
$$

The probability that the system will be in a given state $\Psi(t)$ is given by [19]

$$
\begin{aligned}
P_{i\to f} &= \left|\langle\Psi_f|\Psi(t)\rangle\right|^2 \\
&= \lim_{t\to+\infty, t_0\to-\infty}\left|\langle\Psi_f|\Psi(t)\rangle\right|^2 \\
&= \lim_{t\to+\infty, t_0\to-\infty}\left|\sum_j c_j(t)\langle\Psi_f|U_I(t,t_0)|\chi_j\rangle\right|^2 \\
&= \lim_{t\to t_e/2, t_0\to-t_e/2}\left|\sum_j c_j(t)\langle\Psi_f|U_I(t,t_0)|\chi_j\rangle\right|^2 \\
&= \left|\sum_j c_j(t)\langle\Psi_f|U_I\left(\frac{t_e}{2}, -\frac{t_e}{2}\right)|\chi_j\rangle\right|^2,
\end{aligned}
\tag{29}
$$

where t_e denotes the effective collision time [20], which indicates that

$$
\lim_{t\to+\infty, t_0\to-\infty} V_I(t) = \lim_{t\to t_e, t_0\to-t_e} V_I = 0.
\tag{30}
$$

Under the first-order approximation of group parameter and substituting equation (14) into equation (29) we finally obtain the expression of transition probability

$$
\begin{aligned}
P_{i\to f} = {} & \left|\sum_{j=0} c_j\left\{\delta_{f,j} - \frac{i}{\hbar}\left[(u_1+u_4)\delta_{f,j} + u_2^*\sqrt{j+1}\delta_{f,j+1} + u_2\sqrt{j}\delta_{f,j-1}\right.\right.\right. \\
& \left.\left.\left. + u_3^*\sqrt{(j+1)(j+2)}\delta_{f,j+2} + u_3\sqrt{j(j-1)}\delta_{f,j-2}\right]\right\}\right|^2,
\end{aligned}
\tag{31}
$$

where t and t_0 in the group parameters $u_j = u_j(t, t_0)$ ($j = 1, 2, 3, 4$) are replaced by $t_e/2$ and $-t_e/2$, respectively.

5. Results and discussion

As an application of the expression of transition probability, equation (31), we will calculate the vibrational transition probabilities of the collinear collision systems $H_2 + He$, $H_2 + H$. The total collision energy E_{tot} in the initial state $|i\rangle$ for the collision system is defined by

$$E_{tot} = E_0 + \frac{1}{2}(i + 1)\hbar\omega, \tag{32}$$

hence, the initial kinetic energy is

$$E_0 = E_{tot} - \frac{1}{2}(i + 1)\hbar\omega. \tag{33}$$

Collision time is set to be effective collision time t_e ($t_e \approx 10^{-13}$ s) [20], initial time $t_0 = -t_e/2$. The dynamical parameters used in the calculations are listed in table 2. Similar to [4], for every scattering system we calculated the probabilities of the following transition: $0 \to 1, 0 \to 2, \ldots, 0 \to 7$; $1 \to 2, 1 \to 3, \ldots, 1 \to 7$; $2 \to 3$, $2 \to 4, \ldots, 2 \to 7$; $\ldots$; $5 \to 6, 5 \to 7$. Comparisons with the exact quantum-mechanical calculations [4] for a Harmonic-Exponential potential (HOEXP) and a Morse-Exponential potential (MOEXP) are displayed in tables 3–9 and figures 1–14. In tables 3–9, corresponding to every energy value E ($E = E_{tot}/(\frac{1}{2}\hbar\omega)$) the upper entry is HOEXP result, the middle entry MOEXP result, and the lower entry dynamical Lie algebraic result. Values in parentheses denote $\times 10^{-n}$. From tables 3–9 and figures 1–14 we can see that our calculation results and the exact quantum mechanics calculation results exhibit similar tendency, and the presence of the anharmonic terms indeed has an effect on the vibrational probabilities of the oscillator. It is also found that the smaller the reduced mass of the scattering system, the larger is the effect of anharmonic terms on the transition probabilities. On the other hand, the bigger the quantum number difference between two transition states, the larger is the effect of the anharmonicity. Insofar as the transitions $0 \to 1, 1 \to 2, 2 \to 3, 3 \to 4, 4 \to 5$ of $H_2 + H$ scattering system are concerned, the dynamical Lie algebraic results are similar to HOEXP and MOEXP results in that the probability at the energy 16 is larger than that at the energy 12. This fact reveals that the value of probability corresponding to energy 16 exceeds the first maximum value of transition probability. This is because the reduced mass of $H_2 + H$ is smaller, so that for the transitions $0 \to 1, 1 \to 2, 2 \to 3, 3 \to 4, 4 \to 5$, the first maximum value of transition probability is smaller. As for system $H_2 + He$, although in the HOEXP calculation the probabilities corresponding to transitions $0 \to 1$ and $1 \to 2$ show the phenomenon mentioned above, it is not the case in the MOEXP and dynamical Lie algebraic calculations. In addition, we note that for the two systems, the effect of anharmonicity on the transition probability increases gradually with the increasing of energy. Further examination indicates that our calculations are closer to the MOEXP results than those of HOEXP. This may be accounted for by the fact that the anharmonic oscillator model is closer to the Morse oscillator model. On the whole, the approach of

Table 1
Expansion coefficients in equation (27).

$$D_3 = \left\{ \left[k_1 + E_0 \mathrm{sech}^2\left(\tfrac{v_0 t}{2L}\right) \right] \left(\tfrac{\gamma}{L}\right)^3 \right\} \left(\tfrac{\hbar}{2\mu\omega}\right)^{3/2}$$

$$D_4 = \left\{ \left[k_2 + E_0 \mathrm{sech}^2\left(\tfrac{v_0 t}{2L}\right) \right] \left(\tfrac{\gamma}{L}\right)^4 \right\} \left(\tfrac{\hbar}{2\mu\omega}\right)^2$$

$$A_1 = D_4[1 + \tfrac{i}{\hbar}(8u_3 - 4u_4)]$$

$$A_2 = D_4[1 + \tfrac{i}{\hbar}(4u_4 - 8u_3^*)]$$

$$A_3 = 4D_4[1 + \tfrac{i}{\hbar}(2u_3 + 2u_4 - 6u_3^*)]$$

$$A_4 = 4D_4[1 + \tfrac{i}{\hbar}(6u_3 - 2u_4 - 2u_3^*)]$$

$$A_5 = 6D_4[1 + \tfrac{i}{\hbar}(4u_3 - 4u_3^*)]$$

$$A_6 = 4D_4 \tfrac{i}{\hbar}(u_2 - u_2^*) + D_3[1 + \tfrac{i}{\hbar}(6u_3 - 3u_4)]$$

$$A_7 = 4D_4 \tfrac{i}{\hbar}(u_2 - u_2^*) + D_3[1 + \tfrac{i}{\hbar}(3u_4 - 6u_3^*)]$$

$$A_8 = 4D_4 \tfrac{i}{\hbar}(3u_2 - 3u_2^*) + 3D_3[1 + \tfrac{i}{\hbar}(u_4 - 4u_3^* + 2u_3)]$$

$$A_9 = 4D_4 \tfrac{i}{\hbar}(3u_2 - 3u_2^*) + 3D_3[1 + \tfrac{i}{\hbar}(u_4 - 4u_3^* + 2u_3)]$$

$$A_{10} = 24D_4 \tfrac{i}{\hbar}(u_3 - u_3^*) + 6D_3 \tfrac{i}{\hbar}(u_2 - u_2^*) + 12D_4[1 + \tfrac{i}{\hbar}(u_3 - u_3^*)]$$

$$A_{11} = 6D_4[1 + \tfrac{i}{\hbar}(2u_3 + 2u_4 - 6u_3^*)] + 3D_3 \tfrac{i}{\hbar}(3u_2 - 3u_2^*)$$

$$A_{12} = 6D_4[1 + \tfrac{i}{\hbar}(6u_3 - 2u_4 - 2u_3^*)] + 3D_3 \tfrac{i}{\hbar}(3u_2 - 3u_2^*)$$

$$A_{13} = 6D_3 \tfrac{i}{\hbar}(u_3 - 2u_3^*) + 12D_4 \tfrac{i}{\hbar}(u_2 - u_2^*) + 3D_3 \tfrac{i}{\hbar}u_4 + 3D_3$$

$$A_{14} = 6D_3 \tfrac{i}{\hbar}(2u_3 - u_3^*) + 12D_4 \tfrac{i}{\hbar}(u_2 - u_2^*) - 3D_3 \tfrac{i}{\hbar}u_4 + 3D_3$$

$$A_{15} = 12D_4(u_3 - u_3^*) + 3D_3 \tfrac{i}{\hbar}(u_2 - u_2^*)$$

Table 2
The values (SI) of the dynamical parameters used in the
present calculations.

Dynamic parameter	$H_2 + He$	$H_2 + H$
ω	8.29×10^{14}	8.29×10^{14}
μ	8.36×10^{-28}	8.36×10^{-28}
m	2.23×10^{-27}	1.11×10^{-27}
L	2.0×10^{-11}	2.0×10^{-11}
γ	0.5	0.5
k_1	-5.57×10^{12}	-5.57×10^{12}
k_2	6.31×10^{22}	6.31×10^{22}

dynamical Lie algebra combining with intermediate picture is reasonable in the treating of atom–anharmonic oscillator scattering.

Acknowledgements

Table 3
Comparison of the dynamical Lie algebraic calculation with those of HOEXP and MOEXP calculation [4] for the scattering system $H_2 + He$.

E	$0 \to 4$	$0 \to 5$	$0 \to 6$	$0 \to 7$
6				
	$2.71(-9)$			
8				
	$1.01(-8)$			
10	$4.26(-8)$			
	$1.95(-8)$			
	$2.83(-8)$	$3.86(-9)$		
12	$3.65(-5)$	$5.45(-9)$		
	$1.48(-6)$	$4.95(-9)$		
	$6.11(-6)$	$6.19(-9)$	$4.44(-10)$	$1.00(-10)$
16	$1.06(-2)$	$3.31(-4)$		
	$1.61(-4)$	$7.44(-6)$		
	$3.02(-4)$	$9.82(-6)$	$3.67(-7)$	$5.39(-8)$

Table 4
Comparison of the dynamical Lie algebraic calculation with those of HOEXP and MOEXP calculation [4] for the scattering system $H_2 + He$.

E	$1 \to 4$	$1 \to 5$	$1 \to 6$	$1 \to 7$	$2 \to 5$	$2 \to 6$	$2 \to 7$
6							
	$3.55(-8)$						
8							
	$1.17(-7)$						
10	$1.80(-6)$	$2.95(-10)$					
	$3.12(-6)$				$3.65(-8)$		
	$4.47(-6)$	$3.46(-9)$			$8.27(-8)$		
12	$7.69(-4)$	$1.84(-7)$			$4.11(-6)$		
	$1.38(-4)$	$5.01(-7)$			$4.56(-5)$		
	$3.52(-3)$	$5.52(-6)$	$7.41(-8)$		$3.51(-5)$	$5.66(-7)$	
16	$7.32(-2)$	$4.04(-3)$			$2.58(-2)$		
	$5.16(-3)$	$3.24(-4)$			$5.77(-3)$		
	$1.06(-2)$	$6.76(-4)$	$4.53(-5)$	$1.34(-6)$	$6.35(-3)$	$7.48(-4)$	$3.93(-6)$

Table 5

Comparison of the dynamical Lie algebraic calculation with those of HOEXP and MOEXP calculation [4] for the scattering system $H_2 + He$.

E	$3 \to 4$	$3 \to 5$	$3 \to 6$	$3 \to 7$
6				
	1.72(−6)			
8	3.51(−6)			
	3.51(−6)			
	4.13(−5)			
10	2.76(−3)			
	1.92(−2)	4.47(−6)		
	9.86(−3)	8.36(−6)		
12	9.59(−2)	9.28(−5)		
	5.64(−3)	1.98(−3)		
	1.23(−2)	4.47(−3)	2.53(−6)	
16	3.04(−1)	1.09(−1)		
	6.39(−2)	5.76(−2)		
	8.17(−2)	8.31(−2)	1.24(−2)	4.38(−4)

Table 6

Comparison of the dynamical Lie algebraic calculation with those of HOEXP and MOEXP calculation [4] for the scattering system $H_2 + He$.

E	$4 \to 5$	$4 \to 6$	$4 \to 7$	$5 \to 6$	$5 \to 7$
8					
	7.37(−7)			3.62(−7)	
10					
	9.12(−4)				
	5.69(−4)	6.91(−7)		9.13(−4)	7.02(−7)
12	3.40(−3)				
	5.97(−2)			1.30(−2)	
	9.29(−3)	3.78(−4)	6.63(−6)	2.48(−2)	6.34(−4)
16	3.12(−1)			1.27(−1)	
	3.17(−1)			2.84(−1)	
	4.08(−1)	6.18(−2)	2.77(−3)	3.22(−1)	2.72(−2)

Table 7

Comparison of the dynamical Lie algebraic calculation with those of HOEXP and MOEXP calculation [4] for the scattering system $H_2 + H$.

E	$0 \to 4$	$0 \to 5$	$0 \to 6$	$1 \to 4$	$1 \to 5$	$1 \to 6$
8						
	8.02(−9)			3.73(−7)		
	1.77(−8)			5.44(−7)		
10	2.80(−5)			3.76(−4)		
	1.03(−4)	1.52(−7)		2.32(−3)	5.00(−6)	
	8.63(−5)	9.58(−8)		1.53(−4)	3.84(−6)	
12	3.51(−3)	7.86(−6)		2.49(−2)	9.47(−5)	
	2.57(−3)	8.00(−5)		3.22(−2)	1.58(−3)	
	4.23(−2)	1.20(−4)	4.68(−6)	3.96(−2)	8.65(−4)	3.77(−6)
16	1.54(−1)	2.01(−2)		2.67(−1)	8.49(−2)	
	5.18(−2)	1.02(−2)		2.02(−1)	7.34(−2)	
	9.71(−2)	9.64(−3)	7.75(−4)	3.19(−1)	1.09(−1)	1.45(−3)

Table 8

Comparison of the dynamical Lie algebraic calculation with those of HOEXP and MOEXP calculation [4] for the scattering system $H_2 + H$.

E	$2 \to 5$	$2 \to 6$	$2 \to 6$	$3 \to 4$	$3 \to 5$	$3 \to 6$	$3 \to 7$
6							
				3.49(−6)			
8				5.25(−4)			
				5.25(−4)			
				6.32(−4)	5.66(−7)		
10				3.40(−2)			
	9.59(−5)			1.89(−1)	1.52(−3)		
	3.56(−5)	2.33(−7)	8.58(−8)	8.18(−2)	2.31(−3)	4.34(−6)	
12	7.20(−4)			2.85(−1)	4.90(−3)		
	1.53(−2)			3.49(−1)	9.04(−2)		
	1.13(−3)	6.12(−4)	1.02(−5)	3.22(−1)	6.72(−2)	7.50(−4)	3.63(−5)
16	1.83(−1)			1.75(−3)	2.42(−1)		
	1.95(−1)			2.06(−3)	1.73(−1)		
	2.00(−1)	2.44(−2)	6.76(−3)	4.53(−2)	1.07(−1)	8.49(−2)	2.57(−3)

Table 9

Comparison of the dynamical Lie algebraic calculation with those of HOEXP and MOEXP calculation [4] for the scattering system $H_2 + H$.

E	$4 \to 5$	$4 \to 6$	$4 \to 7$	$5 \to 6$	$5 \to 7$	$6 \to 7$
8						
	7.27(−3)	5.34(−6)		9.90(−4)	4.52(−6)	7.44(−5)
10						
	2.53(−2)					
	1.88(−2)	3.71(−4)	4.58(−6)	5.77(−2)	2.13(−3)	6.32(−3)
12	3.97(−2)					
	3.18(−1)			1.42(−1)		
	1.46(−1)	1.20(−2)	6.52(−3)	1.19(−1)	3.64(−2)	1.78(−2)
16	1.63(−1)			2.93(−1)		
	1.26(−3)			2.77(−2)		
	1.19(−1)	7.94(−2)	1.11(−1)	1.47(−1)	8.39(−2)	9.51(−2)
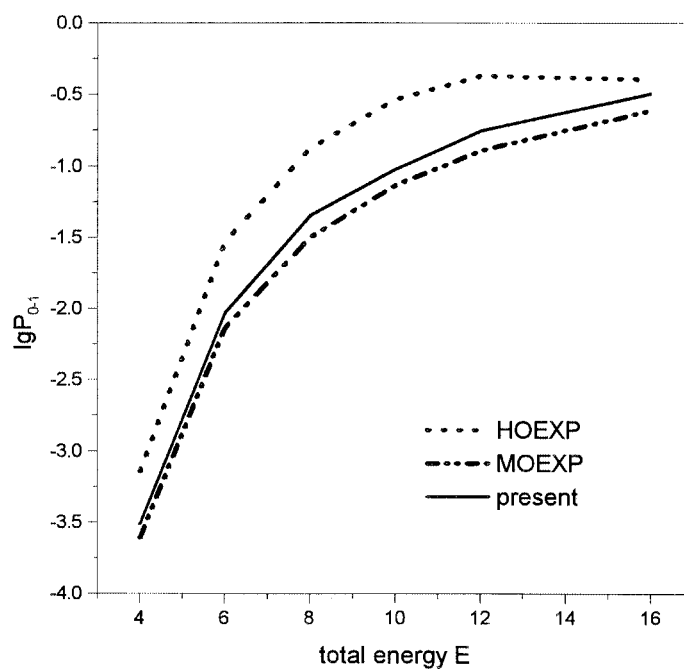
Figure 1. Logarithm of the transition probability $(0 \to 1)$ as a function of the total collision energy E_{tot} for the scattering system $H_2 + He$. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.
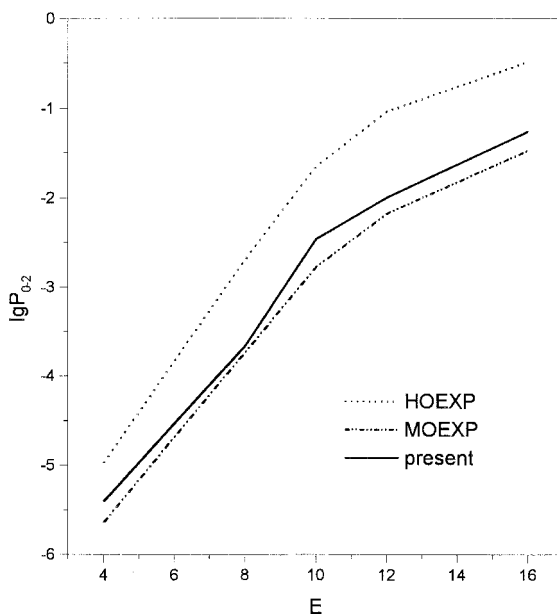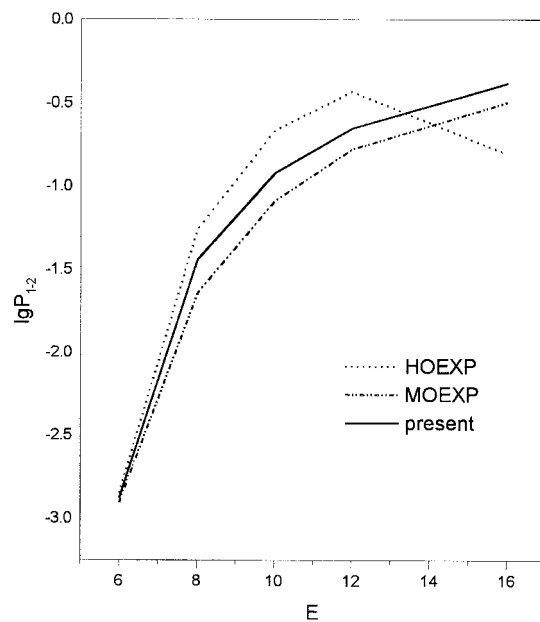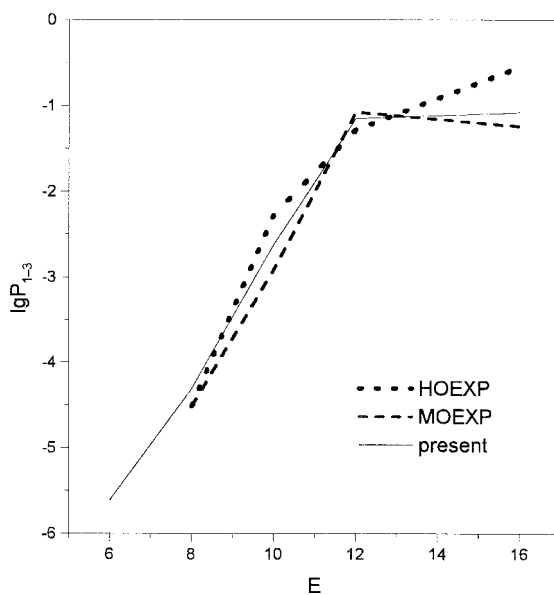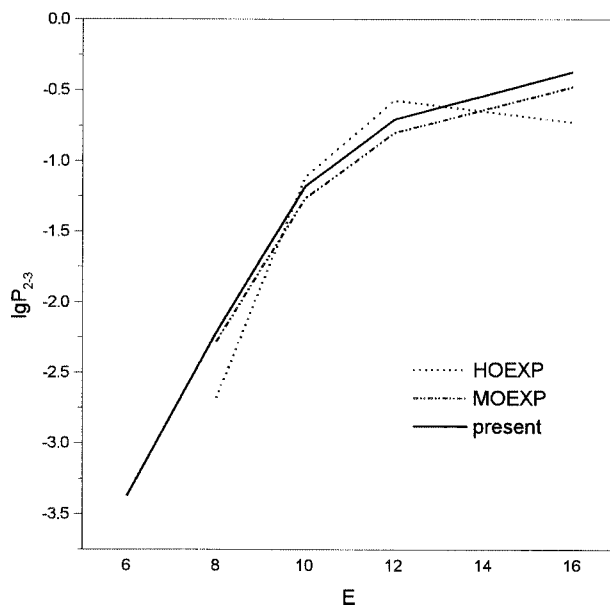
Figure 2. Logarithm of the transition probability ($0 \rightarrow 2$) as a function of the total collision energy E_{tot} for the scattering system H_2 + He. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.
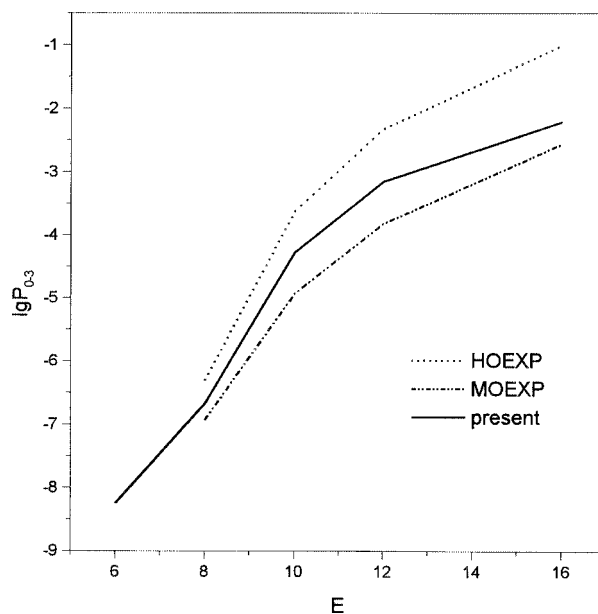
Figure 3. Logarithm of the transition probability ($0 \rightarrow 3$) as a function of the total collision energy E_{tot} for the scattering system H_2 + He. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.
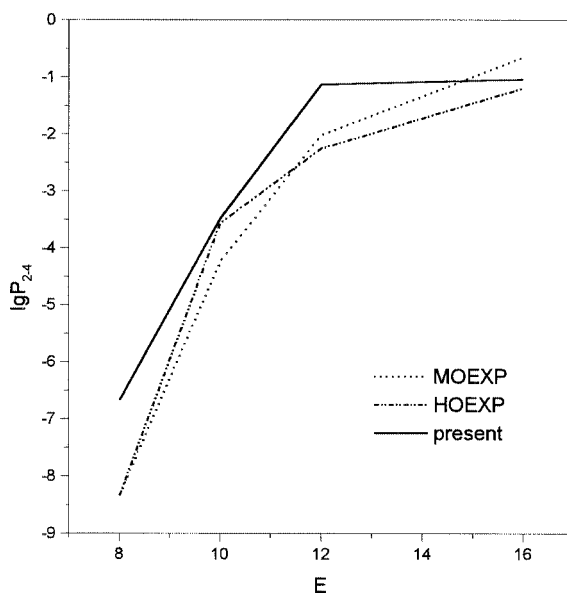
Figure 4. Logarithm of the transition probability ($1 \rightarrow 2$) as a function of the total collision energy E_{tot} for the scattering system H_2 + He. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.
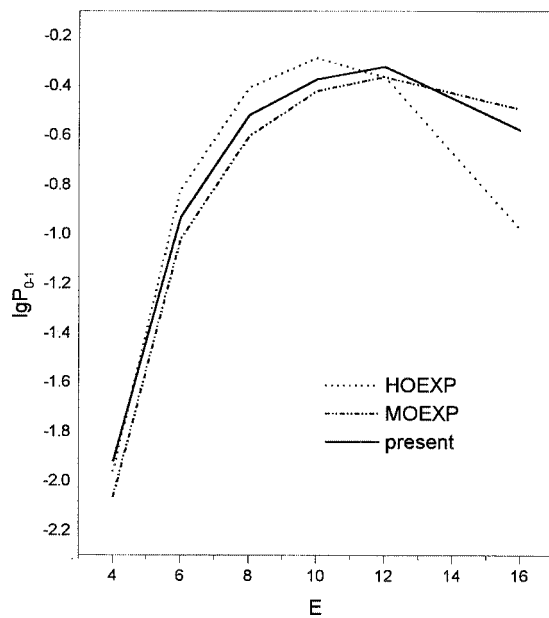

Figure 5. Logarithm of the transition probability ($1 \rightarrow 3$) as a function of the total collision energy E_{tot} for the scattering system H_2 + He. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.

Figure 6. Logarithm of the transition probability $(2 \to 3)$ as a function of the total collision energy E_{tot} for the scattering system $H_2 + He$. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.
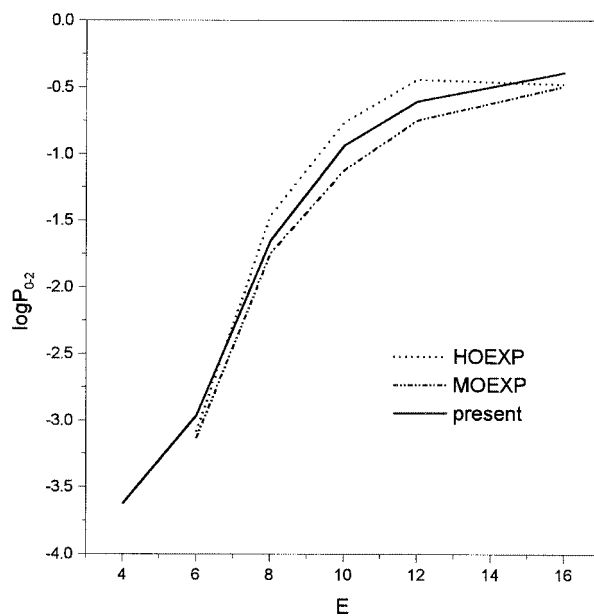

Figure 7. Logarithm of the transition probability $(2 \to 4)$ as a function of the total collision energy E_{tot} for the scattering system $H_2 + He$. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.
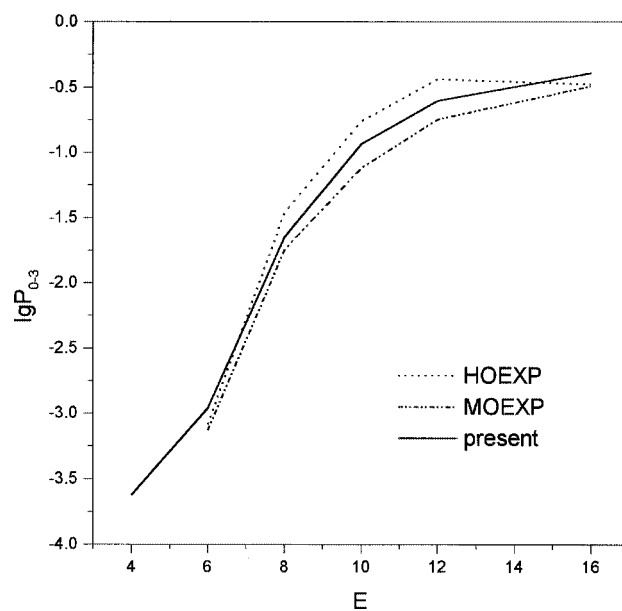
Figure 8. Logarithm of the transition probability $(0 \to 1)$ as a function of the total collision energy E_{tot} for the scattering system $H_2 + H$. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.

Figure 9. Logarithm of the transition probability $(0 \to 2)$ as a function of the total collision energy E_{tot} for the scattering system $H_2 + H$. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.
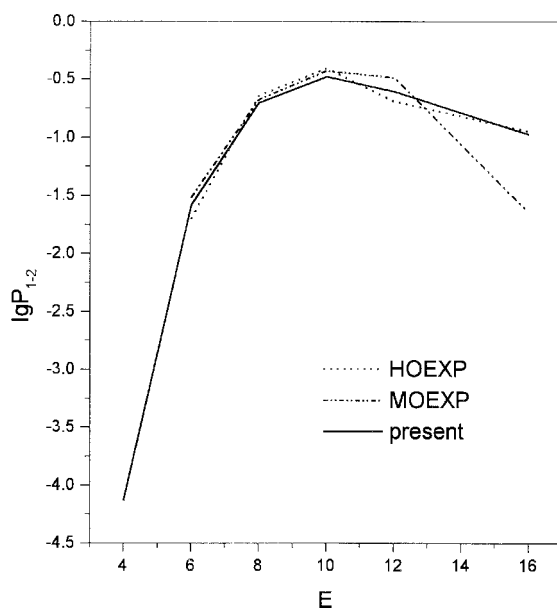
Figure 10. Logarithm of the transition probability ($0 \to 3$) as a function of the total collision energy E_{tot} for the scattering system $H_2 + H$. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.
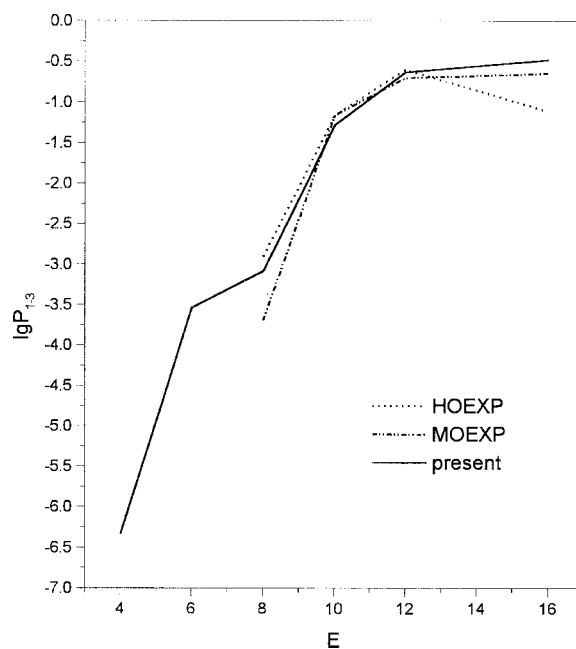
Figure 11. Logarithm of the transition probability ($1 \to 2$) as a function of the total collision energy E_{tot} for the scattering system $H_2 + H$. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.

Figure 12. Logarithm of the transition probability $(1 \rightarrow 3)$ as a function of the total collision energy E_{tot} for the scattering system $H_2 + H$. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.
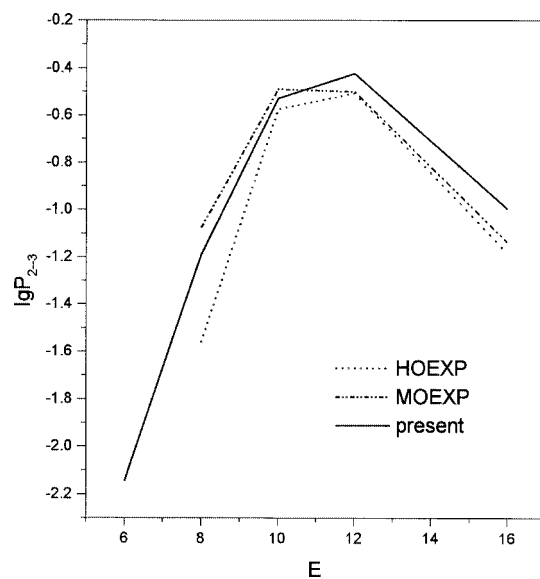

Figure 13. Logarithm of the transition probability $(2 \rightarrow 3)$ as a function of the total collision energy E_{tot} for the scattering system $H_2 + H$. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.
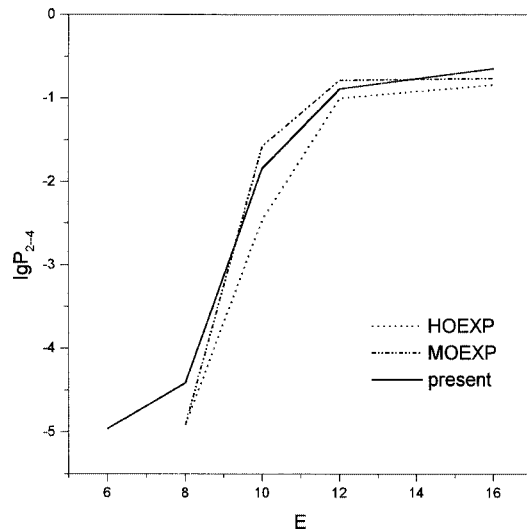
Figure 14. Logarithm of the transition probability ($2 \rightarrow 4$) as a function of the total collision energy E_{tot} for the scattering system $H_2 + H$. The energy is measured in units of $\frac{1}{2}\hbar\omega$. Solid line is for dynamical Lie algebraic results, dotted line for HOEXP results, and dashed line for MOEXP results.

Acknowledgements

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