

## QUANTUM INFORMATION FROM CLASSICAL TRAJECTORIES: SCALING DECONVOLUTION OF MOMENTS IN DIATOM-DIATOM COLLISIONS

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An inversion procedure to obtain quantal transition probabilities from the analysis of classical moments has been applied to various model diatom-diatom collision systems. This inversion relies on the use of a scaling theory to analyse classical moments and the subsequent use of a quantal scaling theory in interpretation of the classical scaling coefficients. We obtain transition probabilities that are in good agreement with exact quantum studies, and also compare favorably with other moment inversion schemes that have been described earlier in the literature.

### 1. Introduction

A problem of continuing interest is the determination of quantum information, e.g. state-to-state transition probabilities, from a classical treatment of molecular collision processes. Various methods [1-8] have been suggested for this purpose in the past few years. These methods can be distinguished as those that directly obtain transition probabilities such as the quasiclassical histogram [1], continuous quantization [2], semiclassical wave packet [3] or classical *S*-matrix [4] methods, and those that attempt to invert [5-9] averaged classical information, such as moments, and are thus indirect. The rationale behind the latter methods [5-9] is that often classical mechanics is likely to be more accurate (when compared with correct quantal results) for phase-averaged quantities [10].

In this paper we study the problem of collinearly colliding diatomic molecules. Our intention is to obtain transition probabilities for the principal inelastic processes by implementing the (indirect) classical methods of moment inversion using energy transfer and cross correlation moments.

There are essentially three methods [5-9] that exploit the classical-quantum equality of moments. If all moments are known exactly, their inversion to obtain transition probabilities is unique. However, the number of accurate classical

moments is usually far smaller than the number of significant transitions, which makes the problem underdetermined. Extra constraints can be incorporated [5] in the form of an entropy maximization principle. This was first implemented by Truhlar and co-workers [5] in the study of a collinear He-H<sub>2</sub> collision, wherein *V*-*T* energy transfer moments were used. Coltrin and Marcus [6] introduced a cross-correlation moment analysis: classical moments from low initial states were directly expressed in terms of transition probabilities and the inversion was effected by solving sets of linear equations. A third method, suggested earlier by us [9], proceeds along entirely different lines. We first employ a classical scaling theory (CST) [11] to express the variation of the moments with the initial states of the molecule. This results in a polynomial expression in the initial quantum numbers (or actions) of the problem. The classical-quantum equivalence of moments is invoked, and the scaling coefficients are expressed in terms of transition probabilities. This is made possible by the use of a quantal scaling theory [12], viz. the energy-corrected sudden (ECS) theory. Under suitable approximations a viable inversion procedure results.

This paper is divided in four parts. The model and relevant details of the classical and quantum scaling theories are described in section 2. The

methodology of the present scaling-based inversion and the applications of all three inversion methods to various diatom-diatom collision systems (for which benchmark quantal calculations

[12] exist) are presented in section 3. For convenience, we have restricted the applications to harmonic systems. A discussion and summary follows in section 4.

## 2. Theory

### 2.1. Model and scaling

The collinear system of two diatomic molecules (AB + CD) studied here has been described earlier [14]. The classical hamiltonian is given in reduced units by (in usual notation)

$$H = \alpha^2 P^2 / 2m + p_1^2 / 2 + V_1(q_1) + p_2^2 / 2 + V_2(\omega_r q_2) + \exp[-R + \alpha(q_1 + \beta q_2)]. \quad (1)$$

All energies are measured in units  $\hbar\omega_{AB}$ ;  $\omega_{AB}$  is the frequency of AB and  $\omega_r$  is the ratio  $\omega_{CD}/\omega_{AB}$ . The classical energy transfer and cross-correlation moments are defined as

$$ET^l(n_1, n_2, E_K) = (1/4\pi^2) \int_0^{2\pi} \int_0^{2\pi} d\theta_1 d\theta_2 \left[ (E_1^f + E_2^f) - (E_{n_1} + E_{n_2}) \right]^l, \quad (2)$$

$$M_{kl}(n_1, n_2, E_K) = (1/4\pi^2) \int_0^{2\pi} \int_0^{2\pi} d\theta_1 d\theta_2 \left[ (E_1^f - E_{n_1})^k (E_2^f - E_{n_2})^l \right], \quad (3)$$

where  $E_1^f$ ,  $E_2^f$  are the final and  $E_{n_1}$ ,  $E_{n_2}$  are the initial energies of AB and CD,  $n_1$ ,  $n_2$  are the initial internal states and  $\theta_1$ ,  $\theta_2$  are the initial internal phase variables respectively; the initial relative kinetic energy is denoted  $E_K$ .

For a collision system with two vibrational modes, the variation of the classical energy transfer moment with initial internal states is given by a polynomial function [15]

$$ET^l(n_1, n_2, E_K) = \sum_{j, m} \gamma_{jm}^l(E_K) n_1^j n_2^m. \quad (4)$$

It can be shown that the scaling form for  $M_{kl}$  is similar,

$$M_{kl}(n_1, n_2, E_K) = \sum_{j, m} \delta_{jm}^{kl}(E_K) n_1^j n_2^m. \quad (5)$$

Quantum mechanically the two moments  $ET^l$  and  $M_{kl}$  are given by

$$ET^l(n_1, n_2, E_K) = \sum_{\substack{\text{open states} \\ n_1', n_2' = 0, 0}} P_{n_1 n_2 \rightarrow n_1' n_2'}(E_K) E_{n_1' n_2'}^l, \quad (6)$$

$$M_{kl}(n_1, n_2, E_K) = \sum_{\substack{\text{open states} \\ n_1', n_2' = 0, 0}} P_{n_1 n_2 \rightarrow n_1' n_2'}(E_K) U_{n_1' n_2'}^{kl}, \quad (7)$$

where

$$E_{n_1' n_2'}^l = \left[ (E_{n_1'} - E_{n_1}) + (E_{n_2'} - E_{n_2}) \right]^l, \quad U_{n_1' n_2'}^{kl} = \left[ (E_{n_1'} - E_{n_1})^k (E_{n_2'} - E_{n_2})^l \right].$$

$P_{n_1 n_2 \rightarrow n_1' n_2'}(E_K)$  is the transition probability for the process  $n_1 n_2 \rightarrow n_1' n_2'$  at kinetic energy  $E_K$ .

In the present study only  $ET^1$  and  $M_{11}$  moments have been used and we restrict the discussion below to harmonic oscillators. For convenience we drop the superscripts in  $ET^1$  and the coefficient  $\gamma_{jm}^1$  and  $\delta_{jm}^{11}$ . Defining  $\Delta_1 = n_1' - n_1$ ,  $\Delta_2 = n_2' - n_2$ , eq. (6) can be rewritten as

$$ET(n_1, n_2, E_K) = \sum_{\Delta_1 = -n_1} \Delta_1 P_{n_1 n_2 \rightarrow n_1 + \Delta_1, n_2} (E_K) + \sum_{\Delta_2 = -n_2} \omega_r \Delta_2 P_{n_1 n_2 \rightarrow n_1, n_2 + \Delta_2} (E_K) \\ + \sum_{\Delta_1 = -n_1} \sum_{\Delta_2 = -n_2} (\Delta_1 + \omega_r \Delta_2) P_{n_1 n_2 \rightarrow n_1 + \Delta_1, n_2 + \Delta_2} (E_K), \quad (8)$$

where contributions from V-T processes (the first two terms), and V-V or V-V,T processes (third term) can be identified. For identical molecules ( $\omega_r = 1$ ) the resonant energy transfer ( $\Delta_1 = -\Delta_2$ ) is extremely efficient but its contribution to ET is zero. Thus the analysis of ET moments is not likely to yield much pertinent information and we need to consider the cross-correlation moment  $M_{11}$ ,

$$M_{11}(n_1, n_2, E_K) \\ = \omega_r \left[ \sum_{\Delta_1 = -1} \sum_{\Delta_2 = 1} \Delta_1 \Delta_2 P_{n_1 n_2 \rightarrow n_1 + \Delta_1, n_2 + \Delta_2} (E_K) + \sum_{\Delta_1 = 1} \sum_{\Delta_2 = 1} \Delta_1 \Delta_2 P_{n_1 n_2 \rightarrow n_1 - \Delta_1, n_2 - \Delta_2} (E_K) \right. \\ \left. - \sum_{\Delta_1 = 1} \sum_{\Delta_2 = 1} \Delta_1 \Delta_2 P_{n_1 n_2 \rightarrow n_1 + \Delta_1, n_2 - \Delta_2} (E_K) - \sum_{\Delta_1 = 1} \sum_{\Delta_2 = 1} \Delta_1 \Delta_2 P_{n_1 n_2 \rightarrow n_1 - \Delta_1, n_2 + \Delta_2} (E_K) \right]. \quad (9)$$

The last two terms of eq. (9) are a measure of V-V processes. At the same time it is clear that the cross-correlation moments do not account for V-T transfer. Thus both the ET and  $M_{11}$  are essential for computing complete state-to-state information.

## 2.2. Scaling-based inversion (SBI)

The scaling-based inversion (SBI) implements the ECS theory [12] in reducing the number of different transition probabilities in eqs. (8) and (9):

$$P_{n_1 n_2 \rightarrow n_1 - \Delta_1, n_2 - \Delta_2} (E_K) = \left| I_{\Delta_1}^{n_1, n_1 - \Delta_1} \right|^2 \left| I_{\Delta_2}^{n_2, n_2 - \Delta_2} \right|^2 \left| A_{n_1 - \Delta_1, n_2 - \Delta_2}^{n_1, n_2, \Delta_1, \Delta_2} \right|^2 P_{\Delta_1 \Delta_2 \rightarrow 00} (E_K), \quad (10)$$

$$P_{n_1 n_2 \rightarrow n_1 + \Delta_1, n_2 - \Delta_2} (E_K) = \left| I_{\Delta_1}^{n_1 + \Delta_1, n_1} \right|^2 \left| I_{\Delta_2}^{n_2, n_2 - \Delta_2} \right|^2 \left| A_{n_1 + \Delta_1, n_2 - \Delta_2}^{n_1, n_2, \Delta_1, \Delta_2} \right|^2 P_{0 \Delta_2 \rightarrow \Delta_1 0} (E_K), \quad (11)$$

where the  $I$  are geometric factors and  $A$  account for adiabaticity corrections. For the case of harmonic oscillators [12],

$$\left| I_m^{n+m, n} \right|^2 = \binom{n+m}{m} \quad \text{and} \quad \left| A_{n_1 \pm \Delta_1, n_2 \pm \Delta_2}^{n_1, n_2, \Delta_1, \Delta_2} \right|^2 = 1.$$

After expanding the binomial coefficients, on combining eqs. (10) and (11) with eq. (8) we get

$$ET(n_1, n_2, E_K) = \sum_{j, m} \gamma_{jm} (E_K) n_1^j n_2^m.$$

Similarly eq. (9) reduces to

$$M_{11}(n_1, n_2, E_K) = \sum_{j, m} \delta_{jm} (E_K) n_1^j n_2^m,$$

so that within the framework of the ECS theory, the quantal scaling form for the moments is identical to the CST. The  $\gamma$  and  $\delta$  coefficients can thus be expressed in terms of the principal transition probabilities, as given in table 1. Within the ECS approximation, the transition probabilities for other processes can be generated from the principal ones,  $P_{ij \rightarrow 00}$  and  $P_{i0 \rightarrow 0j}$ , through eqs. (10) and (11).

### 2.3. Other inversion method:

For completeness we review here the essential features of the other inversion methods [5-8]. The cross-correlation moment inversion (CMI) procedure [6] takes advantage of eq. (7) and inverts the moments  $M_{ki}$  from a given state  $n_1 n_2$  to yield the transition probabilities from this state. For example, if more than two quantum changes are insignificant from initial state  $n_1 = 1, n_2 = 0$  at a given kinetic energy  $E_K$ , then

$$P_{10 \rightarrow 00}(E_K) = (M_{20} - M_{10})/2. \quad (12a)$$

$$P_{10 \rightarrow 01}(E_K) = -(M_{22} + 2\omega_r M_{11})/\omega_r^2. \quad (12b)$$

$$P_{10 \rightarrow 01}(E_K) = (2\omega_r M_{21} + M_{12})/\omega_r^2. \quad (12c)$$

$$P_{10 \rightarrow 20}(E_K) = (M_{20} + M_{10})/2. \quad (12d)$$

There are some difficulties in using the CMI method. Firstly, classical mechanics is less accurate for lower initial states but in order to determine  $P_{10 \rightarrow ij}$  one has to use  $M_{ki}(1, 0)$ . Secondly, for higher initial states, the number of significant transitions is large and it is essential to use the higher-order cross-correlation moments; these are considerably less accurate than the low-order ones. Thirdly, for any transition probability,  $P_{n_1 n_2 \rightarrow n_1' n_2'}$ , a number of equations can be written (e.g., eqs. (12b) and (12c) for  $P_{10 \rightarrow 01}$ ). In some cases [8] these equations give absurd (negative) results and can be rejected immediately. A major problem is encountered when the remaining equations give differing and/or conflicting results. It is then not obvious which equation should be preferred.

The other well-known inversion, the maximization of entropy method (MEM) [5], invokes additional constraints. Within this technique, the inaccurate higher-order moments are unnecessary in effecting the inversion. Successful applications of this method to atom-diatom systems [5,10] have used only the first two moments of energy transfer. Note that the resonant contribution to the ET can be very small (zero for  $\omega_r = 1$ ) and therefore it is necessary to use cross-correlation moments. We have tried various combinations

Table 1

The classical scaling coefficients  $\gamma$  and  $\delta$  in terms of the state-to-state transition probabilities. All the quantities are at the same kinetic energy,  $E_K$

$\gamma_{00} = P_{00 \rightarrow 10} + \omega_r P_{00 \rightarrow 01} + 2P_{00 \rightarrow 20} + 2\omega_r P_{00 \rightarrow 02} + \dots$	(i)
$\gamma_{10} = P_{00 \rightarrow 10} - P_{10 \rightarrow 00} + P_{20 \rightarrow 00} - (1 - \omega_r)P_{10 \rightarrow 01} + (1 - \omega_r)P_{20 \rightarrow 02} + \dots$	(ii)
$\gamma_{01} = \omega_r P_{00 \rightarrow 01} - \omega_r P_{01 \rightarrow 00} + \omega_r P_{02 \rightarrow 00} + (1 - \omega_r)P_{01 \rightarrow 10} + \dots$	(iii)
$\gamma_{20} = -P_{20 \rightarrow 00} - (1 - \omega_r/2)P_{20 \rightarrow 01} - (1 - \omega_r)P_{20 \rightarrow 02} + \dots$	(iv)
$\gamma_{02} = -\omega_r P_{02 \rightarrow 00} - (\omega_r - 1/2)P_{32 \rightarrow 10} + (1 - \omega_r)P_{02 \rightarrow 20} + \dots$	(v)
$\delta_{10} = \omega_r (-P_{10 \rightarrow 01} + P_{10 \rightarrow 02} - 2P_{20 \rightarrow 01} + 2P_{20 \rightarrow 02} + \dots)$	(vi)
$\delta_{01} = \omega_r (-P_{01 \rightarrow 10} + P_{01 \rightarrow 20} - 2\omega_r^2 P_{02 \rightarrow 10} + 2P_{02 \rightarrow 20} + \dots)$	(vii)
$\delta_{20} = \omega_r (-P_{20 \rightarrow 01} - 2P_{20 \rightarrow 02} + \dots)$	(viii)
$\delta_{02} = \omega_r (-P_{02 \rightarrow 10} - 2P_{02 \rightarrow 20} + \dots)$	(ix)

of cross-correlation and energy transfer moments and found that the most reasonable estimates of transition probabilities are provided by ET, ET<sup>2</sup> and M<sub>11</sub> as three constraints in maximizing the entropy, S. This leads to the condition

$$dS = 0 = -k \sum_{n_1, n_2} \left( \ln P_{n_1 n_2} + \bar{a} + \bar{b} E_{n_1 n_2}^1 + \bar{c} E_{n_1 n_2}^2 + \bar{d} U_{n_1 n_2}^{11} \right) dP_{n_1 n_2}, \quad (13)$$

where  $P_{n_1 n_2}$  represents  $P_{n_1 n_2 \rightarrow n_1' n_2'}$  and  $\bar{a}$ ,  $\bar{b}$ ,  $\bar{c}$  and  $\bar{d}$  are the Lagrange multipliers [5].

### 3. Application and results

Vibrational relaxation in collinear molecular collisions is of three types, viz. V-T, V-V, and V-V,T energy transfer. In most systems energy transfer is quite inefficient; the dominant processes involve exchanges of a few quanta of energy at most. Of importance among these are one-quantum de-excitations in a single oscillator, and resonant or near-resonant energy transfers. In the present study we have neglected some multiple quantum exchanges; the errors inherent in the use of classical mechanics are often larger than the magnitudes of transition probabilities for such processes.

The four systems studied here are N<sub>2</sub> + N<sub>2</sub>, N<sub>2</sub> + CO, N<sub>2</sub> + OC, N<sub>2</sub> + O<sub>2</sub>. An advantage in studying these particular model systems is that accurate quantum scattering calculations have been performed earlier [13]. These have served as benchmarks for other (semiclassical forced-oscillator) approximation methods as well [16]. In the present systems, the lower classical moments are in good agreement [14] with the quantal ones and the exact state-to-state transition probabilities follow the ECS scaling law reasonably well – both these being implicit prerequisites for the SBI. Note that the four systems differ considerably in  $\omega_r$  which ranges from 1 for N<sub>2</sub> + N<sub>2</sub> to 0.67 for N<sub>2</sub> + O<sub>2</sub>, and thus represent a sufficiently wide range of model diatom-diatom systems. When  $\omega_r$  is close to 1 the resonant processes  $ij \rightarrow i \pm 1, j \mp 1$  are highly favored, whereas one-quantum de-excitation in the CD molecule is the major process for  $\omega_r$  much different from 1.

The first step in the determination of the state-to-state transition probabilities through the SBI is the computation of scaling coefficients. This is

achieved via the prescription given in ref. [15]; classical moments for various initial states are calculated by the standard procedure [1] and are used as inputs to generate the scaling coefficients [9,15]. We restrict ourselves to a maximum of 25 initial states for purposes of expediency. The lower coefficients which pertain to the low-quantum transitions are then reasonably well converged. In all four systems it is found that  $\gamma_{10}/\gamma_{20}, \delta_{10}/\delta_{20} > 10^3$  and  $\gamma_{20}/\gamma_{30}, \delta_{20}/\delta_{30} > 10^2$ . Since  $\gamma_{n0}, \delta_{n0}$  represent the magnitude of  $n0 \rightarrow 0n'$  processes it is reasonable to assume that all the transitions involving more than two-quantum changes in any of the molecules are negligible [15]. However, the problem is still underdetermined as the number of allowed transitions is greater than the number of available coefficients. An analysis of the sign and magnitude of various coefficients is necessary in order to decide how best to implement the inversion procedure. Such analysis, in all four cases, led to consideration only of processes (except resonant ones) involving less than two-quantum changes in any one of the molecules. For example, in the N<sub>2</sub> + N<sub>2</sub> system at  $E_K = 2.25$ ,

$$\gamma_{20} = -0.264(-7) = -P_{20 \rightarrow 00} - 0.5 P_{20 \rightarrow 01}, \quad (14)$$

$$\delta_{20} = -0.742(-3) = -P_{20 \rightarrow 01} - 2 P_{20 \rightarrow 02}. \quad (15)$$

Since  $\delta_{20} \gg \gamma_{20}$  and all transition probability terms have the same sign, it is evident that  $P_{20 \rightarrow 02} \gg P_{20 \rightarrow 00}$  or  $P_{20 \rightarrow 01}$ . We now have a set of equations which can be inverted to give the transition probabilities at a given kinetic energy  $E_K$ :

$$\delta_{20} = -2\omega_r P_{20 \rightarrow 02}, \quad (16)$$

$$\delta_{02} = -2\omega_r P_{02 \rightarrow 20}, \quad (17)$$

$$\delta_{10} = -\omega_r P_{10 \rightarrow 01} - 2\omega_r P_{20 \rightarrow 02}, \quad (18)$$

$$\delta_{01} = -\omega_r P_{01 \rightarrow 10} - 2\omega_r P_{02 \rightarrow 20}, \quad (19)$$

$$\gamma_{00} = \omega_r P_{00 \rightarrow 01} + P_{00 \rightarrow 10} \quad (20)$$

$$\gamma_{01} = \omega_r P_{00 \rightarrow 01} - \omega_r P_{01 \rightarrow 00} + (1 - \omega_r) P_{01 \rightarrow 10} + (1 - \omega_r) P_{02 \rightarrow 20} \quad (21)$$

$$\gamma_{10} = P_{00 \rightarrow 01} - P_{10 \rightarrow 00} - (1 - \omega_r) P_{10 \rightarrow 01} + (1 - \omega_r) P_{20 \rightarrow 02} \quad (22)$$

All the resonant transition probabilities of interest can be computed from  $\delta$  coefficients [eqs. (17)–(21)], and one-quantum V-T transition probabilities from the  $\gamma$  coefficients. At low energies and when  $\omega_r \approx 1$ ,  $\gamma_{00}$  (the ET from  $n_1, n_2 = 0$ ) is usually negative. In such cases eq. (20) cannot be used. We therefore determined  $P_{01 \rightarrow 00}$  and  $P_{10 \rightarrow 00}$  via eqs. (21) and (22). Note that there are two equations and four unknowns ( $P_{01 \rightarrow 00}$ ,  $P_{10 \rightarrow 00}$ ,  $P_{00 \rightarrow 01}$ ,  $P_{00 \rightarrow 10}$ ). But  $P_{00 \rightarrow 01}(E_K)$  and  $P_{00 \rightarrow 10}(E_K)$  are also  $P_{01 \rightarrow 00}(E_K - \omega_r)$  and  $P_{10 \rightarrow 00}(E_K - 1)$  respectively. The one-quantum transition probabilities may be determined by stepwise computations via eqs. (21) and (22); proceeding higher in initial kinetic energy by steps of  $\omega_r$  and 1 respectively from some sufficiently low energy, say  $E_L$ , at which  $P_{00 \rightarrow 01}$  and  $P_{00 \rightarrow 10}$  can be ignored in comparison with  $P_{01 \rightarrow 00}$  and  $P_{10 \rightarrow 00}$ . The  $P_{01 \rightarrow 00}(E_L)$  and  $P_{10 \rightarrow 00}(E_L)$  computed via eqs. (21) and (22) will now serve as inputs  $P_{00 \rightarrow 01}(E_L + \omega_r)$  and  $P_{00 \rightarrow 10}(E_L + 1)$  in (21) and (22) respectively to yield  $P_{01 \rightarrow 00}(E_L + \omega_r)$  and

$P_{10 \rightarrow 00}(E_L + 1)$ . Similarly these can be used to give  $P_{01 \rightarrow 00}(E_L + 2\omega_r)$  and  $P_{10 \rightarrow 00}(E_L + 2)$ , and so on.

In the symmetric  $N_2 + N_2$  system the magnitude of all other transitions is much lower than  $10 \rightarrow 00$ ,  $10 \rightarrow 01$  and  $20 \rightarrow 02$ . The  $10 \rightarrow 01$  process is  $\approx 100$  times more efficient than the one-quantum de-excitation. In fact the resonant processes dominate to an extent such that even the magnitude of  $20 \rightarrow 02$  transitions is 2.5 times larger than that for  $10 \rightarrow 00$ . Computations from various methods on this system (results are presented in table 2) show that the SBI is able to account properly for this propensity somewhat more accurately than the CMI and MEM methods. Unlike the CMI and MEM the SBI does not require the higher  $M_{kl}$ . The scaling [11] works efficiently at higher energies and so does the SBI. The agreement with quantal results is progressively better as the total energy of the system increases, as can be seen in fig. 1.

These propensities are largely reversed in the  $N_2 + O_2$  system ( $\omega_r = 0.67$ ) where  $01 \rightarrow 00$  is more efficient than near-resonant processes. However, the  $10 \rightarrow 00$  process is much less efficient than  $01 \rightarrow 00$  since it involves a larger energy transfer. The ET moment from state  $n_1 = 0, n_2 = 0$  ( $\gamma_{00}$ ) is positive and can be used to compute  $P_{00 \rightarrow 01}$ . Since all the transition probabilities are at the same

Table 2

Transition probabilities  $P_{ij \rightarrow kl}$  calculated for the  $N_2 + N_2$  system. The reduced parameters in the hamiltonian are:  $\beta = 1.00$ ,  $\omega_r = 1.00$ ,  $m = 1/2$ ,  $\alpha = 0.114$ <sup>23</sup>

$ij \rightarrow kl$	Energy <sup>b)</sup>	CMI	MEM	Exact <sup>c)</sup>	Scaling <sup>d)</sup>
10 → 00	5.25	0.750(-1)	0.990(-3)	0.778(-3)	0.746(-3)
	4.25	0.558(-1)	0.191(-3)	0.158(-3)	0.144(-3)
	3.25	0.572(-1)	0.133(-4)	0.141(-4)	0.107(-4)
	2.25	0.206(-1)	< 1(-10)	0.180(-6)	0.490(-7)
10 → 01	5.25	0.164	0.883(-1)	0.602(-1)	0.600(-1)
	4.25	0.125	0.663(-1)	0.450(-1)	0.448(-1)
	3.25	0.868(-1)	0.451(-1)	0.305(-1)	0.302(-1)
	2.25	0.480(-1)	0.246(-1)	0.167(-1)	0.165(-1)
20 → 02	5.25	0.300(-1)	0.239(-3)	0.200(-2)	0.854(-3)
	4.25	0.198(-1)	0.437(-4)	0.914(-3)	0.371(-3)
	3.25	0.105(-1)	0.332(-5)	0.270(-3)	0.851(-4)

<sup>23</sup>  $p(-q) = p \times 10^{-q}$ .

<sup>b)</sup> Total energy measured in units of  $h\omega_{AB}$  above zero-point energy.

<sup>c)</sup> Exact quantal results are from ref. [13].

<sup>d)</sup> Results from the present method.

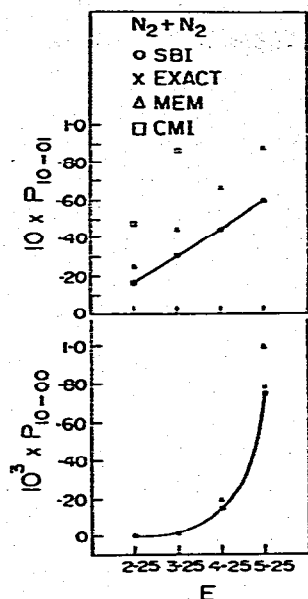


Fig. 1.  $P_{10-01}(E)$  and  $P_{10-00}(E)$  versus total energy  $E$  for the  $N_2 + N_2$  system.  $E$  is measured in units of  $\hbar\omega_{AB}$ . In the lower part CMI results are off scale.

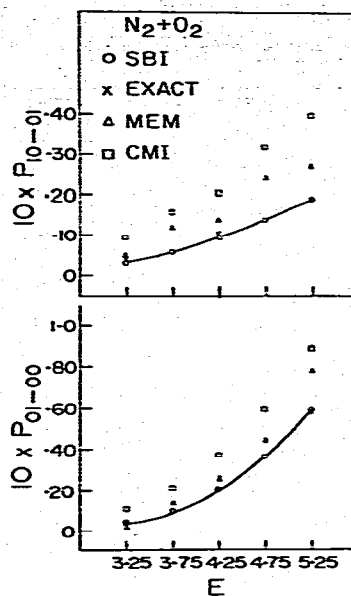


Fig. 2.  $P_{10-01}(E)$  and  $P_{01-00}(E)$  versus total energy  $E$  for the  $N_2 + O_2$  system.  $E$  is measured in units of  $\hbar\omega_{AB}$ .

kinetic energy, SBI will give seven transitions in an unsymmetric system like  $N_2 + O_2$  compared to five in a symmetric system. Some of these transition probabilities will be at different total energies. The transition probabilities increase sharply with increasing total energy and over a wide range, the

SBI yields better results than both CMI and MEM (see fig. 2).

The two other systems studied ( $N_2 + CO/OC$ ) have  $\omega_r = 0.920$ . As may be expected the resonant energy transfer is important. The effect of colliding atom mass is evident in these systems where all

Table 3  
Transition probabilities  $P_{ij \rightarrow kl}$  calculated for the  $N_2 + CO$  system. The reduced parameters in the hamiltonian are:  $\beta = 1.1550$ ,  $m = 1/2$ ,  $\omega_r = 0.920$ ,  $\alpha = 0.114$ <sup>a)</sup>

$ij \rightarrow kl$	Energy <sup>b)</sup>	CMI	MEM	Exact <sup>c)</sup>	Scaling <sup>d)</sup>	SGG <sup>e)</sup>
01 → 00	5.25	0.101	0.435(-2)	0.412(-2)	0.528(-2)	0.412(-2)
	4.25	0.731(-1)	0.197(-2)	0.566(-3)	0.394(-3)	0.558(-3)
10 → 00	5.25	0.987(-1)	0.414(-5)	0.236(-2)	0.198(-2)	0.232(-2)
	4.25	0.722(-1)	< 1(-10)	0.822(-4)	0.138(-3)	0.825(-4)
10 → 01	5.25	0.358(-1)	0.116(0)	0.800(-1)	0.857(-1)	0.709(-1)
	4.25	0.134(-1)	0.851(-1)	0.585(-1)	0.612(-1)	0.534(-1)
20 → 02	5.25	0.397(-1)	0.254(-2)	0.347(-2)	0.322(-2)	0.292(-2)

<sup>a)</sup>  $p(-q) = p \times 10^{-q}$ .

<sup>b)</sup> Total energy measured in units of  $\hbar\omega_{AB}$  above zero-point energy.

<sup>c)</sup> Exact quantal results are from ref. [13].

<sup>d)</sup> Results from the present method.

<sup>e)</sup> Semiclassical results are from ref. [16].

Table 4

Transition probabilities  $P_{ij \rightarrow kl}$  calculated for the  $N_2 + OC$  system. The reduced parameters in the hamiltonian are:  $\beta = 0.8660$ ,  $m = 1/2$ ,  $\omega_r = 0.920$ ,  $\alpha = 0.114$ <sup>a)</sup>

$ij \rightarrow kl$	Energy <sup>b)</sup>	CMI	MEM	Exact <sup>c)</sup>	Scaling <sup>d)</sup>	SGG <sup>e)</sup>
01 $\rightarrow$ 00	5.25	0.594(-1)	0.386(-2)	0.242(-2)	0.209(-2)	0.239(-2)
	4.25	0.419(-1)	0.143(-2)	0.576(-3)	0.422(-3)	0.571(-3)
10 $\rightarrow$ 00	5.25	0.552(-1)	0.509(-3)	0.889(-3)	0.703(-3)	0.887(-3)
	4.25	0.411(-1)	0.350(-6)	0.179(-3)	0.130(-3)	0.179(-3)
10 $\rightarrow$ 01	5.25	0.127	0.668(-1)	0.457(-1)	0.471(-1)	0.404(-1)
	4.25	0.933(-1)	0.484(-1)	0.331(-1)	0.336(-1)	0.303(-1)
20 $\rightarrow$ 02	5.25	- <sup>d)</sup>	0.729(-3)	0.112(-2)	0.943(-3)	0.945(-3)

<sup>a)</sup>  $p(q) = p \times 10^{-q}$ .

<sup>b)</sup> Total energy measured in units of  $\hbar\omega_{AB}$  above zero-point energy.

<sup>c)</sup> Exact quantal results are from ref. [13].

<sup>d)</sup> Results from the present method.

<sup>e)</sup> Semiclassical results are from ref. [16].

<sup>f)</sup> All CMI equations give a negative value.

the energy transfer modes in the  $N_2 + OC$  system are less efficient than in the  $N_2 + CO$  system. The 01  $\rightarrow$  00 process is slightly favored over 10  $\rightarrow$  00. The  $\gamma_{00}$  coefficient is usually negative and therefore  $P_{01 \rightarrow 00}$  and  $P_{10 \rightarrow 00}$  are computed via eqs. (21) and (22). The results of computations on these two systems are given in tables 3 and 4, respectively.

#### 4. Discussion

In this paper we have implemented an inversion procedure which utilizes both classical and quantal scaling theories so as to obtain transition probabilities from classical moments. All these methods are valid at every impact parameter; thus a full three-dimensional inversion scheme is identical in principle to the one-dimensional example treated here. In common with other methods, the present scaling-based inversion relies on the classical-quantum equality of moments [10]. In addition, we further require that the collision system is such that application of the ECS theory [12] would be feasible.

In most collision systems the lower-order moments, e.g. ET,  $M_{11}$ , and  $ET^2$ , are usually more accurate than higher-order ones. An inversion procedure based solely on these should yield better results than methods which involve higher-order

moments as well. While the SBI uses this fact to its advantage, we find that the inaccuracy in a given moment is not uniformly distributed over the scaling coefficients. The 10 and 01 coefficients are usually more accurate than the others. Thus, for example, the SBI  $P_{20 \rightarrow 02}$  is approximately half of its exact value, while  $P_{10 \rightarrow 01}$  is almost exactly the correct quantal result. Within the SBI, note that any inaccuracy in moments is transmitted linearly, as both the CST and ECS are linear theories. Thus the percent error in the moments is reflected directly as a similar error in transition probabilities.

The SBI can be easily used in getting a proper qualitative picture [15], since this merely calls for comparing coefficients in order to elicit trends and propensities. As a *quantitative* tool, though, the use of SBI does require some judgement and as such is difficult to automate. It might be mentioned that all these moment analysis techniques call for some subjective appraisals – which moments to use in eq. (13) in the MEM, or which set of equations to choose from [e.g., eqs. (12b), (12c)] for the CMI.

There are differences among the three methods. The SBI is a fully dynamical theory and incorporates only features of the dynamics in the inversion, as does the CMI. The MEM only provides a least biased estimate of transition probabilities consistent with the dynamical input. This may not always be consistent with the full dynamics as can



be seen in all the four systems studied here. Further, the SBI gives information at a fixed kinetic energy, while the other methods yield information at fixed total energy.

There is one feature within the present SBI which tends to restrict its *full* utility. For anharmonic systems, the quantal ECS formulae [12] analogous to eq. (10) are not particularly simple, and since energies are not always linear in quantum number, the stepwise analysis of scaling coefficients cannot proceed with the same ease as in the present case. There are two possible means of overcoming this drawback: one might use approximate semiclassical scaling formulae [17] to simplify the expressions, or, alternatively, assume a functional dependence of the transition probabilities on the kinetic energy.

In the present applications, we see that the SBI – although slightly more difficult to apply – is uniformly more accurate than the CMI and MEM, and quite often, somewhat surprisingly, of similar or better accuracy than the semiclassical forced-oscillator approach of Skodje et al. [16]. The four systems studied here are very different in their characteristics and represent a sufficiently wide range of generic behaviours. (The case of  $\omega_r$  near zero has not been studied; such systems are close to the atom-diatom collision limit where the SBI method should work with similar ease.)

In addition to its providing of a viable means of obtaining transition probabilities, two facets of the classical scaling theory deserve mention. One of these, the role of the CST in compacting large amounts of trajectory information and in reducing the number of required computations, has been extensively documented [11,15,18]. Further, recall that the angular variables also obey the scaling law [11]. Although such scaling has not been used in the present work, this aspect can be used fruitfully

in locating classical trajectories with the proper boundary conditions – which could then be used in the classical *S*-matrix [4] calculations. In multi-dimensional systems, this feature is likely to be of considerable utility.

## References

- [1] R.N. Porter and L.M. Raff, in: *Dynamics of molecular collisions*, Vol. 1, ed. W.H. Miller (Plenum Press, New York, 1976).
- [2] R. Ramaswamy and A.E. DePristo, *Chem. Phys. Letters* 77 (1981) 190.
- [3] E. Heller, *J. Chem. Phys.* 65 (1976) 1289; H.W. Lee and M.O. Scully, *J. Chem. Phys.* 73 (1980) 2238.
- [4] W.H. Miller, *Advan. Chem. Phys.* 30 (1975) 77; *J. Chem. Phys.* 53 (1970) 1949; R.A. Marcus, *Chem. Phys. Letters* 7 (1970) 525.
- [5] J.W. Duff and D.G. Truhlar, *Chem. Phys.* 9 (1975) 243; D.G. Truhlar, B.P. Reid, D.E. Zurawski and J.C. Gray, *J. Phys. Chem.* 85 (1981) 786.
- [6] M.E. Coltrin and R.A. Marcus, *J. Chem. Phys.* 73 (1980) 4390; 76 (1982) 2379.
- [7] M.E. Coltrin, M.L. Koszykowski and R.A. Marcus, *J. Chem. Phys.* 73 (1980) 3643.
- [8] D.W. Schwenke, D. Thirumalai, D.G. Truhlar and M.E. Coltrin, *J. Chem. Phys.* 78 (1983) 3078.
- [9] R. Ramaswamy and R. Bhargava, *J. Chem. Phys.* 80 (1984) 1095.
- [10] R.J. Gordon, *J. Chem. Phys.* 65 (1976) 4945; R.A. Marcus, *J. Phys. Chem.* 83 (1979) 944.
- [11] A.E. DePristo, *J. Chem. Phys.* 75 (1981) 3384; R. Ramaswamy, *J. Chem. Phys.* 80 (1984) 2462.
- [12] A.E. DePristo, S. Augustin, R. Ramaswamy and H. Rabitz, *J. Chem. Phys.* 71 (1979) 850.
- [13] X. Chapuisat and G. Bergeron, *Chem. Phys.* 36 (1979) 397.
- [14] X. Chapuisat, G. Bergeron and J. Launay, *Chem. Phys.* 20 (1977) 285.
- [15] R. Ramaswamy, *Chem. Phys.* 88 (1984) 7.
- [16] R.T. Skodje, W.R. Gentry and C.F. Giese, *Chem. Phys.* 74 (1983) 347.
- [17] S.D. Augustin, *J. Chem. Phys.* 78 (1983) 206.
- [18] A.E. DePristo, *J. Phys. Chem.* 86 (1982) 1334.