CLASSICAL TRAJECTORY ANALYSIS IN ATOM–TRIATOM COLLISIONS: CONTINUOUS QUANTIZATION AND SCALING BEHAVIOUR

Ramakrishna RAMASWAMY

Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India

A method of analysing classical trajectory data, based on recently derived scaling principles, is applied to a model atom–triatom collinear collision system. Apart from the utility of the scaling idea in extending trajectory computations, the analysis of the scaling coefficients in terms of transition probabilities increases the scope of the classical scaling theory as a means of obtaining (at the very least) qualitative quantum-mechanical information from classical trajectories. As an useful adjunct, the method of continuous quantization is applied to generate approximate transition probabilities. These results are semiquantitative; thus a combination of classical scaling and continuous quantization affords a powerful means of modeling complex collision cases with a minimum of computational effort.

1. Introduction

A central problem in studying molecular collision systems is the difficulty associated with applying exact or accurate theoretical methods [1,2]. Even for molecules containing relatively few atoms, it is customary to use classical mechanics – most commonly the simple and well-known quasiclassical histogram technique (QH) [3]. (A number of alternate scattering methods based on classical mechanics have been suggested in recent years [4–12], some of which involve modifications in order to improve the QH.) The simplicity and convenience of a trajectory method is an attractive feature insofar as application to systems with several degrees of freedom is of concern. Since it is desirable to obtain as much quantum-mechanical information as is possible from such classical calculations, it is of interest to explore different means of analysing classical trajectory data. The primary aim of this paper is to demonstrate the utility of two recently proposed theories in facilitating such analysis, with application to a model atom–triatom system.

We focus on the first moment of the energy transfer (ET) in inelastic collisions, and demonstrate the applicability of a classical scaling princi-

ple [13,14]. This relationship holds over a wide range of collision conditions and makes possible the prediction of the energy transfer from a large number of states based on a small set of trajectory calculations [13,15,16]. One can thus treat a very large number of states – certainly more than can be handled by almost any quantum scattering method. Within the assumption that classical and quantum averages are equal, the classical scaling coefficients can be interpreted [16] in terms of *quantum* state-to-state transition probabilities, which are the primary quantities of interest.

Alternately, state-to-state transition probabilities are obtained here by the continuous quantization (CQ) procedure [12] *. This method utilizes a somewhat elementary mapping concept to analyse the classical *continuous* action variable. In cases treated earlier [12], reasonable accuracy was obtained for most amplitudes that were not too small, i.e. $> 10^{-3}$. However, when classical mechanics is grossly incorrect, CQ offers only marginal

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* The CQ method has been criticized for not reducing to the perturbation result for all transition amplitudes by Dickinson and Richards [17]. However, the CQ method does in fact reduce to the correct classical result, as well as the correct perturbation limit for one-quantum transitions [18].

improvement over QH. There is one advantage even in the case when classical mechanics fails badly – as for example in extremely adiabatic situations. CQ gives good estimates of the *relative* magnitudes for the transition amplitudes, and correctly predicts propensities and trends. In the present cases [*], wherever comparison with exact quantum-mechanical results has been possible, this is seen to be true. The number of trajectories needed for CQ is comparable to that needed to obtain moments, and in addition, the transition probabilities so obtained contain the essential features of the physics of the situation.

Although here the variation of the ET with initial state of the molecular system is studied via the classical scaling theory (CST), a variety of scaling laws for any dynamical variable can be derived [13,14]. Recall that the scaling and CQ can be applied (i) at every value of the impact parameter, (ii) for arbitrary forms of the interaction potential, and (iii) for harmonic as well as anharmonic systems. (An important case when both methods break down is in the case of non-integrable systems [19] when the motion is chaotic, since then proper final action variables cannot always be defined [20]. The model system to which these theories are applied is therefore chosen to be as simple as possible, in order to leave the analysis most transparent; none of these simplifications are restrictive in any essential way. Thus the collision geometry is collinear, and the molecular hamiltonian is asymptotically integrable (and separable). This is described in section 2.

Such systems have been studied before [20–22] by different methods; these previous studies serve as a benchmark against which the present analysis is compared, in section 3. The information derived from the CST is inferential and largely qualitative, but accurate; that obtained from the CQ is semi-quantitative. Thus in larger, more complex collision cases, wherein the application of most dynamical methods (including the QH) remains unfeasible, a combination of CST and CQ can prove practicable. A discussion and summary follows in section 4.

2. Theory

2.1. Collinear model

The classical model system of a symmetric triatomic molecule(XYX)–atom(Z) can conveniently be described in mass-scaled normal coordinates. The hamiltonian is given by

$$H(p, q) = \tfrac{1}{2}\sum_i p_i^2/\mu_i + (q_1^2 + kq_2^2)/2 + V(q), \quad (1)$$

where the interaction potential has the form

$$V(q) = \exp[-\alpha(q_3 - q_1 - q_2)] \quad (2)$$

and the reduced masses are given by

$$\mu_1 = 1,$$
$$\mu_2 = k^{1/2} = (2m_1 + m_2)/m_2 = \omega_2^2,$$
$$\mu_3 = m_3(2m_1 + m_2)/2m_1(2m_1 + m_2 + m_3); \quad (3)$$

$\alpha = (1/2L^2 m_1 k_1)^{1/2}$. m_1, m_2 and m_3 are the masses of atoms X, Y and Z, k_1 is the force constant for the symmetric stretch; in obtaining (1), the intramolecular potential used consists of two uncoupled harmonic oscillator functions, one per XY bond. All energies are measured in units of the symmetric stretch spacing. As usual, the p and q indicate momenta and coordinates, the subscripts 1–3 denote, respectively, the symmetric and asymmetric stretch normal modes, and translation coordinates; L is the range parameter for the interaction potential.

The usual procedure [3] is followed; the hamiltonian (1) is transformed to action–angle variables for the molecular degrees of freedom, $(p_1 q_1 p_2 q_2) \rightarrow (J_1 \theta_1 J_2 \theta_2)$. A given initial state is chosen by the correspondence $n_i = J_i + 1/2$ ($\hbar = 1$); phases θ_1 and θ_2 are sampled uniformly in $[0, 2\pi]$; trajectories are integrated in cartesian space and transformed to final action variables at the end of collision. Moments of a dynamical variable W are computed through the integral

$$\Delta W(E_k; J_1, J_2) = \frac{1}{(2\pi)^2} \int_0^{2\pi} d\theta_1 \int_0^{2\pi} d\theta_2 (W_f - W_i)^l,$$

$$l = 1, 2 \ldots . \quad (4)$$

Note that ΔW is indexed by the kinetic energy and

the initial actions. In eq. (4), the subscripts i and f denote initial and final values. We will primarily be concerned with the first moment of the energy transfer, $\Delta W = ET$, for which W is the molecular hamiltonian.

2.2. Classical scaling theory (CST)

The basic classical scaling formalism has been presented in detail elsewhere [13,14] and we quote only the pertinent results here. If either one of the initial actions is fixed, at a given kinetic energy, the variation of ΔW with the other action is expressed as a polynomial series [16],

$$\Delta W(E_k; \bar{J}, J_2) = \sum_m \beta_m(\bar{J}) J_2^m \qquad (5)$$

(here J_1 is fixed at $\bar{J}$), which can be written in a quantum number form as well ($n = J - 1/2$):

$$\Delta W(E_k; \bar{n}, n_2) = \sum_m \alpha_m(\bar{n}) n_2^m. \qquad (6)$$

Note that the α depend on $\bar{n}$. A similar expression holds for the situation when n_2 is fixed and n_1 is varied. Combining these, it is straightforward to obtain

$$\Delta W(E_k; n_1, n_2) = \sum_{i,j} \gamma_{ij} n_1^i n_2^j. \qquad (7)$$

This is the main scaling form which will be used later. The various $\alpha_m(n_{1_i})$, i.e. the scaling coefficients for *individual* rows of the ΔW matrix are related to the γ by the transformation

$$
\begin{pmatrix} \alpha_l(n_{1_1}) \\ \alpha_l(n_{1_2}) \\ \vdots \\ \alpha_l(n_{1_m}) \end{pmatrix}
=
\begin{pmatrix}
1 & n_{1_1} & n_{1_1}^2 & \cdots & n_{1_1}^m \\
1 & n_{1_2} & n_{1_2}^2 & \cdots & n_{1_2}^m \\
\vdots & \vdots & \vdots & \cdots & \vdots \\
1 & n_{1_m} & n_{1_m}^2 & \cdots & n_{1_m}^m
\end{pmatrix}
\begin{pmatrix} \gamma_{0l} \\ \gamma_{1l} \\ \vdots \\ \gamma_{ml} \end{pmatrix}.
$$
$$(8)$$

A detailed examination of the CST in the present collision case closely follows the analysis given earlier in the case of atom–diatom collisions [16]. Consider the exact quantum-mechanical expres-

sion for the ET

$$ET(E_k; n_1, n_2) = -\sum_{n_1' n_2'} \left[n_1 - n_1' + \omega_2(n_2 - n_2') \right]$$
$$\times P_{n_1 n_2, n_1' n_2'}(E_k). \qquad (9)$$

This can be separated into three terms, corresponding to whether the process $P_{ij,kl}$ is "elastic" in the symmetric stretch, asymmetric stretch, or neither, i.e.

$$ET(E_k; n_1, n_2) = \sum_\nu \nu P_{n_1 n_2, n_1 - \nu n_2} \qquad (10a)$$

$$+ \sum_\nu (\omega_2 \nu) P_{n_1 n_2, n_1 n_2 - \nu} \qquad (10b)$$

$$+ \sum_{\nu_1 \nu_2} (\nu_1 + \omega_2 \nu_2) P_{n_1 n_2, n_1 - \nu_1 n_2 - \nu} \qquad (10c)$$

By applying the quantum energy corrected sudden (ECS) scaling theory [24], it is easy to see that the first term, (10a) reduces to the form

$$-n_1 P_{1n_2, 0n_2} - n_1(n_1 - 1) P_{2n_2, 0n_2} + \dots,$$

which includes *only* powers of n_1; likewise, the second term (10b) contributes only powers of n_2. The final term, (10c), gives the cross terms $n_1^l n_2^m$. Consequently, the scaling coefficients γ_{l0} are composed of transition probabilities $P_{1n_2, 0n_2}$. Similarly γ_{0m} consists of the transition probabilities $P_{n_1 m, n_1 0}$. γ_{00}, the ET when $n_1 = n_2 = 0$, is a combination of both these kinds of terms. Thus the scaling coefficients γ_{l0} or γ_{0m} are indicative of the transfer of energy from a molecular vibrational mode into translation, *namely pure V–T processes.*

The γ_{lm} (with neither l nor m equal to 0) are composed of transition probabilities $P_{l0, 0m}$. Recall that these arise from reexpressing $P_{n_1 n_2, n_1 \pm l n_2 \pm m}$ via the ECS scaling form; hence these γ_{lm} are indicative of energy transfer *between* the modes, i.e. *pure V–V and V–V, T processes.*

As in the case with one degree of freedom [16], the quantum ECS scaling law [24] offers both a justification for the CST, as well as providing a simple interpretation of the individual scaling coefficients. The detailed expressions for the γ can be obtained in a manner analogous to that in ref.

[16]: however, these are substantially more cumbersome in the present instance. The dominant contributions to the various coefficients can be identified as

$$\gamma_{l0} \approx \sum_{n_2} P_{l n_2, 0 n_2}(E_k).$$ (11a)

$$\gamma_{0m} \approx \sum_{n_1} P_{n_1 m, n_1 0}(E_k).$$ (11b)

(The individual transition probabilities usually have a weak dependence on the elastic quantum number.) It is not possible to easily distinguish between the contributions from V–V and V–V,T processes in the cross terms. γ_{lm}. Both $P_{n_1 n_2, n_1 \pm l\, n_2 \pm m}$ and $P_{n_1 n_2, n_1 \pm l\, n_2 \mp m}$ contribute to γ_{lm}. However, since the former process would be expected to have an amplitude of the order of $P_{n_1 n_2, n_1 \pm l\, n_2}$ or $P_{n_1 n_2, n_1 n_2 \pm m}$ or less, any substantial increase of γ_{lm} over γ_{l0}, γ_{0m} may be interpreted as indicative of enhanced V–V transfer. (Resonant V–V transfer becomes possible when one mode frequency is close to being an integral multiple of the other. For example, if $k\omega_1 = k'\omega_2$, the magnitude of $\gamma_{kk'}$ is then an indication of the importance of this resonant process.)

The deconvolution of the γ to obtain individual state-to-state transition probabilities is thus a more complicated scheme. However, as will be seen in section 3, the (absolute) numerical values of the various coefficients, and their dependence on the kinetic energy, can accurately reflect the behaviour of the transition amplitudes themselves.

A measure of the overall inelasticity is the energy transfer when the molecule is classically at rest, $J_1 = J_2 = 0$. This quantity, denoted EZ, which is given in terms of the scaling coefficients by

$$EZ = \sum_{i,j} (-1/2)^{i+j} \gamma_{ij}$$ (12)

serves to characterize the collision system.

3. Application

The general methodology presented in section 2 is applied to a model collision case. In order to make some comparison with other studies [21,22].

this system nominally * corresponds to the case of harmonic CO_2–rare-gas collisions. The primary aim is to demonstrate the scope of the scaling analysis – not only in extending classical computation, but also in extracting as much of the quantum behaviour as is possible. This is complemented by CQ calculations. In the results described here, all calculations employed at least 36 trajectories – 6 per vibrational degree of freedom. When the moments were extremely small, as in CO_2–Kr collisions at low energy, the number of trajectories was increased to 100 to check for accuracy. Convergence was obtained to 3 significant figures for both ET moments and the CQ transition probabilities.

Among the practical problems in the extraction of implicit quantum information from classical trajectory data, a major one lies in the relative errors introduced by the use of classical mechanics [25]. For example. $ET(E_k; 00)$ often turns out to be negative, whereas the quantum-mechanical moment is necessarily ≥ 0. In this paper the analysis proceeds via the scaling coefficients wherein a different problem occurs. The γ are determined by an inversion procedure, eqs. (6)–(8). As the input information is increased these coefficients converge. For predictive accuracy, however, one can use unconverged γ, if the input states are selected carefully to span the region of interest (see especially tables II and III in ref. [16]). The largest terms approach the converged values faster than the smaller ones; even so, the unconverged coefficients are usually of the same magnitude as the converged ones. In the present scattering problem, the number of trajectories needed to generate the converged coefficients is much greater than that needed to be able to achieve excellent scaling predictions for the ET. Thus not much significance will be attached to the smaller γ coefficients except in a broad and qualitative fashion.

At a given kinetic energy, moments are computed for initial states $n_1, n_2 = 0, 4, 8$, i.e. for a total of nine initial states. This suffices in de-

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* The system parameters are those used in refs. [21,22], and thus this is only a crude representation of CO_2–rare-gas collisions. Since the methodology is of greater interest here, such a model is more than adequate for the purpose at hand.

termining the γ coefficients via eqs. (6) and (8), up to and including γ_{22}. The γ are then used in eq. (7) to generate the moments from any other state in the range $0 \leqslant n_1$, $n_2 \leqslant 8$, which maps out the behaviour of the vibrational manifold including 81 possible initial states. Shown in table 2 are the results of such a procedure for CO_2–He and Kr at $E_k = 4$ ($\equiv 0.67$ eV) and in table 3 at $E_k = 8$ ($\equiv 1.34$ eV). The principal γ coefficients are given in table 1.

The major observation regarding this harmonic model system is that a three-term scaling approximation works extremely well along the rows/columns of the ET matrix. In applying the scaling form, we have chosen widely spaced (but symmetrically placed) initial states to determine the coefficients. The difference between the scaling predictions and exact calculations from separate trajectory computations are less than 1% for either collision partner in both tables 2 and 3. (A difference in the two systems is the pattern of the ET. At $E_k = 4$, energy is transferred into translation in He collisions for all states $n_1 \geqslant 1$, n_2; with the heavier rare-gas atom, this occurs only for n_1, low n_2 states.) Initial states with higher excitation in the asymmetric stretch tend to absorb energy into vibrational modes. At higher E_k in table 3 both He and Kr collisions tend to be deactivating except at low n_1 ($n_1 \leqslant 2$ for He and $n_1 = 0$ for Kr). These effects can be understood by examining the moments for the average change in quantum numbers Δn_1 and Δn_2. A detailed analysis of a more realistic model of CO_2–Kr collisions has been given

earlier by Schatz and Mulloney [26], where such behaviour has been noted and discussed. (Note that there can be considerable confidence in the classical calculations: a quantum study of the same collinear CO_2–Kr system by Clary [27] shows good agreement between classical and quantum ET moments at translational energies above 1 eV.)

A glance at table 1 reveals several interesting features. Firstly, $EZ^{He}/EZ^{Kr} \approx 15000$ at $E_k = 4$, and ≈ 500 at $E_k = 8$; the inelasticity in the collision is dramatically reduced with the heavier partner at the same kinetic energy. Secondly, in either system, $|\gamma_{10}| > |\gamma_{01}|$ – i.e. energy transfer progresses more easily out of the symmetric stretch as compared to the asymmetric. The ratio $\omega_2 \gamma_{10}/\gamma_{01}$ gives an estimate of the ratio of the transition probabilities for one-quantum de-excitations (symmetric versus asymmetric). This ratio is larger for Kr than for He, i.e. the asymmetry is more pronounced in the former case. Further, this ratio decreases with increasing kinetic energy, from $\approx$ 700 at $E_k = 2$ to 50 at $E_k = 8$ for He. The largest of the terms that gauge V–V,T transfer, γ_{11}, is of the same order as γ_{01}: this is a direct consequence of the lack of coupling between the two modes of the isolated molecule. With increasing kinetic energy the ratio γ_{11}/γ_{01} decreases; this leads to the expectation that $P_{10.01}/P_{01.00}$ will correspondingly decrease as well.

The above inferences are drawn *entirely* on the basis of the scaling analysis given in section 2.2. This can be contrasted with previous studies of the same systems.

Table 1
Scaling coefficients [a] for CO_2–He, Kr. The input information is from states $n_1 n_2 = 00, 04, 08, 40, 44, 48, 80, 84, 88$

	$E_k = 2$ He	$E_k = 4$		$E_k = 8$	
		He	Kr	He	Kr
γ_{00}	$-0.922(-3)$ [b]	$0.407(-1)$	$0.103(-5)$	0.470	$0.619(-3)$
γ_{10}	$-0.100(-1)$	$-0.625(-1)$	$-0.850(-5)$	-0.173	$-0.914(-3)$
γ_{01}	$-0.287(-4)$	$-0.564(-3)$	$0.198(-5)$	$-0.699(-2)$	$-0.624(-5)$
γ_{20}	$0.153(-4)$	$0.116(-3)$	$-0.113(-5)$	$0.263(-3)$	$-0.347(-5)$
γ_{11}	$-0.357(-4)$	$-0.234(-3)$	$0.483(-5)$	$-0.494(-3)$	$0.282(-5)$
γ_{21}	$0.132(-6)$	$0.112(-5)$	$-0.939(-7)$	$0.677(-6)$	$-0.147(-6)$
EZ	$4.111(-3)$	$7.225(-2)$	$5.233(-4)$	$5.599(-1)$	$1.079(-3)$

[a] The coefficients have dimension of energy, which is measured in units of 1351.23 cm^{-1}.
[b] In this and all other tables, the digits in parentheses indicate the power of 10 by which the preceeding numbers must be multiplied.

Table 2

Scaling in CO_2–rare-gas collisions at $E_k = 4.0(0.67$ eV). The upper and lower figures refer to He and Kr partners; the moments fo CO_2–Kr should be multiplied by a factor of 10^{-4}. The unit of energy is the CO_2 symmetric-stretch normal-mode spacing

n_1	n_2								
	0	1	2	3	4	5	6	7	8
0	0.0407	0.0402	0.0396	0.0390	0.0385	0.0379	0.0373	0.0368	0.0362
	0.0103	0.0304	0.0511	0.0723	0.0940	0.1163	0.1392	0.1625	0.1864
1	−0.0217	−0.0225	−0.0233	−0.0241	−0.0249	−0.0257	−0.0265	−0.0273	−0.0281
			(0.0493) [b]					(−0.0273) [a]	
	−0.0861	−0.0187	0.0490	0.1169	0.1851	0.2535	0.3222	0.3912	0.4604
2	−0.0839	−0.0849	−0.0860	−0.0870	−0.0880	−0.0890	−0.0900	−0.0911	−0.0921
	−0.2051	−0.0923	0.0206	0.1334	0.2463	0.3592	0.4721	0.5850	0.6980
3	−0.1459	−0.1471	−0.1484	−0.1496	−0.1509	−0.1521	−0.1533	−0.1546	−0.1559
				(0.1243) [b]		(−0.1521) [a]			
	−0.3467	−0.1904	−0.0342	0.1218	0.2776	0.4332	0.5887	0.7440	0.8991
4	−0.2076	−0.2090	−0.2106	−0.2120	−0.2135	−0.2150	−0.2165	−0.2179	−0.2194
	−0.5110	−0.3130	−0.1153	0.0821	0.2791	0.4758	0.6721	0.8681	1.064
5	−0.2691	−0.2708	−0.2725	−0.2742	−0.2759	−0.2776	−0.2793	−0.2810	−0.2827
	−0.6980	−0.4601	−0.2227	0.0143	0.2507	0.4868	0.7223	0.9574	1.192
6	−0.3303	−0.3323	−0.3342	−0.3361	−0.3381	−0.3400	−0.3419	−0.3438	−0.3457
	−0.9076	−0.6318	−0.3565	−0.0817	0.1925	0.4662	0.7393	1.012	1.284
7	−0.3914	−0.3935	−0.3957	−0.3978	−0.4000	−0.4021	−0.4042	−0.4064	−0.4085
				(−0.3978) [a]		(0.4137) [b]			
	−1.140	−0.8279	−0.5165	−0.2057	0.1045	0.4141	0.7231	1.032	1.339
8	−0.4522	−0.4546	−0.4569	−0.4593	−0.4616	−0.4640	−0.4663	−0.4687	−0.4710
	−1.395	−1.049	−0.7029	−0.3579	−0.0135	0.3304	0.6737	1.016	1.358

[a] Exact ET from a separate trajectory calculation for CO_2–He; to be compared with the upper number (predicted).
[b] Exact ET for CO_2–Kr to be compared with lower number.

Table 3

Scaling in CO_2–rare-gas collisions at $E_k = 8.0(1.34$ eV). The upper and lower figures refer to He and Kr partners; the moments for CO_2–Kr should be multiplied by a factor of 10^{-2}. The unit of energy is the CO_2 symmetric-stretch normal-mode spacing

n_1	n_2								
	0	1	2	3	4	5	6	7	8
0	0.4702	0.4632	0.4562	0.4492	0.4422	0.4352	0.4283	0.4213	0.4143
	0.0619	0.0613	0.0607	0.0601	0.0594	0.0588	0.0582	0.0576	0.0569
1	0.2979	0.2904	0.2830	0.2755	0.2680	0.2605	0.2530	0.2456	0.2831
				(0.2755) [a]				(−0.0322) [b]	
	−0.0298	−0.0302	−0.0305	−0.0309	−0.0312	−0.0316	−0.0320	−0.0323	−0.0327
2	0.1262	0.1182	0.1102	0.1023	0.0943	0.0863	0.0783	0.0704	0.0624
	−0.1222	−0.1223	−0.1224	−0.1226	−0.1227	−0.1228	−0.1229	−0.1231	0.1232
3	−0.0450	−0.0535	−0.0620	−0.0704	−0.0789	−0.0874	−0.0958	−0.1043	−0.1127
				(−0.2150) [b]				(−0.1043) [a]	
	−0.2153	−0.2152	−0.2151	−0.2150	−0.2150	−0.2149	−0.2148	−0.2147	−0.2147
4	−0.2157	−0.2247	−0.2336	−0.2426	−0.2515	−0.2605	−0.2694	−0.2784	−0.2873
	−0.3091	−0.3088	−0.3085	−0.3083	−0.3090	−0.3078	−0.3075	−0.3073	−0.3071
5	−0.3859	−0.3953	−0.4048	−0.4142	−0.4237	−0.4331	−0.4425	−0.4519	−0.4613
	−0.4036	−0.4031	−0.4027	−0.4023	−0.4019	−0.4015	−0.4011	−0.4008	−0.4004
6	−0.5555	−0.5655	−0.5754	−0.5853	−0.5952	−0.6052	−0.6151	−0.6250	−0.6349
	−0.4987	−0.4982	−0.4977	−0.4972	−0.4966	−0.4961	−0.4956	−0.4951	−0.4946
7	−0.7247	−0.7351	−0.7455	−0.7559	−0.7663	−0.7767	−0.7871	−0.7975	−0.8078
						(−0.5916) [b]		(−0.7975) [a]	
	−0.5946	−0.5940	−0.5934	−0.5928	−0.5921	−0.5916	−0.5910	−0.5904	−0.5898
8	−0.8932	−0.9041	−0.9150	−0.9259	−0.9368	−0.9477	−0.9586	−0.9694	−0.9803
	−0.6912	−0.6905	−0.6898	−0.6891	−0.6886	−0.6878	0.6872	−0.6865	−0.6859

[a] Exact ET from separate trajectory calculation for CO_2–He; to be compared with the upper number (predicted).
[b] Exact ET for CO_2–Kr to be compared with the lower number.

Earlier quantal studies [21,22] of harmonic CO_2 and He, Kr collisions have been carried out at fixed *total* energies of 1 eV and 1.5 eV, on collinear systems closely related to the present hamiltonian (1). These results are summarized for convenience in table 4. The present classical calculations are at a fixed *kinetic* energy, and the scaling coefficients relate only de-excitation transition probabilities at the same kinetic energy. Nevertheless, some comparison is possible.

The effect of increased mass of the colliding particle in decreasing the overall ET is well known, and has been observed earlier [21,22]. The parameter EZ serves to quantify this fact here. From table 4, it can be seen that $P_{00,10}^{He}/P_{00,10}^{Kr}$ at $E_T = 1$ eV is around 15000, and decreases to 600 at $E_T = 1.5$ eV, in a manner similar to the ratio $\gamma_{10}^{He}/\gamma_{10}^{Kr}$ (7000 at $E_k = 4$ to 200 at $E_k = 8$). The one-quantum transition ratio, $P_{10,00}/P_{01,00}$ also behaves in the same way (≈ 900 at $E_T = 1$ eV to 150 at $E_T = 1.5$ eV). As expected, $(P_{10,00}/P_{01,00})^{Kr}$ is much larger

at the same energy. Finally, one may observe that the ratio $P_{10,01}/P_{01,00}$ *decreases* with increasing total energy, as anticipated from the scaling analysis.

Although we have compared transition probabilities at different energies, the conclusions would be similar if it were possible to make the comparison at the same kinetic energy, since the individual transition probabilities are well separated (see fig. 1 in ref. [21]). The very ease of generating the classical moments and performing the scaling analysis makes is possible to treat systems of a size considerably beyond the scope of any quantum calculation.

At this stage therefore, it is appropriate to present some results from the application of the CQ method. An indication of the relative accuracy in using CQ is obtained by comparing the classical ET moments with those obtained by using the CQ transition probabilities. Although the ratios ET(CQ)/ET(classical) and $ET^2(CQ)/ET^2$(classical) can vary considerably, when n_1 or n_2 is large,

Table 4

Quantum-mechanical transition probabilities, $P_{n_1 n_2, n_1' n_2'}$ for the CO_2–He and Kr systems. Unless otherwise indicated, these values are taken from ref. [21]. The upper and lower numbers refer to energies 1 and 1.5 eV respectively. The upper right triangle pertains to the CO_2–He collisions, and the lower left to CO_2–Kr

n_1	n_2	$\epsilon_{n_1 n_2}$ [a]	Kinetic energy [b]	
			$E_T = 1$ eV	$E_T = 1.5$ eV
0	0	1.387	4.58	7.57
1	0	2.387	3.58	6.57
0	1	3.610	2.80	5.79
2	0	3.386	2.58	5.56

$n_1 n_2$	$n_1' n_2'$			
	00	10	01	20
00	–	0.74(−1)	0.82(−4)	0.10(−2)
	–	0.30	0.20(−2)	[d]
10	0.45(−5)	–	0.20(−3)	0.51(−1) [c]
	0.46(−3)	–	0.12(−2)	[d]
01	[e]	0.16(−6)	–	0.11(−4)
	[d]	0.18(−4)	–	0.37(−3)
20	[e]	0.50(−6) [c]	0.29(−5)	–
	[d]	[d]	0.18(−4)	–

[a] The energy of the state $n_1 n_2$ in units of the symmetric stretch normal-mode spacing.
[b] Kinetic energy in the state $n_1 n_2$ (in the present units).
[c] Transition probability given in ref. [22].
[d] Transition probability not available in ref. [21].
[e] Transition probability not available in either refs. [21] or [22].

Table 5

Comparison of exact and CQ transition probabilities $P_{n_1 n_2, n_1' n_2'}$ for CO_2–He collisions

$n_1 n_2 n_1' n_2'$	$E_T = 1$ eV				$E_T = 1.5$ eV			
	QM [a]	CQE [b]	CQD [c]	QM [d]	QM [a]	CQE [b]	CQD [c]	QM [d]
00 10	0.74(−1)	0.16	0.16	0.11	0.30	0.56	0.34	0.34
00 01	0.82(−4)	0.50(−3)	0.24(−3)	0.21(−3)	0.20(−2)	0.22(−2)	0.29(−2)	0.29−(2)
10 01	0.20(−3)	0.78(−4)	0.51(−5)	0.27(−2)	0.12(−2)	0.13(−2)	0.19(−2)	0.72(−2)
10 20	0.51(−1)	0.12	0.89(−1)	0.89(−1)	0.33	0.31	0.38	0.36
01 20	0.11(−4)	0.11(−5)	0.44(−5)	0.91(−3)	0.37(−3)	0.12(−3)	0.11(−3)	0.48(−2)

[a] Quantum results from refs. [21,22].
[b] CQ excitation results. i.e. for the process $n_1 n_2 \rightarrow n_1' n_2'$.
[c] CQ de-excitation results. i.e. for the process $n_1' n_2' \rightarrow n_1 n_2$.
[d] Quantum results from ref. [23].

and the kinetic energy is high, the ratio is close to 1 for *both* the first and second moment of the energy transfer. For example. in CO_2–He at $E_k = 8$. for $n_1 n_2 = 80$. these are $(-0.8932)/(-0.7695) = 0.86$, and $9.53/10.12 = 1.06$ respectively. One can then have reasonable confidence in the actual numerical values of the CQ results. and more importantly, in the physics of the situation as displayed in the propensities and relative magnitudes for the different transitions. Since we have used only *36* trajectories in these calculations. the quasiclassical histogram method would be quantitatively inadequate here.

In table 5, transition probabilities from quantum calculations and the present CQ are compared at fixed total energy. The essential features of the two collision cases seem to be reproduced quite well. At the higher total energy this agreement improves. Also shown are quantum transition probabilities in a similar system (with a different anharmonic molecular potential at the same energies. Except for the process 10–01 which is poorly described. the CQ results are surprisingly good if one allows for the naivety of the method itself and the fact that it involves marginal additional effort to obtain the ET moments.

There are several ways in which the CQ results could be "improved". When both first and second CQ moments show approximately the same deviation from the classical ET moments, one could use this as a constant multiplicative factor to change the transition probabilities, although assuming equal relative errors for all processes is questiona-

ble. A better method at low kinetic energies is to use the quantum ECS law [24] on a transition amplitude known to be more accurate. For example, $P_{40,30}$ ($E_k = 4) = 0.382$, which gives $P_{10,00}$ ($E_k = 4) = 0.96(-1)$ at $E_T = 1.08$ eV, which is closer to the accurate quantum result (see table 4).

4. Discussion

In using classical mechanics in studying molecular collisions. often one can most reliably compute initial state selected quantities. Typically these are moments of dynamical variables that change during the collision, but are constants of the motion asymptotically as $t \rightarrow \pm\infty$. Formally, such a problem is solved by the classical technique of variation of constants, and this leads in a straightforward way to the classical scaling theory [14]. For asymptotically separable or integrable systems, eq. (7) and its generalization to more degrees of freedom holds. For non-integrable systems, the CST is valid only in a restricted regime for regular levels [19].

In the example discussed, the CST is seen to hold to a high degree of accuracy. It suffices to compute the energy transfer from 9 states to predict that from at least 81 (if not more) other levels in the vibrational manifold. As the number of internal degrees of freedom increases, the CST grows in utility, not only as a predictive tool, but also as a means of compacting large amounts of data.

This similarity with the quantum ECS law is worth emphasizing. In a previous collision case [16] as well as the present one, simple classical–quantum correspondences led to an expression of the classical scaling coefficients in terms of quantum state-to-state transition amplitudes. This is a major advantage of the CST: when the number of actual trajectories is insufficient to employ even the quasiclassical histogram method, the scaling analysis can be applied. The information that can be derived from these coefficients is in agreement with the results of separate quantum-mechanical treatments of the same collision cases. However, since examination of scaling coefficients reveals that they consist of complicated combinations of various transition probabilities, this kind of information is at best qualitative. (It is also likely that in most "large" collision systems, such information is adequate and comparable to that obtained by approximate dynamical theories [28].) For model CO_2–He and Kr collisions, it has been possible to show that the trends apparent in the classical scaling coefficients are an accurate reflection of the true quantal behaviour [21,22].

As a useful addition to the largely inferential data obtained through the scaling analysis, the method of continuous quantization was also applied to obtain transition probabilities independently. This was seen to augment the utility of the purely classical analysis; however, the CQ method itself gives no indication of the overall quality of the classical calculations. Where comparison with exact quantum-mechanical results was possible, the CQ results were seen to be in reasonable agreement. (A weakness of the CQ method, however, is that it may not be amenable to the Monte Carlo sampling of the initial phase which is customary in larger systems.)

There are two other methods [6–8] of extracting quantum information from classical moments. One [6,7] uses an information-theoretic constraint of maximum entropy to invert moments of the energy transfer to obtain quantum transition probabilities. The other [8,29], employs cross-correlation moments and is similar in some respects to and complementary to the scaling analysis in section 2.2. The cross-correlation moments, $M_{ij} = \langle \Delta \epsilon_1^i \Delta \epsilon_2^j \rangle$, where $\Delta \epsilon_k$ is the change in energy in the

kth oscillator, and $\langle \ \rangle$ denotes the phase average (as in eq. (4)), from low initial states can be directly expressed in terms of quantum transition probabilities [29]. This latter method works reasonably well, although sometimes the inversion procedure can yield unphysical results (such as negative transition probabilities) due to the errors introduced by the use of classical mechanics. The advantage of the scaling analysis in this context is that the classical calculations can be performed in the regime where classical mechanics is most likely to be accurate – e.g. for high quantum numbers, since the analysis only requires the coefficients γ. On the other hand, the scaling analysis can be more complicated in some cases. A necessary ingredient in the scaling analysis is the quantum ECS theory [24]; for anharmonic oscillator systems, the ECS expressions are often cumbersome, and the quantum-number dependence is not transparent. In such a situation, the cross-correlation method has an advantage. A more detailed comparative study of the various moment analysis methods is presently under way [30].

The extension to more degrees of freedom does not pose any additional problem, unless there is widespread intramolecular chaos. It should be emphasized that although the example chosen here is simple, both the methods, classical scaling and continuous quantization are valid for more complicated cases since they only require that action-like variables be defined. This approach can therefore prove useful in the accurate (e.g. a more realistic intermolecular potential, a proper anharmonic description of the molecular system) modeling of systems of chemical interest.

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