

## SCALING OF MOMENTS IN ROTATIONAL INELASTICITY

Sudeshna SINHA

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

and

Ramakrishna RAMASWAMY

*School of Physical Sciences, Jawaharlal Nehru University, Vedanta Desika Marg, New Delhi 110 067, India*

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We report the scaling behaviour of rotational energy transfer moments. The quantum moments exhibit a polynomial scaling behaviour in the variable  $j_i(j_i+1)$ , whereas the classical moments scale as a polynomial in  $j_i^2$ , where  $j_i$  is the initial rotational quantum number or action. Applications are made to  $\text{Li}^*_2$ -rare gas collisions, as well as to a classical planar-rotor collision model. The scaling theory allows an accurate interpolation and extrapolation of experimental scattering data.

### 1. Introduction

The correlation of inelastic state-to-state quantities through factorization or scaling laws has proven to be a fruitful approach in the study of molecular collisions [1,2]. In particular the use of the energy-corrected sudden (ECS) scaling law is extremely useful in analysing elementary cross sections or kinetic rates [3-5]. For averaged quantities like moments, complementary scaling forms can be deduced through a classical formalism, the classical scaling theory (CST) [6,7]. In the latter case it can be shown that moments have a polynomial dependence on quantum numbers (or actions) with expansion coefficients being related to transition probabilities [8].

In this paper we examine the scaling behaviour of moments in rotationally inelastic collisions. Similar studies have been performed earlier [9] in the somewhat more transparent case of vibrationally inelastic collisions. Our intention here is to examine whether the formalism hitherto developed can be successfully carried over to the present case.

In a sense the scaling theory for moments generalizes the sum rules commonly employed in relaxation studies [10]. The form of dependence of moments on initial quantum numbers has important implications; a linear dependence, for instance, guarantees exponential decay to equilibrium for vibrational inelasticity. Rotational moments are typically strongly non-linear functions of the initial rotor state [11]; however, the question here is whether they can be suitably expressed in polynomial form, which then conveniently allows for accurate interpolation and extrapolation.

The scaling theory is briefly discussed in section 2, and the correct form for polynomial scaling of classical and quantum moments is derived. We also attempt to justify these scaling forms on a purely quantum mechanical basis, using the ECS theory for rotational processes.

In order to verify the scaling behaviour, we consider two approaches. By using the ECS theory along with a power-gap law [12], it is possible to generate kinetic rates for all processes in a given system, and thereby obtain moments. We then examine the validity of scaling for the synthesized moments. A purely classical study is also

made using a classical planar collision model [13], wherein moments are generated and the scaling behaviour is confirmed. These studies are presented in section 3, where we treat the cases of  $\text{Li}^*_2$ -rare gas [14] collisions, as well as the classical model of scattering. This is followed by a discussion and summary.

## 2. Theoretical background

### 2.1. Classical scaling

It is most convenient to work in action-angle variables in setting up the collision problem. We assume for simplicity, the case of a rigid rotor colliding with a structureless partner. The Hamiltonian is given by [13]

$$H(P, R, j, q_j) = P^2/2\mu + V(R, q_j) + Bj^2 + l^2/2\mu R^2, \quad (1a)$$

where

$$V(R, q_j) = (1/R^{12} - 2/R^6)(1 + a_1 \cos q_j + 3a_2 \cos^2 q_j/2). \quad (1b)$$

$P$  and  $R$  are the momentum and coordinate for translational degree of freedom (with reduced mass  $\mu$ ) and  $j$  and  $q_j$  are the action-angle variables for rotational degree of freedom.  $B$  is the rotational constant for the rotor and  $l$  is the orbital angular momentum. The action variable  $j$  is the classical counterpart of the rotational quantum number. Since the interaction potential ( $a_1$  and  $a_2$  are anisotropy parameters)  $V \rightarrow 0$  as  $R \rightarrow \infty$ , the rotor energy is constant before and after the collision. The net change in energy is given by

$$\Delta E(j_i) = B \langle j_f^2 - j_i^2 \rangle, \quad (2)$$

where  $j_i$  and  $j_f$  are the initial and final rotational actions, and  $\langle \rangle$  denotes an average over all angle variables and orbital angular momenta. Through the classical scaling formalism, this change is given by a functional of the Liouville operator [7]

$$\Delta E(j_i) = G_{j_i}(\{V\}; \text{initial actions}) \quad (3)$$

and can be Taylor expanded in the initial rotor action to give a polynomial scaling form. Note that here the symmetry in  $j$  in the Hamiltonian (1) requires that only even powers in  $j$  be included in the expansion, and we therefore have

$$\Delta E(j, E_k) = \alpha_0 + \alpha_1 j^2 + \alpha_2 j^4 + \dots, \quad (4)$$

where  $E_k$  is the kinetic energy of the collision. On the other hand, the angular momentum change  $\Delta L(j_i, E_k) = \langle j_f - j_i \rangle$  is given by polynomial expansion in  $j_i$  itself.

While eq. (4) is the proper form for scaling the classical energy transfer moment, note that the quantum  $j^2$  operator has eigenvalue  $j(j+1)$ . Thus, in taking over eq. (4) to the quantum case, the correct scaling form for the quantum moment would be expected to be

$$\Delta E(j, E_k) = \tilde{\alpha}_0 + \tilde{\alpha}_1 j(j+1) + \tilde{\alpha}_2 j^2(j+1)^2 + \dots \quad (5)$$

The right-hand side can, of course, be rewritten as a series in  $j$  itself. This highlights a basic difference in the classical and quantum scaling forms, and will be borne out in the examples studied in section 3 below.

### 2.2. Quantal formalism

Recall the ECS form for inelastic cross sections [1]

$$\sigma_{i \rightarrow j}(E_k) = (2j+1) \sum_{L=i-j}^{i+j} (2L+1) \begin{pmatrix} i & j & L \\ 0 & 0 & 0 \end{pmatrix}^2 |A_L^i|^2 \sigma_{L \rightarrow 0}(E_k), \quad (6)$$

which relates deexcitation cross sections  $\sigma_{i \rightarrow j}$  at the same initial kinetic energy  $E_k$  to a basic set,  $\sigma_{L \rightarrow 0}$ . In eq. (6)  $\begin{pmatrix} i & j & L \\ 0 & 0 & 0 \end{pmatrix}$  is a 3- $j$  symbol, and  $A_L^i$  is an adiabaticity factor [1]. A similar formula holds for rates  $k_{i \rightarrow j}$  as well. A weighted energy transfer rate from initial state  $j_i$  can be defined at temperature  $T$  as

$$\Delta E(j_i) = \sum_{j_f} k_{j_i \rightarrow j_f}(T)(\epsilon_{j_f} - \epsilon_{j_i}), \quad (7)$$

where  $\epsilon_j = B j(j+1)$ . Rewriting eq. (7) as a sum of excitations and deexcitations, and using eq. (6), one has

$$\begin{aligned} \Delta E(j_i) = & \sum_{\delta=1}^j B(\delta^2 + \delta + 2j_i\delta)(2j_i+1) \sum_{L=\delta}^{2j_i+\delta} (2L+1) \begin{pmatrix} j_i & j_i+\delta & L \\ 0 & 0 & 0 \end{pmatrix}^2 \\ & \times |A_L^{j_i+\delta}|^2 k_{L \rightarrow 0}(T) \exp[-(\delta^2 + \delta + 2j_i\delta)/kt] \\ & - \sum_{\delta=1}^{j_i} B(\delta^2 - \delta - 2j_i\delta)(2j_i+1-2\delta) \sum_{L=\delta}^{2j_i-\delta} (2L+1) \begin{pmatrix} j_i & j_i-\delta & L \\ 0 & 0 & 0 \end{pmatrix}^2 |A_L^{j_i}|^2 k_{L \rightarrow 0}(T), \end{aligned} \quad (8)$$

where the summation index  $\delta$  relates to the quantum number difference between the final and the initial rotational state.

Although it is suggestive, in that the leading term is of order  $j_i^2$ , it is not clear whether this leads to a polynomial law in  $j_i$  or  $j_i^2$ , in contrast to the vibrational case where similar analysis was more transparent. One problem is that 3- $j$  symbols cannot easily be approximated in polynomial form; in a semiclassical approximation by using the Stirlings formula, they reduce (for high enough  $j_i$  and  $L$ ) to

$$\begin{pmatrix} j_i & j_i \pm \delta & L \\ 0 & 0 & 0 \end{pmatrix}^2 = (2j_i \pm \delta + L + 1)^{-1}. \quad (9)$$

However, this does not simplify eq. (8), or further help in making contact with eq. (5).

In arriving at a justification for eq. (5), it is more helpful to use empirical or semi-empirical fitting laws [15],

$$k_{j_i \rightarrow j_f} \sim |\Delta E|^{-\nu} \sim |j_f^2 - j_i^2|^{-\nu} \sim \Delta j^{-\nu}. \quad (10)$$

For small  $\Delta j$  and not too small  $j_i$ ,  $\nu = 1$ . Inserting eq. (10) in eq. (7), it is clear that a polynomial law in  $j_i$  results. The contribution to the coefficients of  $j_i^n$  from excitations is proportional to

$$\sum_{j > j_i} (-1)^n j^{n-1} \exp(-\Delta \epsilon_{j_i}/kT). \quad (11)$$

The exponential factor makes coefficients of large powers of  $j_i$  negligible. The contribution to coefficients of  $j_i^n$  from deexcitations goes as  $(-1)^n \sum_{j < j_i} (1/j^{n+1})$ , and clearly decreases with increasing  $n$ . So the coefficients get progressively smaller, and the series is likely to be convergent. Alternately, in the adiabatic limit, with  $A_L^i = 1$  in eq. (6), and using [16]  $k_{L \rightarrow 0} \sim [L(L+1)]^{-1}$ , eq. (8) can be shown to reduce to a polynomial in  $j_i$ .

This allows, at a heuristic level at least, for a justification of a polynomial type scaling form for quantum mechanical RET moments as well. It is of interest to note that coefficients of both even and odd powers of  $j_i$  appear in the scaling form when the empirical law, eq. (10) is used, in accordance with eq. (5).

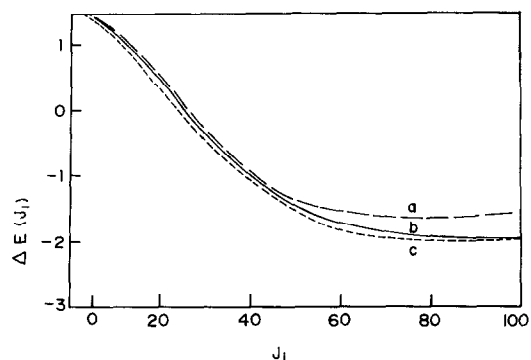


Fig. 1. Quantum number dependence of the rotational energy transfer for the case of  $\text{Li}_2^+$  colliding with (a) Ne, (b) Ar and (c) Xe.  $\Delta E(j)$  is in units of  $10^{-11} \text{ cm}^3 \text{ eV s}^{-1}$ . All relevant parameters were taken from ref. [14].

### 3. Results

The ECS-P law introduced by Pritchard and co-workers [12] combines the ECS scaling theory, and a fit of the basic rates  $k_{L \rightarrow 0}$  (or cross sections) to a power law, modified by an exponentially decreasing term,

$$k_{L \rightarrow 0} = a[L(L+1)]^{-\gamma} \exp[-(L/L^*)^2], \quad (12)$$

where  $a$ ,  $\gamma$  and  $L^*$  are fitting parameters. Using eq. (12), it is possible to generate moments from any initial state  $j_i$ . For  $\text{Li}_2^+$ -rare gas the necessary parameters are given in ref. [14], and the moments can be easily synthesized using  $k_{L \rightarrow 0}$  generated using the ECS-P law. These are plotted in fig. 1, where it can be seen that the general trend in all systems is similar. As  $j_i$  increases there are two opposing effects in operation: the number of lower levels available for transitions increases, but  $k_{j_i \rightarrow j_i \pm \delta} \sim \delta^{-1}$  and this decreases with increasing  $\delta$ . Thus, as  $j$  increases, the RET does not change significantly. This is in accord with results from purely classical studies [17].

We investigate the scaling behavior of the RET moment as a polynomial in  $j(j+1)$  (or equivalently  $j$ ) and

Table 1

Convergence behaviour of scaling coefficients  $\alpha_i$  and  $\tilde{\alpha}_i$  in the  $\text{Li}_2^+$ -Ne system. The parameters used in eq. (10) are:  $a=40$ ,  $\gamma=0.87$ ,  $L^*=36$

$j$ <sup>a)</sup>	RET <sup>b)</sup>	$\alpha_0$ $\tilde{\alpha}_0$	$\alpha_1$ $\tilde{\alpha}_1$	$\alpha_2$ $\tilde{\alpha}_2$	$\alpha_3$ $\tilde{\alpha}_3$	$\alpha_4$ $\tilde{\alpha}_4$
2	1.4849	1.4849				
4	1.4467	1.4976	-0.3183(-2)			
6	1.3872	1.5012	-0.2728(-2)	0.6605(-5)		
8	1.3076	1.4980	-0.3315(-2)	0.7441(-6)		
10	1.2091	1.5013	-0.2748(-2)	0.1031(-4)	-0.6619(-7)	
12	1.0939	1.4982	-0.3367(-2)	0.5299(-6)	0.3730(-8)	
14	0.9641	1.5013	-0.2744(-2)	0.1284(-4)	-0.1357(-6)	0.5788(-9)
16	0.8223	1.4982	-0.3397(-2)	0.4193(-6)	0.4817(-8)	-0.2421(-10)
		1.5013	-0.2743(-2)	0.1465(-4)	-0.1357(-6)	0.1393(-9)
		1.4983	-0.3417(-2)	0.4193(-6)	0.4817(-8)	-0.2421(-10)
		1.5013	-0.2743(-2)	0.1600(-4)	-0.2470(-6)	0.2250(-8)
		1.4984	-0.3431(-2)	0.4667(-6)	0.5596(-8)	-0.3565(-10)
		1.5013	-0.2743(-2)	0.1705(-4)	-0.2893(-6)	0.3069(-8)
		1.4984	-0.3442(-2)	0.4496(-6)	0.6186(-8)	-0.4562(-10)
		1.5013	-0.2743(-2)			

<sup>a)</sup> Rotational quantum number. <sup>b)</sup> Energy transfer moment from state  $j$  (in units of eV).

Table 2  
Comparison of exact and predicted quantum RET moments (in units of eV) for the  $\text{Li}^*_2\text{-Ne}$  system, using eq. (5)

$j$	Exact	Scaled	$j$	Exact	Scaled
4	1.4467	1.4498	54	-1.5701	-1.5705
14	0.9641	0.9635	64	-1.8084	-1.8076
24	0.1888	0.1892	74	-1.9351	-1.9374
34	-0.5798	-0.5800	84	-1.98789	-1.9768
44	-1.1736	-1.1733	94	-1.9932	-2.0841

$j^2$ , following procedures described earlier [9]. Shown in table 1 is the convergence behaviour of the scaling coefficients using eqs. (4) and (5). It is important to note that the coefficients  $\tilde{\alpha}_i$  converge much faster than  $\alpha_i$ . Further the coefficients of increasing order fall off more rapidly in  $j(j+1)$  scaling than in  $j^2$  scaling. It is thus evident that the use of the  $j(j+1)$  scaling form, eq. (5), is superior to eq. (4).

Having determined the scaling coefficients from a small set of input moments, it is possible to use these to predict moments from arbitrary initial states. In table 2 is shown the predictive accuracy of the  $j(j+1)$  scaling form, for the case of the  $\text{Li}^*_2\text{-Ne}$  system. It can be seen that over a wide range of  $j$ , the scaling form yields accurate results especially when used for interpolation.

The classical energy transfer can be directly computed by integrating Hamilton's equations deriving from the Hamiltonian (1). Since the orbital angular momentum is also a parameter in the problem, we have chosen to scale the (partial) RET moment at each value of  $l$  separately. The parameters chosen in the example in table 3 were  $a_1=0.0$ , initial momentum  $P_i=15$ , and  $l=0$ . The scaling coefficients generated by  $j(j+1)$  and  $j^2$  scaling forms are shown. Clearly in the latter case, the coefficients converge more rapidly to a steady value, and also fall off faster with increasing order. This indicates that  $j^2$  scaling is more appropriate than  $j(j+1)$  scaling in contrast to the quantum case, shown in table 1.

In the classical case both interpolation and extrapolation work extremely well, and in fact with only two input moments - a quadratic in  $j$  - the entire range can be predicted. Some representative results, for  $l=12.0$ ,  $a_1=0.0$ , and initial relative momentum  $P_i=15$ , are given in table 4.

Table 3  
Convergence behaviour of scaling coefficients  $\alpha_i$  and  $\tilde{\alpha}_i$  for the classical planar-rotor collision model, at fixed orbital angular momentum  $l=0$

$j$ <sup>a)</sup>	RET <sup>b)</sup>	$\alpha_0$	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\alpha_4$
		$\tilde{\alpha}_0$	$\tilde{\alpha}_1$	$\tilde{\alpha}_2$	$\tilde{\alpha}_3$	$\tilde{\alpha}_4$
10	5.0499	5.0499				
		5.0499				
20	3.3781	5.6071	-0.0055			
		5.6431	-0.0054			
30	0.5958	5.6075	-0.0055	0.1010(-7)		
		5.6395	-0.0054	-0.7631(-7)		
40	-3.2923	5.6076	-0.0055	0.1147(-7)	-0.1167(-11)	
		5.6379	-0.0053	-0.1328(-6)	0.3870(-10)	
50	-8.2830	5.6076	-0.0055	0.1147(-7)	-0.1107(-11)	-0.2031(-16)
		5.6369	-0.0053	-0.1725(-6)	0.8063(-10)	-0.1353(-13)
60	-14.3757	5.6076	-0.0055	0.1147(-7)	-0.8227(-12)	-0.1729(-15)
		5.6363	-0.0053	-0.2011(-6)	0.1175(-9)	-0.3272(-13)

<sup>a)</sup> Rotational quantum number. <sup>b)</sup> Energy transfer moments from state  $j$  (reduced units).

Table 4

Comparison of exact and predicted classical RET (partial) at fixed orbital angular momentum  $l=12$ 

$j$	Exact	Scaled	$j$	Exact	Scaled
10	-0.0071	-0.0071	40	-0.6067	-0.6066
20	-0.0647	-0.0647	50	-1.1832	-1.1836
30	-0.2437	-0.2439	60	-1.9696	-1.9650

#### 4. Discussion

This study has focused on the application of the classical scaling formalism to the case of rotationally inelastic collisions, as a natural extension of previous studies on vibrational processes. Whereas quantum scaling theories treat elementary cross sections or kinetic rates, classical scaling applies mainly for averaged quantities. However, it is possible to deduce the scaling principle that applies to both quantum and classical moments. In the present case, these are not identical: quantal energy transfer moments scale properly as a polynomial in the variable  $j(j+1)$  whereas the corresponding classical moments scale in  $j^2$ , where  $j$  is the rotational quantum number.

In contrast to the vibrational cases studied earlier, it has not been possible to make correspondence between classical scaling coefficients and quantum transition probabilities. Thus, although one can obtain evidence for scaling behaviour, it is not entirely clear as to what the coefficients signify. At the same time the predictive accuracy is excellent, which further underscores the utility of scaling forms as a means of extending scattering data.

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