

# Analytical results from the study of energy relaxation of a forced Morse oscillator

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## Abstract

An exact analytical expression has been derived in the framework of an algebraic model of a forced Morse oscillator for average energy transferred per collision as a function of the initial vibrational state. This model is shown to include the ‘supercollision’ energy transfer events.

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## 1. Introduction

Collisional relaxation of highly vibrationally excited molecules has long been the subject of much research, mainly with the purpose of measuring the average amount of energy transferred per collision with the internal energy of parent molecules [1–3]. The best results available for an understanding of energy transfer processes have been achieved due to theoretical advances in trajectory-based calculations (see, e.g. [4–8] and references therein). Although there is a significant progress in numerical calculations, the analytical approaches allow the insight into the process under investigation, to make general conclusions, and to formulate correctly problems for computer simulation. For many years, a simple model of vibrational-translational energy exchange between a Morse oscillator and structureless atoms in collinear collisions has drawn attention with respect to the analytical calculations of both transition probabilities [9–13] and the average transferred energy [14–18]. An algebraic approach to the vibrational transitions of the Morse oscillator excited by external force has allowed Levine and Wulfman [9] to

find an analytical solution for the probabilities of these transitions. In this Letter, we are going to demonstrate that in the framework of this model the average energy transferred per collision can be calculated precisely without any approximations.

## 2. Theory

The algebraic analysis of vibrational excitation of a forced Morse oscillator introduced by Levine and Wulfman [9] through a dynamical algebra,  $su(2)$ , leads to a closed form result for the transition probabilities between the bound states,  $0 \leq n, n' \leq N$  (there are only  $N + 1$  bound states):

$$P_{n \rightarrow n'} = \left[ d_{\frac{N}{2}-n, \frac{N}{2}-n'}^{(N/2)}(\beta) \right]^2, \quad (1)$$

where  $d$  are the matrix elements for finite rotations [19] and the parameter  $\rho = \tan^2(\beta/2)$  is determined by a forcing function [9,20]. This model describes transitions between the bound states only. Transitions to the continuum are completely absent in the algebraic model. The energy levels correspond to a Morse oscillator are of the form

$$E_n = -D_e + \omega_e \left( n + \frac{1}{2} \right) - x_e \omega_e \left( n + \frac{1}{2} \right)^2, \quad (2)$$

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where  $D_e = \omega_e/4x_e$  is the dissociation energy; the number of the bound states  $N$  is equal to  $(1 - x_e)/2x_e$  because by definition, we get  $E_N = 0$ . The average energy transferred per collision is defined by

$$\langle \Delta E_n \rangle = \sum_{n'=0}^N (E_{n'} - E_n) P_{n \rightarrow n'}. \quad (3)$$

Thus  $\langle \Delta E_n \rangle$  as given by Eq. (3) is the first moment of probabilities (1), i.e., the average over all possible outcomes of a collision with the initial energy  $E_n$ . In other words, to calculate  $\langle \Delta E_n \rangle$ , it is necessary to evaluate the moments  $\langle n' - n \rangle$  and  $\langle n'^2 - n^2 \rangle$  with probabilities (1).

Let us calculate now these moments. We use the multiplication formula with  $3j$ -symbols to put down the product of two elements of  $d$ -matrices [19]

$$\begin{aligned} [d_{mm'}^{(j)}(\beta)]^2 &= (-1)^{m-m'} \sum_{J=0}^{2j} (2J+1) \begin{pmatrix} j & j & J \\ m & -m & 0 \end{pmatrix} \\ &\times \begin{pmatrix} j & j & J \\ m' & -m' & 0 \end{pmatrix} d_{00}^{(J)}(\beta), \end{aligned} \quad (4)$$

where the angular momentum  $j$  is quite arbitrary, i.e., can be either integer or non-integer. Then we give  $m'$  and  $m^2$  in terms of the particular values of  $3j$ -symbols, namely [19]:

$$m' = \frac{(-1)^{m'-j}}{2} \left[ \frac{(2j+2)!}{(2j-1)!} \right]^{1/2} \begin{pmatrix} j & j & 1 \\ m' & -m' & 0 \end{pmatrix} \quad (5)$$

and

$$\begin{aligned} m^2 &= \frac{(-1)^{m'-j}}{3} \left\{ j(j+1) \left[ \frac{(2j+1)!}{(2j)!} \right]^{1/2} \begin{pmatrix} j & j & 0 \\ m' & -m' & 0 \end{pmatrix} \right. \\ &\left. + \frac{1}{2} \left[ \frac{(2j+3)!}{(2j-2)!} \right]^{1/2} \begin{pmatrix} j & j & 2 \\ m' & -m' & 0 \end{pmatrix} \right\}. \end{aligned} \quad (6)$$

The orthogonality condition of  $3j$ -symbols reads the following

$$\sum_{m'=-j}^j \begin{pmatrix} j & j & J \\ m' & -m' & 0 \end{pmatrix} \begin{pmatrix} j & j & k \\ m' & -m' & 0 \end{pmatrix} = \frac{\delta_{Jk}}{2J+1}, \quad (7)$$

where  $k = 0, 1, 2$  in our case. Remember that  $d_{00}^{(1)} = \cos \beta$  and  $d_{00}^{(2)} = (3\cos^2 \beta - 1)/2$ . We can apply these equations to give:

$$\sum_{m'=-j}^j m' [d_{mm'}^{(j)}(\beta)]^2 = m \cos \beta, \quad (8)$$

$$\sum_{m'=-j}^j m^2 [d_{mm'}^{(j)}(\beta)]^2 = \frac{j(j+1)}{2} \sin^2 \beta + \frac{m^2}{2} (3\cos^2 \beta - 1). \quad (9)$$

The equations derived can be used to solve the problem stated. Thus, for the first moment, we can readily determine a simple expression

$$\sum_{n'=0}^N (n' - n) \left[ d_{\frac{n'}{2}-n, \frac{n'}{2}-n'}^{(N/2)}(\beta) \right]^2 = (N - 2n) \sin^2 \frac{\beta}{2}. \quad (10)$$

Expression for the second moment is more complicated

$$\begin{aligned} &\sum_{n'=0}^N (n'^2 - n^2) \left[ d_{\frac{n'}{2}-n, \frac{n'}{2}-n'}^{(N/2)}(\beta) \right]^2 \\ &= (N + 4nN - 6n^2) \sin^2 \frac{\beta}{2} + [N(N-1) - 6n(N-n)] \sin^4 \frac{\beta}{2}. \end{aligned} \quad (11)$$

Based on these results, the average energy transferred per collision from Eq. (3) is of the form

$$\begin{aligned} \langle \Delta E_n \rangle &= \omega_e \left( \frac{\rho}{1+\rho} \right) (N - 2n) - 2x_e \omega_e \left( \frac{\rho}{1+\rho} \right) \\ &\times [(N-n)(2n+1) - n^2] - x_e \omega_e \left( \frac{\rho}{1+\rho} \right)^2 \\ &\times [N(N-1) - 6n(N-n)], \end{aligned} \quad (12)$$

where  $\sin^2 \beta/2$  is substituted by  $\rho/(1+\rho)$  according to the definition of the parameter  $\rho$ , which can be computed from the equations of motion for the group parameters in terms of forcing functions [20] (cf. [10]).

### 3. Results and discussion

Eq. (12) represents our central result. It is seen that the total energy transfer can be written as a sum of three contributions with a different order of magnitude. When  $\rho \ll 1$ , these contributions are of the order  $D_e \rho$ ,  $\omega_e \rho$  and  $D_e \rho^2$ , respectively. The nonlinear dependence on the vibrational quantum number  $n$  arises from the effect of vibrational anharmonicity. In the limit of vanishing anharmonicity ( $N \rightarrow \infty$ ) the parameter  $\rho$  goes to zero, whereas  $N\rho$  stays finite. In this limit, one can recast Eq. (1) to read [21]

$$\left[ d_{\frac{n'}{2}-n, \frac{n'}{2}-n'}^{(N/2)}(\beta) \right]^2 \approx J_{n'-n}^2 \left( 2 \left[ \frac{N\rho(n+n'+1)}{2} \right]^{1/2} \right), \quad (13)$$

where  $J_n$  is the ordinary Bessel function and  $\rho \approx \beta^2/4$ . The linearly perturbed harmonic-oscillator problem has been solved in the Bessel uniform approximation [22,23] and the transition probability is

$$P_{n \rightarrow n'} = J_{n'-n}^2 [2(\bar{\epsilon}\bar{n})^{1/2}], \quad (14)$$

where  $\bar{n}$  is the ‘mean’ quantum number,  $\epsilon$  the phase averaged classical energy (in units  $\omega_e$ ) transferred to the oscillator initially at rest. A direct comparison gives  $N\rho = \epsilon$  in the case of vanishing anharmonicity, hence,  $\langle \Delta E_n \rangle = \omega_e \epsilon$  as is obvious from Eq. (12) under these conditions. Numerous analytical approaches are available in the literature [14–18] for an understanding of the behavior of  $\epsilon$  as a function of the collision energy for an arbitrary ratio of masses.

Two important particular cases follow immediately from the general equation:

- (i) The oscillator is in the ground state before collision

$$\langle \Delta E_0 \rangle = \omega_e (1 - 2x_e) \frac{N\rho}{1+\rho} - x_e \omega_e N(N-1) \left( \frac{\rho}{1+\rho} \right)^2. \quad (15)$$

- (ii) The oscillator comes into collision in the state  $n = N$  (near the continuum)

$$\langle \Delta E_N \rangle = -\omega_e(1 - 2x_c N) \frac{N\rho}{1 + \rho} - x_c \omega_e N(N - 1) \left( \frac{\rho}{1 + \rho} \right)^2. \quad (16)$$

It is clear that the transferred energy  $\langle \Delta E_N \rangle$  (being negative) is of the order  $x_c \langle \Delta E_0 \rangle$ . Once again, we point out that transitions to the continuum were neglected in the algebraic model. Thus, in lower vibrational states, there is the positive change in energy per collision whereas the highly excited oscillator, on the average, only loses energy on every collision. The position of zero is given by the equation

$$n_{\text{zero}} = \frac{N}{3} \left( 1 + \frac{\rho}{4} \right) \left\{ 2 - \left[ \frac{1 + 2x_c + (1 - x_c)(1 + \rho/2)\rho/2}{(1 - x_c)(1 + \rho/4)^2} \right]^{1/2} \right\}. \quad (17)$$

For further  $n$ , the energy transfer reaches a negative maximum at

$$n_{\text{max}} = \frac{2N}{3} \left( 1 + \frac{\rho}{4} \right). \quad (18)$$

For small  $\rho$  the positions of zero and a maximum are actually independent of this parameter and are given as  $N/3$  and  $2N/3$ . This is a distinctive feature of energy transfer intrinsic to the Morse oscillator perturbed by external force.

Fig. 1 illustrates a characteristic behavior of the transferred energy as a function of the vibrational state using hydrogen molecule with  $\omega_e = 4401 \text{ cm}^{-1}$  and  $x_c \omega_e = 121 \text{ cm}^{-1}$  as an example. The value  $\rho = 0.019$  approximately represents the collisions  $\text{H}_2 + \text{He}$  at the total energy  $8\omega_e$  [24].

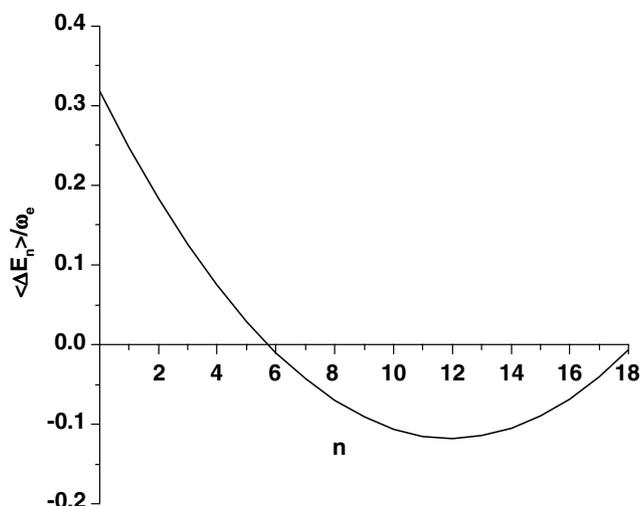


Fig. 1. The average vibrational energy transfer as a function of the initial vibrational quantum number.

Classical trajectory calculations have confirmed the existence of collisions that transfer unusually large amounts of energy ('supercollisions') [5–8]. For example, in the case of excited azulene colliding with Xe atoms [6], supercollision events are observed that are not connected with any particular range of impact parameters or initial kinetic energies but permanently involve the approach of the Xe atom toward a hydrogen atom which is compressed against the carbon backbone of azulene. This close approach then results in an impulsive kick from the azulene to the Xe atom accompanied a large amount of transferred energy. Let us assume that the Morse oscillator is deactivated by means of such impulsive supercollision events. These events leading to large amounts of transferred energy are characterized by large values of the parameter  $\rho$ . When  $\rho \gg 1$ , using Eq. (12) one obtains

$$\langle \Delta E_n \rangle = D_e(1 - x_c)^2 \left( 1 - \frac{2n}{N} \right) - \frac{\omega_e(1 - x_c)}{2\rho} \left( 1 + 4n - \frac{6n^2}{N} \right). \quad (19)$$

In this limiting case, the vibrational relaxation becomes highly efficient. Suffice it to say that when  $n = N$  (or 0); the energy lost (or gained) by the oscillator per collision is approximately equal to the dissociation energy. For these collisions,  $\langle \Delta E_n \rangle$  depends only slightly on the square of vibrational quantum number.

A comparison with classical trajectory calculations also indicates a limited applicability of the algebraic model. In particular, in this model, the energy transferred from the levels located near the dissociation limit is always negative (energy losses) whereas taking transitions to the continuum into account makes this value positive although not large [4]. As mentioned in [4], for  $n \approx N$ , about 80% of the trajectories lead to dissociation. However, the negative maximum position in the dependence of  $\langle \Delta E_n \rangle$  on  $n$  at  $2N/3$  is predicted by the model with much success because for these  $n$  no trajectories leading to dissociation were observed.

Thus, the algebraic model of a forced Morse oscillator provides a simple and instructive framework for the interpretation of the important trends in the numerical calculations of energy transfer from highly excited molecule states.

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