

A comparison of classical and quantum mechanical calculations of vibrational energy transfer. III. Use of the forced quantum oscillator and moment methods for quantization of product state distributions

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Vibrational transition probabilities calculated using the semiclassical forced quantum oscillator model and the information theoretic moment method were compared with exact quantal results in two model systems. In both cases the moment method was generally more accurate. Under conditions leading to a large distortion of the molecular force constant, the forced oscillator model was found to be in significant error. At low collision energies with two or three open states the moment method was inaccurate, and the forced oscillator model is preferred.

I. INTRODUCTION

Despite significant progress in quantum mechanical scattering calculations, classical trajectory analysis remains the most practical method for calculating reaction and relaxation rates in all but the simplest systems. A difficulty inherent in the classical method is the determination of state-to-state transition probabilities and cross sections. Since these are not classically defined observables, it is necessary to postulate a rule for quantizing the classical results. The most popular method is to round off the final values of the dynamical variables (e.g., internal energy or angular momentum) to the nearest quantum number. While this "binning" or histogram method works well for some reactive systems¹ and in rotationally inelastic nonreactive collisions,^{2,3} it can lead to large errors near classical thresholds where there may not be any real valued trajectories connecting the initial and final states,⁴ and near quantal thresholds where classical products may have less than zero-point internal energy.¹

A number of more accurate quantization methods have been described in the literature. Here we compare two of the most promising ones for quantization of nonreactive vibrational energy transfer. The first method is based on the semiclassical assumption that the translational motion can be uncoupled and solved classically to yield a time dependent potential. The motion of the oscillator driven by this potential can then be solved quantum mechanically. It is well known that a harmonic oscillator driven by a potential linear in the oscillator coordinate has an exact quantum mechanical solution.⁵⁻⁸ For this idealized system the motion of the center of the wave packet obeys the classical equations of motion, and the vibrational transition probabilities are given by a simple expression which depends only on the average classical energy transfer. Transition probabilities for an anharmonic oscillator driven by a nonlinear potential have been approximated by the same expression, using the classical energy transfer determined from a representative trajectory.⁹ Different choices of the representative trajectory have resulted in various versions of the method such as the "ITFITS" model of Heidrich, Wilson and Rapp,⁹ and the "DECENT" and "INDECENT" versions of Gentry and Giese.¹⁰⁻¹⁸

Recently Blais and Truhlar¹⁹ used a modification of the Gentry and Giese methods to calculate vibrational energy transfer of H₂ in Ar.

The second approach we have considered is the moment method of Procaccia and Levine^{20,21} and Truhlar and Duff.²² The underlying idea is that fewer than N independent pieces of information are required to describe a distribution of N transition probabilities. In particular, one or two moments (e.g., the average product energy and the average of the square of the energy) may suffice. The least biased distribution²³ satisfying these constraints is often in quantitative agreement with exact quantal calculations. The few lowest moments can be calculated accurately with classical mechanics, using fewer trajectories than needed for a histogram analysis. The moment method has been used by a number of investigators to calculate vibrational^{4,20,22,24-26} and rotational^{21,27,28} product distributions in both nonreactive and reactive²⁵⁻²⁷ collisions.

In this paper we compare the forced oscillator and moment methods with several exact quantal calculations. In previous studies the forced oscillator model was compared with experimental data¹⁰⁻¹² and exact computations.^{13,16,17} The agreement was generally good; however there was some indication in the latter studies that at high energies, where nonlinearity of the potential may be important, the model may be less accurate. Little effort has been made, however, to explore this possible breakdown of the model. The moment method, on the other hand, can fail at low collision energies. For example, a classical harmonic oscillator having an initial vibrational energy of $\frac{1}{2}\hbar\omega$ may lose energy on the average.¹⁸ At higher energies the classical moments are more accurate and yield good results for the classically allowed, and some of the classically forbidden transitions.^{4,22}

In the present study we consider two model systems. First we examine the collinear collision of an atom and a harmonic oscillator, subject to a Lennard-Jones potential. The same system was considered previously by Gentry and Giese¹³; here however we have considerably extended the range of the calculations. The second system is the collision of He + H₂($v=1$) with the *ab initio*

interaction potential of Gordon and Secrest.²⁸ Duff and Truhlar¹⁷ used a number of analytical fits of the Gordon-Secrest surface to compare the forced oscillator predictions with the exact calculations of Alexander and Berard.³⁰ Generally good agreement was obtained. Here we report the moment calculations for the same surfaces and initial conditions.

II. THEORETICAL BACKGROUND

Kerner⁶ and Bartlett and Moyal⁵ showed that for a harmonic oscillator driven by a force $F(t)$, the probability for a transition from state m to state n at time t is given by

$$P_{mn} = m!n! e^{-\epsilon} \epsilon^{m+n} S_{mn}^2, \quad (1)$$

where

$$S_{mn} = \sum_{j=0}^{\min(m,n)} (-1)^j \epsilon^{-j} [(n-j)!j!(m-j)!]^{-1} \quad (2)$$

and $\epsilon \hbar \omega$ is the phase averaged energy absorbed by the classical oscillator at time t . For $m=0$, P_{0n} is simply a Poisson distribution,

$$P_{0n} = \frac{1}{n!} e^{-\epsilon} \epsilon^n. \quad (3)$$

For this system the average classical energy transfer is given by $|f(\omega)|^2 / 2\mu$, where $f(\omega)$ is the Fourier transform of $F(t)$ and μ is the reduced mass of the oscillator. Since $f(\omega)$ is independent of the initial energy of the oscillator, ϵ can be calculated from a single trajectory with the oscillator initially at rest and at equilibrium.

For collisions with anharmonic oscillators and nonlinear potentials, Eq. (1) is inexact, but is assumed to be a reasonable approximation. A further complication arises from the fact that ϵ is no longer independent of the oscillator energy. The procedure which has generally been used is to calculate ϵ from a single representative trajectory, with the oscillator still initially at rest and at equilibrium. An average initial translational energy is chosen so as to satisfy microscopic reversibility. Of the various methods used to obtain ϵ , the INDECENT model of Gentry and Giese¹³ appears to be the most suitable. In this treatment the full potential is used to calculate the trajectory, with the initial translational energy chosen to be some average of the initial and final quantum mechanical translational energies. Here we have chosen the initial velocity v_0 to be the arithmetic average,

$$v_0 = \frac{1}{2}(v_m + v_n), \quad (4)$$

where v_m and v_n are related to the total energy, E_{tot} , by

$$E_{\text{tot}} = \frac{1}{2}\mu v_m^2 + E_m = \frac{1}{2}\mu v_n^2 + E_n, \quad (5)$$

and E_m and E_n are the initial and final quantal energies of the oscillator in states m and n . The resulting value of ϵ is then inserted into Eq. (1) to obtain P_{mn} .

The moments of the energy transfer are given by the expressions

$$\langle \Delta E \rangle = \sum_{j=0}^N P_{mj}(E_j - E_m) \quad (6)$$

$$\langle \Delta E^2 \rangle = \sum_{j=0}^N P_{mj}(E_j - E_m)^2, \text{ etc.}, \quad (7)$$

where $N+1$ is the number of open vibrational states. If N moments are known exactly, these equations can be inverted to yield N transition probabilities. In practice, even very small errors in the moments render the method useless for $N > 2$ or 3. Nevertheless, a plot of P_{mn} vs n usually reveals that fewer than N parameters are needed to fit P_{mn} with tolerable accuracy. Indeed, as few as two independent pieces of information may suffice to describe P_{mn} at any given E_{tot} . A reasonable approximation of P_{mn} is the least biased distribution subject to the constraints that $\langle \Delta E \rangle$ and $\langle \Delta E^2 \rangle$ equal the exact classical values. This distribution is obtained by maximizing the entropy $-\sum_j P_{mj} \ln P_{mj}$, subject to the constraints of Eqs. (6) and (7). The result, using the method of Lagrangian multipliers,³¹ is

$$P_m = \exp\{\lambda_0 + \lambda_1(E_n - E_m) + \lambda_2(E_n - E_m)^2\}. \quad (8)$$

In Eq. (8), λ_0 is a normalization constant, and λ_1 and λ_2 are chosen such that Eq. (8) satisfies Eqs. (6) and (7).

While Eq. (8) is readily generalized to more than two moments, there are two reasons why this was not done. First, the higher classical moments do not correspond as well with the quantal ones at moderate energies. The advantage of a third constraint are more than offset by the inaccuracy of the constraint. Second, even if the moments are exact, numerical inversion of Eqs. (6)–(8) is often difficult to accomplish for $N > 2$.

The classical trajectories used to determine ϵ , $\langle \Delta E \rangle$, and $\langle \Delta E^2 \rangle$ were integrated by standard methods. For the forced oscillator method, one trajectory was computed for each transition probability. The moments of the energy transfer were calculated by averaging over the initial phase of the oscillator having internal energy E_m . (The final internal energy is generally a sinusoidal function of the initial phase.^{4,24}) Using the moment method a minimum of four and a maximum eight trajectories were needed to obtain the entire P_{mn} distribution at each collision energy. Close coupled quantum mechanical calculations for collisions with a harmonic oscillator were carried out using a program written by A. Wagner.³²

III. RESULTS

In our first test we calculated the collinear transition probabilities for collisions of an atom and a harmonic oscillator ($A+BC$) with a Lennard-Jones interaction potential. The dimensionless mass parameter,

$$m = m_A m_C / m_B m_{\text{tot}} \quad (9)$$

was 0.5; the Lennard-Jones distance parameter was 46.71 times half the zero point vibrational amplitude, and the well-depth was $5.707 \times 10^{-3} \hbar \omega$. This model system was first studied quantum mechanically by Gutschick *et al.*,³³ and later semiclassically by Gentry and Giese (Table VIII of Ref. 13). Gentry and Giese considered in their work total energies of up to $6.2 \hbar \omega$. At the highest collision energies the agreement between the semiclassical and exact results was poorer than at lower energies. To see if the trend persisted we doubled the

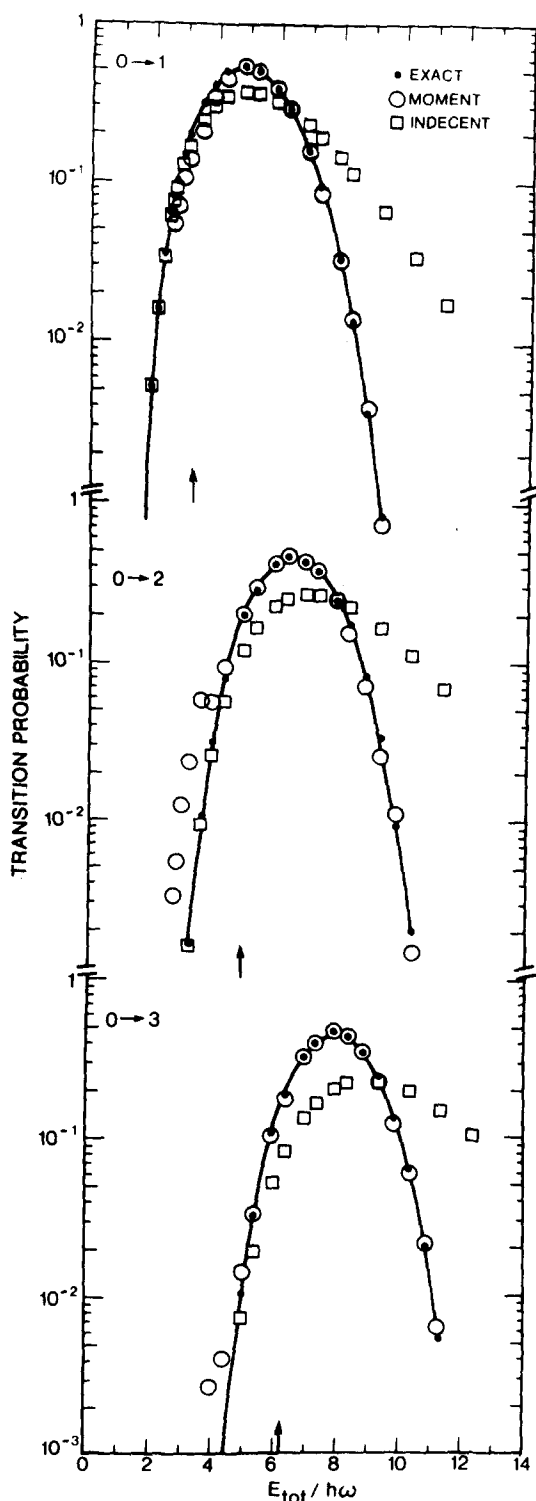


FIG. 1. Transition probabilities for collinear collisions of an atom and a harmonic oscillator with a Lennard-Jones potential, as a function of total energy. Reduced collision parameters are $m=0.5$, $\sigma=46.71$, and $\epsilon=0.005707$. Filled circles and solid curves are exact quantal calculations. Squares are forced oscillator calculations. Open circles were obtained with the moment method using two moments for $E_{\text{tot}} > 3.5 \hbar\omega$ and one moment for $E_{\text{tot}} < 3.5 \hbar\omega$.

energy range. The results, shown in Fig. 1, indicate that at high energies the forced oscillator method can be as much as two orders of magnitude too large. The moment method, on the other hand, is in excellent agree-

ment for all classically allowed transitions. Our experience is that N must exceed the number of constraints. Thus for $N \geq 3$ we used two moments, while for $N=2$ we used only one moment. In Fig. 1 acceptable agreement was obtained for the first forbidden transition only for $N \geq 3$.

Further calculations showed that the transition probabilities are a sensitive function of the reduced mass parameter (i.e., of the skew angle of the potential energy surface). In Fig. 2 P_{01} is plotted against m for $E_{\text{tot}} = 8.2 \hbar\omega$. The exact P_{01} has a strong minimum near $m=0.4$. The moment approximation faithfully reproduces this effect, while the forced oscillator prediction is an order of magnitude too large. For $m \geq 0.8$ both models are fairly accurate, but at still higher values of m the forced oscillator calculations are consistently too low. We note that multiple collisions did not occur in these calculations, even for large values of m .

One might expect that the errors in the forced oscillator model would diminish in three dimensions. To test this we treated the oscillator as a breathing sphere and calculated the transition probability as a function of the orbital angular momentum l . The total cross sections for various mass ratios at a total energy of $8.2 \hbar\omega$ are listed in Table I. We found that at large l the forced oscillator probabilities are smaller than the exact values. At $m=0.4$ cancellation of errors at small and large l (see Fig. 3) brings the semiclassical and quantal cross sections into close agreement. At larger values of m errors do not cancel, and the forced oscillator cross section is consistently too small.

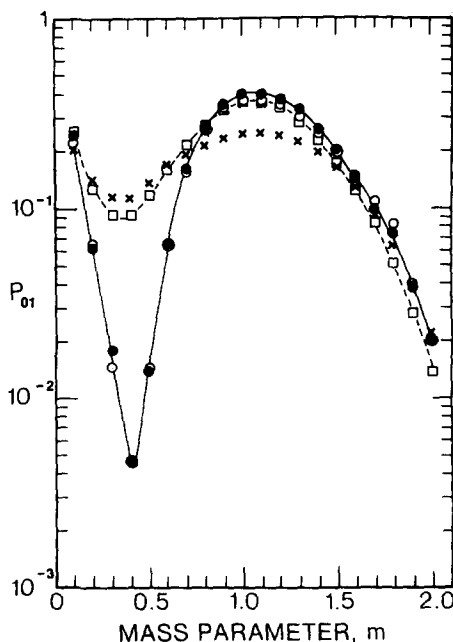


FIG. 2. Transition probabilities for collinear collisions of an atom with a harmonic oscillator with a Lennard-Jones potential, as a function of the mass parameter, m . Reduced collision parameters are $E_{\text{tot}} = 8.2$, $\sigma = 46.71$, and $\epsilon = 0.005707$. Filled circles and solid curve are exact quantal calculations. Squares and dashed curve are forced oscillator calculations. The crosses and open circles were obtained with the moment method, using one and two moments, respectively.

TABLE I. Total cross sections σ_{0l} for a breathing sphere Lennard-Jones potential.^a

m	Total cross section ^b			
	Exact	INDECENT	One moment	Two moment
0.1	0.112	0.099	0.073	0.094
0.4	0.375	0.342	0.256	0.332
1.5	0.449	0.327	0.370	0.403
2.0	0.092	0.075	0.093	0.092

^aReduced parameters: $E_{\text{tot}} = 8.2$, $\sigma = 46.71$, $\epsilon = 0.005707$.

^bIn units of σ^2 .

The second system we studied was $\text{He} + \text{H}_2(v=1)$ at a total energy of 0.14 hartree or $6.98 \hbar\omega_e$. H_2 was treated as a Morse oscillator ($N=9$), and the various numerical fits to the Gordon-Secrest potential²⁹ described by Alexander and Berard³⁰ were used. A zero impact parameter was assumed, and the orientation angle of the oscillator θ was held constant in the fixed-nuclei approximation.³⁴ The results for surfaces GS and AB-4 are displayed in Tables II and III. The INDECENT results are quoted from Ref. 17. As is evident from columns 3-5 in these tables, both methods are in fair agreement with the exact results for P_{10} and P_{12} . However, in nearly every case the moment method is more accurate. (The average error in these tables is 17% for the moment

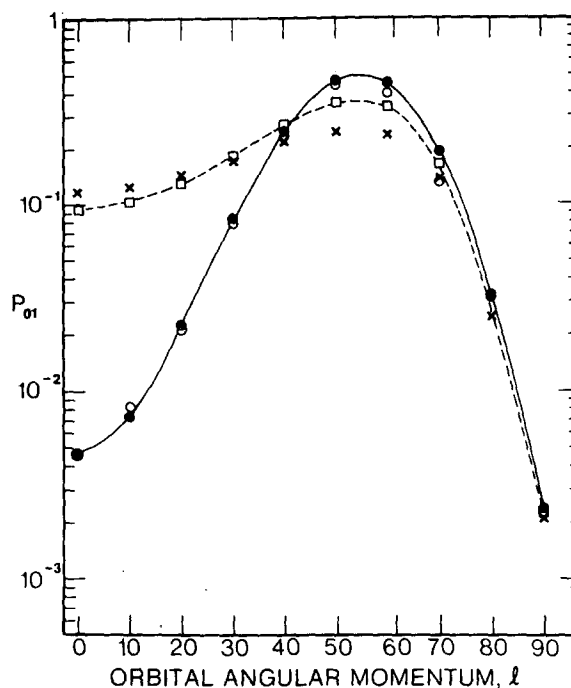


FIG. 3. Opacity function for collision of an atom and a harmonic breathing sphere with a Lennard-Jones potential. The reduced mass parameter is $m=0.4$. Collision parameters and symbols are the same as in Fig. 2.

TABLE II. Calculated transition probabilities for the GS potential energy surface.

Theta (degrees)	Transition	Exact	INDECENT	Classical moments	Quantum moments	Mixed	n_{max}
0	10	3.74-2 ^a	3.06-2	4.24-2	3.86-2		
	12	4.99-2	3.21-2	5.46-2	5.02-2		
	13	5.90-4	1.91-4	2.61-5	1.86-5	1.48-3	1.45
20	10	3.75-2	2.96-2	4.17-2	3.87-2		
	12	5.04-2	3.13-2	5.51-2	5.07-2		
	13	6.02-4	1.81-4	2.64-5	1.92-5	1.49-3	1.45
45	10	2.51-2	1.94-2	2.85-2	2.58-2		
	12	3.77-2	2.10-2	4.13-2	3.79-2		
	13	3.77-4	8.29-5	7.93-6	5.60-6	7.79-4	1.38
57	10	1.29-2	9.24-3	1.35-2	1.31-2		
	12	1.89-2	1.03-2	2.05-2	1.90-2		
	13	1.01-4	2.01-5	5.34-7	4.17-7	1.83-4	1.27
68	10	1.91-3	1.69-3	2.16-3	1.92-3		
	12	2.66-3	2.01-3	2.95-3	2.66-3		
	13	2.44-6	8.09-7	4.57-10	3.09-10	3.91-6	1.10
70	10	9.32-4	9.32-4	1.09-3	9.34-4		
	12	1.14-3	1.16-3	1.31-3	1.14-3		
	13	1.14-6	2.75-7	2.61-11	1.55-11	8.28-7	1.07
75	10	2.01-6	3.05-5	(2.72-6) ^b	5.51-6		
	12	1.14-4	6.62-5	(2.31-4)	1.15-4		
	13	1.81-6	1.32-9	(1.34-14)	3.34-16	1.30-8	1.01
80	10	8.36-4	2.34-4	6.75-4	8.50-4		
	12	2.48-3	1.81-4	2.16-3	2.48-3		
	13	6.57-6	4.18-9	7.13-11	1.29-10	1.49-6	1.08
90	10	2.90-3	1.16-3	2.63-3	2.96-3		
	12	7.36-3	1.08-3	6.85-3	7.38-3		
	13	3.30-5	1.85-7	5.84-9	7.97-9	1.61-5	1.14

^a3.74-2 means 3.74×10^{-2} .

^bValues in parentheses were calculated at 75.9° because the moment equations were unstable at 75.0° .

TABLE III. Calculated transition probabilities for potential energy surface AB-4.

Theta (degrees)	Transition	Exact	INDECENT	Classical moments
0	10	3.65-2	2.73-2	4.34-2
	12	5.46-2	2.81-2	6.35-2
	13	8.65-4	1.41-4	4.20-5
70	10	2.48-2	1.80-2	2.80-2
	12	3.89-2	1.93-2	4.30-2
	13	4.55-4	6.93-5	8.75-6
90	10	1.96-2	1.41-2	2.18-2
	12	3.09-2	1.53-2	3.39-2
	13	2.90-4	4.33-5	3.49-6

method and 192% for the forced oscillator calculation.) For P_{13} both methods are poor, with the moment method considerably worse. As shown in the last column of Table II, all the transitions are classically forbidden. (n_{\max} here is the maximum classical value of the final quantum number.) It is our experience that the first classically forbidden transition (here P_{10} or P_{12}) is predicted reliably by the moment method, while more strongly forbidden transitions are predicted much more poorly.

In order to determine whether the failure of the moment method for P_{13} was due to the inaccuracy of the classical moments or to the inadequacy of only two constraints, we recalculated P_{1n} using the exact first and second quantum mechanical moments. As seen in column 6 of Table II, the "synthesized" values of P_{10} and P_{12} are in excellent agreement with the exact ones, while P_{13} is still very poor. When three moments were used (even exact quantal moments), the Lagrangian equations could not be solved.

An improved value of P_{13} can be obtained by combining the two methods. P_{10} and P_{12} were first computed by the two moment method. Equation (1) was then least squares fitted to these values, treating ϵ as a free parameter. The fitted values of P_{10} and P_{12} generally were within 20% of the moment values. The effective ϵ was then used to predict P_{13} from Eq. (1). The result, labelled "Mixed" in Table II, is generally closer to the exact result than either the INDECENT or moment predictions.

IV. DISCUSSION

Our application of the moment method differs in a number of ways from the information theoretic calculations of Levine, Bernstein, and co-workers. In the vast majority of cases linear surprisals for cross sections and rate constants have been reported, indicating that a single moment should suffice. (One exception is Ref. 26.) On the other hand, we have found that for collinear transition probabilities,³⁵ and for the opacity function $P_{mn}(b)$ evaluated at impact parameter b , two moments are required. For comparison the single moment results are indicated by the crosses in Figs. 2 and 3. Because of a cancellation of errors at different values of b , the single moment cross sections are in reasonable agreement with exact calculations (see Table I); how-

ever, the use of two moments always led to more accurate results. It is interesting to note that the single moment transition probabilities (Fig. 2) and opacity function (Fig. 3) are very similar to the forced oscillator results. This is not unreasonable since the forced oscillator model uses only a single moment for its "input."

In the surprisal synthesis of Procaccia and Levine^{24,21} the conditional probability $P(n|m)$ is defined as

$$P(n|m) = \sigma_{mn} / \sigma_m, \quad (9)$$

where σ_{mn} is the state-to-state cross section, and σ_n is the total cross section out of initial state m . $P(n|m)$ is obtained from solution of the Lagrangian equations. In order to obtain the absolute magnitude of σ_{mn} , σ_m must be determined separately (e.g., from the trajectory calculations). In our approach the opacity function $P_{mn}(b)$ is obtained from solution of the Lagrangian equations [Eq. (8)] at different values of b , and then integrated over b (or l) to obtain σ_{mn} directly.

Another difference is that Levine and co-workers use the absolute value of the energy transfer to calculate the first moment, while we (and Truhlar and Duff²²) use the energy transfer itself. Chapman and Green²⁸ found the latter method more accurate; however, because of the inadequacy of the moment method in their calculations, this point should be checked further.

In a more general treatment²³ P_{mn} is compared to a prior distribution, P_{mn}^0 , leading to the result

$$P_{mn} = P_{mn}^0 \exp\{\lambda_0 + \lambda_1(E_n - E_m) + \lambda_2(E_n - E_m)^2\}. \quad (10)$$

The prior may be an unbiased distribution (e.g., proportional to the product density of translational states), or it can be a "sophisticated" prior incorporating dynamical information. For example, the prior could be the forced oscillator distribution [Eq. (1)]. In Eq. (8) we have used a constant prior, $P_{mn}^0 = 1/N$. We found, however, that all three priors lead to virtually identical results. This is in agreement with the finding of Halavee and Levine.²⁶

Previous tests of the forced quantum oscillator model found it to be in excellent agreement with exact results. We have found here, however, that under some circumstances the model may be in error by more than an order of magnitude. The source of this error is readily traced to nonlinearity in the potential near the turning point of the collision. A useful measure of this nonlinearity is the effective force constant $k(t)$ (i.e., the second derivative of the potential with respect to the oscillator coordinate). It has been shown that the distortion in k produced by a Lennard-Jones intermolecular potential is considerably larger than for a repulsive exponential potential.³⁶ As expected, the maximum value k_m of the effective force constant increases with collision energy and decreases with orbital angular momentum. Defining $k=1$ for an unperturbed harmonic oscillator, we find in Figs. 1 and 3 that the forced oscillator model is inaccurate for $k \gtrsim 1.5$. In Fig. 2, k_m varies from 2.27 at $m=0.1$ to 1.74 at $m=2.0$. In contrast, for a repulsive exponential potential with $m=0.5$, $E_{\text{tot}}=8.2$, and $\alpha=0.29$, during a $0 \rightarrow 1$ transition k_m has a value of only

1.11. Thus, by monitoring $k(t)$ along the trajectory it should be possible to anticipate the accuracy of the model.

As compared with the forced oscillator model, the moment method is much less sensitive to details of the potential energy surface. The method is limited, however, to classically allowed and the first forbidden (either upwards or downwards) transitions. Also, at low energies with only two or three open states, the moment method is unreliable, and the forced oscillator model is preferred. While the usefulness of information theory appears to be quite general, additional tests, particularly in three dimensions, are required before it can be routinely used as part of a quasiclassical trajectory analysis.

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