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# Stochastic theory of vibrational energy transfer in collinear atom–diatom collisions: the role of non-markovian effects

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The role of non-markovian effects in the stochastic treatment of vibrational–translational energy transfer in collinear atom–diatom collisions is examined. A comparison of transition probabilities using both markovian and non-markovian types of master equations, as well as exact time dependent quantum mechanics, is made for various values of the system parameters $m$ and $\alpha$. We find that for certain ranges of the system parameters, the deviations between markovian and non-markovian theories are substantial. Only in the perturbation theory limit and in the limit of low $m/\alpha^2$ values and high enough initial translational energies such that an impulsive approximation for translational motion is accurate are the markovian and non-markovian results similar. An analysis of the collision dynamics indicates that the markovian and non-markovian probabilities agree with each other and with the exact probabilities when action-angle correlations are weak while none of these theories agree (except by accident) when such effects are strong.

## 1. INTRODUCTION

In a recent series of papers [1–6], stochastic models have been developed to deal with problems of interest in molecular collision theory. The various treatments adopted in these papers are based upon quite different starting points. Augustin and Rabitz [1, 2, 5] used phase interference arguments to develop a Pauli-type master equation while Schatz [3] applied a generalized cumulant expansion to obtain an analogous equation but with different time dependent rate coefficients. Both of these master equations inherently assume that the system obeys a markov process, although the details of how this assumption enters and the consequences of it are not always transparent in the equations obtained. In this respect, a more general starting point for developing master equations in collision problems was adopted by Schatz, McLafferty and Ross [4] through the use of the projection operator approach of Zwanzig [7]. In this application a non-markovian master equation similar in form to master equations obtained earlier in a number of investigations in other fields [7–10] was obtained. While the Zwanzig approach enables a more versatile treatment of memory effects in the collision dynamics, the additional difficulty associated with solving a non-markovian master equation makes it desirable to use the corresponding markovian equation whenever that equation represents a satisfactory approximation to the problem. Thus it is important to assess under what conditions it is appropriate to approximate the non-markovian master equation by its markovian counterpart. Here, we examine this point for the restricted problem of vibrational energy transfer associated with the collinear collision of an atom with a diatomic molecule. For this

model, we are able to obtain a fairly simple expression determining the first-order non-markovian correction to the markovian transition probabilities, and we are also able to solve numerically the non-markovian master equation exactly. By comparisons of these results with the results of exact solutions to the Schrödinger equation, we are able to infer when the stochastic models that have been developed within the framework of either the Pauli or Zwanzig formalism present accurate descriptions of the dynamics of this problem.

## 2. Master equations

In the following treatment of vibrational energy transfer we adopt the well established model in which the diatomic molecule BC is treated as a harmonic oscillator, and an exponential interaction potential between atom A and the molecule is assumed. The problem is described by the hamiltonian [6]

$$H=\frac{p^2}{2m}+\tfrac{1}{2}(P^2+Q^2)+\varepsilon_0 \exp(-\alpha q)(1+\alpha Q), \tag{1}$$

where the condition $\alpha Q \ll 1$ has been assumed, and energies have been expressed in units of $\hbar\omega$, with $\omega$ denoting the oscillator frequency. $P$ and $Q$ are scaled vibrational momentum and coordinate variables; $p$, $q$ are scaled translational momentum and coordinate variables, and the parameters $m$, $\alpha$ and $\varepsilon_0$ are defined as

$$\varepsilon_0=\frac{(\frac{1}{2}\tilde{m}v_0{}^2)}{\hbar\omega}=\frac{1}{2}\frac{m_A(m_B+m_C)}{(m_A+m_B+m_C)}\frac{v_0{}^2}{\hbar\omega}, \tag{2}$$

$$m=\frac{m_A m_C}{m_B(m_A+m_B+m_C)}, \tag{3}$$

$$\alpha=\frac{\gamma}{L}\left(\frac{\hbar}{\mu_{BC}\omega}\right)^{1/2}. \tag{4}$$

$v_0$ is the initial translational velocity of atom A with respect to atom B, $L$ is the steepness parameter of the interaction potential, $\mu_{BC}$ is the reduced mass of the molecule BC, $\gamma=m_C/(m_B+m_C)$, where $m_i$ denotes masses of the appropriate atoms, and $\varepsilon_0$ is the initial translational energy in units of $\hbar\omega$. Refinements as to the correct choice of energy factor $\varepsilon_0$ and mass factor $m$ are discussed elsewhere [6, 11, 12].

In the following development, we adopt the usual impulsive approximation for translational motion in which the hamiltonian is partitioned as

$$H=H_V{}^{(0)}+H_T{}^{(0)}+H^{(1)}, \tag{5}$$

where

$$H_V{}^{(0)}=\tfrac{1}{2}(P^2+Q^2), \tag{6}$$

$$H_T{}^{(0)}=p^2/2m+\varepsilon_0 \exp(-\alpha q), \tag{7}$$

$$H^{(1)}=\varepsilon_0\alpha Q \exp(-\alpha q) \tag{8}$$

and the classical equations of motion generated from $H_T{}^{(0)}$ are solved to provide a time dependent perturbation $H^{(1)}(t)$ (with $q(t)$ substituted) on the oscillator

whose hamiltonian is $H_V^{(0)}$. This is equivalent to neglecting translational-vibrational correlations, as discussed in detail elsewhere [4].

To develop a master equation to approximate the time dependent Schrödinger equation for vibration which results from the impulsive treatment of translation, we first consider the equation of motion of the reduced density matrix for vibration $\rho_V(t)$. This is given by [13] (on the neglect of translational-vibrational correlations)

$$i\frac{\partial\rho_V(t)}{\partial t}=L(t)\rho_V(t), \tag{9}$$

where $L(t)$ is the liouvillian appropriate for the vibrational degree of freedom [4]

$$L(t)=L_V^{(0)}+L^{(1)}(t). \tag{10}$$

$L_V^{(0)}$ and $L^{(1)}(t)$ are defined by

$$L_V^{(0)}\rho_V(t)=[H_V^{(0)},\ \rho_V(t)], \tag{11}$$

$$L^{(1)}(t)\rho_V(t)=[\ \mathscr{X}^{(1)},\ \rho_V(t)], \tag{12}$$

where

$$\mathscr{X}^{(1)}=\langle H^{(1)}\rangle_T=\varepsilon_0\alpha Q\langle\exp(-\alpha q)\rangle_T. \tag{13}$$

The angular bracket $\langle\rangle_T$ denotes a quantum ensemble average, which is replaced by a classical average as in reference [4].

We are now interested in the diagonal elements of $\rho_V(t)$. If we denote by $D$ the operator that projects out the diagonal part of $\rho_V(t)$, which we denote with a subscript d, then it is easily shown [9] that $\rho_{V_d}$ exactly satisfies

$$i\frac{\partial\rho_{V_d}(t)}{\partial t}=DL(t)\rho_{V_d}(t)$$

$$-iDL(t)\int_{t_0}^{t}dt'\,T\exp\left[-i\int_{t'}^{t}(1-D)L(s)ds\right](1-D)L(t')\rho_{V_d}(t'), \tag{14}$$

where $T$ is the time ordering operator, and the limit $t_0\to-\infty$ is to be taken.

In the number representation of the harmonic oscillator

$$\langle n|\rho_V(t)|n\rangle=P_n(t) \tag{15}$$

and equation (14) simplifies according to the procedure of Zwanzig [7] to yield

$$\frac{\partial P_n(t)}{\partial t}=-2\sum_{n'}\int_{-\infty}^{t}dt'\cos[\omega_{nn'}(t-t')]\,\mathscr{X}_{nn'}^{(1)}(t)\,\mathscr{X}_{n'n}^{(1)}(t')\{P_n(t')-P_{n'}(t')\}, \tag{16}$$

where

$$\mathscr{X}_{nn'}^{(1)}(t)=\langle n|\ \mathscr{X}^{(1)}(t)|n'\rangle, \tag{17}$$

$$\omega_{nn'}=(E_n-E_{n'})/\hbar \tag{18}$$

and $E_n$ is the energy of the $n$th oscillator state. Equation (16) is the generalized non-markovian master equation from which the various vibrational transition probabilities may be determined. Note that although it is non-markovian, it does not provide an exact description of the dynamics. This is because a Born series expansion of the memory kernel in (14) has been truncated in lowest order in obtaining it [7].

Master equations are classified as non-markovian or markovian according to whether or not a time integration over the appropriate variable is, or is not involved. Although this is the usual interpretation, it may in fact be an improper classification, as Oppenheim and Shuler [14] have pointed out. Nevertheless, we shall retain common usage and refer to equation (16) as non-markovian.

The major step in simplifying equation (16) is to assume markovian behaviour, i.e., the kernel of equation (16) is simplified by writing

$$[P_n(t') - P_{n'}(t')] \sim [P_n(t) - P_{n'}(t)]. \tag{19}$$

The resulting markovian master equation forms the basis of the stochastic method for energy transfer calculations that was employed by Schatz *et al.* [4].

## 3. Non-markovian solution

In this section we consider the direct solution of the non-markovian master equation (16). A partially analytical expression for the transition probabilities $P_{non}(t)$ (i.e., the solution to (16) satisfying $P_n(-\infty) = \delta_{nn_0}$) can be obtained by substituting the expression

$$P_{non}(t) = \int_0^\infty \exp(-x) L_{n_0}(x) L_n(x) h(x, t) dx \tag{20}$$

(where $L_n$ denotes a Laguerre polynomial) into (16). After evaluating the matrix elements in (17) and using the recursion relations for Laguerre polynomials, we obtain the following integrodifferential equation for $h(x, t)$:

$$\frac{\partial h(x, t)}{\partial t} = -x \int_{-\infty}^{t} dt' \cos(t - t') F(t) F(t') h(x, t'), \tag{21}$$

where

$$F(t) = \alpha\varepsilon_0 \exp(-\alpha q(t)) = \alpha\varepsilon_0 \operatorname{sech}^2\left[\alpha t \sqrt{\left(\frac{\varepsilon_0}{2m}\right)}\right] \tag{22}$$

and the boundary condition on $h$ is $h(x, t = -\infty) = 1$. Note that the time variable $t$ in (21, 22) is really a dimensionless (scaled) quantity and is related to the physically meaningful time by $t(\text{physical}) = t(\text{dimensionless})/\omega$.

Although we have been unable to solve equation (21) analytically, it can be solved numerically by re-expressing it as a set of three coupled ordinary differential equations (see Shugard *et al.* [15]). The resulting transition probabilities will be labelled as the total non-markovian (TNM) results.

An approximate but nearly analytical solution to (21) can be obtained if we assume that deviations from markovian behaviour are not too large. We amplify on this statement later and indicate how the following treatment is altered when this assumption does not hold. The approximation involves expanding $P_n(t')$ in (16) in a Taylor series

$$P_n(t') = P_n(t) + (t' - t) \frac{\partial P_n(t)}{\partial t} + \cdots \tag{23}$$

and truncating at the second term. Substituting equation (20) into (23) gives an approximation to equation (21) of the form

$$\frac{\partial h}{\partial t} = -xD(t)h(x, t) - xB(t)\frac{\partial h}{\partial t}, \tag{24}$$

where

$$D(t) = \int_{-\infty}^{t} \cos(t-t')F(t)F(t')dt', \tag{25}$$

$$B(t) = \int_{-\infty}^{t} \cos(t-t')(t-t')F(t)F(t')dt'. \tag{26}$$

The solution to (24) is simply

$$h(x, t) = \exp\left(-x\int_{-\infty}^{t}\frac{D(t')dt'}{1-xB(t')}\right). \tag{27}$$

Expanding the term $[1-xB(t')]^{-1}$ in a power series and taking the limit $t\to\infty$ in $h(x, t)$, we obtain from equation (20) $P_{n0n}(\infty)$, which we abbreviate to $P_{n0n}$, in the form

$$P_{n0n} = \int_{0}^{\infty} L_{n_0}(x)L_n(x)\exp[-x(1+\eta)]\exp(-\zeta x^2)dx, \tag{28}$$

where

$$\eta(t) = \int_{-\infty}^{t} D(t')dt', \tag{29}$$

$$\eta = \eta(\infty) = (2\pi^2m^2/\alpha^2)\,\mathrm{csch}^2\left[\frac{\pi}{\alpha}\left(\frac{m}{2\varepsilon_0}\right)^{1/2}\right] \tag{30}$$

and

$$\zeta = \int_{-\infty}^{\infty} D(t)B(t)dt. \tag{31}$$

In approximating equations (20) and (27) by equation (28), we have assumed that the series expansion of $[1-xB(t')]^{-1}$ can be truncated at the second term, which is valid when $\zeta \gg \int_{-\infty}^{\infty} D(t)B^2(t)dt$ (and $B(t) \ll 1$), and this will be satisfied when deviations from markovian behaviour are small. It is also to be noted that the assumption of small deviation from markovian behaviour implies that $\zeta \ll 1$. The parameter $\eta$ represents the approximate average energy transfer (in units of $\hbar\omega$). Unfortunately, a simple analytic solution of the integral appearing in equation (31) is not possible. However, equation (28) can be evaluated to yield

$$\begin{aligned} P_{n0n} &= n_0!n!\sum_{k=0}^{n_0}\sum_{l=0}^{n}\frac{(-1)^{k+l}\int_0^{\infty}x^{k+l}\exp[-x(1+\eta)-\zeta x^2]dx}{[k!l!]^2(n_0-k)!(n-l)!}, \\ &= n_0!n!\exp\left[\frac{(1+\eta)^2}{8\zeta}\right]\sum_{k=0}^{n_0}\sum_{l=0}^{n}\frac{(-1)^{k+l}(2\zeta)^{-(k+l+1)/2}}{[k!l!]^2(n_0-k)!(n-l)!} \\ &\qquad \Gamma(k+l+1)D_{-(k+l+1)}\left[\frac{1+\eta}{\sqrt{(2\zeta)}}\right], \end{aligned} \tag{32}$$

where $D_n(x)$ are the parabolic cylinder functions. For the present study, the first form of equation (32) was evaluated numerically. The limit $\zeta \to 0$ in equation (32) yields the markov result

$$P_{n_0 n} = \frac{n_0! n! \eta^{n+n_0}}{(1+\eta)^{n+n_0+1}} \sum_{k=0}^{\min(n,\, n_0)} \frac{\eta^{-2k}}{(n_0-k)!(n-k)![k!]^2}. \tag{33}$$

The corresponding result of exact semi-classical theory (obtained by exactly solving the time dependent Schrödinger equation) is given by [16].

$$P_{n_0 n} = n_0! n! \exp(-\eta) \eta^{n_0+n} \left| \sum_{k=0}^{\min(n,\, n_0)} \frac{(-1)^k \eta^{-k}}{(n_0-k)!(n-k)!k!} \right|^2. \tag{34}$$

## 4. Results

In this section, we compare transition probabilities obtained from the exact expression (34), the first-order non-markovian (FONM) expression (32), the markovian expression (33) and the total non-markovian (TNM) expression (equation (20) coupled with the solution to equation (21)). Potential and mass parameters used in determining transition probabilities were chosen to simulate the systems: $H+I_2$, $H+H_2$, and He+HBr. The oscillator frequencies employed were those given by Herzberg [17]. The steepness parameter $L$ was kept constant for all systems; the frequently employed value $L = 0{\cdot}2$ Å [18] was chosen. The $m$ and $\alpha$ values for the systems are: $H+I_2$, $m = 3{\cdot}92 \times 10^{-3}$, $\alpha = 0{\cdot}124$; $H+H_2$, $m = \frac{1}{3}$, $\alpha = 0{\cdot}310$, He+HBr, $m = 3{\cdot}76$, $\alpha = 0{\cdot}561$. In solving for the TNM probabilities using equation (21), convergence of the result was ascertained both by verifying the result proved in reference [4] that the first moment of the final state distribution should equal the exact first moment, and by showing equivalence of TNM and exact transition probabilities in certain limits as described later.

We first consider the $H+I_2$ system for which the mass factor $m$ is very small. In table 1, we compare the transition probabilities $P_{00}$ and $P_{11}$ at low $\varepsilon_0$ (in units of $\hbar\omega$) for the TNM, FONM, markovian, and exact theories. Although all transition probabilities are close to unity, agreement of the master equation transition probabilities with the exact ones and with each other is found to be excellent. At higher $\varepsilon_0$, the TNM results are found to be marginally better than the FONM and markovian results. The analogous comparisons for systems with larger mass factors is quite different as will now be described.

First let us consider the translational energy dependence of the energy transfer parameter $\eta$ and the FONM correction parameter $\zeta$. These are plotted in figure 1 for $H+H_2$. We see that although $\eta > 10\zeta$ for much of the energy range illustrated, $\zeta$ is a more rapidly increasing function of $\varepsilon_0$ for $\varepsilon_0 > 3$. As remarked previously, the approximation leading to the FONM results in equation (28) breaks down when $\zeta$ becomes large compared to unity, so we do not expect the FONM result to be useful for $\varepsilon_0$ greater than about 3 for $H+H_2$. For larger mass parameter systems such as He+HBr, the correction parameter $\zeta$ becomes appreciable at even lower $\varepsilon_0$ (at $\varepsilon_0 = 2$, $\zeta = 0{\cdot}5$), so the range of validity of the FONM result is even more restricted.

A comparison of the TNM, FONM, markovian and exact transition probabilities $P_{11}$ is given in figure 2 for $H+H_2$ and figure 3 for He+HBr. Here we find (i) that the results of all four approaches agree only at very low translational

Table 1. Comparison of total non-markovian, first-order non-markovian, markovian and semiclassical probabilities for $H+I_2$.

| Energy $\varepsilon_0$ | Total non-markovian | | First-order non-markovian | | Markovian | | Exact semi-classical | |
|---|---|---|---|---|---|---|---|---|
| | $P_{00}$ | $P_{01}$ | $P_{00}$ | $P_{11}$ | $P_{00}$ | $P_{11}$ | $P_{00}$ | $P_{11}$ |
| 0·2 | 0·999465 | 0·998398 | 0·999465 | 0·983395 | 0·999465 | 0·998396 | 0·999465 | 0·998395 |
| 0·4 | 0·997581 | 0·992763 | 0·997580 | 0·992755 | 0·997581 | 0·992768 | 0·997578 | 0·992747 |
| 0·6 | 0·995112 | 0·985398 | 0·995110 | 0·985383 | 0·995120 | 0·985455 | 0·995108 | 0·985372 |
| 0·8 | 0·992392 | 0·977306 | 0·992389 | 0·997284 | 0·992418 | 9·977483 | 0·992389 | 0·977283 |
| 1·0 | 0·989547 | 0·968863 | 0·989543 | 0·968838 | 0·989601 | 0·969235 | 0·989547 | 0·968861 |
| 1·4 | 0·983676 | 0·951510 | 0·983668 | 0·951470 | 0·983822 | 0·952505 | 0·983691 | 0·951605 |
| 1·6 | 0·980694 | 0·942732 | 0·980684 | 0·942694 | 0·980904 | 0·944156 | 0·980720 | 0·942907 |

energy; (ii) that the FONM results generally differ substantially from the TNM, especially for the higher mass parameter He + HBr system, and even when $\zeta \ll 1$; and (iii) that the TNM and markovian probabilities differ substantially with each other for $\varepsilon_0 > 1$. The markovian results are actually in better agreement with the exact semiclassical results at intermediate $\varepsilon_0$ ($1 < \varepsilon_0 < 3$) than are the TNM ones. We will analyse the reasons underlying these results in the following paragraphs.

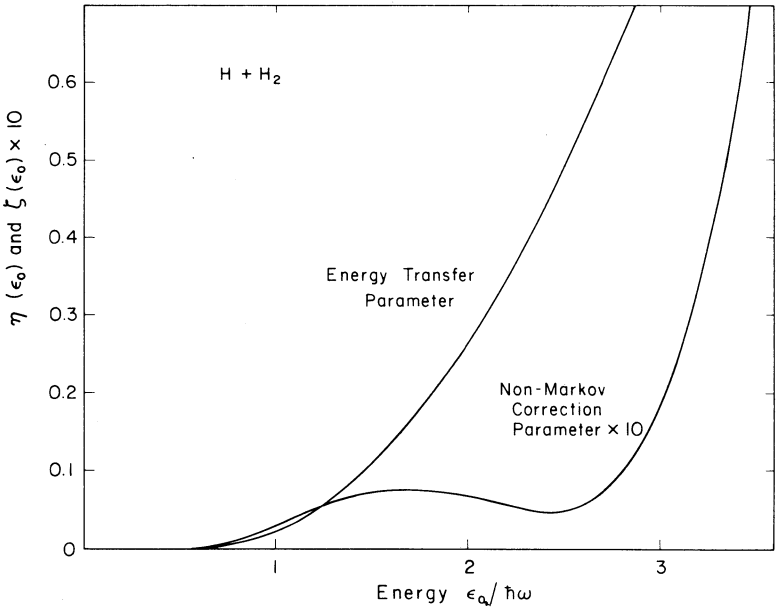


Figure 1. Energy transfer parameter $\eta$ (from equation (30)) and the non-markovian correction parameter $\zeta(\times 10)$ (from equation (31)) as a function of the initial translational energy $\varepsilon_0$ (in units of $\hbar$ ), using parameters appropriate to $H + H_2$.

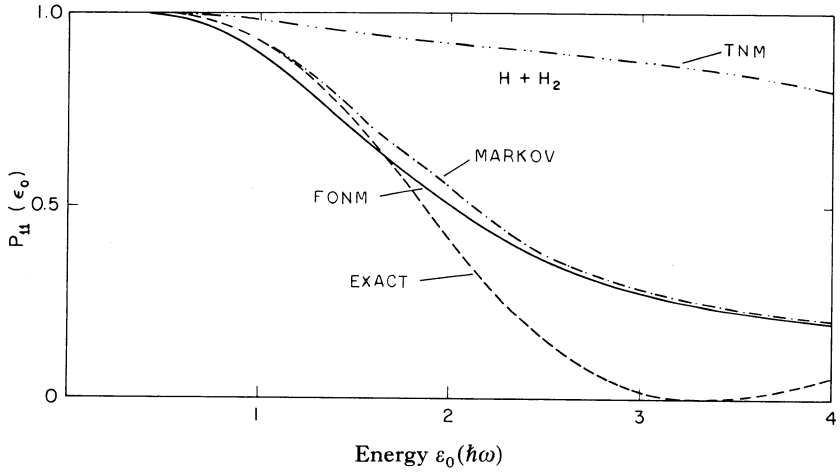


Figure 2. Comparison of probability $P_{11}$ for exact semiclassical (dash-dash), FONM (solid line), TNM (dash-double dot), and markovian (dash-dot) versus the initial translation energy for $H + H_2$.

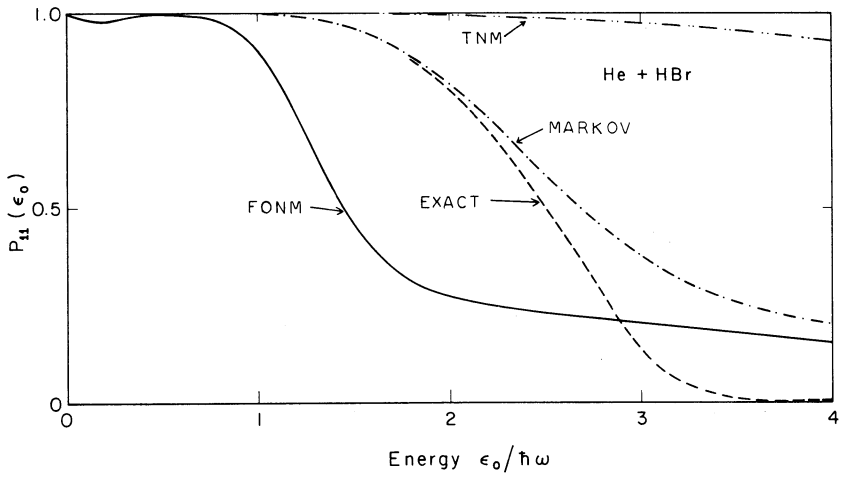


Figure 3. Probability $P_{11}$ as in figure 2 but for He + HBr.

Some of the basic features exhibited in figures 2 and 3 can be understood in a qualitative way by examining the perturbation theory limit of equations (32), (33), and (34) for small values of $\varepsilon_0$. In this limit (small $\eta$ and $\zeta$) $P_{11}$ (FONM) can be determined approximately by expanding the gaussian part of the integrand of equation (32), a valid procedure since $\exp(-x)$ dominates the convergence of the integral for small $\zeta$. For the transition of interest, i.e., $n_0=1$, $n=1$, we have

$$P_{11}(\text{exact}) \sim 1-3\eta+\tfrac{7}{2}\eta^2, \tag{35}$$

$$P_{11}(\text{markov}) \sim 1-3\eta+7\eta^2, \tag{36}$$

$$P_{11}(\text{FONM}) \sim 1-3\eta-14\zeta+78\zeta\eta. \tag{37}$$

(Unfortunately, an analogous simple TNM expression cannot be developed.) The first important result from these equations is that $\{P_{11}(\text{exact})-P_{11}(\text{markov})\} \sim O(\eta^2)$ as $\eta \to 0$, and this result has no explicit dependence on the choice of parameters $m$ and $\alpha$. Reference to figures 2 and 3 illustrates this trend, the markov exact semiclassical results are in close agreement for $\varepsilon_0 \to 0$ for both $H+H_2$ and He + HBr. A rather different behaviour arises for the FONM probability: $\{P_{11}(\text{exact})-P_{11}(\text{FONM})\}$ and $\{P_{11}(\text{markov})-P_{11}(\text{FONM})\}$ both behave like $O(\zeta)$ as $\varepsilon_0 \to 0$. This first-order dependence on $\zeta$ leads to a stronger dependence on the mass parameter $m$. For $H+H_2$ the values of $\eta$ and $\zeta$ determined from figure 1 result in an accidental cancellation of the third and fourth terms in equation (37) at low $\varepsilon_0$, and this results in essentially markovian behaviour for the FONM result. For He + HBr, however, at low $\varepsilon_0$ we find that the third term in equation (37) is quite large (a direct result of the larger mass factor for this system), so the differences $\{P_{11}(\text{exact})-P_{11}(\text{FONM})\}$ and $\{P_{11}(\text{markov})-P_{11}(\text{FONM})\}$ become substantial even at small values of $\varepsilon_0$, as is clearly demonstrated in figure 3.

The rather large difference between FONM and TNM results even for ranges of $\varepsilon_0$ for which $\zeta \lesssim 1$ seems to indicate that the truncation of the expansion in (23) is a more severe approximation than that which leads us from equation (27) to (28). Indeed, a numerical evaluation of equation (20) using (27) for $h(x, t)$ leads to a probability $P_{11}=0{\cdot}9178$ for $H+H_2$ at $\varepsilon_0=1$ compared to a corresponding

value of 0·8980 obtained from equation (28), indicating the validity of the approximate treatment of equation (27). Since the integrand of equation (16) exhibits significant oscillatory behaviour at times during the collision, it is perhaps not surprising that first-order truncation of the Taylor series expansion may not be appropriate under all conditions.

(When second-order terms in equation (23) are included, the probability is given by equation (20) where $h(x, t)$ is the solution of the differential equation

$$xC(t)\frac{\partial^2 h(x,t)}{\partial t^2}+[1-xB(t)]\frac{\partial h(x,t)}{\partial t}+xD(t)h(x,t)=0$$

and $C(t)$ is the second-order correction

$$C(t)=\int_{-\infty}^{t}(t'-t)^2\cos(t-t')F(t)F(t')dt'.$$

This differential equation is not well behaved numerically and could not be solved by the numerical techniques available to us.)

The better agreement of the markovian rather than TNM probabilities with the exact ones at intermediate $\varepsilon_0$ may seem surprising at first, but can be rationalized by examining the time dependence of the energy transfer parameter $\eta(t)$, since this provides a crude measure of the importance of correlations between the vibrational action–angle variables during the collision. From equations (29) and (22), we find

$$\eta(t)=\alpha^2\varepsilon_0{}^2\int_{-\infty}^{t}dt'\int_{-\infty}^{t'}\cos(t'-t'')\exp[-\alpha q(t')]\exp[-\alpha q(t'')]dt'' \qquad (38)$$

and by differentiating this expression and substituting equation (22), it is not difficult to develop a set of coupled ordinary differential equations for accurately determining $\eta(t)$. Plots of $\eta(t)$ for the three systems $H+I_2$, $H+H_2$, and $He+HBr$ at $\varepsilon_0=1$ are given in figure 4. There we see that $\eta(t)$ increases monotonically during the collision for $H+I_2$, but shows oscillatory behaviour for $H+H_2$ and $He+HBr$. Note in particular that $\eta(0)$ is much larger than $\eta(\infty)$ for $He+HBr$ (0·19 versus 0·000 759) and somewhat larger for $H+H_2$ (0·076 versus 0·025). To understand the rather different behaviour of $\eta(t)$ for these systems it is instructive to compare the relative collision durations and vibrational periods. The collision duration $\tau_c$ can be estimated as the period of time for which $\exp[-\alpha q(t)]$ is large (roughly $4/\alpha$ divided by the initial velocity $(2\varepsilon_0/m)^{1/2}$, or $\tau_c=\sqrt{(8m/\varepsilon_0\alpha^2)}$). According to this definition, when $\varepsilon_0=1$, $\tau_c=1{\cdot}43$ for $H+I_2$, 5·27 for $H+H_2$, and 9·78 for $He+HBr$, compared to the (scaled) vibrational period of $2\pi=6{\cdot}28$ for all three systems. This comparison of collisional and vibrational periods indicates that for $H+I_2$, the collision is impulsive at this energy, with essentially no time for the oscillator to respond to the collisional perturbation. For the $He+HBr$, and to a lesser extent for $H+H_2$, the oscillator executes one or more vibrations while the collisional interaction is strong, which is long enough to allow for the transfer of energy first into vibration, then back to translation, one or more times during the collision. By inspection of equation (38) (using equation (22) for $\exp[-\alpha q(t)]$) it is apparent that $\eta(0)\gg\eta(\infty)$ only if significant destructive interference occurs in the integral by virtue of oscillations in $\cos(t'-t'')$. This cancellation effect indicates the importance of correlated motions in the collisions, and this is further substantiated by examination of classical trajectories for He+

HBr and $H+H_2$ where one observes a considerable variation in the amount of energy transfer as a function of initial vibrational phase. Since it is correlation effects which are approximated by the stochastic approaches [4], it is not hard to understand why the TNM result is much less accurate for $He+HBr$ and $H+H_2$ than for $H+I_2$. One might also imagine that the markovian result should also be inaccurate for $He+HBr$, and indeed it is at higher $\varepsilon_0(\varepsilon_0>2{\cdot}5)$. However, for intermediate $\varepsilon_0(1<\varepsilon_0<2{\cdot}5)$, because the combination of approximations leading to equation (33) (namely equation (19) coupled with the approximation inherent in equation (6)) leads to markovian probabilities that are only functions of $\eta$, the markovian result appears to account for correlation more accurately than the non-markovian one. Thus in the present situation, although both the markovian and non-markovian inelastic probabilities first increase then decrease during the collision for $He+HBr$, only the markovian ones follow the exact results quantitatively at intermediate energies since the necessary destructive interference properly occurs only in the markovian master equation. One would not however expect that accurate markovian results would be obtained for other types of collision problems where correlations are important, since the time integral of the rate coefficients appearing in the master equation is not usually equal to the average energy transfer, as it is here. It should also be noted that the collision systems for which we find correlations to be important (i.e., $He-HBr$) are also those for which the impulsive treatment of translational motion is also inaccurate [19].

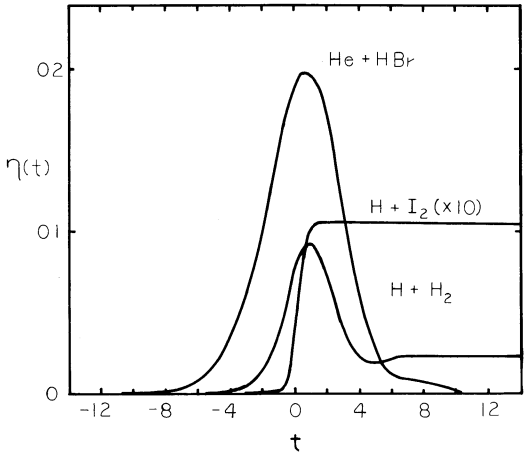


Figure 4. Energy transfer parameter $\eta(t)$ versus time $t$ (in scaled units) for $He+HBr$, $H+H_2$, and $H+I_2$ at a translational energy $\varepsilon_0=1$.

In table 2 we give a comparison of the four theories for the calculation of $P_{01}$ and $P_{12}$ for $He+HBr$. Basically, the same comparisons observed above for $P_{11}$ also apply to $P_{01}$ and $P_{12}$.

Figure 5 illustrates the trends for the multiple transition probabilities. For $H+H_2$ there is fairly close agreement between the markovian, FONM, and exact results; however the TNM results are not in very good agreement with the other theories. For $He+HBr$, the FONM and TNM theories again deviate significantly

Table 2. Comparison of total non-markovian, first-order non-markovian, markovian and exact semiclassical probabilities for the He+HBr.†

| Energy $\varepsilon_0$ | Total non-markovian | | First order non-markovian | | Markovian | | Exact semiclassical | |
|---|---|---|---|---|---|---|---|---|
| | $P_{01}$ | $P_{12}$ | $P_{01}$ | $P_{12}$ | $P_{01}$ | $P_{12}$ | $P_{01}$ | $P_{12}$ |
| 0·2 | 5·15(−4) | 6·11(−4) | 7·56(−3) | 2·91(−2) | 4·19(−12) | 8·38(−12) | 4·19(−12) | 8·38(−12) |
| 0·6 | 3·21(−6) | 9·57(−5) | 4·05(−4) | 1·61(−3) | 8·55(−6) | 1·71(−5) | 8·55(−6) | 1·71(−5) |
| 0·8 | 8·95(−6) | 2·39(−5) | 5·10(−3) | 1·96(−2) | 1·22(−4) | 2·44(−4) | 1·22(−4) | 2·44(−4) |
| 1·0 | 8·03(−5) | −3·54(−5) | 2·71(−2) | 9·32(−2) | 7·49(−4) | 1·49(−3) | 7·49(−4) | 1·50(−3) |
| 1·6 | 9·67(−4) | 1·09(−3) | 2·35(−1) | 2·75(−1) | 1·81(−2) | 3·48(−2) | 1·84(−2) | 3·61(−2) |
| 2·0 | 2·19(−3) | 2·38(−3) | 3·09(−1) | 2·07(−1) | 5·94(−2) | 1·04(−1) | 6·32(−2) | 1·18(−1) |
| 2·4 | 3·77(−3) | 3·75(−3) | 3·04(−1) | 1·80(−1) | 1·27(−1) | 1·86(−1) | 1·47(−1) | 2·44(−1) |

† Number in parentheses indicates the power of 10 by which the number preceding it should be multiplied.

from one another. For even higher multiple transition probabilities than are shown in figure 5, there is a complete lack of agreement between the TNM and exact results, largely because the TNM theory transition probabilities decrease more slowly with increasing energy gap than the exact ones. For example, at $\varepsilon_0 = 3$ for $H + H_2$, $P_{06}(\text{TNM}) \sim 10^{-2}$ compared to the exact probabilities of $10^{-4}$. The markovian and FONM probabilities also decrease in size more slowly than the exact ones (although more rapidly than the TNM). To obtain an overview of the situation for multiple transition probabilities, figure 6 shows the second moments calculated via the four different theories for $H + H_2$. The slow fall-off of the multiple transition probabilities for the TNM theory and to a lesser extent the markov and FONM theories shows up as positive errors in the second moment in that figure. Note here, however, that the first moments are identical for the TNM, markovian, and exact theories [4]. This indicates that the comparison of moments can be a misleading criterion for judging the stochastic models, as the correctness of moments can easily obscure compensatory errors in individual transition probabilities. A point worthy of note is that some of the TNM multiple transition probabilities were found to be negative. Some small negative probabilities were also found using the FONM theory. This is to be contrasted with the markovian and exact semiclassical theories (equations (33) and (34)) for which positive probabilities are guaranteed.

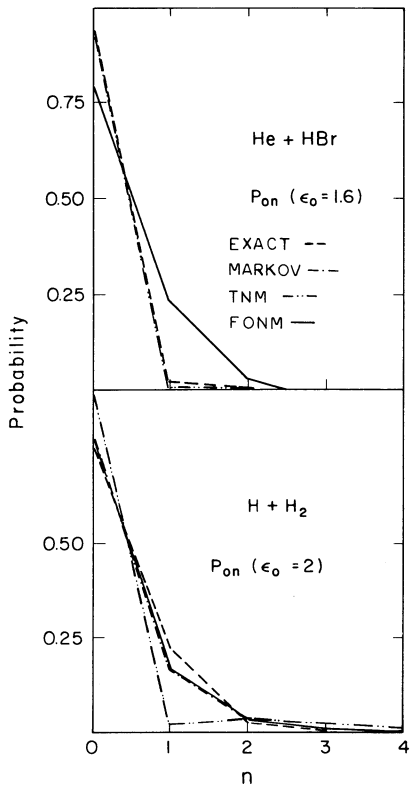


Figure 5. Exact semiclassical (– –), stochastic markov (– · –), FONM (——), and TNM (– · · –) probability distributions $P_{0n}$ versus $n$ for $H + H_2(\varepsilon_0 = 2)$ and $He + HBr$ $(\varepsilon_0 = 1{\cdot}6)$.

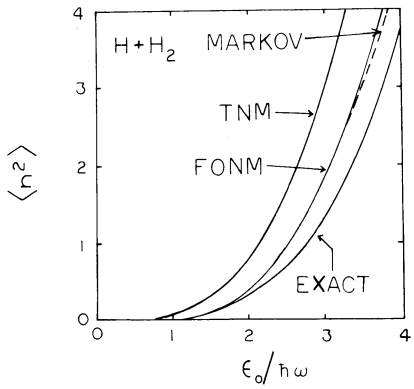


Figure 6. Comparison of second moments as a function of $\varepsilon_0$ for $H+H_2$.

## 5. Discussion

In this paper we have examined transition probabilities for vibrationally inelastic atom–diatom scattering as obtained from both Markovian and non-markovian master equation approximations to the time dependent Schrödinger equation. Except in certain limits, the agreement between these two theories was generally found to be quite poor, which means that the markovian approximation (equation (19)) is in fact not usually very accurate. Exceptions to this in which good agreement between markovian and non-markovian transition probabilities was obtained occurred in the low translational energy perturbation limit where $h(x, t) \simeq 1$ throughout the collision, and for systems like $H+I_2$ which have a collision duration which is short compared to the relevant vibrational period. In the impulsive situation, $\cos(t-t')$ in (21) remains close to unity during the collision, and the expansion in (23) can be accurately truncated at the first term. For systems where the collision duration is comparable to or larger than the vibrational period, motional correlations are much more important (as evidenced by the observed oscillatory exchange of energy between vibration and translation in figure 4), and the markovian approximation becomes inaccurate. Since the collision duration is approximately $\tau_c = (8m/\varepsilon_0\alpha^2)^{1/2}$, it is apparent that for a given $\varepsilon_0$, the shortest $\tau_c$ occurs for systems with the smallest ratio $m/\alpha^2$, and we observe the markovian approximation to be most accurate in this limit. It might also be expected that for any given system (with $m/\alpha^2$ fixed), one can make the markovian approximation accurate simply by increasing $\varepsilon_0$ enough. Although this may be true, $\eta$ also increases with increasing $\varepsilon_0$, and when $\eta$ becomes close to or greater than unity, the lowest order Born approximation inherent in the memory kernel evaluation in (16) becomes inaccurate and makes both the markovian and non-markovian theories inaccurate. Thus we might summarize by saying that *both* master equation approaches tend to be most accurate for systems with small values of $m/\alpha^2$, and for a given system, for energies $\varepsilon_0$ as large as possible consistent with $\eta \ll 1$.

A surprising result of the comparison between markovian, non-markovian and exact transition probabilities was that the markovian results were significantly more accurate than TNM at intermediate $\varepsilon_0$. We regard this as an accident which is somewhat special to the model problem treated. The reason is that the combina-

tion of approximations which leads to the markovian master equation also leads to transition probabilities which depend only on the energy transfer parameter $\eta$; (this is not generally true). The exact probabilities also depend only on $\eta$ and are identical in their lowest order $\eta$ dependence to the markovian probabilities. Thus as long as $\eta$ is small, the markovian and exact transition probabilities will be close. The non-markovian theory (for which the transition probabilities are no longer explicitly functions of $\eta$) fails to be more accurate in treating systems with long collision durations at intermediate $\varepsilon_0$, since in such situations, the necessary interference cancellation which is responsible for making $\eta(0) \geqslant \eta(\infty)$ is not properly described. Presumably this can be overcome by evaluating higher order terms in the Born series expansion of this memory term. Some indication that this is so is provided by the result (derived in reference [20]) that for each addition term in the Born series expansion included, an additional moment of the final state probability distribution becomes exactly predicted by both markovian and non-markovian master equations. This means that in a high order truncation of the Born series in (14), a large number of moments of both probability distributions would be identical. We stress however that caution must be exercised in equating the agreement of moments to the agreement of transition probabilities.

Finally we consider how the results of this work can be used as a guide to future applications of master equation methods to problems in collisional energy transfer for which exact solutions are not available. A conservative statement would be that whenever the markovian and non-markovian results are in good agreement memory effects are presumably weak and the approximations to correlations which are inherent in the stochastic treatment should be accurate. When the two approaches disagree significantly, then memory effects must be more important and neither approach can be trusted to be accurate except in special cases.

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## References

[1] Augustin, S. D., and Rabitz, H., 1976, *J. chem. Phys.*, **64,** 1223.
[2] Augustin, S. D., and Rabitz, H., 1977, *J. chem. Phys.*, **66,** 269.
[3] Schatz, G. C., 1977, *J. chem. Phys.*, **66,** 5220.
[4] Schatz, G. C., McLafferty, F. J., and Ross, J., 1977, *J. chem. Phys.*, **66,** 3609.
[5] Augustin, S. D., and Rabitz, H., 1977, *J. chem. Phys.*, **67,** 2082.
[6] Schatz, G. C., 1977, *Chem. Phys.*, **24,** 263; 1978, *Molec. Phys.*, **35,** 477.
[7] Zwanzig, R., 1961, *Lectures in Theoretical Physics*, Vol. 3, edited by W. E. Brittin, B. W. Downs and J. Downs (Interscience), p. 106.
[8] Montroll, E., 1961, in *Lectures in Theoretical Physics*, Vol. 3, edited by W. E. Brittin, B. W. Downs and J. Downs (Interscience), p. 221.
[9] Agarwal, G. S., 1973, *Progress in Optics*, Vol. 11, edited by E. Wolf (North-Holland), p. 1.
[10] Haake, F., 1973, *Quantum Statistics in Optics and Solid-State Physics*, Springer Tracts in Modern Physics, Vol. 66, edited by G. Höhler, p. 98.
[11] Heidrich, F. E., Wilson, K. R., and Rapp, D., 1971, *J. Chem. Phys.*, **54,** 3885.
[12] Mahan, G. H., 1970, *J. chem. Phys.*, **52,** 5221.
[13] Willis, C. R., and Picard, R. H., 1974, *Phys. Rev.* A, **9,** 1343.

[14] OPPENHEIM, I., and SHULER, K. E., 1965, *Phys. Rev.*, **138,** B1007.
[15] SHUGARD, M., TULLY, J. C., and NITZAN, A., 1977, *J. chem. Phys.*, **66,** 2534.
[16] RAPP, D., and KASSAL, T., 1969, *Chem. Rev.*, **69,** 61.
[17] HERZBERG, G., 1950, *Spectra of Diatomic Molecules* (Van Nostrand).
[18] CLARK, A. P., and DICKINSON, A. S., 1973, *J. Phys.* B, **6,** 164.
[19] KELLEY, J. D., and WOLFSBERG, M., 1966, *J. chem. Phys.*, **44,** 324.
[20] SCHATZ, G. C., 1978, *Chem. Phys. Lett.*, **58,** 368.