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Rate calculations from time-dependent wave packet methods: The relationship of the pure state and canonical total reaction probability

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Reaction rate coefficients for collinear $A + BC \rightarrow AB + C$ exchange reactions computed directly by the time evolution of an initial pure-state wave packet given by $\psi(t = 0) = \phi(q_1)\Sigma_{n=0}^{n'} A_n e^{i\delta n} X_n(q_2)$, where $\phi(q_1)$ describes the distribution of translational states present in the collision, $X_n(q_2)$ is an nth-state vibrational wave function for the BC molecule, A_n is a weighting coefficient dependent upon the nth vibrational-state eigenvalue and temperature, and the δ_n are the relative phases of the initial-state vibrational wave functions, are compared with those obtained using the density operator for a canonical ensemble of noninteracting $A + BC$ molecules. It is shown that the computed total reaction probability for the pure-state wave packet is independent of the δ_n and is the same as that obtained from the density operator for the full canonical ensemble provided certain integrals over the product configuration space vanish. Qualitative arguments are advanced that suggest these integrals may indeed vanish. Numerical computations of the reaction probability for the $T + HD \rightarrow TH + D$ exchange reaction at 1000 and 10 000 K indicate that the contribution of these integrals to the overall reaction probability is small. The immediate consequences of this result are that rate coefficients may be computed using pure-state wave packets that do not include phase factors, and a general theorem that orthogonal reactant states will evolve as orthogonal product states.

I. INTRODUCTION

Recently, Agrawal and Raff[1] have described a time-dependent wave packet method that permits rate coefficients for collinear $A + BC$ exchange reactions to be obtained directly without the necessity of computing separately reaction probabilities out of all statistically significant initial BC vibrational states. The essence of the method is to express the initial state of the system as a pure-state wave function rather than as a diagonal density matrix that models the canonical ensemble. That is, the initial-state wave function is

$$\psi(t = 0) = \phi(q_1)\sum_{n=0}^{n'} A_n X_n(q_2) , \qquad (1)$$

where the A_n are given by

$$A_n = \left[Z_n \Big/ \sum_{n=0}^{n'} Z_n \right]^{1/2} \qquad (2)$$

with

$$Z_n = \exp[- E_n^0/k_B T] , \qquad (3)$$

where k_B is the Boltzmann constant and E_n^0 is the eigenvalue corresponding to the BC vibrational eigenfunction $X_n(q_2)$. By choosing the expansion coefficients A_n such that the A_n^2 correspond to the Boltzmann weights of each of the BC vibrational states at temperature T, the evolution of the wave packet described by Eq. (1) will incorporate the contribution of all statistically significant BC vibrational states into the computed exchange rate. The procedure thereby obviates the need to separately calculate reaction probabilities out of each BC vibrational state.

In a similar manner, $\phi(q_1)$ is the packet representing the relative translational motion. It is chosen such that its Fourier transform yields the desired distribution of relative translational momenta. Consequently, the evolution of the single wave packet described by Eq. (1) will produce the reaction probability averaged over the desired distributions of both translation and vibration. Rate coefficients for the collinear $T + HD \rightarrow TH + D$ reaction at 1000, 1500, and 2400 K computed by this method have been found to be in close agreement with the close-coupling results reported by Garrett *et al.*[2]

At high temperature or for systems having a low vibrational frequency, close-coupling calculations will rapidly increase in difficulty as the number of channels increases. However, the difficulty of this wave packet approach is essentially independent of the number of vibrational states included in Eq. (1). Consequently, under such conditions, the procedure will become the method of choice for the computation of rate coefficients.

In this paper, we wish to examine the above approach in more detail. In particular, we wish to explore the question of the appropriateness of representing the initial state of the system as a pure state in which various vibrational eigenfunctions are combined without consideration of their relative phases rather than using a density matrix formulation of the initial state. We have approached this question in two stages. First, we ask if it is necessary to write Eq. (1) in the form

$$\psi(t = 0) = \phi(q_1)\sum_{n=0}^{n'} A_n e^{i\delta_n} X_n(q_2) , \qquad (4)$$

and then carry out an average over the δ_n to compute the correct rate coefficient for the exchange reaction. Such a requirement might be regarded as being the quantum mechanical analog of phase averaging in a classical trajectory calculation. Secondly, we formulate the problem

in terms of a density operator $\hat{T}_{can}(t)$ for the canonical ensemble in which $\hat{T}_{can}(t=0)$ is represented by a diagonal density matrix. The total reaction probability obtained from the time evolution of $\hat{T}_{can}(t)$ is then compared with that obtained by evolution of the pure-state initial wave packets given by Eqs. (1) and (4).

In the next section, we show that if certain overlap integrals in the product configuration space vanish, all of the approaches to the problem become equivalent. We also develop the necessary equations whereby the deviation of the results obtained with the pure-state procedures from those obtained from a density matrix approach may be quantitatively assessed. Examples are given for the $T + HD \rightarrow TH + D$ reaction. Finally, the analysis presented here goes further in leading to some interesting conclusions regarding the orthogonality of reactant and product states.

II. THEORY

In the notation of Ref. 1, consider two normalized initial wave packets corresponding to the zeroth and first vibrational states:

$$\psi_0(t_0) = \psi_0(t=0) = \phi(q_1)X_0(q_2) , \tag{5}$$

and

$$\psi_1(t_0) = \psi_1(t=0) = \phi(q_1)X_1(q_2) . \tag{6}$$

Let the evolution of these wave packets by the time-dependent Schrödinger equation yield $\psi_0(t=\infty)$ and $\psi_1(t=\infty)$, respectively. The reaction probability for reactants initially in state i is then given by

$$\langle P \rangle_{TD}^i = \int_P |\psi_i(t=\infty)|^2 d\tau , \tag{7}$$

where the integral is taken over the portion of configuration space corresponding to products.

Now consider a pure-state normalized wave packet consisting of a linear combination of ψ_0 and ψ_1 as described by Eq. (4):

$$\psi_{1,0}(t_0) = A_0\psi_0(t_0) + A_1\psi_1(t_0) e^{i\delta_1} , \tag{8}$$

where we have taken $\delta_0 = 0$. This choice involves no loss of generality since it is only the relative phase of ψ_0 and ψ_1 that can be important. To prove the independence of the total reaction probability from the phase factor δ_1, it will be sufficient to show that the reaction probability obtained from the evolution of $\psi_{1,0}(t_0)$ with $\delta_1 \neq 0$ will be

$$\langle P \rangle_{TD}^{1,0} = A_0^2 \langle P \rangle_{TD}^0 + A_1^2 \langle P \rangle_{TD}^1 . \tag{9}$$

The evolution of $\psi_{1,0}(t_0)$ from time t_0 to time t by the time-dependent Schrödinger equation is equivalent to the operator equation

$$\psi(t) = T(t, t_0)\psi(t_0) , \tag{10}$$

where $T(t, t_0)$ is a linear unitary operator.[3] Due to the linearity of $T(t, t_0)$, it is known that if $\psi_0(t_0)$ and $\psi_1(t_0)$ evolve into $\psi_0(t)$ and $\psi_1(t)$, respectively, then $\psi_{1,0}(t_0)$ will evolve into

$$\psi_{1,0}(t) = A_0\psi_0(t) + A_1\psi_1(t) e^{i\delta_1} . \tag{11}$$

We now express $\psi_0(t)$ and $\psi_1(t)$ as the sum of two parts, one part belonging to the reactant configuration space and the other to the product configuration space:

$$\psi_0(t) = a_0^R(t)\psi_0^R(t) + a_0^P(t)\psi_0^P(t) , \tag{12}$$

$$\psi_1(t) = a_1^R(t)\psi_1^R(t) + a_1^P(t)\psi_1^P(t) . \tag{13}$$

Here, the ψ_i^R and ψ_i^P are normalized wave functions, and the a_i^R and a_i^P are complex numbers. The superscripts R and P denote the reactant and product configuration space, respectively.

Theoretically, there exists a line of demarcation between the reactant and product configuration space such that as $t \rightarrow \infty$, ψ^R and ψ^P do not overlap. Therefore we may write

$$\langle \psi^R(t \rightarrow \infty) | \psi^P(t \rightarrow \infty) \rangle = 0 . \tag{14}$$

It is now trivial to see that

$$\langle P \rangle_{TD}^0 = |a_0^P(t \rightarrow \infty)|^2 \tag{15}$$

and

$$\langle P \rangle_{TD}^1 = |a_1^P(t \rightarrow \infty)|^2 . \tag{16}$$

Combination of Eqs. (11)–(13) gives

$$\psi_{1,0}(t \rightarrow \infty) = [a_0^R A_0 \psi_0^R + a_1^R A_1 \psi_1^R e^{i\delta_1}]_{t \rightarrow \infty}$$
$$+ [a_0^P A_0 \psi_0^P + a_1^P A_1 \psi_1^P e^{i\delta_1}]_{t \rightarrow \infty} . \tag{17}$$

The total reaction probability from Eq. (7) is therefore

$$\langle P \rangle_{TD}^{1,0} = \int_P |\psi_{1,0}(t \rightarrow \infty)|^2 d\tau$$
$$= A_0^2 |a_0^P(t \rightarrow \infty)|^2 + A_1^2 |a_1^P(t \rightarrow \infty)|^2 + F(\delta_1) + F^*(\delta_1) . \tag{18}$$

Using Eqs. (15) and (16), this yields

$$\langle P \rangle_{TD}^{1,0} = A_0^2 \langle P \rangle_{TD}^0 + A_1^2 \langle P \rangle_{TD}^1 + F(\delta_1) + F^*(\delta_1) , \tag{19}$$

where

$$F(\delta_1) = [A_0 A_1 a_0^{P*} a_1^P \langle \psi_0^P | \psi_1^P \rangle e^{i\delta_1}]_{t \rightarrow \infty} . \tag{20}$$

Since $T(t, t_0)$ is a unitary operator, its operation on any normalized vector $[C_0\psi_0(t_0) + C_1\psi_1(t_0)]$ yields a normalized vector $[C_0\psi_0(t) + C_1\psi_1(t)]$ for any set of complex numbers C_0 and C_1. Consequently, the orthogonality of $\psi_0(t)$ and $\psi_1(t)$ will be preserved for all values of time t, including $t \rightarrow \infty$.[4] Therefore we have

$$\langle \psi_0(t) | \psi_1(t) \rangle = 0 . \tag{21}$$

Combination of Eqs. (12)–(14) with Eq. (21) gives

$$[a_0^{R*} a_1^R \langle \psi_0^R | \psi_1^R \rangle + a_0^{P*} a_1^P \langle \psi_0^P | \psi_1^P \rangle] = 0 \tag{22}$$

for all values of t.

Chemically, the ψ^R wave functions represent the $(A + BC)$ system while the ψ^P wave functions describe the $(AB + C)$ system. If it is argued that these systems should be independent, the overlap integral $\langle \psi_0^R | \psi_1^R \rangle$ would not be expected to depend upon $\langle \psi_0^P | \psi_1^P \rangle$. Under such conditions, Eq. (22) would require that

$$\langle \psi_0^R | \psi_1^R \rangle = \langle \psi_0^P | \psi_1^P \rangle = 0 , \tag{23}$$

at all values of t. Alternatively, it may be noted that ψ_0^P and ψ_1^P represent chemical states of the products. It

may therefore be appropriate to assume that the scalar product of ψ_0^P and ψ_1^P should not depend upon the coefficients a_0^P, a_1^P, a_0^R, and a_1^R. A similar argument may be advanced for $\langle \psi_0^R | \psi_1^R \rangle$. The independence of the scalar products and the coefficients together with Eq. (22) again leads to Eq. (23).

Equations (23) and (20) thus yield $F(\delta_1) = 0$, and hence

$$\langle P \rangle_{TD}^{1,0} = A_0^2 \langle P \rangle_{TD}^0 + A_1^2 \langle P \rangle_{TD}^1 . \tag{24}$$

That is, $\langle P \rangle_{TD}^{1,0}$ is independent of the phase factor δ_1.

The results of the above analysis may easily be generalized to any number of vibrational states by a straightforward induction proof.

Let us now examine the correspondence (or lack of it) between the pure-state methods utilized in Ref. 1 and a more standard procedure in which the initial state is represented by a density matrix formulation with the off-diagonal elements set to zero. Consider a canonical ensemble of noninteracting A and BC molecules. The density operator for this ensemble is

$$\hat{\tau}_{can} = \exp[-\beta \hat{H}_0]/Z , \tag{25}$$

where $\hat{H}_0$ is the Hamiltonian operator for the noninteracting system for which

$$\hat{H}_0 = \hat{H}_0^A + \hat{H}_0^{BC} \tag{26}$$

and $\beta = (k_B T)^{-1}$. Z is given by the trace of the density matrix,

$$Z = Tr[\exp(-\beta \hat{H}_0)] . \tag{27}$$

If we now employ a basis $\{|K\rangle\}$ in which $\hat{H}_0$ is diagonal, we have

$$\hat{H}_0 |K\rangle = E^0 |K\rangle , \tag{28}$$

and $\hat{\tau}_{can}$ can be represented by a diagonal matrix such that

$$\tau_{KK'} = \exp[-\beta E_K^0] \delta_{KK'} / Z , \tag{29}$$

with

$$Z = \sum_K \exp[-\beta E_K^0] . \tag{30}$$

We may now compare the result for the probability density operator for the pure state with that for the canonical ensemble given by Eqs. (29) and (30). Let $\hat{\tau}_0(t)$ be the density operator for the pure-state representation. This is given by

$$\hat{\tau}_0^{(t=0)} = |\psi(t=0)\rangle\langle\psi(t=0)| . \tag{31}$$

Using Eq. (8) for ψ, this gives

$$\hat{\tau}_0(t=0) = |\psi_{1,0}\rangle\langle\psi_{1,0}|$$

$$= \left[\sum_{K=0}^1 \frac{\exp(i\delta_K)\exp(-\beta E_K^0/2)|\psi_K(t=0)\rangle}{Z^{1/2}} \right] \tag{32}$$

$$\times \left[\sum_{K'=0}^1 \frac{\langle\psi_{K'}(t=0)|\exp(-i\delta_{K'})\exp(-\beta E_{K'}^0/2)}{Z^{1/2}} \right] ,$$

provided we take $\delta_0 = 0$. Expansion of Eq. (32) yields

$$\hat{\tau}_0(t=0) = \frac{1}{Z}\sum_{K=0}^1 |\psi_K(t=0)\rangle \exp(-\beta E_K^0)\langle\psi_K(t=0)|$$

$$+ \frac{1}{Z}\sum_{\substack{K=0 \\ K \neq K'}}^1 \sum_{K'=0}^1 \exp[i(\delta_K - \delta_{K'})] \tag{33}$$

$$\times \exp[-\beta(E_K^0 + E_{K'}^0)/2]|\psi_K(t=0)\rangle\langle\psi_{K'}(t=0)| .$$

It may be seen from Eqs. (29) and (30) that the first summation on the right-hand side of Eq. (33) is the density operator for the canonical ensemble. That is, we have

$$\hat{\tau}_{can}(t=0) = \hat{\tau}_0(t=0) - \hat{\mathfrak{F}}(t=0) , \tag{34}$$

where

$$\hat{\mathfrak{F}}(t) = \frac{1}{Z}\sum_{\substack{K \\ K \neq K'}}\sum_{K'} |\psi_K(t)\rangle\{\exp[i(\delta_K - \delta_{K'})]$$

$$\times \exp[-\beta(E_K^0 + E_{K'}^0)/2]\}\langle\psi_{K'}(t)| . \tag{35}$$

If $\hat{D}(\mathbf{R}_1, \ldots, \mathbf{R}_N)$ is the density operator at point $(\mathbf{R}_1, \ldots, \mathbf{R}_N)$ in configuration space, then the probability density of the canonical ensemble at time t at this point is

$$D(\mathbf{R}_1, \ldots, \mathbf{R}_N, t) = Tr[\hat{D}\hat{\tau}_{can}(t)] = Tr[\hat{D}\{\hat{\tau}_0(t) - \hat{\mathfrak{F}}(t)\}]$$

$$= Tr[\hat{D}\hat{\tau}_0(t)] - Tr[\hat{D}\hat{\mathfrak{F}}(t)] . \tag{36}$$

The first term on the right-hand side of Eq. (36) is the pure-state probability density that has been employed in Ref. 1 to compute the total reaction probability. As can be seen, this result differs from the total canonical probability density by the terms involving $\hat{\mathfrak{F}}(t)$. The difference between the results will therefore involve the scalar product $\langle\psi_0(t)|\psi_1(t)\rangle$ integrated over the product configuration space, and, once again, we are led to a situation similar to Eq. (22). If this scalar product is zero or very small, then the probability density obtained from $\hat{\tau}_0(t)$ will be equal or nearly equal to that computed from $\hat{\tau}_{can}(t)$. In the next section, we present some numerical computation to assess the importance of the terms arising from $\hat{\mathfrak{F}}(t)$.

III. NUMERICAL ANALYSIS

Equations (35) and (36) give a quantitative prescription for the evaluation of the deviation of reaction probabilities computed using a pure-state initial wave function from those obtained from the density matrix for the canonical ensemble. As an illustrative example, we have examined numerically the deviation of the two procedures for the T + HD → TH + D collinear reaction at $T = 1000$ and $10\,000$ K. This latter temperature is sufficiently high to insure that both the $n = 0$ and $n = 1$ vibrational states make significant contributions to the total reaction probability.

The potential-energy surface employed for the (T, HD) system is the analytic fit obtained by Truhlar and Horowitz[5] to the accurate ab initio calculations of Liu and Siegbahn.[6] The pure-state wave packet was written in the form of Eq. (8) where $X_0(q_2)$ and $X_1(q_2)$ were taken to be the ground and first-excited state wave functions for the Morse oscillator approximating the HD potential. The details of the numerical procedures used to effect

TABLE I.   Rate coefficients for the T+HD→TH+D reaction at 1000 K and 10 000 K computed by pure-state wave packet methods using different vibrational-state phase factors. Close-coupling results are also given for comparison.

Temperature (K)	Pure-state wave packet [Eq. (8)]		Close-coupling[a]
	δ_1	K(cm/s)	K(cm/s)
1000	0	4.8×10^3	4.51×10^3
	$\pi/2$	4.3×10^3	
	π	4.3×10^3	
10 000	$-\pi/3$	2.64×10^4	
	0	2.54×10^4	
	$\pi/2$	2.69×10^4	
	$2\pi/3$	2.70×10^4	
	π	2.66×10^4	

[a] Reference 2.

TABLE III.   Computed absolute squares at $t \to \infty$ for various overlap integrals for the T+HD→TH+D system.

	Integral	Value
(a)	$\left| \int\int_T \psi_0^* \, \psi_1 \, d\tau \right|$	3.806×10^{-5}
(b)	$\left| \int\int_R \psi_0^* \, \psi_1 \, d\tau \right|^2$	3.393×10^{-5}
(c)	$\left| \int\int_P \psi_0^* \, \psi_1 \, d\tau \right|^2$	0.464×10^{-5}

[a] Integration over total configuration space.
[b] Integration over reactant configuration space.
[c] Integration over product configuration space.

the evolution of $\psi_{1,0}(t_0)$ have previously been given.[1]

Table I gives the rate coefficients, K, computed using the pure-state probability density operator with $\psi_{1,0}$ given by Eq. (8) with $\delta_1 = -\pi/3$, 0, $\pi/2$, $2\pi/3$, and π. The thermal rate coefficient is obtained from $\langle P \rangle_{TD}^{1,0}$ using the relationship

$$K(T) = [k_B T/2\pi\mu]^{1/2} \langle P \rangle_{TD}^{1,0} , \qquad (37)$$

where μ is the (T, HD) reduced mass. The close-coupling result previously reported by Garrett, Truhlar, Grev, and Walker[2] is also given for comparison purposes. The rate coefficient computed using Eq. (8) is seen to show a slight dependence upon the phase factor. This could be due to a small contribution from the terms contained in $\hat{\mathfrak{F}}(t)$, or it might be an artifact attributable to the numerical errors involved in the evolution of the wave packet and in the computation of the required integrals over the product configuration space.

The total reaction probability for the T + HD → TH + D reaction at 10 000 K has been computed using the density operator for the canonical ensemble. This result is given in Table II where it is compared with the corresponding results using the pure-state density operator with various values for δ_1. As can be seen, the difference in total reaction probability between the pure-state and canonical ensemble computations corresponds to a variation of 1.9%–4.7%. As before, this variation could be the result of contributions from $\hat{\mathfrak{F}}(t)$ or from

numerical error.

In order to evaluate the importance of the phase factor more precisely, we have computed the integrals $\langle \psi_0 | \psi_1 \rangle$, $\langle \psi_0^R | \psi_1^R \rangle$, and $\langle \psi_0^P | \psi_1^P \rangle$ at $t \to \infty$ directly. $\psi_0(t)$ and $\psi_1(t)$ were evolved independently, and the real and imaginary parts of the wave functions at $t \to \infty$ were stored on disk. The above integrals were then computed from the stored values of $\psi_0(t \to \infty)$ and $\psi_1(t \to \infty)$ using a composite Simpson's rule integration procedure. In general, the integrals are complex. The values of their absolute squares are given in Table III. The computed value of $\langle \psi_0(t \to \infty) | \psi_1(t \to \infty) \rangle$ gives a direct measure of the numerical error present in these computations. From Eq. (21), it is seen that this integral should rigorously be zero. The result for this integral given in Table III therefore shows that the computed reaction probabilities are correct only to two significant digits. The numerical error enters in the third significant digit. The result is consistent with previous error estimates obtained by back evolution methods.[1] The computed values for $\langle \psi_0^R | \psi_1^R \rangle$ and $\langle \psi_0^P | \psi_1^P \rangle$ as $t \to \infty$ are both nonzero but their magnitude is within the numerical error of the calculations. Consequently, within the numerical accuracy of the present study, Eq. (23) holds. However, a nonzero contribution from the terms in $\hat{\mathfrak{F}}(t)$ that is of the order 10^{-3} or less cannot be excluded.

IV. DISCUSSION

We have analyzed the accuracy of the procedure of using time-dependent evolution of pure-state wave packets to obtain the total reaction probability of a canonical ensemble of states. We have approached this question by first examining the dependence of the pure-state results upon the relative phases of the orthogonal eigenfunctions included in the pure-state description of the system. Secondly, we have formulated the problem in terms of the probability density operator of the canonical ensemble and then compared the resulting expressions for the total reaction probability with those obtained using the pure-state formulation.

It has been shown that $\langle P \rangle_{TD}^{1,0}$ will be independent of the relative phases of the orthogonal vibrational eigenfunc-

TABLE II.   Total reaction probabilities for T+HD→TH+D at 10 000 K computed using pure-state and canonical ensemble density operators.

	Total reaction probability $\langle P \rangle_{TD}^{1,0}$		
δ_1	Pure-state wave packet	Canonical ensemble	Difference
$-\pi/3$	0.089	0.087	0.002
0	0.086	0.087	0.001
$\pi/2$	0.091	0.087	0.004
$2\pi/3$	0.091	0.087	0.004
π	0.090	0.087	0.003

tions included in the initial wave packet provided $\langle \psi_0^P | \psi_1^P \rangle = 0$ as $t \to \infty$. Direct numerical evaluation of this integral for the T + HD → TH + D system has shown it to be very close to zero. The deviation from zero has been shown to be within the numerical error of the calculations by direct evaluation of $\langle \psi_0 | \psi_1 \rangle$ as $t \to \infty$. Consequently, Eq. (23) is shown to hold for the T + HD system within the numerical accuracy of the method. The general validity of Eq. (23) is equivalent to an important and useful point related to state-to-state chemistry that orthogonal reactant states evolve into orthogonal product states in product space as well as in reactant space. In the notation of this paper, this point may be expressed more clearly: if $\langle \psi_0(t=0) | \psi_1(t=0) \rangle = 0$, then $\langle \psi_0^R | \psi_1^R \rangle = \langle \psi_0^P | \psi_1^P \rangle = 0$ for all values of t.

A comparison of the pure-state and canonical density operators shows that the difference between these operators involves a summation of terms that contain cross products between the orthogonal eigenfunctions representing the states present in the canonical ensemble. The relative importance of the difference terms has been evaluated numerically for the T + HD → TH + D collinear reaction at 1000 and 10 000 K. For this system, the difference in the total canonical and pure-state reaction probabilities at 10 000 K is never more than 4% regardless of the relative phases of the different orthogonal states.

Independent computation of $\langle \psi_0 | \psi_1 \rangle$ at $t \to \infty$ shows that the numerical error in the present calculations is on the order of 10^{-3}. Consequently, the differences between the reaction probabilities obtained from the evolution of the pure-state wave packet given by Eq. (8) and the canonical ensemble are within the numerical error of the method. It is not clear whether the results obtained from $\hat{T}_0(t)$ and $\hat{T}_{can}(t)$ will always be in close agreement or whether there will exist cases where there will be a substantial difference between the results. If the latter is true, then it will be useful to determine the conditions under which $\hat{T}_0(t)$ may accurately replace $\hat{T}_{can}(t)$.

It should be noted that the formation of pure-state initial wave packets by combining various orthogonal translational states without concern for their relative phases has been a standard procedure[7] since the pioneering work of Mazur and Rubin.[8] The present analysis and the agreement of the wave packet results[1] with close-coupling calculations[2,9] provides justification for this approach. Finally, we note that if $\langle \psi_0^P | \psi_1^P \rangle \neq 0$, then $\langle P \rangle_{TD}^{1,0}$ calculated from the pure-state initial wave packet defined by Eq. (8) will depend upon δ_1, and the results may differ significantly from the canonical reaction probabilities. This will lead to the necessity of reinvestigating work which employs pure-state translational wave packets without concern for the relative phases of the translational states.[1,7,8]

ACKNOWLEDGMENTS

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