

Towards a state-to-state transition state theory

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We assume that, having arrived at the transition state, the branching into the different product states is independent of the initial quantum states of the reactants. This assumption plus the familiar transition state approximation (that the reaction rate is the rate of the passage across the barrier) yields an expression for the state-to-state cross section in terms of the state-to-all one, as well as microcanonical rate constants. Models, adiabatic correlations, purely statistical considerations, or collinear computations can provide the required input for the theory. Exact quantal computations on the $3D\ H + H_2$ reaction are found to satisfy the assumed factorization quite well. Furthermore, reaction probabilities derived from a line-of-centers model, with a barrier height dependent on the approach angle, account for the probabilities derived from the exact quantal computation.

I. INTRODUCTION

There are a number of motivations for the development to be discussed in this paper. One, mentioned in the title, is to formulate a state-to-state theory which, upon summing over product states and averaging over an equilibrium distribution of reactant states, will yield the conventional transition state theory TST.¹

Another is to provide a framework where exact collinear reaction probabilities can be used to compute three-dimensional state-to-state cross sections.² Alternatively, one can employ reaction probabilities derived from models for such calculations. One such model³ based on a line-of-centers approach is used here to compare against the results of exact quantal computations⁴ for the $3D\ H + H_2$ reaction. Then, one can regard the present development as a natural extension of the phase space theory⁵ to reactions with a tight transition state.^{6,7} These and other topics closely related to our development have received extensive discussion in the literature. Hence, the list of references in this paper can in no way be complete and we apologize beforehand for our omissions.

The discussion in this paper considers systems at a constant total energy. Results at a given temperature can be obtained by appropriate Boltzmann averages and will be presented elsewhere with additional applications.

In Sec. II we derive a set of exact relations involving state-to-state, state-to-all, and all-to-all cross sections or rate constants in a form appropriate for subsequent TST developments. In Sec. III we introduce a state-to-state reaction cross section factorization, and use it to develop a state-to-state TST. That factorization is tested in Sec. IV against exact $3D\ H + H_2$ quantal calculations. In Sec. V we show that in an adiabatic formalism the condition for validity of the corresponding all-to-all microcanonical rate constant is equivalent to that for the thermal TST one derived previously.⁸ A

simple line-of-centers model is used in Sec. VI to calculate state-to-state and state-to-all cross sections for that reaction and shown to be in agreement with accurate quantum mechanical calculations. Section VII summarizes the conclusions reached.

II. STATE-TO-STATE, STATE-TO-ALL, AND ALL-TO-ALL RELATIONS

Let us consider the partitioning of a polyatomic system into a pair of molecules designated by the arrangement channel index λ and let n_λ represent the set of quantum numbers needed to specify the internal states of those molecules when they are infinitely apart. Let $Q_{\lambda' n'_\lambda}^{\lambda n_\lambda}(E)$ be the integral cross section for the $\lambda n_\lambda \rightarrow \lambda' n'_\lambda$ process at total energy E , which is a bimolecular reaction for $\lambda' \neq \lambda$. The corresponding state-to-state rate constant is given by

$$K_{\lambda' n'_\lambda}^{\lambda n_\lambda}(E) = v_{\lambda n_\lambda}(E) Q_{\lambda' n'_\lambda}^{\lambda n_\lambda}(E) \\ = [k_{\lambda n_\lambda}^2(E)/\pi \hbar \rho_{\lambda n_\lambda}(E)] Q_{\lambda' n'_\lambda}^{\lambda n_\lambda}(E), \quad (2.1)$$

where $\rho_{\lambda n_\lambda}$ is the density of states per unit volume of the relative translational motion of the λ molecules, and $k_{\lambda n_\lambda}$ and $v_{\lambda n_\lambda}$ the corresponding wave number and velocity. These three quantities are interrelated by

$$\rho_{\lambda n_\lambda}(E) = (1/h^3) 4\pi \mu_\lambda^2 v_{\lambda n_\lambda} = (1/h^2) 2\mu_\lambda k_{\lambda n_\lambda}, \quad (2.2)$$

where μ_λ is the reduced mass of the pair of λ molecules. Summing Eq. (2.1) over n'_λ gives

$$K_{\lambda'}^{\lambda n_\lambda}(E) = [k_{\lambda n_\lambda}^2(E)/\pi \hbar \rho_{\lambda n_\lambda}(E)] Q_{\lambda'}^{\lambda n_\lambda}(E), \quad (2.3)$$

where the $Q_{\lambda'}^{\lambda n_\lambda}$ and $K_{\lambda'}^{\lambda n_\lambda}$ are, respectively, the state-to-all cross section and rate constant. Multiplying Eq. (2.3) by $\rho_{\lambda n_\lambda}$ and summing over n_λ gives⁹

$$K_{\lambda'}^\lambda(E) = [\pi \hbar \rho_\lambda(E)]^{-1} \sum_{n_\lambda} k_{\lambda n_\lambda}^2(E) Q_{\lambda'}^{\lambda n_\lambda}(E), \quad (2.4)$$

where ρ_λ and $K_{\lambda'}^\lambda$ are, respectively, the total density of states

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per unit volume and the all-to-all microcanonical rate constant defined by⁹

$$\rho_\lambda(E) = \sum_{n_\lambda} \rho_{\lambda n_\lambda}(E) \quad (2.5)$$

and

$$K_{\lambda'}^{\lambda}(E) = [\rho_\lambda(E)]^{-1} \sum_{n_\lambda} \rho_{\lambda n_\lambda}(E) K_{\lambda'}^{\lambda n_\lambda}(E). \quad (2.6)$$

Equations (2.1), (2.3), and (2.4) express the state-to-state, state-to-all, and all-to-all rate constants at a fixed total energy in terms of appropriate cross sections and serve as a bridge between dynamics and rate theory.^{10,11}

According to the principle of microscopic reversibility⁹

$$k_{\lambda n_\lambda}^2(E) Q_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}(E) = k_{\lambda' n_{\lambda'}}^2(E) Q_{\lambda n_\lambda}^{\lambda' n_{\lambda'}}(E). \quad (2.7)$$

Summing over $n_{\lambda'}$ furnishes

$$k_{\lambda n_\lambda}^2 Q_{\lambda'}^{\lambda n_\lambda} = \pi h \rho_{\lambda'}(E) K_{\lambda n_\lambda}^{\lambda'}(E), \quad (2.8)$$

where $K_{\lambda n_\lambda}^{\lambda'}$ is the total rate constant into state n_λ of λ reaction products from a microcanonical ensemble of λ' reagents at energy E and is given by

$$K_{\lambda n_\lambda}^{\lambda'}(E) = \rho_{\lambda'}^{-1}(E) \sum_{n_{\lambda'}} \rho_{\lambda' n_{\lambda'}}(E) K_{\lambda n_\lambda}^{\lambda' n_{\lambda'}}(E). \quad (2.9)$$

In the spirit of TST, we write the factor $h \rho_{\lambda'} K_{\lambda n_\lambda}^{\lambda'}$ on the right-hand side of Eq. (2.8) as the product of a number $N_{\lambda'}^{\lambda}$ and a probability $P_{\lambda n_\lambda}^{\lambda'}$ and rewrite that equation as

$$k_{\lambda n_\lambda}^2 Q_{\lambda'}^{\lambda n_\lambda} = \pi N_{\lambda'}^{\lambda}(E) P_{\lambda n_\lambda}^{\lambda'}(E), \quad (2.10)$$

where the $P_{\lambda n_\lambda}^{\lambda'}$ are normalized over n_λ :

$$\sum_{n_\lambda} P_{\lambda n_\lambda}^{\lambda'}(E) = 1. \quad (2.11)$$

Equation (2.10) is not an approximation, but together with Eq. (2.11) it constitutes a unique definition of the quantities $N_{\lambda'}^{\lambda}$ and $P_{\lambda n_\lambda}^{\lambda'}$. Indeed, we obtain immediately from these equations the equivalent defining expressions

$$N_{\lambda'}^{\lambda}(E) = \pi^{-1} \sum_{n_\lambda} k_{\lambda n_\lambda}^2(E) Q_{\lambda'}^{\lambda n_\lambda}(E) \quad (2.12)$$

and

$$P_{\lambda n_\lambda}^{\lambda'}(E) = \frac{k_{\lambda n_\lambda}^2(E) Q_{\lambda'}^{\lambda n_\lambda}(E)}{\sum_{\tilde{n}_\lambda} k_{\lambda \tilde{n}_\lambda}^2(E) Q_{\lambda'}^{\lambda \tilde{n}_\lambda}(E)}. \quad (2.13)$$

It is easy to prove from microscopic reversibility that $N_{\lambda'}^{\lambda}$ and $N_{\lambda}^{\lambda'}$ are equal, which is an important property for a TST formulation, as developed in Sec. III, since these numbers will be eventually associated with the number of states of the transition state accessible at energy E and should not depend on whether we approach it from the λ or the λ' directions.

Replacing Eq. (2.10) on the right-hand side of Eq. (2.4) and using Eq. (2.11) gives for the microcanonical rate constant¹⁰⁻¹²

$$K_{\lambda'}^{\lambda}(E) = \frac{N_{\lambda'}^{\lambda}(E)}{h \rho_\lambda(E)}. \quad (2.14)$$

This expression, although exact, has the same form as the

corresponding TST equation, in which N , rather than being defined by Eq. (2.12), is the number of transition state states mentioned in the previous paragraph.

Let us now define a set of state-to-state reaction probabilities¹³

$$\bar{P}_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}(E) = Q_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}(E) / Q_{\lambda'}^{\lambda n_\lambda}(E), \quad (2.15)$$

which are obviously normalized over $n_{\lambda'}$. Using Eq. (2.10) we get

$$Q_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}(E) = [\pi / k_{\lambda n_\lambda}^2(E)] N_{\lambda'}^{\lambda}(E) P_{\lambda n_\lambda}^{\lambda'}(E) \bar{P}_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}(E). \quad (2.16)$$

Once more, this expression is exact but has a form appropriate for TST. In the same spirit we define the transmission factors

$$T_{\lambda n_\lambda}^{\lambda'}(E) = P_{\lambda n_\lambda}^{\lambda'}(E) N_{\lambda'}^{\lambda}(E) \quad (2.17)$$

and

$$\bar{T}_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}(E) = \bar{P}_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}(E) N_{\lambda'}^{\lambda}(E) \quad (2.18)$$

in terms of which Eq. (2.16) can be rewritten in the equivalent exact form

$$Q_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}(E) = [\pi / k_{\lambda n_\lambda}^2(E)] T_{\lambda n_\lambda}^{\lambda'}(E) \bar{T}_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}(E) / N_{\lambda'}^{\lambda}(E). \quad (2.19)$$

Equations (2.16) or (2.19) are useful for the development of state-to-state reaction cross section theories by replacing in them the N , P , \bar{P} , T , or \bar{T} by appropriate approximations.

III. STATE-TO-STATE REACTION CROSS SECTION FACTORIZATION AND TRANSITION STATE THEORY

So far we have only used formal developments, without any approximations. We will now make the first one, by assuming that the following relation holds:

$$\bar{P}_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}(E) = P_{\lambda' n_{\lambda'}}^{\lambda}. \quad (3.1)$$

This expression is equivalent to

$$\frac{Q_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}(E)}{Q_{\lambda'}^{\lambda n_\lambda}(E)} = \frac{k_{\lambda n_\lambda}^2(E) Q_{\lambda'}^{\lambda n_\lambda}(E)}{\sum_{\tilde{n}_\lambda} k_{\lambda \tilde{n}_\lambda}^2(E) Q_{\lambda'}^{\lambda \tilde{n}_\lambda}(E)}. \quad (3.2)$$

Replacement of Eq. (3.1) into Eq. (2.15) gives

$$Q_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}(E) = Q_{\lambda'}^{\lambda n_\lambda}(E) P_{\lambda' n_{\lambda'}}^{\lambda}(E). \quad (3.3)$$

This factorization implies that the n_λ , $n_{\lambda'}$ dependence of $Q_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}$ can be expressed as the product of a factor that depends on n_λ only and one on $n_{\lambda'}$ only.¹⁴ This is in the spirit of TST, in the sense that the partitioning of the reaction flux among the products should not depend on how the system reached its transition state.

Using the definition of $Q_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}$ and the microscopic reversibility expression (2.7) we rewrite Eq. (3.2) as

$$\frac{Q_{\lambda' n_{\lambda'}}^{\lambda n_\lambda}(E)}{Q_{\lambda'}^{\lambda n_\lambda}(E)} = \frac{\sum_{\tilde{n}_\lambda} k_{\lambda \tilde{n}_\lambda}^2(E) Q_{\lambda' n_{\lambda'}}^{\lambda \tilde{n}_\lambda}(E)}{\sum_{\tilde{n}_\lambda} k_{\lambda \tilde{n}_\lambda}^2(E) Q_{\lambda'}^{\lambda \tilde{n}_\lambda}(E)}. \quad (3.4)$$

Generally speaking, it is not expected that this expression should be valid, since it formally contains an n_λ dependence on its left-hand side but not on its right-hand side. However, if the factorization property (3.3) is satisfied, the n_λ dependencies in the numerator and denominator of the left-hand

TABLE I. Rotational branching probabilities \bar{P}_j^j for $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ at $E = 0.6$ eV.

$j \backslash j'$	0	1	2
0	0.262	0.473	0.265
1	0.255	0.482	0.263
2	0.257	0.472	0.272

side of Eq. (3.4) cancel, eliminating this inconsistency.

With the help of Eq. (3.1), we can cast Eqs. (2.16) and (2.19) in the approximate form

$$Q_{\lambda' n_{\lambda'}}^{\lambda n_{\lambda}}(E) = [\pi/k_{\lambda n_{\lambda}}^2(E)] N_{\lambda'}^{\lambda}(E) P_{\lambda n_{\lambda}}^{\lambda'}(E) P_{\lambda' n_{\lambda'}}^{\lambda}(E) \quad (3.5)$$

$$= [\pi/k_{\lambda n_{\lambda}}^2(E)] T_{\lambda n_{\lambda}}^{\lambda'}(E) T_{\lambda' n_{\lambda'}}^{\lambda}(E) / N_{\lambda'}^{\lambda}(E).$$

The description of a test of this equation is given in Sec. IV.

We now introduce TST in Eq. (3.5) by replacing $N_{\lambda'}^{\lambda}(E)$ by $N_{\lambda'}^{\lambda}(E)$, the total number of transition state states¹⁵ or activation barrier tops whose energies do not exceed E . The most obvious way of defining such barrier is based on adiabatic correlations between the transition state and the states of the reagents.⁸ We also replace $P_{\lambda n_{\lambda}}^{\lambda'}$ by an approximate probability $P_{\lambda n_{\lambda}}^{\lambda' \text{app}}$, which is still normalized over n_{λ} as in Eq. (2.11) but is otherwise arbitrary, no longer needing to satisfy Eq. (2.13). We then get the following state-to-state TST cross section expression:

$$Q_{\lambda' n_{\lambda'}}^{\lambda n_{\lambda}}(E) = [\pi/k_{\lambda n_{\lambda}}^2(E)] N_{\lambda'}^{\lambda}(E) P_{\lambda n_{\lambda}}^{\lambda' \text{app}}(E) P_{\lambda' n_{\lambda'}}^{\lambda \text{app}}(E)$$

$$= [\pi/k_{\lambda n_{\lambda}}^2(E)] T_{\lambda n_{\lambda}}^{\lambda' \text{app}}(E) T_{\lambda' n_{\lambda'}}^{\lambda \text{app}}(E) / N_{\lambda'}^{\lambda}(E), \quad (3.6)$$

where the T^{app} are related to the corresponding P^{app} by an expression analogous to Eq. (2.17) in which $N_{\lambda'}^{\lambda}$ is replaced by $N_{\lambda'}^{\lambda}$. Replacement of this expression into Eq. (2.10) and

comparison of the result with Eq. (2.8) gives

$$\rho_{\lambda n_{\lambda}}(E) K_{\lambda'}^{\lambda n_{\lambda}}(E) = \frac{1}{h} N_{\lambda'}^{\lambda}(E) P_{\lambda n_{\lambda}}^{\lambda' \text{app}}(E). \quad (3.7)$$

Summing this expression over n_{λ} and using Eq. (2.6) and the normalization condition of the $P_{\lambda n_{\lambda}}^{\lambda' \text{app}}$ results finally in

$$K_{\lambda'}^{\lambda}(E) = \frac{N_{\lambda'}^{\lambda}(E)}{h \rho_{\lambda}(E)}. \quad (3.8)$$

This is the correct TST version of Eq. (2.14) and shows that regardless of the choice of the normalized model $P_{\lambda n_{\lambda}}^{\lambda' \text{app}}$ used for the calculation of the state-to-state cross section $Q_{\lambda' n_{\lambda'}}^{\lambda n_{\lambda}}$, we will always get the correct TST microcanonical all-to-all rate constant $K_{\lambda'}^{\lambda}(E)$.

IV. A TEST OF FACTORIZATION

Using the state-to-state reaction cross sections for the $\text{H} + \text{H}_2$ system obtained from an exact quantal calculation,⁴ we have tested the factorization assumption of Sec. III. The energy used was 0.6 eV, for which only the ground vibrational state of the reagent and product is open.

The first test was on the summed and averaged cross sections. Replacing in Eq. (2.15) n_{λ} by j , m_j and summing over m_j' and averaging over m_j we get, for the summed and averaged cross sections,

$$Q_j^j = Q^j \bar{P}_j^j. \quad (4.1)$$

Using the values of $Q_{j m_j'}^{j m_j}$ of Table VI of Ref. 4 (and reproduced in Table II of this paper) we calculated the Q_j^j and Q^j , and from those we obtained the values of \bar{P}_j^j given in Table I. From the relatively small variation of these quantities with j we conclude that the factorization of Q_j^j , into a j dependent (but j' independent) factor and a j' dependent (but j independent) factor is a very good one for this case. This is in agreement with the Franck-Condon model proposed and tested previously.¹⁶

TABLE II. Integral reactive cross sections $Q_{j m_j'}^{j m_j}$ for the $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction at $E = 0.6$ eV.^a

$j m_j \backslash j' m_j'$	00	11	10	1-1	22	21	20	2-1	2-2
00	0.432e-01	0.322e-02	0.717e-01	0.322e-02	0.227e-03	0.474e-02	0.338e-01	0.474e-02	0.227e-03
11	0.432e-01	0.337e-02	0.726e-01	0.337e-02	0.226e-03	0.462e-02	0.327e-01	0.462e-02	0.226e-03
10	0.337e-02	0.549e-03	0.596e-02	0.835e-03	0.488e-04	0.709e-03	0.261e-02	0.127e-02	0.774e-04
1-1	0.354e-02	0.276e-03	0.595e-02	0.276e-03	0.185e-04	0.379e-03	0.268e-02	0.379e-03	0.185e-04
22	0.751e-01	0.596e-02	0.128	0.596e-02	0.380e-03	0.812e-02	0.578e-01	0.812e-02	0.380e-03
21	0.761e-01	0.595e-02	0.128	0.595e-02	0.398e-03	0.815e-02	0.577e-01	0.815e-02	0.398e-03
20	0.337e-02	0.835e-03	0.596e-02	0.549e-03	0.774e-04	0.127e-02	0.261e-02	0.709e-03	0.488e-04
2-1	0.354e-02	0.276e-03	0.595e-02	0.276e-03	0.185e-04	0.379e-03	0.268e-02	0.379e-03	0.185e-04
2-2	0.262e-03	0.538e-04	0.419e-03	0.855e-04	0.111e-04	0.811e-04	0.209e-03	0.134e-03	0.146e-04
00	0.432e-01	0.322e-02	0.717e-01	0.322e-02	0.227e-03	0.474e-02	0.338e-01	0.474e-02	0.227e-03
11	0.432e-01	0.337e-02	0.726e-01	0.337e-02	0.226e-03	0.462e-02	0.327e-01	0.462e-02	0.226e-03
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1-1	0.354e-02	0.276e-03	0.595e-02	0.276e-03	0.185e-04	0.379e-03	0.268e-02	0.379e-03	0.185e-04
22	0.751e-01	0.596e-02	0.128	0.596e-02	0.380e-03	0.812e-02	0.578e-01	0.812e-02	0.380e-03
21	0.761e-01	0.595e-02	0.128	0.595e-02	0.398e-03	0.815e-02	0.577e-01	0.815e-02	0.398e-03
20	0.337e-02	0.835e-03	0.596e-02	0.549e-03	0.774e-04	0.127e-02	0.261e-02	0.709e-03	0.488e-04
2-1	0.354e-02	0.276e-03	0.595e-02	0.276e-03	0.185e-04	0.379e-03	0.268e-02	0.379e-03	0.185e-04
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1-1	0.354e-02	0.276e-03	0.595e-02	0.276e-03	0.185e-04	0.379e-03	0.268e-02	0.379e-03	0.185e-04
22	0.751e-01	0.596e-02	0.128	0.596e-02	0.380e-03	0.812e-02	0.578e-01	0.812e-02	0.380e-03
21	0.761e-01	0.595e-02	0.128	0.595e-02	0.398e-03	0.815e-02	0.577e-01	0.815e-02	0.398e-03
20	0.337e-02	0.835e-03	0.596e-02	0.549e-03	0.774e-04	0.127e-02	0.261e-02	0.709e-03	0.488e-04
2-1	0.354e-02	0.276e-03	0.595e-02	0.276e-03	0.185e-04	0.379e-03	0.268e-02	0.379e-03	0.185e-04
2-2	0.262e-03	0.538e-04	0.419e-03	0.855e-04	0.111e-04	0.811e-04	0.209e-03	0.134e-03	0.146e-04
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11	0.432e-01	0.337e-02	0.726e-01	0.337e-02	0.226e-03	0.462e-02	0.327e-01	0.462e-02	0.226e-03
10	0.337e-02	0.549e-03	0.596e-02	0.835e-03	0.488e-04	0.709e-03	0.261e-02	0.127e-02	0.774e-04
1-1	0.354e-02	0.276e-03	0.595e-02	0.276e-03	0.185e-04	0.379e-03	0.268e-02	0.379e-03	0.185e-04
22	0.751e-01	0.596e-02	0.128	0.596e-02	0.380e-03	0.812e-02	0.578e-01	0.812e-02	0.380e-03
21	0.761e-01	0.595e-02	0.128	0.595e-02	0.398e-03	0.815e-02	0.577e-01	0.815e-02	0.398e-03
20	0.337e-02	0.835e-03	0.596e-02	0.549e-03	0.774e-04	0.127e-02	0.261e-02	0.709e-03	0.488e-04
2-1	0.354e-02	0.276e-03	0.595e-02	0.276e-03	0.185e-04	0.379e-03	0.268e-02	0.379e-03	0.185e-04
2-2	0.262e-03	0.538e-04	0.419e-03	0.855e-04	0.111e-04	0.811e-04	0.209e-03	0.134e-03	0.146e-04

^a The top number in each entry is the exact quantal value from Ref. 4, and the bottom one the result of a least-mean-square fit of Eq. (3.5).

In order to test the detailed state-to-state factorization assumption, we least-mean-square fitted the mentioned $Q_{j m_j}^{j m_j}$ values by Eq. (3.5), using N and the six quantities $P_{j|m_j|}$ ($j = 0, 1, 2$) as parameters. The results are given in Table II, where the top number in each entry represents the accurate quantal calculation of Ref. 4 and the lower one the fitted values. The resulting optimal probability parameters are given in the second column of Table III. From these parameters, we can calculate the P_j by summing over the m_j . The results are

$$P_0 = 0.262,$$

$$P_1 = 0.481,$$

$$P_2 = 0.257.$$

These values are in good agreement with the \bar{P}_j values of Table I, which is an indication of the overall validity of Eq. (3.1) when used for the summed and averaged quantities.

A comparison between the quantal and fitted cross sections of Table II indicates an overall qualitative agreement between them, showing that the factorization expression (3.5) is reasonable even on a single quantum state (rather than averaged) level.

The optimal value of N is 5.89. We used Eq. (30) of Ref. 17 to compute the transition state N_{\ddagger} for this system at 0.6 eV. The result was 172. Therefore, although the factorization assumption works quite well, microcanonical TST for this system at this energy is too large by a factor of about 30. This is consistent with deviations between thermal TST and quantal results found previously.^{4,8}

V. AN ADIABATIC STATE-TO-STATE TRANSITION STATE THEORY

As a result of the remarks of Sec. III, we conclude that a necessary and sufficient condition for the validity of microcanonical all-to-all TST is that $N_{\lambda\lambda'}^{\lambda\lambda'}(E)$, defined after Eq. (2.12), be equal to $N_{\lambda\lambda'}^{\lambda\lambda'}(E)$, defined after Eq. (3.5). On the other hand, it was previously proven⁸ that a necessary and sufficient condition for the validity of thermal adiabatic TST is that certain reaction probabilities (not those defined in this paper so far) be step functions of the energy. The mathematical language used on that proof invoked an adiabatic correlation between each state of the reagents and a corresponding state of the transition state. This implies, physically, that the evolution of the system follows separate adiabatic paths.

TABLE III. Probability parameters $P_{j m_j}$.

j, m_j	$P_{j m_j}$	
	a	b
0,0	0.262	0.172
1,0	0.440	0.417
1, ± 1	0.0204	0.02
2,0	0.198	0.308
2, ± 1	0.0280	0.03
2, ± 2	0.0014	0.0012

^a From fit to quantal results—See Sec. IV.

^b From model described in Sec. VI.

ways. Since the microcanonical TST involves less averaging than the thermal one, it is important to show that (in the framework of an adiabatic formalism) the condition for validity of the former is not less restrictive than that of the latter. We will now show that these two necessary and sufficient conditions are actually equivalent. As a result, we shall be able, from Eq. (2.13), to provide explicit expressions for the transition probabilities (or the transmission coefficients) which appear in Eq. (3.6). These are the central practical results of the section. Of course, both the proof and the explicit results are dependent on the aforementioned adiabatic correlation.

The state-to-state cross section can be expressed as

$$Q_{\lambda' n_{\lambda'}}^{\lambda n_{\lambda}}(E) = \frac{\pi}{k_{\lambda n_{\lambda}}^2(E)} \sum_{J=0}^{\infty} (2J+1) \left| [\mathbf{I} - \mathbf{S}'(E)]_{\lambda' n_{\lambda'}}^{\lambda n_{\lambda}} \right|^2, \quad (5.1)$$

where J is the system's total angular momentum quantum number, \mathbf{I} is the identity matrix and \mathbf{S}' a scattering matrix whose open part is symmetric and unitary. As a result, the J partial wave $\lambda n_{\lambda} \rightarrow \lambda' n_{\lambda'}$ transition probability defined by

$$P_{\lambda' n_{\lambda'}}^{J \lambda n_{\lambda}}(E) = \left| [\mathbf{S}'(E)]_{\lambda' n_{\lambda'}}^{\lambda n_{\lambda}} \right|^2 \quad (5.2)$$

is normalized with respect to $\lambda' n_{\lambda'}$:

$$\sum_{\lambda' n_{\lambda'}} P_{\lambda' n_{\lambda'}}^{J \lambda n_{\lambda}}(E) = 1. \quad (5.3)$$

Summing Eq. (5.1) over $n_{\lambda'}$ for $\lambda' \neq \lambda$ (i.e., for reactive processes) we get

$$Q_{\lambda}^{\lambda n_{\lambda}}(E) = \frac{\pi}{k_{\lambda n_{\lambda}}^2(E)} \sum_{JM} P_{\lambda}^{J \lambda n_{\lambda}}(E), \quad (5.4)$$

where

$$P_{\lambda}^{J \lambda n_{\lambda}}(E) = \sum_{n_{\lambda'}} P_{\lambda}^{J \lambda n_{\lambda}}(E) \quad (5.5)$$

is the state-to-all J partial wave reaction probability and M is the quantum number of the projection of the total angular momentum of the system on a laboratory-fixed axis. This probability is degenerate, with respect to M , lies (as any probability should) in the range

$$0 \leq P_{\lambda}^{J \lambda n_{\lambda}}(E) \leq 1 \quad (5.6)$$

and is normalized with respect to λ' but not with respect to n_{λ} . Replacing Eq. (5.4) into Eq. (2.12) we get the exact expression

$$N_{\lambda}^{\lambda}(E) = \sum_{u_{\lambda}} P_{\lambda}^{u_{\lambda}}(E), \quad (5.7)$$

where u_{λ} represents the set of quantum numbers J, M, n_{λ} .

As described previously,⁸ we now define a set of curvilinear coordinates consisting of a reaction coordinate q and a set of transverse coordinates \mathbf{p} , such that as q changes from $-\infty$ to 0 , $+\infty$ the system evolves from the separated reagent molecules in the λ arrangement channel, to the saddle point of the potential energy surface between arrangement channels λ and λ' to the separated product molecules in the λ' arrangement channel. Let $H(\mathbf{p}; q)$ be the Hamiltonian of the system for a fixed q , which describes the transverse \mathbf{p}

motion. For each q let us consider the simultaneous eigenfunctions of $H(\mathbf{p}; q)$, the square of the systems's total angular momentum and its component along the laboratory-fixed axis mentioned above. Let the corresponding energy eigenvalues be denoted by $E_{\lambda', \lambda}^{\lambda u_{\lambda}}(q)$. The $E_{\lambda', \lambda}^{\lambda u_{\lambda}}$ vs q curves usually represent barriers which at the saddle point have values $E_{\lambda', \lambda}^{\lambda u_{\lambda}}(0)$, and in general have maxima $E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max}$ which occur at values $q_{\lambda', \lambda}^{\lambda u_{\lambda}, \max}$ of q which depend on J and n_{λ} (in addition to λ and λ'). The $E_{\lambda', \lambda}^{\lambda u_{\lambda}}(-\infty)$ are the energy eigenvalues of the separated reagents, and are independent of λ' .

It was previously proven⁸ that if we use the $E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max}$ to calculate the transition state partition functions, a necessary and sufficient condition for the validity of all-to-all thermal adiabatic TST is that

$$p_{\lambda', \lambda}^{\lambda u_{\lambda}}(E) = H(E - E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max}) = 0 \text{ for } E < E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max} \quad (5.8)$$

$$= 1 \text{ for } E > E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max},$$

where H denotes the Heavyside step function. Note however that it is possible in principle to use alternative (i.e., nonadiabatic) correlation schemes to define the transition state energy levels and corresponding partition functions.¹⁸ The relation of adiabatic TST to generalized TST has been discussed recently.¹⁹ We now wish to calculate what $N_{\lambda', \lambda}^{\lambda}(E)$ Eq. (5.8) implies. Replacement of this equation into Eq. (5.7) shows that $N_{\lambda', \lambda}^{\lambda}(E)$ is in this case equal to the total number of $E_{\lambda', \lambda}^{\lambda u_{\lambda}}(q)$ barriers (i.e., u_{λ} sets) for which $E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max} < E$. This is by definition the number $N_{\lambda', \lambda}^{\lambda}(E)$ of transition state states whose energy is below E . If we changed the definition of $E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max}$ and used the new $E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max}$ to compute the partition functions of the transition state in this modified TST, the modified $N_{\lambda', \lambda}^{\lambda}(E)$ would still be the number of u_{λ} sets for which the new $E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max} < E$.²⁰ We thus conclude that Eq. (5.8) is a sufficient condition for the validity of

$$N_{\lambda', \lambda}^{\lambda}(E) = N_{\lambda', \lambda}^{\lambda}(E), \quad (5.9)$$

and therefore for the validity of microcanonical transition state theory.

Let us now show that Eq. (5.8) is a necessary condition for the validity of Eq. (5.9) and therefore that Eqs. (5.8) and (5.9) are equivalent. Indeed, replacing Eq. (5.9) into Eq. (5.7) and changing the summation index to \bar{u}_{λ} we get

$$\sum_{\bar{u}_{\lambda}} p_{\lambda', \lambda}^{\lambda \bar{u}_{\lambda}}(E) = N_{\lambda', \lambda}^{\lambda}(E). \quad (5.10)$$

We now order the u_{λ} according to a criterion of increasing $E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max}$ and designate by $u_{\lambda} - 1$ the set of quantum numbers which immediately precedes u_{λ} according to this criterion. Then, over the entire E range, defined by

$$E_{\lambda', \lambda}^{(\lambda u_{\lambda} - 1) \max} < E < E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max}, \quad (5.11)$$

the left-hand side of Eq. (5.10) contains $N_{\lambda', \lambda}^{\lambda}(E)$ terms. Since, according to Eq. (5.6), none of them can exceed unity, the only way in which Eq. (5.10) can be satisfied is if all those terms are unity over this energy range. By allowing E to assume all possible values, we conclude that we must have, in general,

$$p_{\lambda', \lambda}^{\lambda u_{\lambda}}(E) = 1 \text{ for } E > E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max}. \quad (5.12)$$

It is furthermore implicit in any adiabatic TST theory, microcanonical or thermal, that the corresponding $p_{\lambda', \lambda}^{\lambda u_{\lambda}}(E)$ must vanish for $E < E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max}$. As a result of this and of Eq. (5.12), Eq. (5.8) is valid, and the conditions for validity of adiabatic microcanonical and thermal TST are indeed equivalent, as stated.

We turn now to deriving explicit expressions for the transition probabilities in terms of the barrier heights (or energy levels) of the transition state. With the notation introduced after Eq. (5.7) we get, replacing Eq. (5.8) into Eq. (5.4), the adiabatic state-to-all TST cross section

$$Q_{\lambda', \lambda}^{\lambda n_{\lambda} \text{ATST}}(E) = \frac{\pi}{k_{\lambda, n_{\lambda}}^2(E)} \sum_{\bar{J}M} H(E - E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max}). \quad (5.13)$$

Using this result in Eqs. (2.13) and (3.5) we get the corresponding ATST probabilities and state-to-state cross sections. To implement a calculation of these quantities it suffices to obtain the heights $E_{\lambda', \lambda}^{\lambda u_{\lambda}, \max}$ of the barriers which adiabatically connect the λu_{λ} state of the reagents with the λ' products. A calculation of the cross section given by Eq. (5.13) for the $\text{H} + \text{H}_2$ exchange reaction has been reported previously.⁸

VI. MODEL REACTION PROBABILITIES

A model for the reaction cross section as a function of the orientation angle has been described in Ref. 3 and successfully tested for the $\text{H} + \text{D}_2$ reaction. Using θ for the angle between the diatom axis and the vector from the center of mass of the diatom to the atom the result is

$$\sigma_R(\theta) = \pi d^2 [1 - E_0(\theta)/E_{\text{tr}}], \quad (6.1)$$

where $E_0(\theta)$ is the barrier height for a fixed orientation and E_{tr} is the relative translation energy.

To convert Eq. (6.1) to quantal cross sections we average σ_R over a probability distribution of θ for a given j, m_j state, according to²¹

$$Q_R^{jm_j} = \int \sigma_R(\theta) |Y_{jm_j}(\theta, \varphi)|^2 \sin \theta d\theta d\varphi. \quad (6.2)$$

We performed this integration numerically, using the $E_0(\theta)$ from Fig. 1 of Ref. 3. The resulting $Q_R^{jm_j}$ cross sections were used in Eq. (2.10) to compute the model P_{jm_j} . The corresponding values are given in the third column of Table III. The agreement with the ones obtained by the accurate quantal cross sections described in Sec. IV and given in the second column of Table III is quite reasonable [but the numerical values based on Eq. (6.2) are sensitive to the precise value of the translational energy, particularly for $j = 2$]. Using these P_{jm_j} together with Eqs. (2.12) and (3.5) we can calculate the state-to-state cross sections from a remarkably simple model.

The addition theorem of spherical harmonics insures that the degeneracy-averaged reaction cross section

$$Q_R^j = \frac{1}{2j+1} \sum_{m_j} Q_R^{jm_j} \quad (6.3)$$

is given by the classical³ angle-averaged value

$$Q_R^j = \frac{1}{4\pi} \int \sigma_R(\theta) \sin \theta d\theta d\varphi. \quad (6.4)$$

VII. CONCLUSIONS

From a rather simple factorization assumption, given by Eq. (3.3), and tested for the $H + H_2$ system at 0.6 eV, we were able to obtain a simple expression which permits the calculation of state-to-state cross sections in terms of state-to-all cross sections. This assumption also permitted the development of a microcanonical TST theory for state-to-state and state-to-all processes.

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¹For a recent review see D. G. Truhlar, W. L. Hase, and J. T. Hynes, *J. Chem. Phys.* **87**, 2664 (1983).

²For the computation of state-to-all cross sections see J. M. Bowman, G. Z. Ju, and K. T. Lee, *J. Chem. Phys.* **86**, 2232 (1982), and references cited therein.

³R. D. Levine and R. B. Bernstein, *Chem. Phys. Lett.* **105**, 467 (1984).

⁴G. C. Schatz and A. Kuppermann, *J. Chem. Phys.* **65**, 4668 (1976).

⁵J. D. Light, *Discuss. Faraday Soc.* **44**, 14 (1967).

⁶The present results are not however the quantal version of the Strong Coupling Theory of A. F. Wagner and E. K. Parks, *J. Chem. Phys.* **65**, 4343

(1976). The essential difference is that the present state-to-state results are guaranteed to reproduce the transition state theory rate (Ref. 7).

⁷One can also consider extensions of the present results such that the averaged rate is that of the "unified" statistical theory [W. H. Miller, *J. Chem. Phys.* **65**, 2216 (1976)] which is intermediate between a "loose" and a "tight" transition state.

⁸A. Kuppermann, *J. Chem. Phys.* **83**, 171 (1979).

⁹R. D. Levine, *Quantum Mechanics of Molecular Rate Processes* (Clarendon, Oxford, 1969), p. 116.

¹⁰C. A. Coulson and R. D. Levine, *J. Chem. Phys.* **47**, 1235 (1967).

¹¹Reference 9, Section 2.6.3, Eq. (6.48).

¹²R. A. Marcus, *J. Chem. Phys.* **45**, 2138 (1966).

¹³These should not be confused with other kinds of reaction probabilities, such as the square of the absolute values of the elements of the reactive part of the scattering matrix introduced in Eq. (5.2).

¹⁴Factorization properties of this type have been invoked in a variety of contexts. Closest perhaps to our approach is its use to express the reaction rate out of specific states of the reagents in terms of reaction rates into selected states of the reagents from selected states of the products for the reversed reaction [K. G. Anlauf, D. H. Maylotte, J. C. Polanyi, and R. B. Bernstein, *J. Chem. Phys.* **51**, 5716 (1969) and R. A. Marcus, *ibid.* **53**, 604 (1970)]. Note however that the relation between the detailed forward and reverse rate constants can be obtained without invoking the factorization assumption [H. Kaplan, R. D. Levine, and J. Manz, *J. Chem. Phys.* **13**, 447 (1976) or R. D. Levine, in *The New World of Quantum Chemistry*, edited by B. Pullman and R. Parr (Reidel, Dordrecht, 1976)].

¹⁵Reference 9, Section 3.4.0, Eq. (4.15) in particular, or Ref. 12, Eq. (9) in particular. See also K. Morokuma, B. C. Eu, and M. Karplus, *J. Chem. Phys.* **51**, 5193 (1969) and S. H. Lin, K. H. Lau, and H. Eyring, *ibid.* **55**, 5657 (1971).

¹⁶G. C. Schatz and J. Ross, *J. Chem. Phys.* **62**, 3162 (1977).

¹⁷S. H. Harms and R. E. Wyatt, *J. Chem. Phys.* **62**, 3162 (1975).

¹⁸An example of such an alternative scheme is to use the principle of conservation of translational momentum [R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics* (Clarendon, Oxford, 1974), Chap. 1].

¹⁹D. G. Truhlar, A. D. Isaacson, and B. C. Garrett, in *The Theory of Chemical Reaction Dynamics*, edited by M. Baer (Chemical Rubber, Boca Raton, FL, 1984), Appendix I.

²⁰Even if two u_λ sets have the same $E_{\lambda}^{u_\lambda, \max}$ they contribute separately to $N_{\lambda}^{\lambda}(E)$. Therefore, these $E_{\lambda}^{u_\lambda, \max}$ have at least a $2J + 1$ degeneracy corresponding to the M quantum number.

²¹J. M. Bowman and K.-T. Lee, *J. Chem. Phys.* **72**, 5071 (1980).