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 quantum computations on the 3D H + H₂ 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 quantum 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 quantum computations ⁴ for the 3D H + H₂ reaction. Then, one can regard the present development as a natural extension of the phase space theory ⁵ 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 + H₂ quantum 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 nₐ represent the set of quantum numbers needed to specify the internal states of those molecules when they are infinitely apart. Let Qₜₐₙᵢ, λ (E) be the integral cross section for the λnₛ → λ' nᵢₛ process at total energy E, which is a bimolecular reaction for λ' ≠ λ. The corresponding state-to-rate constant is given by

Kₜₐₙᵢ, λ (E) = vₜₐₙᵢ (E) Qₜₐₙᵢ, λ (E)

= [kₜₐₙᵢ (E) / πₚ λₐₙᵢ (E)] Qₜₐₙᵢ, λ (E),  (2.1)

where ρₜₐₙᵢ is the density of states per unit volume of the relative translational motion of the λ molecules, and kₜₐₙᵢ and vₜₐₙᵢ the corresponding wave number and velocity. These three quantities are interrelated by

ρₜₐₙᵢ (E) = (1/ℏ³) ₐₚₜₐₙᵢ vₜₐₙᵢ = (1/ℏ²) ₐₚₜₐₙᵢ kₜₐₙᵢ,  (2.2)

where μₐ is the reduced mass of the pair of λ molecules. Summing Eq. (2.1) over nᵢₛ gives

Kₜₐₙ, λ = kₜₐₙ (E) / πₚ λₐₙ (E) Qₜₐₙ (E),  (2.3)

where the Qₜₐₙ, λ and Kₜₐₙ, λ are, respectively, the state-to-all cross section and rate constant. Multiplying Eq. (2.3) by ρₜₐₙ and summing over nₛ gives

Kₜₐ (E) = [πₚ λ (E)]⁻¹ ∑ₐₙₜₐₙ (E) Qₜₐₙ (E),  (2.4)

where ρₜ and Kₜₐ are, respectively, the total density of states

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*Contribution No. 7150.
per unit volume and the all-to-all microcanonical rate constant defined by
\[ \rho_\lambda(E) = \sum_{\alpha} \rho_{\lambda,\alpha}(E) \] (2.5)
and
\[ K_\lambda^A(E) = [\rho_\lambda(E)]^{-1} \sum_{\alpha} \rho_{\lambda,\alpha}(E) K_{\lambda,\alpha}(E). \] (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 reversibility\(^9\)
\[ k_{\lambda,\alpha}^A(E) Q_{\lambda,\alpha}(E) = k_{\lambda,\alpha}^A(E) Q_{\lambda,\alpha}(E). \] (2.7)
Summing over \(n_\lambda^A\) furnishes
\[ k_{\lambda,\alpha}^A(E) = \pi h \rho_\lambda(E) K_{\lambda,\alpha}(E), \] (2.8)
where \(K_{\lambda,\alpha}\) is the total rate constant into state \(n_\lambda\) of \(\lambda\) reaction products from a microcanonical ensemble of \(\lambda\) reagents at energy \(E\) and is given by
\[ K_{\lambda,\alpha}(E) = \rho_\lambda^{-1}(E) \sum_{\alpha} \rho_{\lambda,\alpha}(E) K_{\lambda,\alpha}(E). \] (2.9)
In the spirit of TST, we write the factor \(h \rho_\lambda(E) K_{\lambda,\alpha}(E)\) on the right-hand side of Eq. (2.8) as the product of a number \(N_{\lambda}^A\) and a probability \(P_{\lambda,\alpha}(E)\) and rewrite that equation as
\[ k_{\lambda,\alpha}^A(E) = \pi N_{\lambda}^A(E) P_{\lambda,\alpha}(E), \] (2.10)
where the \(P_{\lambda,\alpha}(E)\) are normalized over \(\alpha:\)
\[ \sum_{\alpha} P_{\lambda,\alpha}(E) = 1. \] (2.11)
Equation (2.10) is not an approximation, but together with Eq. (2.11) it constitutes a unique definition of the quantities \(N_{\lambda}^A\) and \(P_{\lambda,\alpha}\). Indeed, we obtain immediately from these equations the equivalent defining expressions
\[ N_{\lambda}^A(E) = \pi^{-1} \sum_{\alpha} k_{\lambda,\alpha}^A(E) Q_{\lambda,\alpha}(E) \] (2.12)
and
\[ P_{\lambda,\alpha}(E) = \frac{k_{\lambda,\alpha}^A(E) Q_{\lambda,\alpha}(E)}{\sum_{\alpha} k_{\lambda,\alpha}^A(E) Q_{\lambda,\alpha}(E)}. \] (2.13)
It is easy to prove from microscopic reversibility that \(N_{\lambda}^A\) and \(N_{\lambda}^A\) 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 which direction we approach it from the \(\lambda\) or the \(\lambda\)' directions.
Replacig Eq. (2.10) on the right-hand side of Eq. (2.4) and using Eq. (2.11) gives for the microcanonical rate constant\(^{10-12}\)
\[ K_\lambda^A(E) = \frac{N_{\lambda}^A(E)}{\pi h \rho_\lambda(E)}. \] (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 probabilities\(^3\)
\[ \overline{P}_{\lambda,\alpha}(E) = Q_{\lambda,\alpha}(E) / Q_{\lambda,\alpha}(E), \] (2.15)
which are obviously normalized over \(n_\lambda\). Using Eq. (2.10) we get
\[ Q_{\lambda,\alpha}(E) = \left[ \pi / k_{\lambda,\alpha}(E) \right] N_{\lambda}^A(E) P_{\lambda,\alpha}(E) \overline{P}_{\lambda,\alpha}(E). \] (2.16)
Once more, this expression is exact but has a form appropriate for TST. In the same spirit we define the transmission factors
\[ T_{\lambda,\alpha}(E) = P_{\lambda,\alpha}(E) / N_{\lambda}^A(E) \] (2.17)
and
\[ \overline{T}_{\lambda,\alpha}(E) = \overline{P}_{\lambda,\alpha}(E) / N_{\lambda}^A(E) \] (2.18)
in terms of which Eq. (2.16) can be rewritten in the equivalent exact form
\[ Q_{\lambda,\alpha}(E) = \left[ \pi / k_{\lambda,\alpha}(E) \right] T_{\lambda,\alpha}(E) \overline{T}_{\lambda,\alpha}(E) / N_{\lambda}^A(E). \] (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 \(N, P, \overline{P}, T, \bar{T}\) 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:
\[ \overline{P}_{\lambda,\alpha}(E) = P_{\lambda,\alpha}(E). \] (3.1)
This expression is equivalent to
\[ \frac{Q_{\lambda,\alpha}(E)}{Q_{\lambda,\alpha}(E)} = \frac{k_{\lambda,\alpha}^A(E) \overline{Q}_{\lambda,\alpha}(E)}{\sum_{\alpha} k_{\lambda,\alpha}^A(E) \overline{Q}_{\lambda,\alpha}(E)}. \] (3.2)
Replacement of Eq. (3.1) into Eq. (2.15) gives
\[ Q_{\lambda,\alpha}(E) = \overline{Q}_{\lambda,\alpha}(E) P_{\lambda,\alpha}(E). \] (3.3)
This factorization implies that the \(n_\lambda, n_\lambda\) dependence of \(Q_{\lambda,\alpha}(E)\) can be expressed as the product of a factor that depends on \(n_\lambda\) 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 \(Q_{\lambda,\alpha}(E)\) and the microscopic reversibility expression (2.7) we rewrite Eq. (3.2) as
\[ \frac{Q_{\lambda,\alpha}(E)}{Q_{\lambda,\alpha}(E)} = \frac{\sum_{\alpha} k_{\lambda,\alpha}^A(E) Q_{\lambda,\alpha}(E)}{\sum_{\alpha} k_{\lambda,\alpha}^A(E) Q_{\lambda,\alpha}(E)}. \] (3.4)
Generally speaking, it is not expected that this expression should hold, since it formally contains an \(n_\lambda\) dependence on its left-hand side but not on its right-hand side. However, if the factorization property (3.3) is satisfied, the \(n_\lambda\) dependencies in the numerator and denominator of the left-hand
TABLE I: Rotational branching probabilities $P_f$ for $H + H_2 \rightarrow H_2 + H$ at $E = 0.6 \text{ eV}$.

<table>
<thead>
<tr>
<th>$j$</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.262</td>
<td>0.473</td>
<td>0.265</td>
</tr>
<tr>
<td>1</td>
<td>0.255</td>
<td>0.482</td>
<td>0.263</td>
</tr>
<tr>
<td>2</td>
<td>0.257</td>
<td>0.472</td>
<td>0.272</td>
</tr>
</tbody>
</table>

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

$$Q^a_{\lambda_1 \lambda_2} (E) = \frac{\pi}{k} \lambda_1 \lambda_2 (E) N_{\lambda_1} (E) P^a_{\lambda_1 \lambda_2} (E) P^a_{\lambda_2 \lambda_1} (E)$$

$$= \frac{\pi}{k} \lambda_1 \lambda_2 (E) T^a_{\lambda_1 \lambda_2} (E) T^a_{\lambda_2 \lambda_1} (E) / N_{\lambda_1} (E).$$

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

We now introduce TST in Eq. (3.5) by replacing $N_{\lambda_1} (E)$ by $N_{\lambda_1} (E)$, the total number of transition state states 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. We also replace $P^a_{\lambda_1 \lambda_2}$ by an approximate probability $P^a_{\lambda_1 \lambda_2}$, which is still normalized over $n_1$ 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:

$$Q^a_{\lambda_1 \lambda_2} (E) = \frac{\pi}{k} \lambda_1 \lambda_2 (E) N_{\lambda_1} (E) P^a_{\lambda_1 \lambda_2} (E) P^a_{\lambda_2 \lambda_1} (E)$$

$$= \frac{\pi}{k} \lambda_1 \lambda_2 (E) T^a_{\lambda_1 \lambda_2} (E) T^a_{\lambda_2 \lambda_1} (E) / N_{\lambda_1} (E),$$

where the $T^{app}$ are related to the corresponding $P^{app}$ by an expression analogous to (2.17) in which $N_{\lambda_1}$ is replaced by $N_{\lambda_1}$. Replacement of this expression into Eq. (2.10) and comparison of the result with Eq. (2.8) gives

$$\rho_{\lambda_1 \lambda_2} (E) K^a_{\lambda_1 \lambda_2} (E) = \frac{1}{\hbar} N_{\lambda_1} (E) P^{app}_{\lambda_1 \lambda_2} (E).$$

(3.7)

Summing this expression over $n_1$ and using Eq. (2.6) and the normalization condition of the $P^{app}_{\lambda_1 \lambda_2}$ results finally in

$$K^a_{\lambda_1} (E) = \frac{N^a_{\lambda_1} (E)}{\hbar \rho_{\lambda_1} (E)}.$$

(3.8)

This is the correct TST version of Eq. (2.14) and shows that regardless of the choice of the normalized model $P^{app}_{\lambda_1 \lambda_2}$ used for the calculation of the state-to-state cross section $Q^a_{\lambda_1 \lambda_2}$, we will always get the correct TST microcanonical all-to-all rate constant $K^a_{\lambda_1} (E)$.

IV. A TEST OF FACTORIZATION

Using the state-to-state reaction cross sections for the $H + H_2$ system obtained from an exact quantal calculation, 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) $n_1$ by $j$, $m_1$ and summing over $m_1$ and averaging over $m_j$ we get, for the summed and averaged cross sections,

$$Q^f = Q^a \bar{P}_f.$$

(4.1)

Using the values of $Q^{app}_{\lambda_1 \lambda_2}$ of Table VI of Ref. 4 (and reproduced in Table II of this paper) we calculated the $Q^f_{\lambda_1 \lambda_2}$ and $Q^f$, and from those we obtain the values of $\bar{P}_f$ given in Table I. From the relatively small variation of these quantities with $j$ we conclude that the factorization of $Q^f_{\lambda_1 \lambda_2}$ 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–Condor model proposed and tested previously.

TABLE II: Integral reactive cross sections $Q^{app}_{\lambda_1 \lambda_2}$ for $H + H_2 \rightarrow H_2 + H$ reaction at $E = 0.6 \text{ eV}$.

<table>
<thead>
<tr>
<th>$j$</th>
<th>00</th>
<th>11</th>
<th>10</th>
<th>1</th>
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<tr>
<td>00</td>
<td>0.432e-01</td>
<td>0.322e-02</td>
<td>0.717e-01</td>
<td>0.322e-02</td>
<td>0.227e-03</td>
<td>0.474e-02</td>
<td>0.338e-01</td>
<td>0.474e-02</td>
<td>0.227e-03</td>
</tr>
<tr>
<td>21</td>
<td>0.549e-02</td>
<td>0.783e-02</td>
<td>0.890e-02</td>
<td>0.140e-02</td>
<td>0.811e-02</td>
<td>0.113e-02</td>
<td>0.407e-02</td>
<td>0.228e-02</td>
<td>0.134e-03</td>
</tr>
<tr>
<td>20</td>
<td>0.537e-02</td>
<td>0.419e-03</td>
<td>0.902e-03</td>
<td>0.281e-04</td>
<td>0.575e-03</td>
<td>0.407e-02</td>
<td>0.281e-04</td>
<td>0.575e-03</td>
<td>0.281e-04</td>
</tr>
<tr>
<td>2</td>
<td>0.391e-01</td>
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<td>0.638e-01</td>
<td>0.288e-02</td>
<td>0.209e-01</td>
<td>0.209e-01</td>
<td>0.209e-01</td>
<td>0.209e-01</td>
<td>0.209e-01</td>
</tr>
<tr>
<td>1</td>
<td>0.395e-01</td>
<td>0.549e-02</td>
<td>0.140e-02</td>
<td>0.897e-02</td>
<td>0.783e-03</td>
<td>0.134e-03</td>
<td>0.228e-02</td>
<td>0.281e-04</td>
<td>0.281e-04</td>
</tr>
<tr>
<td>0</td>
<td>0.393e-01</td>
<td>0.549e-02</td>
<td>0.140e-02</td>
<td>0.897e-02</td>
<td>0.783e-03</td>
<td>0.134e-03</td>
<td>0.228e-02</td>
<td>0.281e-04</td>
<td>0.281e-04</td>
</tr>
</tbody>
</table>

*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 $Q^{j}_{m_{j}}$ 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 $P_{j}$ 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 $N_{\lambda}$ 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 $N_{\lambda}^{\lambda}(E)$, defined after Eq. (2.12), be equal to $N_{\lambda}^{\lambda}(E)$, defined after Eq. (3.5). On the other hand, it was previously proven\(^{4}\) 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 pathways. 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 transition 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

$$Q^{j}_{\lambda,m_{j}}(E) = \frac{\pi}{k^{\lambda}_{\lambda,m_{j}}(E)} \sum_{J=0}^{\infty} (2J + 1) \left| \sum_{\lambda = 0}^{\infty} [S'_{\lambda}(E)]^{\lambda_{m_{j}}} \right|^{2},$$

(5.1)

where $J$ is the system's total angular momentum quantum number, $I$ is the identity matrix and $S'$ 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

$$p^{\lambda n_{\lambda}}_{\lambda' n'_{\lambda}}(E) = \left| \sum_{\lambda} [S'_{\lambda'}(E)]^{\lambda_{n'_{\lambda}}} \right|^{2}$$

(5.2)

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

$$\sum_{\lambda} p^{\lambda n_{\lambda}}_{\lambda' n'_{\lambda}}(E) = 1.$$  

(5.3)

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

$$Q^{\lambda}(E) = \frac{\pi}{k^{\lambda}_{\lambda}(E)} \sum_{\lambda} p^{\lambda n_{\lambda}}_{\lambda}(E),$$

(5.4)

where

$$p^{\lambda n_{\lambda}}_{\lambda}(E) = \sum_{n'_{\lambda}} p^{\lambda n_{\lambda}}_{\lambda' n'_{\lambda}}(E)$$

(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

$$0 \leq p^{\lambda n_{\lambda}}_{\lambda}(E) \leq 1,$$

(5.6)

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

$$N^{\lambda}_{\lambda}(E) = \sum_{n_{\lambda}} p^{\lambda n_{\lambda}}_{\lambda}(E),$$

(5.7)

where $n_{\lambda}$ represents the set of quantum numbers $J, M, n_{\lambda}$.

As described previously,\(^{4}\) we now define a set of curvilinear coordinates consisting of a reaction coordinate $q$ and a set of transverse coordinates $p$, such that as $q$ changes from $-\infty$ to $0$, $0$ to $+\infty$ the system evolves from the separated reagent molecules in the $\lambda$ arrangement channel, to the saddle point of the potential energy surface between arrangement channels $\lambda$ and $\lambda'$ to the separated product molecules in the $\lambda'$ arrangement channel. Let $H(p,q)$ be the Hamiltonian of the system for a fixed $q$, which describes the transverse $p$

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**Table III. Probability parameters $P_{m_{j}}$.**

<table>
<thead>
<tr>
<th>$j, m_{j}$</th>
<th>$a$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 0</td>
<td>0.262</td>
<td>0.172</td>
</tr>
<tr>
<td>1, 0</td>
<td>0.440</td>
<td>0.417</td>
</tr>
<tr>
<td>1, ± 1</td>
<td>0.0204</td>
<td>0.02</td>
</tr>
<tr>
<td>2, 0</td>
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<td>0.308</td>
</tr>
<tr>
<td>2, ± 1</td>
<td>0.0280</td>
<td>0.03</td>
</tr>
<tr>
<td>2, ± 2</td>
<td>0.0014</td>
<td>0.0012</td>
</tr>
</tbody>
</table>

*From fit to quantal results—See Sec. IV.

*From model described in Sec. VI.*

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

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

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

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

where $H$ denotes the Heaviside 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. The relation of adiabatic TST to general TST has been discussed recently. We now wish to calculate what $N_{\lambda i}^{\lambda i}(E)$ Eq. (5.8) implies. Replacement of this equation into Eq. (5.7) shows that $N_{\lambda i}^{\lambda i}(E)$ is in this case equal to the total number of $E_{\lambda i}^{\lambda i}(q)$ barriers (i.e., $u_{\lambda i}$ sets) for which $E_{\lambda i}^{\lambda i, \text{max}} < E$. This is by definition the number $N_{\lambda i}^{\lambda i}(E)$ of transition state states whose energy is below E. If we changed the definition of $E_{\lambda i}^{\lambda i, \text{max}}$ and used the new $E_{\lambda i}^{\lambda i, \text{max}}$ to compute the partition functions of the transition state in this modified TST, the modified $N_{\lambda i}^{\lambda i}(E)$ would still be the number of $u_{\lambda i}$ sets for which the new $E_{\lambda i}^{\lambda i, \text{max}} < E$. We thus conclude that Eq. (5.8) is a sufficient condition for the validity of

$$N_{\lambda i}^{\lambda i}(E) = N_{\lambda i}^{\lambda i}(E),$$

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 $\tilde{u}_{\lambda i}$ we get

$$\sum_{\tilde{u}_{\lambda i}} p_{\lambda i}^{\tilde{u}_{\lambda i}}(E) = N_{\lambda i}^{\lambda i}(E).$$

(5.10)

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

$$E_{\lambda i}^{\lambda i, -1, \text{max}} < E < E_{\lambda i}^{\lambda i, \text{max}},$$

(5.11)

the left-hand side of Eq. (5.10) contains $N_{\lambda i}^{\lambda i}(E)$ 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,

$$p_{\lambda i}^{\lambda i}(E) = 1 \text{ for } E > E_{\lambda i}^{\lambda i, \text{max}}.$$

(5.12)

It is furthermore implicit in any adiabatic TST theory, microcanonical or thermal, that the corresponding $p_{\lambda i}^{\lambda i}(E)$ must vanish for $E < E_{\lambda i}^{\lambda i, \text{max}}$. 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

$$Q_{\lambda i}^{\lambda i, \text{ASTST}}(E) = \frac{\pi}{k_{\lambda i}^{\lambda i}(E)} \sum_{M} H(E - E_{\lambda i}^{\lambda i, \text{max}}).$$

(5.13)

Using this result in Eqs. (2.13) and (3.5) we get the corresponding ASTST probabilities and state-to-state cross sections. To implement a calculation of these quantities it suffices to obtain the heights $E_{\lambda i}^{\lambda i, \text{max}}$ of the barriers which adiabatically connect the $\lambda u_{\lambda i}$ state of the reagents with the $\lambda i$ products. A calculation of the cross section given by Eq. (5.13) for the $H + H_2$ exchange reaction has been reported previously.

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 $H + D_2$ reaction. Using $\theta$ for the angle between the diatom axis and the vector from the center of mass of the diatom to the atom the result is

$$\sigma_R(\theta) = \pi d^2 \left[ 1 - E_{0}(\theta)/E_{\nu} \right],$$

(6.1)

where $E_{0}(\theta)$ is the barrier height for a fixed orientation and $E_{\nu}$ is the relative translation energy.

To convert Eq. (6.1) to quantal cross sections we average $\sigma_R$ over a probability distribution of $\theta$ for a given $j, m_j$ state, according to

$$Q_R^{jm} = \int \sigma_R(\theta) \left| Y_{jm}(\theta, \varphi) \right|^2 \sin \theta \, d\theta \, d\varphi.$$

(6.2)

We performed this integration numerically, using the $E_{0}(\theta)$ form of Ref. 3. The resulting $Q_R^{jm}$ cross sections were used in Eq. (2.10) to compute the model $P_{jm}$. 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 $P_{jm}$ 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

$$Q_R^{jm} = \frac{1}{2j + 1} \sum_{m_j} \frac{\sigma_R^{jm}}{Q_R^{jm}}$$

is given by the classical angle-averaged value

$$Q_R^{jm} = \int \sigma_R(\theta) \left| Y_{jm}(\theta, \varphi) \right|^2 \sin \theta \, d\theta \, d\varphi.$$

(6.3)
\[ Q_k = \frac{1}{4\pi} \int \sigma_R(\theta) \sin \theta \ d\theta \ dp. \]  \hfill (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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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 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.
11Reference 9, Section 2.6.3, Eq. (6.48).
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. Maylott, 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. Marz, J. Chem. Phys. 13, 447 (1960) 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, 3657 (1971).
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].
20Even if two \( \alpha_i \) sets have the same \( E_{\alpha_i,m}^{\alpha_i} \), they contribute separately to \( N_{\alpha_i}(E) \). Therefore, these \( E_{\alpha_i,m}^{\alpha_i} \) have at least a 2J + 1 degeneracy corresponding to the \( M \) quantum number.