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# Classical flux integrals in transition state theory: Generalized reaction coordinates

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Transition state theory (TST) approximates the reactive flux in an elementary chemical reaction by the instantaneous flux passing through a hypersurface (the ''transition state'') which completely divides the reactant and product regions of phase space. The rigorous classical evaluation of this instantaneous flux is carried out as a trace in phase space: effectively a multidimensional integral. We present an analysis of the momentum-space component of this flux integral for the case of a generalized reaction coordinate. The classic analysis of the canonical flux by Marcus [J. Chem. Phys. **41**, 2624 (1964)] is refined by reducing the determinant which appears in the transition state partition function to a very simple form, facilitating the ensuing integration over coordinate space. We then extend the analysis to provide analytic expressions for the momentum flux integrals in both the energy-resolved, and the energy+angular-momentum-resolved microcanonical ensembles. These latter expressions allow substantial gains in the efficiency of microcanonical variational implementations of Transition State Theory with generalized reaction coordinates. © *1999 American Institute of Physics.* [S0021-9606(99)00528-0]

## I. INTRODUCTION

The prediction of rate constants for elementary chemical reactions involves the calculation of a potential energy surface (PES), followed by solution of the dynamical problem by evaluating the reactive flux from the reactant region to the product region on the PES. Statistical theories are commonly used for approximate solution of the dynamical problem because, at a certain level of implementation, they are easy to apply and require minimal PES information. This ''user friendly'' aspect has promoted widespread use of Transition State Theory (TST) and popularized concepts of theoretical reaction dynamics in the broad field of chemical kinetics. The relative simplicity of the elementary TST expression for the thermal rate constant also makes it easily parametrized, and hence it enjoys a range of uses from the prediction of rate constants to the fitting of kinetic data (controversy occasionally arises when the latter application is confused with the former!).

The fact that the central component of TST, i.e., the evaluation of flux at a dividing surface specified by a fixed value of the reaction coordinate, is intrinsically classical in nature has been discussed and highlighted in many different ways over the years (e.g., Refs. 1–6). Thus, quantum-mechanical complexities arise when tunneling plays a significant role in the kinetics. Approximate quantum versions of TST exist and have been profitably used (e.g., Refs. 7–12). As with other approximate quantum models, the range of reliability of these quantum TST methods is still the subject of investigation. The introduction of complex absorbing potentials does allow rate constants to be computed rigorously using only ''local'' PES information in the region surrounding the barrier.[13–18] Both formally and in practice,

however, these are well-framed scattering calculations rather than TST-based methods.

There exists a wide range of reaction processes where tunneling is not a dominant factor, and hence classical methods can be profitably used to compute rate constants. In this context, both molecular dynamics (MD) and statistical methods play important and complementary roles. MD gives classically rigorous results, but requires complete PES information, extensive sampling of the system phase space and sometimes very long time simulations. On the other hand, TST and related statistical models are much easier to apply, requiring only sufficient PES information to evaluate the flux at the transition state dividing surface(s) and the density of states of any long-lived intermediates. Hence, there have been extensive and ongoing efforts to develop improved techniques for implementing TST in an efficient manner which is free of auxiliary assumptions or unnecessary parametrizations. In the area of gas-phase chemistry, for instance, this has lead to sophisticated implementations of microcanonical variational transition state theory ($\mu$VTST) to compute rate constants as a function of energy ($E$) and angular momentum ($J$) prior to ensemble averaging for radical–radical or ion-molecule reactions.[19–33]

An important issue in many applications of TST is that a reaction coordinate should be chosen which will make the fundamental transition state assumption (i.e., no recrossing of the dividing surface) a good one for the application at hand (e.g., Refs. 34, 35). Since some trial and error may be involved in the selection of the reaction coordinate, it is important to implement the TST calculations accurately and efficiently in accord with any given definition of the reaction coordinate. The latter problem is the issue that is addressed in this paper. We take the perspective of attempting to develop efficient implementations of TST which as far as pos-

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sible avoid auxiliary approximations. Thus, assuming that one has details of the PES at the transition state dividing surface, the ''partition function'' or ''sum-of-states'' to be evaluated at the transition state will be computed as a multidimensional integral in the classical phase space of the molecular system. Our focus is the development of analytic representations of the necessary momentum-space flux integrals, since this halves the dimensionality of the overall integrals and avoids awkward delta-function constraints in the microcanonical implementations of the theory. Progress has been made in this direction in the past by several authors. In a classic paper, Marcus[36] showed within the context of canonical TST that for a general curvilinear reaction coordinate the momentum-space integrals can be carried out analytically to produce a power of $k_B T$ divided by the square root of the determinant of a certain reduced kinetic energy tensor. Klippenstein[37] later adapted the Marcus result to energy-resolved microcanonical variational transition state theory ($\mu_E$VTST) and applied it to the NCNO dissociation reaction with a bond-length reaction coordinate. Although unable to extend the same approach to $E,J$-resolved microcanonical variational transition state theory ($\mu_{E,J}$VTST) Klippenstein did show how to analytically integrate out the delta functions for the three components of the total angular momentum and that for the energy, evaluating the remaining momentum integrals numerically.[24] In earlier work on $\mu_{E,J}$VTST,[27,28] we have shown that the $(E,J)$-resolved momentum flux integrals can be evaluated analytically for the specific case of a reaction coordinate which is the center-of-mass separation of two dissociating or recombining molecular fragments. This case is simpler than the generalized reaction coordinate because the kinetic energy for motion along this coordinate is separable. Furthermore, we introduced analytic expressions to approximate the momentum flux integrals for a bond-length reaction coordinate.[31] Building on these developments, Robertson et al.[38] have investigated algebraic methods for analytic evaluation of the coordinate-dependent factors appearing in the canonical TST expressions.

In this work we report substantial progress toward more efficient rigorous implementations of canonical variational transition state theory (CVTST), $\mu_E$VTST and $\mu_{E,J}$VTST. Our contribution is two-fold. First, we rederive the Marcus result for canonical TST with a generalized reaction coordinate in a manner which leads to a simple and transparent expression for the determinant of the $(n-1)$-dimensional kinetic energy tensor which arises from analytical evaluation of the momentum flux integral. Second, we present a detailed application of the approach to the evaluation of flux integrals for the transitional modes in barrierless recombination/ simple-fission dissociation reactions, treating the canonical, $E$-resolved microcanonical and $E,J$-resolved microcanonical ensembles. For these reactions, the physical nature of the problem motivates the choice of radial and rigid-body angular coordinates for the two molecular fragments rather than Cartesian coordinates,[39] and microcanonical variational implementations of the theory have played a very important role in elucidation of the reaction dynamics. Remarkably, it will transpire that the analytic microcanonical and canonical expressions proposed in our earlier work on the basis of an

approximate analysis[31] prove under more rigorous examination to be exact results!

The outline of the paper is as follows. In Sec. II, we present the derivation which leads to a refinement of Marcus' result for the canonical momentum flux integral with a generalized reaction coordinate. In Sec. III, we focus our attention on the important cases of recombination reactions without a barrier and the reverse simple-fission dissociation reactions. We derive the expression for the canonical flux integral in Sec. III A, the $E$-resolved microcanonical flux integral in Sec. III B, and finally the $E,J$-resolved microcanonical flux integral in Sec. III C. Section IV concludes.

## II. CANONICAL TST WITH A GENERALIZED REACTION COORDINATE

In canonical TST, the rate constant $k(T)$ can be formally expressed as the ratio of the thermal flux through the transition-state-dividing surface to the canonical density of states of the reactant(s),

$$k(T) = \frac{\text{Tr}[\delta(s-s_0)\dot{s}\Theta(\dot{s})e^{-H/k_B T}]}{\text{Tr}[\wp(\mathbf{q})e^{-H/k_B T}]}. \quad (1)$$

In Eq. (1) $s(\mathbf{q})$ is the reaction coordinate, constrained to the value $s_0$ on the dividing surface. $\dot{s}$ is the flux term and $\Theta(\dot{s})$ is a step function with value 0 for $\dot{s} \leq 0$ and 1 for $\dot{s} > 0$. $\wp(\mathbf{q})$ is a projector onto the relevant region of the reactant ensemble (unit volume for a bimolecular reaction, or the ''strongly coupled'' region of the molecule's configuration space in a unimolecular dissociation). We take $\mathbf{q}$ to represent a convenient set of coordinates $\{q_1,...,q_n\}$ for the molecular system and $\mathbf{p}$ to represent the set of conjugate momenta. $H(\mathbf{q},\mathbf{p})$ is the system Hamiltonian, and $k_B$ is the Boltzmann constant. The traces of Eq. (1) are evaluated classically as integrals over the system phase space,

$$k(T) = \frac{\int \cdots \int d\mathbf{q}\, d\mathbf{p}\, \delta(s-s_0)\dot{s}\Theta(\dot{s})e^{-H/k_B T}}{\int \cdots \int d\mathbf{q}\, d\mathbf{p}\, \wp(\mathbf{q})e^{-H/k_B T}}. \quad (2)$$

Recognizing that the classical partition function for reactants $Q$ is simply $h^{-n}$ times the denominator of Eq. (2) ($h$ being Planck's constant), it is convenient to write $k$ in the ''standard'' TST form

$$k(T) = \frac{k_B T}{h} \frac{Q^+}{Q} e^{-E_0/k_B T}. \quad (3)$$

In Eq. (3) $E_0$ is the critical energy for reaction (classically, the barrier height). $Q^+$ is a quantity which may be defined as

$$Q^+ = \frac{h^{-(n-1)}}{k_B T} e^{E_0/k_B T} \int d\mathbf{q}\, \delta(s-s_0)e^{-V(q)/k_B T}$$

$$\times \int d\mathbf{p}\, \dot{s}\Theta(\dot{s})e^{-E_k/k_B T}, \quad (4)$$

where $V$ is the potential energy and $E_k$ is the kinetic energy. In the simple approach to deriving Eq. (3), one assumes that the kinetic energy for motion along the reaction coordinate is separable (at least at the transition state) from the other degrees of freedom.[36] Thus, the flux term involving the velocity $\dot{s}$ along the reaction coordinate in Eq. (4) integrates out to

produce the characteristic prefactor $k_B T$ in Eq. (3), and $Q^+$ is indeed a partition function in the usual sense for the degrees of freedom orthogonal to the reaction coordinate. For example, suppose that the kinetic energy tensor is diagonal with respect to the momentum $p_1$,

$$E_k = \tfrac{1}{2}\mathbf{p}^T\mathbf{G}\mathbf{p}, \tag{5a}$$

with

$$G_{il} = G_{li} = 0, \quad i \neq 1 \tag{5b}$$

and that $(q_1, p_1)$ are in fact the reaction coordinate $s$ and momentum $p_s$, respectively. $Q^+$ then reduces to the standard partition function for the "orthogonal" modes,

$$Q^+ = \frac{e^{E_0/k_B T}}{h^{(n-1)}} \int \cdots \int d\mathbf{q}^\perp \, d\mathbf{p}^\perp e^{-H^\perp/k_B T}, \tag{6}$$

where $\mathbf{q}^\perp = \{q_2, \ldots, q_n\}$, $\mathbf{p}^\perp = \{p_2, \ldots, p_n\}$, and $H^\perp = E_k^\perp(\mathbf{p}^\perp) + V^\perp(\mathbf{q}^\perp; s = s_0)$, $s_0$ being the value of $s$ which defines the position of the transition state. If the transition state lies at a saddle point on the PES, this can often be regarded as a good approximation for energies not far above the barrier, since the saddle point is by definition a stationary point on the PES and the kinetic energy tensor will be locally separable along the direction of the reaction coordinate. For energies not far above $E_0$, trajectories crossing the barrier will not deviate far from the saddle point and so the separability of the kinetic energy should hold quite well. However, for thermal systems incorporating significant populations at energies markedly higher than $E_0$ one might not expect this separability to hold. Furthermore, for reactions proceeding without a saddle point on the PES between reactants and products, such as the barrierless recombination/simple-fission dissociation classes explicitly considered in Sec. III below, this problem is exacerbated. Clearly, it is desirable to remove the approximation of a separable kinetic energy for motion along the reaction coordinate, and this is the problem which Marcus addressed in his pioneering work.[36]

We now take a somewhat different approach to develop a result which is manifestly equivalent to, but simpler and more physically transparent than that of Marcus. Since our principle focus is the analytic evaluation of the momentum flux integral, it is useful to write it as follows:

$$\Phi(T,\mathbf{q}) = \frac{1}{k_B T} \int d\mathbf{p} \, \dot{s} \, \Theta(\dot{s}) e^{-E_k/k_B T}, \tag{7}$$

so that

$$Q^+ = \frac{e^{E_0/k_B T}}{h^{(n-1)}} \int d\mathbf{q} \, \delta(s - s_0) e^{-V(\mathbf{q})/k_B T} \, \Phi(T,\mathbf{q}). \tag{8}$$

It is convenient, but not absolutely necessary, to assume that we have set up the Hamiltonian in terms of Cartesian coordinates, since in this case the kinetic energy tensor $\mathbf{G}$ will be diagonal which will simplify some of the ensuing equations. Since the motion of the center of mass is strictly separable, the corresponding partition function can always be factored out of the final result (although it will in any case cancel in the expression for the rate coefficient). Thus, we assume without loss of generality that

$$G_{ij} = \delta_{ij} m_i^{-1} \tag{9}$$

and the determinant of $\mathbf{G}$ is then

$$|\mathbf{G}| = \left[ \prod_i m_i^{-1} \right]. \tag{10}$$

Note that with this labeling scheme, $m_{3r-2} = m_{3r-1} = m_{3r} = m^{(r)}$, where $m^{(r)}$ is the mass of the $r$th particle. The time derivative of the reaction coordinate $s$ is written

$$\dot{s} = \sum_{i=1}^{n} \frac{\partial s}{\partial q_i} \dot{q}_i = \sum_{i=1}^{n} \frac{\partial s}{\partial q_i} \frac{p_i}{m_i} = (\nabla s)^T \mathbf{G} \mathbf{p}. \tag{11}$$

In order to evaluate the integral in Eq. (7), it will be necessary to transform to a new set of momenta $\mathbf{v} = \{\nu_1, \ldots, \nu_n\}$ such that the following conditions are satisfied: (a) the Jacobian for the transformation should be a constant (i.e., independent of the momenta), and (b) one of the momenta, which we label $\nu_1$, satisfies the relation

$$\frac{\partial E_k}{\partial \nu_1} = c\dot{s} \tag{12}$$

with $c$ a constant. Condition (a) will be satisfied if we require the transformation to be linear. Our method of satisfying condition (b) will further require that the transformation matrix be orthogonal, so that the Jacobian for the transformation will in fact be unity. Thus, we write

$$\mathbf{v} = \mathbf{U}\mathbf{p}; \tag{13a}$$

$$\mathbf{U}^T\mathbf{U} = \mathbf{I}. \tag{13b}$$

The kinetic energy now becomes

$$E_k = \tfrac{1}{2}\mathbf{p}^T\mathbf{G}\mathbf{p} = \tfrac{1}{2}\mathbf{v}^T\mathbf{U}\mathbf{G}\mathbf{U}^T\mathbf{v} = \tfrac{1}{2}\mathbf{v}^T\mathbf{G}^*\mathbf{v} \tag{14}$$

and the next task is the specification of $\nu_1$ so as to satisfy Eq. (12). This amounts to specifying the first row of the transformation matrix $\mathbf{U}$. Using Eq. (14) we have

$$\frac{\partial E_k}{\partial \nu_1} = \sum_i G_{i1}^* \nu_i = (\mathbf{G}^*\mathbf{e}_1)^T\mathbf{v}, \tag{15}$$

where $\mathbf{e}_1$ is the elementary vector $(1,0,\ldots,0)$ (for notational convenience here and below, its dimension can be inferred from the matrix beside which it appears). Use of Eqs. (13)–(14) then leads to

$$\frac{\partial E_k}{\partial \nu_1} = \mathbf{e}_1^T\mathbf{U}\mathbf{G}\mathbf{p}.$$

Equating this to $c\dot{s}$ via Eqs. (11) and (12) then gives

$$\mathbf{e}_1^T\mathbf{U}\mathbf{G}\mathbf{p} = c(\nabla s)^T\mathbf{G}\mathbf{p},$$

which then implies that

$$\mathbf{U}^T\mathbf{e}_1 = c\nabla s.$$

Thus, the first row of the transformation matrix $\mathbf{U}$ is proportional to $\nabla s$. Recalling that $\mathbf{U}$ must be orthogonal, one finally has

$$\mathbf{U}^T\mathbf{e}_1 = \frac{\nabla s}{|\nabla s|}, \tag{16}$$

i.e., the constant $c = |\nabla s|^{-1}$. The only restriction on the remaining momenta $\nu_2, \ldots, \nu_n$ is that they should be orthonormal to $\nu_1$ [Eq. (13b)]. Thus, virtually any method of determining a set of $(n-1)$ vectors in $\mathbb{R}^n$ orthonormal to the first row of $\mathbf{U}$ will suffice to define the remaining rows of the transformation matrix, and thence the remaining momenta. The Lanczos algorithm is useful in this context, since it will choose $\nu_2, \ldots, \nu_n$ such that the new kinetic energy tensor $\mathbf{G}^*$ is symmetric tridiagonal, which simplifies the ensuing analysis. Using the notation $\mathbf{u}_i$ to refer to the $i$th row of $\mathbf{U}$ (i.e., $\mathbf{u}_i = \mathbf{U}^T \mathbf{e}_i$), we begin by setting $\mathbf{u}_1$ from Eq. (16) as the seed vector for the algorithm, and generate the remaining vectors in the standard manner (e.g., Ref. 40),

$$\beta_i \mathbf{u}_{i+1} = (\mathbf{G} - \alpha_i)\mathbf{u}_i - \beta_{i-1}\mathbf{u}_{i-1}, \tag{17a}$$

where

$$\alpha_i = \mathbf{u}_i{}^T \mathbf{G} \mathbf{u}_i. \tag{17b}$$

This three-term recursion generates a sequence of vectors $\mathbf{u}_i$ which are orthonormal, and in terms of which the new representation of the kinetic energy tensor is tridiagonal,

$$\mathbf{G}^* = \mathbf{U}\mathbf{G}\mathbf{U}^T = \begin{pmatrix} \alpha_1 & \beta_1 & 0 & 0 & 0 \\ \beta_1 & \alpha_2 & \cdot & 0 & 0 \\ 0 & \cdot & \cdot & \cdot & 0 \\ 0 & 0 & \cdot & \alpha_{n-1} & \beta_{n-1} \\ 0 & 0 & 0 & \beta_{n-1} & \alpha_n \end{pmatrix}. \tag{18}$$

For later reference, note in particular the form of $\alpha_1$:

$$\alpha_1 = \mathbf{u}_1{}^T \mathbf{G} \mathbf{u}_1 = \frac{1}{|\nabla s|^2}(\nabla s)^T \mathbf{G} \nabla s$$

$$= \frac{1}{|\nabla s|^2} \left\{ \sum_{i=1}^{n} \left( \frac{\partial s}{\partial q_i} \right)^2 m_i^{-1} \right\}. \tag{19}$$

The integrals of Eq. (7) are now ordered as follows:

$$\Phi(T, \mathbf{q}) = \frac{1}{k_B T} \int d\mathbf{v}^\perp e^{-E_k^\perp / k_B T}$$

$$\times \int d\nu_1 \dot{s} \Theta(\dot{s}) e^{-(\alpha_1 \nu_1^2 + 2\beta_1 \nu_2 \nu_1)/2k_B T}, \tag{20}$$

where $\mathbf{v}^\perp = (\nu_2, \ldots, \nu_n)$ and

$$E_k^\perp = \tfrac{1}{2}(\mathbf{v}^\perp)^T \mathbf{G}^\perp \mathbf{v}^\perp, \tag{21a}$$

$$\mathbf{G}^\perp = \begin{pmatrix} \alpha_2 & \beta_2 & 0 & 0 & 0 \\ \beta_2 & \alpha_3 & \cdot & 0 & 0 \\ 0 & \cdot & \cdot & \cdot & 0 \\ 0 & 0 & \cdot & \alpha_{n-1} & \beta_{n-1} \\ 0 & 0 & 0 & \beta_{n-1} & \alpha_n \end{pmatrix}. \tag{21b}$$

The step function $\Theta(\dot{s})$ can now be accounted for by examining the relation between $\dot{s}$ and $\nu_1$. Recalling that $c = |\nabla s|^{-1}$, one has from Eqs. (12) and (15) that

$$\dot{s} = |\nabla s| \frac{\partial E_k}{\partial \nu_1} = |\nabla s|(\alpha_1 \nu_1 + \beta_1 \nu_2), \tag{22}$$

thus $\dot{s} = 0$ implies that $\nu_1 = -(\beta_1/\alpha_1)\nu_2$. Since $\mathbf{G}$ in Eq. (19) is positive definite, $\alpha_1$ is positive. Thus, $\dot{s} > 0$ implies that $\nu_1 > -(\beta_1/\alpha_1)\nu_2$, so that the step function $\Theta(\dot{s})$ will be exactly accounted for by integration over the following boundaries:

$$\Phi(T, \mathbf{q}) = \frac{1}{k_B T} \int_{-\infty}^{\infty} d\mathbf{v}^\perp e^{-E_1^\perp / k_B T}$$

$$\times \int_{-(\beta_1/\alpha_1)\nu_2}^{\infty} d\nu_1 \dot{s} e^{-(\alpha_1 \nu_1^2 + 2\beta_1 \nu_2 \nu_1)/2k_B T}. \tag{23}$$

We now substitute

$$\eta = \tfrac{1}{2}(\alpha_1 \nu_1^2 + 2\beta_1 \nu_2 \nu_1) \tag{24a}$$

$$\frac{\partial \eta}{\partial \nu_1} = \frac{\partial E_k}{\partial \nu_1} = \frac{\dot{s}}{|\nabla s|} \tag{24b}$$

into Eq. (23) to give

$$\Phi(T, \mathbf{q}) = \frac{|\nabla s|}{k_B T} \int_{-\infty}^{\infty} d\mathbf{v}^\perp e^{-E_k^\perp / k_B T} \int_{-(\beta_1^2/2\alpha_1)\nu_2^2}^{\infty} d\eta \, e^{-\eta / k_B T}.$$

Integration over $\eta$ then yields

$$\Phi(T, \mathbf{q}) = |\nabla s| \int_{-\infty}^{\infty} d\mathbf{v}^\perp e^{-E_k^+ / k_B T} \tag{25}$$

with

$$E_k^+ = \tfrac{1}{2}(\mathbf{v}^\perp)^T \mathbf{G}^+ \mathbf{v}^\perp, \tag{26a}$$

$$\mathbf{G}^+ = \mathbf{G}^\perp - \frac{\beta_1^2}{\alpha_1} \mathbf{e}_1 \mathbf{e}_1{}^T. \tag{26b}$$

The remaining integrals in Eq. (25) can now be evaluated in standard fashion[41] to give the result

$$\Phi(T, \mathbf{q}) = \frac{|\nabla s|(2\pi k_B T)^{(n-1)/2}}{|\mathbf{G}^+|^{1/2}}. \tag{27a}$$

and thence

$$Q^+ = \frac{(2\pi k_B T)^{(n-1)/2} e^{E_0/k_B T}}{h^{(n-1)}}$$

$$\times \int d\mathbf{q}\, \delta(s - s_0) \frac{e^{-V(\mathbf{q})/k_B T} |\nabla s|}{|\mathbf{G}^+|^{1/2}}. \tag{27b}$$

Equation (27b) is entirely equivalent to the result of Marcus.[36] The factor $|\nabla s|$ appears here because of our slightly different definition of the momentum ''conjugate'' to $\dot{s}$ [Eq. (12)]. Our present formulation, however, reveals that a significant additional simplification can be achieved by examination of the determinant of $\mathbf{G}^+$, since

$$|\mathbf{G}^+| = |\mathbf{G}^\perp| - \frac{\beta_1^2}{\alpha_1} \begin{vmatrix} \alpha_3 & \beta_3 & 0 & 0 & 0 \\ \beta_3 & \alpha_4 & \cdot & 0 & 0 \\ 0 & \cdot & \cdot & \cdot & 0 \\ 0 & 0 & \cdot & \alpha_{n-1} & \beta_{n-1} \\ 0 & 0 & 0 & \beta_{n-1} & \alpha_n \end{vmatrix}.$$

This, however, is directly related to the determinant of $\mathbf{G}$ as follows:

$$\alpha_1|\mathbf{G}^+| = \alpha_1 \begin{vmatrix} \alpha_2 & \beta_2 & 0 & 0 & 0 \\ \beta_2 & \alpha_3 & \cdot & 0 & 0 \\ 0 & \cdot & \cdot & \cdot & 0 \\ 0 & 0 & \cdot & \alpha_{n-1} & \beta_{n-1} \\ 0 & 0 & 0 & \beta_{n-1} & \alpha_n \end{vmatrix}$$

$$-\beta_1^2 \begin{vmatrix} \alpha_3 & \beta_3 & 0 & 0 & 0 \\ \beta_3 & \alpha_4 & \cdot & 0 & 0 \\ 0 & \cdot & \cdot & \cdot & 0 \\ 0 & 0 & \cdot & \alpha_{n-1} & \beta_{n-1} \\ 0 & 0 & 0 & \beta_{n-1} & \alpha_n \end{vmatrix}$$

$$= \begin{vmatrix} \alpha_1 & \beta_1 & 0 & 0 & 0 \\ \beta_1 & \alpha_2 & \cdot & 0 & 0 \\ 0 & \cdot & \cdot & \cdot & 0 \\ 0 & 0 & \cdot & \alpha_{n-1} & \beta_{n-1} \\ 0 & 0 & 0 & \beta_{n-1} & \alpha_n \end{vmatrix} = |\mathbf{G}^*| = |\mathbf{G}|, \quad (28)$$

where we have made use of the fact that $\mathbf{G}^*$ is related to $\mathbf{G}$ by an orthogonal transformation [Eq. (14)], and hence the two matrices have the same determinant. Substitution of Eqs. (10), (19) and (28) into Eq. (27a) finally yields

$$\Phi(T,\mathbf{q}) = (2\pi k_B T)^{(n-1)/2} \left[ \sum_{i=1}^{n} \left( \frac{\partial s}{\partial q_i} \right)^2 m_i^{-1} \right]^{1/2} \left[ \prod_{i=1}^{n} m_i \right]^{1/2}$$
(29a)

and

$$Q^+ = \frac{(2\pi k_B T)^{(n-1)/2} e^{E_0/k_B T}}{h^{(n-1)}} \left[ \prod_{i=1}^{n} m_i \right]^{1/2} \int d\mathbf{q}\, \delta(s-s_0)$$

$$\times \left[ \sum_{i=1}^{n} \left( \frac{\partial s}{\partial q_i} \right)^2 m_i^{-1} \right]^{1/2} e^{-V(\mathbf{q})/k_B T}. \quad (29b)$$

Equation (29) is the main result of this section. Its utility lies in the fact that the coordinate-dependence of the momentum flux integral, given by the terms inside the square brackets, is very simple and easy to evaluate. It also lends itself to physical interpretation in terms of an effective reduced mass $\mu$ for instantaneous motion along the reaction coordinate. Defining $\mu$ as follows;

$$\mu^{-1} = \sum_{i=1}^{n} \left( \frac{\partial s(\mathbf{q})}{\partial q_i} \right)^2 m_i^{-1}. \quad (30)$$

Equation (29b) then takes the form

$$Q^+ = \frac{(2\pi k_B T)^{(n-1)/2} e^{E_0/k_B T}}{h^{(n-1)}}$$

$$\times \int d\mathbf{q}\, \frac{\prod_{i=1}^{n} m_i^{1/2}}{\mu(\mathbf{q})^{1/2}} e^{-V(\mathbf{q})/k_B T} \delta(s-s_0). \quad (31)$$

We note that the simplicity of the above result stems from the fact that the preceding analysis avoids full canonical transformation to curvilinear coordinates, focusing solely on orthogonal transformations in momentum space to evaluate the momentum flux integral. This allows us to take advan-

tage of the intrinsic simplicity of the underlying Cartesian coordinate system and its associated kinetic energy tensor $\mathbf{G}$. In rigorous implementations of the theory, the ensuing integration over coordinate space is usually carried out by Monte Carlo methods and the efficiency of the overall procedure is greatly enhanced by simplifying the evaluation of the integrand. In the present approach, one retains the flexibility to choose subsequent coordinate transformations so as to (a) integrate analytically over external coordinates and any cyclic internal coordinates, and (b) minimize the numerical effort involved in evaluating $V(\mathbf{q})$ and $\mu(\mathbf{q})$, thus optimizing the performance of the overall algorithm.

## III. RECOMBINATION/SIMPLE-FISSION DISSOCIATION REACTIONS WITH A VARIABLY DEFINED REACTION COORDINATE

We now turn to a specific class of reactions where variational TST methods have played a crucial role in successful modeling and prediction of thermal and microcanonical rate constants.[39,42–44] These are reactions involving unimolecular species with one or more dissociative channels having no pronounced chemical barrier (i.e., no saddle point on the PES). Examples of such reactions include radical–radical recombinations, ion-molecule associations, collision-complex-forming bimolecular reactions, and single or multichannel simple-fission dissociation reactions. The model for these reactions has been described in some detail previously (e.g., Refs. 19, 22, 27). Theoretical modeling of experimentally measured product vibrational state distributions suggests that the internal vibrational modes of the recombining or separating fragments behave essentially adiabatically in the region of the PES between the variational transition state and the infinitely separated products.[21] Thus, these so-called "conserved" modes are assumed to be adiabatically decoupled from the remaining degrees of freedom, which are collectively termed the "transitional modes." The model Hamiltonian thus takes the form

$$H = H_C + H_{TM} + V_{\min}(s). \quad (32)$$

$H_C$ for the conserved modes is typically weakly parametrically dependent on $s$, since the internal vibrational frequencies of the fragments are typically close to their asymptotic values. The transitional modes correlate at large separations to the rotational degrees of freedom of the fragments and their relative translational motion, and in the unimolecular species to vibrations and overall rotation. Thus, $H_{TM}$ for the transitional modes is strongly dependent on $s$. In the absence of a well-defined barrier, it is the interplay of the entropic and enthalpic changes along the reaction coordinate associated with the transitional modes which causes the variational implementation of TST to be an important factor in the modeling of these reactions. This is done at the most detailed level by $\mu_{E,J}$VTST, and successively more approximately by $\mu_E$VTST and CVTST.[45]

Rigorous implementations of $\mu_{E,J}$VTST were originally carried out for the simpler case of a reaction coordinate defined as the center-of-mass separation of the two molecular fragments (e.g., Refs. 19, 20, 29). Although the earlier implementations involved numerical integration over angular

coordinates and momenta, the momentum flux integrals are now known to be analytic which considerably simplifies the procedure.[28,29] Investigations of a more general type of reaction coordinate, defined as the separation between any two points fixed relative to the respective frames of the two molecular fragments, were pioneered by Klippenstein.[22,23,46] For energies significantly above the reaction threshold, his work clearly showed that the variably defined reaction coordinate, which might typically be the length of the forming or breaking bond, allows significant further minimization of the computed reaction flux in comparison with the center-of-mass separation reaction coordinate. Klippenstein's $\mu_{E,J}$VTST algorithm involved numerical integration over the angular momenta and coordinates,[22,24] although he showed that Marcus' result for the canonical momentum flux discussed in Sec. II above could be readily applied to $\mu_E$VTST and CVTST in this context.[22,37] On the basis of an approximate analysis, we proposed in an earlier paper analytic expressions for the momentum flux integrals in $\mu_{E,J}$VTST with a variably defined reaction coordinate, and found the computed results in excellent agreement with Klippenstein's calculations for the NC+NO reaction. Karas and Gilbert,[47] and more recently Robertson et al.,[38] have investigated canonical implementations of the variable reaction coordinate approach.

In this section we adapt the general treatment of Sec. II to derive exact analytic expressions for the momentum flux integrals associated with the transitional modes in this important class of reactions.

## A. Canonical momentum flux integral

Given the assumed separability of the Hamiltonian into $H_C$ for the conserved modes and $H_{TM}$ for the transitional modes [Eq. (32)], Eq. (3) becomes

$$k(T) = \frac{k_B T}{h} \frac{Q_c Q_{TM}^+}{Q} e^{-E_0/k_B T}, \tag{33}$$

where $Q_c$ is the partition function for the conserved modes at the given value of $s$, and $Q_{TM}^+$ is that for the transitional modes at the same value of $s$. Note that, in the context of variational implementations of the TST formulas here and below, the energy restrictions imposed by adiabatic[48] or complete[26] decoupling of certain modes in the region of the PES from the transition state out to infinite separation are readily accounted for. However, to keep the notation simple, we will not explicitly consider this in the equations below. Recall that the variably defined reaction coordinate is chosen as the separation between two points fixed relative to the rigid-body frames of the respective fragments, which are themselves defined either for the optimized geometry at the given value of $s$ or possibly for some vibrationally averaged geometry. In either case, the value of $s$ defined in this way is independent of vibrational fluctuations associated with the conserved modes, so that the flux factor $\dot{s}$ affects only $Q_{TM}^+$. Thus, our analysis focuses on the quantity $Q_{TM}^+$

$$Q_{TM}^+ = \frac{1}{\sigma_1 \sigma_2} \left( \frac{k_B T}{h} \right)^{-1}$$

$$\times \int dR \, d\phi \, d\theta \, d\phi_1 \, d\theta_1 \, d\psi_1 \, d\phi_2 \, d\theta_2 \, d\psi_2 \, \delta(s - s_0)$$

$$\times \frac{1}{h^9} \int dp_R \, dp_\phi \, dp_\theta \, dp_{\phi_1} \, dp_{\theta_1} \, dp_{\psi_1} \, dp_{\phi_2} \, dp_{\theta_2} \, dp_{\psi_2}$$

$$\times \dot{s} \Theta(\dot{s}) e^{-H_{TM}/k_B T}. \tag{34}$$

In Eq. (34), $R$ is the center-of-mass separation, $\phi$ and $\theta$ are the spatially referenced Euler angles which locate the orientation of the line joining the centers of mass, $(\phi_1, \theta_1, \psi_1)$ are the spatially referenced Euler angles locating the orientation of the rigid-body frame of fragment 1 and $(\phi_2, \theta_2, \psi_2)$ are those for fragment 2. $P_R$ and the Euler momenta are conjugate to $R$ and the Euler angles as indicated. The symmetry numbers of the fragments are specified by $\sigma_1$ and $\sigma_2$, respectively. In the following derivations, we treat the most general case for a binary collision, i.e., two asymmetric-top fragments. The final working equations, however, are presented in a form which covers also the specific cases of linear or monatomic collision partners.

Some preliminary transformations, which have been described in detail previously,[27] are necessary to bring Eq. (34) into a form which is useful for our purposes. First, the Euler momenta of the fragments and the orbital rotation are transformed to the corresponding principal-axis angular momentum components in units of $\hbar$ with Jacobian $J_c$ as indicated,

$$(p_{\phi_1}, p_{\theta_1}, p_{\psi_1}, p_{\phi_2}, p_{\theta_2}, p_{\psi_2}, p_\phi, p_\theta)$$

$$\xrightarrow{\quad j_c = n^2 \sin\theta_1 \sin\theta_2 \sin\theta \quad} (j_{1A}, j_{1B}, j_{1C}, j_{2A}, j_{2B}, j_{2C}, l_x, l_y). \tag{35}$$

The components $l_x$ and $l_y$ of the orbital angular momentum vector $\mathbf{l}$ are its projections onto the "body-fixed" $x$ and $y$ axes perpendicular to the line joining the centers of mass of the two fragments, which defines the body-fixed $z$ axis. Note that the principal axes of the fragments will, in general, not coincide with each other or with the body-fixed axes. This complication does not concern us here as there are no vector constraints to be accounted for; however, it will be dealt with in Sec. II C below where the constraint of a fixed total angular momentum vector is imposed. In terms of these principal-axis momenta, Eq. (34) becomes

$$Q_{TM}^+ = \frac{1}{\sigma_1 \sigma_2} \frac{1}{k_B T} \frac{1}{(2\pi)^8}$$

$$\times \int dR \, d\phi \, d\theta \, d\phi_1 \, d\theta_1 \, d\psi_1 \, d\phi_2 \, d\theta_2 \, d\psi_2 \, \delta(s - s_0)$$

$$\times \sin\theta \sin\theta_1 \sin\theta_2 \frac{1}{\pi^3} \int dp_R \, d\mathbf{j}_1 \, d\mathbf{j}_2 \, d\mathbf{l} \, \dot{s} \Theta(\dot{s})$$

$$\times e^{-H_{TM}/k_B T} \tag{36}$$

and the transitional-mode Hamiltonian is

$$H_{\mathrm{TM}} = \frac{p_R^2}{2\mu} + A_1 j_{1A}^2 + B_1 j_{1B}^2 + C_1 j_{1C}^2 + A_2 j_{2A}^2 + B_2 j_{2B}^2 + C_2 j_{2C}^2$$

$$+ B_0(l_x^2 + l_y^2) + V_{\mathrm{TM}}(\mathbf{q})$$

$$= T_{\mathrm{TM}} + V_{\mathrm{TM}}(\mathbf{q}). \tag{37}$$

It is useful also at this point to make the following transformations for $R$, $\mu$ and $p_R$, so that the kinetic energy tensor for the transitional modes can be defined with common units (i.e., Joules) for all of its elements,

$$\tilde{R} = R/1\ \mathrm{m},$$

$$\tilde{\mu} = \mu \times 1\ \mathrm{m}^2, \tag{38}$$

$$\tilde{p}_R = \tilde{\mu}\dot{\tilde{R}}/\hbar.$$

Thus, $\tilde{R}$ and $\tilde{p}_R$ are dimensionless, and $\tilde{\mu}$ carries units of kgm$^2$ [note that the quantities $(\mu,\tilde{\mu})$ and $(R,\tilde{R})$ are, respectively, numerically identical in the following equations, the differences being simply semantic and related to units]. The kinetic energy for the transitional modes can now be written

$$T_{\mathrm{TM}} = \mathbf{w}^{\mathrm{T}} \mathbf{G}_{\mathrm{TM}} \mathbf{w}, \tag{39}$$

where $\mathbf{w} = (\tilde{p}_R, l_x, l_y, j_{1A}, j_{1B}, j_{1C}, j_{2A}, j_{2B}, j_{2C})$. $\mathbf{G}_{\mathrm{TM}}$ is a diagonal matrix with diagonal elements $\{(\hbar^2/2\tilde{\mu}), B_0, B_0, A_1, B_1, C_1, A_2, B_2, C_2\}$. $B_0$ here is the rotational constant for the orbital rotation of the fragment centers of mass about the overall center of mass, i.e., $B_0 = \hbar^2/2\mu R^2$. The determinant of $\mathbf{G}_{\mathrm{TM}}$ is then given by

$$|\mathbf{G}_{\mathrm{TM}}| = \left(\frac{\hbar^2}{2\tilde{\mu}}\right) B_0^2 \prod_{i=1}^{2} A_i B_i C_i. \tag{40}$$

Analogous to Sec. II, we define the canonical momentum flux integral as

$$\Phi(T,\mathbf{q}) = \frac{\hbar}{k_B T} \frac{1}{\pi^3} \int d\mathbf{j}_1\, d\mathbf{j}_2\, d\mathbf{l}\, d\tilde{p}_R\, \dot{s}\, \Theta(\dot{s})\, e^{-T_{\mathrm{TM}}/k_B T} \tag{41}$$

so that

$$Q_{\mathrm{TM}}^+ = \frac{1}{\sigma_1 \sigma_2} \frac{1}{N} \int d\phi\, d\theta\, d\phi_1\, d\theta_1\, d\psi_1\, d\phi_2\, d\theta_2\, d\psi_2\, dR$$

$$\times \delta(s-s_0) \sin\theta \sin\theta_1 \sin\theta_2 e^{-V_{\mathrm{TM}}(\mathbf{q})/k_B T} \Phi(T,\mathbf{q}). \tag{42}$$

The factor $N$ in Eq. (42) is the normalizing constant for the angular integrals ($2^8 \pi^5$). Next, one transforms the Euler angles to a set of external angles $\{\phi,\theta,\psi\}$ and body-fixed internal angles $\{\phi',\theta_1',\psi_1',\theta_2',\psi_2'\}$.[19,27,49] Here, $\phi$ and $\theta$ are unchanged (i.e., the orbital Euler angles), and $\psi$ is a third Euler angle necessary to specify the overall orientation of the body. $\phi'$ is the torsional angle between the two fragments, and $\{\theta_1',\psi_1',\theta_2',\psi_2'\}$ are body-fixed Euler angles for the fragments. The Jacobian for this transformation is unity. Invariance of the Hamiltonian with respect to overall rotation then allows analytic integration over $\phi$, $\theta$ and $\psi$, reducing the angular configuration space integration to at most five dimensions,

$$Q_{\mathrm{TM}}^+ = \frac{1}{\sigma_1 \sigma_2} \frac{1}{N'} \int d\phi'\, d\theta_1'\, d\psi_1'\, d\theta_2'\, d\psi_2'\, dR\, \delta(s-s_0)$$

$$\times \sin\theta_1' \sin\theta_2' e^{-V_{\mathrm{TM}}(\mathbf{q})/k_B T} \Phi(T,\mathbf{q}), \tag{43}$$

where $N'$ is the normalizing factor for integration over the five internal angles ($2^5 \pi^3$). Evaluation of the integral over $R$ then gives

$$Q_{\mathrm{TM}}^+ = \frac{1}{\sigma_1 \sigma_2} \frac{1}{N'} \int d\phi'\, d\theta_1'\, d\psi_1'\, d\theta_2'\, d\psi_2' \left(\frac{\partial s}{\partial R}\right)^{-1}$$

$$\times \sin\theta_1' \sin\theta_2' e^{-V_{\mathrm{TM}}(\mathbf{q})/k_B T} \Phi(T,\mathbf{q})\Big|_{s=s_0}$$

$$= \frac{1}{\sigma_1 \sigma_2} \left\langle \left(\frac{\partial s}{\partial R}\right)^{-1} e^{-V_{\mathrm{TM}}(\mathbf{q})/k_B T} \Phi(T,\mathbf{q}) \right\rangle_{s=s_0}. \tag{44}$$

Thus, $Q_{\mathrm{TM}}^+$ can be calculated either by direct quadrature for specific cases of reduced dimension or by computing the average value of the integrand using Monte Carlo sampling.

With the preliminary transformations complete and notation established, we now address the central issue of evaluating the momentum flux integral $\Phi(T,\mathbf{q})$ analytically. The development here is largely summarized since it follows that of the previous section closely. First, the time derivative of the reaction coordinate $s$ is written as

$$\dot{s} = \frac{\partial s}{\partial \tilde{R}}\dot{\tilde{R}} + \frac{\partial s}{\partial \gamma_{0x}}\dot{\gamma}_{0x} + \frac{\partial s}{\partial \gamma_{0y}}\dot{\gamma}_{0y} + \sum_{i=1}^{2} \frac{\partial s}{\partial \gamma_{iA}}\dot{\gamma}_{iA}$$

$$+ \frac{\partial s}{\partial \gamma_{iB}}\dot{\gamma}_{iB} + \frac{\partial s}{\partial \gamma_{iC}}\dot{\gamma}_{iC} = \frac{2}{\hbar}(\nabla s)^{\mathrm{T}} \mathbf{G}_{\mathrm{TM}} \mathbf{w}, \tag{45}$$

where $\gamma_{0x}$ and $\gamma_{0y}$ are the angles of rotation about the body-fixed $x$ and $y$ axes (which are principal axes for the orbital rotation), and $(\gamma_{iA}, \gamma_{iB}, \gamma_{iC})$ are the angles of rotation about the principal axes of fragment $i$. An orthogonal transformation to a new set of momenta $\mathbf{v}$ follows,

$$\mathbf{v} = \mathbf{U}\mathbf{w}; \tag{46a}$$

$$\mathbf{U}^{\mathrm{T}}\mathbf{U} = \mathbf{I}, \tag{46b}$$

where $\mathbf{U}$ is a $9 \times 9$ orthogonal matrix whose first row, $\mathbf{u}_1$, is defined as

$$\mathbf{u}_1 = \mathbf{U}^{\mathrm{T}} \mathbf{e}_1 = \frac{\nabla s}{|\nabla s|}. \tag{46c}$$

For our purposes, the remaining momenta $\nu_2,\ldots,\nu_9$, specified in the transformation by rows $\mathbf{u}_2,\ldots,\mathbf{u}_9$, need only be orthonormal to $\mathbf{v}_1$. For convenience, one may envisage using the Lanczos algorithm [Eq. (17)] to generate these momenta, in which case the resulting kinetic energy tensor $\mathbf{G}_{\mathrm{TM}}^*$ is symmetric tridiagonal [Eq. (18)]:

$$T_{\mathrm{TM}} = \mathbf{w}^{\mathrm{T}} \mathbf{G}_{\mathrm{TM}} \mathbf{w} = \mathbf{v}^{\mathrm{T}} \mathbf{U} \mathbf{G}_{\mathrm{TM}} \mathbf{U}^{\mathrm{T}} \mathbf{v} = \mathbf{v}^{\mathrm{T}} \mathbf{G}_{\mathrm{TM}}^* \mathbf{v}. \tag{47}$$

For later reference we note that the expression analogous to Eq. (19) for $\alpha_1$ is

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$$\alpha_1 = \frac{1}{|\nabla s|^2}\left\{\left(\frac{\partial s}{\partial \tilde{R}}\right)^2\left(\frac{\hbar^2}{2\tilde{\mu}}\right)+\left[\left(\frac{\partial s}{\partial \gamma_{0x}}\right)^2+\left(\frac{\partial s}{\partial \gamma_{0y}}\right)^2\right]B_0\right.$$

$$\left.+\sum_{i=1}^2\left(\frac{\partial s}{\partial \gamma_{iA}}\right)^2 A_i+\left(\frac{\partial s}{\partial \gamma_{iB}}\right)^2 B_i+\left(\frac{\partial s}{\partial \gamma_{iC}}\right)^2 C_i\right\}. \quad (48)$$

The momentum flux integral now becomes

$$\Phi(T,\mathbf{q})=\frac{\hbar}{k_BT}\frac{1}{\pi^3}\int d\nu_2\cdots d\nu_9\int d\nu_1\dot{s}\Theta(\dot{s})e^{-T_{TM}/k_BT}. \quad (49)$$

Analogous to the proof of Sec. II, we note that with $\nu_1$ defined as in Eq. (46c) the following identity holds:

$$\dot{s}=\frac{|\nabla s|}{\hbar}\frac{\partial T_{TM}}{\partial \nu_1}=\frac{2|\nabla s|}{\hbar}(\alpha_1\nu_1+\beta_1\nu_2). \quad (50)$$

Since $|\nabla s|$ and $\alpha_1$ are both positive, the step function $\Theta(\dot{s})$ is exactly accounted for by integrating over $\nu_1$ as follows:

$$\Phi(T,\mathbf{q})=\frac{\hbar}{k_BT}\frac{1}{\pi^3}\int d\nu_2\cdots d\nu_9\int_{-(\beta_1/\alpha_1)\nu_2}^\infty d\nu_1\dot{s}e^{-T_{TM}/k_BT}. \quad (51)$$

Now $\eta$ is defined as follows:

$$\eta=\alpha_1\nu_1^2+2\beta_1\nu_2\nu_1, \quad (52a)$$

$$\frac{\partial \eta}{\partial \nu_1}=\frac{\partial T_{TM}}{\partial \nu_1}=\frac{\hbar}{|\nabla s|}\dot{s}. \quad (52b)$$

Substitution of $\eta$ into Eq. (51) gives

$$\Phi(T,\mathbf{q})=\frac{1}{k_BT}\frac{|\nabla s|}{\pi^3}\int d\nu_2\cdots d\nu_9 e^{-T_{TM}^\perp/k_BT}$$

$$\times\int_{-(\beta_1^2/\alpha_1)\nu_2^2}^\infty d\eta e^{-\eta/k_BT}, \quad (53)$$

where $\mathbf{v}^\perp=(\nu_2,\ldots,\nu_9)$ and

$$T_{TM}^\perp=\tfrac{1}{2}(\mathbf{v}^\perp)^T\mathbf{G}_{TM}^\perp\mathbf{v}^\perp. \quad (54)$$

$\mathbf{G}_{TM}^\perp$ here is defined analogous to Eq. (21b). Integration over $\eta$ in Eq. (53) then leads to

$$\Phi(T,\mathbf{q})=\frac{|\nabla s|}{\pi^3}\int d\nu_2\cdots d\nu_9 e^{-T_{TM}^+/k_BT} \quad (55)$$

with

$$T_{TM}^+=\tfrac{1}{2}(\mathbf{v}^\perp)^T\mathbf{G}_{TM}^+\mathbf{v}^\perp \quad (56)$$

and $\mathbf{G}_{TM}^+$ defined analogous to Eq. (26b). One now integrates over the remaining momenta in Eq. (55) to obtain the result

$$\Phi(T,\mathbf{q})=\frac{\pi|\nabla s|(k_BT)^4}{|\mathbf{G}_{TM}^+|^{1/2}}. \quad (57)$$

Now from Eqs. (28), (40) and (48) one has finally

$$\Phi(T,\mathbf{q})=\frac{\pi(k_BT)^4}{B_0\Pi_{i=1}^2(A_iB_iC_i)^{1/2}}\left\{\left(\frac{\partial s}{\partial \tilde{R}}\right)^2+\left[\left(\frac{\partial s}{\partial \gamma_{0x}}\right)^2\right.\right.$$

$$\left.+\left(\frac{\partial s}{\partial \gamma_{0y}}\right)^2\right]\left(\frac{1}{\tilde{R}^2}\right)+\sum_{i=1}^2\left(\frac{\partial s}{\partial \gamma_{iA}}\right)^2\left(\frac{\tilde{\mu}}{I_{iA}}\right)$$

$$\left.+\left(\frac{\partial s}{\partial \gamma_{iB}}\right)^2\left(\frac{\tilde{\mu}}{I_{iB}}\right)+\left(\frac{\partial s}{\partial \gamma_{iC}}\right)^2\left(\frac{\tilde{\mu}}{I_{iC}}\right)\right\}^{1/2}. \quad (58a)$$

Equation (58) is the exact classical result for the transitional-mode canonical momentum flux with a variably defined reaction coordinate. Together with Eq. (44), it provides a very simple procedure for rigorously implementing CVTST in this class of reactions. The configurational dependence of $\Phi(T,\mathbf{q})$ is compactly represented in terms of the gradients of the reaction coordinate $s$ with respect to rotations about the principal axes of the system. The corresponding result for arbitrary combinations of fragments is

$$\Phi(T,\mathbf{q})=\frac{\pi^{(n-m)/2}(k_BT)^{(n/2+1)}}{B_0\Pi_{i=1}^n\Lambda_i^{1/2}}\left\{\left(\frac{\partial s}{\partial \tilde{R}}\right)^2+\left[\left(\frac{\partial s}{\partial \gamma_{0x}}\right)^2\right.\right.$$

$$\left.+\left(\frac{\partial s}{\partial \gamma_{0y}}\right)^2\right]\left(\frac{1}{\tilde{R}^2}\right)+\sum_{i=1}^n\left(\frac{\partial s}{\partial \gamma_i}\right)^2\left(\frac{\tilde{\mu}}{I_i}\right)\right\}^{1/2}, \quad (58b)$$

where $n$ is the combined number of rotational degrees of freedom of the two fragments, whose rotational constants and moments of inertia are generically labeled $\Lambda_i$ and $I_i$, respectively. The integer $m=2$ if one of the fragments is monatomic, otherwise $m=4$. This result is in fact identical to that proposed in our earlier work on the basis of an approximate analysis.[31]

## B. E-resolved microcanonical momentum flux integral

In this section we consider the momentum flux integral for the $E$-resolved microcanonical ensemble. As noted above, Klippenstein has previously implemented an extension of Marcus' canonical approach to the microcanonical case.[37] Our result will follow in a straightforward manner from the techniques established in the previous sections. It is equivalent to that of Klippenstein, but simpler in form and potentially faster in numerical computations. The statistical expression for the $E$-resolved microcanonical rate constant, $k(E)$, is written classically as

$$k(E)=\frac{\int\cdots\int d\mathbf{q}\,d\mathbf{p}\delta(s-s_0)\dot{s}\Theta(\dot{s})\delta(E-H)}{\int\int\cdots\int d\mathbf{q}\,d\mathbf{p}\wp(\mathbf{q})\delta(E-H)}. \quad (59)$$

Recognizing that the classical density of states $\rho(E)$ for the reactant(s) is $h^{-n}$ times the denominator of Eq. (59), it is convenient to write $k(E)$ in the standard form

$$k(E)=\frac{W(E)}{h\rho(E)}, \quad (60)$$

where $W(E)$ may be defined as

$$W(E)=h^{-(n-1)}\int\cdots\int d\mathbf{q}\,d\mathbf{p}\delta(s-s_0)\dot{s}\Theta(\dot{s})\delta(E-H). \quad (61)$$

As a result of the neglect of coupling between the conserved and transitional modes in Eq. (32), the expression for $W(E)$ can be written as a convolution of the conserved-mode density of states $\rho_{\mathrm{vib}}(E)$ with the transitional mode ''sum of states'' $W_{\mathrm{TM}}(E)$,

$$W(E) = \int_0^{E^*} dE_+ W_{\mathrm{TM}}(E_+)\rho_{\mathrm{vib}}(E^*-E_+), \qquad (62)$$

where $E^* = E - V_{\min}(s)$. As above, the definition of the reaction coordinate implies that the flux factor will affect only $W_{\mathrm{TM}}(E)$ in Eq. (62). Hence, our focus will be on deriving a compact and efficient expression for this quantity,

$W_{\mathrm{TM}}(E)$

$$= \frac{1}{\sigma_1\sigma_2}\int\cdots\int dR\,d\phi\,d\theta\,d\phi_1\,d\theta_1\,d\psi_1\,d\phi_2\,d\theta_2 d\psi_2$$

$$\times\delta(s-s_0)\frac{1}{h^8}\int dp_R\,dp_\phi\,dp_\theta\,dp_{\phi_1}\,dp_{\theta_1}\,dp_{\psi_1}$$

$$\times dp_{\phi_2}\,dp_{\theta_2}\,dp_{\psi_2}\,\dot{s}\Theta(\dot{s})\delta(E-H). \qquad (63)$$

Analogous to Sec. III A above, we introduce (1) a transformation of angular momenta to the principal-axis components, (2) a transformation of $R$ and $p_R$ so that they are dimensionless ($\tilde{p}_R$ in units of $\hbar$) and the corresponding element of the kinetic energy tensor $\mathbf{G}_{\mathrm{TM}}$ is $(\hbar^2/2\tilde{\mu})$ [Eqs. (38) and (39)], (3) a transformation of angles to body-fixed external and internal Euler angles, followed by integration over the external angles and $R$. Next, we define the $E$-resolved momentum flux integral as

$$\Phi(E,\mathbf{q}) = \frac{\hbar}{\pi^3}\int d\mathbf{j}_1\,d\mathbf{j}_2\,d\mathbf{l}\,d\tilde{p}_R\,\dot{s}\Theta(\dot{s})\delta(E-H_{\mathrm{TM}}), \qquad (64a)$$

so that $W_{\mathrm{TM}}(E)$ is written

$$W_{\mathrm{TM}}(E) = \frac{1}{\sigma_1\sigma_2}\frac{1}{N'}\int d\phi'\,d\theta_1'\,d\psi_1'\,d\theta_2'\,d\psi_2'\left(\frac{\partial s}{\partial R}\right)^{-1}$$

$$\times\sin\theta_1'\sin\theta_2'\Phi(E,\mathbf{q})\bigg|_{s=s_0}$$

$$= \frac{1}{\sigma_1\sigma_2}\left\langle\left(\frac{\partial s}{\partial R}\right)^{-1}\Phi(E,\mathbf{q})\right\rangle_{s=s_0}. \qquad (64b)$$

The orthogonal transformation of momenta now proceeds as in Eqs. (45)–(48), after which $\Phi(E,\mathbf{q})$ takes the form

$$\Phi(E,\mathbf{q}) = \frac{\hbar}{\pi^3}\int d\nu_2\cdots d\nu_9\int_{-(\beta_1/\alpha_1)\nu_2}^{\infty} d\nu_1\,\dot{s}\,\delta(E-H_{\mathrm{TM}}), \qquad (65)$$

where we have taken account of the boundaries imposed by $\Theta(\dot{s})$ as in Eq. (51). Introducing the variable $\eta$ as in Eq. (52), Eq. (65) now becomes

$$\Phi(E,\mathbf{q}) = \frac{|\nabla s|}{\pi^3}\int d\nu_2\cdots d\nu_9\int_{-(\beta_1^2/\alpha_1)\nu_2^2}^{\infty} d\eta$$

$$\times\delta(E-V_{\mathrm{TM}}(\mathbf{q})-T_{\mathrm{TM}}^{\perp}-\eta) \qquad (66)$$

with $T_{\mathrm{TM}}^{\perp}$ as in Eq. (54). Integration over $\eta$ now yields

$$\Phi(E,\mathbf{q}) = \frac{|\nabla s|}{\pi^3}\int d\nu_2\cdots d\nu_9\Theta(E-V_{\mathrm{TM}}(\mathbf{q})-T_{\mathrm{TM}}^{+}) \qquad (67)$$

with $T_{\mathrm{TM}}^{+}$ as in Eq. (56). The remaining integrals are cast into a standard form (e.g., Dirichlet's integral[50]) and evaluated to give

$$\Phi(E,\mathbf{q}) = \frac{\pi|\nabla s|}{4!}\frac{[E-V_{\mathrm{TM}}(\mathbf{q})]^4}{|\mathbf{G}_{\mathrm{TM}}^{+}|^{1/2}}. \qquad (68)$$

Substituting for $|\mathbf{G}_{\mathrm{TM}}^{+}|$ using Eqs. (28), (40) and (48), one obtains the result

$$\Phi(E,\mathbf{q}) = \frac{\pi}{4!}\frac{[E-V_{\mathrm{TM}}(\mathbf{q})]^4}{B_0\Pi_{i=1}^2(A_iB_iC_i)^{1/2}}\left\{\left(\frac{\partial s}{\partial\tilde{R}}\right)^2+\left[\left(\frac{\partial s}{\partial\gamma_{0x}}\right)^2\right.\right.$$

$$+\left(\frac{\partial s}{\partial\gamma_{0y}}\right)^2\left]\left(\frac{1}{\tilde{R}^2}\right)+\sum_{i=1}^2\left(\frac{\partial s}{\partial\gamma_{iA}}\right)^2\left(\frac{\tilde{\mu}}{I_{iA}}\right)\right.$$

$$\left.+\left(\frac{\partial s}{\partial\gamma_{iB}}\right)^2\left(\frac{\tilde{\mu}}{I_{iB}}\right)+\left(\frac{\partial s}{\partial\gamma_{iC}}\right)^2\left(\frac{\tilde{\mu}}{I_{iC}}\right)\right\}^{1/2} \qquad (69a)$$

and its equivalent for arbitrary combinations of fragments,

$$\Phi(E,\mathbf{q}) = \frac{\pi^{(n-m)/2}}{\Gamma(n/2+2)}\frac{[E-V_{\mathrm{TM}}(\mathbf{q})]^{(n/2+1)}}{B_0\Pi_{i=1}^n\Lambda_i^{1/2}}$$

$$\times\left\{\left(\frac{\partial s}{\partial\tilde{R}}\right)^2+\left[\left(\frac{\partial s}{\partial\gamma_{0x}}\right)^2+\left(\frac{\partial s}{\partial\gamma_{0y}}\right)^2\right]\left(\frac{1}{\tilde{R}^2}\right)\right.$$

$$\left.+\sum_{i=1}^n\left(\frac{\partial s}{\partial\gamma_i}\right)^2\left(\frac{\tilde{\mu}}{I_i}\right)\right\}^{1/2}. \qquad (69b)$$

In Eq. (69b), $\Gamma(n)$ is the gamma function, i.e., $\Gamma(n+1) = n\Gamma(n)$, with $\Gamma(1) = 1$ and $\Gamma(1/2) = \pi^{1/2}$. The quantities $n$, $m$ $\Lambda_i$, and $I_i$ are as defined beneath Eq. (58b).

## C. $E,J$-resolved microcanonical momentum flux integral

For an isolated bimolecular collision or unimolecular dissociation in the gas phase, both the total energy and total angular momentum are conserved quantities. The conservation of angular momentum has important consequences for the dynamics and kinetics of such reactions, hence it is very important to develop statistical theories which account correctly for this effect.[39,42,43,45,51,52]

In this final section, we extend the developments above to allow for angular-momentum resolution in the calculation of the flux through the TS hypersurface with a variably defined reaction coordinate. The tools for the angular momentum analysis have been largely developed in our earlier work on the center-of-mass separation reaction coordinate,[28] hence the reader is referred to that reference for background details.

The statistical approximation for the $J$-resolved microcanonical rate constant is written

$$k(E,J) = \frac{\int\int \cdots \int\int d\mathbf{q}\, d\mathbf{p}\, \delta(s-s_0)\dot{s}\,\Theta(\dot{s})\,\delta(E-H)\,\delta(J-j)}{\int\int \cdots \int\int d\mathbf{q}\, d\mathbf{p}\,\wp(\mathbf{q})\,\delta(E-H)\,\delta(J-j)}$$

$$= \frac{W(E,J)}{h\rho(E,J)}, \tag{70}$$

where $\rho(E,J)$ is the $J$-resolved microcanonical density of states of the reactant(s).[19,29,51,53] As in Eq. (62) above, $W(E,J)$ is written as a convolution of the transitional mode "sum of states," $W_{TM}(E,J)$, and the conserved mode density of states,

$$W(E) = \int_{E_{\min}(J)}^{E^*} dE_+ W_{TM}(E_+,J)\rho_{vib}(E^*-E_+), \tag{71}$$

where $E_{\min}(J)$ is the minimum energy required to generate the total angular momentum $J$ and $E^*$ is as in Eq. (62). Note we assume here that only the high-amplitude motions in the transitional modes contribute significantly to the total angular momentum. Thus, both the reaction coordinate flux factor and the angular momentum constraint affect only $W_{TM}$ in Eq. (71). Analogous to Eq. (64), we have for the $J$-resolved quantities

$$\Phi(E,J,\mathbf{q}) = \frac{\hbar}{\pi^3}\int d\mathbf{j}_1\, d\mathbf{j}_2\, d\mathbf{l}\, d\tilde{p}_R \dot{s}\,\Theta(\dot{s})\,\delta(E-H_{TM})\,\delta(J-j) \tag{72a}$$

so that

$$W_{TM}(E,J) = \frac{1}{\sigma_1\sigma_2}\frac{1}{N'}\int d\phi'\, d\theta_1'\, d\psi_1'\, d\theta_2'\, d\psi_2' \left(\frac{\partial s}{\partial R}\right)^{-1}$$

$$\times \sin\theta_1'\sin\theta_2'\,\Phi(E,J,\mathbf{q})\bigg|_{s=s_0}$$

$$= \frac{1}{\sigma_1\sigma_2}\left\langle \left(\frac{\partial s}{\partial R}\right)^{-1}\Phi(E,J,\mathbf{q})\right\rangle_{s=s_0}. \tag{72b}$$

Our approach is to consider first the momentum flux integral for a fixed total angular-momentum vector $\mathbf{J}$, and then integrate this over the different orientations of $\mathbf{J}$. Thus, we write the momentum flux integral for a given total angular-momentum vector $\mathbf{J}$ as

$$\Phi(E,\mathbf{J},\mathbf{q}) = \frac{\hbar}{\pi^3}\int d\mathbf{j}_1\, d\mathbf{j}_2\, d\mathbf{l}\, d\tilde{p}_R \dot{s}\,\Theta(\dot{s})\,\delta(E-H_{TM})\,\delta(\mathbf{J}-\mathbf{j}), \tag{73}$$

whence

$$\Phi(E,J,\mathbf{q}) = \int d\mathbf{j}\,\Phi(E,\mathbf{j},\mathbf{q})\,\delta(J-j). \tag{74}$$

The first step in evaluating Eq. (73) is the recognition that each of the angular momenta can be separated into a component which is dictated by the instantaneous overall rotation of the system associated with the vector $\mathbf{J}$ and a component which is associated with purely internal rotation. Furthermore, the kinetic energy for the transitional modes also separates into that for overall rotation and that for internal rotation and translation.[28] Thus, we write

$$\mathbf{j}_1 = \mathbf{j}_1^{\mathbf{J}} + \mathbf{p}_1, \tag{75a}$$

$$\mathbf{j}_2 = \mathbf{j}_2^{\mathbf{J}} + \mathbf{p}_2, \tag{75b}$$

$$\mathbf{l} = \mathbf{l}^{\mathbf{J}} + \mathbf{p}_0. \tag{75c}$$

In Eq. (75), the quantities $\mathbf{j}_1^{\mathbf{J}}$, $\mathbf{j}_2^{\mathbf{J}}$ and $\mathbf{l}^{\mathbf{J}}$ are vector constants which give the individual angular momenta of the fragments and the orbital rotation arising from the instantaneous overall rotation associated with the total angular-momentum $\mathbf{J}$. They are completely defined by $\mathbf{J}$ through the fact that they correspond to a *common angular velocity vector* $\boldsymbol{\omega}^{\mathbf{J}}$ which is itself related to $\mathbf{J}$ through the overall inertia tensor. This definition is expressed through the following equations:[28]

$$\mathbf{j}_1^{\mathbf{J}'} = \mathbf{I}_1'\boldsymbol{\omega}^{\mathbf{J}'} = \mathbf{I}_1'\mathbf{I}'(\mathbf{q})^{-1}\mathbf{J}', \tag{76a}$$

$$\mathbf{j}_2^{\mathbf{J}'} = \mathbf{I}_2'\boldsymbol{\omega}^{\mathbf{J}'} = \mathbf{I}_2'\mathbf{I}'(\mathbf{q})^{-1}\mathbf{J}', \tag{76b}$$

$$\mathbf{l}^{\mathbf{J}'} = \mathbf{I}_2'\boldsymbol{\omega}^{\mathbf{J}'} = \mathbf{I}_0'\mathbf{I}'(\mathbf{q})^{-1}\mathbf{J}', \tag{76c}$$

where $\mathbf{I}'(\mathbf{q})$ is the inertia tensor for the overall body,

$$\mathbf{I}'(\mathbf{q}) = \mathbf{I}_1' + \mathbf{I}_2' + \mathbf{I}_0'. \tag{77}$$

In Eq. (76) and below, a superscript prime on vectors and tensors indicates that these quantities are represented with respect to the common body-fixed axes $(x,y,z)$ of the system. Vectors and tensors *without* a prime are assumed to be projected onto the relevant principal axes. With the definition of Eq. (76), it is readily shown that

$$\mathbf{J}' = \mathbf{j}_1^{\mathbf{J}'} + \mathbf{j}_2^{\mathbf{J}'} + \mathbf{l}^{\mathbf{J}'} \tag{78}$$

and so the delta function constraint of Eq. (73) becomes

$$\delta(\mathbf{J}-\mathbf{j}) = \delta(\mathbf{J}'-\mathbf{j}')$$

$$= \delta[\mathbf{J} - (\mathbf{j}_1' + \mathbf{j}_2' + \mathbf{l}')]$$

$$= \delta[\mathbf{J} - (\mathbf{j}_1^{\mathbf{J}'} + \mathbf{j}_1^{\mathbf{J}'} + \mathbf{l}^{\mathbf{J}'}) - (\mathbf{p}_1' + \mathbf{p}_2' + \mathbf{p}_0')]$$

$$= \delta(\mathbf{p}_1' + \mathbf{p}_2' + \mathbf{p}_0'). \tag{79}$$

This constraint reflects the fact that the angular momenta $(\mathbf{p}_0, \mathbf{p}_1, \mathbf{p}_2)$ are required to describe purely *internal* motion and must have no contribution to the overall angular momentum. In terms of the decomposition in Eq. (75), the kinetic energy for the transitional modes becomes[28]

$$T_{TM} = \mathbf{J}^T\mathbf{G}_{TM}^{ext}\mathbf{J} + \hbar(\boldsymbol{\omega}^{\mathbf{J}'})^T(\mathbf{p}_0' + \mathbf{p}_1' + \mathbf{p}_2') + \mathbf{p}^T\mathbf{G}_{TM}\mathbf{p}, \tag{80}$$

where $\mathbf{p} = (\tilde{p}_R, p_{0x}, p_{0y}, p_{1A}, p_{1B}, p_{1C}, p_{2A}, p_{2B}, p_{2C})$, $\mathbf{G}_{TM}$ is diagonal as defined beneath Eq. (39), and $\mathbf{G}_{TM}^{ext}$ is a diagonal matrix whose elements $\mathbf{G}_{11} = A(\mathbf{q})$, $\mathbf{G}_{22} = B(\mathbf{q})$, and $\mathbf{G}_{33} = C(\mathbf{q})$ are the overall rotational constants for the system at the specified configuration. Note that, since $p_{0z}$ (the orbital angular momentum about the line joining the fragment centers of mass) is identically zero, it is suppressed for notational convenience in the last term of Eq. (80) which describes the internal kinetic energy. From Eq. (80), it is clear that the delta-function constraint of Eq. (79) will also ensure that the coupling term between internal and external momenta in the kinetic energy expression is zero.

As is already apparent from Eqs. (76)–(80), in order to account for the vector correlations imposed by fixing the total angular-momentum vector $\mathbf{J}$, it will be necessary to

project vectors and tensors as appropriate onto a common axial system. For this purpose, we choose the body-fixed Cartesian axes $(x,y,z)$; hence it is appropriate to make some comment on the structure of $\mathbf{G}'_{TM}$. $\mathbf{G}_{TM}$ is diagonal because it is represented in terms of the respective principal axes of the fragments and the orbital rotation. Since $\mathbf{G}'_{TM}$ is represented with respect to the body-fixed axes, however, the blocks involving fragments 1 and 2 will in general not be diagonal. If the kinetic energy tensor for fragment 1 is denoted as $\mathbf{G}_1$ and that for fragment 2 as $\mathbf{G}_2$ then we have

$$\mathbf{G}'_i = \mathbf{A}_i \mathbf{G}_i \mathbf{A}_i^{-1}, \tag{81}$$

where $\mathbf{A}_i$ is the rotation matrix which relates the principal axes of fragment $i$ to the body-fixed axes.[54] Thus, $\mathbf{G}'_{TM}$ is block diagonal, with nonzero elements $\{(\hbar^2/2\tilde{\mu}),B_0,B_0,\mathbf{G}'_1,\mathbf{G}'_2\}$ with $\mathbf{G}'_1$ and $\mathbf{G}'_2$ constituting $3\times3$ blocks as indicated in Eq. (81).

The next step is to examine the functional dependence of the flux factor $\dot{s}$ in light of the decomposition represented by Eq. (75). In Eq. (45), $\dot{s}$ was represented in terms of infinitesimal rotations and corresponding angular velocities about the principal axes of the fragments, which in general are not co-aligned. For the present purposes, it is more useful to express $\dot{s}$ in terms of infinitesimal rotations about axes which are co-aligned with the body-fixed axes of the system,

$$\dot{s} = \frac{\partial s}{\partial \tilde{R}}\dot{\tilde{R}} + \frac{\partial s}{\partial \gamma_{0x}}\dot{\gamma}_{0x} + \frac{\partial s}{\partial \gamma_{0y}}\dot{\gamma}_{0y} + \sum_{i=1}^{2}\frac{\partial s}{\partial \gamma_{ix}}\dot{\gamma}_{ix} + \frac{\partial s}{\partial \gamma_{iy}}\dot{\gamma}_{iy}$$
$$+ \frac{\partial s}{\partial \gamma_{iz}}\dot{\gamma}_{iz}. \tag{82}$$

Analogous to Eqs. (75) and (76), we now decompose the angular velocity vectors $\omega'_0 = (\dot{\gamma}_{0x},\dot{\gamma}_{0y},0)$, $\omega'_1 = (\dot{\gamma}_{1x},\dot{\gamma}_{1y},\dot{\gamma}_{1z})$, $\omega'_2 = (\dot{\gamma}_{2x},\dot{\gamma}_{2y},\dot{\gamma}_{2z})$ from Eq. (82) into the common component $\boldsymbol{\omega}^{\mathbf{J}'}$ associated with the coherent overall rotation generating the total angular-momentum vector $\mathbf{J}'$ and the remaining components $\tilde{\boldsymbol{\omega}}'_i$ which describe internal rotation (corresponding to the internal angular momenta $\mathbf{p}'_i$),

$$\boldsymbol{\omega}'_i = \boldsymbol{\omega}^{\mathbf{J}'} + \tilde{\boldsymbol{\omega}}'_i. \tag{83}$$

Substitution into Eq. (82) leads to

$$\dot{s} = \frac{\partial s}{\partial \tilde{R}}\dot{\tilde{R}} + \frac{\partial s}{\partial \gamma_{0x}}\tilde{\omega}_{0x} + \frac{\partial s}{\partial \gamma_{0y}}\tilde{\omega}_{0y} + \sum_{i=1}^{2}\frac{\partial s}{\partial \gamma_{ix}}\tilde{\omega}_{ix}$$
$$+ \frac{\partial s}{\partial \gamma_{iy}}\tilde{\omega}_{iy} + \frac{\partial s}{\partial \gamma_{iz}}\tilde{\omega}_{iz} + \omega^{\mathbf{J}}_x\left(\frac{\partial s}{\partial \gamma_{0x}} + \frac{\partial s}{\partial \gamma_{1x}} + \frac{\partial s}{\partial \gamma_{2x}}\right)$$
$$+ \omega^{\mathbf{J}}_y\left(\frac{\partial s}{\partial \gamma_{0y}} + \frac{\partial s}{\partial \gamma_{1y}} + \frac{\partial s}{\partial \gamma_{2y}}\right)$$
$$+ \omega^{\mathbf{J}}_z\left(\frac{\partial s}{\partial \gamma_{0z}} + \frac{\partial s}{\partial \gamma_{1z}} + \frac{\partial s}{\partial \gamma_{2z}}\right). \tag{84}$$

Examining the first term in parentheses in Eq. (84), one notes that it gives the change in $s$ which results from simultaneous and identical infinitesimal rotations about the $x$ axis of fragment 1, fragment 2 and the line joining their respective centres of mass. This, of course, is an infinitesimal rigid-body rotation of the overall system. Recalling that $s$ is defined as a

separation distance *internal* to the overall system, it is apparent that $s$ cannot change as a result of such a rotation. Since the same conclusion holds for the $y$ and $z$ axes, the expressions in parentheses in Eq. (84) sum, respectively, to zero and we have

$$\dot{s} = \frac{\partial s}{\partial \tilde{R}}\dot{\tilde{R}} + \frac{\partial s}{\partial \gamma_{0x}}\tilde{\omega}_{0x} + \frac{\partial s}{\partial \gamma_{0y}}\tilde{\omega}_{0y} + \sum_{i=1}^{2}\frac{\partial s}{\partial \gamma_{ix}}\tilde{\omega}_{ix} + \frac{\partial s}{\partial \gamma_{iy}}\tilde{\omega}_{iy}$$
$$+ \frac{\partial s}{\partial \gamma_{iz}}\tilde{\omega}_{iz} = \frac{2}{\hbar}(\nabla's)^T\mathbf{G}'_{TM}\mathbf{p}', \tag{85}$$

where the primes again indicate that vectors and tensors are projected onto the common body-fixed axes. Thus, $\dot{s}$ is a function solely of the internal angular momenta $\mathbf{p}'_0$, $\mathbf{p}'_1$ and $\mathbf{p}'_2$.

Using Eqs. (75)–(79) and (85), we can now rewrite the momentum flux integral in Eq. (73) as

$$\Phi(E,\mathbf{J},\mathbf{q}) = \frac{\hbar}{\pi^3}\int d\mathbf{p}'\dot{s}(\mathbf{p}')\Theta(\dot{s})\delta[E-H_{TM}]$$
$$\times \delta(p_{0x}+p_{1x}+p_{2x})\delta(p_{0y}+p_{1y}+p_{2y})$$
$$\times \delta(p_{1z}+p_{2z}), \tag{86}$$

where $\mathbf{p}' = (\tilde{p}_R,p_{0x},p_{0y},p_{1x},p_{1y},p_{1z},p_{2x},p_{2y},p_{2z})$. The angular-momentum delta functions in Eq. (86) have the effect of collapsing three of the integrals. For example, if we choose to integrate over $p_{2x}$, $p_{2y}$ and $p_{2z}$ then Eq. (86) becomes

$$\Phi(E,\mathbf{J},\mathbf{q}) = \frac{\hbar}{\pi^3}\int d\mathbf{p}'_{int}\dot{s}(\mathbf{p}'_{int})\Theta(\dot{s})\delta[E-V(\mathbf{q})-E^J-T^{int}_{TM}], \tag{87}$$

where $d\mathbf{p}'_{int} = d\tilde{p}_R\,dp_{0x}\,dp_{0y}\,dp_{1x}\,dp_{1y}\,dp_{1z}$,

$$T^{int}_{TM} = (\mathbf{p}'_{int})^T\mathbf{G}'_{int}\mathbf{p}'_{int}, \tag{88}$$

and $\mathbf{G}'_{int}$ may be deduced from Eq. (80) by setting $\mathbf{p}'_2 = -(\mathbf{p}'_0+\mathbf{p}'_1)$. Likewise, the functional form of $\dot{s}(\mathbf{p}'_{int})$ may be obtained from Eq. (85) by setting $\mathbf{p}'_2 = -(\mathbf{p}'_0+\mathbf{p}'_1)$. It remains to integrate Eq. (87) over the six internal momenta. The procedure to perform this integral is entirely analogous to that used in the evaluation of Eq. (64a) above, the only difference being that the number of integrals here is six, as opposed to nine in that case. The difference in dimensionality is trivially accounted for, since the generic form of the integral remains the same [cf. Eq. (69b)]. Thus, we can write the solution for Eq. (87) formally as follows:

$$\Phi(E,\mathbf{J},\mathbf{q}) = \frac{\pi^{-1/2}|\nabla s|}{\Gamma(5/2+1)}\frac{\tilde{\alpha}_1^{1/2}}{|\mathbf{G}'_{int}|^{1/2}}[E-V_{TM}(\mathbf{q})-E^J]^{5/2}, \tag{89}$$

where $\tilde{\alpha}_1$ is the top-left-hand element of the appropriate tridiagonal kinetic energy tensor [cf. Eqs. (17) and (18)]. Although it is possible to write explicit formulas for the terms $|\mathbf{G}'_{int}|$ and $\tilde{\alpha}_1$ by working through the details of the transformations, one can save trees and clumsy notation by noting that integration of Eq. (89) over all energetically allowed components of the total angular momentum $\mathbf{J}$ must yield $\Phi(E,\mathbf{q})$ [Eq. (69a)],

$$\Phi(E,\mathbf{q}) = \int d\mathbf{J}\,\Phi(E,\mathbf{J},\mathbf{q})$$

$$= \frac{\pi^{-1/2}|\nabla s|}{\Gamma(5/2+1)}\frac{\widetilde{\alpha}_1^{1/2}}{|\mathbf{G}'_{\text{int}}|^{1/2}}\int dJ_A\,dJ_B\,dJ_C$$

$$\times [E - V_{\text{TM}}(\mathbf{q}) - A(\mathbf{q})J_A^2 - B(\mathbf{q})J_B^2 - C(\mathbf{q})J_C^2]^{5/2}$$

$$= \frac{\pi}{4!}\frac{[E - V_{\text{TM}}(\mathbf{q})]^4}{[A(\mathbf{q})B(\mathbf{q})C(\mathbf{q})]^{1/2}}\frac{|\nabla s|\,\widetilde{\alpha}_1^{1/2}}{|\mathbf{G}'_{\text{int}}|^{1/2}}. \qquad (90)$$

Comparison of Eq. (90) with Eq. (69a) shows that

$$\frac{|\nabla s|\,\widetilde{\alpha}_1^{1/2}}{|\mathbf{G}'_{\text{int}}|^{1/2}} = \frac{[A(\mathbf{q})B(\mathbf{q})C(\mathbf{q})]^{1/2}}{B_0\Pi_{i=1}^2(A_iB_iC_i)^{1/2}}\left\{\left(\frac{\partial s}{\partial \widetilde{R}}\right)^2 + \left[\left(\frac{\partial s}{\partial \gamma_{0x}}\right)^2\right.\right.$$

$$\left. + \left(\frac{\partial s}{\partial \gamma_{0y}}\right)^2\right]\left(\frac{1}{\widetilde{R}^2}\right) + \sum_{i=1}^2\left(\frac{\partial s}{\partial \gamma_{iA}}\right)^2\left(\frac{\widetilde{\mu}}{I_{iA}}\right)$$

$$\left. + \left(\frac{\partial s}{\partial \gamma_{iB}}\right)^2\left(\frac{\widetilde{\mu}}{I_{iB}}\right) + \left(\frac{\partial s}{\partial \gamma_{iC}}\right)^2\left(\frac{\widetilde{\mu}}{I_{iC}}\right)\right\}^{1/2}. \qquad (91)$$

Substituting Eq. (91) into Eq. (89) then gives the result

$$\Phi(E,\mathbf{J},\mathbf{q}) = \frac{[A(\mathbf{q})B(\mathbf{q})C(\mathbf{q})]^{1/2}}{B_0\Pi_{i=1}^2(A_iB_iC_i)^{1/2}}\frac{\pi^{-1/2}}{\Gamma(5/2+1)}[E - V_{\text{TM}}(\mathbf{q})$$

$$- E^{\mathbf{J}}]^{5/2}\left\{\left(\frac{\partial s}{\partial \widetilde{R}}\right)^2 + \left[\left(\frac{\partial s}{\partial \gamma_{0x}}\right)^2 + \left(\frac{\partial s}{\partial \gamma_{0y}}\right)^2\right]\left(\frac{1}{\widetilde{R}^2}\right)$$

$$+ \sum_{i=1}^2\left(\frac{\partial s}{\partial \gamma_{iA}}\right)^2\left(\frac{\widetilde{\mu}}{I_{iA}}\right) + \left(\frac{\partial s}{\partial \gamma_{iB}}\right)^2\left(\frac{\widetilde{\mu}}{I_{iB}}\right)$$

$$+ \left(\frac{\partial s}{\partial \gamma_{iC}}\right)^2\left(\frac{\widetilde{\mu}}{I_{iC}}\right)\right\}^{1/2}. \qquad (92a)$$

The corresponding result for arbitrary combinations of fragments is

$$\Phi(E,\mathbf{J},\mathbf{q}) = \frac{[A(\mathbf{q})B(\mathbf{q})C(\mathbf{q})]^{1/2}}{B_0\Pi_{i=1}^n\Lambda_i^{1/2}}\frac{\pi^{n-m-3/2}}{\Gamma[(n+1)/2]}$$

$$\times [E - V_{\text{TM}}(\mathbf{q}) - E^{\mathbf{J}}]^{(n-1)/2}$$

$$\times \left\{\left(\frac{\partial s}{\partial \widetilde{R}}\right)^2 + \left[\left(\frac{\partial s}{\partial \gamma_{0x}}\right)^2 + \left(\frac{\partial s}{\partial \gamma_{0y}}\right)^2\right]\left(\frac{1}{\widetilde{R}^2}\right)\right.$$

$$\left. + \sum_{i=1}^n\left(\frac{\partial s}{\partial \gamma_i}\right)^2\left(\frac{\widetilde{\mu}}{I_i}\right)\right\}^{1/2}. \qquad (92b)$$

Equation (92) is the exact classical momentum flux integral for the transitional modes with a specified configuration $\mathbf{q}$, total energy $E$, total angular-momentum vector $\mathbf{J}$ and a variably defined reaction coordinate $s$. It is interesting to compare this with the corresponding result when the reaction coordinate is the center-of-mass separation $R$. Labeling the latter $\Phi^*(E,\mathbf{J},\mathbf{q})$, one has[28]

$$\Phi^*(E,\mathbf{J},\mathbf{q}) = \frac{[A(\mathbf{q})B(\mathbf{q})C(\mathbf{q})]^{1/2}}{B_0\Pi_{i=1}^n\Lambda_i^{1/2}}\frac{\pi^{n-m-3/2}}{\Gamma[(n+1)/2]}$$

$$\times [E - V_{\text{TM}}(\mathbf{q}) - E^{\mathbf{J}}]^{(n-1)/2}. \qquad (93)$$

Thus, it is apparent that the *exact* result of Eq. (92) is related to $\Phi^*(E,\mathbf{J},\mathbf{q})$ by inclusion of a multiplicative correction factor given by the terms in curly brackets. Indeed, it was in the spirit of finding a correction factor that we arrived at this same result previously via an approximate analysis.[31]

Ensuing integration of $\Phi(E,\mathbf{J},\mathbf{q})$ over orientations of the angular-momentum vector to obtain $\Phi(E,J,\mathbf{q})$ [Eq. (74)] proceeds in a fashion entirely analogous to our earlier work, where somewhat lengthy analytical expressions for $\Phi^*(E,J,\mathbf{q})$ are presented.[28] Thus, one concludes that

$$\Phi(E,J,\mathbf{q}) = \left\{\left(\left(\frac{\partial s}{\partial \widetilde{R}}\right)^2 + \left[\left(\frac{\partial s}{\partial \gamma_{0x}}\right)^2 + \left(\frac{\partial s}{\partial \gamma_{0y}}\right)^2\right]\left(\frac{1}{\widetilde{R}^2}\right)\right)\right.$$

$$\left. + \sum_{i=1}^n\left(\frac{\partial s}{\partial \gamma_i}\right)^2\left(\frac{\widetilde{\mu}}{I_i}\right)\right\}^{1/2}\Phi^*(E,J,\mathbf{q}). \qquad (94)$$

Equation (94) completes our analysis of the momentum flux integral for $E,J$-resolved ensembles. Coupled with Monte Carlo integration, or direct quadrature as appropriate, over the internal angular configuration space [Eq. (72b)] it provides a very convenient and efficient method for implementation of $\mu_{E,J}$ VTST in this important class of reactions.

## IV. CONCLUSION

In this paper, we have reported significant new developments in the implementation of TST with a generalized reaction coordinate. Our derivation of the canonical flux integral (Sec. II), while equivalent to Marcus' pioneering analysis of this problem,[36] yields a simpler and more physically transparent result which should prove much easier to work with in numerical implementations of the theory. The essential advantage of the analysis which we have introduced is that it invokes only orthogonal transformations in momentum space to evaluate the momentum flux integral, rather than full canonical transformations. In this way we are able to take advantage of simplicity of an underlying Cartesian coordinate system to derive our final result. In Sec. III, we have extended the analysis to treat the important class of gas phase reactions involving barrierless recombination/simple-fission dissociation processes. We have derived simple analytic forms for the momentum flux integrals associated with the transitional modes in these reactions, including the canonical ensemble, the $E$-resolved microcanonical ensemble and the $E,J$-resolved microcanonical ensemble. These expressions have been shown in previous work to enable dramatic enhancements in the efficiency of rigorous numerical implementations of variational TST for this class of reactions,[28,31] and hence are already coded in our unimolecular kinetics package. The present work reveals that the expressions, which we had previously arrived at on the basis of an approximate analysis, are in fact exact.

## ACKNOWLEDGMENTS

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