Kinematic Factors in Transition State Theory with a Generalized Reaction Coordinate[†]

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Different approaches to the evaluation of the momentum flux integral in classical transition state theory (TST) with a generalized reaction coordinate (GRC) have yielded superficially contrasting results for the kinematic factor which must be included in the ensuing configurational integral. In this work, Smith's recent solution for the momentum flux integral in TST with a GRC (*J. Chem. Phys.* **1999**, *111*, 1830) is rederived and generalized in order to establish equivalence with several different approaches in the literature: (a) the pioneering work of Marcus (*J. Chem. Phys.* **1964**, *41*, 2624), (b) the reaction path Hamiltonian result of Miller (in *Potential Energy Surfaces and Dynamics Calculations*; Truhlar, D. G., Ed.; Plenum: New York, 1981), and (c) the flexible TST expression of Robertson, Wagner, and Wardlaw (*Faraday Discuss.* **1995**, *102*, 65). We conclude that, while each of these approaches is distinct, the results are consistent. For the general case, a coordinate-dependent kinematic factor does arise from the analytical evaluation of the momentum flux integral, and it is now apparent that this factor can be very simply and efficiently evaluated for incorporation into the ensuing configurational integral on the dividing surface. The same kinematic factor appears in canonical and microcanonical TST expressions for the rate constant, even when total angular momentum is explicitly resolved in the flux integrals.

I. Introduction

Transition state theory (TST) has a long and venerable history, almost as long as the field of reaction dynamics itself. The theory bases itself upon the assumption that there exists a region somewhere along the reaction path at which one may identify a distinct bottleneck in the quantum or classical flux. This is an assumption which can now be explicitly verified by exact quantum scattering calculations for three- or four-atom direct reactions,[1] where not surprisingly the "bottleneck region" is that part of the potential energy surface (PES) at or close to the potential barrier. Quantum scattering calculations are expensive in terms of computer time and memory, however, and often require a substantial new code to be written for each extra atom or degree of freedom that is included explicitly into the calculation. Hence, it is exceedingly important to continue the development of fast and reliable approximate theories for chemical rate constants.

In order to develop a good approximate theory, the task is to find a suitable approximation for the net reactive flux. The presence of a distinct bottleneck in the flux at some part of the PES between reactants and products implies that reaction is a rare event in a molecular history, such that once this region of the PES is crossed it is unlikely to be recrossed on a short time scale. In TST this last statement is exploited by approximating the *net* flux with the *one-way* flux of an equilibrium canonical or microcanonical ensemble across a dividing surface positioned somewhere in the bottleneck region. The transition state dividing surface (TSDS), defined in configuration space as a hypersurface associated with a constant value of the reaction coordinate, completely separates reactant and product regions of configuration space. If the TSDS is placed in the bottleneck region of the PES where recrossing dynamics is minimal, one should obtain a good approximation to the classical reactive flux. Thus, from a conceptual point of view, there are two fundamental dynamical approximations involved in classical TST: (1) The assumption that an equilibrium ensemble adequately represents the real molecular population. For direct bimolecular reactions this is usually chosen as a canonical ensemble. For unimolecular, recombination, or chemical activation reactions where the competition between reaction and collisional relaxation of the long-lived intermediates must be explicitly incorporated via a master equation treatment, the microcanonical equilibrium ensemble (with energy E and preferably also angular momentum J resolved) should be used. (2) The use of the *one-way* flux across the TSDS to approximate the actual reactive flux implies, of course, the assumption that trajectories which reach this surface (from either side) will not recross it. There are a number of elegant derivations of classical TST and its unimolecular variant, Rice−Ramsperger−Kassel−Marcus (RRKM) theory, in the literature (see, e.g.,refs 2−5 and references therein) which highlight these fundamental dynamical assumptions.

In addition to the two assumptions summarized above, it is well-known that there is an implementational issue in TST which relates to the kinematic coupling between the generalized (curvilinear) reaction coordinate, s, and the remaining degrees of freedom in the molecular system.[6] Consider the standard TST expression for the thermal rate constant $k(T)$

$$k(T) = \frac{k_B T}{h} \frac{Q^{+}}{Q} e^{-E_0/k_B T} \tag{1}$$

Here Q^{+} is the partition function for the "degrees of freedom orthogonal to the reaction coordinate", Q is that for the reactant(s), E_0 is the classical barrier height and the other symbols carry their usual meanings. Assuming for the moment that Q^{+} is being evaluated classically, one would naïvely write this quantity in the usual manner

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$$Q^{+} = \frac{e^{E_0/k_BT}}{h^{(n-1)}} \int \ldots \int d\mathbf{q}^{\perp}\, d\mathbf{p}^{\perp}\, e^{-[E_k^{\perp} + V(\mathbf{q}^{\perp};s)]/k_BT} \qquad (2)$$

where $\mathbf{q}^{\perp}$ represents the remaining coordinates and $\mathbf{p}^{\perp}$ their conjugate momenta, $E_k^{\perp}$ is the appropriate kinetic energy for these degrees of freedom, and V is the potential (if V is expressed relative to the barrier height, then the preexponential factor will not be necessary). Now, if there exist coupling terms in the full kinetic energy expression, E_k, between s and the remaining coordinates $\mathbf{q}^{\perp}$, how should we write the kinetic energy expression $E_k^{\perp}$ in eq 2—by setting $\dot{s}$ or rather p_s to zero? This question was answered in general terms by Marcus,[6] who concluded that the correct expression for the kinetic energy of the remaining degrees of freedom in eq 2 is obtained from the full kinetic energy of the system, E_k, by setting $\dot{s}$ to zero. This leads to a coordinate-dependent kinematic factor appearing in the subsequent configurational integrals, which Marcus interpreted as a volume element associated with integration over the TSDS. Furthermore, in general this differs from the (incorrect) result one would obtain by setting p_s to zero.

Until recently, Marcus' interpretation of the meaning of Q^{+} in the context of a generalized reaction coordinate has not been exploited to any significant extent in the calculation of rate constants via TST. One suspects this has been largely due to the lack of a compelling application for the theory in which the kinematic issue discussed above has important consequences. For a reaction proceeding over a chemical barrier, the common approach is to place the TSDS at the saddle point, where the Hamiltonian is locally separable. As Marcus himself noted,[6] there is essentially no ambiguity in the definition of Q^{+} in this case, since most of the reactive flux will cross the TSDS close to the saddle-point where separability of the Hamiltonian makes the kinematic issue redundant. While a variational approach would allow the TSDS to move away from the saddle point (subject to further minimization of the calculated flux), the enhancement obtained thereby is not large, especially in comparison with uncertainties introduced by the need for approximate tunneling corrections.[2] Hence, interest in TST for barrier-crossing reactions has focused rather on the issue of quantum mechanical extensions to the theory which can better predict the tunneling contribution to the rate.[7−12]

A significant development in this regard was the introduction of the reaction path Hamiltonian (RPH) by Miller et al.,[13] which constituted a generalization to the case of polyatomic systems of the "natural collision coordinates" of Marcus.[14] Classical and quantum mechanical Hamiltonians were formulated with reference to a set of coordinates comprising of the reaction path, defined as the minimum energy pathway (MEP) in mass-weighted Cartesians, and coordinates orthogonal to it which are specified by diagonalization of the projected force-constant matrix (this diagonalization being carried out parametrically along the reaction path).[13] The formulation of this exact Hamiltonian was not only an important conceptual advance but also allowed the exploration of a range of approximate scattering methods based on quadratic expansion of the potential about the MEP.[15] In addition, Miller investigated the evaluation of the microcanonical flux integrals at any position along the reaction path for zero total angular momentum.[16] Regardless of the fact that coupling terms between the reaction coordinate and the orthogonal modes *do* exist in the RPH kinetic energy, exact analytical evaluation of the momentum flux integrals revealed that for this coordinate system the naïve TST expression for the microcanonical flux (which one might have derived by setting p_s to zero and hence ignoring the coupling) applies without modification!

In recent years, a "compelling application" which demands correct kinematic implementation of variational TST has arisen, accompanied by a renewed focus on the kinematic aspect of the theory. This has been due to the recognition that several very important classes of chemical reaction, including radical−radical recombinations, radical−alkene additions, and ion−molecule reactions, can occur without any significant potential energy barrier (in the unimolecular vernacular, these are the so-called "type II" potentials[17]). The absence of a barrier has two important ramifications which favor the application of a judiciously formulated version of variational TST: (a) tunneling is unlikely to be important, and (b) with no obvious a priori location for the transition state, a variational implementation of the theory (including different possible specifications of the reaction coordinate itself) is essential. The correct kinematic implementation of TST for any given definition of the reaction coordinate (or, equivalently, the TSDS) then becomes a central issue.

The "judiciously formulated" version of variational TST referred to above owes many of its features to pioneering work by Wardlaw and Marcus in the mid-1980s.[18−20] It is a hybrid classical/quantum implementation of TST in which the system is divided into two groups of modes. First, the internal vibrations of the two recombining (or dissociating) moieties are labeled "conserved modes" because their vibrational character is preserved in the dissociation process. These frequencies approach their asymptotic values quite soon as the bond length increases, changing only slowly in the region of separations where the variational transition states are typically found (usually with a bond length greater than 2 Å). The second group of modes are labeled "transitional modes" because they change in character from vibrations in the unimolecular species to free rotations and relative translations of the infinitely separated moieties. The anisotropy in the potential governing these motions changes dramatically as a function of the bond length, and it is the interplay between enthalpic and entropic factors in the transitional modes which has the dominant affect on the variational location of the transition state and the final value of the predicted rate coefficient. Since the time scale for internal vibrations of the moieties is generally much shorter than that for motions of the "looser" transitional modes, the densities of states of the former are evaluated quantum mechanically (usually by direct count of harmonic oscillator states). The flux associated with the transitional modes is evaluated classically via rigorous phase space integration, with the moieties being treated as rigid rotors in formulating the expression for the kinetic energy. In their pioneering work, Wardlaw and Marcus chose the separation between the centers of mass of the two moieties, R_{cm}, as the reaction coordinate. The advantage of this choice of reaction coordinate is simplicity: there are no coupling terms between R_{cm} and the remaining Jacobi coordinates (angles describing the rotations of the moieties about their respective centers of mass and the relative orbital rotation), such that the kinematic issue discussed above need not be addressed.

The center-of-mass separation is not necessarily the most intuitive choice of reaction coordinate, however. Klippenstein[21] noted that when the bond length is not too great, the transitional modes take on a more vibrational character, which one typically describes in terms of bond-length−bond-angle coordinates. Hence the bond length R_{b} may be a more "natural" choice of reaction coordinate than R_{cm} at smaller separations. Klippenstein extended the Wardlaw/Marcus model by developing a phase space integration scheme which explicitly imposes the constraint $\dot{s} = 0$, where s is defined as the bond length, or more generally the separation between any two points fixed in the respective frames of the two moieties.[21-24] This work clearly showed that, at smaller separations of the moieties, the use of a bond-length reaction coordinate enables a significant reduction in the computed flux and hence this is a better choice of reaction coordinate. Only at energies close to the reaction threshold, in which case the variational transition state lies at large separations, is R_{cm} the optimal reaction coordinate.[21,22,25] It should be recognized that the testing and refinement of this variational TST model has hinged on the availability of careful and precise experimental rate measurements of medium-sized molecules with well-defined energy and angular momentum, a fundamental area to which Brad Moore has made seminal contributions.[26-31]

The variational TST methodology described above has proven to be a valuable tool for the accurate modeling of chemical reactions involving "barrierless" channels. These types of reaction are exceedingly numerous in combustion, atmospheric and astrophysical fields. Furthermore, they can often involve very complex PESs which support multiple long-lived intermediate species and multiple dissociation and/or rearrangement channels. Hence, in order to be able to implement such calculations on a routine basis, it is essential to strip the algorithms down and make them fast, efficient, and capable of making optimal use of expensive ab initio data. Important advances have been made in this regard with the recognition that the momentum flux integrals can in fact be carried out analytically, which halves the dimensionality of the Monte Carlo integrals and dramatically speeds up the algorithms. That this ought to be possible was implicit in the generic canonical treatment of TST by Marcus.[6] The fact was recognized and exploited by Klippenstein, who developed expressions for the canonical transitional mode (TM) flux integral with a bond-length reaction coordinate[21] and later adapted the approach to carry out efficient E-resolved microcanonical calculations.[32] Robertson et al. have also addressed the analytical evaluation of canonical and E-resolved microcanonical TM flux integrals, both when R_{cm} is the reaction coordinate[33] and more generally.[34,35] Our own contribution to this effort has been to demonstrate that the TM momentum flux integrals can be evaluated analytically in the more complex case where calculations must be carried out with explicit resolution of the total angular momentum. This was shown originally for the R_{cm} reaction coordinate,[36] and more recently for a completely arbitrary definition of the reaction coordinate.[37]

The summary above portrays impressive advances in the efficient and accurate implementation of variational TST with a generalized reaction coordinate, and indicates that there are compelling and immediate applications for such work. However, despite the fact that the general principles are clear, a cursory comparison of the analytical results obtained for the momentum flux integrals by different authors does not indicate any obvious equivalence. Although it is easy to miss since it is subsumed into the volume element for the surface integral, Marcus' work indicated that there is a coordinate-dependent factor which must be included in the configurational integral over the TSDS.[6] Miller's result indicated that, at least for the RPH, there is no special coordinate dependence above and beyond the potential itself.[16] The independent works of Klippenstein,[21,32,38] of Robertson et al.[34,35] and of Smith[25,37] on the TM flux integrals yield coordinate-dependent kinematic factors. However, although in principle their different approaches should lead to the same final result, the equivalence is not obvious.

The purpose of this paper is to reanalyze our recent treatment[37] in a more general manner so that the relationship to Marcus' pioneering work, to Miller's RPH result and also to the results of Robertson et al. becomes transparent. In section II below, our derivation is outlined and generalized, highlighting certain aspects which will enable the equivalence to the other approaches to be established. In section III we show how Miller's RPH result, which yields no special coordinate dependence in the configurational integral, may be recovered from the present treatment. In section IV we consider the TM flux integrals and establish exact equivalence between our kinematic factor and the recent work of Robertson et al.[35] Section V concludes.

II. Flux through a Hypersurface Defined by a Generalized Reaction Coordinate: Coordinate Dependence of the Kinematic Factor

In the present section we deal with the canonical version of TST. It will be apparent that the corresponding microcanonical version is easily obtained without introducing any fundamentally new physics, either by recasting the derivation with the microcanonical density function [$\delta(E-H)$] instead of the canonical (Boltzmann) function[37,36,32] or via inverse Laplace transform of the canonical result.[35,33] Note that evaluation of the canonical or microcanonical flux integrals with explicit resolution of the total angular momentum (a very important feature for correct treatment of multichannel systems) *does* involve additional physics to that presented herein. This development is explicitly laid out in previous publications,[36,37] hence in the present work we shall not consider angular momentum issues further.

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)

$$k(T) = \frac{\mathrm{Tr}\lfloor \delta(s - s_0)\dot{s}\Theta(\dot{s})\mathrm{e}^{-H/k_\mathrm{B}T}\rfloor}{\mathrm{Tr}[p(\mathbf{q})\mathrm{e}^{-H/k_\mathrm{B}T}]} \tag{3}$$

In eq 3 the reaction coordinate $s(\mathbf{q})$ has the value s_0 on the TSDS. $\dot{s}$ is the flux term and $\Theta(\dot{s})$ is a step function with value 0 for $\dot{s} \leq 0$ and 1 for $\dot{s} > 0$. $p(\mathbf{q})$ 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. $H(\mathbf{q},\mathbf{p}) = E_\mathrm{k} + V$ is the system Hamiltonian. The traces of eq 3 are evaluated classically as integrals over the system phase space

$$k(T) = \frac{\int ... \int \mathrm{d}\mathbf{q}\,\mathrm{d}\mathbf{p}\ \delta(s - s_0)\dot{s}\Theta(\dot{s})\mathrm{e}^{-H/k_\mathrm{B}T}}{\int ... \int\ \mathrm{d}\mathbf{q}\,\mathrm{d}\mathbf{p}\ p(\mathbf{q})\mathrm{e}^{-H/k_\mathrm{B}T}} \tag{4}$$

Recognizing that the classical partition function for reactants Q is simply h^{-n} times the denominator of eq 4 (h being Planck's constant and n the number of degrees of freedom), one writes k in the standard TST form of eq 1 with Q^+ defined as

$$Q^{+} = \frac{h^{-(n-1)}}{k_{\mathrm{B}}T} \mathrm{e}^{E_0/k_{\mathrm{B}}T} \int \mathrm{d}\mathbf{q}\ \delta(s - s_0) \mathrm{e}^{-V(\mathbf{q})/k_{\mathrm{B}}T} \int \mathrm{d}\mathbf{p}\ \dot{s}\Theta(\dot{s}) \mathrm{e}^{-E_k/k_{\mathrm{B}}T} \tag{5}$$

Since our principal focus is the analytic evaluation of the momentum flux integral, it is useful to write it as follows

$$\Phi(T,\mathbf{q}) = \frac{1}{k_{\mathrm{B}}T} \int \mathrm{d}\mathbf{p}\ \dot{s}\Theta(\dot{s}) \mathrm{e}^{-E_k/k_{\mathrm{B}}T} \tag{6}$$

so that

$$Q^{+} = \frac{\mathrm{e}^{E_0/k_{\mathrm{B}}T}}{h^{(n-1)}} \int \mathrm{d}\mathbf{q}\ \delta(s - s_0) \mathrm{e}^{-V(\mathbf{q})/k_{\mathrm{B}}T} \Phi(T,\mathbf{q}) \tag{7}$$

The time derivative of the reaction coordinate s is written

$$\dot{s} = \sum_{i=1}^{n} \frac{\partial s}{\partial q_i} \dot{q}_i = \nabla s^{\mathrm{T}} \dot{\mathbf{q}} = \nabla s^{\mathrm{T}} \mathbf{G}(\mathbf{G}^{-1}\dot{\mathbf{q}}) = (\nabla s)^{\mathrm{T}} \mathbf{G}\mathbf{p} \tag{8}$$

The canonical momenta $\mathbf{p}$ in eq 11 are defined in the standard manner[39]

$$p_i = \frac{\partial L}{\partial \dot{q}_i} = \frac{\partial E_{\mathrm{k}}}{\partial \dot{q}_i} \tag{9}$$

where $L = E_{\mathrm{k}} - V$ is the Lagrangian. Let $\mathbf{A}$ be the kinetic energy tensor when E_{k} is expressed in terms of the velocities

$$E_{\mathrm{k}} = {}^{1}\!/_{2} \mathbf{q}^{\mathrm{T}} \mathbf{A} \dot{\mathbf{q}} \tag{10}$$

Then eqs 12 and 13 imply that

$$\mathbf{p} = \mathbf{A}\dot{\mathbf{q}} \tag{11}$$

and

$$E_{\mathrm{k}} = {}^{1}\!/_{2} \mathbf{p}^{\mathrm{T}} \mathbf{A}^{-1} \mathbf{p} = {}^{1}\!/_{2} \mathbf{p}^{\mathrm{T}} \mathbf{G} \mathbf{p} \tag{12}$$

The identification $\mathbf{p} = \mathbf{G}^{-1}\dot{\mathbf{q}}$ in eq 8 then follows from this.

The traditional approach to the evaluation of the flux integral in eq 6 is to carry out a canonical transformation so that the reaction coordinate s and its conjugate momentum p_s become integration variables.[6,35] Our approach focuses rather on an orthogonal transformation in the momentum space only.[37] One transforms to a new set of momenta $v = \{v_1, ..., v_n\}$ such that v_1, satisfies the relation

$$\frac{\partial E_{\mathrm{k}}}{\partial v_1} = c\dot{s} \tag{13}$$

Writing

$$\mathbf{v} = \mathbf{U}\mathbf{p} \tag{14a}$$

$$\mathbf{U}^{\mathrm{T}}\mathbf{U} = \mathbf{I} \tag{14b}$$

the kinetic energy now becomes

$$E_{\mathrm{k}} = \frac{1}{2}\mathbf{p}^{\mathrm{T}}\mathbf{G}\mathbf{p} = \frac{1}{2}\mathbf{v}^{\mathrm{T}}\mathbf{U}\mathbf{G}\mathbf{U}^{\mathrm{T}}\mathbf{v} = \frac{1}{2}\mathbf{v}^{\mathrm{T}}\mathbf{G}^{*}\mathbf{v} \tag{15}$$

and the next task is the specification of v_1 so as to satisfy eq 13. This amounts to specifying the first row of the transformation matrix $\mathbf{U}$. Using eqs 8 and 13−15 one finally concludes that[37]

$$v_1 = \frac{1}{|\nabla s|} \nabla s^{\mathrm{T}} \mathbf{p} \tag{16}$$

The only restriction on the remaining momenta v_2, ..., v_n is that they should be orthonormal to v_1 (eq 14b). Thus, virtually any method of determining a set of $(n - 1)$ vectors in 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. We use the Lanczos recursion here, since it has the convenient property that the new kinetic energy tensor $\mathbf{G}^{*}$ is symmetric tridiagonal

$$\mathbf{G}^{*} = \mathbf{U}\mathbf{G}\mathbf{U}^{\mathrm{T}} = \begin{bmatrix} \alpha_1 & \beta_1 & 0 & 0 & 0 \\ \beta_1 & \alpha_2 & \bullet & 0 & 0 \\ 0 & \bullet & \bullet & \bullet & 0 \\ 0 & 0 & \bullet & \alpha_{n-1} & \beta_{n-1} \\ 0 & 0 & 0 & \beta_{n-1} & \alpha_n \end{bmatrix} \tag{17}$$

It will turn out that α_1 is the only one of these tensor elements that shows up in the final expression. It has the form

$$\alpha_1 = \frac{1}{|\nabla s|^2} (\nabla s)^{\mathrm{T}} \mathbf{G} \nabla s \tag{18}$$

The momentum flux integral in terms of these new momenta is written

$$\Phi(T,\mathbf{q}) = \frac{1}{k_{\mathrm{B}}T} \int \mathrm{d}\mathbf{v}^{\perp}\ \mathrm{e}^{-E_{k}^{\perp}/k_{\mathrm{B}}T} \int \mathrm{d}v_1\ \dot{s}\Theta(\dot{s}) \mathrm{e}^{-(\alpha_1 v_1^{2} + 2\beta_1 v_2 v_1)/2k_{\mathrm{B}}T} \tag{19}$$

where $\mathbf{v}^{\perp} = (v_2, ..., v_n)$ and

$$E_{\mathrm{k}}^{\perp} = \frac{1}{2} (\mathbf{v}^{\perp})^{\mathrm{T}} \mathbf{G}^{\perp} \mathbf{v}^{\perp} \tag{20a}$$

$$\mathbf{G}^{\perp} = \begin{bmatrix} \alpha_2 & \beta_2 & 0 & 0 & 0 \\ \beta_2 & \alpha_3 & \bullet & 0 & 0 \\ 0 & \bullet & \bullet & \bullet & 0 \\ 0 & 0 & \bullet & \alpha_{n-1} & \beta_{n-1} \\ 0 & 0 & 0 & \beta_{n-1} & \alpha_n \end{bmatrix} \tag{20b}$$

Recognition of the bounds on the v_1 integral imposed by the $\Theta(\dot{s})$ function, and subsequent evaluation of this integral proceeds in an established manner,[6,32,35,37] yielding an integral over the remaining momenta with a modified kinetic energy tensor

$$\Phi(T,\mathbf{q}) = |\nabla s| \int_{-\infty}^{\infty} \mathrm{d}\mathbf{v}^{\perp}\ \mathrm{e}^{-E_{k}^{+}/k_{\mathrm{B}}T} \tag{21}$$

with

$$E_{\mathrm{k}}^{+} = {}^{1}\!/_{2} (\mathbf{v}^{\perp})^{\mathrm{T}} \mathbf{G}^{+} \mathbf{v}^{\perp} \tag{22a}$$

$$\mathbf{G}^{+} = \mathbf{G}^{\perp} - \frac{\beta_1^{\,2}}{\alpha_1} \mathbf{e}_1 \mathbf{e}_1^{\mathrm{T}} \tag{22b}$$

The quantity E_{k}^{+} is an expression for the kinetic energy of the system with the constraint $\dot{s} = 0$ imposed. In this sense, the equivalence of this somewhat different derivation to the more traditional line of approach based on canonical transformations[6,13,16,21,32,34,35] is clear. The contrast is that the momenta $\mathbf{v}$ here are not required to be conjugate to a predefined set of coordinates, but rather have been defined via the orthogonal transformation of eq 14 to facilitate a minimalist approach to the final simple result, eq 26 below.

The remaining integrals in eq 21 are evaluated in standard fashion[40] to give the formal result

$$\Phi(T,\mathbf{q}) = \frac{|\nabla s|(2\pi k_\mathrm{B}T)^{(n-1)/2}}{|\mathbf{G}^+|^{1/2}} \tag{23}$$

The remaining issue is to find a simple way to evaluate the determinant of the $(n-1) \times (n-1)$ modified kinetic energy tensor $\mathbf{G}^+$. At this stage, some comparison of approaches taken by different authors to evaluate this determinant is instructive. Klippenstein[21,32] adopts a numerical approach to the evaluation of $|\mathbf{G}^+|$. Marcus[6] makes general observations which suggest two possible approaches.

(i) He first notes that the modified kinetic energy tensor $\mathbf{G}^+$ is the inverse of the corresponding velocity-referenced kinetic energy tensor $\mathbf{A}^+$. Since, as noted above, $E_\mathrm{k}{}^+$ gives the kinetic energy of the system under the constraint $\dot{s} = 0$, $\mathbf{A}^+$ is obtained from the full tensor $\mathbf{A}^*$ by striking out the row and column corresponding to the reaction coordinate velocity $\dot{s}$ (where $\mathbf{A}^*$ is the kinetic energy tensor for the set of canonical variables which includes s and p_s). A formal proof of the conjugate relation between $\mathbf{G}^+$ and $\mathbf{A}^+$ is given by Robertson et al.[35] Thus, one can seek to construct the tensor $\mathbf{A}^*$ and then evaluate the determinant of its minor $\mathbf{A}^+$ by either numerical or analytical methods. Robertson et al.[34,35] have pursued this latter analytical approach to obtain results which will be shown below to be equivalent to those of Smith.

(ii) Marcus also notes that

$$|\mathbf{A}^+| = G^*_{11}|\mathbf{A}^*| = \frac{G^*_{11}}{|\mathbf{G}^*|} \tag{24}$$

The first equality is straightforward to prove using Cramer's rule. This provides another avenue for evaluation of the required determinant, but still requires the construction of $\mathbf{G}^*$.

Returning to the approach of this paper, it will be apparent that we have made no reference to coordinates or velocities relating to the momenta $\upsilon_2, ..., \upsilon_n$—these were simply chosen to be orthogonal to υ_1. Neither is it necessary to do so, since (i) the fact that $\mathbf{G}^*$ is tridiagonal and (ii) the fact that $\mathbf{G}^*$ is related to $\mathbf{G}$ by an orthogonal transformation (i.e., $|\mathbf{G}^*| = |\mathbf{G}|$) make it easy to prove a direct relationship between $|\mathbf{G}^+|$ and $|\mathbf{G}|$ without reference to the conjugate tensor $\mathbf{A}^+$.[37] One finds that

$$|\mathbf{G}^+| = |\mathbf{G}|/\alpha_1 \tag{25}$$

Substitution into eq 23, with α_1 as given in eq 18, then leads to

$$\Phi(T,\mathbf{q}) = (2\pi k_\mathrm{B}T)^{(n-1)/2}\frac{(\nabla s^\mathrm{T}\mathbf{G}\nabla s)^{1/2}}{|\mathbf{G}|^{1/2}} \tag{26}$$

and consequently

$$Q^+ = \frac{(2\pi k_\mathrm{B}T)^{(n-1)/2}\mathrm{e}^{E_0/k_\mathrm{B}T}}{h^{(n-1)}}\int \mathrm{d}\mathbf{q}\ \delta(s-s_0)\frac{(\nabla s^\mathrm{T}\mathbf{G}\nabla s)^{1/2}}{|\mathbf{G}|^{1/2}}\mathrm{e}^{-V(\mathbf{q})/k_\mathrm{B}T} \tag{27}$$

As a first comment on the very simple result of eq 27, it should be recalled that, in contrast to the traditional line of approach based on canonical transformations,[6,13,35] the reaction coordinate s is not necessarily one of the coordinates $\mathbf{q}$. Thus, it becomes apparent that there is no need to construct a specific canonical transformation and subsequent kinetic energy tensor in order to accommodate a given definition of the reaction coordinate s: all one need do is evaluate the gradients of s with respect to a convenient coordinate system in which $\mathbf{G}$ is already known. This realization represents a substantial simplification over the pioneering work of Marcus, since it allows one to more easily envisage the construction of a generic ("black-box") variational TST code which could rigorously implement arbitrary GRC definitions input by the user, always in terms of a common set of coordinates. For example, if the application is such that a classical treatment of all rovibrational degrees of freedom is acceptable, the natural choice of coordinates for the representation of the kinetic energy is Cartesians. In this case, the result of eq 27 becomes

$$Q^+ = \frac{(2\pi k_\mathrm{B}T)^{(n-1)/2}\mathrm{e}^{E_0/k_\mathrm{B}T}}{h^{(n-1)}}\left(\prod_{i=1}^{n}\boldsymbol{m}_i{}^{1/2}\right)\int \mathrm{d}\mathbf{x}\ \delta(s-s_0) \times \left[\sum_{i=1}^{n}\left(\frac{\partial s}{\partial x_i}\right)^2\boldsymbol{m}_i{}^{-1}\right]^{1/2}\mathrm{e}^{-V(\mathbf{x})/k_\mathrm{B}T} \tag{28}$$

[in this labeling scheme, the coordinates (x_{3r-2}, x_{3r-1}, x_{3r}) are actually the Cartesians ($x^{(r)}$, $y^{(r)}$, $z^{(r)}$) of the rth atom, and $m_{3r-2} = m_{3r-1} = m_{3r} = m^{(r)}$, where $m^{(r)}$ is the mass of the rth atom].

A second comment on the result of eq 27 relates to the identification of the coordinate dependence in the integrand which one would ascribe to a "kinematic factor" in the spirit of the title of this work. There are three sources of coordinate dependence in eq 27: the potential $V(\mathbf{q})$, $|\mathbf{G}|$, and the factor $(\nabla s^\mathrm{T}\mathbf{G}\nabla s)$. The potential is an expected part of the configurational integral. It is expensive to calculate, but requires no further comment in the present context. In considering the possible coordinate dependence of $|\mathbf{G}|$, one notes that there is no such coordinate dependence in the Cartesian representation of eq 28. Consider, then, the transformation from the Cartesian coordinates $\mathbf{x}$ in eq 28 to the general coordinates $\mathbf{q}$ in eq 27. We write the differential relation between the two sets of coordinates as

$$\dot{\mathbf{q}} = \mathbf{K}\dot{\mathbf{x}} \tag{29}$$

which implies that the Jacobian factor for the coordinate transformation is $|\mathbf{K}|^{-1}$. The kinetic energy tensors $\mathbf{A}$ and $\mathbf{G}$ for the general coordinate system will be related to those of the Cartesian system, $\mathbf{A}^\mathrm{c}$ and $\mathbf{G}^\mathrm{c}$ by the equations

$$\mathbf{A} = (\mathbf{K}^{-1})^\mathrm{T}\mathbf{A}^\mathrm{c}\mathbf{K}^{-1} \tag{30a}$$

$$\mathbf{G} = \mathbf{A}^{-1} = \mathbf{K}(\mathbf{A}^\mathrm{c})^{-1}\mathbf{K}^\mathrm{T} = \mathbf{K}\mathbf{G}^\mathrm{c}\mathbf{K}^\mathrm{T} \tag{30b}$$

Noting that the mass factor in eq 28 is $|\mathbf{G}^\mathrm{c}|^{-1/2}$, and including the Jacobian factor for the transformation to the general coordinates $\mathbf{q}$ leads to

$$Q^+ = \frac{(2\pi k_\mathrm{B}T)^{(n-1)/2}\mathrm{e}^{E_0/k_\mathrm{B}T}}{h^{(n-1)}} \times \int \mathrm{d}\mathbf{q}\ |\mathbf{K}|^{-1}\delta(s-s_0)\ \frac{(\nabla s^\mathrm{T}\mathbf{G}\nabla s)^{1/2}}{|\mathbf{G}^\mathrm{c}|^{1/2}}\mathrm{e}^{-V(\mathbf{q})/k_\mathrm{B}T} \tag{31}$$

which in light of eq 30b is manifestly equivalent to eq 27. Thus, the factor $|\mathbf{G}|^{-1/2}$ in eq 27 is seen to comprise of a coordinate-independent mass factor $|\mathbf{G}^\mathrm{c}|^{-1/2}$ and a coordinate-dependent Jacobian factor $|\mathbf{K}|^{-1}$. The Jacobian $|\mathbf{K}|^{-1}$ is merely a product of the choice of coordinate system $\mathbf{q}$, which in the present context need not have anything to do with the choice of reaction coordinate (it might, for instance, be a convenient coordinate system for the evaluation of the potential energy function). Since $|\mathbf{K}|^{-1}$ therefore has no intrinsically dynamical origin, one may reasonably associate a coordinate-dependent "kinematic factor" associated with kinetic energy coupling to a generalized reaction coordinate in TST with the term $(\nabla s^{\mathrm{T}}\mathbf{G}\nabla s)^{1/2}$. Granted this is simply a question of definition. Marcus[6] associated the entire expression $(\nabla s^{\mathrm{T}}\mathbf{G}\nabla s)^{1/2}/|\mathbf{G}|$ with the volume element of integration on a hypersurface in configuration space with the constraint $\mathrm{d}s = 0$ (or, equivalently, $\dot{s} = 0$) imposed. He did not therefore define a kinematic factor. However, while the Jacobian $|\mathbf{K}|^{-1}$ necessarily gives the correct volume element for *any* integral over the coordinates $\mathbf{q}$, the constraint $\mathrm{d}s = 0$ derives specifically from the fundamental TST assumption. Since the latter constraint has no more general meaning outside of TST, subsuming the factor $(\nabla s^{\mathrm{T}}\mathbf{G}\nabla s)^{1/2}$ which arises from it into a volume element is somewhat artificial. Hence, the interpretation of $|\mathbf{K}|^{-1}$ (or equivalently any coordinate dependence in $|\mathbf{G}|$) as a static Jacobian factor and of $(\nabla s^{\mathrm{T}}\mathbf{G}\nabla s)^{1/2}$ as a kinematic factor would seem more appropriate in the light of this discussion.

Finally in this section, although it is implicit in the derivation above, it is useful to provide an explicit proof of the fact that the kinematic factor $(\nabla s^{\mathrm{T}}\mathbf{G}\nabla s)^{1/2}$ is independent of the particular representation chosen for the kinetic energy. Let us assume, then, that the form of the kinetic energy is known in terms of two different sets of canonical coordinates and momenta $(\mathbf{q},\mathbf{p})$ and $(\mathbf{q}',\mathbf{p}')$. The differential relationship between the two coordinate systems is written:

$$\dot{\mathbf{q}}' = \mathbf{K}\dot{\mathbf{q}} \tag{32}$$

where $K_{ij} = \partial q'_i/\partial q_j$. Analogous to eq 30 above, the momentum-referenced kinetic energy tensors, $\mathbf{G}$ and $\mathbf{G}'$, are then related by the equation

$$\mathbf{G}' = \mathbf{K}\mathbf{G}\mathbf{K}^{\mathrm{T}} \tag{33}$$

It is now necessary to establish the relationship between ∇s and $\nabla' s$. Noting that the absolute time derivative $\dot{s}$ is independent of the coordinate system, one has

$$\nabla s^{\mathrm{T}}\dot{\mathbf{q}} = \dot{s} = \nabla' s^{\mathrm{T}}\dot{\mathbf{q}}' \tag{34}$$

Substituting eq 32 into the right-hand equality of eq 34 then gives

$$\nabla s^{\mathrm{T}}\dot{\mathbf{q}} = \dot{s} = \nabla' s^{\mathrm{T}}\dot{\mathbf{q}}$$

with the conclusion that

$$\nabla s = \mathbf{K}^{\mathrm{T}}\nabla' s \tag{35}$$

Using eqs 33 and 35, the invariance of the kinematic factor with respect to the representation of the kinetic energy follows:

$$\begin{aligned}(\nabla' s^{\mathrm{T}}\mathbf{G}'\nabla' s) &= \lfloor \nabla s^{\mathrm{T}}\mathbf{K}^{-1}(\mathbf{K}\mathbf{G}\mathbf{K}^{\mathrm{T}})(\mathbf{K}^{\mathrm{T}})^{-1}\nabla s \rfloor \\ &= (\nabla s^{\mathrm{T}}\mathbf{G}\nabla s)\end{aligned} \tag{36}$$

We shall utilize this fact in section IV below to establish the equivalence of different approaches to the TM flux integral with a generalized reaction coordinate.

III. Flux through a Hypersurface Defined by the Reaction Path

The reaction path is a locus in mass-weighted Cartesian space defined by the minimum energy pathway from reactants to products. Marcus[14,41] proposed that the arc length along such a locus would prove a useful definition for the reaction coordinate s. He defined the "natural collision coordinates" for a triatomic system in terms of this definition for s and remaining coordinates defined as parametrically orthogonal to the locus which defines s. Miller and co-workers[13] developed the multidimensional generalization of these coordinates and the corresponding reaction path Hamiltonian (RPH). Miller subsequently examined the classical flux integral through a TSDS defined as the hyperplane orthogonal to the reaction path at any given value of s.[16] As discussed in the Introduction, the curious feature of his result was that, despite the fact that there are coupling terms in the kinetic energy tensor between s and the remaining degrees of freedom, one obtains the same result which would be naïvely derived by neglecting such terms. In this section, we examine the RPH flux integral in the light of the present discussion of kinematic factors in TST with a generalized reaction coordinate. For the sake of brevity, we treat only canonical TST and do not explicitly consider rotations. The details of microcanonical implementations with account for angular momentum can be found elsewhere.[13,36,37]

We begin by transforming the configurational integral in eq 28 above into mass-weighted Cartesian coordinates

$$y_i = m_i^{1/2}x_i, \quad i = 1, n \tag{37}$$

The Jacobian for this transformation is $\prod_{i=1}^{n} m_i^{-1/2}$, and the new kinetic energy tensor is the identity matrix; thus

$$Q^{+} = \frac{(2\pi k_{\mathrm{B}}T)^{(n-1)/2}\mathrm{e}^{E_0/k_{\mathrm{B}}T}}{h^{(n-1)}}\int \mathrm{d}\mathbf{y}\ \delta(s - s_0)|\nabla s|\mathrm{e}^{-V(\mathbf{y})/k_{\mathrm{B}}T} \tag{38}$$

Equation 38 indicates that there is a kinematic factor, $|\nabla s|$, which is associated with the "reaction path" definition for s. To see why this disappears in Miller's result,[16] one must transform the configurational integral from mass-weighted Cartesians to the curvilinear coordinates of the RPH, $\{Q_1, ..., Q_{n-1}, Q_n = s\}$. Following the procedure of the previous section, we write the differential relationship between the two sets of coordinates as

$$\dot{\mathbf{Q}} = \mathbf{K}\dot{\mathbf{y}} \tag{39}$$

which implies that the Jacobian factor for the coordinate transformation is $|\mathbf{K}|^{-1}$

$$Q^{+} = \frac{(2\pi k_{\mathrm{B}}T)^{(n-1)/2}\mathrm{e}^{E_0/k_{\mathrm{B}}T}}{h^{(n-1)}}\int \mathrm{d}Q_1\ ...\ \mathrm{d}Q_{n-1}|\mathbf{K}|^{-1}|\nabla s|\mathrm{e}^{-V(\mathbf{y})/k_{\mathrm{B}}T} \tag{40}$$

In eq 40 the variable $Q_n = s$ has been integrated out with use of the delta function constraint in eq 38. It remains to show that $|\mathbf{K}|^{-1}$ and $|\nabla s|$ cancel to produce a result identical to that which would be obtained by neglecting coupling between s and the remaining degrees of freedom. Now, since at any given value of s the coordinates $\{Q_1, ..., Q_{n-1}\}$ are by construction orthogonal to s, in this representation we have $\nabla' s = \mathbf{e}_n$, the elementary unit vector (0...,0,1). Thus, from eq 35 we have

$$\nabla s = \mathbf{K}^{\mathrm{T}}\mathbf{e}_n \tag{41}$$

i.e., ∇s is the bottom row of the transformation matrix $\mathbf{K}$. To proceed further it is necessary to examine the transformation to the RPH coordinates in detail. The absolute relation between the mass-weighted Cartesians $\mathbf{y}$ and the RPH coordinates $\mathbf{Q}$ may be expressed as[13]

$$y_i = a_i(s) + \sum_{j=1}^{n-1} L_{ij}(s) Q_j \tag{42}$$

Here $a_i(s)$ is the ith component of the vector $\mathbf{a}(s)$ which locates the reaction path in mass weighted Cartesian space at any given value of the arc length s. Differentiation of the vector $\mathbf{a}(s)$ with respect to s yields a unit vector $\mathbf{v}_n$ tangential to the reaction path. This vector is then used to symmetrically deflate the matrix of second derivatives of the potential $V(\mathbf{y})$, thereby forming a projected force constant matrix of rank $n - 1$.[13] The projected force constant matrix is diagonalized to obtain $n - 1$ frequencies for harmonic motion orthogonal to s and a set of eigenvectors $\mathbf{v}_1(s),...,\mathbf{v}_{n-1}(s)$ which specify the axial directions of the orthogonal coordinates $Q_1,...,Q_{n-1}$. Together, the set of vectors $\mathbf{v}_1(s),...,\mathbf{v}_n(s)$ form a complete orthonormal basis in the n-dimensional mass-weighted Cartesian space, a fact which we utilize below (of course, their directions change parametrically with the value of s). In eq 42, the quantities $L_{ij}(s)$ are elements of an orthogonal matrix $\mathbf{L}(s)$ whose columns are the vectors $\mathbf{v}_1(s),...,\mathbf{v}_n(s)$. Equation 42 allows us to specify the derivative matrix $\mathbf{K}$ (or rather its inverse) explicitly, since

$$\begin{aligned} \dot{y}_i &= \sum_{j=1}^{n-1} L_{ij}(s)\dot{Q}_j + \left[\frac{\partial a_i(s)}{\partial s} + \sum_{m=1}^{n-1} \frac{\partial L_{im}(s)}{\partial s} Q_m\right]\dot{s} \\ &= \sum_{j=1}^{n-1} L_{ij}(s)\dot{Q}_j + \left[L_{in}(s) + \sum_{m=1}^{n-1} \frac{\partial L_{im}(s)}{\partial s} Q_m\right]\dot{s} \end{aligned} \tag{43}$$

where we have utilized the fact that $\partial\mathbf{a}/\partial s = \mathbf{v}_n$, which is in fact the last column of $\mathbf{L}(s)$. In matrix form (recall $s = \dot{Q}_n$), eq 43 is

$$\dot{\mathbf{y}} = \mathbf{K}^{-1}\dot{\mathbf{Q}} \tag{44a}$$

with

$$\begin{aligned} K_{ij}^{-1} &= L_{ij}, \quad i = 1, n; j = 1, n - 1 \\ &= L_{ij} + \eta_i, \quad i = 1, n; j = n \end{aligned} \tag{44b}$$

and

$$\eta_i = \sum_{m=1}^{n-1} \frac{\partial L_{im}(s)}{\partial s} Q_m \tag{44c}$$

In other words, $\mathbf{K}^{-1}$ is equal to the orthogonal matrix $\mathbf{L}(s)$ except that the vector $\boldsymbol{\eta}$ is added to the last column. We now devise a factorization of $\mathbf{K}^{-1}$ which will allow us to identify its determinant. First, define $\{c_j, j=1,\mathrm{n}\}$ as the projection coefficients of $\boldsymbol{\eta}$ onto the orthogonal columns of $\mathbf{L}$

$$\eta = \sum_{j=1}^{n} c_j \mathbf{v}_j = \sum_{j=1}^{n} (\mathbf{v}_j^{\mathrm{T}} \eta)\mathbf{v}_j \tag{45}$$

The following factorization of $\mathbf{K}^{-1}$ then holds

$$\mathbf{K}^{-1} = \mathbf{L}\mathbf{C}^{(n)}\mathbf{C}^{(n-1)}...\mathbf{C}^{(1)} \tag{46a}$$

where

$$\mathbf{C}^{(j)} = \mathbf{I} + c_j \mathbf{e}_j \mathbf{e}_n^{\mathrm{T}} \tag{46b}$$

$\mathbf{I}$ is the $n \times n$ identity matrix, and the product of the canonical vectors $\mathbf{e}_j$ and $\mathbf{e}_n^{\mathrm{T}}$ is an $n \times n$ matrix with zero elements everywhere except the jnth, which is unity. Thus, $\mathbf{C}^{(j)}$ differs from the identity matrix only in that the jnth element takes the value c_j. The effect of this sequence of multiplications onto $\mathbf{L}$ from the right is to add the different components of $\boldsymbol{\eta}$ in eq 45 one at a time onto the last column of the matrix. The determinants of the $\mathbf{C}^{(j)}$ matrices are as follows:

$$\begin{aligned} |\mathbf{C}^{(j)}| &= 1, \quad j = 1, n - 1 \\ &= 1 + c_n, \quad j = n \end{aligned} \tag{47}$$

while the determinant of the orthogonal matrix $\mathbf{L}$ is unity. Hence, from eqs 46a and 47, the product rule for determinants gives us

$$\begin{aligned} |\mathbf{K}|^{-1} = |\mathbf{C}^{(n)}| &= 1 + c_n \\ &= 1 + \sum_{i=1}^{n} L_{in}(s) \sum_{m=1}^{n-1} \frac{\partial L_{im}(s)}{\partial s} Q_m \\ &= 1 + \sum_{m=1}^{n-1} Q_m B_{m,n}(s) \end{aligned} \tag{48}$$

and we now have an explicit expression for the Jacobian in eq 40. It will be apparent from the last equality in eq 48 that we have defined the quantity $B_{m,n}(s)$ in a manner consistent with Miller et al.[13] in order to facilitate comparison. To prove that this Jacobian factor cancels against $|\nabla s|$ in eq 40, it is necessary to examine the last row of the matrix $\mathbf{K}$, since this is the vector ∇s (eq 41). The tensor $\mathbf{K}$ is easily constructed by inversion of eq 46a. First, note that

$$[\mathbf{C}^{(j)}]^{-1} = \mathbf{I} - c_j\, \mathbf{e}_j\, \mathbf{e}_n^{\mathrm{T}}, \quad j = 1, n - 1 \tag{49a}$$

$$[\mathbf{C}^{(n)}]^{-1} = \mathbf{I} + [(1 + c_n)^{-1} - 1]\mathbf{e}_n\mathbf{e}_n^{\mathrm{T}} \tag{49b}$$

so that

$$\mathbf{K} = [\mathbf{C}^{(1)}]^{-1}[\mathbf{C}^{(2)}]^{-1} ... [\mathbf{C}^{(n)}]^{-1}\mathbf{L}^{\mathrm{T}} \tag{50}$$

Examination of the sequence of multiplications in eq 50 leads to the conclusion that the last row of $\mathbf{K}$ is actually the last column of $\mathbf{L}$, rescaled by the factor $(1 + c_n)^{-1}$

$$\nabla s = (1 + c_n)^{-1}\mathbf{v}_n = (1 + c_n)^{-1} \frac{\partial \mathbf{a}(s)}{\partial s} \tag{51}$$

Finally, since $\mathbf{v}_n$ is normalized, we have

$$\begin{aligned} |\nabla s| &= (1 + c_n)^{-1} \\ &= [1 + \sum_{m=1}^{n-1} Q_m B_{m,n}(s)]^{-1} \end{aligned} \tag{52}$$

Equations 40, 48, and 52 then lead to the result

$$Q^{+} = \frac{(2\pi k_{\mathrm{B}} T)^{(n-1)/2} \mathrm{e}^{E_0/k_{\mathrm{B}}T}}{h^{(n-1)}} \int \mathrm{d}Q_1 ... \mathrm{d}Q_{n-1} \mathrm{e}^{-V(\mathbf{y})/k_{\mathrm{B}}T} \tag{53}$$

Assuming, in the spirit of the RPH, that the potential is harmonic about the minimum energy pathway

$$V(\mathbf{y}) = E_0 + \sum_{i=1}^{n-1} \frac{1}{2} w_i Q_i^2 \tag{54}$$

it is then clear that evaluation of the coordinate integrals in eq 53 gives the standard harmonic oscillator result for the partition function of the orthogonal modes

$$Q^{+} = \prod_{i=1}^{n-1} \left(\frac{k_B T}{h v_i} \right) \tag{55}$$

where $v_i = w_i/2\pi$. Equation 55 is the canonical equivalent of Miller's microcanonical result.[16]

In conclusion, the reaction path Hamiltonian has the interesting feature that a rigorous evaluation of the flux integral through the TSDS leads to the same result which one would obtain with a naïve approach that neglected kinetic coupling between the reaction coordinate and the orthogonal modes. This is a consequence of the cancellation of the kinematic factor (eq 52) against the Jacobian factor for transformation to the RPH coordinate system (eq 48). We also note in passing that eq 33 (where in the present case $\mathbf{G} = \mathbf{I}$ for the mass-weighted Cartesians) in conjunction with eqs 49 and 50 provides an alternative route to the RPH from that used by Miller et al.[13]

IV. Flux Integrals for a Generalized Reaction Coordinate in a Subspace of Transitional Modes

As indicated in the Introduction, a powerful motivation for exploring and extending methodologies of variational TST with a generalized reaction coordinate (GRC) has arisen in recent years. This came with the realization that rate constants for a large and very important class of reactions involving barrierless formation (or the reverse dissociation) of collision complexes can be accurately modeled with a judiciously formulated variational TST model.[20,24,42] Crucially, work to date has indicated that the transitional modes (TM) forming the space within which the GRC is defined can be acceptably treated classically. The important ramification of this is that a classical analysis of the effect of a generalized definition for the reaction coordinate on the resulting flux integrals is pertinent, and indeed vital for enhancing the efficiency of the calculations.

Klippenstein has demonstrated the importance of the definition of the reaction coordinate to obtaining accurate results.[21,22,38] The sensitivity of calculated rate constants to the definition of a GRC has prompted work in recent years to explore this effect. Independent approaches by Smith[25] and by Robertson et al.[34] lead to simple expressions for kinematic factors associated with a generalized definition of the reaction coordinate in the TM flux integrals. Their results, however, were superficially very different in nature and both treatments involved ad hoc assumptions. More recently, both groups have established rigorous foundations for their respective approaches,[37,35] with the favorable conclusion that the earlier results, while derived approximately, were correct. Another outcome of the recent works is that the respective expressions for the kinematic factor in the TM flux integral now bear a much closer similarity to each other. In the developments of section II above, we have generalized certain aspects of our derivation which will allow us in this section to establish complete equivalence between this approach and that of Robertson et al.

A brief outline of our approach to the TM flux integrals serves to establish notation.[37] The reasoning behind the assumed separability of the Hamiltonian into H_C for the conserved modes and H_{TM} for the transitional modes has been summarized in the Introduction. Equation 1 then becomes

$$k(T) = \frac{k_B T}{h} \frac{Q_c Q^{+}_{TM}}{Q} e^{-E_0/k_B T} \tag{56}$$

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. The analysis focuses on the quantity Q^{+}_{TM}

$$Q^{+}_{TM} = \frac{1}{\sigma_1 \sigma_2} \left(\frac{k_B T}{h} \right)^{-1} \int \times \\ dR_{cm}\, d\phi\, d\theta\, d\phi_1\, d\theta_1\, d\psi_1\, d\phi_2\, d\theta_2\, d\psi_2\, \delta(s - s_0) \frac{1}{h^9} \int \times \\ dp_{Rcm}\, dp_\phi\, dp_\theta\, dp_{\phi_1} dp_{\theta_1}\, dp_{\psi_1}\, dp_{\phi_2}\, dp_{\theta_2}\, dp_{\psi_2}\, \dot{s}\Theta(\dot{s}) e^{-H_{TM}/k_B T} \tag{57}$$

In eq 57, R_{cm} is the center-of-mass separation, ϕ and θ are the spatially referenced Euler angles which locate the orientation of the line joining the centers of mass, (ϕ_1,θ_1,ψ_1) are the spatially referenced Euler angles locating the orientation of the rigid-body frame of fragment 1 and (ϕ_2,θ_2,ψ_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 σ_1 and σ_2 respectively.

Some preliminary transformations, which have been described in detail previously,[43] are now carried out. First, the Euler momenta of the fragments and the orbital rotation are transformed to the corresponding principal-axis angular momentum components in units of h with Jacobian J_c as indicated

$$(p_{\phi_1}, p_{\theta_1}, p_{\psi_1}, p_{\phi_2}, p_{\theta_2}, p_{\psi_2}, p_\phi, p_\theta) \xrightarrow{J_c = h^8 \sin\theta_1 \sin\theta_2 \sin\theta} \\ (j_{1A}, j_{1B}, j_{1C}, j_{2A}, j_{2B}, j_{2C}, l_x, l_y) \tag{58}$$

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. In terms of these principal-axis momenta, eq 57 becomes

$$Q^{+}_{TM} = \\ \frac{1}{\sigma_1 \sigma_2} \frac{1}{k_B T} \frac{1}{(2\pi)^8} \int dR_{cm}\, d\phi\, d\theta\, d\phi_1\, d\theta_1\, d\psi_1\, d\phi_2\, d\theta_2\, d\psi_2\, \delta \\ (s - s_0) \sin\theta \sin\theta_1 \sin\theta_2 \frac{1}{\pi^3} \int \times \\ dp_{R_{cm}}\, d\mathbf{j}_1\, d\mathbf{j}_2\, d\mathbf{l}\, \dot{s}\Theta(\dot{s}) e^{-H_{TM}/k_B T} \tag{59}$$

and the transitional-mode Hamiltonian is

$$H_{TM} = \frac{{p_{R_{cm}}}^2}{2\mu} + A_1 j_{1A}^2 + B_1 j_{1B}^2 + C_1 j_{1C}^2 + A_2 j_{2A}^2 + B_2 j_{2B}^2 + \\ C_2 j_{2C}^2 + B_0 (l_x^2 + l_y^2) + V_{TM}(\mathbf{q}) = T_{TM} + V_{TM}(\mathbf{q}) \tag{60}$$

Some unit-related transformations for R_{cm}, μ, and $p_{R_{cm}}$ allow the kinetic energy tensor for the transitional modes can be defined with common units (i.e., Joules) for all of its elements[37]

$$\tilde{R}_{\mathrm{cm}} = R_{\mathrm{cm}}/1\mathrm{m}$$
$$\tilde{\mu} = \mu \times 1\mathrm{m}^2$$
$$\tilde{p}_{\mathrm{Rcm}} = \tilde{\mu}\dot{\tilde{R}}_{\mathrm{cm}}/\hbar \qquad (61)$$

Thus, $\tilde{R}_{\mathrm{cm}}$ and $\tilde{p}_{R_{\mathrm{cm}}}$ are dimensionless, and $\tilde{\mu}$ carries units of kg m^2 (their numerical values are unchanged). The kinetic energy for the transitional modes is now written in compact tensor form

$$T_{\mathrm{TM}} = \mathbf{w}^{\mathrm{T}}\mathbf{G}_{\mathrm{TM}}\mathbf{w} \qquad (62)$$

where $\mathbf{w} = (\tilde{p}_{\mathrm{Rcm}}, l_x, l_y, j_{1A}, j_{1B}, j_{1C}, j_{2A}, j_{2B}, j_{2C})$. $\mathbf{G}_{\mathrm{TM}}$ 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., $B_0 = \hbar^2/2\mu R_{\mathrm{cm}}{}^2$. The determinant of $\mathbf{G}_{\mathrm{TM}}$ is then given by

$$|\mathbf{G}_{\mathrm{TM}}| = \left(\frac{\hbar^2}{2\tilde{\mu}}\right)B_0{}^2\prod_{i=1}^{2}A_iB_iC_i \qquad (63)$$

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

$$\Phi(T,\mathbf{q}) = \frac{\hbar}{k_{\mathrm{B}}T}\frac{1}{\pi^3}\int \mathrm{d}\mathbf{j}_1\,\mathrm{d}\mathbf{j}_2\,\mathrm{d}\mathbf{l}\,\mathrm{d}\tilde{p}_{R_{\mathrm{cm}}}\,\dot{s}\,\Theta(\dot{s})\mathrm{e}^{-T_{\mathrm{TM}}/k_{\mathrm{B}}T} \qquad (64)$$

so that

$$Q^{+}_{\mathrm{TM}} = \frac{1}{\sigma_1\sigma_2}\frac{1}{N}\int \mathrm{d}\phi\,\mathrm{d}\theta\,\mathrm{d}\phi_1\,\mathrm{d}\theta_1\,\mathrm{d}\psi_1\,\mathrm{d}\phi_2\,\mathrm{d}\theta_2\,\mathrm{d}\psi_2\,\mathrm{d}R_{\mathrm{cm}} \times \delta(s-s_0)\sin\theta\sin\theta_1\sin\theta_2\,\mathrm{e}^{-V_{\mathrm{TM}}(\mathbf{q})/k_{\mathrm{B}}T}\,\Phi(T,\mathbf{q}) \qquad (65)$$

The factor N in eq 65 is the normalizing constant for the angular integrals ($2^8\pi^5$). Next, one transforms from the spatially fixed Euler angles to a set of external angles $\{\phi,\theta,\psi\}$ and body-fixed internal angles $\{\mathbf{\Gamma}_{\mathrm{int}}\} = \{\phi',\theta'_1,\psi'_1,\theta'_2,\psi'_2\}$.[18,19,43] Here, ϕ and θ are unchanged (i.e., the orbital Euler angles), and ψ is a third Euler angle necessary to specify the overall orientation of the body. ϕ' 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 $\sin\theta'_1\sin\theta'_2/\sin\theta_1\sin\theta_2$. Invariance of the Hamiltonian with respect to overall rotation then allows analytic integration over ϕ, θ, and ψ

$$Q^{+}_{\mathrm{TM}} = \frac{1}{\sigma_1\sigma_2}\frac{1}{N'}\int \mathrm{d}\mathbf{\Gamma}_{\mathrm{int}}\,\mathrm{d}R_{\mathrm{cm}}\,\delta(s-s_0) \times \sin\theta'_1\sin\theta'_2\,\mathrm{e}^{-V_{\mathrm{TM}}(\mathbf{q})/k_{\mathrm{B}}T}\,\Phi(T,\mathbf{q}) \qquad (66)$$

where N' is the normalizing factor for integration over the five internal angles ($2^5\pi^3$). Evaluation of the integral over R_{cm} then leaves a configurational integral over at most five dimensions

$$Q^{+}_{\mathrm{TM}} = \frac{1}{\sigma_1\sigma_2}\frac{1}{N'}\int \mathrm{d}\mathbf{\Gamma}_{\mathrm{int}}\sin\theta'_1\sin\theta'_2\mathrm{e}^{-V_{\mathrm{TM}}(\mathbf{q})/k_{\mathrm{B}}T} \times (\partial s/\partial R_{\mathrm{cm}})^{-1}\Phi(T,\mathbf{q})|_{s=s_0} = \frac{1}{\sigma_1\sigma_2}\langle \mathrm{e}^{-V_{\mathrm{TM}}(\mathbf{q})/k_{\mathrm{B}}T}(\partial s/\partial R_{\mathrm{cm}})^{-1}\,\Phi(T,\mathbf{q})\rangle_{s=s_0} \qquad (67)$$

Thus, Q^{+}_{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, the analytical evaluation of the momentum flux integral $\Phi(T,\mathbf{q})$ proceeds as discussed in detail previously.[37] The result for two asymmetric-top moieties is

$$\Phi(T,\mathbf{q}) = \frac{\pi(k_{\mathrm{B}}T)^4}{B_0\prod_{i=1}^{2}(A_iB_iC_i)^{1/2}}\left(\frac{2\tilde{\mu}}{\hbar^2}\right)^{1/2}(\nabla s^{\mathrm{T}}\mathbf{G}_{\mathrm{TM}}\nabla s)^{1/2} \qquad (68)$$

and consequently

$$Q^{+}_{\mathrm{TM}} = \frac{1}{\sigma_1\sigma_2}\frac{1}{N'}\frac{\pi(k_{\mathrm{B}}T)^4}{B_0\prod_{i=1}^{2}(A_iB_iC_i)^{1/2}}\int \mathrm{d}\Gamma_{\mathrm{int}}\sin\theta'_1\sin\theta'_2\,\mathrm{e}^{-V_{\mathrm{TM}}(\mathbf{q})/k_{\mathrm{B}}T} \times \left(\frac{2\tilde{\mu}}{\hbar^2}\right)^{1/2}(\partial s/\partial R_{\mathrm{cm}})^{-1}(\nabla s^{\mathrm{T}}\mathbf{G}_{\mathrm{TM}}\nabla s)^{1/2}|_{s=s_0} \qquad (69)$$

The kinetic energy tensor is most simply expressed in terms of the radial momentum $p_{R_{\mathrm{cm}}}$ and the principal axial angular momenta, in which case $\mathbf{G}_{\mathrm{TM}}$ is diagonal (eq 62 above). However, one is not restricted to this representation. Robertson et al. construct kinetic energy tensors $\mathbf{A}^0$ and $\mathbf{G}^0$ associated with the set of coordinates $\{R_{\mathrm{cm}}, \phi, \theta, \psi, \mathbf{\Gamma}_{\mathrm{int}}\}$ in their approach.[33−35] The result of their recent analysis of the TM flux integral, expressed in terms of the present notation, is

$$Q^{+}_{\mathrm{TM}} = \frac{1}{\sigma_1\sigma_2}\frac{1}{N'}\frac{\pi(k_{\mathrm{B}}T)^4}{B_0\prod_{i=1}^{2}(A_iB_iC_i)^{1/2}}\int \mathrm{d}\Gamma_{\mathrm{int}}\sin\theta'_1\sin\theta'_2\,\mathrm{e}^{-V_{\mathrm{TM}}(\mathbf{q})/k_{\mathrm{B}}T} \times \left[1+\left(\frac{2\tilde{\mu}}{\hbar^2}\right)(\nabla R_{\mathrm{cm}}{}^{\mathrm{T}}\mathbf{G}^0_r\nabla R_{\mathrm{cm}})\right]^{1/2}|_{s=s_0} \qquad (70)$$

Some explanation of terms is necessary here. The $(n-1)\times(n-1)$ tensor $\mathbf{G}^0_r$ is obtained from $\mathbf{G}^0$ by eliminating the row and column associated with $p_{R_{\mathrm{cm}}}$. We have taken the liberty of attributing units of energy to these tensors for consistency with our definition of $\mathbf{G}_{\mathrm{TM}}$ above (eqs 61 and 62). For the purposes of evaluating the gradient vector in eq 70, $R_{\mathrm{cm}} = R_{\mathrm{cm}}(s,\phi,\theta,\psi,\Gamma_{\mathrm{int}})$ (i.e., s takes the place of R_{cm} as an independent variable) and the $(n-1)$ elements of ∇R_{cm} are gradients taken with respect to the angles. Since θ, ϕ, and ψ are external angles, the corresponding elements of the gradient vector are zero, so that only the last five elements associated with the angles $\mathbf{\Gamma}_{\mathrm{int}}$ are nonzero.

It is necessary to establish the equivalence of eqs 69 and 70. In section II the invariance of the kinematic factor $(\nabla s^{\mathrm{T}}\mathbf{G}\nabla s)$ with respect to different representations of the kinetic energy was established. Thus, we can rewrite this factor in terms of the coordinates $\{R_{\mathrm{cm}}, \phi, \theta, \psi, \Gamma_{\mathrm{int}}\}$ and their conjugate momenta. Equation 69 becomes

$$Q_{\mathrm{TM}}^{+} = \frac{1}{\sigma_1\sigma_2}\frac{1}{N'}\frac{\pi(k_{\mathrm{B}}T)^4}{B_0\prod_{i=1}^{2}(A_iB_iC_i)^{1/2}}\int \mathrm{d}\Gamma_{\mathrm{int}} \sin\theta'_1 \sin\theta'_2\, \mathrm{e}^{-V_{\mathrm{TM}}(\mathbf{q})/k_{\mathrm{B}}T} \times \left(\frac{2\tilde{\mu}}{\hbar^2}\right)^{1/2} (\partial s/\partial R_{\mathrm{cm}})^{-1}(\nabla' s^{\mathrm{T}}\mathbf{G}^0\,\nabla' s)^{1/2}|_{s=s_0} \quad (71)$$

Bringing $(\partial s/\partial R_{\mathrm{cm}})^{-1}$ inside the latter set of parentheses yields

$$Q_{\mathrm{TM}}^{+} = \frac{1}{\sigma_1\sigma_2}\frac{1}{N'}\frac{\pi(k_{\mathrm{B}}T)^4}{B_0\prod_{i=1}^{2}(A_iB_iC_i)^{1/2}}\int \mathrm{d}\Gamma_{\mathrm{int}} \sin\theta'_1 \sin\theta'_2\, \mathrm{e}^{-V_{\mathrm{TM}}(\mathbf{q})/k_{\mathrm{B}}T} \times \left(\frac{2\tilde{\mu}}{\hbar^2}\right)^{1/2} (\nabla'' s^{\mathrm{T}}\mathbf{G}^0\nabla'' s)^{1/2}|_{s=s_0} \quad (72)$$

where the elements of the gradient vector $\nabla'' s$ have the following form

$$(\nabla'' s)_1 = \frac{\partial R_{\mathrm{cm}}}{\partial s}\frac{\partial s}{\partial R_{\mathrm{cm}}} = 1$$

$$(\nabla'' s)_i = \frac{\partial R_{\mathrm{cm}}}{\partial s}\frac{\partial s}{\partial \gamma_i} = \frac{\partial R_{\mathrm{cm}}}{\partial \gamma_i} = 0, \quad \gamma_i = \phi, \theta, \psi$$

$$(\nabla'' s)_i = \frac{\partial R_{\mathrm{cm}}}{\partial s}\frac{\partial s}{\partial \gamma_i} = \frac{\partial R_{\mathrm{cm}}}{\partial \gamma_i}, \quad \gamma_i = \phi', \theta'_1, \psi'_1, \theta'_2, \psi'_2 \quad (73)$$

Noting that $\mathbf{G}_{11}^0 = \hbar^2/2\tilde{\mu}$, one then moves the factor $(2\tilde{\mu}/\hbar^2)^{1/2}$ inside the latter parentheses in eq 72 which, together with eq 73, leads directly to the result of Robertson et al. in eq 70. Thus, the equivalence of the expressions derived by Smith[25,37] and by Robertson et al.[34,35] for the TM flux integral is proven.

V. Conclusion

In this article we have explored the classical evaluation of the flux integral appearing in transition state theory with a generalized reaction coordinate. This is an integration in phase space which computes the exact classical one-way flux of an equilibrium ensemble across the chosen TSDS. One can analytically evaluate the momentum flux integrals for canonical, *E*-resolved microcanonical, and *E,J*-resolved microcanonical versions of the theory. It has become apparent that the presence of coupling terms in the kinetic energy between the GRC and the remaining degrees of freedom generally leads to a coordinate-dependent kinematic factor appearing in the configurational integral after the momentum integrals have been evaluated. We choose to distinguish between the kinematic factor and coordinate-dependent Jacobian factors which arise because of the choice of coordinates for the configurational integration. The kinematic factor, $(\nabla s^{\mathrm{T}}\mathbf{G}\nabla s)^{1/2}$, is independent of the particular set of coordinates and conjugate momenta used to represent the kinetic energy. This fact is very important from an implementational perspective, since it allows the kinematic factor to be routinely evaluated in terms of a convenient coordinate system in which the form of the **G** tensor is already known. It completely avoids the necessity for explicitly constructing a kinetic energy tensor in terms of the GRC and remaining coordinates—a feature which appeared unavoidable prior to our recent recasting of the theory.[37]

We have examined the intriguing result of Miller for the reaction path Hamiltonian flux integral,[16] which showed that rigorous evaluation of the momentum flux integrals leads to the same result which one would have obtained naïvely by neglecting coupling terms between the reaction coordinate the orthogonal modes. Miller's result is verified by our investigation, with the additional conclusion that this feature is the result of a fortunate cancellation between the coordinate-dependent kinematic factor and the coordinate-dependent Jacobian factor for configurational integration in the RPH coordinates. Our analysis also provides a novel alternative route to the derivation of the RPH.

Our result for the transitional-mode flux integral with a generalized reaction coordinate[37] has been compared with the later result of Robertson et al.,[35] with the conclusion that both groups have converged to equivalent results, albeit via quite distinct approaches.

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