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Beyond Transition-State Theory: A Rigorous Quantum Theory of Chemical Reaction Rates

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Introduction

Transition-state theory (TST),[1] as all chemists know, provides a marvelously simple and useful way to understand and estimate the rates of chemical reactions. The fundamental assumption[2] of transition-state theory (i.e., direct dynamics, no recrossing trajectories; see below), however, is based inherently on *classical* mechanics, so the theory must be quantized if it is to provide a *quantitative* description of chemical reaction rates. Unlike classical mechanics, though, there seems to be no way to construct a rigorous quantum mechanical theory that contains as its only approximation the transition-state assumption of "direct dynamics". Pechukas[3] has discussed this quite clearly (and it will be reviewed below): as soon as one tries to rid a quantum mechanical version of transition-state theory of all approximations (e.g., separability of a one-dimensional reaction coordinate) beyond the basic transition-state assumption itself, one is faced with having to solve the full (multidimensional) quantum reaction dynamics problem. But a correct treatment of the full quantum dynamics must yield the *exact* rate constant and is no longer a transition-state "theory".

Though there is no rigorous quantum prescription for determining the rate constant of a chemical reaction that avoids, in one guise or another, the necessity of solving the Schrödinger equation, there is nevertheless a rigorous theoretical approach[4] that avoids having to solve the complete state-to-state reactive scattering problem; one does not avoid solving the Schrödinger equation, but needs to solve it only *locally*, in the vicinity of the transition state, with no explicit information about reactant and product states being required. After reviewing some of the notions alluded to above, the purpose of this Account is to describe this "direct" theoretical approach for calculating chemical reaction rates, the logical conclusion in the quest for a "rigorous" quantum mechanical version of transition-state theory.

Classical Mechanics

It is useful first to review very briefly the situation[3,5] within the realm of classical mechanics and establish some definitions. For comparison with quantum expressions later it is convenient to express the thermal rate constant $k(T)$ as a Boltzmann average of the *cumulative reactive probability* $N(E)$,

$$k(T) = [2\pi\hbar Q_r(T)]^{-1} \int_{-\infty}^{\infty} dE\, e^{-E/kT} N(E) \qquad (1a)$$

where N is given by

$$N(E) = (2\pi\hbar)^{-(F-1)} \int d\mathbf{p} \int d\mathbf{q}\, \delta[E-H(\mathbf{p},\mathbf{q})]\, F(\mathbf{p},\mathbf{q})\, \chi(\mathbf{p},\mathbf{q}) \qquad (1b)$$

and $Q_r(T)$ is the partition function (per unit volume) of reactants.

[Equations 1a and 1b can be combined to express the thermal rate constant more explicitly,

$$k(T) = Q_r(T)^{-1}(2\pi\hbar)^{-F} \int d\mathbf{p} \int d\mathbf{q}\, e^{-H(\mathbf{p},\mathbf{q})/kT}\, F(\mathbf{p},\mathbf{q})\, \chi(\mathbf{p},\mathbf{q}) \qquad (1c)$$

but in this paper we will focus on the cumulative reaction probability $N(E)$ as the primary object of interest. Sometimes, in fact, usually for unimolecular reactions, it is the *microcanonical* rate constant $k(E) \equiv [2\pi\hbar\rho_r(E)]^{-1}N(E)$ which is the quantity of interest, where $\rho_r(E)$ is the density of reactant states per unit energy.]

The integrand of eq 1b giving the cumulative reaction probability consists of three factors: a statistical factor $\delta[E-H(\mathbf{p},\mathbf{q})]$ (the microcanonical density), the flux $F(\mathbf{p},\mathbf{q})$, and a dynamical factor $\chi(\mathbf{p},\mathbf{q})$. [The classical Hamiltonian $H(\mathbf{p},\mathbf{q})$ is assumed throughout this paper (for simplicity of presentation; it is not essential) to be of Cartesian form,

$$H(\mathbf{p},\mathbf{q}) = \mathbf{p}^2/2m + V(\mathbf{q}) \qquad (2)$$

where $(\mathbf{q},\mathbf{p}) \equiv (q_k,p_k)$, $k = 1, ..., F$ are the coordinates and momenta of the system.] The flux $F(\mathbf{p},\mathbf{q})$ is defined with respect to a *dividing surface* in coordinate space which separates the reactant side from the product side. If the dividing surface is defined by the equation

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[1] (a) An interesting set of papers by many of the founders of the theory—Wigner, M. Polanyi, Evans, and Eyring—is in the following: Reaction Kinetics—a General Discussion. *Trans. Faraday Soc.* **1938,** *34,* 1–127. (b) For a reasonably recent review, see: Truhlar, D. G.; Hase, W. L.; Hynes, J. T. *J. Phys. Chem.* **1983,** *87,* 2664.

[2] Wigner, E. *Trans. Faraday Soc.* **1938,** *34,* 29.

[3] Pechukas, P. In *Dynamics of Molecular Collisions,* Part B (Vol. 2 of *Modern Theoretical Chemistry*); W. H., Miller, Ed.; Plenum: New York, 1976; Chapter 6.

[4] (a) Seideman, T.; Miller, W. H. *J. Chem. Phys.* **1992,** *96,* 4412. (b) Seideman, T.; Miller, W. H. *J. Chem. Phys.* **1992,** *97,* 2499. (c) Miller, W. H.; Seideman, T. Cumulative and State-to-State Reaction Probabilities via a Discrete Variable Representation—Absorbing Boundary Condition Green's Function. In *Time Dependent Quantum Molecular Dynamics: Experiments and Theory*; Broeckhove, J., Ed.; NATO ARW.

[5] Miller, W. H. *Acc. Chem. Res.* **1976,** *9,* 306.

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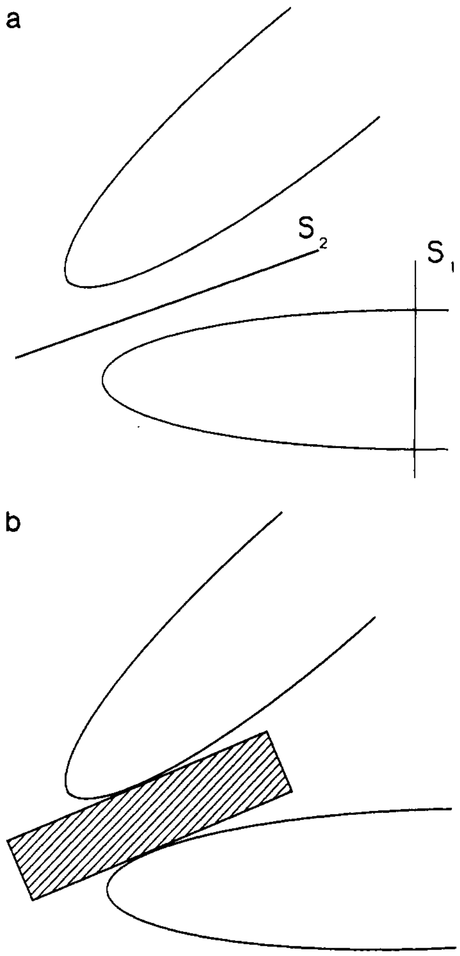

Figure 1. (a) Schematic depiction of the contours of a potential energy surface with two possible choices of the dividing surface (actually a *line* in this two-dimensional case), S_1 in the reactant region and S_2 through the transition-state region. (b) Same as part a, but indicating a region of some width about the dividing surface S_2.

$$f(\mathbf{q}) = 0 \tag{3a}$$

e.g., $f(\mathbf{q}) < 0$ on the reactant side and $f(\mathbf{q}) > 0$ on the product side, then the flux through it is given by

$$F(\mathbf{q},\mathbf{p}) \equiv \frac{\mathrm{d}}{\mathrm{d}t} h[f(\mathbf{q})] = \delta[f(\mathbf{q})] \frac{\partial f(\mathbf{q})}{\partial \mathbf{q}} \cdot \mathbf{p}/m \tag{3b}$$

where $h(\xi)$ is the Heaviside function,

$$h(\xi) = 1 \quad \text{for} \quad \xi > 0$$

$$h(\xi) = 0 \quad \text{for} \quad \xi < 0$$

(Note that $h'(\xi) = \delta(\xi)$, the Dirac δ function.) That is, $h[f(\mathbf{q})] = 0$ and 1, respectively, on the reactant and product sides of the dividing surface, and the flux is the rate (the time derivative) of crossing the dividing surface from reactants to products. Often the dividing surface is specified by a given value of a reaction coordinate, coordinate q_F, say. In this case $f(\mathbf{q}) = q_F - q_F^{\ddagger}$, where $q_F^{\ddagger}$ is the value of the reaction coordinate which defines the dividing surface, and eq 3b for the flux simplifies to

$$F(\mathbf{q},\mathbf{p}) = \delta(q_F - q_F^{\ddagger}) p_F/m \tag{3c}$$

The third factor in the integrand of eq 1b, $\chi(\mathbf{p},\mathbf{q})$, is the *characteristic function for reaction*; it can be defined in several equivalent ways,[3] but the one that is perhaps the most intuitive (at least in classical mechanics) is as follows: $\chi(\mathbf{p},\mathbf{q}) = 1$ if the trajectory determined by initial conditions $(\mathbf{p},\mathbf{q})$ at time $t = 0$ goes from reactants in the infinite past ($t \rightarrow -\infty$) to products in the infinite future ($t \rightarrow +\infty$), and $\chi(\mathbf{p},\mathbf{q}) = 0$ otherwise. Because the integrand of the phase space average in eq 1b contains the δ function $\delta[f(\mathbf{q})]$, all trajectories begin on the dividing surface, with initial conditions $(\mathbf{p},\mathbf{q})$, and one runs them forward and backward in time to determine whether $\chi(\mathbf{p},\mathbf{q})$ is 1 or 0. Because of the other δ function, the microcanonical density $\delta[E-H(\mathbf{p},\mathbf{q})]$, all trajectories have the same total energy E.[6]

The rigorous dynamical expression for $N(E)$, eq 1b, is independent of the choice of the dividing surface (by virtue of Liouville's theorem), but a wise choice for it facilitates the calculation. Figure 1a shows a schematic contour plot of a potential energy surface and two possible choices of the dividing surface. For dividing surface S_1 one thus begins trajectories in the reactant valley and integrates long enough to determine which ones react, i.e., the values of $(\mathbf{p},\mathbf{q})$ for which $\chi(\mathbf{p},\mathbf{q}) = 1$. The calculation of $N(E)$ [and therefore $k(T)$] is greatly simplified,[7] however, by choosing the dividing surface S_2, which cuts through the transition-state region, because it is then necessary to run the trajectory (i.e., numerically integrate the classical equations of motion) for only a *short time* in order to determine whether the trajectory came from reactants in the past and goes to products in the future.

Transition-state theory, in fact, corresponds to running the trajectory for *zero time*, i.e., to the *approximation* that $\chi(\mathbf{p},\mathbf{q})$ is 1 or 0 depending only on whether or not the trajectory starts off pointing in the reactive direction. It is thus the assumption of "direct dynamics", that no trajectories recross the dividing surface at later (or earlier) times. Stated algebraically, the transition-state approximation is

$$\chi_{\mathrm{TST}}(\mathbf{p},\mathbf{q}) = h\left[\frac{\partial f(\mathbf{q})}{\partial \mathbf{q}} \cdot \mathbf{p}\right] \tag{4a}$$

or if $f(\mathbf{q}) = q_F - q_F^{\ddagger}$, then

$$\chi_{\mathrm{TST}}(\mathbf{p},\mathbf{q}) = h(p_F) \tag{4b}$$

It is a straightforward procedure to show that with the approximation eq 4, eq 1 leads to conventional transition state theory rate expressions: e.g., if $f(\mathbf{q}) = q_F - q_F^{\ddagger}$, one finds that

$$N_{\mathrm{TST}}(E) = (2\pi\hbar)^{-(F-1)} \int \mathrm{d}\mathbf{p}' \int \mathrm{d}\mathbf{q}' \, h[E - H_{F-1}(\mathbf{p}',\mathbf{q}')] \tag{5a}$$

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(6) Because of the two δ functions in the integrand of eq 1b, it is possible to carry out the integration over the reaction coordination q_F and its conjugate momentum p_F. For example, if $f(\mathbf{q}) = q_F - q_F^{\ddagger}$, then one obtains

$$N(E) = (2\pi\hbar)^{-(F-1)} \int \mathrm{d}\mathbf{p}' \int \mathrm{d}\mathbf{q}' \, h[E - H_{F-1}(\mathbf{p}',\mathbf{q}')][\chi_+(\mathbf{p}',\mathbf{q}';E) - \chi_-(\mathbf{p}',\mathbf{q}';E)]$$

with

$$\chi_\pm(\mathbf{p}',\mathbf{q}';E) = \chi[\mathbf{p}',\mathbf{q}',q_F = q_F^{\ddagger}, p_F = \pm[2m[E - H_{F-1}(\mathbf{p}',\mathbf{q}')]]^{1/2}]$$

where $\mathbf{q}',\mathbf{p}' = (q_k, p_{,}k)$, $k = 1, ..., F-1$, and H_{F-1} is the classical Hamiltonian for the system with the Fth degree of freedom frozen at $q_F^{\ddagger}$, i.e., $H_{F-1}(\mathbf{p}',\mathbf{q}') = (\mathbf{p}')^2/2m + V(\mathbf{q}',q_F^{\ddagger})$.

(7) (a) Keck, J. C. *Adv. Chem. Phys.* **1967**, *13*, 85. (b) Horiuti, J. *Bull. Chem. Soc. Jpn.* **1938**, *13*, 210.

where $(\mathbf{q}',\mathbf{p}') = \{q_k,p_k\}$, $k = 1, ..., F-1$, and $H_{F-1} = (\mathbf{p}')^2/2m + V(\mathbf{q}',q_F^{\ddagger})$ is the classical Hamiltonian for the system with $F-1$ degrees of freedom (i.e., *on* the dividing surface defined by $q_F \equiv q_F^{\ddagger}$). In words, eq 5a says that $N_{\text{TST}}(E)$ is the volume of phase space on the dividing surface (i.e., of the $F-1$ dimensional system) with energy less than or equal to E. The thermal rate constant then follows from eq 1a,

$$k(T) = \frac{kT}{h}\frac{Q^{\ddagger}(T)}{Q_{\text{r}}(T)} \qquad (5b)$$

where $Q^{\ddagger}$ is the partition function on the dividing surface,

$$Q^{\ddagger}(T) = (2\pi\hbar)^{-(F-1)}\int d\mathbf{p}'\int d\mathbf{q}'\, e^{-H_{F-1}(\mathbf{p}',\mathbf{q}')/kT} \qquad (5c)$$

To summarize, the exact (classical) result for $N(E)$ [and thus $k(T)$] requires that one solve the classical reaction dynamics, i.e., begin trajectories on the dividing surface and follow them long enough to determine whether or not they are reactive. The result is independent of the choice of dividing surface, but a clever choice makes the calculation easier (i.e., the trajectories do not need to be followed for as long a time). Transition-state theory requires no dynamical (i.e., trajectory) calculation; it is the *approximation* that a trajectory is reactive if at $t = 0$ it starts out in the reactive direction. The transition-state approximation for $N(E)$ (eq 5a) is clearly not independent of the dividing surface; i.e., in Figure 1a, the assumption of no recrossing trajectories appears as though it would be reasonably good for the dividing surface S_2, but would surely be poor for the choice S_1. For *any* dividing surface the transition-state approximation for $N(E)$, eq 5a, can be shown to be an upper bound (i.e., any error in eq 4 is to count some nonreactive trajectories as reactive ones),

$$N_{\text{TST}}(E) \geq N(E) \qquad (6)$$

The best transition-state approximation is thus the one that makes $N_{\text{TST}}(E)$ a minimum, and this provides the criterion for choosing the best dividing surface.[8]

Quantum Transition-State Theory?

In attempting to construct a quantum mechanical version of transition-state theory it is fairly obvious how to quantize the motion *on* the dividing surface, i.e., the $(F-1)$ degrees of freedom in the Hamiltonian H_{F-1}, because these degrees of freedom correspond to bounded motions. The Hamiltonian H_{F-1} simply becomes the quantum Hamiltonian operator; the partition function of the activated complex $Q^{\ddagger}$ in eq 5c, for example, becomes a quantum partition function.

It is more problematic to quantize the Fth degree of freedom, the reaction coordinate. At the simplest level of approximation one typically assumes that it is separable from the $(F-1)$ degrees of freedom on the dividing surface. In this case the cumulative reaction probability is given by

$$N(E) = \sum_{\mathbf{n}^{\ddagger}} P_{\text{tun}}(E-\epsilon_{\mathbf{n}^{\ddagger}}) \qquad (7a)$$

where P_{tun} is the tunneling probability for the one-dimensional reaction coordinate motion, E is the total energy, and $\{\epsilon_{\mathbf{n}^{\ddagger}}\}$ are the energy levels of the "activated complex", i.e., of the Hamiltonian H_{F-1} for motion on the dividing surface; $E - \epsilon_{\mathbf{n}^{\ddagger}}$ is thus the energy in the reaction coordinate. It is then easy to show that with eq 7a for $N(E)$, eq 1 leads to the following quantum transition state theory rate constant with a one-dimensional tunneling correction:

$$k(T) = \kappa(T)\frac{kT}{h}\frac{Q^{\ddagger}(T)}{Q_{\text{r}}(T)} \qquad (7b)$$

where $Q^{\ddagger}$ is the quantum partition function for motion on the dividing surface,

$$Q^{\ddagger}(T) = \sum_{\mathbf{n}^{\ddagger}} e^{-\epsilon_{\mathbf{n}^{\ddagger}}/kT} \qquad (7c)$$

and $\kappa(T)$, the tunneling correction, is the Boltzmann average of the one-dimensional tunneling probability,

$$\kappa(T) = (kT)^{-1}\int_{-\infty}^{\infty} dE_F\, e^{-E_F/kT}\, P_{\text{tun}}(E_F) \qquad (7d)$$

Whereas the *classical* transition state theory rate expression, eq 5, requires knowledge of the potential energy surface only *on* the dividing surface, the quantum expression above (eq 7) requires knowledge of the potential energy surface for some *region about* the dividing surface (cf. Figure 1b) because of the quantum nature of the reaction coordinate (i.e., the tunneling correction). Furthermore, it is clearly an approximation to assume that the reaction coordinate, the Fth degree of freedom, is separable from the other $(F-1)$ degrees of freedom. To have a quantum transition-state theory that is free of this approximation requires a *multidimensional tunneling* treatment. Johnson and Rapp[9] were, to my knowledge, the first to address multidimensional tunneling in a serious way. More recent treatments[5,10] have been approximations that are based on semiclassical tunneling theory.[11] All of these treatments are inherently approximate, however, and as Pechukas[3] has noted, if one deals with multidimensional tunneling fully correctly, without approximation, then one must in effect solve the multidimensional Schrödinger equation.

One attempt at constructing a rigorous quantum transition-state theory (i.e., free of the separability approximation) was based on "quantizing" eqs 1 and 4 directly. For example, it is fairly clear that the classical phase space average in eq 1b should become a quantum mechanical trace,

$$(2\pi\hbar)^{-F}\int d\mathbf{p}\int d\mathbf{q}[\cdots] \rightarrow \text{tr}[\cdots] \qquad (8)$$

and $H(\mathbf{p},\mathbf{q})$ and $F(\mathbf{p},\mathbf{q})$ become quantum operators $\hat{H}$ and $\hat{F}$. The flux operator $\hat{F}$ is in general defined by

$$\hat{F} = \frac{i}{\hbar}[\hat{H},h(f(\hat{\mathbf{q}}))] \qquad (9a)$$

i.e., the Heisenberg time derivation of $h(f(\mathbf{q}))$ (cf. eq 3b). If $f(\mathbf{q}) = q_F - q_F^{\ddagger}$, then this commutator is easily evaluated, to give

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(8) For a review of many applications and ramifications of this variational feature, see: (a) Truhlar, D. G.; Garrett, B. C. *Acc. Chem. Res.* **1980**, *13*, 440. (b) *Annu. Rev. Phys. Chem.* **1984**, *35*, 159.

(9) Johnston, H. S.; Rapp, D. *J. Am. Chem. Soc.* **1961**, *83*, 1.

(10) (a) Marcus, R. A.; Coltrin, M. E. *J. Chem. Phys.* **1977**, *67*, 2609. (b) Reference 8b. (c) Makri, N.; Miller, W. H. *J. Chem. Phys.* **1989**, *91*, 4026.

(11) (a) George, T. F.; Miller, W. H. *J. Chem. Phys.* **1972**, *57*, 2458. (b) Hornstein, S. M.; Miller, W. H. *J. Chem. Phys.* **1974**, *61*, 745.

$$\hat{F} = {}^1/_2\{\delta(\hat{q}_F - q_F^{\ddagger})(\hat{p}_F/m) + (\hat{p}_F/m)\delta(\hat{q}_F - q_F^{\ddagger})\} \quad (9b)$$

where $\hat{p}_F = (\hbar/i)(\partial/\partial q_F)$ is the momentum operator for the reaction coordinate; eq 9b is clearly the quantum analog of the classical flux, eq 3c. Using the quantum analog of the classical transition-state approximation, eq 4b, then gives

$$N_{\mathrm{QMTST}}(E) = 2\pi\hbar\ \mathrm{tr}[\delta(E - \hat{H})\,\hat{F}\,h(\hat{p}_F)] \quad (10a)$$

and

$$k_{\mathrm{QMTST}}(T) = \mathrm{tr}[\mathrm{e}^{-\hat{H}/kT}\,\hat{F}\,h(\hat{p}_F)]/Q_{\mathrm{r}}(T) \quad (10b)$$

McLafferty and Pechukas[12] and Miller[5,13] independently developed theories of this type, but though they do avoid having to make the separability approximation, they have the disappointing feature that they do not give the correct quantum result in the separable limit, eq 7, even though the dynamics is clearly "direct" in this limit. This difficulty is related to the nature of the "zero time" approximation inherent in eq 4; i.e., quantum mechanics requires finite time (of order $\hbar/kT$) to describe even direct dynamics correctly. To correct for this "zero time" defect, Tromp and Miller[14] used flux time correlation functions to define a quantum transition-state theory based on short (but finite) time quantum dynamics, but this also has ad hoc features and sometimes gives unphysical results.

The conclusion, therefore, is that, unlike classical mechanics, there is no rigorous (e.g., nonseparable) quantum version of transition-state theory that does not require a solution of the full multidimensional reaction dynamics. It does not seem appropriate, however, to refer to such a treatment as a transition-state "theory" (i.e., approximation) since ipso facto it must yield the exact result.

Rigorous Quantum Rate Theory

Though transition-state theory does not survive the transformation from classical to quantum mechanics in a rigorous fashion,[15] there is a rigorous quantum analog of the classical approach which begins trajectories on a dividing surface in the transition-state region and follows them for only short times. Thus the quantum rate constant can also be written in the form of eq 1, where the rigorous quantum expression for the cumulative reaction probability[13b] is

$$N(E) = \sum_{n_{\mathrm{p}}}\sum_{n_{\mathrm{r}}}|S_{n_{\mathrm{p}},n_{\mathrm{r}}}(E)|^2 \quad (11)$$

where n_{r} (n_{p}) denotes all the quantum numbers of the reactants (products), and the square moduli of the S-matrix elements are the reaction probabilities for the $n_{\mathrm{r}} \rightarrow n_{\mathrm{p}}$ (state-to-state) transition. It is eq 11, in fact, which suggests the term "cumulative reaction probability" for $N(E)$: i.e., the *total* reaction probability from initial reactant state n_{r} is given by

$$P_{n_{\mathrm{r}}}(E) \equiv \sum_{n_{\mathrm{p}}}|S_{n_{\mathrm{p}},n_{\mathrm{r}}}(E)|^2 \quad (12a)$$

and if one idealized matters by assuming that some initial states are completely reactive and others completely nonreactive, i.e., $P_{n_{\mathrm{r}}} = 0$ or 1, then clearly $N(E)$,

$$N(E) \equiv \sum_{n_{\mathrm{r}}} P_{n_{\mathrm{r}}}(E) \quad (12b)$$

would be the number of reactive states. This interpretation as the "number of reactive states" also comes from classical transition-state theory; e.g., if one neglects tunneling in eq 7a, then

$$N_{\mathrm{TST}}(E) = \sum_{\mathbf{n}^{\ddagger}} h(E - \epsilon_{\mathbf{n}^{\ddagger}}) \quad (12c)$$

i.e., N_{TST} is the number of states $\mathbf{n}^{\ddagger}$ of the activated complex that lie below total energy E, i.e., which have positive kinetic energy $E - \epsilon_{\mathbf{n}^{\ddagger}}$ in the reaction coordinate at the transition state. In reality, of course, reaction probabilities can take on any values between 0 and 1, but the interpretation of $N(E)$ as the effective number of quantum states which react is still qualitatively useful. It is also useful to note that the cumulative reaction probability of eq 11 is closely related to the *yield function* introduced by Coulson and Levine.[16]

Though eq 11 provides a rigorous quantum definition of the cumulative reaction probability, is not helpful in a practical sense because a complete state-to-state reactive scattering calculation is required to obtain the S-matrix. Is it possible to determine $N(E)$ more "directly" (and thus presumably more efficiently), but without approximation, by anything short of such a complete solution of the quantum reactive scattering Schrödinger equation?

A *formal* answer to this question was given some years ago, namely, that $N(E)$ is given completely rigorously, and thus equivalently to eq 11, by the following expression:[17]

$$N(E) = {}^1/_2(2\pi\hbar)^2\,\mathrm{tr}[\delta(E - \hat{H})\,\hat{F}\,\delta(E - \hat{H})\hat{F}] \quad (13)$$

where $\hat{F}$ is the flux operator of eq 9. This expression for $N(E)$ is manifestly independent of any reference to asymptotic quantum states of reactants or products. To see (at least heuristically) how it comes about one "quantizes" the classical expression eq 1b according to eqs 8 and 9. Noting that the characteristic function χ can also be expressed as[13,17]

$$\chi(\mathbf{p},\mathbf{q}) = \lim_{t\rightarrow\infty} h[f(\mathbf{q}(t))] = \int_0^{\infty}\mathrm{d}t\,\frac{\mathrm{d}}{\mathrm{d}t}h[f(\mathbf{q}(t))] = \int_0^{\infty}\mathrm{d}t\,F(t) \quad (14)$$

the classical expression, eq 1b, becomes

$$N(E) = 2\pi\hbar\int_0^{\infty}\mathrm{d}t\ \mathrm{tr}[\delta(E - H)F\,F(t)] \quad (15)$$

Quantum mechanically, however, the time-evolved flux operator is given by

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(12) McLafferty, F. J.; Pechukas, P. *Chem. Phys. Lett.* **1974**, *27*, 511.

(13) Miller, W. H. *J. Chem. Phys.* **1974**, *61*, 1823. (b) Miller, W. H. *J. Chem. Phys.* **1975**, *62*, 1899.

(14) Tromp, J. W.; Miller, W. H. *J. Phys. Chem.* **1986**, *90*, 3482.

(15) Interestingly, at the *semiclassical* level there actually does exist a nontrivial version of transition-state theory that includes nonseparable coupling between all degrees of freedom, including the reaction coordinate. It involves the locally "good" action variables about the saddle point on the potential energy surface, in terms of which the classical motion, though nonseparable, is *integrable*. See: (a) Miller, W. H. *Faraday Discuss. Chem. Soc.* **1977**, *62*, 40. (b) Miller, W. H.; Hernandez, R.; Handy, N. C.; Jayatilaka, D.; Willets, A. *Chem. Phys. Lett.* **1990**, *62*, 172.

(16) Coulson, C. A.; Levine, R. D. *J. Chem. Phys.* **1967**, *47*, 1235. See also: Levine, R. D. *Quantum Theory of Molecular Rate Processes*; Oxford: New York, 1969; pp 120–122.

(17) Miller, W. H.; Schwartz, S. D.; Tromp, J. W. *J. Chem. Phys.* **1983**, *79*, 4889.

$$\hat{F}(t) = \mathrm{e}^{i\hat{H}t/\hbar}\hat{F}\mathrm{e}^{-i\hat{H}t/\hbar}$$

and the real part of the integral is even, so that

$$N(E) = {}^1/_2(2\pi\hbar)\int_{-\infty}^{\infty}\mathrm{d}t\ \mathrm{tr}[\delta(E-\hat{H})\hat{F}\mathrm{e}^{i\hat{H}t/\hbar}\hat{F}\mathrm{e}^{-i\hat{H}t/\hbar}] \quad (16)$$

But the operator $\mathrm{e}^{-i\hat{H}t/\hbar}$ can be replaced by the scalar $\mathrm{e}^{-iEt/\hbar}$ since this operator sits next to $\delta(E-\hat{H})$ (with a cyclic permutation inside the trace), and with the identity

$$\int_{-\infty}^{\infty}\mathrm{d}t\ \mathrm{e}^{i(H-E)t/\hbar} = 2\pi\hbar\delta(E-\hat{H}) \quad (17)$$

one obtains the quoted result, eq 13.

Equation 13 is quite a beguiling expression. For example, in the classical expression for $N(E)$, eq 1b, there are a *statistical* factor $\delta(E-H)$, the flux factor F, and a *dynamical* factor χ. A similar structure exists in the quantum expression, eq 15, where the dynamical factor is the time integral of the time-evolved flux operator, i.e., $\chi(\mathbf{p},\mathbf{q}) \rightarrow \int_0^{\infty}\mathrm{d}t\ \hat{F}(t)$. The manipulations following eq 15, however, lead to the result eq 13, which appears to have *no* dynamical information, i.e., only the statistical operator $\delta(E-\hat{H})$ and flux operator $\hat{F}$ are involved in eq 13. The steps which convert eq 15 into eq 13, however, are reversible, so that the dynamical information must be contained implicitly in eq 13. This is another example of the fact that, in quantum mechanics, dynamics and statistics are inseparably intertwined; e.g., a wavefunction describes the *dynamical motion* of the particles and also their *statistics*. Finally, I note that one cannot convert eq 13 directly into a corresponding classical expression by replacing the trace by a phase space average and the operators by the corresponding functions (as one *can* do for eq 15). If one tries, the result is

$$N(E) = {}^1/_2(2\pi\hbar)^2(2\pi\hbar)^{-F}\int\mathrm{d}\mathbf{p}\int\mathrm{d}\mathbf{q}\ \delta(E-H(\mathbf{p},\mathbf{q}))^2\ F(\mathbf{p},\mathbf{q})^2 \quad (18)$$

which appears to be infinite (because of the squares of the δ functions); the factor $\hbar^2$ (which doesn't divide out in normalization) is 0 in the classical limit, however, so eq 18 is simply indeterminant.

The difficult part of eq 13 to evaluate is the microcanonical density operator, $\delta(E-\hat{H})$, which is usually[18] expressed in terms of the outgoing wave Green's function (actually an *operator*),

$$\delta(E-\hat{H}) = -\frac{1}{\pi}\,\mathrm{Im}\ \hat{G}^+(E) \quad (19a)$$

where

$$\hat{G}^+(E) = \lim_{\epsilon\to 0}(E + i\epsilon - \hat{H})^{-1} \quad (19b)$$

ϵ is a positive constant which imposes the outgoing wave boundary condition on the Green's function (hence the "+" designation), or it may be thought of as a convergence factor in the expression for G^+ in terms of the time evolution operator $\mathrm{e}^{-i\hat{H}t/\hbar}$:

$$\hat{G}^+(E) = (i\hbar)^{-1}\int_0^{\infty}\mathrm{d}t\ \mathrm{e}^{i(E+i\epsilon)t/\hbar}\mathrm{e}^{-i\hat{H}t/\hbar}$$

the factor $\exp(-\epsilon t/\hbar)$ in the integrand makes the time integral well-behaved in the long time ($t \rightarrow \infty$) limit.

The parameter ϵ in eq 19b usually plays a purely formal role in quantum scattering theory, but it has recently[4] been pointed out that one may think of it as the *absorbing potential* that a number of persons[19] have used in numerical wavepacket propagation calculations to prevent reflections at the edge of the coordinate space grid. In this latter approach one adds a negative imaginary potential to the true potential energy function,

$$V(\mathbf{q}) \rightarrow V(\mathbf{q}) - i\epsilon(\mathbf{q}) \quad (20a)$$

but this is clearly equivalent to adding the positive (operator) ϵ to E in $E - H$,

$$E - \hat{H} \rightarrow E + i\hat{\epsilon}(q) - \hat{H} \quad (20b)$$

Allowing ϵ to be a (positive) function of coordinates, i.e., a potential energy operator, is better than taking it to be a constant, because it can be chosen to be 0 in the physically relevant region of space and only "turned on" at the edges of this region to impose the outgoing wave boundary condition. Absorbing flux in this manner, and thus not allowing it to return to the interaction region, is analogous in a classical calculation to terminating trajectories when they exit the interaction region.

Figure 2 shows a sketch of the potential energy surface for the generic reaction $H + H_2 \rightarrow H_2 + H$, with several different choices for the absorbing potential $\epsilon(\mathbf{q})$ (indicated by dashed contours). $\epsilon(\mathbf{q})$ is 0 in the transition-state region, where the reaction dynamics (i.e., tunneling, recrossing dynamics, etc.) takes place, and is turned on outside this region. All the choices in Figure 2 are possible, i.e., give correct results, but the one in Figure 2c was found to be the most efficient, i.e., the one that allowed one to make the interaction region as small as possible.

With the microcanonical density operator given by eq 19 (with some choice for ϵ), straightforward algebraic manipulations (using eqs 9a and 19) lead to the following even simpler form for the cumulative reaction probability:

$$N(E) = 4\ \mathrm{tr}[\hat{G}^+(\mathrm{E})^*\hat{\epsilon}_\mathrm{p}\hat{G}^+(\mathrm{E})\hat{\epsilon}_\mathrm{r}] \quad (21a)$$

where ϵ_r (ϵ_p) is the part of the adsorbing potential in the reactant (product) valley, and $\epsilon \equiv \epsilon_\mathrm{r} + \epsilon_\mathrm{p}$. This expression may be evaluated in any convenient basis set which spans the interaction region and also extends some ways into the absorbing region. The explicit matrix expression is then

$$N(E) = 4\ \mathrm{tr}[(E - i\epsilon - \mathbf{H})^{-1}\cdot\epsilon_\mathrm{p}\cdot(E + i\epsilon - \mathbf{H})^{-1}\cdot\epsilon_\mathrm{r}] \quad (21b)$$

with

$$\epsilon = \epsilon_\mathrm{r} + \epsilon_\mathrm{p}$$

It is interesting to note that in eq 21 all reference to a specific dividing surface has vanished; it is implicit that a dividing surface lies somewhere between the reactant and product "absorbing strips" (cf. Figure 2c), but there is no dependence on its specific choice. This is consistent with the earlier discussion that in classical mechanics $N(E)$ is independent of the choice of the

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(18) See, for example: Newton, R. G. *Scattering Theory of Waves and Particles*; Springer-Verlag: Berlin, 1982; p 176 ff.

(19) (a) Goldberg, A.; Shore, B. W. *J. Phys. B* **1978**, *11*, 3339. (b) Leforestier, C.; Wyatt, R. E. *J. Chem. Phys.* **1983**, *78*, 2334. (c) Kosloff, R.; Kosloff, D. *J. Comput. Phys.* **1986**, *63*, 363. (d) Neuhauser, D.; Baer, M. *J. Chem. Phys.* **1989**, *90*, 4351.

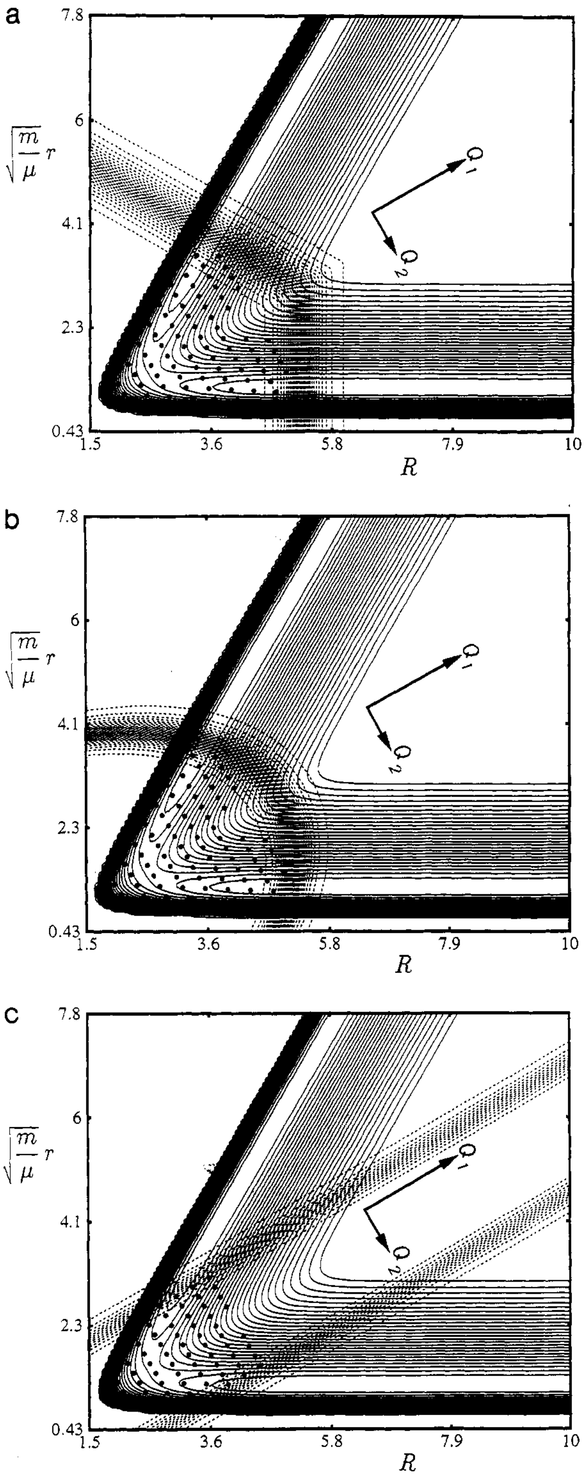

Figure 2. Solid lines are contours of the potential energy surface for the $H + H_2 \rightarrow H_2 + H$ reaction. Broken lines are contours of the absorbing potential (which is 0 in the central part of the interaction region and "turned on" at the edge), for three possible choices of it. The points are the grid points which constitute the "basis set" for the evaluation of the quantum trace, eqs 21 and 22.

dividing surface provided that one actually determines the exact dynamics, as is being done here quantum mechanically.

Equation 21 provides the first practical scheme for determining the rate constant for a chemical reaction absolutely *correctly*, but *directly*, i.e., without having to solve the complete reactive scattering problem. This is not a transition-state "theory" since calculation of the Green's function, the matrix inverse of $(E + i\epsilon - \mathbf{H})$, is equivalent to solving the Schrödinger equation, i.e., it generates the complete quantum dynamics. Since this is required only in the transition-state region (between the reactant and product absorbing strips), one may think of this quantum mechanical calculation as the analog of a classical trajectory calculation which begins trajectories on a dividing surface in the transition-state region and follows them for a short time to see which ones are reactive.

Illustrative Examples

In recent applications[4] it has proved useful to employ a set of *grid points* in coordinate space as the basis set in which to evaluate eq 21b. These discrete variable,[20] pseudospectral,[21] or collocation methods[22] are proving quite useful for a variety of molecular quantum mechanical calculations. The primary advantages of such approaches are that (1) no integrals are required in order to construct the Hamiltonian matrix (e.g., the potential energy matrix is diagonal, the diagonal values being the values of the potential energy function at the grid points) and (2) the Hamiltonian matrix is extremely sparse (so that large systems of linear equations can be solved efficiently).

Since the absorbing potential is diagonal in a grid point representation, eq 21b for the cumulative reaction probability simplifies to

$$N(E) = 4\sum_{i,i'} \epsilon_i^{\mathrm{r}} |G_{i,i'}|^2 \epsilon_{i'}^{\mathrm{p}} \qquad (22)$$

where the index labels the grid points (the "basis functions") and $G_{i,i'}$ is the (i,i') element of the inverse of the matrix $\{\delta_{i,i'}(E+i\epsilon_i) - H_{i,i'}\}$, with $\epsilon_i = \epsilon_i^{\mathrm{r}} + \epsilon_i^{\mathrm{p}}$. The sum over i and i' includes only points in the reactant and product absorbing regions, respectively, since ϵ_i^{r} and $\epsilon_{i'}^{\mathrm{p}}$ are 0 at other grid points.

Figure 2c shows the set of grid points and the absorbing potentials which yield accurate results for the standard test problem, the collinear $H + H_2 \rightarrow H_2 + H$ reaction. The important feature to see here is how close the absorbing potentials can be brought in and how localized the grid can be taken about the transition-state region. This is the region in which it is necessary to determine the quantum dynamics in order to obtain the correct result for $N(E)$ [and thus $k(T)$]. No information about reactant and product quantum states is involved in the calculation.

Figure 3a shows the cumulative reaction probability so obtained[4a] for the collinear $H + H_2$ reaction. Apart from noting that it is correct (by comparison with any number of earlier scattering calculations using eq 11), it is interesting to observe that at the higher energies $N(E)$ is not a monotonically increasing function of energy. This is a signature[23] of transition-state theory-violating dynamics, i.e., recrossing trajectories in a classical picture, and the result of a short-lived collision complex that causes resonances in a quantum description.

For the $H + H_2$ reaction in three-dimensional space one needs to add in the bending degree of freedom in

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(20) (a) Lill, J. V.; Parker, G. A.; Light, J. C. *J. Chem. Phys.* **1986**, *85*, 900. (b) Muckerman, J. T. *Chem. Phys. Lett.* **1990**, *173*, 200.

(21) (a) Friesner, R. A. *Chem. Phys. Lett.* **1985**, *116*, 39. (b) Friesner, R. A. *J. Chem. Phys.* **1986**, *85*, 1462.

(22) (a) Peet, A. C.; Miller, W. H. *Chem. Phys. Lett.* **1988**, *149*, 257. (b) Yang, W.; Peet, A. C.; Miller, W. H. *J. Chem. Phys.* **1989**, *91*, 7537.

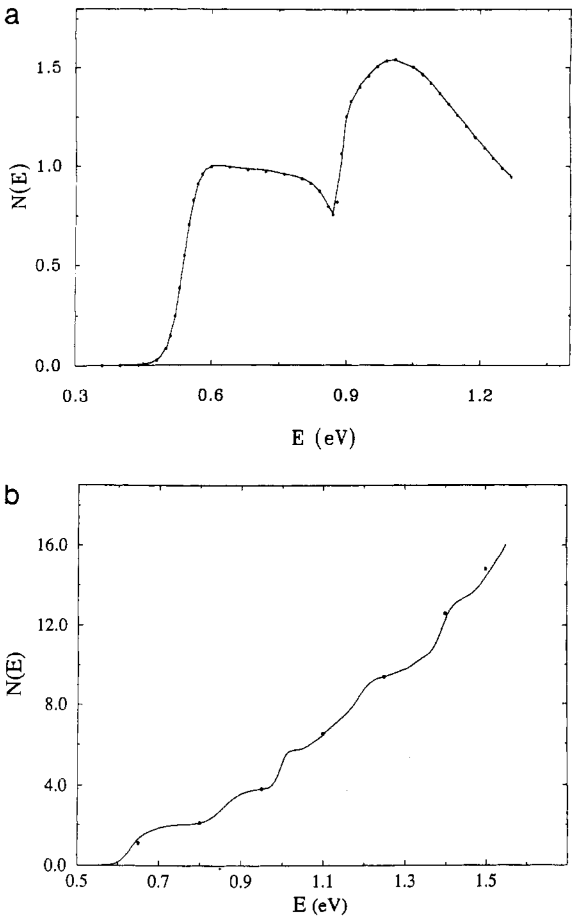

Figure 3. Cumulative reaction probability for the $H + H_2 \rightarrow H_2 + H$ reaction: (a) for collinear geometry (ref 4a); (b) three-dimensional space for total angular momentum $J = 0$ (ref 4b).

the transition-state region and also allow the three-atom system to rotate. Figure 3b shows the cumulative reaction probability obtained[4b] for zero total angular momentum ($J = 0$), and again it is in complete agreement with results[24] obtained from eq 11 via full scattering calculations. The number of grid points needed for convergence ranges from somewhat less than ~170 at the lowest energies shown to ~1200 at the highest energies. (The presence of shorter de Broglie wavelengths at higher energy requires a smaller spacing between the grid points.)

For the three-dimensional case (Figure 3b), $N(E)$ is seen (to the eye, at least) to increase monotonically with E, and in fact one has known[25] for many years that the reaction dynamics tends to behave more transition-state-like in higher physical dimensions (other things being equal). (Figure 3b also shows the staircase structure[24] which is a remnant of microcanonical transition-state theory in the separable approximation,[26] i.e., eq 7a.) Resonances do exist in three dimensions; they are simply masked more by the nonresonant (direct) scattering in three dimensions than they are in one dimension. They can be observed in more detailed state-to-state differential scattering cross sections for the $H + H_2$ reaction,[27] but not in $N(E)$, or $k(T)$, which are highly averaged quantities.

It will be possible to carry out these rigorous quantum calculations/simulations for a variety of simple chemical reactions, e.g., atom–diatom ($A + BC \rightarrow AB + C$) reactions and even some four-atom reactions (e.g., $H + H_2O \rightarrow H_2 + OH$), but for larger systems it will of course be necessary to introduce approximations. If the reaction takes place through a well-defined transition state, then it is fairly clear how an approximate calculation would proceed: using normal coordinates appropriate to the transition state,[4b] it is typical that only a few modes are strongly coupled to the reaction coordinate, so that one would treat these degrees of freedom by full matrix inversion to obtain the Green's function, with other degrees of freedom being included perturbatively. This is standard fare for molecular quantum calculations, e.g., as for vibrational eigenvalues,[28] and there is room for much physical insight in implementing these schemes (sudden/adiabatic separations, sequential decoupling or contractions, etc.).

Concluding Remarks

Though there is no rigorous quantum mechanical version of transition state theory, i.e., a quantum theory whose only approximation is the assumption of "direct dynamics", there is a quantum analog of the classical approach which requires only localized, or short time dynamics to determine the reaction rate completely correctly. Thus eq 21 (or 22) gives an absolutely rigorous expression for the cumulative reaction probability (and then the rate constant via eq 1a), and one is required to solve the quantum dynamics (i.e., invert the matrix $(E + i\epsilon - \mathbf{H})$, which is equivalent to solving the Schrödinger equation) only *locally*, in the transition-state region bounded by the absorbing strips across the reactant and product valleys, with no information about reactant or product quantum states being required. This provides a framework for carrying out completely rigorous calculations ("quantum simulations") for the rate constants of simple reactions, and it is also a rigorous starting point for making systematic approximations (e.g., quantum perturbation theory) necessary to treat more complex chemical systems. The dividing

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[23] $N(E)$ will always increase monotonically with E in a transition-state approximation. It is easy to prove this classically, e.g., from eq 5a. If the dividing surface is held fixed as E varies, then from eq 5a one has

$$\frac{\mathrm{d}}{\mathrm{d}E}N_{\mathrm{TST}}(E) = (2\pi\hbar)^{-(F-1)}\int \mathrm{d}\mathbf{p}'\int \mathrm{d}\mathbf{q}'\ \delta[E-H_{F-1}]$$

which is clearly positive. Furthermore, if the dividing surface is parametrized and allowed to vary with energy, the above equation still holds because any parameters in the dividing surface are chosen variationally. Thus if the dividing surface (and thus the Hamiltonian H_{F-1}) depend on some parameters $c_1, c_2, ... \equiv \{c_k\}$, then the expression for N_{TST} will depend not only on the energy E but also on these parameters, $N_{\mathrm{TST}}(E,c_1,c_2,...)$. The values of the c_k's are chosen, however, by the variational condition

$$0 = \frac{\partial}{\partial c_k}N_{\mathrm{TST}}(E,\{c_k\})$$

which determines specific values $c_k(E)$. Thus the variationally optimized result for the cumulative reaction probability is $N_{\mathrm{TST}}(E,c_1(E),c_2(E),...) \equiv N_{\mathrm{TST}}(E)$. Then

$$\frac{\mathrm{d}}{\mathrm{d}E}N_{\mathrm{TST}}(E) = \frac{\partial}{\partial E}N_{\mathrm{TST}}(E,\{c_k\}) + \sum_k \frac{\partial N_{\mathrm{TST}}}{\partial c_k}c_k'(E)$$

but the last terms are all 0 because of the variational conditions.

[24] Chatfield, D. C.; Friedman, R. S.; Truhlar, D. G.; Garrett, B. C.; Schwenke, D. W. *J. Am. Chem. Soc.* **1991**, *113*, 486.

[25] Chapman, S.; Hornstein, S. M.; Miller, W. H. *J. Am. Chem. Soc.* **1975**, *97*, 892.

[26] See, for example: Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley: New York, 1972; p 93 ff.

[27] Miller, W. H.; Zhang, J. Z. H. *J. Phys. Chem.* **1991**, *95*, 12.

[28] See, for example: (a) Bacic, Z.; Light, J. C. *Annu. Rev. Phys. Chem.* **1989**, *40*, 469. (b) Bowman, J. M., Ed. Special issue on "Molecular Vibrations". *Comput. Phys. Commun.* **1988**, *51*.

surface (cf. Figure 1a) so central to classical transition-state theory has been effectively replaced by a dividing *region*, the region between the two absorbing strips [cf. Figures 1b and 2c]. By solving the quantum dynamics in this region one is determining multidimensional, nonseparable tunneling effects and also any recrossing dynamics that violates the transition theory assumption of "direct dynamics"; i.e., as has been emphasized throughout this Account, a treatment that describes multidimensional tunneling effects correctly must also describe all the dynamics in the transition-state region correctly, including recrossing dynamics that violates transition-state theory. Equation 21 (or 22) provides the basis for carrying out such a local calculation of the quantum reaction dynamics.

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