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CHAPTER

QUANTUM THEORY OF CHEMICAL REACTION RATES*

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Introduction

If one wishes to describe a chemical reaction at the *most* detailed level possible, i.e., its state-to-state differential scattering cross section, then it is necessary to solve the Schrödinger equation (with scattering boundary conditions) to obtain the S-matrix $\{S_{n_p,n_r}(E,J)\}$ as a function of total energy E and total angular momentum J, in terms of which the cross sections can be calculated as follows,[1]

$$\sigma_{n_p,n_r}(\theta,E) = \left|(2ik_r)^{-1} \sum_J (2J+1)\, d^J_{m_p,m_r}(\theta) S_{n_p,n_r}(E,J)\right|^2 . \tag{1}$$

(Here $n_r(n_p)$ label the reactant (product) quantum states, $m_p(m_r)$ is the projection of total angular momentum onto the relative velocity vector of the reactants (products), and $d^J_{mm'}(\theta)$ is the Wigner rotation matrix.) For the simplest chemical reactions, e.g., H or D+H_2(para) $\rightarrow$ H+H_2(ortho) or HD, H+D_2 $\rightarrow$ HD+D, F+H_2 $\rightarrow$ HF+H, it is actually possible[2] nowadays to carry out such calculations that are effectively exact (numerically).

All other physically observable attributes of the reaction can be derived from the above cross sections. Often, in fact, one is primarily interested in the *least* detailed quantity which characterizes the reaction, namely its thermal rate constant, which is obtained by integrating Eq. (1) over all scattering angles, summing over all product quantum states, and Boltzmann-averaging over all initial quantum states of reactants. With the proper weighting factors, all of these averages are conveniently contained in the cumulative reaction probability[3] (CRP), which is defined by

$$N(E) = \sum_{J=0} (2J+1) \sum_{n_p,n_r} |S_{n_p,n_r}(E,J)|^2 , \tag{2}$$

and in terms of which the thermal rate constant is

$$k(T) = [2\pi\hbar\, Q_r(T)]^{-1} \int_{-\infty}^{\infty} dE\, e^{-E/kT} N(E) . \tag{3}$$

(Q_r is the reactant partition function per unit volume.) Thus, having carried out a full state-to-state scattering calculation to obtain the S-matrix, one can obtain the CRP from Eq. (2), and then rate constant from Eq. (3), but this seems like "overkill"; i.e., if one only wants the rate constant, it would clearly be desirable to have a theory that allows one to calculate it, or the CRP, more *directly* than via Eq. (2), yet also *correctly*, i.e., without inherent approximations. Such a theory[4] is the

*Based on an address presented by William H. Miller before "The Robert A. Welch Foundation, 38th Conference on Chemical Research, Chemical Dynamics of Transient Species," which was held in Houston, Texas, October 24-25, 1994.

subject of this paper.

Brief Review of Transition State Theory

What one is looking for is something like transition state theory (TST).[5-7] It provides a *direct* route to the rate, but unfortunately is not *correct*. TST is actually a theory based on classical mechanics, and its quantization unavoidably entails additional approximations. In its most commonly used form TST expresses the rate constant as

$$k_{TST}(T) = \frac{kT}{h}\frac{Q^{\ddagger}(T)}{Q_r(T)}, \tag{4}$$

where $Q^{\ddagger}(T)$ is the partition function of the "activated complex",

$$Q^{\ddagger}(T) = \sum_n e^{-\varepsilon_n^{\ddagger}/kT}, \tag{5}$$

$\varepsilon_n^{\ddagger}$ being the energy levels for motion of the molecule on a dividing surface which separates reactants from products, i.e., the molecular system with one degree of freedom (the reaction coordinate) removed. The corresponding approximation for the CRP is

$$N_{TST}(E) = \sum_n h(E-\varepsilon_n^{\ddagger}), \tag{6}$$

where $h(\zeta)$ is the Heaviside (or step) function (= 1 or 0 for $\zeta>0$ or <0, respectively).

The next better version of TST is to allow for tunneling along the reaction coordinate, whereby Eq. (6) becomes

$$N_{TST}(E) = \sum_n P_{1d}(E-\varepsilon_n^{\ddagger}), \tag{7}$$

and from Eq. (3) it is easy to show that the corresponding result for the rate constant is

$$k_{TST}(T) = \kappa(T)\frac{kT}{h}\frac{Q^{\ddagger}(T)}{Q_r(T)}, \tag{8a}$$

where κ is the tunneling correction factor

$$\kappa(T) = (kT)^{-1}\int_{-\infty}^{\infty} dE_t\, e^{-E_t/kT}\, P_{1d}(E_t). \tag{8b}$$

$P_{1d}(E_t)$ in Eq. (7) and (8) is a one dimensional transmission probability, effectively a smoothed out version of the step function in Eq. (6).

As soon as motion along the reaction coordinate is allowed, however, one realizes that it is not separable from the degrees of freedom of the activated complex, so that more rigorously one needs a multidimensional tunneling correction factor. Many models exist for determining these,[7-11] most based on semiclassical theory.[12] The only *rigorous* full dimensional tunneling/transmission factor, however, is that obtained by solving the full dimensional Schrödinger equation; one then no longer has a "theory" (i.e., approximation), however, but simply the exact answer (a "quantum simulation") which is, of course, what one would like if it is possible to obtain it.

The theory described below[13] is such a fully exact quantum theory and can be thought of as the "end of the line" in the quest for increasingly more rigorous quantum versions of transition state theory. It does, in fact, have some of the attributes of TST; e.g., though it is necessary (in effect) to solve the Schrödinger equation, it is necessary only to solve it *locally*, in the interaction region, and not to obtain the state-to-state S-matrix. The actual numerical prescription that results will also be seen to have some striking resemblances to TST.

Rigorous Quantum Expression for the CRP

A rigorous and "direct" expression for the CRP has actually been known for over ten years, but until recently not much progress has been made in utilizing it. The expression is[14]

$$N(E) = \frac{1}{2}(2\pi\hbar)^2 \, \mathrm{tr}\,[\delta(E-\hat{H})\hat{F}\,\delta(E-\hat{H})\hat{F}] \,, \tag{9}$$

which is formally equivalent to Eq. (2) but is "direct" in the sense that it does not involve any explicit information about asymptotic reactant and product quantum states; all that appears in Eq. 9 is the microcanonical density operator, $\delta(E-\hat{H})$, which involves the Hamiltonian of the system, and a flux operator $\hat{F}$,

$$\hat{F} = \frac{i}{\hbar}[\hat{H},h(f(\mathbf{q}))] = \frac{1}{2}\left[\frac{\hat{\mathbf{p}}}{m}\cdot\frac{\partial f(\mathbf{q})}{\partial \mathbf{q}}\,\delta(f(\mathbf{q})) + \delta(f(\mathbf{q}))\,\frac{\partial f(\mathbf{q})}{\partial \mathbf{q}}\cdot\frac{\hat{\mathbf{p}}}{m}\right], \tag{10}$$

where h( ) is given again the Heaviside function and $f(\mathbf{q})$ is a function of coordinates which defines, through the equation

$$f(\mathbf{q}) = 0 \,, \tag{11}$$

a "dividing surface" which separates reactants (where $f(\mathbf{q})<0$) and products (where $f(\mathbf{q})>0$).

Since Eq. (9) is the basis of all further theoretical developments, it is useful to see more intuitively how it arises. In *classical* mechanics the expression for the CRP is

$$N_{CL}(E) = 2\pi\hbar\,(2\pi\hbar)^{-F}\int d\mathbf{p}_0\int d\mathbf{q}_0\,\delta(E-H(\mathbf{p}_0,\mathbf{q}_0))\,F(\mathbf{p}_0,\mathbf{q}_0)\,\mathbb{P}(\mathbf{p}_0,\mathbf{q}_0)\,, \tag{12}$$

where here the coordinates and momenta $(\mathbf{p}_0,\mathbf{q}_0)$ are the initial conditions for a classical trajectory. The delta function in the integrand is the microcanonical distribution for the phase space of initial conditions, and $F(\mathbf{p}_0,\mathbf{q}_0)$ is a flux factor of the same form as the quantum operator [Eq. (10)]. $\mathbb{P}(\mathbf{p}_0,\mathbf{q}_0)$ is the characteristic function for reaction, equal to 1 if the trajectory with these initial condition is on the product ($f(\mathbf{q})>0$) side of the dividing surface in the infinite future ($t\to\infty$), and 0 otherwise; $\mathbb{P}$ can thus be expressed algebraically as

$$\mathbb{P}(\mathbf{p}_0,\mathbf{q}_0) = \lim_{t\to\infty} h[f(\mathbf{q}(t;\mathbf{p}_0,\mathbf{q}_0))]\,. \tag{13}$$

The rigorous quantum mechanical version[15] of Eq. (12) looks almost the same,

$$N_{QM}(E) = 2\pi\hbar\,\mathrm{tr}[\delta(E-\hat{H})\hat{F}\,\widehat{\mathbb{P}}]\,, \tag{14}$$

where the classsical phase space average has become a trace, $\hat{H}$ and $\hat{F}$ have become the

corresponding operators, and the (projection) operator $\widehat{\mathbb{P}}$ is also the rather obvious quantum analog of Eq. (13),

$$\widehat{\mathbb{P}} = \lim_{t\to\infty} e^{i\widehat{H}t/\hbar}\, h(f(\mathbf{q}))\, e^{-i\widehat{H}t/\hbar}\,, \tag{15}$$

where the time evolution is now generated quantum mechanically. The long time limit in Eq. (15) can also be written as the integral of the time derivative.

$$\begin{aligned}\widehat{\mathbb{P}} &= \int_0^\infty dt \frac{d}{dt} e^{i\widehat{H}t/\hbar}\, h(f(\mathbf{q}))\, e^{-i\widehat{H}t/\hbar} \\ &= \int_0^\infty dt\; e^{i\widehat{H}t/\hbar} \frac{i}{\hbar} [\widehat{H}, h(f(\mathbf{q}))]\, e^{-i\widehat{H}t/\hbar} \\ &= \int_0^\infty dt\; e^{i\widehat{H}t/\hbar}\, \widehat{F}\, e^{-i\widehat{H}t/\hbar}\,,\end{aligned} \tag{16}$$

and with this form for $\widehat{\mathbb{P}}$ substituted into Eq. (14) — and interchanging the order of the trace and the time integral, and noting that the (real part of the) integrand is even — one obtains

$$N(E) = (2\pi\hbar)\frac{1}{2}\int_{-\infty}^{\infty} dt\, \mathrm{tr}\, [\delta(E-\widehat{H})\widehat{F} e^{i\widehat{H}t/\hbar}\, \widehat{F} e^{-i\widehat{H}t/\hbar}]\,. \tag{17}$$

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

$$\int_{-\infty}^{\infty} dt\, e^{i(\widehat{H}-E)t/\hbar} = 2\pi\hbar\delta(E-\widehat{H})\,, \tag{18}$$

one obtains Eq. (9).

Equation (9) is quite a beguiling expression. E.g., in the classical expression for the CRP, Eq. (12), there is a *statistical* factor $\delta(E-H)$, the flux factor F, and a *dynamical* factor $\mathbb{P}$. A similar structure exist in the quantum expression, Eq. (14), where the dynamical factor is the projection operator $\widehat{\mathbb{P}}$. Eq. (9), however, appears to have *no* dynamical information; i.e., only the statistical operator $\delta(E-\widehat{H})$ and flux operator $\widehat{F}$ are involved. This is an example of the fact that dynamics and statistics are inseparably intertwined in quantum mechanics; e.g., a wavefunction describes the *dynamical motion* of the particles and also their *statistics*.

The difficult part of Eq. (9) to evaluate is the microcanonical density operator, $\delta(E-\widehat{H})$, which is usually[16] expressed in terms of the outgoing wave Green's function (actually an *operator*),

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

where

$$\widehat{G}^{+}(E) = \lim_{\varepsilon\to 0} (E+i\varepsilon-\widehat{H})^{-1}\,. \tag{19b}$$

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

$$\hat{G}^+(E) = (i\hbar)^{-1} \int_0^\infty dt\, e^{i(E+i\varepsilon)t/\hbar} e^{-i\hat{H}t/\hbar} ;$$

the factor $\exp(-\varepsilon t/\hbar)$ in the integrand makes the time integral well-behaved in the long time ($t \to \infty$) limit. The parameter ε in Eq. (19b) usually plays a purely formal role in quantum scattering theory, but it has recently[13a] been pointed out that one may think of it as the *absorbing potential* that a number of persons[17] have used in numerical wavepacket propagation calculations to prevent reflections at the edge of the coordinate space grid. Absorbing potentials have also been used in other ways for time-independent scattering calculations.[18] In this latter approach one adds a negative imaginary potential to the true potential energy function,

$$V(\mathbf{q}) \to V(\mathbf{q}) - i\varepsilon(\mathbf{q}) , \tag{20a}$$

but this is clearly equivalent to adding the positive (operator) $\hat{\varepsilon}$ to E in E-H,

$$E-\hat{H} \to E + i\hat{\varepsilon}(\mathbf{q}) - \hat{H} . \tag{20b}$$

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 zero 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 1 shows a sketch of the potential energy surface for the generic reaction $H+H_2 \to H_2+H$, with the absorbing potential $\varepsilon(\mathbf{q})$ indicated by dashed contours. $\varepsilon(\mathbf{q})$ is zero in the transition state region, where the reaction dynamics (i.e., tunneling, re-crossing dynamics, etc.) takes place, and is turned on outside this region. In practice one chooses the interaction region (that between the absorbing potentials) to be as small as possible, so that as small a basis set as possible can be used to represent the operators and evaluate the trace. Choosing it too small, though, will cause the absorbing potentials to interfere with reaction dynamics one is attempting to describe.

With the microcanonical density operator given by Eq. (19) (with some choice for ε), straightforward algebraic manipulations (also using Eq. (10)) lead to the following even simpler form for the cumulative reaction probability,[13b]

$$N(E) = 4\, \mathrm{tr}\, [\hat{G}^+(E)^* \hat{\varepsilon}_p \hat{G}^+(E) \hat{\varepsilon}_r] , \tag{21a}$$

where $\varepsilon_r(\varepsilon_p)$ is the part of the adsorbing potential in the reactant (product) valley, and $\varepsilon \equiv \varepsilon_r + \varepsilon_p$. 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

$$N(E) = 4\, \mathrm{tr}\, [(E-i\varepsilon-\mathbf{H})^{-1} \bullet \varepsilon_p \bullet (E+i\varepsilon-\mathbf{H})^{-1} \bullet \varepsilon_r] , \tag{21b}$$

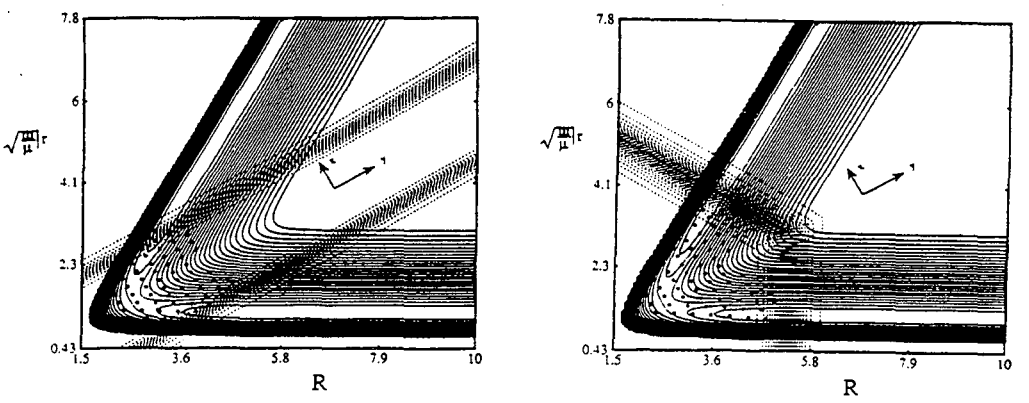


FIGURE 1

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 zero in the central part of the interaction region and "turned on" at the edge), for two possible choices of it. The points are the grid points which constitute the "basis set" for the evaluation of the quantum trace in Eq. (21) below.

with

$$\varepsilon = \varepsilon_r + \varepsilon_p \,. \tag{21c}$$

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. Fig. 1), but there is no dependence on its specific choice. This is just as it should be, for it has been long recognized[15] that these formally exact rate expressions are invariant to the choice of the dividing surface (a result of Liouville's theorem).

Finally, in recent calculations it has been shown[13c] that the most efficient way to evaluate the trace in Eq. (21) is to symmetrize the matrix inside the trace operation as follows,

$$N(E) = \mathrm{tr}[\widehat{P}(E)] \,, \tag{22a}$$

where

$$\widehat{P}(E) \equiv 4\widehat{\varepsilon}_r^{\,1/2}\widehat{G}(E)^*\widehat{\varepsilon}_p\widehat{G}(E)\widehat{\varepsilon}_r^{\,1/2} \,. \tag{22b}$$

$\widehat{P}(E)$ is seen to be a Hermitian operator (or matrix), so that its eigenvalues $\{p_k(E)\}$ are all real, and from Eq. (22a) the CRP is their sum,

$$N(E) = \sum_k p_k(E) \,. \tag{23}$$

It is also easy to see that $\widehat{P}(E)$ is a positive operator, so that its eigenvalues are all positive. It is not as obvious — but can be readily shown[13c] — that $\widehat{P}(E)$ is also bounded by the identity operator

$$\widehat{P}(E) \le 1 \,, \tag{24a}$$

from which it follows that

$$0 \le p_k(E) \le 1 \,. \tag{24b}$$

The eigenvalues $\{p_k\}$ can thus be thought of as *probabilities*, and then Eq. (23) bears an interesting resemblance to the simple transition state expression, Eq. (7), in which N(E) is given (approximately) as a sum of one-dimensional tunneling (or transmission) probabilities over all states of the activated complex. The *exact* N(E) is given in Eq. (23) as the sum of the "eigen reaction probabilities" $\{p_k\}$, the eigenvalues of the operator $\hat{P}$ defined by Eq. (22b).

Eqs. (21)-(23) provide a 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 $(E+i\varepsilon-\mathbf{H})$, 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.

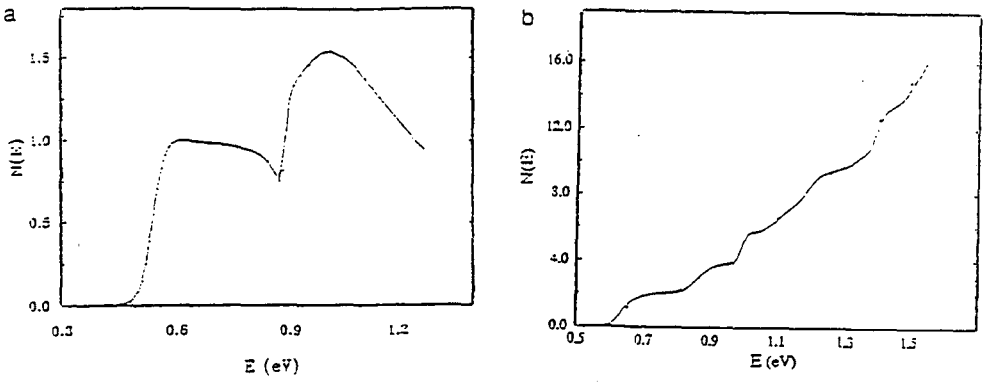
Some Recent Applications

In recent applications[13] it has proved useful to employ a set of *grid points* in coordinate space as the basis set in which to evaluate Eq. (21b) or (22)-(23). These discrete variable,[19] pseudo-spectral,[20] or collocation methods[21] 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).

Figure 1 shows the set of grid points and several possible choices for 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 2a shows the cumulative reaction probability so obtained[13a] 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. (2)), it is interesting to observe that at the higher energies N(E) is not a monotonically increasing function of energy. This is a signature of transition state theory-violating dynamics, i.e., re-crossing 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 the transition state region and also allow the three-atom system to rotate. Fig. 2b shows the cumulative reaction probability obtained[13b] for zero total angular momentum (J=0), and again it is in complete agreement with results[22] obtained from Eq. (2) via full scattering calculations. Even though collision complexes also form in the three-dimensional version of the $H+H_2$ reaction, N(E) in Fig. 2b appears (to the eye, at least) to increase monotonically with energy in transition state-like fashion. This is an example of the fact that dynamics appears to behave more transition state-like the higher the physical dimensional of space.[23]



(a) (b)

FIGURE 2
Cumulative reaction probability for the $H+H_2 \rightarrow H_2+H$ reaction, (a) for collinear geometry (ref. 13a), (b) three dimensional space for total angular momentum J=0 (ref. 13b).

A more challenging application[24] is to the reaction

$$H+O_2 \rightarrow OH+O\ , \tag{25}$$

which is one of the most important reactions for modeling the combustion of hydrocarbons. Fig. 3 shows a schematic of the potential surface, and one sees why this is a more complicated reaction to deal with: the deep well (~2 eV) in the interaction region leads to the formation of a moderately long-lived collision complex, strongly violating the transition state assumption of "direct dynamics". The rigorous quantum methodology described above, however, is nevertheless applicable: absorbing potentials are introduced just outside the interaction region where all the reaction dynamics (tunneling, re-crossings, etc.) is determined, and the grid points cover the region in between. Figure 4 shows the cumulative reaction probability for this reaction (for J=0 total angular momentum), and structure resulting from the collision complex is readily observable.

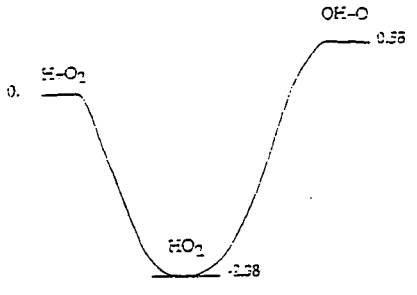


FIGURE 3
Energetics (in eV) of the H-O-O potential energy surface.

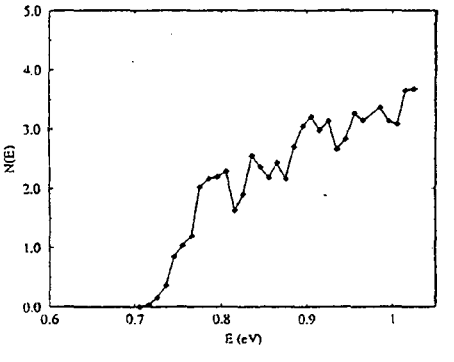
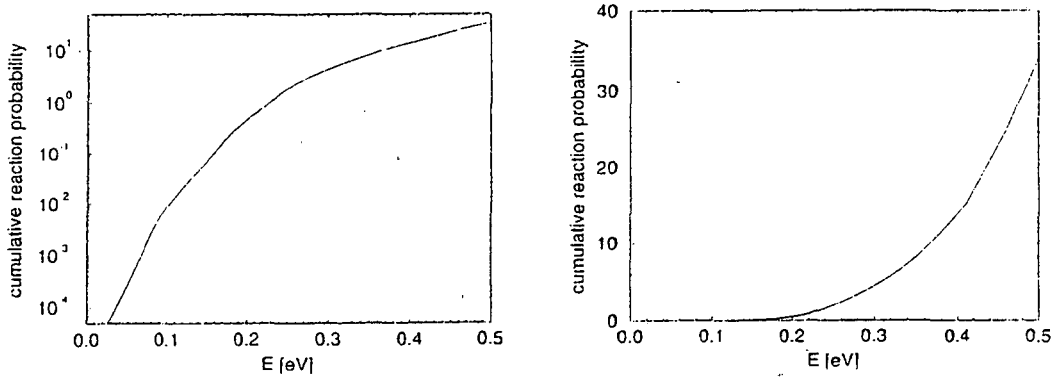


FIGURE 4
The cumulative reaction probability for the $H+O_2 \rightarrow OH+O$ reaction as a function of total energy, for total angular momentum J=0 (ref. 24).



(a) (b)

FIGURE 5
The cumulative reaction probability, for the H_2+OH → H_2O+H reaction as a function of total energy, for total angular momentum J=0 (ref. 25). (a) logarithmic scale, (b) linear scale.

Finally, full (six) dimensional calculations for the CRP of the reaction[25]

$$H_2+OH \rightarrow H+H_2O \tag{26}$$

have also been carried out and are shown in Fig. 5 (for total angular momentum J=0), the first such calculation of the CRP for a four atom reaction. This reaction is very "transition state-like" because there is a simple saddle point separating reactants and products. One qualitative feature that one notes, compared for example to the CRP for the three-dimensional H+H_2 reaction in Fig. 2b, is that the "stair case structure" that is a hold-over from the classical sum of step functions [Eq. (6)] is absent in Fig. 5. This is readily understood by looking at the individual eigenreaction probabilities $\{p_k(E)\}$ in Fig. 6; the higher density of states for the four atom system results in the "overlap" of the various threshold structures.

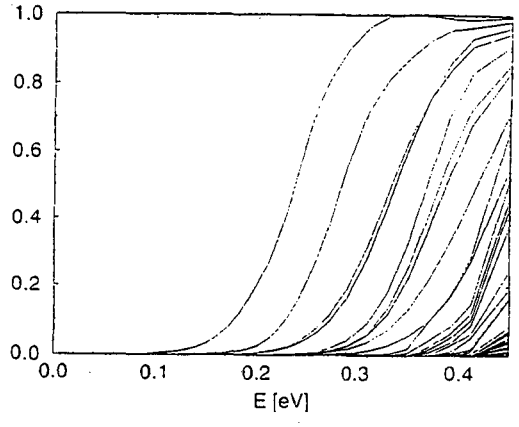


FIGURE 6
Eigenreaction probabilities $\{p_k(E)\}$ for the H_2+OH → H_2O+H reaction, as a function of total energy.

Concluding Remarks

Considerable progress has thus been made in the ability to compute a chemical reaction rate *directly*, without having to solve the complete state-to-state reactive scattering problem, but also *correctly*, i.e., without inherent approximation. One does not avoid having to solve the Schrödinger equation, but must only solve it locally, in the transition state region between reactants and products. In this sense the rigorous theory retains a flavor of transition state theory. More specifically, the cumulative reaction probability is most efficiently calculated by determining the eigenreaction probabilities $\{p_k\}$ [Eq. (23)], which are the rigorous analog of the TST transmission probabilities [Eq. (7)].

Even with this progress, though, rigorous calculations of the type described above for $H+O_2$ and $OH+H_2$ are feasible only for relatively small molecular systems (though "small" is somewhat larger than it used to be!). To deal with more complex systems one would like to be able to combine rigorous quantum treatments such as these for the few degrees of freedom most strongly involved in the chemical reaction with an approximate treatment of the (perhaps many) remaining degrees of freedom that are not so intimately involved. One would ideally like this "approximate treatment" to be based on classical mechanics, perhaps in a *semi*classical framework, so that classical trajectory simulation methodology can be brought to bear. Various ideas of this type exist,[26,27] and one expects to see progress along these lines.

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