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Roles of Classical Dynamics and Quantum Dynamics on Activated Processes Occurring in Liquids

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This paper reviews the reactive flux correlation function approach to studying the classical dynamics of activated processes in liquids. The possibilities and consequences of nonadiabatic electronic transitions in affecting this dynamics is also considered. We emphasize the feasibility of quantitative trajectory studies and the fact that these studies have yet to be fully exploited in the development of approximate theories of activated processes.

KEY WORDS: Barrier crossing; activation; correlation functions; nonadiabatic transitions; liquids.

1. INTRODUCTION

This paper reviews some of the principles relevant to activated processes occurring in liquids and other random fluctuating environments. An activated process is an infrequent event which carries a system between two or more relatively stable states. It is infrequent because barriers separate stable states. Barriers are regions of low probability which, in the simplest cases, correspond to configurations of relatively high energy. More generally, because of entropic considerations, we may consider barriers to be located in regions of high *free* energy. In the realm classical mechanics, a transition between stable states must occur by passing over a barrier. (In quantum theory, the barrier can be circumvented by tunneling.) Thus a barrier region is a *transition state*—a state that must be visited during the passage from one stable state to another.

The study of barrier crossing has a long history in chemistry and physics. The renaissance of interest in the topic in the field of condensed

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matter theory has often focused on the ideas introduced long ago by Kramers.(1) Since so much has been written on Kramers' perspective, there is no need to review it here. Instead, when considering classical dynamics, I will emphasize the correlation function approach which orginated with Yamamoto.(2) Calculations based upon generalizations(3,4) of this approach have enabled exact numerical studies of such varied phenomena as interstitial diffusion in solids,(5) desorption and diffusion rates on surfaces,(6) the kinetics of isomerization of small solvated molecules,(7) ergodicity and chaos in isolated molecules,(8) and the rates of conformational transitions in biopolymers.(9) Indeed, the methodology is now at such a stage that is often straightforward and practical to perform accurate trajectory calculations of rates of classical activated processes in liquids. In focusing on the feasibility of trajectory studies, I am not belittling the advantages of approximate analytical theories. I am, however, calling attention to the fact that nontrivial classical model systems can be examined quantitatively, and existing theoretical treatments have yet to grapple with and successfully explain those simulations.

The word "classical" implies a dynamics for which the relevant degrees of freedom evolve in accord with Newton's equations of motion. In such a model, the role of quantum mechanics is to determine the Born–Oppenheimer potential energy surface on which the classical dynamics occurs. This simplified model is limited for two reasons. First, within the Born–Oppenheimer or adiabatic approximation, the true dynamics of nuclei may exhibit the quantum mechanical effects of diffraction and tunneling. For any chemical reaction involving the transfer of protons, these effects can be particularly important. For more massive particles, however, these considerations are less significant.

A second reason for the breakdown of the classical model is the possibility of nonadiabatic transitions. In particular, electronic transitions between different Born–Oppenheimer potential surfaces will alter the course of a classical trajectory and thereby exert a strong influence on activated processes. When these electronic transitions are relatively infrequent (in a sense made more precise below), their effects can be treated with stochastic surface hopping approximations,(10) the simplest and oldest of which is the Landau–Zener–Stueckelberg model.(10,11) These methods have been very useful in treating gas phase chemical dynamics. In adopting these successful theories to treat the effects of nonadiabatic transitions on activated processes in condensed phases, however, an important generalization must be made. In particular, one must account for the fact that nonadiabatic transitions are promoted not only by the dynamics of the reaction coordinates, but also by the time dependence of fluctuations of the condensed phase environment.

Unlike the state-of-the-art for classical activated transitions in condensed phases, the appropriate methodology for treating the quantum mechanical aspects of these processes is not well understood. In my discussion of these effects, I will focus primarily on the role of nonadiabatic transitions, and I describe how for chemical reactions involving charge transfer, the dynamics of the condensed phase environment can significantly alter the rate of nonadiabatic transitions from that in the absence of the environment.

2. CLASSICAL ACTIVATION AND SEPARATION OF TIME SCALES

To begin, let us consider the transitions between states *A* and *B* as pictured in Fig. 1. We will imagine that the reaction coordinate *q* is a classical variable and that it is coupled to a classical bath of other degrees of freedom. The "bath" can both donate and remove energy from the reaction coordinate. Both are crucial to an activated process. The coordinate orginally trapped in well *A* must acquire energy to become activated and mount the barrier, and subsequently it must lose energy to become trapped in well *B*.

For real molecules which contain more than one degree of freedom, part of the bath is intramolecular involving modes of the reacting species other than the reaction coordinate(s). The rest of the bath is intermolecular involving the degrees of freedom in the surrounding solvent environment.

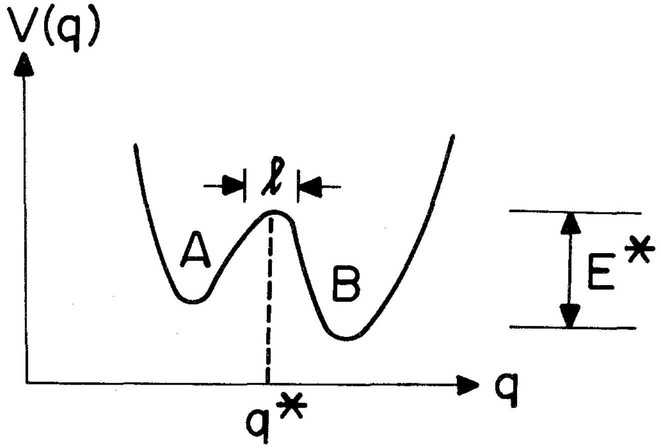

Fig. 1. A potential, $V(q)$, for the reaction coordinate, q involved in activated transitions between region $A(q<q^*)$ and region $B(q>q^*)$.

The size of the energy fluctuations in the bath are characterized by a temperature T. We assume that the activation energy, E^*, is much larger than k_BT (k_B is Boltzmann's constant). According to the principle of equipartition, $k_BT/2$ is the average energy of each mode or degree of freedom in the bath. Indeed, this principle can serve as our definition of T. Further, k_BT is the characteristic size of energy fluctuations for a given degree of freedom. It is for this reason that the condition

$$E^*/k_BT \gg 1 \tag{1}$$

guarantees that the transitions between regions A and B will be *infrequent events*. In particular, $\exp(-E^*/k_BT)$ is approximately the probability of being at the transition state located in the vicinity of $q = q^*$, and the system must pass through that state in changing from A to B. Thus the rate of an activated process is a factor of $\exp(-E^*/k_BT)$ smaller than those not requiring activation. In other words, activated processes are infrequent events due to the unlikely occurrence of a spontaneous fluctuation in which the modes in the bath (each with an average energy of $k_BT/2$) conspire to deposit energy E^* in the reaction coordinate.

Once the reaction coordinate is activated, it proceeds from region A to region B in a time of roughly $l/\langle |v| \rangle$, where $\langle |v| \rangle \propto T^{1/2}$ is the average speed of the reaction coordinate. If we now assume that activated trajectories are undeterred in crossing the transition state, we can estimate the rate constant to go from A to B (or vice versa) as

$$k \approx (\langle |v| \rangle / l) \exp(-E^*/k_BT) = k_{\mathrm{TST}} \tag{2}$$

The approximation that the trajectory moves through the transition state undeterred (i.e., the activated trajectory will not recross the transition state) is the *transition state theory* (TST) approximation. This observation is our reason for using the notation k_{TST} for the right-hand side of Eq. (2). The reader might object that I am making no distinction between $A \to B$ and $B \to A$ transition rate constants. They are, of course, different, and the difference is related to an equilibrium constant by the principle of detailed balance. For simplicity, we can assume the differences contribute a factor of the order of unity. The precise details will be ironed out, however, when we consider the exact formula for the rate constants, Eq. (6) below.

The time $k^{-1} = \tau_{rxn}$ is the average time between reactions, i.e., transitions carrying the system from state A to state B. If we sit and watch the system as it evolves coupled to a fluctuating bath, we will need to wait a time of roughly τ_{rxn} before seeing a transition between states A and B. The typical time scale for nonactivated molecular processes, however, is

$\tau_{\mathrm{mol}}^{-1} \approx v_0 = \langle |v| \rangle / l$. The *separation of time scales* inherent to an activated process is

$$(1/\tau_{\mathrm{mol}}) \approx v_0 = (\langle |v| \rangle / l) \gg k = 1/\tau_{rxn} \tag{3}$$

In making the distinction between the time scales for activated and non activated processes, I have adopted an over simplified picture in which all the fast or frequent dynamics is characterized by one time, τ_{mol}. In reality, things are much more complicated. Here are just a few of the many fast times or frequencies that may be of relevance: the frequency for motions in either of the stable wells, the time for an activated trajectory to cross the barrier, the time for an activated trajectory to lose energy $k_B T$ to the bath, and the correlation time(s) for fluctuating forces imposed on the reaction coordinate by the bath. The precise specification of all these time scales will be important in a quantitative theory of specific activated processes, but what is crucial to our general discussion is that all these times are very small in comparison to τ_{rxn}. In this context, τ_{mol} refers to the collection of all those short times characterizing dynamics relevant to an activated process. The degree of relevance is determined by how much the dynamics creates deviations from TST.

3. THE TRANSMISSION COEFFICIENT, COUPLING, AND ENERGY FLOW

The corrections to the TST estimate of rate constants are conveniently expressed in terms of the *transmission coefficient*, κ. It is defined by

$$k = \kappa k_{\mathrm{TST}} \tag{4}$$

and roughly speaking, κ is the fraction of successful or undeterred activated trajectories. This quantity κ depends upon the topography of the potential surface of the reaction coordinate and upon the nature of the coupling of the coordinate to the bath and the time scales associated with that coupling. While it is therefore a highly system-specific quantity, we can still make some general qualitative statements about its behavior.

In particular, we know that if there is no coupling of the reaction coordinate to the bath, then there is no way to activate a trajectory. Nor is there any way to deactivate one: If already possessing the energy E^*, the reaction coordinate will retain that energy, rebound off the potential wall, recross the transition state, thereby violating the TST approximation, and fail to react. From this description, it is seen that κ is zero when the coupling to the bath is zero. Further, an increase in that coupling will lead to an increase in κ and an increase in rate. These observations are the basis of the

Lindemann and Hinshelwood mechanisms(12) of unimolecular kinetics. These mechanisms say that for very low coupling, the rate constant is proportional to collision frequency or pressure of the environment.

The opposite extreme is the regime of high coupling. Here, as first explained by Kramers,(1) the reaction coordinate will be buffeted by the fluctuating environment. The resulting diffusive motion leads to a lowering of the rate as the coupling increases. The transmission coefficient is, therefore, a nonmonatonic function of the coupling as illustrated schematically in Fig. 2.

It is clear that the nonmonatonic behavior of κ is inarguable. But it is also clear that the precise behavior of κ, arising from a competition between inertial and diffusive effects, is highly system specific. Because of this specificity, it is a difficult experimental and theoretical issue to determine where to locate a given system on the curve drawn in Fig. 2. The "coupling" referred to in Fig. 2 is a quantity that determines the time required for the bath to remove energy and/or alter the direction of an activated reaction coordinate. The proper choice for parameterizing such a quantity is not always obvious. For example, consider an isomerization in a polyatomic molecule. If the time scale for intramolecular vibrational energy to be transferred is short enough [i.e., if the intramolecular vibrational rearrangement (IVR) rate is rapid enough], then the isolated molecule may already be in the high coupling regime, and the increase of rate with increasing coupling will not be observed. Further, when the

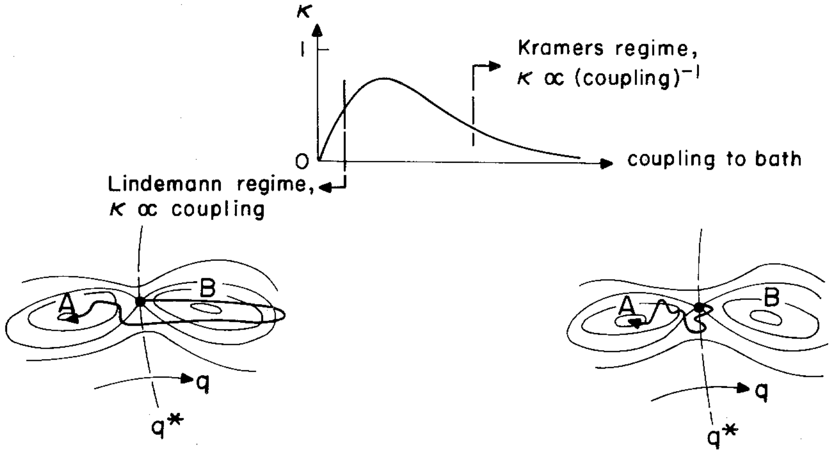

Fig. 2. The transmission coefficient, κ, for a classical activated process, and typical non-transition state theory trajectories characteristic of the low-coupling (Lindemann) and high-coupling (Kramers) regimes. The latter are pictured at the bottom left and right, respectively.

effects of a liquid environment are to be considered, the simplest ideas would say that in the high coupling regime, κ is proportional to a diffusion constant or the reciprocal of a friction constant. The appropriate friction, however, depends upon the frequencies of motion of the reaction coordinate during the activated process and the ability of the bath to respond to and affect motions at those intrinsic frequencies.(13,14) Here, the relevant time scale is τ_{mol}, and the response of an environment at the frequency τ_{mol}^{-1} is generally quite different than that at the much lower frequency τ_{rxn}^{-1}.

4. Trajectory Calculations and Statistical Considerations

Useful guidance for understanding these complicated issues can be obtained from exact trajectory calculations. Indeed, any approximate efforts to resolve these issues should be tested against simulations of model systems, the models constructed to show these effects. To perform exact trajectory calculations, however, requires some thought since straightforward computer simulations are not necessarily practical because of the infrequency of activated events. A typical time step for integrating molecular motions is no larger than 10^{-14} sec. Yet the time between completed activated events is no less than $10^2\tau_{\mathrm{mol}}$ corresponding to perhaps 10^{-10} or 10^{-9} sec in a liquid. Thus, a straightforward trajectory must be followed for thousands of time steps to see just one activated process, and statistically meaningful results require thousands of these observations.

To devise an efficient method, one wants to avoid spending computation time observing portions of trajectories which are not intimately involved in the activated event. Here it is useful to note that all activated processes pass through the transition state—the bottleneck from which the infrequency arises. Thus imagine studying only those trajectories which at time $t=0$ are at the transition state. Since this state is unstable, typical transient dynamics away from it and towards a stable situation will occur in a relatively rapid time $t \sim \tau_{\mathrm{mol}}$. This idea leads one to the *reactive flux* correlation function defined as follows:

$$k(t) = \langle v(0)\,\delta[q(0)-q^*]\,H_B[q(t)]\rangle \tag{5}$$

Here, $q(t)$ is the reaction coordinate at time t; $v(t)=q(t)$ is the velocity of that coordinate; $H_B[q(t)]$ is the characteristic function for stable state B, i.e., it is 1 for $q(t)>q^*$ and it is zero otherwise (we can construct more general criteria for the transition surface between stable states A and B, and such generalization will not alter our discussion in any fundamental way). Finally, the angle brackets indicate the equilibrium ensemble average over the initial conditions (coordinates and momenta at $t=0$) of all degrees of freedom, both the reaction coordinate and the bath.

To compute $k(t)$, one begins all trajectories with $q(0)=q^*$, and then averages the velocity (i.e., the flux) for all of those trajectories for which at time t, $q(t)>q^*$. Since each trajectory begins in the unstable transition state, the relaxation of $k(t)$ to a plateau value, k, will occur in a rapid time τ_{mol}. After a very long time $t \gtrsim \tau_{rxn}$, however, at least a few subsequent completed activated events will have occurred, $H_B[q(t)]$ will then be uncorrelated from the initial flux, and $k(t)$ will have relaxed to zero. This anticipated qualitative behavior of $k(t)$ is sketched in Fig. 3. The initial decay to the plateau (it *appears* to be a plateau on the scale of short times) is a *transient relaxation* from the transition state. This transient relaxation occurs in the time it takes enough energy to flow from the activated reaction coordinate to cause a trapping of the trajectory in a region of one of the stable states. The longer time decay corresponds to the *population relaxation* which characterizes the relaxation of spontaneous fluctuations in the concentration $H_B(t)$ from its equilibrium value $\langle H_B[q(t)]\rangle = x_B = 1 - x_A$ (x_A and x_B are the equilibrium mole fractions of states A and B, respectively).

5. Correlation Function Formula for the Rate Constant

The dynamics of the spontaneous fluctuations and the decay to equilibrium of nonequilibrium concentrations are connected by the fluctuation–dissipation theorem.(15) Through this connection, it can be shown(2,4) that the plateau value, k, is the generic rate constant for the $A \rightleftarrows B$ activated processes. In particular,

$$k_{A\to B} = k(\Delta t)/x_A \equiv k/x_A \tag{6}$$

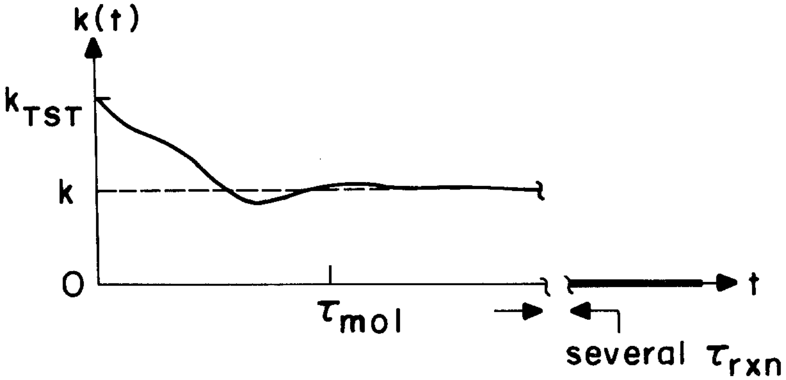

Fig. 3. Reactive flux correlation function for a classical activated process.

where Δt is a time in the plateau region, i.e.,

$$\tau_{\mathrm{mol}} < \Delta t \ll \tau_{rxn} \tag{7}$$

Further, the TST estimate of the rate constant is

$$\begin{aligned} k_{A \to B}^{(\mathrm{TST})} &= k(0^+)/x_A \\ &= \langle v\theta(v) \rangle_{q^*} \langle \delta(q - q^*) \rangle / 2x_A \end{aligned} \tag{8}$$

and, therefore, the transmission coefficient is

$$\begin{aligned} \kappa &= k/k(0^+) \\ &= \langle v H_B[q(t)] \rangle_{q^*} / \langle v\theta(v) \rangle_{q^*} \end{aligned} \tag{9}$$

Here, $\langle \cdots \rangle_{q^*}$ indicates the average over initial conditions performed with $q(0) = q^*$, q and v are abbreviations for $q(0)$ and $v(0)$, respectively, and $\theta(v)$ is 1 for positive v and zero otherwise.

The derivation of Eq. (8) follows directly form considering the dynamics involved in Eq. (5) for very small t.(4) The average of the δ function in Eq. (8) is the probability density for observing the reaction coordinate at the transition state. From the reversible work principle of statistical mechanics, we know that this probability is proportional to the Boltzmann factor for the *free* energy of activation. Thus, for example, when considering a thermal system the quantity E^* introduced in our qualitative discussion above is a Helmholtz free energy. It is interesting to note that when the microcanonical ensemble is employed in the averaging, the TST rate constant obtained from Eq. (8) is the RRKM rate constant of unimolecular kinetics.(8,12)

A correlation function formula for the rate constant like that shown in Eq. (6) was first derived by Yamamoto on the basis of a physical argument.(2) I rederived the relationship in 1978 by essentially rephrasing Yamamoto's arguments in terms of projecton operator methods.(4) At the price of some rigor, elementary derivations of the result can also be formulated.(16) The derivation in Ref. 4 shows that Eq. (6) is an approximation in the sense that it applies only to activated processes. In particular, the formula contains relative errors of the order of $\exp(-E^*/k_B T)$. It differs from other correlation function formulas for rate constants(4,17) by terms of similar size. For an activated transition where E^* is large compared to $k_B T$, the errors and differences are negligible. If E^* was not large, the process would not be infrequent, and the utility of Eq. (6) in making efficient the simulation of such events would no longer be especially significant.

It is important to appreciate that the validity of Eq. (6) is relatively independent of the nature of the activated dynamics. For example, use of Eq. (6) does not imply that trajectories evolve diffusively as appropriate in the high coupling regime; the formula applies equally well to the circumstances where the reaction coordinate moves inertially.

Equation (6) rests on two fundamental assumptions: (1), the validity of the fluctuation–dissipation theorem and (2) the separation of time scales where the activated event is the only slow process of relevance. The first of these is the statement that we believe a nonlinear dynamical system under investigation at or near equilibrium is sufficiently robust that it remains stable and responds linearly to arbitrarily small disturbances. While it is unlikely that one will ever derive it for any interesting system, it is equally unlikely that we will ever see any significant violations to it for activated processes in chemistry and biology. The second assumption, however, is more questionable. It is a statement about phenomenology and the existence of a rate constant. If other slow processes are important or if $A \rightleftarrows B$ transitions are not activated events and occur on a fast time scale, then the linear or unimolecular kinetics in which $k_{A \to B}$ is defined becomes invalid. At the microscopic level of molecular dynamics, one may note that the plateau value behavior of $k(t)$ is a necessary and sufficient condition for the existence of the rate constant. This important aspect of considering the time dependence of $k(t)$ was first discussed and explored in the paper by Montgomery *et al.*(18) When the plateau value behavior is not observed, one must conceive of a different phenomenology (or higher-order kinetics) that may involve several transport coefficients or relaxation times.

Equation (6) is analogous to the Green–Kubo formulas for the transport coefficients relevant to hydrodynamic relaxation.(15) Hydrodynamic fluctuations can evolve over macroscopic times, yet the dissipation which determines the transport coefficients generally occurs over much shorter microscopic times. The mathematical structure of the analogy is discussed in Ref. 4.

6. CALCULATIONS OF RATES FROM CORRELATION FUNCTION FORMULA

Calculations of rate constants based upon Eq. (6) break into two parts as is evident from the factorization exhibited in Eqs. (8) and (9). The time independent or equilibrium calculation involved in Eq. (8) can be performed by Monte Carlo umbrella or importance sampling.(19–21) It should be appreciated, however, that calculations based upon the Pratt–Chandler theory of solvation(21–23) and the RISM equation(23) are also possible, and this approach can be both accurate and less computationally intensive than simulations.[2] Analogous theories for the dynamical calculations involved in Eq. (9) have yet to be fully tested. (Some recent suggestions,(25) however, seem quite promising.) At present, reliable results for nontrivial systems must be obtained by sampling several thousand short trajectories (each of time duration τ_{mol}) orginating with $q(0) = q^*$.

This two-step approach of determining the equilibrium statistics of the transition state [Eq. (8)], and the subsequent running of short trajectories from that state is nearly identical to Bennett's algorithm for the molecular dynamics simulation of infrequent events.(3) [Bennett suggests running trajectories both forward and backward in time, but Eq. (6) requires only those for positive time. In Ref. 4 it is shown that as a consequence of averaging over initial conditions, both procedures yield the same final result though Eq. (6) appears to be the more efficient by a factor of 2.] These procedures are closely related to earlier ideas adopted in trajectory studies of gas phase kinetics.(25) Berne(27) has recently reviewed the work on simulations. Though computationally intensive, the methodology is indeed practical. In addition to Bennett's application to the diffusion of interstitial particles in solids,(5) the approach has been applied to study isomerization dynamics of chain molecules both with full molecular dynamics of several hundred liquid particles(7b) and with stochastic models of the solvent.(7a) Further, as mentioned in the Introduction, the method has also been used with profit to study desorption dynamics from solid–gas interfaces(6a) and diffusion on solid surfaces.(6b) Simple models for intramolecular dynamics of isolated molecules have been examined with this technique,(8) and the method also forms the basis for analyzing conformational rearrangements in biopolymers.(9)

The results of these simulations provide benchmarks for approximate treatments of activated dynamics. Satisfactory theoretical explanations of the existing simulations have yet to be developed,[3] but when they are, we will have moved a long way toward unraveling the complexities of condensed phase effects on activated molecular processes.

7. ROLES OF QUANTUM DYNAMICS

The complexities we have referred to above become even more interesting when quantum mechanical effects are included in our considerations. While it is not always possible, let us assume that we can partition our thoughts on this subject into two categories: (1) those referring

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[2] For recent work along these lines see Ref. 24.

[3] One might imagine, for example, a detailed comparison between the simulations in Ref. 7 and the recent theories presented in Ref. 28.

to dynamics of nuclei evolving on a single Born–Oppenheimer surface, and (2) those concerned with the effects on nonadiabatic electronic transitions between different Born–Oppenheimer states.

In the first case, quantum effects are due to nuclear zero point motion and tunneling. There is an extensive literature examining the role these phenomena for gas phase reaction.(29) For condensed phase reactions, much less has been done. The parameter which signals the importance of these quantum effects is the thermal wavelength

$$\lambda = \hbar/(k_B T m)^{1/2} \tag{10}$$

where m is the reduced mass of the reaction coordinate and $2\pi\hbar$ is Planck's constant. Quantum dispersion—tunneling and zero point motion—are significant when λ is comparable to or larger than the typical lengths characterizing the intermolecular potential (e.g., the length l in Fig. 1). For a proton at room temperature, $\lambda \approx 0.3$ Å.

The appropriate starting point for a systematic treatment of the effects of the uncertainty principle or dispersion in nuclear coordinates would seem to be the quantum mechanical generalization of Eq. (6). This generalization was in fact written down by Yamamoto(2) in his seminal paper on the time correlation function formulation of rate constants. In the quantum mechanical case, it is interesting to note that in the limit $t \to 0^+$, the reactive flux $k(t)$ approaches zero rather than the finite value of k_{TST} that it attains in the classical case.(30) This fact exasperates systematic efforts to define the meaning of quantum transition state theory.

The first attempt at using this formulation to treat a quantum-activated process coupled to a fluctuating environment was made by Wolynes.(31) This calculation determined the transmission coefficient for a reaction coordinate which moves on an inverted parabolic potential and is linearly coupled to a harmonic bath. When the dispersion in the reaction coordinate is large enough (i.e., when quantum effects are large due to a large spatial extent of the wave function for the reaction coordinate), the unphysical nature of the inverted parabolic potential model becomes apparent, and Wolynes' calculation exhibits an unphysical divergence. To correct this deficiency, one must consider the nonlinear corrections to Wolynes' harmonic approximation.(32) Many other applications of the quantum generalization of Eq. (6) are possible by exploiting the techniques employed in gas phase reaction dynamics calculations and adding to these the models for fluctuating environments developed in classical liquid state theory. Undoubtedly, we will see much work along these lines in the near future.[4]

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[4] For an example of recent work along these lines see the study of proton tunneling in colinear FH...F complexes by J. T. Hynes in this issue (Ref. 33).

8. NONADIABATIC TRANSITIONS

The second category of quantum effects, the role of nonadiabatic transitions, involves the mediation of activated processes by the dynamics of electronic states. In Fig. 4, we show two neighboring potential surfaces corresponding to two different adiabatic electronic states. If confined to the ground state potential surface, the movement from region A to B involves a classical activated process. Owing to the proximity of the excited state surface in the barrier region, however, electronic transitions may occur which can significantly alter the course of a barrier crossing. Further, in the case shown in Fig. 4, the alteration will lower the transmission coefficient from its classical behavior since motion in the excited potential will be oscillatory and therefore violate the unidirectionality assumed in transition state theory.

Incidentally, the type of potential surfaces shown in Fig. 4 are typical of reactions which involve a significant degree of charge transfer as the nuclei move through the transition state.(34) In that case, at the transition state for the nuclei, $\Delta/\hbar$ is the frequency with which the electronic charge will fluctuate between two localized regions (i.e., between two diabatic states). When this frequency is very high compared to τ_{mol}^{-1}, the electrons will successfully adjust and equilibrate to the nuclear motions, and the dynamics will be adiabatic, evolving on the ground state surface. When $\Delta/\hbar$ is not much larger than τ_{mol}^{-1}, however, nonadiabatic effects due to the relatively low frequency of transitions between diabatic states will be important. From the golden rule of time-dependent perturbation theory,(35) we may estimate the rates of the transitions between diabatic surfaces. A precise answer will be system specific, but in general, the rate estimated in this way will scale as Δ^2. Since several such transitions may occur while the

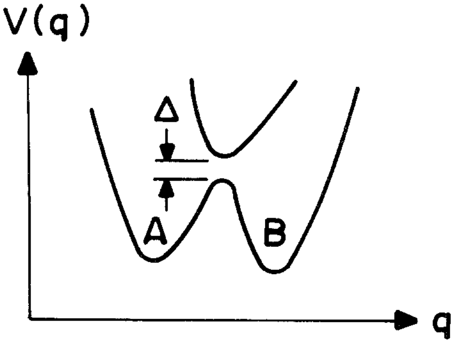

Fig. 4. Two neighboring Born–Oppenheimer (i.e., adiabatic) potential surfaces for the reaction coordinate q.

nuclei are in the transition state region, we must consider their cumulative effect. If we assume each transition is uncorrelated from the rest, we obtain an exponential relaxation law for the equilibration of the electronic states to the nuclear configuration.[5] Within this approximate approach, one predicts that the probability for electronic state equilibration (i.e., the probability for *not* making a transition between adiabatic states) is given by

$$p \approx 1 - \exp(-z\Delta^2) \tag{11}$$

where z will depend upon the nature of the classical dynamics of the nuclei as they pass through the transition state. For example, z will increase with the time spent in the transition state region. The degree with which it increases can be estimated from Landau–Zener–Stueckelberg theory.(11,34) This traditional theory of nonadiabatic transitions produces a formula of the type given in Eq. (11).

Let us adopt this equation. Further, assume that any transition to the excited Born–Oppenheimer surface totally randomizes the directionality of a classical trajectory. Then we arrive at the following estimate for the transmission coefficient (i.e., the fraction of undeterred trajectories crossing the transition state)

$$\kappa \approx \kappa_{cl} p \approx \kappa_{cl}(1 - e^{-z\Delta^2}) \tag{12}$$

where κ_{cl} is the transmission coefficient that would be obtained from classical dynamics occuring on the ground electronic state potential surface. Formulas of this type have provided the basis for recent qualitative discussions of the role of nonadiabatic transition in charge transfer reactions.(37,38) The equation leads us to expect a strong dependence of rate constants on the energy splitting Δ when $z\Delta^2$ is not large. This is the nonadiabatic regime. In the opposite adiabatic regime, the rate will be insensitive to Δ.

9. SURFACE HOPPING MODELS AND CHOICE OF ADIABATIC STATES

The ideas that surround this type of discussion can be made more quantitative with surface hopping models.(39,40) Here, one performs trajectory calculations which are interrupted stochastically be transitions to different electronic states. The probability for making such a transition is determined self-consistently based upon the nature of the nuclear dynamics

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[5] An explicit calculation of this type has been described by Chakravarty and Leggett (Ref. 36).

and the coupling of that dynamics to the electronic states. There are various formulations of this methodology,(10) and one such method(40) has been modified and applied to the problem of iodine recombination in a liquid.(41) One may expect more applications of this type in the future, but the accuracy of such calculations will depend upon the choice of adiabatic states.

The issue we refer to here is understood as follows. The surface hopping approach is a correct dynamical model in the limit for which transitions between adiabatic surfaces occur relatively infrequently. If this condition is not met, phase interference will be more complicated than that depicted in the surface hopping picture. If transitions are indeed infrequent, it must mean that the adiabatic states are very nearly good stationary electronic states. Now the natural question to ask is what are reasonable approximations to stationary electronic states when the activated molecular complex under consideration is coupled to a time-dependent fluctuating environment? An answer to this question is required to obtain accurate results from a surface hopping calculation of nonadiabatic transitions in liquids. One possible answer is obtained from the so-called "effective adiabatic" (EA) approximation which Carmeli and I have developed.(42)

The basic idea in the EA theory is to construct a reference system in which the environment contains only zero frequency (i.e., adiabatic) fluctuations. The parameters which define this reference system are adjusted variationally to optimize the ability of the reference system to mimic the behavior of the full nonadiabatic system. The stationary states of the reference system are then the optimum adiabatic states.

To make the discussion a bit more specific, let us consider a Hamiltonian of the form

$$H=\sum_{i} |i\rangle\, E_i \langle i| + \sum_{i,j} |i\rangle\, V_{ij}(x) \langle j| + H_B(x;\omega_B) \tag{13}$$

where $|i\rangle$ and E_i are the Born–Oppenheimer electronic states and energies, respectively, of the isolated molecular complex, $V_{ij}(x)$ is the coupling of those states with the bath, x denotes the fluctuating variable(s) of the bath, H_B is the bath Hamiltonian, and ω_B denotes the frequency(ies) characterizing the bath fluctuations. When $\omega_B \to 0$, the bath is adiabatic, and the form of the EA reference Hamiltonian is

$$H_{\mathrm{EA}}=\sum_{i} |i\rangle\, E'_i \langle i| + \sum_{i,j} |i\rangle\, V'_{ij}(x) \langle j| + H_B(x;0) \tag{14}$$

where E'_i and $V'_{ij}(x)$ are the quantities to be determined variationally. In particular, one exploits the standard Gibbs–Bogoliubov–Feynman bound(43) for the partition function, Q,

$$Q \geqslant Q_{\mathrm{EA}} \exp(\langle \Delta S \rangle_{\mathrm{EA}}) \tag{15}$$

where ΔS is the differences between the action in Euclidian time of the actual system and that of the reference system. The notation $\langle \cdots \rangle_{\mathrm{EA}}$ indicates an average over all quantum paths weighted in accord with the EA reference action functional. One determines the variational parameters characterizing the reference system by maximizing the right-hand-side of Eq. (15). The technical details are discussed in Ref. 42.

10. IMPLICATIONS OF THE EFFECTIVE ADIABATIC APPROXIMATION

The simplest case for which this theory can be applied is the spin-boson Hamiltonian with a monochromatic bosonic field. In particular, i spans only the two states 1 and 2, the energy difference between them is $\Delta = E_2 - E_1$, the coupling matrix is $V_{ij}(x) \propto x(1 - \delta_{ij})$, and the bath contains only one harmonic with fundamental frequency ω_B. This model is a two-level system linearly coupled to an Einstein crystal. It represents a nonlinear and infinite state quantum problem that cannot be solved in closed form. Nevertheless, the EA treatment of the model casts it in the form of a statistical distribution of two state problems requiring the diagonalization of a 2×2 matrix; and this simple treatment has been shown to yield quantitatively accurate results for correlation functions and the partition function.(42)

In Fig. 5 we consider the results of the EA theory applied to the monochromatic spin-boson Hamiltonian. The choice of parameters employed in the illustrated calculations are typical of those that might be encountered in liquid state activated processes involving charge transfer. The coupling to the bath would then be primarily of a dipolar nature, and the bath variable x would correspond to the local fluctuating electric field. Figure 5 shows how the renormalized energy splitting, Δ', changes as a function of the bath frequency, ω_B. The reduction of the energy splitting is due to the fact that in this class of models, fluctuations in the environment lead to localization—a diminution of tunneling or resonances of electrons. It is this reduced or renormalized splitting that properly belongs in the estimate made in Eq. (12) since it is $\Delta'/\hbar$ which characterizes the electronic tunneling rate under the influence of a fluctuating medium. Therefore,

$$\kappa \approx \kappa_{cl}(1 - e^{-z\Delta'^2}) \tag{16}$$

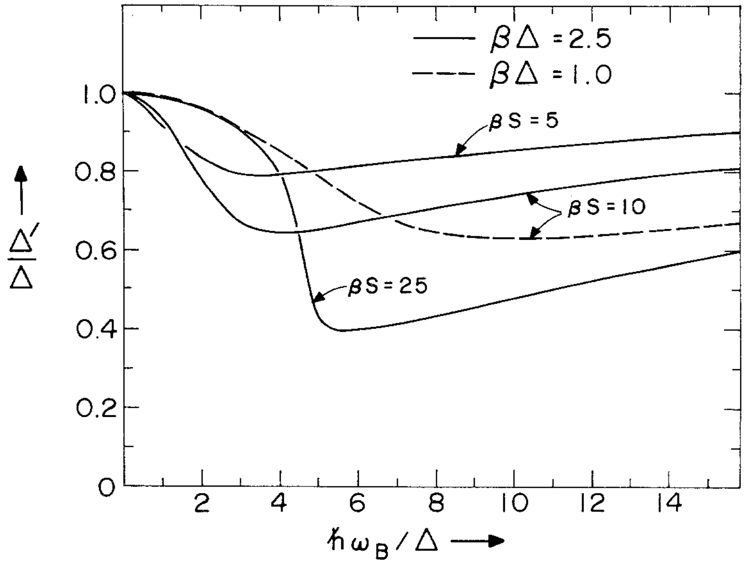

Fig. 5. Renormalized energy splitting of a two-state system coupled to an Einstein crystal (i.e., a monchromatic Gaussian bathe) as a function of the frequency of the bath, ω_B, at a few values of Δ and S. The latter characterizes the strength of coupling between the two states system and the bath. In particular, S is the solvation energy in the "classical limit" ($\Delta/\omega_B \to 0$), and β is $k_B^{-1}T$. Note that in the convention employed in this paper, Δ is the spacing between the levels, while in Ref. 42, Δ is half the spacing between the levels.

accounts for the nonadiabatic transitions induced by the time dependence of the fluctuations in the environment. Since Δ'^2 can be significantly smaller than Δ^2, we see that it is possible for the bath fluctuations to alter the dynamics of an activated process from a purely classical adiabatic barrier crossing to a dynamics strongly influenced by nonadiabatic electronic transitions. This prediction, I believe, deserves serious consideration in any theoretical work concerned with the role of nonadiabatic transitions in condensed phase activated processes.

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