Vibrational Nonadiabaticity and Tunneling Effects in Transition State Theory

R. A. Marcus

Arthur Amos Noyes Laboratory of Chemical Physics,[†] *California Institute of Technology, Pasadena, California 91125*

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The usual quantum mechanical derivation of transition state theory is a statistical one (a quasi-equilibrium is assumed) or dynamical. The typical dynamical one defines a set of internal states and assumes vibrational adiabaticity. Effects of nonadiabaticity before and after the transition state are included in the present derivation, assuming a classical treatment of the reaction coordinate. The relation to a dynamical derivation of classical mechanical transition state theory is described, and tunneling effects are considered.

Introduction

Derivations of transition state theory include a classical mechanical one due to Wigner[1,2] and several based on quantum mechanics.[3-6] One of the latter assumes a quasi-equilibrium between reactants and transition state[3] and another assumes vibrational adiabaticity along the reaction coordinate.[4,5] Apart from the use of classical mechanics, Wigner's derivation is the most general of these: its principal dynamical assumption is that a dividing surface ("transition state") can be found in phase space such that no classical trajectories recross it. Thereby, it provides insight into possible situations where transition state theory can break down because of dynamical effects. When this dividing surface in phase space is assumed to be independent of the momenta the usual (but classical) form of transition state theory, with its familiar kT/h factor, is obtained.

The vibrationally-adiabatic quantum mechanical derivation[4,5] is a dynamical one, adiabaticity being a particular dynamical approximation, while the quasi-equilibrium derivation is a statistical one (more ad hoc). As such, the former can be more revealing. Vibrational nonadiabaticity is important in some reactions and in the present paper a derivation which considers such nonadiabatic effects before and after the transition state is described. The problem of nuclear tunneling is also considered.

Quantum Mechanical State Theory

The following expressions arise in transition state theory for k_E and k_T, the microcanonical and canonical rate constants, respectively, when the motion along the reaction coordinate can be treated classically and the remaining coordinates are treated quantum mechanically: k_E is given by[7,8]

$$k_E = N_E^{\ddagger}/h\rho_E \qquad (1)$$

where $N_E^{\ddagger}$ is the total number of internal states of the transition state with energy equal to or less than E; ρ_E is the density of states of the reactant(s) at energy E. Instead, if certain quantum numbers, whose totality is denoted by J, are conserved during the elementary step, the rate constant for a microcanonical ensemble of given J is[7,8]

$$k_{EJ} = N_{EJ}^{\ddagger}/h\rho_{EJ} \qquad (2)$$

$N_{EJ}^{\ddagger}$ and ρ_{EJ} being the number of states of the transition state and the density of states of the reactant(s), respectively, for the given E and J. The k_E and $N_E^{\ddagger}$ in (1) equal the sum over J of k_{EJ} and $N_{EJ}^{\ddagger}$, respectively.

Like $N_E^{\ddagger}$, $N_{EJ}^{\ddagger}$ is a step function of E, increasing by unity each time E exceeds a new energy level $E_n(q_n^{\ddagger})$ of the transition state. $E_n(q_n^{\ddagger})$ is the value of the energy of the nth internal state at a value of the reaction coordinate $q = q_n^{\ddagger}$ selected as the transition state for a system in state n. $q_n^{\ddagger}$ and E_n may both depend on J, but for brevity the J is suppressed in the notation.

The canonical rate constant at temperature T, k_T, is the probability of being in the interval $(E, E + \mathrm{d}E)$ and having a particular J, multiplied by k_{EJ}, integrated over E and summed over J. The probability (at high enough pressures) is the equilibrium value, $\rho_{EJ} \exp(-E/kT)\, \mathrm{d}E/Q$, where Q is the partition function of the reactant(s). Thereby

$$k_T = (kT/h)\sum_J \int N_{EJ}^{\ddagger} \exp(-E/kT)\, \mathrm{d}(E/kT)Q \qquad (3)$$

Since $N_{EJ}^{\ddagger}$ is the step function of E described above, $\mathrm{d}N_{EJ}^{\ddagger}/\mathrm{d}E$ is a sum of Dirac-delta functions, $\sum_n \delta(E - E_n(q_n^{\ddagger}))$. Integration by parts thus yields the familiar

$$k_T = (kT/h)Q^{\ddagger}/Q \qquad (4)$$

where $Q^{\ddagger}$ equals $\sum_{Jn} \exp(-E_n(q_n^{\ddagger})/kT)$. This $E_n(q)$ includes any potential energy increment $V(q)$ from reactants to that value of q.

To count the states in $N_{EJ}^{\ddagger}$ one introduces a basis set of states n. The set may be the vibrationally-adiabatic set (VA), in which the Schrodinger equation is solved at each value of a reaction coordinate q, yielding a set of levels $E_n(q)$. If, instead, the coupling between the internal degrees of freedom is neglected (as is usually the case in practical applications of transition state theory) one has what one might call a partially vibrationally-adibatic basis set (PVA). There is, here, coupling only to q.

Regardless of which of these basis sets is used, the transition state in vibrationally-adiabatic transition state theory is taken to be a value of q, $q_n^{\ddagger}$, which can depend on n and J, and is chosen to be at the maximum of the $E_n(q)$ vs. q curve. If we denote by $[n]$ the set of these (VA or PVA) states in $N_{EJ}^{\ddagger}$, and indicate after a colon the condition satisified by those states we have in VA (or PVA) theory

$$N_{EJ}^{\ddagger} = \sum_n 1,\ [n\colon\ \max E_n(q) \le E] \qquad q \qquad (5)$$

Instead of (5) another and simpler count for $N_{EJ}^{\ddagger}$ is the total number of states at a given q, $N_{EJ}^{\ddagger}(q)$ where q (denoted by $q^{\ddagger}$) is chosen such that $N_{EJ}^{\ddagger}$ is as small as possible, i.e.

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$$N_{EJ}^{\ddagger}(q) = \sum 1,\ [n\colon\ E_n(q) \le E] \qquad \text{(6a)}$$

$$N_{EJ}^{\ddagger} = \min_{q}\ N_{EJ}^{\ddagger}(q),\ q = q^{\ddagger} \text{ at the minimum } N_{EJ}^{\ddagger}(q) \qquad \text{(6b)}$$

For simplicity we shall confine our attention here to systems or conditions where there is only one minimum in (6b).

The $N_{EJ}^{\ddagger}(q)$ given by (6a) equals or exceeds that in (5), exceeding it when there are any states for which

$$\max_{q} E_n(q) > E > E_n(q^{\ddagger}) \qquad (7)$$

Thus, by choosing q so that $N_{EJ}^{\ddagger}(q)$ is as small as possible, as in (6b), the number of states obeying (7) becomes as small as possible, and so (6) approaches the VA (PVA) eq 5.

Before proceeding with nonadiabatic effects it is useful to recall a VA (or PVA) derivation of (2). An ensemble of quantum states in $(E, E + \mathrm{d}E)$ and with the given J is considered, there being $\rho_{EJ}\,\mathrm{d}E$ such states. In the reactants' region the probability of finding the system in any specified internal state n and also in $\mathrm{d}q\ \mathrm{d}p$ (p is the momentum canonically conjugate to the reaction coordinate q) equals the number of quantum states in $\mathrm{d}q\ \mathrm{d}p$, divided by $\rho_{EJ}\,\mathrm{d}E$. The probability thus equals $\mathrm{d}q\ \mathrm{d}p/h\rho_{EJ}\ \mathrm{d}E$, since each quantum state in (q,p) space occupies an area h. This probability per unit q (i.e., the above divided by $\mathrm{d}q$), when multiplied by the velocity $\dot{q}$, yields the probability flux of this nth state, $\dot{q}\ \mathrm{d}p/h\rho_{EJ}\ \mathrm{d}E$. Since $\dot{q}\ \mathrm{d}p$ equals $\mathrm{d}E$,[9] this flux equals $1/h\rho_{EJ}$. A channel n is "open" if $E_n(q) \le E$ for all q. If one sums the flux over all open channels and if the sum of these open channels is denoted by $N_{EJ}^{\ddagger}$, one obtains the reactive probability flux, i.e., the rate constant k_{EJ} given by (2).

This derivation is the same regardless of whether a VA or PVA basis set is employed, but $N_{EJ}^{\ddagger}$ then refers to a VA or to a PVA count, respectively.[10] The other assumptions are those of an equilibrium distribution in the ensemble of states of the reactant(s), and a classical treatment of this reaction coordinate.

The connection of this derivation with the dynamical one of classical mechanical transition state theory[1,2] may be noted: In the latter, it was assumed that no trajectory, regardless of where it started, recrossed the dividing surface ("transition state") in phase space. Vibrational adiabaticity was not assumed. In the above quantum mechanical derivation, the assumption of vibrational adiabaticity provides a prescription for finding out whether "trajectories" recross the "dividing surface". (The dividing surface is now the set of points $q_n^{\ddagger}$ at the maximum of each $E_n(q)$ in eq 5. For a given n the system either crosses this "dividing surface" once (when $\max_q E_n(q) < E$, i.e., the so-called open channel n) or not at all (when $\max_q E_n(q) > E$), but it never can recross this dividing surface in this vibrationally-adiabatic approximation. However, when a single value of $q_n^{\ddagger}$ is used, namely, the $q^{\ddagger}$ in (6b), recrossings can occur in this VA (PVA) case, and so then (6) exceeds (5) in this case, namely by the states satisfying (7).

Vibrationally-Nonadiabatic Effects

Vibrationally-nonadiabatic effects arise from two main sources:[11] (1) variation in the frequencies of the internal motions (motions perpendicular to the reaction coordinate) along the reaction coordinate, and (2) curvilinear effects of the reaction coordinate, such as a sharp change of direction of that coordinate in the usual[3] skewed-axes diagram. Both effects participate in reactions which are nearly adiabatic.[11] Reactions which are highly vibrationally nonadiabatic, such a highly exothermic reactions which produce very vibrationally-excited products, are probably so because of the sharp change of direction of reaction coordinate effect. (The reaction coordinate in this description is chosen to parallel the "reaction path".[12])

Of the two equations for $N_{EJ}^{\ddagger}$ in the previous section, (5) and (6), eq 5 treats each channel (internal state) from reactants to products as either open or closed. A channel n is open if $E_n(q) < E$ for all q and closed otherwise. In the presence of vibrationally-nonadiabatic transitions, each channel can become partially open and then eq 5 no longer applies when such transitions are important. Equation 6 on the other hand merely counts states at some q, regardless of whether they are at a later or earlier q open, closed, or partially open, and we shall focus our attention on it.

Several nonadiabatic effects arise. Clearly, a vibrationally-nonadiabatic transition which occurs at a $q > q^{\ddagger}$ and which does not result in a reflection back across the transition state has no effect on the forward reactive flux. However, certain localized nonadiabatic transitions occurring at $q < q^{\ddagger}$ also have no effect on this reactive flux. Consider two channels m and n, which undergo their first nonadiabatic transition. Each has the same initial flux j^0 ($= 1/h\rho_{EJ}$) in the ensemble. We consider rather localized nonadiabatic transition probabilities between the two states at a q, $P_{m\leftarrow n}$, which do not in themselves cause a reflection at that q. The forward flux in the nth channel after this transition is $j^0 P_{n\leftarrow n} + j^0 P_{n\leftarrow m}$. Since $P_{n\leftarrow n}$ equals $1 - P_{m\leftarrow n}$ and since by microscopic reversibility $P_{m\leftarrow n}$ and $P_{n\leftarrow m}$ are equal, the flux in the nth channel after the transition is again j^0, as is that in the mth channel. Thus, such transitions at q's less than $q^{\ddagger}$ do not result in net flux changes in each channel, and so do not affect the forward reactive flux. Similar remarks apply to later vibrationally-nonadiabatic transitions which each of these channels may undergo with other channels at $q < q^{\ddagger}$. In the present discussion we shall neglect any transition which occurs at $q = q^{\ddagger}$, for simplicity. It would lead to an expression less simple than (2).

Thus, in a derivation which includes nonadiabatic effects we may proceed as follows. The initial probability flux of internal states is $1/h\rho_{EJ}$, as shown earlier, summed over all states with energy equal to or less than E and having the given J. These states may then undergo nonadiabatic transitions but the transitions described above do not affect the forward flux of states in each channel. We then select as the transition state some q, denoted by $q^{\ddagger}$, and assume that there will be very few reactants' states which have a turning point at $q > q^{\ddagger}$ (i.e., states arising from reactants such that $E_n(q^{\ddagger}) < E < E_n(q)$ at a $q > q^{\ddagger}$), very few products' states which have a turning point at $q < q^{\ddagger}$ (i.e., states arising from products which crossed $q^{\ddagger}$ from the products' direction then met a turning point and recrossed $q^{\ddagger}$), and very few bound states containing $q^{\ddagger}$ (which have, accordingly, both turning points). Under these conditions, the flux crossing $q = q^{\ddagger}$ is almost all reactive flux and one obtains (6a), where $N_{EJ}^{\ddagger}$ is the number of internal states n at $q = q^{\ddagger}$. Because of recrossings, which occur where any of the above conditions is violated, this rate constant is an upper bound (apart from other neglected effects), and so (6b) is imposed to minimize the error. Some other prescription for the transition state, other than q equal to a single value at a given E and J, could also be introduced, giving $q^{\ddagger}$ an n dependence for example (as well as the E and J dependence it already may have).

Further Comparison with Classical Theory

In the most general form of classical mechanical transition state theory the dividing surface (the transition state) is one which depends on both the coordinates and the momenta.[1,2] In the transition state theory described by (2) and (6), the dividing surface depends on a limited number of momentum-like variables (E and the J's, recalling that quantum numbers correspond to the classical action variables, which are momenta[13]). In (2) and (5) the dividing surface also depends on other momentum-like variables, the n's, but suffered by neglecting nonadiabatic effects. In none of these cases was the dividing surface crossed by momentum velocity components ($\dot{p}$, $\dot{J}$, or $\dot{n}$), only by $\dot{q}$ (nor by velocity components for coordinates conjugate to J or n, the "angle variables" velocities[14]). In one case there was no $\dot{J}$ because J was a constant of the motion while in the other case the effects of nonadiabatic transitions and hence of $\dot{n}$'s were considered before and after but not at the transition state. Typically, momentum velocity components at the transition state have been used mainly (in classical mechanical transition state theory) to treat atom recombination reactions[1,2]

$$2X + M \rightarrow X_2 + M \tag{8}$$

since to avoid immediate redissociation of any newly formed X_2 bond some of the energy of the newly formed bond must be transferred to the other coordinates.

The variational form of classical mechanical transition state theory, in which the dividing surface is chosen so as to make the reactive flux as small as possible,[2] has (6b) as its analogue in the present quantum treatment.

Tunneling

In transition state theory nuclear tunneling along the reaction coordinate is usually treated by calculating the potential energy barrier along the "reaction path" (path of steepest ascent to a saddle point from the reactants' and products' valleys).[3] For a given vibrational quantum number n of the internal motion(s) (in the vibrationally-adiabatic approximation) $E_n(q)$ includes the potential energy increment, $V(q)$, and acts as an effective barrier for tunneling. It was recently shown[15] for the $H + H \rightarrow H_2 + H$ reaction that semiclassically a better tunneling path (one with the less $\mathrm{Im}\int \mathbf{P}\cdot d\mathbf{Q}$ integral for the paths examined[15]) was for any specified n the path of vibrational end points for that n (cf. Figure 1 of ref 15). (Im is the "imaginatory part of ", $d\mathbf{Q}$ an element of the path, and $\mathbf{P}$ momentum along the path.) This path yielded improved values of the reaction probability when compared with exact quantum mechanical results for the collinear collision treated.

The best tunneling path (one with minimum $\mathrm{Im}\int \mathbf{P}\cdot d\mathbf{Q}$) will depend upon the reaction. As an example one can consider the transfer of a light particle H between two heavy particles A and B, in $AH + B \rightarrow A + HB$. When A and B are sufficiently heavy only the motion of the H need be considered in the tunneling. The path with the smallest $\mathrm{Im}\int \mathbf{P}\cdot d\mathbf{Q}$ now involves, at the distance of closest approach of A and B for the given E and n, the motion of the H alone.[16] In other cases, where the masses of A and B are not so large, they take part in the motion too. In the usual skewed-axis diagram, one selects as the initial point of tunneling the translational-vibrational end point in the reactants' channel (P in Figure 1 of ref 15) for the given n and E. As the final point of tunneling one would select the translational-vibrational end point for state m of the products (P′ in Figure 1 of ref 15). [Here, m equals n in the case of a sufficiently symmetric reaction.] One would, presumably, for any given (n,m) pair find the path with the smallest $\mathrm{Im}\int \mathbf{P}\cdot d\mathbf{Q}$, and eventually select that m for which this $\mathrm{Im}\int \mathbf{P}\cdot d\mathbf{Q}$ is also the smallest. Similar remarks apply to a reaction $AC + B \rightarrow A + CB$. In the case of fully three-dimensional reactions, the local $E_n(q)$ includes an energy for the bending motions of the A–C–B system, which at large separation distances are AC or CB rotations.

It is not yet known, in the present absence of detailed calculations apart from those in ref 15 for collinear $H + H_2$, how well the above simple prescription applies. It depends on the very existence of these states of energy $E_n(q)$.

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(7) For unimolecular reactions, cf. R. A. Marcus, *J. Chem. Phys.*, **20**, 359 (1952); **43**, 2658 (1965), eq 3; **52**, 1018 (1970).

(8) For bimolecular reactions the derivation is similar to that in ref 7.

(9) Since $\dot{q}$ equals p/μ, where μ is the reduced mass for motion along the reaction coordinate, then for any given $E_n(q)$ and q, $\dot{q}\,dp = d(p^2/2\mu) = dE$.

(10) Typically, the $N_{EJ}^{\ddagger}$ defined in (5) is smaller for a VA than for a PVA basis. For example, a coupling between two PVA states, n and m, causes a splitting at any intersection of their (PVA) energies $E_n(q)$ and $E_m(q)$. Thereby, when E lies within this "gap" arising from the splitting, the contribution to $N_{EJ}^{\ddagger}$ of the two states is zero in the PVA case but can be zero or unity in the VA case. It is unity if the lower VA state formed from the coupling has an energy which nowhere exceeds this E. (For this condition to be fulfilled it is at least necessary that the PVA $E_n(q)$ and $E_m(q)$ curves have slopes of opposite sign at the intersection.)

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Discussion

David M. Golden (Stanford Research Institute). If reported A factors for $R + H\text{-}R' \rightarrow RH + R'$ are correct as reported, they can be understood using simple transition state theory as described in my paper in this symposium. Does this mean that the dynamic corrections discussed by Kuppermann and the tunneling corrections discussed by Marcus tend to cancel each other?

R. A. Marcus. The transfer of a light particle (H) between two relatively heavy ones (R,R′) is very different dynamically from the $H + H_2 \rightarrow H_2 + H$ reaction, and should be treated separately. I have commented in the paper on tunneling paths for the transfer of a light particle between two heavy ones. It would be very useful, of course, to have three-dimensional quantum mechanical calculations for these systems.

J. TROE (Institut für Physikalische Chemie der Universitat Gottingen). I agree with your remarks about the importance of the vibrational adiabatic channel states. Now we have to ask what is important to do in the future? Certainly we need better potential surfaces. Then, we have to learn how, with these surfaces, we can construct a better set of channel states. This has to be done so that we obtain the best zeroeth order set of channels for which only a minimum of dynamical coupling is left over. We also must learn to what extent vibrational adiabaticity holds for a given set of channel states.

R. A. MARCUS. I certainly agree. In the written version of the paper, which is an elaboration of the verbal one, it is pointed out how nonadiabaticity affects possible definitions of the transition state—leaving one essentially intact but making the other quite uncertain.

H. O. PRITCHARD (York University). I would like to suggest that in any reaction for which quantum-mechanical tunneling is conceived to be an important contributing mechanism, it is going to be extremely difficult to calculate reliable rates from first principles. We have recently [M. Kuriyan and H. O. Pritchard, *Can. J. Chem.*, 55, 3420 (1977)] calculated the energy levels for H_2^+ with both adiabatic and nonadiabatic (effective) potentials. Inclusions of the nonadiabatic Born–Oppenheimer corrections shifts the quasi-bound levels of H_2^+ by about 3 cm^{-1}, but it alters the lifetimes by as much as a factor of 4. Thus, with less-than-perfect potential surfaces, the chances of getting reliable answers will be worst when the barrier is low and wide, as it is in a quasi-bound resonance, but will improve somewhat if the barrier is strongly peaked and very narrow.