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Abstract

Semiclassical and quantum mechanical transition state theory is reviewed and two new approaches described. One is a general implementation of a semiclassical rate expression [Miller, Faraday Disc. Chem. Soc. 62, 40 (1977)] that involves the 'good' action-angle variables associated with the saddle point (i.e., transition state) of a potential energy surface. The other is an evaluation of a formally exact quantum expression for the rate [Miller, Schwartz, and Tromp, J. Chem. Phys. 79, 4889 (1983)] in terms of Siegert eigenvalues associated with the transition state. Siegert eigenvalues are usually associated with scattering resonances, so their identification with the saddle point of a potential surface, and the expression for the reaction rate in terms of them, is quite an unexpected and novel development.

1. Introduction

Transition state theory[1] is without a doubt the most commonly used theory for describing chemical reaction rates (and also rate processes in many other fields), for both unimolecular and bimolecular reactions. The purpose of this paper is to suggest two new transition state-like theoretical approaches for determining such rates, the first a semiclassical one and the second fully quantum mechanical. In order to focus on the basic theoretical ideas which are the subject of the paper, all expressions below will be written explicitly for total angular momentum J=0; for applications to real molecular systems it is of course necessary to carry out the transition state calculation for each value of J separately and then combine them appropriately. The remainder of the Introduction summaries the basic notions of transition state theory and earlier related work.

The microcanonical and canonical rate constants are both conveniently expressed in terms of the cumulative reaction probability N(E),

$$k(E) = [2\pi\hbar\rho(E)]^{-1}N(E) \tag{1.1a}$$

$$k(T) = [2\pi\hbar Q_r(T)]^{-1}\int^{\infty} dE\, e^{-\beta E}N(E)\,, \tag{1.1b}$$

where E is the total energy of the molecular system, T the temperature [$\beta = (kT)^{-1}$], ρ is the density of reactant states per unit energy, and Q_r is the reactant partition function. (k(E) is usually of more interest for unimolecular reactions, where it is known as RRKM theory, and k(T) typically of more interest for bimolecular reactions.) The cumulative reaction probability is in turn given by the sum of tunneling, or transmission probabilities over all states $\mathbf{n} = (n_1,\ldots,n_{F-1})$ of the "activated complex"

$$N(E) = \sum_{\mathbf{n}} P_{\mathbf{n}}(E)\,. \tag{1.2}$$

The activated complex is the system of F-1 degrees of freedom (F is the total number of degrees of freedom of the molecular system) for motion in the dividing surface normal to the reaction coordinate (the Fth degree of freedom) which separates reactants from products. If for some states $\mathbf{n}$, $P_{\mathbf{n}}$ were to equal 1, and for all other states equal to zero, then N(E) would simply be the number of states for which the transmission probability is unity. In general, therefore, one may think qualitatively of N(E) as the "number of quantum states that react", as a function of the total energy of the system. In the limit of classical mechanics N(E) is also proportional to the microcanonical average of the one-way flux through the dividing surface.[2]

The transmission probabilities $\{P_{\mathbf{n}}(E)\}$ are thus the primary objects which must be calculated, and then Eqs. (1.2) and (1.1) give the reaction rates.[3] The <u>simplest</u> approximation for them is obtained by assuming that the reaction coordinate (mode F) is separable from the (F-1) modes of the activated complex. In this limit

$$P_{\mathbf{n}}(E) = P_{1d}(E-\varepsilon_{\mathbf{n}}^{\ddagger}) , \tag{1.3a}$$

where $\varepsilon_{\mathbf{n}}^{\ddagger}$ is the energy eigenvalue for state $\mathbf{n}$ of the activated complex, often approximated as harmonic,

$$\varepsilon_{\mathbf{n}}^{\ddagger} \equiv \sum_{k=1}^{F-1} \hbar\omega_k^{\ddagger}(n_k+1/2) , \tag{1.3b}$$

and $P_{1d}(E_F)$ is a one-dimensional tunneling probability, often approximated by the uniform semiclassical expression

$$P_{1d}(E_F) \equiv \left[1+e^{2\theta(E_F)}\right]^{-1} , \tag{1.3c}$$

where $\theta(E_F)$ is the one-dimensional WKB barrier penetrating integral

$$\theta(E_F) = \int_{\text{barrier}} dq_F \sqrt{2m[V(q_F)-E_F]/\hbar^2} . \tag{1.3d}$$

If the barrier potential $V(q_F)$ is furthermore assumed to be harmonic (i.e., a parabolic barrier), then

$$\theta(E_F) = \frac{\pi(V_0-E_F)}{\hbar|\omega_F|} , \tag{1.3e}$$

where $\omega_F = -i|\omega_F|$ is the imaginary barrier frequency. (From Eqs. (1.3) one can readily see the general characteristic $P_n(E) \rightarrow 1$ for $E_F \equiv E-\varepsilon_n^{\ddagger} >> V_0$.) The totally harmonic limit of the theory thus requires only a normal mode analysis at the transition state (saddle point of the potential surface) in order to determine the frequencies $\{\omega_k\}$, k=1, ..., F, and also, of course, the barrier height V_0. As simple as this totally harmonic result is, it is the general basis for describing the effects of dissapation on reaction rates (i.e., Kramers' theory).[4]

A more rigorous expression for the transmission probabilities is given by the "instanton" model,[5] i.e., a semiclassical theory that involves a periodic classical trajectory on the upside-down potential surface. In this case, $2\theta(E)$ is the classical action integral (in pure imaginary time) for a complete cycle about the periodic orbit, and $\{\omega_k(E)\}$, k=1, ..., F-1 are the stability frequencies for an infinitesimal perturbation about the periodic orbit. The major advantage of this theory is that one need not choose the reaction path, or even the dividing surface, in some *ad hoc* manner, but rather the full F-dimensional (classical) dynamics selects the reaction path (i.e., the periodic orbit). The transmission probabilities are given in this theory by

$$P_n(E) = \left\{1 + \exp\left[2\theta(E) - 2\theta'(E)\sum_{k=1}^{F-1} \hbar\omega_k(E)(n_k+1/2)\right]\right\}^{-1}, \tag{1.4}$$

which one sees is very similar in structure to the separable result given by Eq. (1.3a) - (1.3d), i.e.,

$$P_n^{\mathrm{separable}}(E) = \left\{1 + \exp\left[2\theta\left(E - \sum_{k=1}^{F-1} \hbar\omega_k^{\ddagger}(n_k+1/2)\right)\right]\right\}^{-1}. \tag{1.5}$$

The primary differences are, first of all, that $\theta(E)$ in Eq. (1.4) is computed along the periodic orbit and not along a separable one dimensional path as in Eq. (1.5). Also, the constant frequencies $\{\omega_k^{\ddagger}\}$ in Eq. (1.5) are replaced in (1.4) by the energy-dependent stability frequencies of the periodic orbit. *And finally, the periodic orbit result, Eq. (1.4), inherently assumes that the energy* in the activated complex is small compared to the total energy, and the exponent in Eq. (1.4) is expanded to first order in this energy. If the action integral θ(E) were a linear function of E - i.e., if the barrier were assumed to be parabolic, as in Eq. (1.3e) - then this would not be an approximation, but in general it is. Thus the periodic orbit result, though clearly better in many ways than the separable approximation, has the defect that it is not correct in the separable limit if the barrier is anharmonic.

II. Semiclassical Transmission Probabilities Including Anharmonicity

A more rigorous way of including anharmonicity into the transition state transmission probabilities is based on the set of 'good' action-angle variables associated with the saddle point on the potential surface.[6] The good action variables about a saddle point are in complete analogy with those associated with a minimum on a potential surface. In the latter case one can compute classical trajectories, determine the invariant tori, calculate the topologically independent action integrals, etc., in order to determine them,[7] but this is not possible for the case of a saddle point *because the trajectories will "run away". It is necessary to express the classical Hamiltonian in* terms of the good action variables by some analytic prescription.[8]

The general result of this approach[6] begins with the classical Hamiltonian expressed as a function of its 'good' (i.e., conserved) action variables, $E(I_1, ..., I_F)$. One of these actions is identified with the reaction coordinate, I_F say, and realized to be imaginary,

$$I_F \equiv -i\hbar\theta/\pi \qquad (2.1a)$$

while the other (F-1) actions are quantized in the usual semiclassical fashion,

$$I_k = (n_k+1/2)\hbar\ , \qquad (2.1b)$$

k=1, ..., F-1. The equation

$$E = E(n_1, ..., n_{F-1},\theta) \equiv E(\mathbf{n},\theta) , \tag{2.2}$$

is then solved to express $\theta \equiv \theta(\mathbf{n},E)$ as a function of E and the F-1 quantum number $\mathbf{n}$. The transmission probability then has the semiclassical form

$$P_{\mathbf{n}}(E) = [1+e^{2\theta_{\mathbf{n}}(E)}]^{-1} . \tag{2.3}$$

As an elementary example of this general prescription, consider a harmonic saddle point, for which

$$E(I_1, ..., I_F) = V_0 + \sum_{k=1}^{F} \omega_k I_k . \tag{2.4a}$$

Making the replacements in Eq. (2.1), with $\omega_F = -i|\omega_F|$, and solving Eq. (2.2) leads to

$$\theta(\mathbf{n},E) = \frac{\pi}{\hbar|\omega_F|}\left(V_0 + \sum_{k=1}^{F-1} h\omega_k(n_k+1/2) - E\right) , \tag{2.4b}$$

i.e., Eq. (1.3e), the harmonic result discussed above.

A less trivial application of this general prescription Eq. (2.1)-(2.3) was given recently[9] by using perturbation theory to include the effects of cubic and quartic anharmonicities about a saddle point. If $\{q_k\}$, k=1, ..., F denote the usual mass-weighted normal mode coordinates at the saddle point (i.e., the harmonic potential is $V_0 + \sum_k 1/2\omega_k{}^2 q_k{}^2$), and

$$f_{kj\ell} = \left(\frac{\partial^3 V}{\partial q_k \partial q_j \partial q_\ell}\right)_{q=0} \tag{2.5a}$$

$$f_{kj\ell m} = \left(\frac{\partial^4 V}{\partial q_k \partial q_j \partial q_\ell \partial q_m}\right)_{q=0} \tag{2.5b}$$

are the cubic and quartic force constants, then the classical energy is given in terms of the good *actions* $\{I_k\}$ *by*

$$E(I_1, \ldots, I_F) = V_0 + \sum_{k=1}^{F} \omega_k I_k + \sum_{k \le k'=1}^{F} x_{kk'} I_k I_{k'} \,, \tag{2.6}$$

where the anharmonic constants $\{x_{k,k'}\}$ are given in terms of the cubic and quartic force constants,

$$x_{kk} = \frac{1}{16\omega_k^2}\left[f_{kkkk} - \sum_{\ell=1}^{F} \frac{f_{kk\ell}^2(8\omega_k^2-3\omega_\ell^2)}{\omega_\ell^2(4\omega_k^2-\omega_\ell^2)}\right] \tag{2.7a}$$

$$x_{k\ell} = \frac{1}{4\omega_k\omega_\ell}\left[f_{kk\ell\ell} - \sum_{m=1}^{F} \frac{f_{kkm}f_{\ell\ell m}}{\omega_m^2} + \sum_{m=1}^{F} \frac{2f_{k\ell m}^2(\omega_k^2+\omega_\ell^2-\omega_m^2)}{[(\omega_k+\omega_\ell)^2-\omega_m^2]\,[(\omega_k-\omega_\ell)^2-\omega_m^2]}\right], \tag{2.7b}$$

for $k \neq \ell$. With the replacements indicated by Eq. (2.1), Eq. (2.2) is a quadratic equation for θ which is readily solved to give

$$\theta(\mathbf{n},E) = \frac{\pi\Delta E}{\hbar\Omega_F}\left(\frac{2}{1+\sqrt{1+4x_{FF}\Delta E/(\hbar\Omega_F)^2}}\right), \tag{2.8}$$

where

$$\Delta E = V_0 + \varepsilon_{\mathbf{n}}^{\ddagger} - E \tag{2.9a}$$

with

$$\varepsilon_{\mathbf{n}}^{\ddagger} = \sum_{k=1}^{F-1} \hbar\omega_k(n_k+1/2) + \sum_{k \le k'=1}^{F-1} \hbar^2 x_{kk'}(n_k+1/2)(n_{k'}+1/2) \,, \tag{2.9b}$$

and

$$\hbar\Omega_F = \hbar\tilde{\omega}_F - \sum_{k=1}^{F-1} \hbar^2 \tilde{x}_{kF}(n_k+1/2) \,, \tag{2.10a}$$

with

$$\tilde{\omega}_F = i\omega_F = |\omega_F| \,, \tag{2.10b}$$

$$\tilde{x}_{kF} = -ix_{kF} \,, \tag{2.10c}$$

($\tilde{x}_{kF}$ is real). Eqs. (2.8)-(2.10) incorporate anharmonicity in the energy levels of the activated complex (cf. Eq. (2.9b)), anharmonicity in the reaction coordinate itself (via x_{FF}), and coupling between the reaction coordinate and modes of the activated complex (i.e., reaction path curvature) through the anharmonic constants $\tilde{x}_{kF}$ in Eq. (2.10a).

It is useful to note that having the energy to quadratic order in the actions, Eq. (2.6), can describe anharmonic effects quite realistically. Morse oscillator vibrational eigenvalues, for example, are given exactly through second order in (n+1/2). Also, consider the popular Eckart potential barrier

$$V(x) = V_0 \operatorname{sech}^2(\alpha x)\,, \tag{2.11a}$$

which is often used to model anharmonic barriers. The one-dimensional WKB action integral for it is given by

$$\theta(E) = \pi\sqrt{\frac{2m}{\hbar^2\alpha^2}}\,(\sqrt{V_0} - \sqrt{E})\,, \tag{2.11b}$$

so that the energy as a function of θ is

$$E(\theta) = V_0 - \frac{\theta}{\pi}\hbar\alpha\sqrt{\frac{2V_0}{m}} + \left(\frac{\theta}{\pi}\right)^2 \frac{\hbar^2\alpha^2}{2m}\,; \tag{2.11c}$$

i.e., the energy is given exactly as a quadratic function of the action. One thus feels that Eq. (2.6), and the transmission probability that results from it, can have a useful range of validity for including the effects of anharmonicity of the transition state.

Is it possible to apply the general semiclassical theory of Eq. (2.1) - (2.3) <u>non-perturbatively</u>? The following procedure is one scenario. The idea is to use <u>quantum mechanics</u> to obtain the energy in terms of the quantum numbers (i.e., action variables) by diagonalizing a Hamiltonian matrix.

Thus suppose that the potential is harmonic plus cubic and quartic anharmonic terms. One first imagines that <u>all</u> the frequencies $\{\omega_k\}$ k=1, ..., F are real and writes out the simple (analytic) matrix representation of the Hamiltonian, $H_{n,n'}$, in the harmonic oscillator basis (where here n and

n' denote F quantum numbers). After the matrix elements are calculated, one makes the replacement

$$\omega_F \rightarrow -i|\omega_F| ,$$

whereby the matrix $H_{\mathbf{n},\mathbf{n}'}$ becomes complex symmetric. Diagonalizing it thus gives complex eigenvalues, i.e., the complex energies that would result in the perturbation expression Eq. (2.6) if all the actions were replaced by $I_k = (n_k+1/2)\hbar$, k=1, ..., F. That is, when diagonalizing a Hamiltonian matrix to obtain eigenvalues - the non-perturbative quantum mechanical procedure - all the actions have "automatically" been set to their quantum values, i.e., (half-integers)x$\hbar$. To apply Eqs. (2.1) - (2.3), therefore, it is necessary to fit these numerically obtained eigenvalues to an analytic function of the quantum numbers, such as Eq. (2.6) or possibly a more general function, e.g., a Pade approximant. Once the analytic function E(**n**) is determined, one can then make the replacement Eq. (2.1a), solve Eq. (2.2) and obtain the transmission probability via Eq. (2.3).

III. A Fully Quantum Rate Expression

The discussion at the end of the previous section describes a quantum mechanical calculational procedure (diagonalizing a particular complex symmetric Hamiltonian matrix), the result of which is then used in a semiclassical theory. This seems wasteful; i.e., after one has done a quantum calculation, one would like to be able to determine the rate fully quantum mechanically.

This is possible by realizing that the complex eigenvalues discussed at the end of Section II are the Siegert eigenvalues[10] of the system. This is clear when one considers the boundary conditions satisfied by the corresponding eigenfunctions. For modes k=1, ..., F-1 the harmonic oscillator functions have real frequencies so that the eigenfunctions will decay in these coordinates in the usual fashion. For mode F, though, with $\omega_F = -i|\omega_F|$, the harmonic oscillator functions have the form

$$\phi_{n_F}(q_F) \sim \exp(i|\omega_F|q_F^2/2\hbar) \times H(q_F) , \tag{3.1}$$

where H is a polynomial in q_F. This function is an <u>outgoing</u> wave in both directions $q_F \to \pm\infty$, i.e., the Siegert boundary condition.

As has been used recently in quantum reactive scattering theory,[11] though, an outgoing wave basis set is what is necessary to construct a finite basis set representation of the Green's function $G^+(E)$ (provided one is interested in matrix elements of G^+ between short-range states). Thus if $\{E_\ell\}$, $\{\psi_\ell(q)\}$, $\ell=1, \ldots$ are the complex eigenvalues ($\mathrm{Im}E_\ell<0$) and corresponding eigenfunctions that result from the calculation described at the end of Section II, then one has the approximation[11]

$$G^+(E) = \sum_{\ell=1} \frac{|\psi_\ell\rangle\langle\psi_\ell|}{E-E_\ell} , \tag{3.2}$$

which becomes exact in the limit of a complete basis. (Note that there is no complex conjugation of the wavefunction in the bra symbol.) The microcanonical density operator is then given by[12]

$$\begin{aligned}\delta(E-H) &= -\frac{1}{\pi}\,\mathrm{Im}G^+(E)\\ &= -\frac{1}{2\pi i}(G^+(E)-G^-(E))\\ &= -\frac{1}{2\pi i}\left[\sum_\ell \frac{|\psi_\ell\rangle\langle\psi_\ell|}{E-E_\ell} - \frac{|\psi_\ell^*\rangle\langle\psi_\ell^*|}{E-E_\ell^*}\right] .\end{aligned} \tag{3.3}$$

Since the time evolution operator can be expressed as

$$e^{-iHt/\hbar} = \int_{-\infty}^{\infty} dE\, e^{-iEt/\hbar}\, \delta(E-H) , \tag{3.4a}$$

use of Eq. (3.3) in (3.4a) - and noting that $\mathrm{Im}E_\ell<0$, $\mathrm{Im}E_\ell^*>0$ - and evaluating the integral over E by closing the contour in the lower half plane, gives

$$e^{-iHt/\hbar} = \sum_{\ell} e^{-iE_{\ell}t/\hbar} |\psi_{\ell}\rangle\langle\psi_{\ell}| . \tag{3.4b}$$

Eqs. (3.3) and (3.4) make it possible to carry out a direct evaluation of the exact quantum rate expressions given by Miller, Schwartz, and Tromp.[13] Thus the canonical rate constant is given by

$$k(T) = Q_r^{-1} \int_0^{\infty} dt\, C_f(t) , \tag{3.5a}$$

where the flux correlation function is

$$C_f(t) = \mathrm{tr}\left[e^{iHt/\hbar}\, e^{-\beta H/2} F\, e^{-\beta H/2}\, e^{-iHt/\hbar} F\right] , \tag{3.5b}$$

where F is the flux-through-the-surface operator. Use of Eq. (3.4) in (3.5b) (and some straightforward manipulation) gives the flux correlation function as

$$C_f(t) = - \sum_{\ell,\ell'} \left\langle \psi_{\ell'}^{*} | F | \psi_{\ell} \right\rangle^2 e^{-\beta\left(E_{\ell}+E_{\ell'}^{*}\right)/2}\, e^{it\left(E_{\ell'}^{*}-E_{\ell}\right)/\hbar} . \tag{3.6}$$

Since $\mathrm{Im}(E_{\ell'}^{*}-E_{\ell})>0$, this correlation function decays exponentially as t → ∞, the correct behavior (which has <u>not</u> been obtained in previous basis set calculations of this correlation function[13,14]). With Eq. (3.6), the time integral in Eq. (3.5a) can be readily carried out, giving

$$k(T) = \frac{\hbar}{Q_r}\, \mathrm{Im} \sum_{\ell,\ell'} \left(\left\langle \psi_{\ell'}^{*} | F | \psi_{\ell} \right\rangle\right)^2 e^{-\beta\left(E_{\ell'}^{*}+E_{\ell}\right)/2} \Big/ \left(E_{\ell'}^{*}-E_{\ell}\right) . \tag{3.7}$$

One can similarly use Eq. (3.3) to evaluate the flux expression for the cumulative reaction probability N(E),

$$N(E) = \tfrac{1}{2}(2\pi\hbar)^2\, \mathrm{tr}\left[F\delta(E-H)F\delta(E-H)\right] . \tag{3.8}$$

The result of this calculation is

$$N(E) = \hbar^2 \,\mathrm{Re} \sum_{\ell,\ell'} \frac{\langle\psi_{\ell'}^{*}|F|\psi_{\ell}\rangle^{2}}{(E-E_{\ell'}^{*})(E-E_{\ell})} - \frac{\langle\psi_{\ell'}|F|\psi_{\ell}\rangle^{2}}{(E-E_{\ell'})(E-E_{\ell})} . \tag{3.9}$$

It remains to apply Eqs. (3.7) and (3.9) and test their ease of use, generality, and efficiency (i.e., how rapidly convergence is achieved with increasing size of basis set). It is nevertheless interesting to see how these formally exact quantum rate expression can be expressed in terms of the Siegert eigenvalues (and eigenfunctions) which are related to the transition state. Siegert eigenvalues usually are discussed only with regard to scattering <u>resonances</u>,[10] for which the imaginary parts of the eigenvalues are small. Here, on the other hand, the imaginary parts are <u>large</u> - e.g., for a parabolic saddle point

$$\mathrm{Im}\, E_n = -\hbar|\omega_F|(n_F+1/2)$$

$n_F = 0, 1, 2, \ldots$ - and have nothing to do with resonances. This appears to be a totally new context for these quantities.

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   $$P(k) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt\, e^{ikt} \prod_{n} [1+2itP_n(E)/2\pi\rho(E)]^{-1/2} .$$

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