

Semi-Classical Theory for Non-separable Systems:

Construction of "Good" Action-Angle Variables for Reaction Rate Constants*

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A semiclassical expression for bimolecular rate constants for reactions which have a single activation barrier is obtained in terms of the "good" action variables of the (classical) Hamiltonian that are associated with the saddle point region of the potential energy surface. The formulae apply to non-separable, as well as separable saddle points.

1. INTRODUCTION

A semiclassical expression for reaction rate constants has recently been derived which is of interest because it has the form of a generalization of transition state theory which correctly takes into account non-separability of the Hamiltonian about the saddle point of the potential energy surface.^{1,2} Application³ of this theory to the collinear $H + H_2$ reaction gives reasonably good agreement with (numerically) exact results of quantum scattering calculations⁴ over a wide range of energies near and below the effective threshold for reaction, much better agreement than the usual (i.e., separable) quantum mechanical version of transition state theory. This is of some practical importance, since for chemical reactions with significant activation energy it is the threshold region that primarily determines the thermal rate constant.

This semiclassical reaction rate theory^{1,3} involves certain *periodic* classical trajectories of the molecular system and is very similar in its mathematical structure to the periodic orbit theory of semi-classical eigenvalues derived by Gutzwiller⁵ (see also the important modification by Miller).⁶ As has been discussed,⁶ however, the quantum condition produced by periodic orbit theory, although qualitatively correct, contains dynamical approximations in addition to the semiclassical approximation itself, and semiclassical quantization of non-separable systems is in general more accurately achieved by the Hamilton-Jacobi approach of the old quantum theory.⁷ In this approach it is necessary to construct the total non-separable Hamiltonian as a function of the complete set of "good" action variables (or adiabatic invariants) of the system, and recently a great deal of progress has been made in finding ways to do this non-perturbatively (i.e., numerically). The preceding paper⁸ in this volume,

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for example, describes an application of the Hamilton-Jacobi approach to semiclassical eigenvalues and also gives more references to this topic.

Just as the periodic orbit theory for eigenvalues involves implicit dynamical approximations, so does the periodic orbit version^{1,3} of the semiclassical reaction rate theory. To overcome these dynamical limitations of periodic orbit theory one would like to construct a Hamilton-Jacobi theory for reaction rate constants analogous to that for the eigenvalue problem. Such is the object of this paper.

To motivate the form of the general result section 2 first discusses the separable case. Section 3 then shows that the expression suggested there is also the correct semiclassical result for the general, non-separable case. The relation between this new semiclassical rate theory and the earlier one^{1,3} based on periodic orbits is discussed in section 4.

2. SEPARABLE CASE

For notational simplicity, formulae below are all written without taking explicit account of total angular momentum conservation; the modifications necessary to account for this are minor and have been given before.^{1,3}

The rate constant for a bimolecular reaction, such as $A + BC \longrightarrow AB + C$, can be written in the form^{1,3}

$$k(T) = (2\pi h Q_r)^{-1} \int_0^\infty dE e^{-\beta E} N(E); \quad (1)$$

where Q_r is the partition function (per unit volume) for reactants, β is related to temperature in the usual way, and E is the total energy. The exact expression for $N(E)$ is^{1,3}

$$N(E) = \sum_{n',n} |S_{n',n}(E)|^2, \quad (2)$$

where the reactive S -matrix elements must in general be determined by carrying out a quantum mechanical scattering calculation. n ($\equiv n_1, n_2, \dots, n_{F-1}$) and n' are the quantum numbers for the $F - 1$ internal degrees of freedom of reactants and products, respectively, and F is the total number of degrees of freedom of the complete system in its overall centre of mass.

If motion along a reaction coordinate (the F 'th degree of freedom) is *separable* from the $F - 1$ internal degrees of freedom, then the S -matrix is diagonal,

$$|S_{n',n}(E)|^2 = \delta_{n',n} P(E - \epsilon_n), \quad (3)$$

where $P(E_i)$ is the one-dimensional tunnelling probability for a translational energy E_i along the reaction coordinate; ϵ_n is the energy of internal state n . Since the semiclassical approximation for $P(E_i)$ is

$$P(E_i) = [1 + e^{2\theta(E_i)}]^{-1}, \quad (4)$$

where $\theta(E_i)$ is the usual barrier penetration integral,

$$\theta(E_i) = \int dq_F \sqrt{2m[v_F(q_F) - E_i]}, \quad (5)$$

eqn (2) becomes

$$N(E) = \sum_{n=0} [1 + e^{2\theta(E - \epsilon_n)}]^{-1}, \quad (6)$$

where

$$\sum_{n=0} \equiv \sum_{n_1=0} \sum_{n_2=0} \dots \sum_{n_{F-1}=0}.$$

The action variable for the F 'th degree of freedom, n_F , is defined in the usual one-dimensional fashion (setting $\hbar = 1$),

$$\begin{aligned} (n_F + \frac{1}{2})\pi &= \int dq_F \sqrt{2m[E_t - v_F(q_F)]} \\ &= i\theta(E_t), \end{aligned} \quad (7)$$

so that the expression for $N(E)$ finally takes the form

$$N(E) = \sum_{n=0} [1 + e^{2\pi \text{Im } n_F(E,n)}]^{-1}. \quad (8)$$

To see the meaning of eqn (8) in a simple example, consider a particle first in a two-dimensional harmonic potential *well*. The total (classical) Hamiltonian is given in terms of the two action variables (i.e., semi-classical quantum numbers) in this case by

$$E(n_1, n_2) = \hbar\omega_1(n_1 + \frac{1}{2}) + \hbar\omega_2(n_2 + \frac{1}{2}). \quad (9)$$

Making the replacement $\omega_2 \rightarrow i\omega_2$ corresponds to *inverting* the harmonic potential of this degree of freedom, so that the two dimensional well becomes a *saddle point region*, a harmonic potential well in one direction and a parabolic barrier in the other. The hamiltonian in eqn (9) thus becomes

$$E(n_1, n_2) = \hbar\omega_1(n_1 + \frac{1}{2}) + i\hbar\omega_2(n_2 + \frac{1}{2}), \quad (10)$$

and one notes the important point that there are "good" action variables associated with a saddle point region of a potential surface just as there are those associated with a minimum. Rather than requiring both action variables to be integers, as is done for the semiclassical eigenvalue problem, one solves the following equation,

$$E = E(n_1, n_2), \quad (11)$$

to express n_2 as a function of E and n_1 ; for eqn (10) this is

$$n_2(E, n_1) = -\frac{1}{2} + i[\hbar\omega_1(n_1 + \frac{1}{2}) - E]/(\hbar\omega_2), \quad (12)$$

and eqn (8) in this case gives

$$N(E) = \sum_{n_1=0} \left\{ 1 + e^{\left(\frac{2\pi}{\hbar\omega_2} [\hbar\omega_1(n_1 + \frac{1}{2}) - E]\right)} \right\}^{-1}. \quad (13)$$

For this harmonic-parabolic saddle point eqn (13) is actually the exact quantum mechanical result, the "bonus" one often obtains with harmonic potential functions in semiclassical theory; i.e., if eqn (13) is substituted into eqn (1), the result is

$$k(T) = \Gamma\left(\frac{kT}{\hbar}\right) \frac{Q^\ddagger}{Q_r}, \quad (14)$$

where Q^\ddagger is the partition function of the "activated complex" and Γ is the tunnelling correction:

$$Q^\ddagger = \frac{1}{2}\hbar\omega_1\beta/\sinh(\frac{1}{2}\hbar\omega_1\beta) \quad (15a)$$

$$\Gamma = \frac{1}{2}\hbar\omega_2\beta/\sin(\frac{1}{2}\hbar\omega_2\beta). \quad (15b)$$

The next section shows that eqn (8), derived here for the separable case, is also the correct semiclassical expression for $N(E)$ for the general, non-separable case. In the non-separable situation, however, the total (classical) Hamiltonian is of course not a separable function of the F "good" action variables as in eqn (10), and the

partition function for the activated complex and the tunnelling correction thus do not enter as separate factors as they do in eqn (14), and to construct the function $E(n_1, n_2, \dots, n_F)$ is the primary task of the theory. It can be done, for example, using the procedure devised by Chapman, Garrett, and Miller⁹ for solving the Hamilton-Jacobi equation in action-angle variables. (Interestingly, it does not appear that the approach of Eastes and Marcus¹⁰ would be possible because the classical trajectories about a saddle point are not quasi-periodic.) One action variable, n_F say, is identified as the one associated with the "reactive direction", and one then solves the equation

$$E = E(n_1, n_2, \dots, n_F) \quad (16)$$

to obtain $n_F(E, n_1, n_2, \dots, n_{F-1})$. Eqn (8) then gives $N(E)$ and eqn (1) $k(T)$.

3. NON-SEPARABLE CASE

Another formally exact expression for the rate constant, completely equivalent to eqn (1) and (2), is¹¹

$$k(T) = Q_r^{-1} \text{tr}[e^{-\beta H} \delta(f) \dot{f} \mathcal{P}], \quad (17)$$

where f is an operator that defines a surface which divides reactants and products, \dot{f} is the Heisenberg time derivative of f ,

$$\dot{f} = \frac{i}{\hbar} [H, f], \quad (18)$$

and \mathcal{P} is a projection operator that projects onto all states which have evolved in the infinite past from reactants.¹¹ It is easy to see that eqn (17) can be written as eqn (1) with $N(E)$ given by

$$N(E) = 2\pi\hbar \text{tr}[\delta(E - H) \delta(f) \dot{f} \mathcal{P}], \quad (19)$$

an expression formally equivalent to eqn (2) but more useful for present purposes. The plan is to evaluate eqn (19) semiclassically.

For notational simplicity consider the case of two degrees of freedom, i.e., a collinear $A + BC \rightarrow AB + C$ reaction. If n_1 and n_2 are the two "good" action variables, then the quantum mechanical states $|n_1 n_2\rangle$ are eigenstates of the total hamiltonian,

$$H|n_1 n_2\rangle = E(n_1, n_2) |n_1 n_2\rangle. \quad (20)$$

Evaluating the trace in eqn (19) in this representation gives

$$N(E) = 2\pi\hbar \sum_{n_1} \int dn_2 \delta[E - E(n_1, n_2)] \langle n_1 n_2 | \delta(f) \dot{f} \mathcal{P} | n_1 n_2 \rangle, \quad (21)$$

where

$$\langle n_1 n_2 | \delta(f) \dot{f} \mathcal{P} | n_1 n_2 \rangle = \int_{-\pi}^{\pi} dq_1 \int_{-\infty}^{\infty} dq_2 \psi_{n_1 n_2}(q_1, q_2)^* \delta(f) \dot{f} \mathcal{P} \psi_{n_1 n_2}(q_1, q_2); \quad (22)$$

q_1 and q_2 are the angle variables conjugate to n_1 and n_2 , and $E(n_1, n_2)$ is the total (classical) hamiltonian, in general non-separable, expressed in terms of the "good" action variables. [Superposition of amplitudes from the different 2π intervals of q_1 leads to n_1 being integral, and this is why the domain of q_1 is limited to $(-\pi, \pi)$ rather

than $(-\infty, \infty)$.^{12]} Since (n_1, n_2) and (q_1, q_2) are conjugate variables, the semiclassical wavefunctions are¹²

$$\psi_{n_1 n_2}(q_1, q_2) = \sqrt{(2\pi)^{-2}} e^{i(n_1 q_1 + n_2 q_2)}, \quad (23)$$

so that eqn (21) becomes

$$\langle n_1 n_2 | \delta(f) \hat{f} \mathcal{P} | n_1 n_2 \rangle = \left[(2\pi)^{-1} \int_{-\pi}^{\pi} dq_1 e^{-in_1 q_1} e^{in_1 q_1} \right] \times \left[(2\pi)^{-1} \int_{-\infty}^{\infty} dq_2 e^{-in_2 q_2} \delta(f) \hat{f} \mathcal{P} e^{in_2 q_2} \right], \quad (24)$$

where the fact has been used that n_1 is real (an integer) and that n_2 may not be, and where f has been taken to involve only the (n_2, q_2) degree of freedom. (The final result cannot depend on the specific choice for f .)¹¹ The first factor in eqn (24) is clearly unity, and the second factor is essentially a one-dimensional flux for the (n_2, q_2) degree of freedom that depends parametrically on n_1 . The flux through a one-dimensional barrier has the standard form of the frequency ν of the (n_2, q_2) motion,

$$\nu = \frac{\partial E(n_1, n_2)}{\partial n_2} \bigg/ 2\pi\hbar, \quad (25)$$

multiplied by the tunnelling, or transmission probability P ,

$$P = (1 + e^{2\pi \operatorname{Im} n_2})^{-1} = e^{-2\pi \operatorname{Im} n_2} (1 + e^{-2\pi \operatorname{Im} n_2})^{-1}. \quad (26)$$

Eqn (24) thus becomes

$$\langle n_1 n_2 | \delta(f) \hat{f} \mathcal{P} | n_1 n_2 \rangle = (2\pi\hbar)^{-1} \frac{\partial E(n_1, n_2)}{\partial n_2} (1 + e^{2\pi \operatorname{Im} n_2})^{-1}. \quad (27)$$

Before proceeding to the final result, it is interesting to note the simple illuminating interpretation eqn (27) has if one expands the tunnelling probability in a geometric series:

$$P = e^{-2\theta} - e^{-4\theta} + e^{-6\theta} \dots \quad (28a)$$

where

$$\theta = \pi \operatorname{Im} n_2. \quad (28b)$$

Eqn (27) then reads

$$\langle n_1 n_2 | \delta(f) \hat{f} \mathcal{P} | n_1 n_2 \rangle = \nu e^{-2\theta} - \nu e^{-4\theta} + \nu e^{-6\theta} \dots, \quad (29)$$

and each term can be thought of as the flux contribution of one of the classical trajectories that comes from reactants and crosses the dividing surface $f=0$. The trajectories (classical trajectories in complex time¹²) are pictured in fig. 1; the reactive ones contribute positive flux and the non-reactive ones negative flux. The Appendix shows how eqn (29) results directly from eqn (24) if one makes a particular choice for f .

The final expression is now obtained by substituting eqn (27) into (21),

$$N(E) = 2\pi\hbar \sum_{n_1} \int dn_2 \delta[E - E(n_1, n_2)] (2\pi\hbar)^{-1} \frac{\partial E(n_1, n_2)}{\partial n_2} (1 + e^{2\pi \operatorname{Im} n_2})^{-1}, \quad (30)$$

which gives

$$N(E) = \sum_{n_1=0} [1 + e^{2\pi \operatorname{Im} n_2(E, n_1)}]^{-1}, \quad (31)$$

where $n_2(E, n_1)$ is determined by $E = E(n_1, n_2)$. This is eqn (8) for the case $F = 2$.

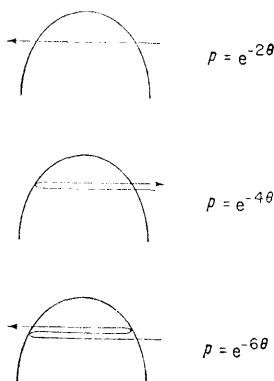


FIG. 1.— Sketch of the potential energy along a reaction coordinate through a saddle point region and the different classical trajectories [in complex time—see ref. (12)] that come from reactants and pass through the saddle point region at least once. P is the probability associated with the trajectory in each case.

4. RELATION TO PERIODIC ORBIT THEORY

It is easy to see how the periodic orbit expression¹ for the rate constant is recovered if one uses eqn (8) with the periodic orbit quantum condition⁶ for determining $E(n_1, n_2, \dots, n_F)$. Periodic orbit theory determines $E(n_1, n_2, \dots, n_F)$ implicitly by the equation⁶

$$\Phi(E) - \Phi'(E) \sum_{i=1}^{F-1} \hbar \omega_i(E) (n_i + \frac{1}{2}) = 2\pi \hbar (n_F + \frac{1}{2}), \quad (32)$$

where $\Phi(E)$ is the action integral for one pass around the periodic orbit and $\{\omega_i(E)\}$ are the $F - 1$ stability frequencies. For the case of a saddle point Φ is pure imaginary,

$$\Phi(E)/\hbar \equiv 2i\theta(E); \quad (33)$$

so that eqn (32) gives

$$2\pi (n_F + \frac{1}{2}) = i[2\theta(E) - 2\theta'(E) \sum_{i=1}^{F-1} \hbar \omega_i(E) (n_i + \frac{1}{2})],$$

or

$$2\pi \operatorname{Im} n_F(E, n_1, \dots, n_{F-1}) = 2\theta(E) - 2\theta'(E) \sum_{i=1}^{F-1} \hbar \omega_i(E) (n_i + \frac{1}{2}), \quad (34)$$

which, with eqn (8), is the expression obtained¹ via periodic orbit theory for $N(E)$.

5. CONCLUDING REMARKS

This paper has shown how a semiclassical approximation for the rate constant for a bimolecular reaction with a single activation barrier can be constructed in terms of the complete set of "good" action variables associated with the saddle point of the potential energy surface. This new expression for the rate constant bears the same relation to the earlier semiclassical rate expression in terms of periodic orbits that the old quantum theory for semiclassical eigenvalues bears to the periodic orbit quantization rule. Since the expressions based on the "good" action variables

of Hamilton-Jacobi theory should in general be more accurate than their periodic orbit approximations, this new expression for the rate constant is expected to be more accurate than the one based on periodic orbit theory.

APPENDIX

If in eqn (24) f is chosen as

$$f = -\sin q_2, \quad (\text{A1})$$

then the effect of \mathcal{P} is simply to require $q_2 > 0$. The operator \hat{f} is

$$\hat{f} = \frac{\partial f}{\partial q_2} \frac{\partial E(n_1, n_2)}{\partial n_2} \Big|_{n_2 = (n_2)_{\text{op}}} \quad (\text{A2})$$

$$\text{where } (n_2)_{\text{op}} = \frac{1}{i} \frac{\partial}{\partial q_2}; \quad (\text{A3})$$

thus

$$\hat{f} e^{in_2 q_2} = -\cos q_2 \frac{\partial E(n_1, n_2)}{\partial n_2} e^{in_2 q_2}. \quad (\text{A4})$$

This then gives (setting $\hbar = 1$)

$$\begin{aligned} \langle n_1 n_2 | \delta(f) \hat{f} \mathcal{P} | n_1 n_2 \rangle &= (2\pi)^{-1} \frac{\partial E(n_1, n_2)}{\partial n_2} \int_{0+}^{\infty} dq_2 \delta(\sin q_2) (-\cos q_2) e^{-2q_2 \text{Im } n_2} \\ &= (2\pi)^{-1} \frac{\partial E(n_1, n_2)}{\partial n_2} [e^{-2\pi \text{Im } n_2} - e^{-4\pi \text{Im } n_2} + e^{-6\pi \text{Im } n_2} \dots] \\ &= (2\pi)^{-1} \frac{\partial E(n_1, n_2)}{\partial n_2} e^{-2\pi \text{Im } n_2} (1 + e^{-2\pi \text{Im } n_2})^{-1} \\ &= (2\pi)^{-1} \frac{\partial E(n_1, n_2)}{\partial n_2} (1 + e^{2\pi \text{Im } n_2})^{-1}, \end{aligned} \quad (\text{A5})$$

which is eqn (27).

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