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SEMICLASSICAL METHODS IN CHEMICAL DYNAMICS

W.H. Miller

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# SEMICLASSICAL METHODS IN CHEMICAL DYNAMICS

William H. Miller

Department of Chemistry, University of California, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

A general semiclassical (multidimensional WKB-type) approximation to quantum mechanics is reviewed. The principal feature of the approach is that it is able to incorporate the exact classical mechanics of the system and also the quantum principle of superposition. Applications to inelastic and reactive scattering, and to statistical mechanics and reaction rates are discussed.

## 1. Introduction

The use of semiclassical methods in chemical and molecular problems has become so pervasive over the last twenty years that it is somewhat intimidating to attempt a short review with the present title.<sup>1</sup> Since a comprehensive review is impossible, I have chosen several examples which illustrate the variety of quantum phenomena that semiclassical theory is able to describe correctly.

Perhaps the most dramatic quantum phenomenon is that of quantization itself, the fact that only discrete values of the energy are allowed for a system whose motion is bounded. The grandfather of all semiclassical descriptions of quantization is the Bohr model of the hydrogen atom and its generalization which became known as the Old Quantum Theory.<sup>2</sup> For a diatomic molecule with potential function  $V(r)$ , for example, the Bohr-Sommerfeld (or WKB) quantization condition is

$$(n + 1/2)\pi = \int_{r_1}^{r_2} dr \sqrt{\frac{2\mu}{\hbar^2} \left[ E - V(r) - \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} \right]} \quad (1.1)$$

where  $(r_1, r_2)$  are the two classical turning points in the effective potential ( $V(r)$  plus the centrifugal term). Eq. (1.1) is an implicit equation for the energy levels  $E(n, \ell)$  in terms of the vibrational and rotational quantum numbers.

For molecular systems, i.e., diatomic molecules, Eq. (1.1) is actually quite accurate: ground state energies are given to better than 1% accuracy even for

H<sub>2</sub>, and more accurately for heavier systems and for excited states. Furthermore, it is possible to invert Eq. (1.1) and construct the potential function V(r) in terms of experimentally determined energy levels E(n,λ). This Rydberg-Klein-Rees<sup>3</sup> method produces potential curves that are essentially the exact (errors < 1 meV) Born-Oppenheimer potential.

The generalization of this quantization rule to multi-dimensional systems, those with more than one degree of freedom (and which are not integrable), is non-trivial, primarily because the classical trajectories of the system cannot be determined analytically. The Old Quantum Theory laid out the correct formal prescription for determining the semiclassical eigenvalues<sup>2b</sup> even though computers were not then available to make it possible to carry out calculations except in low order perturbation theory. The essential task is to express the classical Hamiltonian of the system in terms of its "good" action-angle variables and then to require the "good" action variables to be integers (or half integers). Because lasers are making it increasingly possible to access highly vibrationally excited states of polyatomic molecules, there is currently a great deal of effort in the chemical physics community in developing numerical procedures for determining semiclassical eigenvalues of non-separable multidimensional systems. A variety of methods have been reported in recent years.<sup>4</sup>

The remainder of the paper discusses the semiclassical description of inelastic and reactive scattering (Section 2) and of statistical operators and Boltzmann rate constants (Section 3).

## 2. The Classical S-Matrix

The basic semiclassical approximation is the stationary phase approximation to the Feynman path integral representation of the quantum time evolution operator:<sup>5</sup>

$$\langle \mathbf{q}_2 | e^{-iH(t_2-t_1)/\hbar} | \mathbf{q}_1 \rangle = \sum \left[ \frac{1}{(2\pi i \hbar)^F} \left| \frac{\partial^2 S(\mathbf{q}_2, \mathbf{p}_1)}{\partial \mathbf{p}_1^2} \right| \right]^{-1/2} e^{iS(\mathbf{q}_2, \mathbf{q}_1)/\hbar} \quad (2.1)$$

where F is the number of degrees of freedom, S<sub>2</sub>(q<sub>2</sub>, p<sub>1</sub>) is the coordinate at time t<sub>2</sub> that results from a classical trajectory with initial condition (p<sub>1</sub>, q<sub>1</sub>) at time t<sub>1</sub>, the sum is over all values of p<sub>1</sub> that (for fixed q<sub>1</sub>) satisfy the equation

$$q_2(q_1, p_1) = q_2 \quad , \quad (2.2)$$

and  $\phi$  is the classical action along this trajectory

$$\phi(q_2, q_1) = \int_{t_1}^{t_2} dt [p(t) \cdot \dot{q}(t) - H(p, q)] \quad . \quad (2.3)$$

In a momentum representation the semiclassical expression is<sup>1b</sup>

$$\langle p_2 | e^{-iH(t_2 - t_1)\hbar} | p_1 \rangle = \sum [(-2\pi i\hbar)^F \left| \frac{\partial p_2(q_1, p_1)}{\partial q_1} \right|]^{-1/2} e^{i\phi(p_2, p_1)\hbar} \quad , \quad (2.4)$$

where  $p_2(p_1, q_1)$  is the momentum at time  $t_2$  that results from the classical trajectory with the indicated initial conditions, the sum is over all values of  $q_1$  that (for fixed  $p_1$ ) satisfy the equation

$$p_2(p_1, q_1) = p_2 \quad , \quad (2.5)$$

and here the action integral is

$$\phi(p_2, p_1) = \int_{t_1}^{t_2} dt [-q(t) \cdot \dot{p}(t) - H(p, q)] \quad . \quad (2.6)$$

Eqs. (2.1) - (2.6) apply for any set of canonically conjugate coordinates and momenta; i.e., they are invariant to a canonical transformation.<sup>1b</sup>

From the propagator it is not hard to construct the semiclassical expression for the S-matrix for a multichannel scattering system.<sup>1b,1c,6</sup> For a collinear atom-diatom collision system, for example, the classical Hamiltonian is of the form

$$H((R, P), (n, q)) = \frac{P^2}{2\mu} + \epsilon(n) + V(R, n, q) \quad , \quad (2.7)$$

where  $(R, P)$  are the coordinate and momentum for relative translation of the atom and diatom,  $(n, q)$  are the action-angle variables for the free diatom, and  $V$  is the interaction which vanishes as  $R \rightarrow \infty$ .  $\epsilon(n)$  is the MB eigenvalue function of the free diatom. To construct this "classical S-matrix" for

vibrationally inelastic collisions one must factor out the energy-conserving delta function from the semiclassical propagator. The result of this gives the classical S-matrix as

$$S_{n_2, n_1}(E) = \sum \left[ -2\pi i M \frac{\partial n_2(q_1, n_1; E)}{\partial q_1} \right]^{-1/2} e^{i\phi(n_2, n_1; E)}, \quad (2.8)$$

where  $n_2(q_1, n_1; E)$  is the final value of the action (as  $t_2 \rightarrow \infty$ ) for the trajectory with initial conditions  $(q_1, n_1)$  and

$$R_1 = \text{arbitrarily large}$$

$$P_1 = -\sqrt{2\mu[E - \epsilon(n_1)]}$$

The sum is over all roots of the equation (for fixed  $n_1$  and  $E$ )

$$n_2(q_1, n_1; E) = n_2 \text{ (an integer)} \quad (2.9)$$

and the action integral  $\phi$  is

$$\phi(n_2, n_1; E) = \int_{-\infty}^{\infty} dt [-R(t)\dot{\phi}(t) - q(t)\dot{n}(t)] \quad (2.10)$$

The initial action  $n_1$  is also taken to be an integer, the initial vibrational state.

An important feature of Eqs. (2.8) - (2.10) is that the function  $n_2(q_1)$  (disregarding the dependence on  $n_1$  and  $E$  for the moment) is a periodic function of  $q_1$ ; cf. Figure 1.

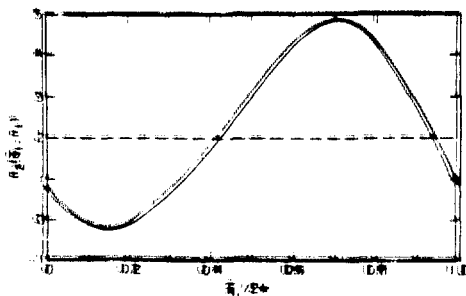


FIGURE 1  
Quantum number function for vibrational excitation,  $n_1 = 1$ .

Eq. (2.9) thus has an even number of roots, two in the generic case indicated in Figure 1. The classical S-matrix, Eq. (2.8), then has two terms so that interference structure appears in the transition probability

$$P_{n_2, n_1}(E) = |S_{n_2, n_1}(E)|^2 \quad . \quad (2.11)$$

Typical values for these are shown in Figure 2.

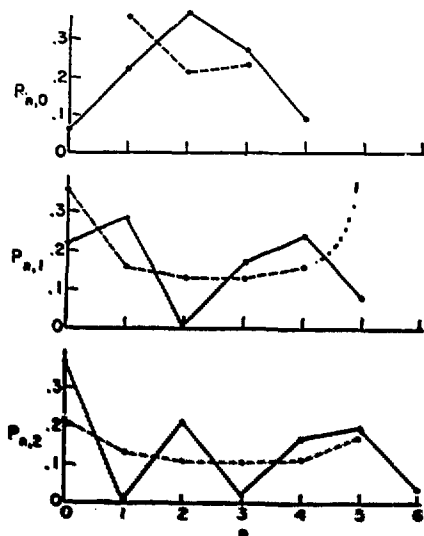


FIGURE 2

Vibrational transition probabilities for initial states  $n_1=0,1$ , and 2. The dashed lines connect the completely classical values, and the solid lines the semiclassical values which show interference effects.

There are thus interference effects in internal state distributions quite analogous to interference effects in angular distributions (differential cross sections), and they originate because there is more than one classical trajectory which connects the specific initial and final states. Because the "quantum number function"  $n_2(q_1)$  -- which here plays the same role as the classical deflection function  $\alpha(b)$  in elastic scattering -- has a maximum (and a minimum), there are "rainbow" maxima in the distribution of final vibrational states, analogous to rainbows in angular distributions.<sup>10</sup>

Other interesting quantum features are revealed if the interaction potential displays discrete symmetries.<sup>6b,7</sup> This is best illustrated by considering the collision of a plane rotor with an atom. The Hamiltonian has the same form as

Eq. (2.7), where  $n$  is now the angular momentum quantum number and designated  $j$ , and the angle variable  $q$  is the physical angle of orientation of the rotor. Eqs. (2.8) - (2.11) also apply (with  $n$  replaced by  $j$ ).

If the rotor is a homonuclear diatomic molecule, then the transformation

$$q \rightarrow q + \pi \quad (2.12)$$

interchanges the identical atoms and thus leaves the system unchanged. The quantum number function  $j_2(q_1)$  thus has the symmetry

$$j_2(q_1 + \pi) = j_2(q_1) \quad (2.13)$$

and is therefore periodic in the interval  $(0, \pi)$ . For every root to the equation

$$j_2(q_1) = j_2 \quad (2.14)$$

in the interval  $(0, \pi)$  there is thus a symmetrically related root in the interval  $(\pi, 2\pi)$ . It is easy to see that the action integral, Eq. (2.10), changes as follows with the transformation  $q_1 \rightarrow q_1 + \pi$

$$\phi(j_2(q_1 + \pi), j_1) = \phi(j_2(q_1), j_1) - \pi[j_2(q_1) - j_1] \quad .$$

so that the classical S-matrix, Eq. (2.8), takes the form

$$S_{j_2, j_1} = [1 + e^{-i\pi\Delta j}] \sum \left[ -2\pi i \hbar \frac{\partial j_2}{\partial q_1} \right] e^{-i/2 \pi (j_2, j_1) \hbar} \quad (2.15)$$

$$\Delta j \equiv j_2 - j_1$$

where here the sum is only over roots of Eq. (2.14) in the primary interval  $(0, \pi)$ .

Eq. (2.15) reveals the selection rule

$$\Delta j = 0, \pm 2, \pm 4, \dots \quad (2.16)$$

for rotationally inelastic transitions of a homonuclear diatomic molecule, and one sees that it results from interference of symmetrically related trajectories. Classical trajectories exist for which  $\Delta j$  is odd, but

destructive interference gives no net probability amplitude for such transitions.

One can easily generalize the above discussion to consider the case of a rotor with M-fold rotational symmetry. The quantum number function in this case is periodic in the interval  $(0, 2\pi/M)$  and has the symmetry

$$j_2(q_1) = j_2(q_1 + \frac{2\pi}{M}) = j_2(q_1 + \frac{4\pi}{M}) = \dots = j_2(q_1 + 2\pi(\frac{M-1}{M})) \quad (2.17)$$

The classical S-matrix then has the same form as Eq. (2.15) with the "symmetry factor" replaced by

$$\begin{aligned} & [1 + e^{-i\frac{2\pi}{M}(\Delta j)} + e^{-i\frac{4\pi}{M}(\Delta j)} + \dots] \\ & = \sum_{k=0}^{M-1} e^{-i\frac{2\pi k}{M}(\Delta j)} = \frac{1 - e^{-2i\pi\Delta j}}{1 - e^{-2i\pi\Delta j/M}} \quad (2.18) \end{aligned}$$

and the sum in the second factor of Eq. (2.15) is only over roots in the primary interval  $(0, 2\pi/M)$ . Eq. (2.18) reveals the selection rule

$$\Delta j = 0, \pm M, \pm 2M, \dots \quad ; \quad (2.19)$$

i.e., the interference of symmetrically related trajectories is completely destructive if  $\Delta j/M$  is non-integral.

This analysis also shows the correct limit if there is continuous rotational symmetry. This is the limit that  $M \rightarrow \infty$ , in which  $j_2(q_1)$  becomes completely independent of  $q_1$ . The "selection rule" in this limit is

$$\Delta j = 0, \pm 1, \dots \quad ; \quad (2.20)$$

thus only elastic transitions,  $j_2 = j_1$ , are possible, i.e., one has conservation of the rotational angular momentum  $j$ . It is well-known in classical mechanics how to deal with such continuous symmetries, for they correspond to a conserved action variable and thus produce a constant of the motion. The semiclassical analysis shows how to deal with discrete symmetries,



e.g., a 2- or 3- fold symmetric rotor, one for which angular momentum is not conserved but for which there is still quantum mechanical manifestation of the symmetry, i.e., a selection rule.

The above description is particularly useful in showing how to deal with weakly broken symmetries, which produce weak selection rules. The molecule CO, for example, is an "almost homonuclear" molecule; i.e., the odd anisotropy in its interaction with other molecules is smaller than the even anisotropy. The rotational quantum number function, though not identical in  $(0, \pi)$  and  $(\pi, 2\pi)$ , is nevertheless similar; cf. Figure 3.

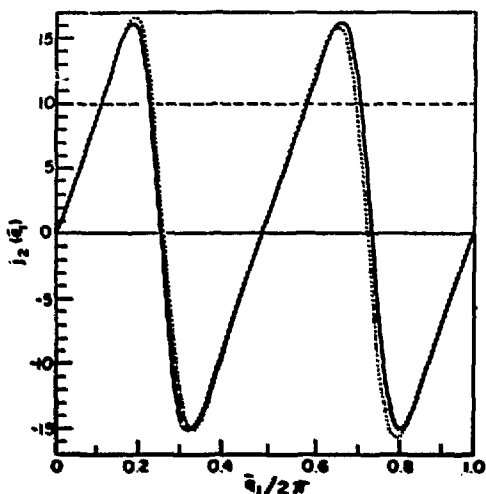


FIGURE 3

Quantum number function for rotational excitation of a diatomic molecule by collision with an atom. The solid curve is for a homonuclear diatom and the dotted curve for an "almost" homonuclear molecule.

Odd  $\Delta j$  transitions are thus not completely eliminated by destructive interference, but their probabilities are much smaller than for even  $\Delta j$ .

Finally, it should be noted that this semiclassical theory is also able to describe classically forbidden processes, <sup>1b, 1c, 8</sup> a kind of generalized tunneling phenomena analogous to tunneling through barriers in one dimension. An example of this is the 1-5 vibrational transition shown in Figures 1 and 2. For  $m_1 = 1$  there is no real root to the equation

$$m_2(q_1) = 5$$

((2.27))

but there are in general complex roots. (The quantum number function  $n_2(q_1)$  is obtained for complex  $q_1$  most generally by actually integrating the classical equations of motion with complex initial conditions. Alternatively, it is sometimes possible to obtain  $n_2(q_1)$  at complex  $q_1$  by analytic continuation via Padé approximants using only real values of  $q_1$ .) The action integral  $\phi(n_2, n_1)$  is complex in this case, and the probability of such a transition is

$$P_{n_2 \rightarrow n_1} = \left[ 2\pi\hbar \left| \frac{\partial n_2}{\partial q_1} \right| \right]^{-1} e^{-2\text{Im}\phi(n_2, n_1)/\hbar} \quad (2.22)$$

with  $\text{Im}\phi > 0$ . If  $q_1$  is a complex root of Eq. (2.21), then  $q_1^*$  also is, and the action integral for it has  $\text{Im}\phi < 0$ . This would lead to an exponentially large transition probability and is clearly unphysical. The situation is analogous to the exponentially growing and decaying WKB wavefunction in classically forbidden regions, and a similar analysis rejects the unphysical term.

This analytic continuation of classical mechanics is also useful for describing barrier tunneling (e.g., chemical reactions) on multidimensional potential energy surfaces.<sup>1b,1c,8c</sup> Here the situation is more subtle conceptually than the above non-reactive case because at energies below the potential barrier all classical trajectories are non-reactive; there is thus no reactive quantum number  $n_2(q_1)$  to analytically continue. The resolution of the difficulty is illustrated by considering the case of one-dimensional barrier tunneling (cf. Figure 4).

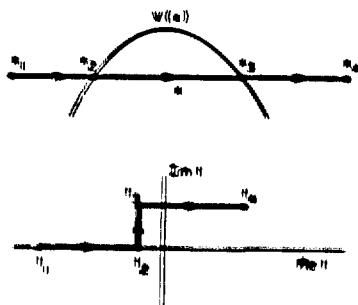


FIGURE 4

Sketch of a one-dimensional classical trajectory  $x(t)$ , and the appropriate complex time contour, which tunnels through a potential barrier at an energy below  $E_0$ . ( $x_k \equiv x(t_k)$ ,  $k=1,2,3,4,\dots$ )

where it is indicated that by integrating the classical equations of motion along complex time contours one can find classical trajectories that react (i.e., go through the barrier) at energies below it. Analogously, for a collinear  $A+BC(n_1) \rightarrow AB(n_2)+C$  reaction there exist reactive trajectories (integrated along complex time contours) at energies below the potential barrier, and by varying the initial angle variable  $q_1$  one can also satisfy the boundary condition Eq. (2.9), i.e., that the vibrational action of the final diatom be integral. Figure 5 shows two such reactive trajectories (at two different energies) for the  $H+H_2 \rightarrow H_2+H$  reaction. The reaction probability is still given by Eq. (2.22).

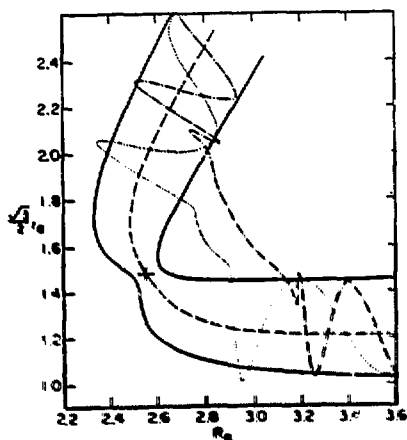


FIGURE 5

Reactive (i.e., tunneling) trajectories along a complex time contour for the  $H+H_2 \rightarrow H_2+H$  reaction. The dash-dot curve is the trajectory for an energy far below the barrier maximum and the dotted curve for an energy only slightly below the barrier. The solid curves are equipotential contours of the potential energy surface and the dashed curve the steepest descent path from reactants to products.

### 3. Semiclassical Statistical Mechanics and Reaction Rates

#### A. Semiclassical Boltzmann Operator

By making the transcription  $\hbar \rightarrow \hbar_s$  in Eq. (2.11) one immediately obtains a semiclassical approximate to matrix elements of the Boltzmann operator.<sup>9</sup> It is useful to use the (real) variable  $\tau$ , which is related to the time  $t$  by

$$\tau = \hbar t \quad , \quad (3.1)$$

and also to specialize to the case of cartesian coordinates  $x$ , so that the

Hamiltonian has the generic form

$$H(p, x) = \frac{p^2}{2m} + V(x) \quad .$$

Then if  $\bar{p}$  is the real quantity

$$\bar{p}(\tau) = m\dot{x}'(\tau) \quad , \quad (3.2)$$

-- i.e.,  $\bar{p}(\tau) = -ip(t)$ , where  $p$  is the (pure imaginary) momentum -- Eqs. (2.1)  
- (2.3) give

$$\langle x_2 | e^{-\beta H} | x_1 \rangle = \int \left[ (2\pi\hbar)^F \left| \frac{\partial x_2}{\partial \bar{p}_1} \right| \right]^{-1/2} e^{-\phi(x_2, x_1; \hbar\beta)/\hbar} \quad , \quad (3.3)$$

where

$$\phi(x_2, x_1; \hbar\beta) = \int_0^{\hbar\beta} d\tau \left[ \frac{\bar{p}(\tau)^2}{2m} + V(x(\tau)) \right] \quad , \quad (3.4)$$

and  $x_2(x_1, \bar{p}_1)$  is the value of the coordinate at imaginary time  $\tau = \hbar\beta$  that results from a classical trajectory with initial conditions

$$x(0) = x_1 \quad , \quad \dot{x}'(0) = \bar{p}_1/m \quad . \quad (3.5)$$

The sum in Eq. (3.3) is over values of  $\bar{p}_1$  that satisfy (for fixed  $x_1$ )

$$x_2(x_1, \bar{p}_1) = x_2 \quad . \quad (3.6)$$

Because the time is pure imaginary it is easy to see that the equations of motion in this case have the form

$$m \frac{d^2 x(\tau)}{d\tau^2} = - \frac{\partial V(x)}{\partial x} \quad , \quad (3.7)$$

and

$$\overline{p}(\tau) \equiv m\dot{x}'(\tau) \quad (3.8)$$

Eq. (3.7) shows that the classical motion in the  $\tau$ -variable (imaginary time) is the same as ordinary classical motion in real time in the inverted potential function ( $V \rightarrow -V$ ). If the potential  $V$  is a potential well, then the classical motion used in constructing the semiclassical Boltzmann operator is that of a particle moving over a potential barrier, and conversely if  $V$  is a potential barrier, the classical motion on the up-side-down potential is as that in a potential well. One also notes that Eqs. (3.3) - (3.7) involve only real-valued quantities.

An important special case of Eq. (3.3) is the diagonal matrix element  $x_2 = x_1$ , which is the equilibrium particle density

$$\rho_B(x_1) \equiv \langle x_1 | e^{-\beta H} | x_1 \rangle \quad (3.9)$$

This semiclassical Boltzmann density is generally much more accurate than the Wigner-Kirkwood semiclassical correction to the classical density,

$$\rho_{CL}(x_1) = \left( \frac{m}{2\pi\hbar^2\beta} \right)^{F/2} e^{-\beta V(x_1)} \quad (3.10)$$

An even more accurate and easier-to-use result is obtained for the particle density by first using the quantum identity

$$\rho_B(x_1) = \int dx_2 \langle x_2 | e^{-\frac{\beta H}{2}} | x_2 \rangle^2 \quad (3.11)$$

and then invoking the semiclassical approximation for the integrand. Changing integration variables from  $x_2$  to  $\overline{p}_1$  gives

$$\rho_B(x_1) = (2\pi\hbar)^{-F} \int d\overline{p}_1 e^{-\frac{2}{\hbar} \left( \overline{p}_1 \cdot x_1 - \frac{\beta E}{2} \right)} \quad (3.12)$$

where

$$\phi(\bar{p}_1, x_1; \frac{\hbar\beta}{2}) = \int_0^{\frac{\hbar\beta}{2}} d\tau \left[ \frac{\bar{p}(\tau)^2}{2m} + V(x(\tau)) \right] \quad ; \quad (3.13)$$

$x(\tau)$  is the solution of Eq. (3.7) with initial condition (3.5). Eqs. (3.12) - (3.13) are easy to apply because they involve only the initial conditions of the trajectory  $x(\tau)$ .

### B. Semiclassical Transition State Theory

The thermal (i.e., Boltzmann average over reactant states) rate constant for a reaction can be expressed as<sup>10</sup>

$$k_{b \rightarrow a} Q_a = \text{tr}(e^{\beta H} F P) \quad , \quad (3.14)$$

where  $Q_a$  is the partition function for reactants "a",  $F$  is a flux operator,

$$F = \delta(s) \dot{s} \quad (3.15)$$

$s$  is the reaction coordinate, and  $P$  is a projection operator which projects into all states that have evolved from reactants in the infinite past. The transition state approximation corresponds to the following replacement

$$F P = \frac{1}{2} \delta(s) |\dot{s}| \quad (3.16)$$

and the semiclassical approximation for the Boltzmann operator converts Eq. (3.14) into<sup>11</sup>

$$k_{b \rightarrow a} Q_a = \int dq_1 \langle q_2 | e^{-\beta H} | q_1 \rangle \frac{1}{2} \delta(s) |\dot{s}| \quad .$$

$$\langle q_2 | e^{-\beta H} | q_1 \rangle = \left[ \left| \frac{\partial q_2}{\partial p_1} \right| F \right]_{q_2=q_1}^{-1/2 - \phi(q_1, q_1; \hbar\beta)} \quad . \quad (3.17)$$

and the trace (the integral over  $q_1$ ) is to be evaluated via the stationary

phase approximation. The stationary phase condition is

$$\frac{\partial}{\partial q_1} \phi(q_1, q_1; \hbar\beta) = \bar{p}_2 - \bar{p}_1 = 0 \quad , \quad (3.18)$$

which means that points  $q_1$  which contribute to the integral must lie on a classical trajectory such as

$$\begin{aligned} q_2 &= q_1 \\ \bar{p}_2 &= \bar{p}_1 ; \end{aligned} \quad (3.19)$$

i.e., the classical trajectory must be a periodic orbit with period  $\hbar\beta$ . This result that the tunneling takes place along a periodic orbit on the inverted potential surface has been discovered independently in other fields under the term "instanton methods".<sup>12</sup>

It is useful to express the final result of the calculation<sup>11</sup> as a Boltzmann average of the microcanonical result,

$$k_{b \rightarrow a} Q_a = \frac{1}{2\pi\hbar} \int dE e^{-\beta E} P(E) \quad , \quad (3.20)$$

where the microcanonical cumulative reaction probability  $P(E)$  is given by

$$P(E) = \sum_{k=1}^{\infty} (-1)^{k-1} e^{-k\phi(E)/\hbar} \prod_{i=1}^{F-1} \frac{1}{2\sinh[ku_i(E)/2]} \quad . \quad (3.21)$$

Here  $\phi(E)$  is the action integral,

$$\phi(E) = \int_0^{T(E)} dt \bar{p}(\tau) \cdot \dot{\bar{q}}(\tau) \quad . \quad (3.22)$$

along the periodic orbit (on the inverted potential surface) at energy  $E$ ,  $T(E)$  is the period of the periodic orbit, and  $\{u_i(E)\}$ ,  $i=1, \dots, F-1$ , are the stability parameters of the periodic trajectory. The product of factors in Eq. (3.21) involving the stability parameters comes from the Jacobian factor in the semiclassical propagator and is a result of path-integrating over harmonic

fluctuations about the classical path (periodic orbit in this case). The sum in (3.21) is over multiple passes over the periodic orbit; if the tunneling probability is small, then only the  $k=1$  term need be retained.

The nature of the above result is made especially clear by expanding the sinh functions in Eq. (3.21) using the identity

$$\frac{1}{2\sinh(ku_1/2)} = \sum_{n_1=0}^{\infty} e^{-(n_1+1/2)ku_1} \quad ; \quad (3.23)$$

the sum over  $k$  (multiple passes over the periodic orbit) can then be carried out, giving

$$P(E) = \sum_{n=0}^{\infty} \frac{1}{1 + \exp[\phi(E)/M + \sum_{i=1}^{F-1} (n_i+1/2)u_i(E)]} \quad . \quad (3.24)$$

Upon defining the stability frequencies,  $\omega_i(E) \equiv u_i(E)/T(E)$ , and noting that  $T(E) = -\phi'(E)$ , the exponent in Eq. (3.24) becomes

$$\frac{1}{M} [\phi(E) - \phi'(E) \sum_{i=1}^{F-1} (n_i+1/2)M\omega_i(E)] \quad . \quad (3.25)$$

which to terms of order  $M$  is the same as

$$\frac{1}{M} \phi(E_n) \quad , \quad (3.26)$$

with

$$E_n \equiv E - \sum_{i=1}^{F-1} (n_i+1/2)M\omega_i(E) \quad . \quad (3.27)$$

Using Eqs. (3.26) and (3.27) in Eq. (3.24) gives the final expression for the cumulative reaction probability



$$P(E) = \sum_{n=0}^{\infty} P_1(E_n) \quad , \quad (3.28)$$

where  $P_1$  is the usual one-dimensional WKB tunneling probability (which is uniformly valid for small or large tunneling probabilities),

$$P_1(E_n) = [1 + e^{\phi(E_n)/\hbar}]^{-1} \quad . \quad (3.29)$$

$E_n$  of Eq. (3.27) is interpreted as the one-dimensional energy in motion along the periodic orbit (the reaction coordinate mode) for the case that  $\{n_j\}$  quanta are in the F-1 quasi-harmonic modes (with energy-dependent frequencies  $\{\omega_j(E)\}$ ) orthogonal to it. (E is the total energy of all F modes.) Eq. (3.28) has the form of the cumulative reaction probability for a separable system, the essential difference being that here the frequencies of the F-1 "activated complex" modes are energy-dependent.

Finally, I would like to take this opportunity to discuss an example for which it has been suggested that these WKB-type models are inadequate. Consider the one-dimensional potential sketch in Figure 6, which has been used to illustrate the "decay of the false vacuum".<sup>12</sup> The above

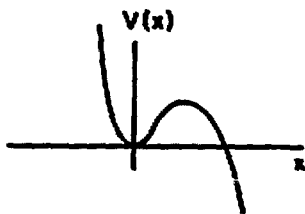


FIGURE 6  
One dimensional potential illustrating "decay of the false vacuum".

analysis degenerates to standard WKB theory (because F=1), which gives the decay rate of the metastable state with energy E as

$$k(E) = \frac{\omega}{2\pi} e^{-\phi(E)/\hbar} \quad , \quad (3.30)$$

where  $\omega$  is the harmonic frequency of the well and it has been assumed that the

tunneling probability is small ( $<10^{-1}$ ). Notwithstanding claims to the contrary,<sup>12</sup> Eq. (3.30) is quite accurate even for decay of the ground state,  $E = 1/2 \hbar\omega$ ; i.e.,

$$k_0 = \frac{\omega}{2\pi} e^{-\phi(1/2 \hbar\omega)/\hbar} \quad (3.31)$$

The only subtle feature arises if one wishes to expand the action  $\phi(E = 1/2 \hbar\omega)$  in powers of  $\hbar$  to obtain an explicit expression for the  $\hbar$ -dependence in the formal limit  $\hbar \rightarrow 0$ ; this is because  $\phi(E)$  does not have a finite derivative at  $E=0$ . This is well-known,<sup>13</sup> though, and for  $E \rightarrow 0$  one has

$$\phi(E) = \phi(0) + (E/\omega) \ln(2E/\omega) + cE + O(E^2) \quad (3.32)$$

where  $c$  is a constant that depends on the potential. With Eq. (3.31) this becomes

$$\lim_{\hbar \rightarrow 0} k_0 = \frac{\omega}{2\pi} e^{-\frac{c\omega}{2}} \hbar^{-1/2} e^{-\phi(0)/\hbar} \quad (3.33)$$

For the standard example,

$$V(x) = \frac{1}{2} x^2 - \frac{1}{3} x^3 \quad ,$$

and with  $m\omega=1$ , one has  $\phi(0) = \frac{6}{5}$  and  $e^{-\frac{c}{2}} = 6e$ , which is essentially identical to the result obtained by more sophisticated methods.<sup>12</sup>

#### 4. Concluding Remarks

All quantum effects result, ultimately, from the superposition principle of probability amplitudes. Since the kind of semiclassical theory we have described incorporates the principle of superposition, all quantum effects -- interference, tunneling (which is analytically continued interference), selection rules, and quantization itself -- are accounted for, at least qualitatively. For chemical and molecular systems, for which the potential functions are smooth and the particles relatively heavy, semiclassical theory is often quite accurate quantitatively. Perhaps more important, though, is that it provides a simple and comprehensive way of understanding the quantum effects observed in chemical dynamics.

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