LBL-4998

RECENT DEVELOPMENTS IN SEMICLASSICAL MECHANICS: EIGENVALUES AND REACTION RATE CONSTANTS*

William H. Miller†

Department of Chemistry and Materials and Molecular Research Division of the Lawrence Berkeley Laboratory, University of California, Berkeley CA 94720 and University Chemical Laboratory, Lensfield Road, Cambridge England

ABSTRACT

A semiclassical treatment of eigenvalues for a multidimensional non-separable potential function and of the rate constant for a chemical reaction with an activation barrier is presented. Both phenomena are seen to be described by essentially the same semiclassical formalism, which is based on a construction of the total Hamiltonian in terms of the complete set of "good" action variables (or adiabatic invariants) associated with the minimum in the potential energy surface for the eigenvalue case, or the saddle point in the potential energy surface for the case of chemical reaction.

I. INTRODUCTION

Semiclassical methods are the natural way of describing the effects of quantum mechanics in classical-like systems, and they have been an extremely powerful tool for describing quantum effects in atomic and molecular collision processes. Ford and Wheeler's papers[1] in 1959 showed how interference and tunneling effects in elastic scattering[2] could be described in a beautifully simple way: the collision dynamics are treated *via* classical mechanics but used to construct scattering *amplitudes* rather than the scattering probabilities (i.e., cross sections) themselves. This means that the quantum *principle of superposition* is included in the description, and this is the essential contribution of quantum mechanics. This approach provides a quantitative description of all quantum effects in elastic scattering; recently, for example, it has been shown[3,4] that a slight extension of the Ford and Wheeler analysis (to include "classically forbidden" contributions to the amplitude) even describes diffraction from purely repulsive potentials, a quantum effect heretofore thought to defy a simple semiclassical treatment.

Beginning in 1970 this semiclassical idea of "classical dynamics plus quantum superposition" was generalized to inelastic and reactive collision processes.[5-7] Although originally designed to deal with molecular collision phenomena, this "classical S-matrix" theory has also found application to electron scattering,[8] diffraction of atoms from crystal surfaces,[9,10] and coulomb excitation and fission dynamics in nuclear physics.[11-13] One of the predictions of this theory, for example, is that analogous to interference structure in the differential cross section for elastic scattering, there is an interference structure in the distribution of final states in inelastic-reactive scattering processes;[14] e.g., the cross section for the product molecule being in final vibrational state v_f, plotted as a function of v_f, in general has an interference structure. Although these interference effects in final state distributions have not yet been seen experimentally, it is certain that they exist and will presumably be seen when more refined techniques for state analysis becomes available.

This paper reviews some of the more recent developments in "semiclassical mechanics"--the semiclassical approximation to eigenvalues for multidimensional non-separable systems and the semiclassical approximation for the rate constants of chemical reactions which have simple activation barriers. It is an interesting feature of semiclassical theory that these two problems are described by essentially the same formalism.

Section II first discusses the semiclassical eigenvalue problem for multidimensional systems using both periodic orbit theory and the more rigorous Hamilton-Jacobi theory. In parallel fashion, Section III then discusses the semiclassical description of reaction rate constants--first the periodic orbit version of the theory and then the more rigorous Hamilton-Jacobi formulation.

II. SEMICLASSICAL EIGENVALUES

a. Periodic Orbit Theory

One of the truly new approaches to a multidimensional semiclassical quantum condition is the recent work of Gutzwiller[15] (with the modification of Miller[16]). The beginning point is to consider the trace of the resolvent operator, or green's function

$$\mathrm{tr}\ G(E) \equiv \mathrm{tr}\ (E-H)^{-1} \quad , \tag{2.1}$$

which is given quantum mechanically by

$$\mathrm{tr}\ G(E) = \sum_n (E-E_n)^{-1} \quad , \tag{2.2}$$

indicating that it has simple poles where E equals one of the quantum mechanical eigenvalues $\{E_n\}$. The green's function can be expressed in terms of the propagator,

$$G(E) = (i\hbar)^{-1} \int_0^\infty dt\ e^{iEt/\hbar}\ e^{-iHt/\hbar} \quad , \tag{2.3}$$

and the trace can be evaluated in a coordinate representation, so that

$$\mathrm{tr}\ G(E) = (i\hbar)^{-1} \int_0^\infty dt\ e^{iEt/\hbar} \int d\underset{\sim}{q}\ \langle \underset{\sim}{q} | e^{-iHt/\hbar} | \underset{\sim}{q} \rangle \quad . \tag{2.4}$$

Eq. (2.4) is still formally exact quantum mechanics, but one now injects the semiclassical approximation for matrix elements of the propagator,[17]

$$\langle \underset{\sim}{q} | e^{-iHt/\hbar} | \underset{\sim}{q} \rangle \sim e^{i\phi(\underset{\sim}{q},\underset{\sim}{q};t)/\hbar} \quad , \tag{2.5}$$

where ϕ is the classical action integral along the trajectory that goes from position $\underset{\sim}{q} \equiv \{q_i\}$, $i=1,\ldots,f$ at time $t = 0$ (f = number of degrees of freedom) back to $\underset{\sim}{q}$ at time t, and consistent with semiclassical mechanics, the integrals over $\underset{\sim}{q}$ and over t in Eq. (2.4) are all evaluated via the stationary phase approximation. The stationary phase condition for the $\underset{\sim}{q}$ integrals, for example, is

$$\begin{aligned} 0 &= \frac{\partial\phi(\underset{\sim}{q},\underset{\sim}{q};t)}{\partial\underset{\sim}{q}} \\ &= \left[\frac{\partial\phi(\underset{\sim}{q}_2,\underset{\sim}{q}_1;t)}{\partial\underset{\sim}{q}_2} + \frac{\partial\phi(\underset{\sim}{q}_2,\underset{\sim}{q}_1;t)}{\partial\underset{\sim}{q}_1}\right]_{\underset{\sim}{q}_1=\underset{\sim}{q}_2=\underset{\sim}{q}} \\ &= \underset{\sim}{p}_2-\underset{\sim}{p}_1 \quad ; \end{aligned} \tag{2.6}$$

i.e., the values of $\underset{\sim}{q}$ which are points of stationary phase must be such that the initial and final momenta, as well as coordinates, are the same, or in other words, $\underline{q}$ must lie on a periodic orbit of the system. In this very simple way, therefore, one sees how periodic orbits play a central role in this approach to the semiclassical eigenvalue problem.

The algebraic details involved in carrying out the stationary phase evaluation of the integrals in Eq. (2.4) are quite tedious but straight-forward, and the result of the calculation is[15]

$$\mathrm{tr}\, G(E) = -\frac{i\Phi'(E)}{\hbar} \sum_{n=1}^{\infty} \frac{e^{in[\Phi(E)/\hbar - \lambda \frac{\pi}{2}]}}{\prod_{k=1}^{f-1} 2i \sin(\frac{n}{2}\, \omega_k(E)\Phi'(E))} \quad . \tag{2.7}$$

In Eq. (2.7) $\Phi(E)$ is the action integral for one pass about the periodic orbit with energy E,

$$\Phi(E) = \int_0^{T(E)} dt\; \underline{p}(t)\cdot\dot{\underline{q}}(t) \quad , \tag{2.8}$$

where $T(E) \equiv \Phi'(E)$ is the period of the periodic orbit, $\{\omega_k(E)\}$, $k=1,\ldots, f-1$, are the stability frequencies of the (stable) periodic orbit, and λ is the number of "conjugate points" experienced in one pass about the periodic orbit. (In most cases λ is 0 or 2). The sum over n in Eq. (2.7) is a sum of amplitudes for all possible numbers of passes about the periodic orbit.

In order to identify the polar singularities in Eq. (2.7)--and thus the eigenvalues via Eq. (2.2)--it is useful to expand the sine functions in the denominator according to the identity

$$\frac{1}{2i \sin(\frac{x}{2})} = \frac{e^{-i\frac{x}{2}}}{1-e^{-ix}} = \sum_{n=0}^{\infty} e^{-i(n+\frac{1}{2})x} \quad . \tag{2.9}$$

Since there are f-1 sine factors in Eq. (2.7), this gives[16]

$$\mathrm{tr}\, G(E) = -\frac{i\Phi'(E)}{\hbar} \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_{f-1}=0}^{\infty} \sum_{n=1}^{\infty} e^{inA} \quad , \tag{2.10a}$$

where

$$A = \Phi(E)/\hbar - \lambda\,\frac{\pi}{2} - \Phi'(E) \sum_{k=1}^{f-1} \omega_k(E)(n_k+\tfrac{1}{2}) \quad . \tag{2.10b}$$

The sum over n (i.e., over multiple passes about the periodic orbit) in Eq. (2.10a) is easily accomplished,

$$\sum_{n=1}^{\infty} e^{inA} = e^{iA}(1-e^{iA})^{-1} \quad , \tag{2.11}$$

whereby the polar singularities in tr G(E) are seen to be those values of E for which $e^{iA} = 1$, or

$$A = 2\pi\, n_f \quad , \tag{2.12}$$

where n_f is an integer. Eqs. (2.10b) and (2.2) thus give the quantum condition of periodic orbit theory as[16]

$$\Phi(E) - \Phi'(E) \sum_{k=1}^{f-1} \hbar\, \omega_k(E)(n_k+\tfrac{1}{2}) = 2\pi\hbar\,(n_f+\tfrac{\lambda}{4}) \quad . \tag{2.13}$$

The energy levels are thus characterized by f quantum numbers, n_f being the number of quanta in motion *along* the periodic orbit, and n_k, k=1, ..., f-1, being the number of quanta in the kth harmonic mode of perturbation *about* the periodic orbit.

Although physically realistic and meaningful in many ways, Eq. (2.13) nevertheless has some fundamental shortcomings, primarily the implicit assumption that most of the energy is in motion along the periodic orbit, with deviations from it being treated only within a harmonic approximation. To see this, consider a completely separable system where the periodic orbit is chosen to be along the fth degree of freedom. The *correct* semiclassical eigenvalue condition in this case is

$$\Phi\left(E - \sum_{k=1}^{f-1} \varepsilon_k(n_k)\right) = 2\pi\hbar\,(n_f+\tfrac{1}{2}) \quad , \tag{2.14}$$

where $\varepsilon_k(n_k)$ is the one-dimensional eigenvalue for the kth degree of freedom, and in this case Φ is the one-dimensional action integral for the fth degree of freedom. To convert this into the expression given by periodic orbit theory, Eq. (2.13), two approximations are necessary: (1) All degrees of freedom except the fth one must be assumed to be harmonic, i.e.,

$$\varepsilon_k(n_k) \simeq \omega_k(n_k+\tfrac{1}{2}) \quad , \tag{2.15a}$$

and (2) Φ must be approximated by the first two terms of a Taylor's series expansion,

$$\Phi\left(E - \sum_{k=1}^{f-1} \hbar\omega_k(n_k+\tfrac{1}{2})\right) \simeq \Phi(E) - \Phi'(E) \sum_{k=1}^{f-1} \hbar\omega_k(n_k+\tfrac{1}{2}) \quad . (2.15b)$$

Assumption (1), Eq. (2.15a), is in general only valid for small n_k, and (2), Eq. (2.15b), is in general valid only if

$$E \gg \sum_{k=1}^{f-1} \hbar\omega_k(n_k+\tfrac{1}{2}) \quad , \qquad (2.16)$$

both of which imply that most of the total energy E is in one mode, the $f^{\underline{th}}$ one. If it should be that the first f-1 modes are harmonic, then Eq. (2.15a) is of course not an approximation; and further, if the $f^{\underline{th}}$ mode is also harmonic, then Eq. (2.15b) is also exact. Thus the one (trivial) case in which periodic orbit theory is actually exact is the completely separable, completely harmonic case.

Since these limitations implicit in periodic orbit theory stem directly from the stationary phase approximation used to evaluate the integrals in Eq. (2.4), it is difficult to see how to avoid them and stay within the present formalism. What would be required is some sort of uniform asymptotic evaluation of the integrals in Eq. (2.4), but it is not clear how to go about this. Fortunately, the approach described in the next section by-passes these difficulties by taking a different approach to the problem.

b. Hamilton-Jacobi Theory

The "Old Quantum Theory", as described by Born,[18] provides an alternate (much older) approach to the semiclassical eigenvalue problem[19] that has the major advantage of treating all degrees of freedom on an equal footing. Recently it has been shown[20] that the equations which result in this formulation can be cast in a form that permit efficient numerical solution, so that this approach is no longer limited to the realm of perturbation theory.[18]

In this approach the classical Hamiltonian for the system is divided into a separable reference Hamiltonian H_o and a residual non-separable interaction V,

$$H(\underset{\sim}{p},\underset{\sim}{x}) = H_o(\underset{\sim}{p},\underset{\sim}{x}) + V(\underset{\sim}{x}) \qquad (2.17)$$

with

$$H_o(\underset{\sim}{p},\underset{\sim}{x}) = \frac{p^2}{2\mu} + V_o(\underset{\sim}{x}) \quad , \tag{2.18}$$

where $V_o(\underset{\sim}{x})$ is separable,

$$V_o(\underset{\sim}{x}) = \sum_{i=1}^{f} v_i(x_i) \quad . \tag{2.19}$$

It is convenient then to change canonical variables from the cartesian variables (p,x) to the "zeroth order" action-angle variables $(\underset{\sim}{n},\underset{\sim}{q})$ which refer to H_o, in terms of which the Hamiltonian has the form

$$H(\underset{\sim}{n},\underset{\sim}{q}) = H_o(\underset{\sim}{n}) + V(\underset{\sim}{q},\underset{\sim}{n}) \quad . \tag{2.20}$$

Often the one-dimensional reference potentials $\{v_i(x_i)\}$ in Eq. (2.19) are taken to be harmonic, as we will now do, but this is not necessary. $H_o(\underset{\sim}{n})$ is then given explicitly by

$$H_o(\underset{\sim}{n}) = \sum_{i=1}^{f} \omega_i(n_i+\tfrac{1}{2}) \quad , \tag{2.21}$$

units being used so that $\hbar = 1$.

The presence of the non-separable interaction in Eq. (2.20) prevents the action variables n from being constants of the motion and thus the "good" quantum numbers of the system. The next step, therefore, is to carry out a canonical transformation from these zero$^{\underline{th}}$ order action-angle variables $(\underset{\sim}{n},\underset{\sim}{q})$ to the "good" action-angle variables (N,Q) such that in terms of these latter variables the total Hamiltonian is a function only of the action variables N:

$$H(\underset{\sim}{N},\underset{\sim}{Q}) = E(\underset{\sim}{N}) \quad . \tag{2.22}$$

The $\{N_i\}$ are thus constants of the motion, and the semiclassical eigenvalues are given by $E(\underset{\sim}{N})$ with all the $\{N_i\}$ required to be non-negative integers.

The (n,q) → (N,Q) transformation is effected by a generating function $F(\underset{\sim}{q},\underset{\sim}{N})$ which is required to be a solution of the Hamilton-Jacobi equation,

$$\begin{aligned} E(\underset{\sim}{N}) &= H\left(\frac{\partial F(\underset{\sim}{q},\underset{\sim}{N})}{\partial \underset{\sim}{q}}, \underset{\sim}{q}\right) \\ &= \underset{\sim}{\omega}\cdot\left(\frac{\partial F}{\partial \underset{\sim}{q}} + \frac{1}{2}\right) + V\left(\underset{\sim}{q}, \frac{\partial F}{\partial \underset{\sim}{q}}\right) \quad . \end{aligned} \tag{2.23}$$

F is taken to be of the form

$$F(\mathbf{q},\mathbf{N}) = \mathbf{N}\cdot\mathbf{q} + i\sum_{\mathbf{k}}{}' B_{\mathbf{k}}(\mathbf{N})\, e^{i\mathbf{k}\cdot\mathbf{q}} \quad , \tag{2.24}$$

the first term being that which generates the identity transformation, which is correct in the limit $V \to 0$, and where the prime on the summation indicates that the term $k = 0$ is omitted. Substituting this Fourier expansion into Eq. (2.23) and projecting out individual Fourier components leads to the following algebraic equations:

$$E\,\delta_{\mathbf{k},\mathbf{0}} = \boldsymbol{\omega}\cdot(\mathbf{N}+\tfrac{1}{2})\,\delta_{\mathbf{k},\mathbf{0}} - (\boldsymbol{\omega}\cdot\mathbf{k})B_{\mathbf{k}} + (2\pi)^{-f}\int_{\mathbf{0}}^{2\pi} d\mathbf{q}\; e^{-i\mathbf{k}\cdot\mathbf{q}}\, V(\mathbf{q},\mathbf{N} - \sum_{\mathbf{k}}{}' \mathbf{k}'\, B_{\mathbf{k}'}\, e^{i\mathbf{k}'\cdot\mathbf{q}}) \; . \tag{2.25}$$

For $\mathbf{k} \neq \mathbf{0}$, Eq. (2.25) is a set of (non-linear) equations for the Fourier coefficients $B_{\mathbf{k}}$,

$$(\boldsymbol{\omega}\cdot\mathbf{k})B_{\mathbf{k}} = (2\pi)^{-f}\int_0^{2\pi} d\mathbf{q}\; e^{-i\mathbf{k}\cdot\mathbf{q}}\, V(\mathbf{q},\mathbf{N} - \sum_{\mathbf{k}}{}' \mathbf{k}'\, B_{\mathbf{k}'}\, e^{i\mathbf{k}'\cdot\mathbf{q}}) \tag{2.26a}$$

and for $k = 0$ Eq. (2.25) gives the eigenvalue $E(\mathbf{N})$ in terms of the Fourier coefficients,

$$E(\mathbf{N}) = \boldsymbol{\omega}\cdot(\mathbf{N}+\tfrac{1}{2}) + (2\pi)^{-f}\int_0^{2\pi} d\mathbf{q}\; V(\mathbf{q},\mathbf{N} - \sum_{\mathbf{k}}{}' \mathbf{k}'\, B_{\mathbf{k}'}\, e^{i\mathbf{k}'\cdot\mathbf{q}}) \tag{2.26b}$$

One thus first sets N equal to the desired quantum numbers and solves Eq. (2.26a) for the Fourier coefficients $B_{\mathbf{k}}$; the eigenvalue corresponding to this set of quantum numbers is then given by Eq. (2.26b).

For the non-degenerate situation--i.e., the case that $\boldsymbol{\omega}\cdot\mathbf{k}$ is not too small for all $\mathbf{k}$ which contribute significantly to the Fourier expansion--Eq. (2.26a) can often be solved by a simple successive substitution algorithm. Eq. (2.26a) is written as

$$B_{\mathbf{k}} = \frac{1}{\boldsymbol{\omega}\cdot\mathbf{k}}\;(2\pi)^{-f}\int_0^{2\pi} d\mathbf{q}\; e^{-i\mathbf{k}\cdot\mathbf{q}}\, V(\mathbf{q},\mathbf{N} - \sum_{\mathbf{k}}{}' \mathbf{k}'\, B_{\mathbf{k}'}\, e^{i\mathbf{k}'\cdot\mathbf{q}}) , \tag{2.27}$$

which is seen to be of the form

$$B_{\underset{\sim}{k}} = \text{function}\ [B_{\underset{\sim}{k}}] \quad .$$

The iterative procedure is then

$$B_{\underset{\sim}{k}}^{(\ell+1)} = \text{function}\ [B_{\underset{\sim}{k}}^{(\ell)}] \quad ,$$

$\ell = 0,1,2...$, with the initialization

$$B_{\underset{\sim}{k}}^{(0)} = 0 \quad .$$

Application[20] of this procedure for solving Eq. (2.26a) to a model two-dimensional potential well has shown that the semiclassical eigenvalues so obtained are in good agreement with accurate quantum mechanical values--comparable to the agreement for one-dimensional WKB eigenvalues--even for very strong nonseparable coupling. Essentially the same procedure has also been used[21] to determine a number of vibrational eigenvalues of H_2O and SO_2 with realistic potential functions. This is the first application of a multidimensional semiclassical quantum condition to real molecular systems.

If there are low order degeneracies in $H_0(\underset{\sim}{n})$--i.e., if $\omega \cdot k=0$ for some $\underset{\sim}{k}$ that contribute significantly to the Fourier series--then the above procedure for solving Eq. (2.26a) will clearly not be applicable. In such cases other algorithms--such as the multidimensional Newton iteration--must be used to solve Eq. (2.26a). For the two dimensional potential functions

$$V(x,y) = \frac{1}{2}\,\omega_1{}^2\ x^2 + \frac{1}{2}\,\omega_2{}^2\ y^2 + \lambda(xy^2 - \frac{1}{3}\,x^3) \quad ,$$

and

$$V(x,y) = \frac{1}{2}\,\omega_1{}^2\ x^2 + \frac{1}{2}\,\omega_2{}^2\ y^2 + \lambda\ x^2\ y^2 \quad ,$$

with $\omega_1 = \omega_2$, a multidimensional Newton procedure has been used[22] successfully to solve Eq. (2.26a) and thus obtain semiclassical eigenvalues.

III. RATE CONSTANTS FOR CHEMICAL REACTION

For a bimolecular exchange reaction of the general type

$$A + BC \rightarrow AB + C \quad ,$$

the thermal rate constant is given quantum mechanically by[23]

$$k(T) = Q_r^{-1}\ \mathrm{tr}(e^{-\beta H}\ F\ P) \quad , \qquad (3.1)$$

where Q_r is the partition function (per unit volume) for reactants, H is the total Hamiltonian, F is a flux operator, and P is the projection operator which projects onto states that have evolved in the infinite past from reactants.

Since the Boltzmann operator $e^{-\beta H}$ can be expressed in terms of the green's function by

$$e^{-\beta H} = \frac{-1}{2\pi i} \int^{\infty} dE\ e^{-\beta E}\ G(E) \quad , \qquad (3.2)$$

the rate constant can be expressed equivalently as

$$k(T) = (2\pi\hbar\ Q_r)^{-1} \int^{\infty} dE\ e^{-\beta H}\ N(E) \quad , \qquad (3.3)$$

where $N(E)$ is[24]

$$N(E) = i\hbar\ \mathrm{tr}[G(E)\ F\ P] \quad . \qquad (3.4)$$

Semiclassical approximations for $N(E)$, and thus for the rate constant via Eq. (3.3), are then obtained by introducing semiclassical approximations for $G(E)$ and for the evaluation of the trace.

a. Periodic Orbit Theory

The periodic orbit analysis of Section IIa can also be used to evaluate the trace in Eq. (3.4). The factor FP in Eq. (3.4) makes only minor difference to the calculation, and if there is a simple activation barrier separating reactants and products (as, for example, with $H + H_2$) one obtains[25]

$$N(E) = \sum_{n=1}^{\infty} \frac{-e^{in[\Phi(E)/\hbar - \lambda \frac{\pi}{2}]}}{\prod_{k=1}^{f-1} 2i \sin[\frac{n}{2}\ \omega_k(E)\ \Phi'(E)]} \quad , \qquad (3.5)$$

which is the analog of Eq. (2.7). In this case, though, the periodic orbit is for an imaginary time increment (because $e^{-\beta H} \equiv e^{-iHt/\hbar}$ for $t = -i\hbar\beta$), so that the action integral $\Phi(E)$ is pure imaginary. (The periodic motion is basically an oscillation back and forth through the potential barrier.[25]) The real quantity $\theta(E)$ is defined by

$$\phi(E)/\hbar = i2\theta(E) \quad , \tag{3.6}$$

and since $\lambda = 2$ in this case, Eq. (3.6) becomes

$$N(E) = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}\, e^{-n2\theta(E)}}{\prod_{k=1}^{f-1} \sinh\ [-n\hbar\omega_k(E)\theta'(E)]} \tag{3.7}$$

The sinh functions in the denominator of Eq. (3.7) are expanded in the analogous way as Eq. (2.9), so that Eq. (3.7) becomes

$$N(E) = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_{f-1}=0}^{\infty} \sum_{n=1}^{\infty} (-1)^{n-1}\, e^{-n[2\theta(E) - 2\theta'(E) \sum_{k=1}^{f-1} \hbar\omega_k(E)(n_k+\frac{1}{2})]} \quad , \tag{3.8}$$

and the sum over n--the number of "tunneling oscillations" inside the barrier--is easily carried out to give[25]

$$N(E) = \sum_{\underset{\sim}{n}=0}^{\infty} [1 + e^{2\theta(E) - 2\theta'(E)\hbar\underset{\sim}{\omega}(E)\cdot(\underset{\sim}{n}+\frac{1}{2})}]^{-1} \quad , \tag{3.9}$$

where $\underset{\sim}{\omega}(E) = \{\omega_k(E)\}$, $k=1, \ldots, f-1$, $\underset{\sim}{n} = \{n_i\}$, $i=1, \ldots, f-1$, and

$$\sum_{\underset{\sim}{n}=0}^{\infty} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_{f-1}=0}^{\infty} \quad .$$

Eq. (3.9) is the final expression for N(E) within periodic orbit theory, the rate constant then being given by Eq. (3.3).

Although Eq. (3.9) does provide a qualitatively correct physical picture of the reaction rate constant, this periodic orbit limit of the theory suffers from the same quantitative shortcomings as those in the eigenvalue problem discussed in Section IIa, namely that most of the energy is implicitly assumed to be in one mode (motion along the "reaction coordinate") with deviations from it being treated only within a harmonic approximation. To see this, consider the situation that motion along a reaction coordinate is separable from the remaining f-1 degrees of freedom; it is then easy to show that the exact quantum mechanical expression for N(E) in this case is

$$N(E) = \sum_{\underset{\sim}{n}=0} P_{tun}(E-\varepsilon_{\underset{\sim}{n}}) \quad , \tag{3.10}$$

where $P_{tun}(E_t)$ is the one dimensional tunneling probability with an energy E_t in translational motion along the reaction coordinate. The semiclassical approximation for the tunneling probability is

$$P_{tun}(E_t) = [1 + e^{2\theta(E_t)}]^{-1} \quad , \tag{3.11}$$

and if the f-1 degrees of freedom of the "activated complex" are approximated as harmonic,

$$\epsilon_{\underset{\sim}{n}} \simeq \underset{\sim}{\omega}\cdot(\underset{\sim}{n}+\tfrac{1}{2}) \quad , \tag{3.12}$$

then the correct semiclassical limit of Eq. (3.10) is

$$N(E) = \sum_{\underset{\sim}{n}} \{1 + e^{2\theta[E - \hbar\underset{\sim}{\omega}\cdot(\underset{\sim}{n}+\frac{1}{2})]}\}^{-1} \quad . \tag{3.13}$$

To obtain the result given by periodic orbit theory, Eq. (3.9), it is also necessary to approximate the exponent in Eq. (3.13) by the first two terms of its Taylor's series expansion,

$$\theta[E - \hbar\underset{\sim}{\omega}\cdot(\underset{\sim}{n}+\tfrac{1}{2})] \simeq \theta(E) - \theta'(E)\hbar\underset{\sim}{\omega}\cdot(\underset{\sim}{n}+\tfrac{1}{2}) \quad . \tag{3.14}$$

As for the eigenvalue problem discussed in Section IIa, the approximations in Eqs.(3.12) and (3.14) are in general valid only if most of the total energy E is in motion along the reaction coordinate. As there, too, the periodic orbit expression happens to be exact for the (trivial) case that all the f-1 modes are harmonic and the barrier for the fth mode is parabolic (i.e., an inverted harmonic potential).

Just as for the eigenvalue problem, therefore, the periodic orbit approach gives a result that is qualitatively correct but which can be inaccurate quantitatively because of dynamical assumptions implicit in it. Here too, though, there exists a Hamilton-Jacobi approach that treats all the degrees of freedom on an equal dynamical footing.

b. Hamilton-Jacobi Theory

A Hamilton-Jacobi analysis,[26] similar to that of the eigenvalue problem described in Section IIb, can be used to overcome the limitations in periodic orbit theory described in the previous section. This is possible by realizing that there are "good" action variables associated with the saddle point of a potential surface just as there are those related to a minimum in a potential surface.

Consider first, for example, the case discussed in the previous section that motion along the reaction coordinate (the $f^{\underline{th}}$ degree of freedom) is separable from the other f-1 degrees of freedom. The correct semiclassical expression for N(E) is given in this case by Eqs. (3.10) and (3.11):

$$N(E) = \sum_{\underset{\sim}{n}=0} [1 + e^{2\theta(E-\varepsilon_{\underset{\sim}{n}})}]^{-1} \quad , \tag{3.15}$$

where $\underset{\sim}{n} \equiv \{n_k\}$, k=1, ..., f-1. An action variable for the reaction coordinate, n_f, can be defined in the usual one-dimensional fashion,

$$\begin{aligned}(n_f+\tfrac{1}{2})\pi &= \int dq_f \sqrt{2\mu[E_t-V_f]} \\ &= i\int dq_f \sqrt{2\mu[V_f-E_t]} \\ &\equiv i\theta(E_t) \quad , \end{aligned} \tag{3.16}$$

with $E_t = E-\varepsilon_{\underset{\sim}{n}}$, where θ is the (real) barrier penetration integral. Eq. (3.15) can thus be written equivalently as

$$N(E) = \sum_{\underset{\sim}{n}=0} [1 + e^{2\pi \, \mathrm{Im} \, n_f(E,\underset{\sim}{n})}]^{-1} \quad , \tag{3.17}$$

where $n_f(E,\underset{\sim}{n})$ is given as a function of the total energy E and the f-1 action variables (or quantum numbers) by Eq. (3.16).

Although deduced for the separable case, Eq. (3.17) is also the result of the more rigorous Hamilton-Jacobi theory[26] for a general non-separable potential function. In the general case one must first construct the total Hamiltonian in terms of the complete set of "good" action variables $\{n_i\}$, i=1, ..., f using, for example, the methods of Section IIb. Then the equation

$$E = H(n_1,n_2, \ldots, n_{f-1},n_f) \tag{3.18}$$

is solved for $n_f(E,n_1, \ldots, n_{f-1})$, and N(E) is given by Eq. (3.17). This result of the Hamilton-Jacobi analysis is seen to have the same qualitative structure as that of periodic orbit theory, Eq. (3.9), but it does not incorporate any approximation about the distribution of energy among the various modes nor approximate any of the modes as harmonic.

Eq. (3.17) can be derived for the general non-separable case by evaluating the trace in Eq. (3.4) in the representation of the "good" action variables $\{n_i\}$, $i=1, \ldots, f$:

$$\begin{aligned} N(E) &= i\hbar \, \mathrm{tr}[G(E)FP] \\ &= i\hbar \sum_{\underset{\sim}{n}=0} \int dn_f \, \langle \underset{\sim}{n}, n_f | G(E)FP | \underset{\sim}{n}, n_f \rangle \\ &= i\hbar \sum_{\underset{\sim}{n}=0} \int dn_f \, \frac{\langle \underset{\sim}{n}, n_f | FP | \underset{\sim}{n}, n_f \rangle}{E - E(\underset{\sim}{n}, n_f)} \quad , \end{aligned} \tag{3.19}$$

where $\underset{\sim}{n} \equiv \{n_i\}$, $i=1, \ldots, f-1$, and $E(\underset{\sim}{n}, n_f) \equiv H(n_1, n_2, \ldots, n_f)$. Because of the simple pole in the integrand, the integral over n_f can be evaluated by contour integration, giving

$$N(E) = 2\pi\hbar \sum_{\underset{\sim}{n}=0} \langle \underset{\sim}{n}, n_f | FP | \underset{\sim}{n}, n_f \rangle \Big/ \frac{\partial E(\underset{\sim}{n}, n_f)}{\partial n_f} \tag{3.20}$$

with $n_f = n_f(E, \underset{\sim}{n})$ determined by the pole condition, Eq. (3.18). It is shown elsewhere,[26] along with more details of the calculation, that the flux integral is given by

$$\langle \underset{\sim}{n}, n_f | FP | \underset{\sim}{n}, n_f \rangle = \frac{\partial E(\underset{\sim}{n}, n_f)}{\partial n_f} \left(1 + e^{2\pi \mathrm{Im}\, n_f}\right)^{-1} \Big/ 2\pi\hbar \quad , \tag{3.21}$$

which, inserted into Eq. (3.20), gives Eq. (3.17).

Application[27] of the periodic orbit version of this rate theory, Eq. (3.9), has been seen to give reasonably good results for the collinear H + H_2 exchange reaction <u>if</u> the exponent in Eq. (3.9) is modified in the following manner:

$$\theta(E) - \theta'(E)\, \hbar \underset{\sim}{\omega}(E) \cdot (\underset{\sim}{n} + \tfrac{1}{2}) \rightarrow \theta(E_{\underset{\sim}{n}}) \quad , \tag{3.22}$$

with $E_{\underset{\sim}{n}}$ determined by the equation

$$E_{\underset{\sim}{n}} = E - \hbar \underset{\sim}{\omega}(E_{\underset{\sim}{n}}) \cdot (\underset{\sim}{n} + \tfrac{1}{2}) \quad . \tag{3.23}$$

This modification has the effect of correcting, in an approximate fashion, for the assumption in periodic orbit theory that all but infinitesimal of the total energy is in motion along the reaction coordinate. Use of Eq. (3.9) without this modification gives poor results because $\hbar\omega(E)(n+\frac{1}{2})$ is not at all small compared to E in the range of interest for this system. Since the Hamilton-Jacobi approach involves no such approximations, it is anticipated that it will provide a more satisfactory description of the rate constant for this (and similar) chemical reaction.

IV. CONCLUDING REMARKS

One thus sees that within the framework of semiclassical mechanics eigenvalues in a multidimensional potential well and chemical reaction through a saddle point region of a potential energy surface can be described by essentially the same formalism. In both cases the periodic orbit version of the theory provides a simple, physically correct picture of the phenomenon but can be inaccurate quantitatively because of certain assumptions implicit in it.

The Hamilton-Jacobi approach avoids the limitations of periodic orbit theory. It provides a way of constructing the total Hamiltonian for the non-separable system in terms of a complete set of "good" (i.e., conserved) action variables. In the eigenvalue case these action variables are required to be integers (i.e., quantum numbers), and this discretizes the energy. For chemical reaction through a saddle point region one of the action variables is identified as a "generalized barrier penetration integral", and its imaginary part (as a function of the other action variables and the total energy) gives the reaction probability. Applications of this approach to real molecular systems, either for eigenvalues or for rate constants of chemical reactions, have only begun but promise to be a useful way of describing these phenomena.

REFERENCES

* Supported in part by the U.S. Energy Research and Development Administration, and by the National Science Foundation under grant GP-41509X.

† Camille and Henry Dreyfus Teacher-Scholar; J. S. Guggenheim Memorial Fellow on sabbatical leave from the Department of Chemistry, University of California, Berkeley, CA 94720.

1. K. W. Ford and J. A. Wheeler, Ann. Phys. N.Y. **7**, 259, 287 (1959).
2. For reviews of semiclassical theory of elastic scattering, see R. B. Bernstein, Adv. Chem. Phys. **10**, 75 (1966), and M. V. Berry and K. E. Mount, Rept. Prog. Phys. **35**, 315 (1972).
3. G. E. Zahr and W. H. Miller, Mol. Phys. **30**, 951 (1975).
4. R. J. Gordon, J. Chem. Phys. **63**, 3109 (1975).
5. W. H. Miller, J. Chem. Phys. **53**, 1949 (1970).
6. R. A. Marcus, Chem. Phys. Lett. **7**, 525 (1970).

7. For reviews, see W. H. Miller, Adv. Chem. Phys. 25, 69 (1974); 30, 77 (1975).

8. F. T. Smith, D. L. Huestis, D. Mukherjee, and W. H. Miller Phys. Rev. Lett. 35, 1073 (1975).

9. J. D. Doll, J. Chem. Phys. 61, 954 (1974).

10. R. I. Masel, R. P. Merrill, and W. H. Miller, Surf. Sci. 46, 681 (1974); J. Chem. Phys. 64, 45 (1976).

11. S. Levit, U. Smilansky, and D. Pelte, Phys. Lett. 53B, 39 (1974).

12. H. Massmann and J. O. Rasmussen, Nucl. Phys. A243, 155 (1975); H. Massmann, P. Ring, and J. O. Rasmussen, Phys. Lett. 57B, 417 (1975).

13. R. A. Malfliet, Lecture Notes in Physics (Springer Verlag) 33, 86 (1975); T. Koeling and R. A. Malfliet, Phys. Reports (Section C of Phys. Lett.) 22C, 182 (1975).

14. W. H. Miller, J. Chem. Phys. 53, 3578 (1970).

15. M. D. Gutzwiller, J. Math. Phys. 12, 343 (1971).

16. W. H. Miller, J. Chem. Phys. 63, 996 (1975).

17. R. P. Feynman and A. R. Hibbs, Quantum Mechanics and Path Integrals, McGraw-Hill, New York, 1965.

18. M. Born, The Mechanics of the Atom, Ungar, New York, 1960.

19. Other recent work on the semiclassical eigenvalue problem that is related to that discussed here is (a) I. C. Percival, J. Phys. B 6, L229 (1973); J. Phys. A 7, 794 (1974); (b) W. Eastes and R. A. Marcus, J. Chem. Phys. 61, 4301 (1974); D. W. Noid and R. A. Marcus, J. Chem. Phys. 62, 2119 (1975). These authors basically follow the formulation of Keller [J. B. Keller, Ann. Phys. N.Y. 4, 180 (1958); J. B. Keller and S. I. Rubinow, Ann. Phys. N.Y. 9, 24 (1960)] which is based on the Hamilton-Jacobi equation in cartesian coordinates, rather than that in action-angle variables used by Born.

20. S. Chapman, B. C. Garrett, and W. H. Miller, J. Chem. Phys. 64, 502 (1976).

21. N. C. Handy, S. M. Colwell, and W. H. Miller, Faraday Disc. Chem. Soc. 62, to be published.

22. N. C. Handy and W. H. Miller, unpublished results.

23. W. H. Miller, J. Chem. Phys. 61, 1823 (1974).

24. The more conventional expression for N(E) is in terms of the S-matrix elements of scattering theory,

$$N(E) = \sum_{\underset{\sim}{n}_a,\underset{\sim}{n}_b} |S_{\underset{\sim}{n}_b,\underset{\sim}{n}_a}(E)|^2$$

where $\underset{\sim}{n}_a$ and $\underset{\sim}{n}_b$ are the internal quantum numbers of the reactants and products, respectively.

25. W. H. Miller, J. Chem. Phys. 62, 1899 (1975).

26. W. H. Miller, Faraday Disc. Chem. Soc. 62, to be published.

27. S. Chapman, B. C. Garrett, and W. H. Miller, J. Chem. Phys. 63, 2710 (1975).