Title
Semiclassical Methods for Nonseparable Systems

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SEMICLASSICAL METHODS FOR NONSEPARABLE SYSTEMS

Bruce Campbell Garrett

ABSTRACT

Semiclassical techniques have been widely used for describing the dynamics of molecular collisions. The calculation of discrete energy eigenvalue spectra in bound systems has also employed semiclassical methods, a well-known example being the Bohr-Sommerfeld quantum condition for a one-dimensional potential well. Work has been done towards developing semiclassical theories for rate constants in reactive systems and semiclassical eigenvalues in bound systems. Application of these theories have been made to nonseparable multidimensional systems.

Transition state theory has played an important role in chemical kinetics and is very useful for approximating reaction rate constants for molecular systems. Many shortcomings of transition state theory can be attributed to the assumption of separability of motion along the reaction coordinate which is inherent in traditional formulations of the theory. A quantum mechanical version of transition state theory for nonseparable systems has been given by Miller. Semiclassical approximations have been made to the quantum rate expression and the resulting semiclassical theory has been applied to the reactive H + H_2 system. Comparison of this nonseparable theory with quantum scattering calculations shows agreement which is quite good. This is marked improvement over traditional separable formulations of transition state theory.

Although the quantum condition for one-dimensional bound systems is well-known, generalization of these results to multidimensional nonseparable systems is not obvious and has drawn the attention of many authors. Work has been done towards a semiclassical quantum condition which is closest to the approach of Born. The Hamilton-Jacobi equation for the systems is solved in action-angle variables, allowing the classical Hamiltonian to be expressed as a function of action variables which are constants of motion for the system. Requiring the action variables to be integers provides the semiclassical eigenvalues. Numerical calculations have been performed on a two-dimensional coupled potential well with good agreement with the quantum eigenvalues. Application of the theory has also been made a two-dimensional symmetric double-well potential which mimic the inversion motion in ammonia. Effects of coupling upon the energy level splittings have been studied.

I. INTRODUCTION

Semiclassical methods have proven to be a very powerful tool for describing the dynamics of gas phase molecular collisions. More recently, considerable progress has been made in applying semiclassical techniques to the determination of the discrete energy eigenvalue spectra of bound systems. The present work addresses itself to both these topics, the emphasis being upon applications of the methods to systems in which a simple separation of variables cannot be made.

The importance of considering nonseparable systems is twofold. First, separable systems are already solvable by existing semiclassical methods. A separable system can be reduced to many one-dimensional problems which in turn can be treated by the well-known method of Jeffrey, Wentzel, Kramers, and Brillioun - the JWKB or WKB approximation[1]. Ford and Wheeler[2] have shown how the WKB solution to the Schrodinger equation can be applied to the effective one-dimensional problem in the elastic scattering of two atoms. For bound one-dimensional potentials, the WKB approximation gives the Bohr-Sommerfeld quantization rules of the old quantum theory.

Second, and most important, systems of physical importance are in general nonseparable. Vibrational excitation in atom-diatom collisions arise solely from the coupling between the internal degree of freedom and the relative translation of the two particles. The reactive case is even more pathalogical since the coordinates relevant to the reactants are different from those relevant to the products. The vibrational energy spectrum of a molecule is regular for the lowest eigenvalues where the vibrational modes are approximately harmonic and weakly coupled. However the coupling of modes for higher eigenvalues eventually leads to irregular spectra in which identification of mode excitation becomes meaningless. Although we will be dealing with the general case of non-separable potentials, a useful test of the methods presented here will be their comparison with the correct separable semiclassical limit given by the WKB approximation.

An important contribution to the semiclassical description of molecular scattering has been the development of methods by Miller[3] and Marcus[4] which use classical mechanics for all degrees of freedom of a system to construct the pertinent parameters of quantum scattering theory. The full dynamics of the system are obtained through classical trajectories; however, instead of constructing the probabilities (or cross sections) directly as in classical calculations, the scattering amplitudes are obtained. This effectively includes the quantum principle of superposition and allows for interference effects. This method also allows for the description of tunneling in reactive systems.

The work presented in chapter II is concerned with the semiclassical description of reactive collisions using approximate dynamics. This is based upon the transition state theory[5] of chemical kinetics, which is inherently a classical method for approximating reaction rates. Recent work by Miller[6] has given a formulation of transition state theory based upon quantum dynamics, i.e., a full quantum mechanical transition state theory. The semiclassical approximations to this quantum theory use classical trajectories to construct the proper quantum mechanical functions—in this case the matrix elements of the Boltzman operator.

The most common semiclassical approach to the eigenvalue problem has been through the asymptotic solution to the Schrodinger equation (the $\hbar \to 0$ limit), which leads to the Hamilton-Jacobi equation. The multi-valued solutions to this classical equation parameterize the semiclassical wavefunction. Restricting the wavefunction to be single valued imposes the proper quantization condition. Another different and interesting approach to semiclassical eigenvalues is based upon the semiclassical approximation to the density of states. This semiclassical approximation is parameterized by classical trajectories which are periodic in nature. Singularities in this function of energy specify the eigenvalues. Both of these methods are reviewed in chapter III and a practical method of solving the Hamilton-Jacobi equation to obtain the semiclassical eigenvalues is presented.

The semiclassical quantization condition can also be viewed as finding "good" action variables for the system: action variables which are constants of the motion. The eigenvalues are then specified by requiring the action variables to be integers. However one is not restricted to bound state systems when constructing "good" action variables. One can find "good" action variables for scattering situations, in particular for the saddle point region of a potential surface describing a reactive system. In chapter IV it is shown how one can use these action variables to parameterize the reaction rate for such a system.

II. TRANSITION STATE THEORY

The transition state theory[5] of rate constants (also known as absolute rate theory and activated complex theory) has been a very useful tool in chemical kinetics, being very successful for parameterizing rate constants for chemical reactions with activation barriers. The reason for this success lies in the fact that the fundamental assumption of transition state theory is quite good in the energy regime which is most important in determining the thermal rate constant—the threshold region of energies very close to the barrier height. Traditional formulations of transition state theory, however, contain other approximations which tend to degrade the quantitative description of the rate constants. Recent interest has been in examing these assumptions and their validity.[6-13]

Transition state theory is inherently a classical model, using approximate classical dynamics to estimate reaction rate constants. The assumptions of the theory are therefore best couched in the language of classical mechanics. Section A reviews classical transition state theory and its approximations with particular emphasis on the fundamental assumption.

For energies in the threshold region where transition state theory would be expected to be most accurate, quantum mechanical effects such as tunneling become most pronounced. Attempts to include quantum effects into traditional formulations of transition state theory have, for the most part, been in an ad hoc manner, introducing quantum mechanics into the classical equations after the simplifying assumptions have been made. A rigorous formulation of quantum mechanical transition state theory has been given by Miller[6] and is briefly reviewed in section B.

The desire to obtain an easily calculable model which retains quantum effects has lead to two different semiclassical approximations to the quantum mechanical transition state rate expression. These semiclassical models are presented in section C as well as applications to model systems including the H + H_2 reactive system. A detailed description of the calculations performed in this chapter is presented in the appendix.

A. Classical Transition State Theory

Except for the simplest cases of elastic scattering of atoms, classical rate constants are obtained from the computation of many classical trajectories which entail knowing the exact dynamics of the system[14]. It is the aim of transition state theory to obviate the need for this detailed information by introducing special assumptions. We begin by first presenting an exact (within classical mechanics) rate constant expression, then introduce the simplifying approximations and examine their physical consequences.

It is initially assumed that the dynamics of the systems we will be treating can be adequately described by classical mechanics on a single Born-Oppenheimer potential energy surface, and that reactants are in a Boltzmann distribution of internal states and relative translation. Given these assumptions, the "exact" rate expression is the Boltzmann average of the flux of reactive trajectories through a surface which divides reactants (arrangement a) from products (arrangement b):

$$k^{cl}_{b\leftarrow a}(T) = Q_a^{-1}(T)\, h^{-N} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\;\; e^{-\beta H(\underset{\sim}{p},\underset{\sim}{q})}\; F(\underset{\sim}{p},\underset{\sim}{q})\;\; \chi_{b\leftarrow a}(\underset{\sim}{p},\underset{\sim}{q}) \qquad (2.1)$$

where Q_a is the partition function per unit volume for reactants; $\beta = (kT)^{-1}$; $(\underset{\sim}{p},\underset{\sim}{q}) = (p_i,q_i)$, i - 1,2,...,N, are the momenta and coordinates respectively for the N degrees of freedom; $H(p,q)$ is the total classical Hamiltonian; $F(\underset{\sim}{p},\underset{\sim}{q})$ is the flux through a surface; and $\chi_{b\ a}(\underset{\sim}{p},\underset{\sim}{q})$ is the characteristic function for reaction. If $f(\underset{\sim}{q})$ is a yet unspecified function of coordinates which defines the dividing surface by $f(q) = 0$, then

$$F(\underset{\sim}{p},\underset{\sim}{q}) = \delta\left(f(\underset{\sim}{q})\right) \frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \frac{\underset{\sim}{p}}{m} \qquad (2.2)$$

is just the flux normal to the dividing surface, where δ is the Dirac delta function which changes the volume integral over the N coordinates to one over N - 1 coordinates and restricted to the dividing surface. The characteristic function $\chi_{b\leftarrow a}(\underset{\sim}{p},\underset{\sim}{q})$ is defined as 1 if a trajectory determined by the phase space point $(\underset{\sim}{p},\underset{\sim}{q})$ is a reactive one going from reactants to products, and is zero otherwise. An important advantage to this way of formulating the rate expression is that all the dependence of the rate constant on trajectory information is contained in the characteristic function $\chi_{b\leftarrow a}(\underset{\sim}{p},\underset{\sim}{q})$. This fact will be used later in making the fundamental transition state theory approximation.

We have not yet specified where the dividing surface defined by $f(\underset{\sim}{q}) = 0$ should be placed. However, it is a direct consequence of the classical continuity equation that the classical rate expression is independent of where the surface is located,[7] as long as it is specified that all reactive trajectories pass through it. The classical continuity equation states that for a closed surface, the steady state flux through the surface must be zero. More precisely,

$$\int d\underset{\sim}{p} \int d\underset{\sim}{q} \quad \rho(\underset{\sim}{p},\underset{\sim}{q}) \quad \delta\left(f(\underset{\sim}{q})\right) \frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \underset{\approx}{m}^{-1}\!\!\!\!\quad \frac{\underset{\sim}{p}}{\underset{\approx}{m}} \tag{2.3}$$

where $f(\underset{\sim}{q}) = 0$ defines the closed surface; $\rho(\underset{\sim}{p},\underset{\sim}{q})$ is a distribution function which is restricted to remain constant along a classical trajectory determined by the phase space point $(\underset{\sim}{p},\underset{\sim}{q})$. The rate expression eq. (2.1) can be put into this form if we define $\rho(\underset{\sim}{p},\underset{\sim}{q}) = e^{-\beta H(\underset{\sim}{p},\underset{\sim}{q})} \chi_{b\leftarrow a}(\underset{\sim}{p},\underset{\sim}{q})$ and take the closed surface to be two different choices of dividing surface with segments joining them at infinity. Along a trajectory the Hamiltonian is a conserved quantity, the energy, and the characteristic function is constant for any given trajectory, thus implying that the distribution function is indeed constant along a trajectory. Since no flux reaches the segment of the closed surface at infinity, the flux in either direction, reactants to products or vice versa, must be exactly equal but opposite in sign through the two sufaces. (Flux into the closed surface through one dividing surface is flux out of the closed surface through the other dividing surface.) Since the reactive flux is equal through any two arbitrary dividing surfaces, eq.(2.1) must be independent of the location of the surface.

As an illustrative example of a choice of dividing surface consider the case where the surface is placed in the asymptotic region of channel a (reactants). If we choose coordinates in terms of a relative coordinate between the centers of mass of the colliding pair, R, and all other internal coordinates $\underset{\sim}{q}, \{\underset{\sim}{q}\}=\{q_i\}, i=1,2,\ldots,N-1$, then this choice of surface is just $f(R,\underset{\sim}{q}) = R_{max} - R = 0$. The Hamiltonian can be expressed as follows:

$$H(P,R,\underset{\sim}{p},\underset{\sim}{q}) = P^2/2\mu + h_{N-1}(\underset{\sim}{p},\underset{\sim}{q}) + V(R,\underset{\sim}{q}) \quad , \tag{2.4}$$

where $P,\underset{\sim}{p}$ are the momentum conjugate to $R,\underset{\sim}{q}$ respectively, μ is the reduced mass for the relative translational motion, $h_{N-1}(\underset{\sim}{p},\underset{\sim}{q})$ is the Hamiltonian for the N-1 internal degrees of freedom of the isolated reactants, and $V(R,\underset{\sim}{q})$ is the coupling between the internal and relative translational degrees of freedom. For $R = R_{max}$ in the asymptotic region of the reactant channel $V(R,\underset{\sim}{q}) \to 0$, and eq. (2.1) becomes

$$\begin{aligned} k^{CL}_{b\leftarrow a}(T) &= Q_a^{-1} h^{-N} \int d\underset{\sim}{p} \int d\underset{\sim}{q} \int dP \;\; P/\mu \; e^{-\beta P^2/2\mu} \; e^{-\beta h_{N-1}(\underset{\sim}{p},\underset{\sim}{q})} \; \chi_{b\leftarrow a}(P,R,\underset{\sim}{p},\underset{\sim}{q}) \Big|_{R=R_{max}} \\ &= Q_a^{-1} h^{-N} \int dE_t \; e^{-\beta E_t} \int d\underset{\sim}{p} \int d\underset{\sim}{q} \;\; e^{-\beta h_{N-1}(\underset{\sim}{p},\underset{\sim}{q})} \; \chi_{b\leftarrow a}(E_t, R_{max}, \underset{\sim}{p}, \underset{\sim}{q}) \end{aligned} \tag{2.5}$$

where $E_t = P^2/2\mu$ is the translational energy. This is just a standard expression used in Monte-Carlo trajectory calculations[14]. The internal coordinates and momentum and translational energy are Monte-Carlo selected from their distributions to determine the initial conditions for a trajectory starting at $R = R_{max}$. The rate constant is then the sum of the characteristic function $\chi_{b\leftarrow a}$ over many such trajectories, normalized by $h^N Q_a$.

Now we wish to make the fundamental approximation[15] of transition state theory to eliminate this need for the detailed trajectory information contained in $\chi_{b\leftarrow a}$. This can be done by replacing $\chi_{b\leftarrow a}$ by some other function which depends only on the phase space point $(\underset{\sim}{p},\underset{\sim}{q})$ and not the trajectory determined by it. The choice is a function which picks out all trajectories which have flux headed towards products at the dividing surface. Mathematically this can be expressed as a step function,

$$h(x) = \begin{cases} 1 \;, & x > 0 \\ 0 \;, & x < 0 \end{cases}$$

where x is the flux $\frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \frac{\underset{\sim}{p}}{m}$ at the surface. (We imply that positive flux is that which is pointed twards products.) However if we replace $\chi_{b\leftarrow a}(\underset{\sim}{p},\underset{\sim}{q})$ by $h\left(\frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \frac{\underset{\sim}{p}}{m}\right)$ in eq. (2.1) the expression will no longer be independent of the location of the dividing surface. If we choose the dividing surface in the reactant region many trajectories which start at the surface with flux headed towards products will not be reactive but turn around and recross the surface. Alternatively if the dividing surface is placed in the product region, many trajectories which have positve flux at the surface will have actually originated from the products and not be reactive (running the trajectory backwards in time would show such a trajectory to recross the dividing surface.) The fundamental assumption of transition state theory is that all trajectories which reach a dividing surface placed at the saddle point for the reaction with flux headed towards products will indeed be reactive ones. With this approximation eq. (2.1) becomes

$$k_{b\leftarrow a}^{CL\ TST}(T) = Q_a^{-1}(T)\, h^{-N} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\ e^{-\beta H(\underset{\sim}{p},\underset{\sim}{q})}\, \delta\left(f(\underset{\sim}{q})\right) \frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \frac{\underset{\sim}{p}}{m}\, h\left(\frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \frac{\underset{\sim}{p}}{m}\right) \qquad (2.6)$$

where it is understood that $f(\underset{\sim}{q})$ is chosen such that the dividing surface is at the saddle point.*

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* A more rigorous formulation of transition state theory is given by variationally adjusting the dividing surface to give the best results. This is discussed in detail by other authors.[8]

The case of an atom plus diatom reacting collinearly is depicted in fig. 1. Here the dividing surfaces S_1, S_2, S_3 are actually lines in the reactant region, the product region, and at the saddle point respectively. For the transition state theory choice of surface, S_3, a trajectory with energy infinitesimally above the barrier at the saddle point started from the surface in either direction will move away from the saddle point region very slowly picking up velocity as it moves down toward either reactants or products and will never return to the surface. For energies low enough there will be no recrossing trajectories and transition state theory will be exact. However for higher energies there will be trajectories which cross the surface towards products, rebound off the repulsive wall to recross the surface and be nonreactive. Before giving a more quantitative assessment of the validity of this assumption, it is convenient first to give a more formal expression for the rate expression and to describe a microcanonical formulation of the rate constant.

If the classical phase space average is identified as a classical trace,

$$h^{-N}\int d\underset{\sim}{p}\int d\underset{\sim}{q}\;\; A(\underset{\sim}{p},\underset{\sim}{q}) \;=\; \mathrm{tr}_{\mathrm{CL}}[A(\underset{\sim}{p},\underset{\sim}{q})]$$

then the rate expression takes the form

$$k^{\mathrm{CL}}_{b\leftarrow a}(T) \;=\; Q_a^{-1}(T)\;\; \mathrm{tr}_{\mathrm{CL}}\left[e^{-\beta H(\underset{\sim}{p},\underset{\sim}{q})}\; F_R(\underset{\sim}{p},\underset{\sim}{q})\right] , \qquad (2.7)$$

where $Q_a = \mathrm{tr}_{CL}[e^{-\beta H_o(\underset{\sim}{p},\underset{\sim}{q})}]$, H_o is the Hamiltonian in the reactant channel, and $F_R(\underset{\sim}{p},\underset{\sim}{q}) = F(\underset{\sim}{p},\underset{\sim}{q})\ \chi_{b\to a}(\underset{\sim}{p},\underset{\sim}{q})$ is the reactive flux. The transition state approximation gives

$$k_{b\leftarrow a}^{CL\ TST}(T) = Q_a^{-1}(T)\ \ \mathrm{tr}_{CL}\left[e^{-\beta H(\underset{\sim}{p},\underset{\sim}{q})}\ F(\underset{\sim}{p},\underset{\sim}{q})\ h\left(\frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}}\cdot\frac{\underset{\sim}{p}}{\underset{\sim}{m}}\right)\right] \tag{2.8}$$

A microcanonical formulation of the rate constant can be given by use of the microcanonical distribution function, $\delta(e\text{-}H)$, in place of the canonical distribution function, $e^{-\beta H}$. The two distribution functions are related by

$$e^{-\beta H} = \int dE\ e^{-\beta E}\ \delta(E\text{-}H) \tag{2.9}$$

If a dimensionless function $N^{CL}(E)$ is defined by

$$N^{CL}(E) \equiv 2\pi\hbar\ \mathrm{tr}_{CL}\ \left[\delta\left(E\text{-}H(\underset{\sim}{p},\underset{\sim}{q})\right)\ \ F_R(\underset{\sim}{p},\underset{\sim}{q})\right] \tag{2.10}$$

then it is related to the rate constant by

$$k^{CL}_{b\leftarrow a}(T) \;=\; Q_a^{-1}(T)\;(2\pi\hbar)^{-1}\int dE\; e^{-\beta E}\, N^{CL}(E) \qquad (2.11)$$

The transition state approximation can be made for the microcanonical version of the rate constant exactly as it was for the canonical case to give

$$N^{CL\;TST}(E) \;=\; 2\pi\hbar\;\mathrm{tr}_{CL}\left[\delta\!\left(E-H(\underset{\sim}{p},\underset{\sim}{q})\right)\;F(\underset{\sim}{p},\underset{\sim}{q})\;h\!\left(\frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}}\cdot\frac{\underset{\sim}{p}}{m}\right)\right] \qquad (2.12)$$

An interesting form for $N^{CL\;TST}(E)$ can be obtained by further reducing eq. (2.12). If the coordinates are chosen such that q_1 measures distance normal to the dividing surface then $f\,(q_1) = 0$ defines the surface at the saddle point and

$$F(\underset{\sim}{q},\underset{\sim}{p})\quad h\left(\frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}}\cdot\frac{\underset{\sim}{p}}{m}\right) = \;\delta\,(q_1)\;\frac{p_1}{m}\,h(p_1) \qquad (2.13)$$

which is equivalent to

$$F(\underset{\sim}{p},\underset{\sim}{q})\;h\!\left(\frac{\partial f}{\partial \underset{\sim}{q}}\cdot\frac{\underset{\sim}{p}}{m}\right) \;=\; \delta(q_1)\quad |p_1/2m| \qquad (2.14)$$

since $p_1 h(p_1) = \frac{1}{2}\,[p_1 + |p_1|]$, and $\mathrm{tr}_{CL}[\rho(\underset{\sim}{p},\underset{\sim}{q})\;\partial(q_1)\;p_1] = 0$, for either $\rho(\underset{\sim}{p},\underset{\sim}{q}) = e^{-\beta H(\underset{\sim}{p},\underset{\sim}{q})}$ or $\rho(\underset{\sim}{p},\underset{\sim}{q}) = \delta\left(E-H(\underset{\sim}{p},\underset{\sim}{q})\right)$. Using eq. (2.14) in eq. (2.12) gives

$$\begin{aligned} N^{CL\ TST}(E) &= 2\pi\hbar\; h^{-N} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\; \delta\left(E-H(\underset{\sim}{p},\underset{\sim}{q})\right)\, \delta(q_1)\, \frac{1}{2}\left|\frac{p_1}{m}\right| \\ &= h^{-(N-1)} \int d\underset{\sim}{p}_{N-1} \int d\underset{\sim}{q}_{N-1}\; h\left(E-H_{N-1}\right) \end{aligned} \tag{2.15}$$

where $\underset{\sim}{q}_{N-1},\underset{\sim}{p}_{N-1}$ are all coordinates and momentum except (q_1,p_1) and H_{N-1} is the classical Hamiltonian for all degrees of freedom except (q_1,p_1) evaluated for $q_1=0$. This has the interpretation of the classical approximation to the number of quantum states for the N-1 degrees of freedom $(q_1=0)$ with energy less than E, or the microcanonical partition function. This is just the form of the flux integral N(E) that is used in statistical theories for complex formation.[16-18]

As a quantitative test of the validity of the transition state approximation in classical mechanics, comparison should be made between the transition state theory rate expression and exact classical dynamical calculations (i.e. trajectories). Pechukas and McLafferty[11] showed by geometrical arguments that the microcanonical transition state rate expression was exact for energies up to about 0.1 eV above the barrier height for the collinear $H + H_2$ reaction. Calculations by Chapman et. al.[12] comparing microcanonical rate constants of transition state theory with dynamically exact trajectory calculations for both the collinear and full three-dimensional H + H_2 reaction have given similar results which are shown on figs. 1 and 2 respectively. It is seen that for energies up to 0.2 eV for the collinear case and to 0.4 eV for the three-dimensional calculation that the transition state results are essentially exact. These are energies that are well above the barrier height which indicates that the transition state assumption is a good one for energies near the threshold region of a reaction.

If the coordinates are chosen so that q_1 is normal to the dividing surface at the saddle point and measures progress along the reaction coordinate then the transition state approximation to the reactive flux is given by eq. 2.13. We assume that motion in the other N-1 degrees of freedom is bound and can be treated independently from q_1. More precisely,

$$H(\underset{\sim}{p},\underset{\sim}{q}) = h_1(p_1,q_1) + h_b\left(\underset{\sim}{p}_{N-1},\underset{\sim}{q}_{N-1}\right) \qquad (2.16)$$

where $(\underset{\sim}{p}_{N-1},\underset{\sim}{q}_{N-1}) = (p_i,q_i)$, i=2,...N; $h_1(p_1,q_1)$ is the Hamiltonian for motion along q_1 and $h_b(\underset{\sim}{p}_{N-1},\underset{\sim}{q}_{N-1})$ is the Hamiltonian for motion in the N-1 bound degrees of freedom. For this case eq. (2.6) reduces to

$$k^{CL\ TST}_{b\leftarrow a}(T) = Q_a^{-1}(T)\, h^{-N} \int dp_1 \int dq_1 \; e^{-\beta h_1(p_1,q_1)} \frac{p_1}{m} h\left(\frac{p_1}{m}\right) \delta(q_1) \int d\underset{\sim}{p}_{N-1} \int d\underset{\sim}{q}_{N-1}\, e^{-\beta h_b(\underset{\sim}{p}_{N-1},\underset{\sim}{q}_{N-1})}$$

$$= \frac{kT}{h} \frac{Q^{\ddagger}}{Q_o} e^{-\beta V_o} \tag{2.17}$$

where $Q^{\ddagger} = h^{-(N-1)} \int d\underset{\sim}{p}_{N-1} \int dq_{N-1}\, e^{-\beta\left(h_b(\underset{\sim}{p}_{N-1},\underset{\sim}{q}_{N-1}) - V_o\right)}$ is the partition function of the activated complex, $Q_o = Q_a/Q_{tr}$ is the partition function for the internal degrees of freedom of the reactants, where Q_{tr} is the translational partition function of the reactants, and V_0 is the value of the potential at the saddle point. This is the standard form of transition state theory found elsewhere.[5,19] It is in general possible to define these coordinates such that they diagonalize the kinetic energy, therefore coupling between motion along the reaction path and the bound N-1 degrees of freedom arises soley through the potential. However since the delta function in q_1 restricts evaluations of the potential on the surface, the potential effectively depends only on $\underset{\sim}{q}_{N-1}$, and the motion in q_1 is effectively separated from the other N-1 degrees of freedom. This is exemplified in the collinear A + BA reaction for which the potential energy surface is shown in fig. 1. The choice of coordinates s and u shown on the figure diagonalize the kinetic energy giving

$$H(p_s,p_u,s,u) = p_s^2/2m_s + p_u^2/2m_u + V(s,u) \quad , \tag{2.18}$$

where V(s,u) is the potential surface and p_s, p_u are the momentum conjugate to s,u respectively. For this system eq. (2.6) gives eq. (2.17) where

$$Q^{\ddagger} = \int du \int dp_u \quad e^{-\beta\left(p_u^2/2m_u + V(u,o)\right)} \qquad (2.19)$$

It is interesting to note that we have arrived at the standard transition state rate expression with no recourse to arguments of equilibrium between reactants and the activated complex, the distribution of states at the dividing surface, or vibrational adiabacity of the reaction which are often found in textbook descriptions of transition state theory. The approximations used here are 1) Boltzmann distribution of reactant internal states and relative translation, 2) the use of classical mechanics to describe the dynamics of the system, and 3) the dynamical approximation termed the fundamental assumption.

B. Quantum Mechanical Transition State Theory

Although approximations used to derive the classical transition state rate expression may be valid for classical mechanics, it is not clear they will remain valid if a rigorous quantum mechanical treatment of the theory is used. However the usual method of including quantum effects into the traditional transition state expression, eq. (2.17), is to assume the partition functions to be quantum mechanical ones and to include a tunnelling correction factor, Γ(T),

$$k(T) = \frac{kT}{h} \Gamma(T) \frac{Q^{\ddagger}(T)}{Q_0(T)} e^{-\beta Vo} . \qquad (2.20)$$

This method of introducing quantum mechanics into eq. (2.17) contains two critical assumptions: the fundamental assumption and a separability approximation. The separability approximation arises through the introduction of the tunneling correction factor which is assumed to be one-dimensional. Detailed comparison of this type of expression with exact quantum scattering calculations have shown very poor agreement in some situations suggesting that the validity of these assumptions should be tested.

Evidence that the fundamental assumption may still be valid is shown in the work of Kuppermann, Adams, and Truhlar.[20] Streamlines of flux plotted as a function of coordinate for the collinear H + H_2 system show that at low energies the flux is a well-behaved function moving monotonically through the saddle point region. Only at higher energies do whirlpool effects in the flux contours begin to appear analagous to recrossing trajectories in the classical system. The semiclassical calculations of George and Miller[21] for collinear H + H_2 show tunneling trajectories in complex time which move monotonically through the saddle point region with no recrossings of the dividing surface suggesting that the fundamental assumption should be good quantum mechanically.

These same two previous works also indicate that the separability approximation may not be valid. In both these works it was shown that the dynamics took the system through the dividing surface in classical forbidden regions away from the saddle point. It is in just these regions away from the saddle point that one expects the separation of the Hamiltonian no longer to be valid. This was realized by Johnston and Rapp[22] in work which tried to account for this nonseparability.

Still, a more quantitative assessment of the applicability of these assumptions is needed. An important contribution towards this end was given through Miller's formulation of a quantum mechanical version of transition state theory which does not include the separability approximation.[6] A brief review of this work is given below which treats the collinear atom plus diatom explicitly.

An exact expression for the thermal rate constant for the collinear reaction of A + BC(arrangement a) going to AB + C (arrangement b) is

$$k^{QM}_{b\leftarrow a}(T) = h^{-1}\, Q_a^{-1}(T) \sum_{n_a} \sum_{n_b} \int_0^\infty dE_t\, e^{-\beta(E_t+\varepsilon_{n_a})} \left| S_{n_b,n_a}(E_t) \right|^2 \qquad (2.21)$$

where $\beta = (kT)^{-1}$, n_a and n_b are vibrational quantum numbers in channels a and b respectively, E_t is the initial translational energy, $S_{n_b,n_a}(E_t)$ is the S-matrix element for reaction from initial state n_a to final state n_b, and Q_a is the total partition function per unit volume for reactants,

$$Q_a = Q_{BC}\,(2\pi\hbar)^{-1}\int_{-\infty}^{\infty} dp\; e^{-\beta p^2/2u}$$

$$Q_{BC} = \sum_{n_a} e^{-\beta\varepsilon_{n_a}} \qquad (2.22)$$

is the vibrational partition function of molecule BC. The goal is to transform this expression into one which is amenable to the fundamental assumption of transition state theory, that is, to express the rate constant as a reactive flux through a surface which divides products and reactants. The problem arises then to express the quantum flux in terms of the quantity which contains the dynamical information, the S matrix elements. The flux through a surface can be defined as

$$-\int_S dS\,\mathrm{Re}\left(\psi^* \frac{\hbar}{i\mu}\,\underset{\sim}{\nabla}\,\psi\right) \quad , \qquad (2.23)$$

where S defines the surface. If one takes for example surface S_1 in figure 1, defined by $R = R_{max}$, eq. (2.23) becomes

$$-\mathrm{Re}\int_{-\infty}^{\infty} dr\; \psi^*(r,R)\;\frac{\hbar}{i\mu}\,\frac{\partial}{\partial R}\,\psi(r,R)\Big|_{R=R_{max}} \quad . \qquad (2.24)$$

One can introduce the S-matrix into this expression for the flux by using the asymptotic form of the scattering wavefunction in the reactant channel n_a:

$$\psi_{p,n_a}(r\ R) \xrightarrow[R\to\infty]{} \frac{-e^{-ik_{n_a}R}}{(2\pi\hbar)^{1/2}}\ \phi_{n_a}(r) + \sum_{n_a'} \frac{e^{ik_{n_a}'R}}{(2\pi\hbar)^{1/2}}\ \phi_{n_a}'(r) \left(\frac{v_{n_a}}{v_{n_a'}}\right) S_{n_a',n_a}\ (E_t) \tag{2.25}$$

where $E_t = P^2/2\mu$; $k_{n_a} = 2\mu\ E_t/\hbar^2$; $v_{n_a} = \hbar k_{n_a}/\mu$ is the asymptotic velocity in channel n_a; and $\{\phi_{n_a}(r)\}$ are the internal state wavefunctions for vibration. The flux then reduces to

$$v_{n_a}\ (2\pi\hbar)^{-1} \left[1 - \sum_{n_a'} \left|S_{n_a',n_a}\ (E_t)\right|^2\right] \tag{2.26}$$

using the orthonormality of the internal state wavefunctions.

The flux through a surface in the product arrangement can be similarly defined as

$$v_{n_a}\ (2\pi\hbar)^{-1} \sum_{n_b} \left|S_{n_b,n_a}\ (E_t)\right|^2 \tag{2.27}$$

(the absence of the one in this form arises from the fact that there is no incident plane wave contribution to the wavefunction in the product channels.) From the unitarity of the S-matrix one knows that

$$1 = \sum_{n_a'} \left| S_{n_a',n_a}(E_t) \right|^2 + \sum_{n_b} \left| S_{n_b,n_a}(E_t) \right|^2 \tag{2.28}$$

indicating that equations (2.26) and (2.27) are identical, the flux through the two surfaces are equal. This can also be seen from the quantum mechanical continuity equation[23] which states that for time independent wavefunction, the flux through a close suface is zero:

$$\mathrm{Re} \oint d\underset{\sim}{S} \circ \left(\psi^* \frac{\hbar}{2\mu i} \underset{\sim}{\nabla} \psi = 0 \right) \quad . \tag{2.29}$$

As in the classical case two surfaces can be joined with segments at infinity to give a closed surface for which eq. (2.29) holds proving that the reactive flux through any two dividing surfaces must be the same.

By introducing a function of coordinates $f(\underset{\sim}{q})$ such that $f(\underset{\sim}{q}) = 0$ defines the dividing surface the flux can be expressed as a volume integral:

$$\mathrm{Re} \int d\underset{\sim}{q}\ \delta\left(f(\underset{\sim}{q})\right) \psi^*(\underset{\sim}{q}) \frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{v}\ \psi(\underset{\sim}{q}) = \mathrm{Re} \langle \psi | F_{op} | \psi \rangle \tag{2.30}$$

and $F_{op} = \delta\left(f(\underset{\sim}{q})\right)\frac{\partial f}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{v}$, with $v_k = \frac{\hbar}{i\mu}\,\frac{\partial}{\partial q_k}$; $k = 1,2,\ldots,N$ for the N degrees of freedom. Substituting eq. (2.27) and (2.30) into (2.21) gives

$$k^{QM}_{b\leftarrow a}(T) = Q_a^{-1}(T) \sum_{n_a} \int_0^\infty dE_t\, v_{n_a}^{-1} \langle \psi_{P,n_a} | e^{-\beta H} F | \psi_{P,n_a} \rangle \tag{2.31}$$

where use has been made of the fact that Ψ is an eigenfunction of the Hamiltonian and thus $e^{-\beta H}\, \psi_{P,n_a} = e^{-\beta(E_t+\varepsilon_{n_a})}\, \psi_{P,n_a}$. This can be put into the form of a quantum mechanical trace by changing variable of integration from E_t to P and then introducing a projection operator to change the limits of integration on P,

$$\begin{aligned} k^{QM}_{b\ a}(T) &= Q_a^{-1}(T) \sum_{n_a} \int_{-\infty}^{0} dP\ \langle \psi_{P,n_a} | e^{-\beta H} F | \psi_{P,n_a} \rangle \\ &= Q_a^{-1}(T) \sum_{n_a} \int_{-\infty}^{\infty} dP\, \langle \psi_{P,n_a} | e^{-\beta H} F \mathscr{P} | \psi_{P,n_a} \rangle \\ &= Q_a^{-1}(T)\ \mathrm{tr}\left[e^{-\beta H} F \mathscr{P}\right] \end{aligned} \tag{2.32}$$

where

$$\mathscr{P} = \sum_{n_a} \int_{-\infty}^{\infty} dP \, |\psi_{P,n_a}> h(-P) < \psi_{P,n_a}| \qquad (2.33)$$

This is very similar to eq. (2.7) from section A, where the classical functions H(p,q) and f(p,q) have been replaced by their quantum mechanical operators, the trace is a quantum mechanical one, and the characteristic function $\chi(\underset{\sim}{p},\underset{\sim}{q})$ is replaced by a projection operator $\mathscr{P}$. The projection operator picks out those states which have negative relative momentum P in the reactant arrangement. More precisely it is an operator which projects onto those states which evolved from reactants in the infinite past,

$$\mathscr{P} = \lim_{t\to-\infty} e^{iHt/\hbar} \, h(-P) \, e^{-iHt/\hbar} \qquad (2.34)$$

Just as in the classical case with $\chi(\underset{\sim}{p},\underset{\sim}{q})$, $\mathscr{P}$ contains all the dynamical information through the propagator $e^{iHt/\hbar}$. We now wish to make an approximation analagous to fundamental assumption of classical transition state theory to obviate this need for exact dynamical information.

Equation (2.32) is an exact expression for the rate constant assuming only a Boltzmann distribution of reactant internal states and relative translation. Information concerning the location of the dividing surface is contained in the expression F_{op} through $f(\underset{\sim}{q})$. As in the classical expression the exact quantum rate expression is independent of the location of the surface. The transition state approximation for the quantum mechanical rate expression parallels that of classical transition state theory, $\mathscr{P} \rightarrow h\left(\frac{\partial f(\underset{\sim}{q})}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{v}\right)$ and we now define the surface to be at the saddle point region. Thus the exact projection operator is replaced by an approximate one which projects onto those states which have flux in the produce direction at the dividing surface. Since the approximate rate expression is no longer independent of the location of the dividing surface, the classical transition state choice is used. For the collinear A + BC reaction this corresponds to surface S_3 of fig. 1 and

$$h\left(\frac{\partial f}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{v}\right) = h(p_s) \tag{2.35}$$

where p_s is the momentum conjugate to the coordinate s at the saddle point.

Finally the transition state rate constant can be written

$$k^{QM\ TST}_{b \leftarrow a}(T) = Q_a^{-1}(T) \ \mathrm{tr} \left[e^{-\beta H} \, \delta(f) \, \frac{\partial f}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{v} \, h\left(\frac{\partial f}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{v}\right)\right] \tag{2.36}$$

However one ambiguity arises from the introduction of the transition state approximation. For the exact projection operator $\mathcal{P}$, F and $\mathcal{P}$ commute within the trace,

$$\mathrm{tr}[e^{-\beta H}\, F\,] = \mathrm{tr}[e^{-\beta H}\mathcal{P}F] \qquad (2.37)$$

This is not true for $h\left(\frac{\partial f}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{v}\right)$ though,

$$\mathrm{tr}\left[e^{-\beta H}\, F\, h\left(\frac{\partial f}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{v}\right)\right] \neq \mathrm{tr}\left[e^{-\beta H}\, h\left(\frac{\partial f}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{v}\right)\, F\right] \qquad (2.38)$$

This can be viewed alternatively as not knowing the proper transition state approximation to the exact reactive flux operator, $F_R = F\mathcal{P} = \mathcal{P}F$. Classically the exact reactive flux is $F_R(\underset{\sim}{p},\underset{\sim}{q}) = F(\underset{\sim}{p},\underset{\sim}{q})\chi(\underset{\sim}{p},\underset{\sim}{q})$ and its subsequent transition state approximation is $F_R^{TST} = F(\underset{\sim}{p},\underset{\sim}{q})\; h\left(\frac{\partial f}{\partial \underset{\sim}{q}} \cdot \underset{\sim}{v}\right)$. An approximate method of identifying the transition state reactive flux operator is through the Weyl correspondence rule[24] which gives a prescription for finding an approximate quantum operator that corresponds to the classical function. For the case that the classical function is a function of coordinates only or momenta only, the Weyl prescription becomes exact. In the situation that the classical function is a non-additive function of coordinates and momenta, the quantum operator is not well-defined since q and p operators do not commute, however, the

Weyl prescription supplies a unique operator. The use of the Weyl approximation to the reactive flux in equation (2.36) is mathematically equivalent to replacing the quantum mechanical trace by a classical phase space average and replacing the Boltzmann operator $e^{-\beta H}$ by the Wigner distribution function $W(\underset{\sim}{p},\underset{\sim}{q})$,[25]

$$W(\underset{\sim}{p},\underset{\sim}{q}) = h^{-N}\int d\underset{\sim}{q}'\; e^{-i\underset{\sim}{p}\cdot\underset{\sim}{q}'}\,\langle \underset{\sim}{q}+\tfrac{1}{2}\underset{\sim}{q}'|e^{-\beta H}|\underset{\sim}{q}-\tfrac{1}{2}\underset{\sim}{q}'\rangle \qquad (2.39)$$

to give

$$k^{QM\ TST}_{b\leftarrow a}(T) = Q_a^{-1}(T)\int d\underset{\sim}{p}\int d\underset{\sim}{q}\; W(\underset{\sim}{p},\underset{\sim}{q})\; F(\underset{\sim}{p},\underset{\sim}{q})\; h\!\left(\frac{\partial f}{\partial \underset{\sim}{q}}\cdot\frac{\underset{\sim}{p}}{m}\right) . \qquad (2.40)$$

This will be denoted the Weyl prescription to quantum mechanical transition state theory. It should be noted that besides the fundamental transition state approximation it has become necessary to introduce another approximation of a semiclassical nature to identify the reactive flux operator within the transition state approximation.

A microcanonical version of the exact quantum mechanical rate expression is given by

$$N^{QM}(E) = 2\pi\hbar\ \mathrm{tr}\,[\delta(E-H)\ F_R] \qquad (2.41)$$

which is related to the canonical formulation by

$$k_{b\leftarrow a}^{QM}(T) = Q_a^{-1}(T)\ (2\pi\hbar)^{-1} \int_0^\infty dE\ e^{-\beta E}\ N^{QM}(E) \qquad (2.42)$$

The dimensionless quantity N(E) can also be expressed as

$$N^{QM}(E) = \sum_{n_a,n_b} |S_{n_a,n_b}(E)|^2 \qquad (2.43)$$

thus reproducing equation (2.21). The probability of going from state n_a in arrangement a to state n_b in arrangement b is $|S_{n_a,n_b}(E)|^2$. The sum over all initial and final states of these probabilities is N(E), the cumulative reaction probability. The transition state approximation to eq. (2.41) is straightforward, although the same ambiquity arises in the ordering of the operators. This can be dealt with by using the Weyl correspondence rule to identify the reactive flux operator for the transition state theory.

The transition state rate expression (2.36) is free of auxiliary approximations that are common in conventional forms of transition state theory. It is interesting to see that by making a separability approximation we can arrive at the conventional form of the theory. We assume that we can define a set of coordinate $\underset{\sim}{q}$ with conjugate momenta $\underset{\sim}{p}$ such that $q_1 = 0$ defines the dividing surface at the saddle point region. Furthermore, it is assumed that a separation of variables can be performed on the Hamiltonian as in eq. (2.16) where the momenta are now the quantum mechanical operators. The traditional expression of transition state theory is easily derived:

$$k_{b\leftarrow a}(T) \;=\; \Gamma(T)\,\frac{kT}{h}\,\frac{Q^{\ddagger}(T)}{Q_o(T)}\,e^{-\beta V_o}\;, \tag{2.44}$$

where

$$Q^{\ddagger}(T) \;=\; \mathrm{tr}_{N-1}\left[e^{-\beta h_b}\right] \tag{2.45}$$

is the partition function of the activated complex, and

$$\Gamma(T) \;=\; 2\pi\hbar\beta\;\mathrm{tr}_1\left[e^{-\beta h_1}\;\delta(q_1)\,\frac{p_1}{m}\,h(p_1)\right] \tag{2.46}$$

is a one-dimensional tunneling probability. The tunneling probability can be evaluated easily for two sample potentials, the free particle $h_1 = p_1^2/2m_1$, and the harmonic barrier $h_1 = p_1^2/2m_1 - m_1\omega_1 q_1^2/2$.

$$\Gamma(T) = 2\pi\hbar\beta \int_{-\infty}^{\infty} dp_1 \int_{-\infty}^{\infty} dq_1 \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dq_1' \, e^{ip_1 \cdot q_1'/\hbar} \, \delta(q_1) \frac{p_1}{m} h(p_1) \, \langle q_1 + \tfrac{1}{2} q_1' \, | e^{-\beta h_1} | \, q_1 - \tfrac{1}{2} q_1' \rangle \tag{2.47}$$

and

$$\Gamma(T) = \beta \int_{0}^{\infty} dp_1 \int_{-\infty}^{\infty} dq_1' \; e^{ip_1 q_1'/\hbar} \frac{p_1}{m_1} \langle \tfrac{1}{2} q_1' \, | e^{-\beta h_1} | \, -\tfrac{1}{2} q_1' \rangle \tag{2.48}$$

For the free particle Hamiltonian

$$\langle \tfrac{1}{2} q_1 \, | \, e^{-\beta h_1} \, | \, -\tfrac{1}{2} q_1 \rangle = \sqrt{\frac{m}{2\pi\hbar^2\beta}} \; e^{\frac{-m}{\hbar^2\beta}} \; \frac{q_1^{\,2}}{2} \tag{2.49}$$

which gives $\Gamma = 1$, the expected result since there should be no tunneling. For the harmonic barrier Hamiltonian

$$\langle \tfrac{1}{2} q_1 \, | \, e^{-\beta h_1} \, | \, -\tfrac{1}{2} q_1 \rangle = \sqrt{\frac{m\omega}{2\pi\hbar \, \sin(\hbar \;\beta)}} \quad \exp\left[\frac{-m\omega}{\hbar} \cot \; \frac{\hbar\omega\beta}{2} \; q_1^{\,2} \right] \tag{2.50}$$

which gives

$$\Gamma = \frac{\hbar\omega\beta}{2} \Big/ \sin\left(\frac{\hbar\omega\beta}{2}\right) \tag{2.51}$$

which is the correct result - the Wigner correction factor.[26]

As a more rigorous test of the quantitative validity of the fundamental assumption of transition state theory and the separability approximation, it was desired to apply eq. (2.36) to a multidimensional system in which the separation of the Hamiltonian is not rigorous. The collinear H + H_2 system is an excellent candidate for this purpose for several reasons: it is one of the smallest multidimensional systems (two mathematical dimensions), thus reducing effort in the calculation; there are many exact quantum scattering calculations with which to compare; the atoms are sufficiently light so that quantum effects should be prominent necessitating a quantum mechanical description of the system; and previous work by Kupperman and Truhlar[27] has compared conventional forms of transition state theory with exact results and shown poor agreement.

A straighforward method of evaluating eq. (2.36) for the collinear H + H_2 system by expanding the trace in a discrete basis set using the Weyl form for the reactive flux was attempted. Progressively larger basis sets of finite size were used checking for convergence of the trace with respect to the basis size. This approach was unsuccessful due to the ill behaved nature of the matrix elements of the Weyl reactive flux operator. To further test this basis set approach, calculations were carred out by McCurdy and Miller on a sample one-dimensional tunneling problem: the symmetric Eckart potential

$$V(x) = V_o \operatorname{sech}^2 (x/a) \quad . \tag{2.52}$$

Exact quantum calculations have been tabulated by Johnston[29] for the two dimensionless parameters

$$u = \frac{\hbar\beta}{a}\left(\frac{2V_o}{m}\right)^{1/2} \quad , \quad \alpha = \frac{a}{\hbar}\,(2mV_o)^{1/2} \quad ,$$

where u is proportional to β, and α, which is proportional to $am^{1/2}$, is a measure of how quantum-like the system is (lower α implies a more quantum-like system.) The results were similar to those for the collinear $H + H_2$ system in that they never converged with respect to basis size due to the ill-behaved nature of the Weyl flux operator.

Further calculations by McCurdy and Miller seem to indicate that the Weyl prescription to transition state theory may not be valid. A path integral approach[30] to evaluating eq. (2.47) for the Ekhart barrier was used resulting in very poor results for the cases in which tunneling was important. This is not a totally unexpected result, however. The Weyl prescription for operators is intrinsically tied in with the Wigner distribution function in that one can be rigorously derived from the other. It is known that the Wigner distribution function is not guaranteed to be a positive number. If one tries to interpret the distribution function as the probability of a system being at the phase space point $(\underset{\sim}{p},\underset{\sim}{q})$ a negative number makes no physical sense. This is because a question is being asked (what is the probability of a system having position q and momenta p?) which is not a legitimate one to ask quantum mechanically.

Other methods of treating the ambiquity of the ordering of the operators in eq. (2.36) which retain a full quantum mechanical treatment of the problem are not obvious. However, it seems that semiclassical methods should be very useful in obtaining a workable form of transition state theory which retains quantum effects. The semiclassical limit of eq. (2.36) is presented in the next section.

C. Semiclassical Limit of Quantum Mechanical Transition State Theory

The classical S-matrix theory of Miller[31] can be used to obtain a semiclassical approximation to eq. (2.21). The use of complex valued trajectories to describe tunneling has been successful although difficult to carry out due to the necessity to know the full dynamics of the system. The rate expression of quantum mechanical transition state theory avails itself to a different type of semiclassical approximation which one would expect to be easier to apply since the full dynamics are no longer needed. Two different types of semiclassical models are reviewed here, both based upon the classical path approximation for matrix elements of the Boltzmann operator,[32] $e^{-\beta H}$, which is briefly described below.

As Feynman[33] noted, the Boltzman operator can be viewed as the quantum mechanical propagator, $e^{iH(t_2-t_1)/\hbar}$, for an imaginary time increment, $t_2-t_1 = -i\hbar\beta$. Since the propagator is dependent on the time difference, t_2-t_1, and not the absolute values of t_1,t_2, we take $t_1 = 0$ and $t_2 = t$. The semiclassical approximation to the coordinate matrix elements of the propagator is well known,[3]

$$\langle \underset{\sim}{q}_2 | e^{-iHt/\hbar} | \underset{\sim}{q}_1 \rangle = \left[(2\pi i\hbar)^N \left| \frac{\partial \underset{\sim}{q}_2}{\partial \underset{\sim}{p}_1} \right|_{\underset{\sim}{q}_1} \right]^{-1/2} \left[\exp \frac{i}{\hbar}\, \phi(\underset{\sim}{q}_2,\underset{\sim}{q}_1) \right] \qquad (2.53)$$

where

$$\phi(\underset{\sim}{q}_2,\underset{\sim}{q}_1) = \int_0^t dt' \left[\underset{\sim}{p}(t') \cdot \underset{\sim}{q}(t') - H\Big(\underset{\sim}{p}(t'),\, \underset{\sim}{q}(t')\Big) \right] , \qquad (2.54)$$

is the classical action along the classical trajectory which goes from $\underset{\sim}{q}_1$ to $\underset{\sim}{q}_2$ in time t. Instead of having the initial conditions problem usually encountered in classical trajectories, we now have a boundary value problem in which the initial and final coordinates and the time increment determine the initial momenta (and final momenta), i.e. $\underset{\sim}{q}_2(\underset{\sim}{p}_1,\underset{\sim}{q}_1) = \underset{\sim}{q}_2$ is the equation to be solved for $\underset{\sim}{p}_1$ given $\underset{\sim}{q}_1,\underset{\sim}{q}_2$, and the time interval t, where $\underset{\sim}{q}_2$ is the value of $\underset{\sim}{q}(t')$ at $t' = t$ for a trajectory with momenta and coordinates $(\underset{\sim}{p}_1,\underset{\sim}{q}_1)$ at $t = 0$. The determinate of the Jacobian $\left(\partial\underset{\sim}{q}_2/\partial\underset{\sim}{p}_1\right)_{q_1}$ is evaluated for this trajectory. The formal substitution of $\tilde{t} = i\hbar\beta$ into eq. (2.53) gives the semiclassical approximation to the Boltzmann density matrix in terms of a trajectory in purely imaginary time. This can be reduced to dynamics in purely real time by introducing $\tau = it$ and $\underset{\sim}{\bar{p}} = m\left(\partial\underset{\sim}{q}/\partial\tau\right) = -im\, d\underset{\sim}{q}/dt = -i\underset{\sim}{p}$. This change of variables has an interesting effect on the equations of motion, $\dot{\underset{\sim}{p}} = -\partial H/\partial\underset{\sim}{q} = \partial\underset{\sim}{p}/\partial t = -\partial\underset{\sim}{\bar{p}}/\partial\tau = -\underset{\sim}{\bar{p}}'$, which implies that $\underset{\sim}{\bar{p}}' = +\partial V(\underset{\sim}{q})/\partial\underset{\sim}{q}$ for Cartesian coordinates. This has the effect of replacing $V(\underset{\sim}{q})$ by $-V(\underset{\sim}{q})$ in the equations of motion. Therefore running a trajectory in purely imaginary time is equivalent to running trajectories in real time but on the inverted potential. If H(t) is defined as

$$H(\tau) = \frac{\underset{\sim}{\bar{p}}^2(\tau)}{2m} + V\left(\underset{\sim}{q}(\tau)\right) = \frac{\underset{\sim}{\bar{p}}(\tau)\cdot\underset{\sim}{q}'(\tau)}{2} + V\left(\underset{\sim}{q}\,(\tau)\right), \qquad (2.55)$$

it is no longer a conserved quantity, and the Boltzmann density matrix becomes

$$\langle\underset{\sim}{q}_2|e^{-\beta H}|\underset{\sim}{q}_1\rangle = \left[(2\pi\hbar)^N \left|\frac{\partial\underset{\sim}{q}_2}{\partial\underset{\sim}{p}_1}\right|_{\underset{\sim}{q}_1}\right]^{-1/2} \exp\left[-\frac{1}{\hbar}\int_0^{\hbar\beta} H(\tau)\, d\tau\right] \qquad (2.56)$$

where the bar notation has been dropped.

1. Semiclassical Phase Space Distribution

The Weyl prescription for the quantum mechanical transition state rate constant, eq. (2.40), identifies the rate constant as a classical phase space average over an approximate distribution function: Wigner's function $W(\underset{\sim}{p},\underset{\sim}{q})$. However, Wigner's distribution still contains a quantum mechanical matrix element of the Boltzmann operator. The semiclassical approach described here is to replace the Wigner distribution function in eq. (2.40) by a semiclassical function - i.e., one which is constructed from classical mechanics but still contains quantum effects.

A semiclassical distribution function, $\rho_{SC}(\underset{\sim}{p},\underset{\sim}{q})$ can be identified by examining the partition function

$$Q_{SC} = h^{-N} \int d\underset{\sim}{p} \int d\underset{\sim}{q} \quad \rho_{SC}(\underset{\sim}{p},\underset{\sim}{q}) \quad . \tag{2.57}$$

The exact quantum mechanical partition function is

$$\begin{aligned} Q_{QM} &= \mathrm{tr}\left[e^{-\beta H}\right] = \int d\underset{\sim}{q}_o \ \langle \underset{\sim}{q}_o | e^{-\beta H} | \underset{\sim}{q}_o \rangle \\ &= \int d\underset{\sim}{q}_o \int d\underset{\sim}{q}_1 \ \left| \langle \underset{\sim}{q}_o | e^{-\frac{\beta H}{2}} | \underset{\sim}{q}_1 \rangle \right|^2 \end{aligned} \tag{2.58}$$

Inserting the classical path approximation to the Boltzmann density matrix into eq. (2.58) gives

$$Q_{SC} = \int d\underset{\sim}{q}_o \int d\underset{\sim}{q}_1 \left[(2\pi\hbar)^N \left| \frac{\partial \underset{\sim}{q}_1}{\partial \underset{\sim}{p}_o} \right|_{\underset{\sim}{q}_o} \right]^{-1} \exp\left[-\frac{2}{\hbar} \int_0^{\hbar\beta/2} d\tau\, H(\tau) \right]$$

$$= h^{-N} \int d\underset{\sim}{q}_o \int d\underset{\sim}{p}_o \quad \exp\left[-\frac{2}{\hbar} \int_0^{\hbar\beta/2} d\tau\, H(\tau) \right] \tag{2.59}$$

where the Jacobian $(\partial \underset{\sim}{p}_o/\partial \underset{\sim}{q}_1)_{\underset{\sim}{q}_o}$ has been used to make the change in variables of integration. The independent variables are now the initial coordinates and momenta $\left(\underset{\sim}{p}(\tau=0),\ \underset{\sim}{q}(\tau=0)\right)$ with the time increment determining the final conditions.

One ambiquity inherent in eq (2.59) is that a change of integration variables to any $\left(\underset{\sim}{p}(\tau_o),\ \underset{\sim}{q}(\tau_o)\right)$ along the trajectory leaves the partition function invariant (Liouville's theorem implies that $dp(\tau)\ dq(\tau) = dp_o dq_o$ for any τ.) This change of variable is equivalent to replacing

$$\exp\left[\frac{-2}{\hbar} \int_0^{\hbar\beta/2} d\tau\, H(\tau) \right] \quad \text{by} \quad \exp\left[\frac{-2}{\hbar} \int_{-\tau_o}^{\hbar\beta/2-\tau_o} d\tau\, H(\tau) \right]$$

in eq. (2.59) while leaving $dp_o dq_o$ as the integration variables, thus placing the ambiquity in the distribution function.

Comparison of eq. (2.57) and (2.59) identifies ρ_{SC} as

$$\rho_{SC}(\underset{\sim}{p}_o\ \underset{\sim}{q}_o) = \exp\left[\frac{-2}{\hbar}\int_{-\tau_0}^{\hbar\beta/2-\tau_0} d\tau\ H(\tau)\right] \tag{2.60}$$

The classical high temperature limit ($\beta \to 0$) gives

$$\rho_{SC}(\underset{\sim}{p},\underset{\sim}{q}) \longrightarrow e^{-\beta H(\tau_0)}$$

for $\tau_o = 0$ this gives $e^{-\beta H(\underset{\sim}{p}_o,\underset{\sim}{q}_o)}$ which is the classical Boltzmann distribution function.

Classically one used information just at the phase space point to calculate the distribution probabilities. However, quantum mechanically it is impossible to have a phase space distribution since simultaneous knowledge of coordinates and momenta is not possible. The semiclassical "compromise" is to average over the phase space around the phase space point of interest. The volume of phase space that is average over is related to β, as β becomes more quantum-like (large) the volume becomes larger.

Replacing $W(\underset{\sim}{p},\underset{\sim}{q})$ by $\rho_{SC}(\underset{\sim}{p},\underset{\sim}{q})$ in eq. (2.40) gives the semiclassical approximation

$$Q_a\, k^{SC}_{b\leftarrow a}(T) \;=\; h^{-N} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\;\; F_R(\underset{\sim}{p},\underset{\sim}{q})\; \exp\left[\frac{-2}{\hbar}\;\; d\int_{-\tau_o}^{\hbar\beta/2-\tau_o} H(\;)\right] \qquad (2.61)$$

where we must still specify τ_o. The partition function was independent of the choice of $\tau_{o,}$ however this is not true for eq. (2.61). A change of τ_o will change the weighting function $\rho_{SC}(\underset{\sim}{p},\underset{\sim}{q})$ for each phase space point. To help determine a good choice of τ_o it is instructive to examine a separable system, i.e., the Hamiltonian is given by eq. (2.16) and the reactive flux is given by eq. (2.13). Thus eq. (2.61) becomes

$$Q_a\, k^{SC}_{b\leftarrow a}(T) \;=\; \frac{kT}{h}\,\Gamma(T)\; e^{-\beta Vo}\, Q^{\ddagger} \qquad (2.62)$$

where the partition function for the activated complex is

$$Q^{\ddagger} = h^{-(N-1)} \int d\underset{\sim}{p}_{N-1} \int d\underset{\sim}{q}_{N-1} \; \exp\left[\frac{-2}{\hbar}\int_{-\tau_o}^{\hbar\beta/2-\tau_o} d\tau \, h_b(\tau)\right] , \qquad (2.63)$$

and the tunneling correction factor is

$$\Gamma(T) = 2\pi\hbar\beta \int_{-\infty}^{\infty} dp_1 \int_{-\infty}^{\infty} dq_1 \, \frac{p_1}{m_1} h(p_1) \; \exp\left[\frac{-2}{\hbar}\int_{-\tau_o}^{\hbar\beta/2-\tau_o} h_1(\tau)\right] \qquad (2.64)$$

The partition function for the activated complex is independent of the choice of τ_o, however $\Gamma(T)$ is not. For a harmonic barrier, $h_1 = p_1^2/2m_1 - m_1\omega_1^2 q_1^2/2$, $\tau_o = h\beta/4$ gives the exact result,

$$\Gamma(T) = \frac{\hbar\omega_1\beta}{2} \Bigg/ \sin\left(\frac{\hbar\omega_1\beta}{2}\right)$$

A more realistic barrier is the previously described symmetric Eckhart barrier, eq. (2.52). The semiclassical expression for $\tau_o = h\beta/4$ is compared with Johnston's results[29] in fig. 4, for two values of α. Agreement is excellent for $\alpha = 20$ but tends to deviate for $\alpha = 4$. The barrier for the H + H_2 system corresponds to $\alpha = 10$-12, indicating that the semiclassical description of tunneling should be quite good for this system.

Application of eq. (2.61) was made to the collinear $H + H_2$ system using the Truhlar-Kupperman[34] potential surface for H_3 (a Wall-Porter[35] fit to the scaled Shavitt-Stevens-Minn-Karplus[36] potential surface) and also the Porter-Karplus[37] potential surface. The results for the two potentials are shown on figs. 5 and 6 respectively. The semiclassical results are the points which are compared with exact quantum scattering results[38] (upper solid line) as well as the rate constant of conventional transition state theory (lower solid line),

$$k_{b\leftarrow a}(T) \;=\; Q_a^{-1}(T)\,\frac{kT}{h}\left[2\,\sinh\left(\frac{\hbar\omega^{\ddagger}\beta}{2}\right)\right]^{-1} \qquad (2.65)$$

where $\omega^{\ddagger}$ is the symmetric stretch frequency at the saddle point. No tunneling correction factor was used as Truhlar and Kuppermann[27] found that use of any type of one-dimensional corrections tended to degrade the results. One can see that the semiclassical theory is a marked improvement over traditional forms of transition state theory. At 200 K for example, the conventional theory is about a factor of 30 and 70 too small for the two surfaces, while the semi-classical theory is correspondingly 1.6 and 2.3 too small.

Application to the full three-dimensional $D + H_2 \rightarrow DH + H$ for the Yates-Lester[39] fit to Liu's[40] potential surface was also made. Results for 300 K and 1000 K agree well with the experimental measurements of Mitchell and LeRoy[41]: log k(cm/molecule-sec) = 8.2 ± 0.2 at 300 K compared to the experimental results of 8.26, and log k = 12.1 ± 0.2 at 1000 K compared to the experimental results of 12.04, the error estimates being the residual error in the Monte-Carlo integration of the phase space integral.

The quality of the results for both the collinear and three-dimensional calculations seem to indicate that the fundamental assumption is a good approximation. The marked improvement over conventional transition state theory which assumes separability seems to indicate that the separability approximation may not be valid.

2. Periodic Orbit Theory

Another type of semiclassical approximation to the quantum mechanical rate expression can be made by first introducing a local type approximation:

$$
\begin{aligned}
Q_a k_{b\leftarrow a} &= \int d\underset{\sim}{q} \; \langle \underset{\sim}{q} | \, e^{-\beta H} F_R | \underset{\sim}{q} \rangle \\
&= \int d\underset{\sim}{q} \int d\underset{\sim}{q}' \; \langle \underset{\sim}{q} | \, e^{-\beta H} | \underset{\sim}{q}' \rangle \; \langle \underset{\sim}{q}' | \, F_R \, | \underset{\sim}{q} \rangle \qquad (2.66) \\
&\cong \int d\underset{\sim}{q} \; F_R(\underset{\sim}{p},\underset{\sim}{q}) \; \langle \underset{\sim}{q} | \, e^{-\beta H} | \underset{\sim}{q} \rangle
\end{aligned}
$$

where it is understood that $F_R(\underset{\sim}{p},\underset{\sim}{q})$ is the classical function corresponding to the quantum operator, F_R, and that we want to use the classical path approximation to the Boltzmann density matrix. (This is derived by Miller[42] using the classical path approximation in the Weyl prescription to the transition state rate expression eq. (2.40), with the integrals over $\underset{\sim}{p}$ and $\underset{\sim}{q}_2$ being evaluated by stationary phase[43].) Using eq. (2.13) for the flux eq. (2.66) becomes

$$Q_a\, k_{b\leftarrow a} = \int dq \ldots \int dq_N \; \tfrac{1}{2}|\dot{q}_1| \; \delta(q_1) \; \langle \underset{\sim}{q}|e^{-\beta H}|\underset{\sim}{q}\rangle \tag{2.67}$$

where q_1 is the corrdinate orthogonal to the dividing surface. Stationary phase evaluation of the integrals over $\underset{\sim}{q}$ in eq. (2.67) gives the stationary phase condition that $\underset{\sim}{p}_1 = \underset{\sim}{p}_2$, the initial and final momenta are equal. This together with $\underset{\sim}{q}_1 = \underset{\sim}{q}_2 = \underset{\sim}{q}$ defines a periodic orbit on the inverted surface (the dynamics defined by the classical path approximation to $\langle \underset{\sim}{q}|e^{-\beta H}|\underset{\sim}{q}\rangle$ can be viewed as real time trajectories on the inverted surface.) A more exact evaluation of eq. (2.67) is desired however and we refer to the previous work of Gutzwiller.[44]

Gutzwiller was interested in the semiclassical evaluation of the trace of the Green's function. For q_1 defined as motions along the periodic trajectory and q_i $i = 2,\ldots,N$ defined as displacements orthogonal to q_1, Gutzwiller evaluated the integral over $q_2 \ldots q_N$ by stationary phase to give

$$\int dq_2 \cdots \int dq_N \, \langle \underset{\sim}{q}|G(E)|\underset{\sim}{q}\rangle = \frac{i}{\hbar}\frac{1}{|\dot{q}_1|} \sum_{k=1}^{\infty} (-1)^k \, e^{ik\phi(E)/\hbar} \prod_{i=1} \frac{1}{2\sinh\left[\frac{ku_i(E)}{2}\right]} \tag{2.68}$$

where $G(E) = (E-H)^{-1}$, $\phi(E)$ is the classical action around one period of the periodic trajectory, $T(E)$ is the period of the trajectory, $\{u_1\}, i=1,\ldots,N-1$ are stability parameters which characterize the periodic orbit, and the sum over k is over multiple passes around the periodic trajectory. This expression can be related to the rate constant expression eq. (2.67) by noting the relationship between the propagator in time and the Green's function

$$e^{-iHt/\hbar} = -\frac{1}{2\pi i}\int dE \; e^{-iEt/\hbar} \, G(E) \quad , \tag{2.69}$$

and using the relationship between the propagator and the Boltzmann operator

$$e^{-\beta H} = -\frac{1}{2\pi i}\int dE \; e^{-\beta E} \, G(E) \quad . \tag{2.70}$$

Evaluation of the integral over q_1 in eq. (2.67) by virtue of the delta function and use of equations (2.70) and (2.68) gives

$$k_{b\leftarrow a}(T)\ Q_a(T) = (2\pi\hbar)^{-1} \int dE\ e^{-\beta E}\ N(E) \tag{2.71}$$

where

$$N(E) = \sum_{k=1}^{\infty} (-1)^{k-1}\ e^{-k\Phi(E)/\hbar} \prod_{i=1}^{N-1} \frac{1}{2\sinh\left[\frac{ku_i(E)}{2}\right]} \tag{2.72}$$

We have arrived at a microcanonical formulation of "semiclassical transition state theory" which is characterized by a periodic trajectory going from $\tilde{q}$ back to $\tilde{q}$ in an energy dependent time T(E). The initial conditions are picked so that they will determine a periodic trajectory for the given energy E. For the canonical case we showed that the time increment was proportional to β and was purely imaginary, $t = -i\hbar\beta$, leading to the interpretation of real trajectories on the inverted surface. In the microcanonical case it is unclear that T(E) should necessarily be purely imaginary as in the canonical case. This ambiguity can be resolved by a closer examination of Gutzwiller's work.

In obtaining a semiclassical approximation to $\langle \tilde{q}|G(E)|\tilde{q}\rangle$, Gutzwiller essentially used the inverse Fourier transform of the semiclassical approximation to the propagator,

$$\langle \underset{\sim}{q}|G(E)|\underset{\sim}{q}\rangle \cong -\frac{i}{\hbar}\int_{-\infty}^{\infty} dt\ e^{iEt/\hbar}\left[(2\pi i\hbar)^N\left(\frac{\partial \underset{\sim}{q}_2}{\partial \underset{\sim}{p}_1}\right)_{\underset{\sim}{q}_1}\right]^{-1/2} e^{-i\phi/\hbar} \quad , \qquad (2.73)$$

evaluating the time integral by stationary phase. However to obtain a microcanonical version of the rate constant we want to use the inverse Laplace transform of eq (2.70):

$$\langle \underset{\sim}{q}|G(E)|\underset{\sim}{q}\rangle = -\int_{\beta_0-i\infty}^{\beta_0+i\infty} d\beta\ e^{\beta E}\ \langle \underset{\sim}{q}|e^{-\beta H}|\underset{\sim}{q}\rangle\ . \qquad (2.74)$$

Inserting the classical path approximation to $\langle \underset{\sim}{q}|e^{-\beta H}|\underset{\sim}{q}\rangle$ and evaluating the β contour integral by steepest descent[45] gives the steepest descent condition, $E - \frac{\partial\phi}{\partial\beta} = 0$, which defines the relationship between β and E. The phase then becomes

$$\begin{aligned}\Phi(E) &= E\beta(E) - \frac{1}{\hbar}\int_0^{T(E)} dt\left(\underset{\sim}{p}(t)\cdot\dot{\underset{\sim}{q}}(t) - H\right)\\ &= -\frac{1}{\hbar}\int_0^{T(E)} dt\ \underset{\sim}{p}(t)\cdot\dot{\underset{\sim}{q}}(t)\end{aligned}$$

we can now identify this to be the proper phase to use in eq. (2.72).

This analysis could be done equivalent by using eq. (2.73) but realizing that the time increment is purely imaginary and doing the integral by steepest descent. Thus Gutzwiller's results are straightforward for our purposes with the periodic trajectory now being one in purely imaginary time. Changing to real time trajectories on the upside down potential surface gives the following results for the phase.

$$-i\Phi(E) = 2\theta(E) = \hbar^{-1}\int_0^{\tau_f(E)} d\tau\, \bar{\underset{\sim}{p}}(\tau)\cdot \underset{\sim}{q}'(\tau)$$

$$\tau_f(E) = iT(E) = \hbar\beta(E) \qquad (2.76)$$

For the case of the collinear reaction of an atom with a diatom as depicted in fig. 1, the potential surface at the saddle point is a barrier in the s direction and bound in the u motion. Inverting the surface gives a well in the s degree of freedom and u becomes unbound. In general, for an inverted potential surface of N degrees of freedom, there will be one bound degree of freedom giving rise to the periodic motion and N-1 degrees of freedom unbound making the periodic motion unstable. The measure of this instability, the stability parameters, are directly related to the Jacobian, $\frac{\partial(\underset{\sim}{q}_2,\underset{\sim}{p}_2)}{\partial(\underset{\sim}{q}_1,\underset{\sim}{p}_1)}$, which arises from the classical path approximation and the stationary phase integrations. More precisely, the stability parameters are the natural logarithms of the eigenvalues of the 2N x 2N Jacobian matrix.

It is useful to expand the sinh functions in their geometric series representation and resume the k index in eq. (2.72) to give

$$N(E) = \sum_{\underset{\sim}{n}=0}^{\infty} \left\{ 1 + \exp\left[2\theta(E) + \sum_{i=1}^{N-1} \left(n_i + \frac{1}{2}\right) u_i(E) \right] \right\}^{-1} \tag{2.77}$$

where

$$\underset{\sim}{n} = \{n_i\}, i = 1,\ldots,N-1; \text{ and } \sum_{\underset{\sim}{n}=0}^{\infty} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_{N-1}=0}^{\infty}$$

The period of the trajectory is related to the action integral by

$$\tau_f(E) = -2\hbar\, \theta'(E) \tag{2.78}$$

and defining the frequency $\omega_i(E)$ as

$$\omega_i(E) = u_i(E)/\tau_f(E) , \tag{2.79}$$

implying that $u_i(E) = -2\hbar\theta'(E)\,\omega_i(E)$, gives

$$N(E) = \sum_{\underset{\sim}{n}=0}^{\infty} \left\{ 1 + \exp\left[2\theta(E) - 2\theta'(E) \sum_{i=1}^{N-1} \left(n_i + \frac{1}{2}\right)\hbar\omega_i(E)\right]\right\}^{-1} \qquad (2.80)$$

In the limit that the system is separable the periodic trajectory moves only in the bound degree of freedom for the inverted surface. Thus $\theta(E)$ becomes a one-dimensional barrier penetration integral, and the frequencies become the energy independent harmonic frequencies for the wells on the upright surface. However eq. (2.80) is not the correct separable limit. The WKB approximation to the tunneling probability is

$$P(E_t) = [1 + e^{2\theta(E_t)}]^{-1} \qquad (2.81)$$

where $\theta(E_t)$ is the barrier penetration integral for translational energy E_t.

The separable limit of N(E) should then be

$$N(E) = \sum_{\underset{\sim}{n}} \left[1 + e^{2\theta(E_{\underset{\sim}{n}})}\right]^{-1} \qquad (2.82)$$

where

$$E_{\underset{\sim}{n}} = E - \varepsilon_{\underset{\sim}{n}} \, , \quad \varepsilon_{\underset{\sim}{n}} = \sum_{i-1}^{N-1} \left(n_i + \frac{1}{2}\right) \hbar\omega_i \quad ,$$

and $E_{\underset{\sim}{n}}$ is the translation energy for a system with total energy E and internal state $\underset{\sim}{n}$. If we recognize

$$2\theta(E) - 2\theta'(E) \sum_{i=1}^{N-1} \left(n_i + \frac{1}{2}\right) \hbar\omega_i$$

as the first two terms in a Taylor series expansion, then "unexpanding" the series gives $2\theta(E_n)$, where

$$E_n = E - \hbar\underset{\sim}{\omega}(E_n) \cdot \left(\underset{\sim}{n} + \frac{1}{2}\right) \quad . \tag{2.83}$$

The modified expression for periodic orbit theory is then given by eq. (2.82) with the translational energy, $E_{\underset{\sim}{n}}$, given by eq. (2.83). This gives the correct semiclassical separable limit if the bound degrees of freedom are harmonic; i.e, it is the multi-dimensional generalization of the WKB tunneling probability in one-dimension.

This semiclassical model was also applied to the collinear $H + H_2$ system for the same two potential surface described earlier. Figure 7 shows the periodic trajectory for two different energies E, one just below the barrier and one far below it. So long as $E<V_{sp}$ the trajectories are all real valued and relatively easy to find because of their high symmetry. There is only one such trajectory for a given energy. As $E \to V_{sp}$ the trajectory becomes infinitesimally short in length and moves to the saddle point of the potential surface; for lower energies the periodic trajectory cuts the corner of the potential surface, the more so the lower the energy.

Figures 8 and 9 show the action integral $\theta(E)$ and the stability parameter $\omega(E)$ as a function of the total energy for the Truhlar-Kuppermann potential surface. One notes that

$$\lim_{E \to V_{sp}} \theta(E) = 0 \tag{2.84}$$

$$\lim_{E \to V_{sp}} \omega(E) = \omega_{sp} \tag{2.85}$$

where ω_{sp} is the symmetric stretch frequency at the saddle point, the quantity which appears in conventional transition state theory. It is tempting to suspect that the zero energy limit of $\omega(E)$ might be the vibrational frequency of the isolated H_2 molecule:

$$\lim_{E \to 0} \omega(E) = \omega_{H_2} . \tag{2.86}$$

Although this is clearly the trend seen in fig. 8, it does not appear to be quantitatively true.

The cumulative reaction probability for the two potential surfaces is shown in figs. 10 and 11. The solid lines are the exact quantum mechanical values,[38] and the dashed lines are the semiclassical transition state theory approximation given by eq. (2.82). The agreement between the two is seen to be reasonably good. The accuracy of this semiclassical transition state theory is, in fact, almost as good as the results of classical S-matrix theory.[21]

D. Summary

The results of both types of semiclassical approximations to the quantum transition state rate expression are in good agreement with the exact quantum scattering calculation, indicating that the fundamental assumption of transition state theory is valid quantum mechanically as well as classically. The marked improvement of these semiclassical models over traditional formulations of transition state theory which include separability seems to indicate that the separability approximation is not valid. It is not possible however to determine whether the remaining discrepancies between the exact quantum and semiclassical results are a result of the transition state approximation or the semiclassical approximation. There are obvious shortcomings of the semiclassical methods however.

Recent work of Stratt and Miller[46] has shown that the semiclassical phase space distribution as described in this work is not a rigorous result of semiclassical mechanics. We wish to know the semiclassical approximation to the Boltzmann average of an operator F:

$$\langle F \rangle = Q_a^{-1} \, \mathrm{tr} \left[e^{-\beta H} \, F \right] \tag{2.87}$$

however, we only know how to take the semiclassical approximation to the Boltzmann density matrix $\langle \underset{\sim}{q} | e^{-\beta H} | \underset{\sim}{q} \rangle$. The Boltzmann average of F can be rigorously defined as

$$\langle F \rangle = -\frac{1}{\beta} \lim_{\lambda \to 0} \frac{d}{d\lambda} \left\{ \mathrm{tr} \left[e^{-\beta(H+\lambda F)} \right] \right\} \tag{2.88}$$

The semiclassical approximation can be made to eq. (q.88) by treating $H + \lambda F$ as an effective Hamiltonian and using the classical path approximation. By taking the λ derivative of the semiclassical expression followed by the $\lambda \to 0$ limit gives the correct semiclassical approximation. For the rate constant the result is:

$$Q_a\, k^{SC}_{b\leftarrow a} = \lim_{\lambda\to} h^{-N} \int d\underset{\sim}{q} \int d\underset{\sim}{p}\ \frac{2}{\hbar\beta} \left[\int_0^{\hbar\beta/2} F_R(\tau)\,d\tau\right] \exp\left[\frac{-2}{\hbar}\int_0^{\hbar\beta/2} d\tau\,\Big(H(\tau) + \lambda\, F_R(\tau)\Big)\right] \qquad (2.89)$$

The ambiquity in eq. (2.61) of the correct weighing (how to choose τ_o) is no longer present. This ambiguity was equivalent to the problem of where to evaluate the classical function $F(\underset{\sim}{p},\underset{\sim}{q})$ along the semiclassical trajectory. This has been replaced by averaging $F(\underset{\sim}{p},\underset{\sim}{q})$ over the entire trajectory. Work is in progress[46] to find the proper $\lambda\to 0$ limit of eq. (2.88).

One obvious error inherent in periodic orbit theory is the harmonic approximation for the internal state energies. This arises from the stationary phase evaluation of the $\underset{\sim}{q}$ integrals in eq. (2.67) which assumes that motion orthogonal to the periodic orbit is harmonic. This can be circumvented by doing the $\underset{\sim}{q}$ integrals numerically. A microcanonical version of the local approximation eq. (2.66), is

$$N(E) = 2\pi\hbar \int d\underset{\sim}{q}\ \delta(q_1)\ |\dot{q}_1|\ \langle \underset{\sim}{q}\,|\ \partial(E-H)\ |\,\underset{\sim}{q}\rangle \qquad (2.90)$$

$$\langle \underset{\sim}{q}|\delta(E-H)\,|\,\underset{\sim}{q} = \frac{1}{2\pi i}\int_{\beta_o-i\infty}^{\beta_o+i\infty} d\beta\ e^{\beta E}\ \langle\ \underset{\sim}{q}|e^{-\beta H}|\underset{\sim}{q}\rangle \qquad (2.91)$$

$$= \frac{1}{2\pi i}\left[(2\pi\hbar)^{N-1}\ \frac{\partial \underset{\sim}{q}_2}{\partial \underset{\sim}{p}_1}\ \frac{\partial E}{\partial(\hbar\beta)}\right]^{-1/2} e^{-\Phi/\hbar}$$

the phase is given in eq. (2.75), and the Jacobian, $\frac{\partial E}{\partial(\hbar\beta)}$, arises from the steepest descent evaluation of the β integral. Thus,

$$N(E) = -i\hbar\int d\underset{\sim}{q}\;\delta(q_1)\,|\dot{q}_1|\left[(2\pi\hbar)^{N-1}\frac{\partial\underset{\sim}{q}_2}{\partial\underset{\sim}{p}_1}\;\frac{\partial E}{\partial(\hbar\beta)}\right]^{-1}\;e^{-\Phi/\hbar} \qquad (2.92)$$

(stationary phase evaluation of the q integrals in eq. (2.92) gives periodic orbit theory.) Numerical integration of eq. (2.92) was carried out for the collinear H + H_2 system and comparison was made to periodic orbit theory without the modification of unexpanding the Taylor series. The results shown in fig. 12 indicate that the harmonic approximation has very little effect in the H + H_2 system. However, comparison of the modified periodic orbit theory results with these indicate that the "unexpansion" of the Taylor series is necessary. The fact that a modification to the original theory is needed to give the correct separable limit is a little unsettling and a derivation of the theory which gives the correct separable limit is desirable although unavailable at this time.

Finally it is interesting to note that all attempts to use the Weyl prescription for quantum mechanical transition state theory have failed, but the semiclassical method using the local approximation, eq. (2.67), which identify the reactive flux by the classical function have been very successful. To further test the validity of the Weyl prescription for transition state theory, a semiclassical model using the Weyl prescription for the reactive flux operator was examined. The Weyl prescription to the reactive flux for a one-dimensional system can be written (see ref. 6):

$$\langle x'|F_R|x\rangle = \delta\left(\frac{x'+x}{2}\right)\frac{\hbar}{2\pi m}\,\frac{-1}{(x'-x)^2} \tag{2.93}$$

giving for the one-dimensional tunneling correction factor, eq. (2.47),

$$\Gamma(T) = 2\pi\hbar\beta\int_{-\infty}^{\infty} dx\,\frac{\hbar}{2\pi m}\left(\frac{-1}{2x^2}\right)\langle x|e^{-\beta h_1}|-x\rangle \tag{2.94}$$

Integration by parts gives:

$$\Gamma(T) = \frac{\hbar^2\beta}{2m}\int_{-\infty}^{\infty} dx\,\left(-\frac{1}{x}\right)\frac{d}{dx}\langle x|e^{-\beta h_1}|-x\rangle, \tag{2.95}$$

Replacing the quantum matrix element in eq. (2.95) by the semiclassical approximation eq. (2.56) and assuming that the Jacobian is a slowly varying function of x as compared to the exponential of the phase so that the derivative is taken only of the exponential, gives the semiclassical result:

$$\Gamma(T) = e^{\beta V_0} \frac{\hbar\beta}{2m} \int_{-\infty}^{\infty} dx \frac{-(p_2+p_1)}{x} \left(2\pi\hbar \frac{\partial x_2}{\partial p_1}\right)^{-1/2} e^{-\Phi/\hbar} \tag{2.96}$$

where $\Phi = \int_0^{\hbar\beta} H(\tau)d\tau$ is the classical action for a trajectory which goes from x to -x in time $\hbar\beta$ on the upside down potential surface, and $\frac{\partial}{\partial x}\Phi(x_1,x_2) = -p_2-p_1$, $p_2(p_1)$ is the final (initial) momentum of the trajectory. This expression can be evaluated analytically for the harmonic barrier. The inverted barrier becomes a harmonic well for which the equations of motions are known:

$$\begin{aligned} x(\tau) &= x_1\cos(\omega\tau) + \frac{p_1}{m}\sin(\omega\tau) \\ p(\tau) &= p_1\cos(\omega\tau) + m\,x_1\sin(\omega\tau) \end{aligned} \tag{2.97}$$

The initial and final momenta for the desired trajectory are

$$p_1 = p_2 = -m\omega x_1\left(\frac{1+\cos u}{\sin u}\right) = -m\omega x_1 \frac{\cos\frac{u}{2}}{\sin\frac{u}{2}} , \tag{2.98}$$

the Jacobian becomes

$$\frac{\partial x_2}{\partial p_1} = \frac{\sin u}{m\omega} \tag{2.99}$$

and the phase is

$$\Phi = m\omega x_1^{\;2}\left(\frac{1+\cos u}{\sin u}\right) = m\omega x_1^{\;2}\,\frac{\cos\frac{u}{2}}{\sin\frac{u}{2}} \qquad (2.100)$$

$V_o=0$, and $u = \hbar\beta$. For $0<u<\pi$, $p_1<0, \phi>0$, and $\frac{\partial x_2}{\partial p_1}>0$. This corresponds to a trajectory which goes directly from x to -x. Evaluation of the integral in eq. (2.96) gives the correct results, $\Gamma = \frac{u}{2}\Big/\sin\frac{u}{2}$. For $\pi<u<2\pi, p_1>0, \Phi<0$ and $\frac{\partial x_2}{\partial p_1} < 0$. This corresponds to a trajectory which starts with momentum moving away from -x (positive momentum), reflects off the repulsive wall, goes past -x and is reflected a second time before getting to -x in time $\hbar\beta$. In this case the integrand has a negative Jacobian under the square root giving a complex number while the argument of the exponential is positive. However, the integral can still be evaluated by changing integration variables from x to ix, where $i = \sqrt{-1}$. The contour integration is then rotated back on the real axis while the pieces at infinity are thrown away. This in effect analytically continues the result from the interval $0<u<\pi$ to the interval $\pi<u<2\pi$, giving $\Gamma = \frac{u}{2}\sin\frac{u}{2}$.

If one tries to do the same analysis on a more general potential such as the symmetric Eckhart barrier, one is faced with a difficulty. The harmonic oscillator has the property that the period of a trajectory going from x back to x is $2\pi/\omega$ which is independent of the energy. This has the subtle consequence that for a given time increment $\hbar\beta$ the initial momentum will have the same sign for trajectories going from x to -x for all x. For $p_1 = 0$ any x gives a trajectory which goes to -x in the time $\hbar\beta = \pi/\omega$. This is just a trajectory which starts at the classical turning point with zero momentum and rolls down the side of the well to end up at -x with zero momentum in half of one period π/ω. For the time interval to be longer, the initial momentum must be positive for all x and for the time interval to be shorter than π/ω the initial momentum must be negative for all x. For a general potential such as the Eckart barrier this will not be true. For a given time increment one can find a value for x, x_{cr}, such that $p_1 = 0$ gives the desired trajectory and for $x<x_{cr}$,p_1 must be negative and for $x>x_{cr}$,p_1 must be postive. Thus we have both types of trajectories for one value of β. This makes the integrand real and imaginary for different regions of the x axis, making it impossible for the change of variable and contour rotation that we performed for the harmonic case. This type of behaviour strongly argues that the Weyl prescription for transition state theory is not valid. Since no alternative means for a rigorous quantum mechanical interpretation of the transition state approximation to the reactive flux is obvious, semiclassical methods were used for verifying the validity of the transition state approximation in quantum mechanics. The weakness of the separability approximation necessitated the development of nonseparable semiclassical techniques for transition state theory.

APPENDIX

DETAILS OF NUMERICAL CALCULATIONS

The details of the calculations using semiclassical transition state theory to evaluate reaction rate constants for the collinear $H + H_2$ reaction as well as the three-dimensional $D + H_2$ reaction are contained in this appendix. The collinear system is treated first with both periodic orbit theory and the semiclassical phase space distribution. Details of the numerical evaluation of the thermal rate constant for the three-dimensional system using the semiclassical phase space distribution conclude this section.

In all of the calculations detailed here classical trajectories are computed by integration of Hamilton's equations of motion;

$$\dot{\underset{\sim}{p}}(t) = -\frac{\partial H(\underset{\sim}{p},\underset{\sim}{q})}{\partial \underset{\sim}{q}} \quad , \quad \dot{\underset{\sim}{q}}(t) = \frac{\partial H(\underset{\sim}{p},\underset{\sim}{q})}{\partial \underset{\sim}{p}} \qquad \text{(A2.1)}$$

Equation (A2.1) represents 2N coupled first order differential equations. Their solution is numerically obtained by use of a fifth order Adams-Moulton predictor-corrector variable step size integration algorithm.[47] By specifying the initial conditions and the derivatives of the Hamiltonian given in eq. (A2.1), the trajectory is unambiguously specified.

Invariably the classical action along the trajectory is also desired

$$\phi(t) = \int_0^t dt' \; \underset{\sim}{p}(t') \cdot \underset{\sim}{\dot{q}}(t') \qquad \text{(A2.2)}$$

This can be easily computed by adding one further equation to those given in eq. (A2.1), that is,

$$\dot{\phi}(t) = p(t) \cdot \dot{q}(t) \qquad \text{(A2.3)}$$

Numerical integration of eq. (A2.3) with $\big(p(t),q(t)\big)$ specified by eq. (A2.1) and with the initial condition that $\phi(t=0) = 0$ gives the desired result, a solution to eq. (A2.2).

Since transition state theory requires calculations done in the saddle point region of the potential, it is convenient to use the coordinates that diagonalize the kinetic energy in that region. These are the (s,u) coordinates specified on fig. 1. If (r,R) are the internal coordinate for H_2 vibration and the distance between the atom and the center of mass of the H_2 molecule, respectively, then s and u can be expressed in terms of r and R as

$$\begin{aligned} s &= R - \frac{3}{2}\, r \\ u &= \frac{1}{2} R + \frac{1}{4} r \end{aligned} \qquad \text{(A2.4)}$$

for the collinear H + H_2 system.

The Hamiltonian in these new coordinates is

$$H(s,u,p_s,p_u) = p_s^2/2m_s + p_u^2/2m_u + V(s,u) \qquad \text{(A2.5)}$$

where $m_s = m_H/6$, $m_u = 2m_H$, and m_H is the mass of hydrogen.

To apply the periodic orbit theory of reaction rates to this system requires trajectories which begin at a phase point (s,u,p_s,p_u) and return to this phase point in a time T(E). The equations of motion governing this trajectory are given by eq. (A2.1), except the potential is inverted, $V \to -V$. The equations of motion are then given by

$$\dot{p}_s(t) = +\frac{\partial V(u,s)}{\partial s}\ ,\ \dot{p}_u(t) = +\frac{\partial V(u\ s)}{\partial u}\ ,\ \dot{s}(t) = \frac{p_s}{m_s}\ ,\ \dot{u}(t) = \frac{p_u}{m_u}\ . \qquad \text{(A2.6)}$$

For the upside-down potential, motion in the u degree of freedom is unbound whereas motion in s is bound in the immediate vicinity of the saddle point. The coordinate s corresponds to q_1 in eq. (2.67) -- it is orthogonal to the dividing surface (the u-axis). Therefore the trajectory is required to begin with s=0, that is, start on the dividing surface, S_3 of fig. 1, and return to it. Since the potential is bound for the s motion, trajectories can have multiple turning points in the s degree of freedom. It is clear that in order for a trajectory to return to a point on the dividing surface with the same momentum, i.e., the same sign, the trajectory must go through at least two turning points in s. For two turning points in s, then, a trajectory would cross the line S_3 twice.

The motion in u has at most one turning point on the inverted surface. If the initial value of u is greater than the saddle point value, u_{sp}, the turning point will be for some u less than u_{sp}. Therefor if a trajectory starts with the initial momentum in u, p_{u_i}, greater than zero it will encounter no turning point in u and would never return to u. Conversely if the initial momentum p_{u_i} is less than zero, for the trajectory to be periodic a second turning point must be encountered for some u outside the initial value of u. Since this cannot happen, we can infer that the initial value of the momentum in u must be zero.

The procedure for finding the periodic trajectory for a given total energy is to specify the coordinates ($s=0$, $u=u_i$) and calculate the initial momentum from energy conservation ($p_s=p_{s_i}$, $p_u=0$). The trajectory is run (eq. (A2.6) are numerically integrated) until it crosses the line S_3 twice or appears to be in a region of the potential where it will never return to S_3. One varies u_i systemmatically until $u_i=u_f$. Due to the high symmetry of the potential this ensures that p_u final is also zero. The result is then a periodic trajectory.

Once the periodic trajectory is found for a given energy, we need to evaluate the action integral, $\theta(E)$, and the stability parameter, $\omega(E)$. The action integral is calculated by numerical integration of the equation

$$\dot{\Phi}(t) = P_s(t)\,\dot{s}(t) + P_u(t)\,\dot{u}(t) \tag{A2.7}$$

along the trajectory; $\theta(E)$ is given by

$$\theta(E) = \frac{1}{2}\Phi\left(T(E)\right) \tag{A2.8}$$

where $T(E)$ is the period of the trajectory.

The collinear $H + H_2$ ststem has two degrees of freedom therefore there will be only one stability parameter, and eq. (2.82) becomes

$$N(E) = \left[1 + e^{2\,(E_n)}\right]^{-1} \quad , \tag{A2.9}$$

where

$$E_n = E - \hbar\omega(E_n)\left(n + \frac{1}{2}\right) \tag{A2.10}$$

The stability parameter is defined in terms of the eigenvalues of the Jacobian matrix, $\frac{\partial(s_f,u_f,p_{s_f},p_{u_f})}{\partial(s_i,u_i,p_{s_i},p_{u_i})}$, where subscript i indicates initial conditions and subscript f denotes final conditions. This is a 4 x 4 matrix and therefore will have four eigenvalues. However the eigenvalues come in pairs, $\lambda = e^{\pm u_i}$, $i = 1,2$, where λ are the eigenvalues and u_i are the two stability parameters. Two eigenvalues are guaranteed to be unity, therefore one stability parameter will be zero.[48] The stability frequency, $\omega(E)$, is given in terms of the nonzero stability parameter as

$$\omega(E) = u(E)/T(E) \quad . \tag{A2.11}$$

Evaluation of the matrix elements is carried out using the method outlined by Miller.[48] If one defines a time dependent matrix $\underset{\approx}{R}(t)$ as follows:

$$\underset{\approx}{R}(t) = \begin{pmatrix} \frac{\partial s(t)}{\partial s_i} & \frac{\partial s(t)}{\partial u_i} & \frac{\partial s(t)}{\partial p_{s_i}} & \frac{\partial s(t)}{\partial p_{u_i}} \\ \frac{\partial u(t)}{\partial s_i} & \frac{\partial u(t)}{\partial u_i} & \frac{\partial u(t)}{\partial p_{s_i}} & \frac{\partial u(t)}{\partial p_{u_i}} \\ \frac{\partial p_s(t)}{\partial s_i} & \frac{\partial p_s(t)}{\partial u_i} & \frac{\partial p_s(t)}{\partial p_{s_i}} & \frac{\partial p_s(t)}{\partial p_{u_i}} \\ \frac{\partial p_u(t)}{\partial s_i} & \frac{\partial p_u(t)}{\partial u_i} & \frac{\partial p_u(t)}{\partial p_{s_i}} & \frac{\partial p_u(t)}{\partial p_{u_i}} \end{pmatrix} \tag{A2.12}$$

then $\underset{\approx}{R}\big(t = T(E)\big)$ is the desired Jacobian matrix. The time evolution of $\underset{\approx}{R}(t)$ is given by

$$\frac{d}{dt}\underset{\approx}{R}(t) + \underset{\approx}{F}(t)\,\underset{\approx}{R}(t) = 0 \tag{A2.12}$$

where

$$\underset{\approx}{F}(\cdot) = \begin{pmatrix} 0 & 0 & -\frac{1}{m_s} & 0 \\ 0 & 0 & 0 & -\frac{1}{m_u} \\ \frac{\partial^2 V}{\partial s^2} & \frac{\partial^2 V}{\partial s \partial u} & 0 & 0 \\ \frac{\partial^2 V}{\partial u \partial s} & \frac{\partial^2 V}{\partial u^2} & 0 & 0 \end{pmatrix}$$

Equation (A2.12) represents sixteen coupled differential equations which depend upon the trajectory $(s(t),u(t),p_s(t),p_u(t))$, therefore one can solve these equations by simply including these sixteen additional equations in the numerical integration of the classical trajectory. The proper initial condition is

$$\underset{\approx}{R}(t=0) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} . \qquad \text{(A2.14)}$$

The final values of the sixteen variables form the Jacobian matrix which can be diagonalized by standard methods. It should be noted that the matrix is nonsymmetric and therefore can have complex eigenvalues. A subroutine -SPCTRM- is available at the Lawrence Berkeley Laboratory Computing Center for this purpose. In practice the complex components of the eigenvalues were found to be negligible, however the accuracy of the eigenvalues was diminished due to the large difference in the magnitudes of the eigenvalues -- five orders of magnitude in the worst cases. However, the largest eigenvalue was computed to enough accuracy to be useful, and this was the only eigenvalue needed to determine the stability frequency.

One further note concerning the evaluation of the force constants needed in eq. (A2.13). Although derivatives of the potential, $\partial V/\partial s$ and $\partial V/\partial u$, are analytically obtained by differentiation of the potential forms (ref. 34 and 37), the force constants were obtained numerically by finite difference methods.

The procedure at this point is quite simple. For a given energy one has evaluates θ and ω. If we call this energy E_n then eq. (A2.10) can be easily inverted to give E. Since $\theta(E_n)$ is already computed, eq. (A2.9) gives N(E). The results of this calculation can be found in Chapter II section C. 2.

The semiclassical phase space distribution method uses eq. (2.61) with $\tau_o = \hbar\beta/4$. For the collinear H + H_2 system in s and u coordinates this becomes

$$Q_a \cdot k = (2\pi\hbar)^{-2} \int ds_1 \int du_1 \int dp_{s_i} \int dp_{u_i} \delta(s_1) \frac{1}{2} \frac{p_{s_i}}{m_s} - \exp \frac{2}{\hbar} \int_{-\hbar\beta/4}^{\hbar\beta/4} d\tau \, H(\tau) \qquad \text{(A2.15)}$$

where the Hamiltonian is given in eq. (A2.5) and the equations of motion are given in eq. (A2.6). The variables $u_1, s_1, p_{u_1}, p_{s_1}$ are the initial conditions for a trajectory run on the inverted surface. Actually two trajectories are computed, one which starts at this initial phase point and proceeds forward in time until $\tau = \hbar\beta/4$, the other proceeding backwards in time from the same initial phase point until $\tau = -\hbar\beta/4$. The sum of the integrals of the time dependent Hamiltonian along these two trajectories exponentiated replaces the usual Boltzmann average in the phase space average. Although $H(\tau)$ is no longer conserved for the equations of motion given in eq. (A2.6), the quantity $p_s^2(\tau)/2m_s$ + $p_u^2(\tau)/2m_u - V\big(s(\tau),u(\tau)\big)$ is conserved. Therefore

$$p_s^2(\tau)/2m_s + p_u^2(\tau)/2m_u - V(s,u) = p_{s_1}^2/2m_s + p_{u_1}^2/2m_u - V(s_1,u_1)$$

and

$$\begin{aligned} H(\tau) &= p_s^2(\tau)/2m_s + p_u^2(\tau)/2m_u + V(s_1,u_1) - p_{s_1}^2/2ms - p_{u_1}^2/2m_u \\ &= p_s(\tau)\ \dot{s}(\tau) \quad p_u(\tau)\ \dot{u}(\tau) + V(s_1,u_1) - p_{s_1}^2/2m_s - p_{u_1}^2/2m_u \end{aligned} \tag{A2.16}$$

and

$$-\frac{2}{\hbar}\int_{-\hbar\beta/4}^{\hbar\beta/4} d\tau\, H(\tau) = \phi + \beta\left(V(s_1,u_1) - p_{s_i}{}^2/2m_s - p_{u_i}{}^2/2m_u\right) \tag{A2.17}$$

where

$$\phi = \frac{2}{\hbar}\int_{-\hbar\beta/4}^{\hbar\beta/4} d\tau\left(p_s(\tau)\ \dot{s}(\tau) + p_u(\tau)\ \dot{u}(\tau)\right) . \tag{A2.18}$$

The quantity ϕ can be calculated by the method previously given for numerical integration of the classical action.

The procedure is to integrate numerically over the initial conditions u_1, p_{s_1}, p_{u_1} where $s_1 = 0$ by virtue of the delta function. For every phase point determined by these initial conditions the integration can be easily calculated by computing the classical trajectory to obtain ϕ, all other functions in the integrand are then just simple algebraic functions of the initial conditions.

The behavior of the integrand upon the phase space point is strongly dependent upon the temperature at which the calculation is being evaluated. As the temperature gets lower β becomes larger and the time for running the trajectories becomes longer. In general, the longer a trajectory is allowed to run, the more action it will accumulate, and therefore the phase space point will be exponentially damped in the integral. For this reason very few regions of phase space give non-negligible contributions to the integrand, these regions becoming smaller for lower temperatures. This pathology in the integrand made the numerical integration of eq. (A2.15) difficult. The method used for the three dimensional integration was first to map out contours of the integrand for (u,p_s) planes for a fixed value of p_u. From these maps limits of integration could be put upon the integrals. The integrals in p_s and p_u were evaluated by Gaussian Legendre quadrature. It was found that the pathology of the integrand could be adequately treated by using an adaptive Simpson's rule integration in the u integration. The adaptive algorithm adds more and more equally space points into a region of the u axis until the integrand in that region has converged to within a desired accuracy. Results from these calculations can be found in Chapter II section C.1.

The partition function Q_a is given in eq. (2.22), where the energy levels for the H_2 vibration are easily obtained by the Morse oscillator fit to the H_2 vibrational motion.

Application of the semiclassical phase space distribution to the three-dimensional D + H_2 system begins with eq. (2.61) also. However for this system the phase space average is originally 12-dimensional:

$$Q_a\, k_{b\leftarrow a} = (2\pi\hbar)^{-6} \int d_3\vec{r} \int d_3\vec{R} \int d_3\vec{p} \int d_3\vec{P}\ F_R(\vec{r},R,\vec{p},\vec{P})\ e^{-\frac{2}{\hbar}\int_{-\hbar\beta/4}^{\hbar\beta/4} d\tau\, H(\tau)} , \qquad (A2.19)$$

where $\vec{r}$ is the vector between the two H atoms and $\vec{R}$ is the vector between D and the center of mass of H_2. The momentum $\vec{p},\vec{P}$ are those conjugate to $\vec{r},\vec{R}$ respectively. In these coordinates the Hamiltonian is given by

$$H = p^2/2m + P^2/2\mu + V \qquad (A2.20)$$

where $p = |\vec{p}|$, $P = |\vec{P}|$, $m = \frac{1}{2}m_H$, $\mu = m_H$, and m_H is the mass of hydrogen (this assumes that the mass of deuterium is just twice that of hydrogen.) Since the relative spatial configuration of the three atoms can be specified by just three coordinates, the potential can be expressed in terms of just three variables. The pertinent coordinates for this calculation are the three internuclear distances r_1, r_2, r_3. These can be defined in terms of r and R as follows:

$$\begin{aligned}
\vec{r}_1 &= \vec{R} - \tfrac{1}{2}\vec{r}\ ; & |\vec{r}_1| &= r_1 = \sqrt{R^2 + r^2/4 - rR\cos\gamma} \\
\vec{r}_2 &= \vec{r}\ ; & |\vec{r}_2| &= r_2 = r \\
\vec{r}_3 &= \vec{R} + \tfrac{1}{2}\vec{r}\ ; & |\vec{r}_3| &= r_3 = \sqrt{R^2 + r^2/4 + rR\cos}
\end{aligned} \tag{A2.21}$$

where $r = |\vec{r}|$, $R = |\vec{R}|$, and $\cos\gamma = \frac{\vec{r}\cdot\vec{R}}{rR}$.

Trajectories on the inverted surface for the calculation of the semiclassical phase space distribution were carried out in the $\vec{r},\vec{R}$ coordinates by numerical integration of the 12 differential equations,

$$\dot{\vec{r}} = \vec{p}/m\ , \quad \dot{\vec{R}} = \vec{P}/\mu\ , \quad \dot{\vec{p}} = \frac{\partial\, V(r_1,r_2,r_3)}{\partial\vec{r}}\ , \quad \dot{\vec{P}} = \frac{\partial\, V(r_1,r_2,r_3)}{\partial\vec{R}} \tag{A2.22}$$

It is convenient to express the vectors in both Cartesian and polar coordinates:

$$\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} = r \begin{pmatrix} \sin\theta_r \sin\phi_r \\ \sin\theta_r \cos\phi_r \\ \cos\theta_r \end{pmatrix} , \vec{R} = \begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = R \begin{pmatrix} \sin\theta_R \sin\phi_R \\ \sin\theta_R \cos\phi_R \\ \cos\theta_R \end{pmatrix}$$

$$\vec{p} = \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} = p \begin{pmatrix} \sin\theta_p \sin\phi_p \\ \sin\theta_p \cos\phi_p \\ \cos\theta_p \end{pmatrix} , \vec{P} = \begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = P \begin{pmatrix} \sin\theta_P \sin\phi_P \\ \sin\theta_P \cos\phi_P \\ \cos\theta_P \end{pmatrix} \qquad (A2.23)$$

The trajectories are integrated in the Cartesian components, therefore one needs $\frac{\partial V}{\partial x}$, $\frac{\partial V}{\partial y}$, etc. These are evaluated in terms of chain rule differentiation in terms of $\frac{\partial V}{\partial r_1}$, $\frac{\partial V}{\partial r_2}$, and $\frac{\partial V}{\partial r_3}$.

The integrals of eq. (A2.19) are best expressed in the polar coordinates. Since space is isotropic and we need only three coordinates to specify the orientation of the three atoms, we may replace the integrals over θ_r, ϕ_r, ϕ_R by $8\pi^2$ and set the three angles equal to zero. This also allows the identification of θ_R as γ.

The now nine-dimensional integral can be further reduced by use of the delta function contained in the flux function F_R. The dividing surface is defined by

$$f(\vec{r},\vec{R}) = r_1^2(\vec{r},\vec{R}) - r_2^2(\vec{r},\vec{R}) - R^2 - 3/4\ r^2 - rR\cos\gamma = 0 . \qquad (A2.24)$$

With the dividing surface defined we can identify the reactive flux normal to it as

$$F_R = \delta\left(f(\vec{r},\vec{R})\right) \frac{1}{2} \left| -\left(\frac{3}{2}\vec{r} + \vec{R}\right)\cdot \frac{\vec{p}}{m} + \left(2\vec{R} - \vec{r}\right)\cdot \frac{\vec{P}}{\mu} \right| \qquad \text{(A2.25)}$$

Using the delta function to eliminate the R integral restricts r to be

$$R = \frac{r}{2}\left(\cos\gamma + \sqrt{3 + \cos^2\gamma}\right) \qquad \text{(A2.26)}$$

and gives for eq. (A2.19)

$$Q_a k_{b\leftarrow a} = \frac{8\pi^2}{(2\pi\hbar)^6} \int_0^\infty dr\, r^2 \int_{-1}^{1} d(\cos\gamma)\, \frac{r}{4} \frac{\left(\cos\gamma + 3\sqrt{\cos^2\gamma}\right)^2}{\sqrt{3 + \cos^2\gamma}}$$

$$\times \int_0^\infty dp\, p^2 \int_0^\infty dP\, P^2 \int_{-1}^{1} d(\cos\theta p) \int_{-1}^{1} d(\cos\theta_P) \int_0^\pi d\phi_p \int_0^\pi d\phi_P\, \frac{1}{2} \left|\text{flux}\right| e^{-\frac{2}{\hbar}\int_{-\hbar\beta/4}^{\hbar\beta/4} d\tau H(\tau)} \qquad \text{(A2.27)}$$

Equation (A2.28) is an 8-dimensional integral which is most efficiently evaluated by Monte-Carlo methods.[14] Two further modifications were made to eq. (A2.27) to give more convenient integration variables. First, define ρ,α such that

$$p = \rho\sqrt{2m}\,\cos\frac{\alpha}{2}\quad,\quad P = \rho\sqrt{2u}\,\sin\frac{\alpha}{2}$$

$$\text{(A2.28)}$$

$$dpdP = \sqrt{m\mu}\,\rho\;d\rho\;d\alpha$$

and ρ is then just the total initial kinetic energy and α gives the partitioning between p and P. It is also desirable to replace the ρ integral by a total energy integral. This is done by Boltzmann averaging the existing expression over the total energy with the function $\delta(E-H)e^{+\beta H}$ included inside the other eight integrals. Clearly evaluating the energy integral by virtue of the delta function will give back eq. (A2.27), therefore this does not alter the expression. However we wish to keep the E integral and use the delta function to evaluate the ρ integral. This is done to give

$$\rho = (E - V)^{1/2} \qquad \text{(A2.29)}$$

and eq. (A2.27) becomes

$$Q_o k_{b\leftarrow a}^{SC\ TST} = \frac{4\pi^2\ (m\mu)^{3/2}}{(2\pi\hbar)^6} \int_0^{\infty} dE\ e^{-\beta E} \int_0^{\infty} dr\ \frac{r^4}{4} \int_{-1}^{1} d(\cos\gamma)\ \frac{\cos\gamma + \sqrt{3+\cos^2\gamma}}{\sqrt{3+\cos^2\gamma}}\ (E-V)^{5/2}$$

$$\times \int_{-1}^{1} d(\cos\beta)\ \sin\beta \int_{-1}^{1} d(\cos\theta_p) \int_{-1}^{1} d(\cos\theta_p) \int_0^{\pi} d\phi_p \int_0^{\pi} d\phi_p\ \ \mathrm{fcn}\left(E_1, r, \gamma, \beta, \theta_p, \theta_p, \phi_p, \phi_p\right)$$

where

$$\mathrm{fcn} = \frac{1}{2}\left|\sqrt{\frac{2}{u}}\ \sin\frac{\beta}{2} \left\{\left(\cos\gamma + \sqrt{3+\cos^2\gamma}\right)\left(\cos\gamma\ \cos\theta_p + \sin\gamma\ \sin\theta_p\ \cos\phi_p\right) - \cos\theta_p\right\}\right.$$

(A2.30)

$$\left.\frac{1}{2}\sqrt{\frac{2}{m}}\ \cos\frac{\beta}{2} \left\{\left(\cos\gamma + \sqrt{3+\cos^2\gamma}\right)\left(\cos\gamma\ \cos\theta_p + \sin\gamma\ \sin\theta_p\ \cos\phi_p\right) + 3\ \cos\theta_p\right\}\right|$$

$$\times \exp\left[-\frac{2}{\hbar}\int_{-\hbar\beta/4}^{\hbar\beta/4} d\tau H(\tau) + \beta E\right]$$

One integrates over the 8 variables and constructs the vectors $\vec{r},\vec{R},\vec{p},\vec{P}$ from eq. (A2.23) with $\theta_r = \phi_r=\phi_R = 0$, and R given by eq. (A2.26). The vectors then specify the initial conditions for the trajectories needed to evaluate $\exp\left[-2/\hbar \int_{-\hbar\beta/4}^{\hbar\beta/4} d\tau H(\tau)\right]$. This exactly parallels the collinear calculation.

The introduction of the energy variable into the integration does present a complication. This is that one must specify the variables r and γ such that the potential is less than or equal to E. This is effectively done by sampling the r and γ variable by a rejection technique.

The motivation behind using the energy variable is that classical calculation of the energy dependent cross section showed a $E^4e^{-\beta E}$ dependence in this function. This argues that for high enough energies the semiclassical microcanonical rate should also exhibit this dependence. For this reason the Monte-Carlo sampling of the energy variable was weighted by $E^4e^{-\beta E}$. Other weighting functions used were r^4, $\sin^2(\beta)$ for r and β respectively. This method worked quite well for temperatures of 300K and 1000K, the results being given in section C.1 of this chapter. However the pathology of the semiclassical phase space distribution function for lower temperatures as mentioned in the collinear case made the calculations impossible. No efficient Monte-Carlo method - i.e., no set of weighting functions - could be found to improve convergence of the integration with respect to quadrature points.

Finally it should be mentioned that the partition function Q_a now is for the three-dimensional H_2 molecule:

$$Q_a = Q_{vib} Q_{rot} Q_{tr} \quad ,$$

where

$$Q_{tr} = (2\pi\hbar)^{-3} \int d_3\vec{P}\, e^{-\beta P^2/2\mu} \qquad \text{(A2.31)}$$

$$= (2\pi\hbar)^{-3}\, 4\pi \int dP\, P^2\, e^{-\beta P^2/2}$$

and we have assumed that the vibrational and rotational motion is separable. The vibrational partition function is exactly the same as in the collinear case. In general one need not include the nuclear partition function into the total partition function as it remains the same in the transition state region and is cancelled out. However for H_2 the nuclear and rotational contributions are coupled by symmetry considerations which give rise to ortho and para hydrogen. The effect upon the rotational partition function is to add a degeneracy factor to the sum, thus Q_{rot} is given by

$$Q_{rot} = f_J (2J+1)\, e^{-\beta BJ(J+1)} \quad , \quad f_J = 1/4 \text{ for even } J \qquad \text{(A2.32)}$$

$$= 3/4 \text{ for odd } J$$

and $B = \hbar^2/2I$, I is the moment of inertia for the diatom.

III. SEMICLASSICAL EIGENVALUES

Semiclassical methods have been very useful in describing quantum effects in reactive systems.[3,49] Indeed, in the last section it was shown how semiclassical models could be used to describe tunneling effects in chemical reactions near the threshold energy. The discretization of energy levels in bound systems is a purely quantum mechanical consequence, however recently much progress has been made towards developing methods for quantization of the energy levels using classical mechanics.

For a one-dimensional system, the semiclassical results come from the "Old Quantum Theory" and is the Bohr-Sommerfeld quantization condition:[1]

$$(n+1/2)\pi = \int_{x_<}^{x_>} dx\ \{2m[E-V(x)]/\hbar^2\}^{1/2}, \tag{3.1}$$

for n = 0,1,..., which defines the eignevalues E(n) implicitly for the potential. This is only applicable to one-dimensional systems or multidimensional systems which can be separated into many one-dimensional systems. However there is a need for semiclassical quantization conditions for multidimensional systems which are nonseparable. For most systems of interest the lowest few eigenenergies can be obtained fairly easily by diagonalizing the Hamiltonian in a basis set. For the higher eigenstates this quantum mechanical procedure becomes increasingly difficult due to the size of the basis set required. But it is just for these higher bound states that semiclassical approximations such as WKB are the best. Semiclassical methods should be useful for finding the energy levels for these higher eigenstates where the motion of the system becomes coupled.

The first progress made towards obtaining a semiclassical quantization condition for multidimensional nonseparable systems was by Einstein[50] in 1917 before the advent of quantum mechanics. Other work on this problem done within the "Old Quantum Theory" is described in Born's book.[51] With the formulation of quantum mechanics this semiclassical approach saw little development until the more recent work of Keller.[52] Using the semiclassical wave function approach of Kramer[53] and Brillouin[54], Keller modified the results of Einstein to give the proper half-integer quantum numbers for simple oscillators. This result is the Einstein-Brillouin-Keller (EBK) quantization rule and is briefly described in section A with further modifications and improvements made by other authors being mentioned.

Another different approach to the problem of semiclassical quantization is that taken by Gutzwiller.[44] Gutzwiller developed a semiclassical expression for the trace of the Green's function, G(E), using the semiclassical approximation to the propagator which is based upon periodic trajectories of the bound system. Energy eigenvalues are obtained by finding singularities in the trace of G(E) as a function of energy. Because of the applicability of Gutzwiller's results to transition state theory, it is felt that a brief review of the work is worthwhile. This is given in section B.

Pechukas[55] has also presented a different approach to the problem using a generalized Miller-Good transformation to map the nonseparable potential onto a separable one.

A method for semiclassical quantization has been given by Chapman, Garrett, and Miller[56] which follows the approach of Born. The Hamilton-Jacobi equation is solved in action-angle variables to construct "good" action-angle variables such that the action variables are constants of the motion. Imposing the quantum condition is done simply by requiring the action variables to be half-integers. This method is detailed in section C. Application of this method to a model two-dimensional nonseparable system is made in section D. Finally the problem of semiclassical eigenvalues for degenerate systems is discussed in section E.

A. Trajectory Methods

The EBK quantization rule can best be desribed using Keller's approach. The semiclassical wavefunction is given by

$$\Psi(\underset{\sim}{q}) = A(\underset{\sim}{q})\, e^{iS(\underset{\sim}{q})/\hbar} \quad , \tag{3.2}$$

where $\underset{\sim}{q}$ is the vector of Cartesian coordinates. Requiring $\Psi(\underset{\sim}{q})$ to obey the Schrödinger equation in Cartesian coordinates to lowest order in $\hbar$ is equivalent to $S(\underset{\sim}{q})$ obeying the Hamilton-Jacobi equation[57]

$$H\left(\underset{\sim}{q}, \frac{\partial S(\underset{\sim}{q})}{\partial \underset{\sim}{q}}\right) = E \tag{3.3}$$

where

$$S(\underset{\sim}{q}) = \int_{\underset{\sim}{q}_0}^{\underset{\sim}{q}} \underset{\sim}{p} \cdot d\underset{\sim}{q}$$

is Hamilton's characteristic function, and $(\underset{\sim}{p},\underset{\sim}{q}) = (p_i,q_i)$, i - 1,2,...,N. The function $S(\underset{\sim}{q})$ is multivalued, its value determined by the path from $\underset{\sim}{q}_0$ to $\underset{\sim}{q}$. Two topologically distinct paths, C_1 and C_2, can be joined to give one closed path, $C_\Sigma = C_2 - C_1$, where the minus sign indicates motion in a backwards sense along path C_1. If $S_1 = \int_{C_1} \underset{\sim}{p}\cdot d\underset{\sim}{q}$ and $S_2 = \int_{C_2} \underset{\sim}{p}\cdot d\underset{\sim}{q}$ are the two values of $S(\underset{\sim}{q})$ for these two paths then

$$\Delta S = S_2 - S_1 = \oint_{C_\Sigma} \underset{\sim}{p}\cdot d\underset{\sim}{q} \tag{3.4}$$

is the change in $S(\underset{\sim}{q})$ in going around the closed path C_Σ. Requiring $\Psi(\underset{\sim}{q})$ to be a single valued function of $\underset{\sim}{q}$ then restricts ΔS to be an integer multiple of $2\pi\hbar$ plus any contribution to the phase of $\Psi(\underset{\sim}{q})$ from the pre-exponential factor $A(\underset{\sim}{q})$. The fact taht $A(\underset{\sim}{q})$ changes sign for every turning point crossed gives half integers or

$$\Delta S = 2\pi\hbar\ (n + \tfrac{1}{2}) \tag{3.5}$$

for n = 0,1,....

The intergral over closed path C_Σ in eq. (3.4) is a line integral and therefore independet of the path. In order to use this method to evaluate the energy eigenvalues, it is necessary to specify N such relationships as given by eq. (3.5) for N topologically independent closed paths, C_i, i - 1,2,...,N. (One topologically independent path cannot be deformed into another one without a change in the value of the integral.) In terms of these paths the EBK quantization condition is

$$2\pi\hbar\ (n_i + 1/2) = \oint_{C_i} \underset{\sim}{p} \cdot d\underset{\sim}{q}\ ,\ i = 1,2,\ldots N\ . \tag{3.6}$$

The problem in application of eq. (3.6) then is to identify the proper line integrals, that is, one must know the topology of the system.

Einstein realized that eq. (3.6) was not applicable to systems in general, but that it was required of the system that for a given point in $\underset{\sim}{q}$-space a finite number of branches of the $\underset{\sim}{p}(\underset{\sim}{q})$ function existed. Therefore although $\underset{\sim}{p}$ is a multivalued function of $\underset{\sim}{q}$ it is not infinitely so and thus the closed paths C_i can be defined. Work by Kolomogorov, Arnol'd, and Moser[58] (KAM theory) has shown that nonseparable systems can display such behavior and that such behavior is equivalent to a trajectory filling only a portion of the total allowable phase space, this region being contained within 2N well defined caustic curves (turning points in N-dimensions). For behavior of the trajectories that is more disordered so that the caustic curves are no longer well defined, the region of phase space is called "irregular." The methods reviewed here are concerned with the "regular" region and its energy spectrum.

The existence of N relationships given by eq. (3.6) restricts motion of the system to an N-dimensional surface, called invariant toroids by others, embedded in the 2N-dimensional phase space. A method due to Percival and Pomphrey[59] uses a variational approach to construct the invariant toroids directly.

The work of Marcus and coworkers[60] has also been along these lines, solving the Hamilton-Jacobi equation in Cartesian coordinates for the multivalued soltions $S(\underset{\sim}{q})$. Of particular interest is the method using Poincare's surfaces of section.[60(b)] For simplicity this is exemplified using a two-dimensional system (thus a four-dimensional phase space.) A surface of section is constructed by defining a phase plane such as (x,p_x) for a fixed value of y. A quasiperiodic trajectory cuts this phase plane and creates a smooth curve for all passes of the trajectory through the phase plane with $p_y > 0$. Two surfaces of section, one for each phase plane (x,P_x) and (y,p_y), will generate two closed curves which can be used to evaluate the line integrals of eq. (3.6). Variation of the initial conditions (including energy) until eq. (3.6) is satisfied yields the semiclassical energy eigenvalues.

A modification of Marcus' results by Sorbie[61] has yielded a method which is much more versatile in its applicability. The action integrals $\oint_C p_i dq_i - M_i J_i$, $i = 1,\ldots,N$, are integrated along the actual trajectory until the trajectory has closed one itself to a desired accuracy. Requiring $J_i - (n_i + 1/2)\, 2\pi\hbar$; $i - 1,2,\ldots,N$, is equivalent to Marcus' result, where N_i is one half of the number of turning points in the i direction. One further modification of this semiclassical quantization condition by Sorbie and Handy[62] has enabled this method to treat the troublesome case of degeneracy. A discussion of this aspect is delayed until section E.

B. Periodic Orbit Theory

Miller[63] has reviewed Gutzwiller's[44] semiclassical quantization condition as well as making an important modification to it. For details the interested reader is referred to this previous work, as only the results of the derivation are described here.

Gutzwiller's results are based upon the semiclassical approximation to the response function, g(E), defined by

$$\begin{aligned} g(E) &= \mathrm{Tr}\,[G(E)] \\ &= \int d\underset{\sim}{q}\;\; G(\underset{\sim}{q},\underset{\sim}{q};E) \end{aligned} \tag{3.7}$$

The response function is related to the density of states, $\rho(E)$, defined by

$$\begin{aligned} \rho(E) &= \mathrm{Tr}\,[\delta(E-H)] \\ &= \sum_n \delta(E-E_n) \end{aligned} \tag{3.8}$$

by the relationship $\mathrm{Im}\,G(E) = -\pi\,\delta(E-H)$. Miller expressed Gutzwiller's results in terms of the density of states as

$$\rho(E) = \frac{\Phi'(E)}{2\pi} \;\mathrm{Re} \sum_{n=-\infty}^{\infty} \exp\left\{in\left[\Phi(E) - \lambda\pi/2\right] \prod_{j=1}^{N-1} \frac{1}{2i\,\sin\left[\frac{1}{2}n\hbar\omega(E)\Phi'(E)\right]}\right\} \tag{3.9}$$

where the quantities $\Phi(E)$, λ, and $\{\omega_j(E)\}$ are all defined by a periodic classical trajectory (one that starts at a phase point $(\underset{\sim}{p},\underset{\sim}{q})$ and returns to that phase point in a time $T(E)$, the period of the orbit.) The classical action $\Phi(E)$ is defined by

$$\Phi(E) = \hbar^{-1}\int_0^{T(E)} dt\; \underset{\sim}{p}\cdot\underset{\sim}{\dot{q}} \tag{3.10}$$

λ is the number of turning points encountered along the trajectory, and $\{\omega_j(E)\}$ are the set of N-1 stability frequencies characterizing the periodic orbit. The modification due to Miller is to express the sin functions as sums of exponentials,

$$\prod_{j=1}^{N-1} \frac{1}{2i\sin\left(\frac{x_j}{2}\right)} = \prod_{j=1}^{N-1} \frac{e^{-ix_j/2}}{1-e^{-ix_j}} = \sum_{\underset{\sim}{m}=0}^{\infty} \exp\left[\sum_{j=1}^{N-1} -i\ (m_j+1/2)x_j\right] \tag{3.11}$$

where

$$\sum_{\underset{\sim}{m}=0}^{\infty} = \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \cdots \sum_{m_{N-1}=0}^{\infty} .$$

Use of the Poisson sum formula

$$\sum_{n=-\infty}^{\infty} e^{inx} = 2\pi \sum_{n=-\infty}^{\infty} \delta(x-2\pi n) \tag{3.12}$$

gives

$$\rho(E) = \Phi'(E) \sum_{\underset{\sim}{m}=0}^{\infty} \sum_{n=0}^{\infty} \delta\left[\Phi(E) - \sum_j (m_j+1/2)\hbar\omega_j\Phi'(E) - 2\pi(n+\lambda/4)\right] . \tag{3.13}$$

The quantization condition is specified by comparison of equations (3.8) with (3.13),

$$\Phi(E) - \sum_{i=0}^{-N-1}(m_i+1/2)\ \hbar\omega_i(E)\ \Phi'(E) = 2\pi(n+\lambda/4) \tag{3.14}$$

which implicitly determines the energy eigenvalues $E(n,m_1,m_2,\ldots,m_{N-1})$, for integer values of n and m_i, i - 1,2,...,N-1.

For the one-dimensional case (N=1), there are two turning points along the periodic trajectory ($\lambda = 2$), and eq. (3.14) reduces to

$$\begin{aligned}\Phi(E) &= \hbar^{-1}\int d\tau\ p\ \frac{dx}{d\tau} = \hbar^{-1}\ 2\int_{x_<}^{x_>} dx\ p \\ &= 2\pi(n+1/2)\end{aligned} \tag{3.15}$$

which is the Bohr-Sommerfeld quantization conditions, eq. (3.1). However for the case of a multidimensional but separable system, eq. (3.14) does not in general give the correct semiclassical result. For example consider a two-dimensional system with coordinates (x,y) and conjugate momentum (p_x,p_y) where these two degrees of freedom are uncoupled. For a nondegenerate system there are two possible periodic trajectories obtained by putting all the energy in one degree of freedom. Because the two modes are uncoupled the energy will remain in only one of the modes and

and motion will be in that degree of freedom only. For the case of one harmonic potential and one anharmonic potential (Morse oscillator) in which the motion is in the anharmonic degree of freedom the results can be anlytically obtained,

$$\Phi(E) = \frac{2\pi}{\hbar} \frac{\sqrt{2mD}}{a} [1 - \sqrt{E/D}]$$

and $\omega(E) = \omega =$ harmonic frequency

for

$$V_{morse}(x) = D\,(1-e^{-ax})^2 \quad . \tag{3.16}$$

Use of these expressions in eq. (3.14) does not give the correct semiclassical eigenvalues. However a simple modification can be made to eq. (3.14) to give the correct result for this case. This is analogous to the modification made in the application of the theory to transition state theory. Recognizing eq. (3.14) as the first two terms in a Taylor series expansion and "unexpanding" it gives

$$\Phi\left(E - \sum_{i=1}^{N-1} (m_i+1/2)\hbar\omega_i(E)\right) = 2\pi(n+\lambda/4) \quad . \tag{3.17}$$

It is easy to show that using the expressions give by eq. (3.16) in this equation does give the correct separable quantization condition for this example,

$$E(n,m) = D\left[1 - \left(1 - \frac{2n+1}{\sqrt{2mD}}\right)^2\right] + \hbar\omega(m+1/2) \tag{3.18}$$

It is interesting to examine this same system with the periodic trajectory taken to be in the harmonic degree of freedom. For this case

$$\Phi(E) = \frac{2\pi}{\hbar}\,\frac{E}{\omega} \quad , \quad \omega(E) = a\sqrt{2D/m}$$

$$E(n,m) = (n+1/2)\hbar\omega + (m+1/2)\hbar\, a\sqrt{2D/m}$$

Clearly the harmonic degree of freedom has been treated correctly but a harmonic approximation has been made to the anharmonic degree of freedom. This can be understood in light of the approximations that went into the derivation of eq. (3.9) from the response function in eq. (3.7). The integrals over the coordinates in eq. (3.7) were evaluated by the method of stationary phase, which inherently builds in this harmonic approximation to the theory. This is a rather unsettling aspect of the theory in that it treats the degrees of freedom in an unsymmetric way, handling the periodic motion exactly but treating all other motion within a harmonic approximation.

This nonsymmetric treatment of the degrees of freedom was not a problem in the application of the theory to transition state theory since one degree of freedom, that of motion along the reaction path, is quite different from the other bound degrees of freedom in the scattering situation. The periodic orbit pertinent to the transition state was along the reaction path and it was shown that treating the bound degrees of freedom within a harmonic approximation was quite good.

The major similarity between Gutzwiller's work and the semiclassical quantization condition of Marcus[60] and that of Sorbie [61] is the use of classical trajectories to generate an action integral which is then quantized. In the methods of Marcus and Sorbie a quasiperiodic trajectory is used to determine the topology of the problem and enable the construction of N topologically independent phase integrals for an N-dimensional system. Quantization of these phase integrals determines the energy eigenvalue implicitly. The major drawback of this method is the restriction to the regular spectrum of systems. The method of Gutzwiller calculates only one phase integral along a periodic trajectory, treating all motion orthogonal to the periodic motion as harmonic. Although Gutzwiller's method is not restricted to the regular part of the spectrum (as long as a periodic trajectory can still be found in the irregular regions of phase space), motion in the irregular regions is expected to be highly anharmonic; thus giving poor results for this method.

C. Solution on to the Hamilton-Jacobi Equation in Action-Angle Variables

The method of obtaining semiclassical eigenvalues presented here is based upon the work of Born.[51] As in the previously reviewed semiclassical quantization conditions of section A, Born's method is based upon the solution to the Hamilton-Jacobi equation, the difference being the equation is solved in action-angle variables instead of Cartesian coordinates. (For a review of action-angle variables for simple one-dimensional potentials see the appendix.) Action-angle variables are introduced by assuming the Hamiltonian to be of the form

$$H(\underset{\sim}{p},\underset{\sim}{x}) = H_0(\underset{\sim}{p},\underset{\sim}{x}) + H_1(\underset{\sim}{p},\underset{\sim}{x}) \qquad (3.20)$$

where $(\underset{\sim}{p},\underset{\sim}{x}) = (p_i,x_i)$, $i \quad 1,2,\ldots,f$ are the Cartesian momenta and coordinates for an f-dimensional system. The zeroth order Hamiltonian, $H_0(\underset{\sim}{p},\underset{\sim}{x})$ is assumed to be separable and of the form

$$H_0(\underset{\sim}{p},\underset{\sim}{x}) = \sum_{i=1}^{f} \left(p_i^2/2m + v(x_i)\right) \qquad (3.21)$$

A canonical transformation can be made from Cartesian coordinates to action-angle variables $(\underset{\sim}{n},\underset{\sim}{q})$ for the f one-dimensional potentials, $v(x_i)$. In these variables eq. (3.20) becomes

$$H(\underset{\sim}{n},\underset{\sim}{q}) = H_0(\underset{\sim}{n}) + H_1(\underset{\sim}{n},\underset{\sim}{q}) \tag{3.22}$$

where H_0 is now a function of only $\underset{\sim}{n}$. In the limit that H_1 becomes zero the system is separable and $\underset{\sim}{n}$ are constants of the motion:

$$\frac{d\underset{\sim}{n}(\tau)}{d\tau} = -\frac{\partial H}{\partial \underset{\sim}{q}} = -\frac{\partial H_0}{\partial \underset{\sim}{q}} = 0 \quad . \tag{3.23}$$

In the separable case semiclassical eigenvalues are obtained by requiring the set of action variables $\{n_i\}$, i-1,...f to be half-integers. Examination of eq. (A3.6) shows the similarity to the Bohr-Sommerfeld quantization condition.

A form for the Hamiltonian has been chosen, eq. (3.20), such that the zeroth order part is separable and all nonseparability is in the perturbation, H_1. Therefore H_1 will be a function of both $\underset{\sim}{n}$ and $\underset{\sim}{q}$ and $\underset{\sim}{n}$ will not be constants of the motion for the full Hamiltonian. It is desired to find "good" action-angle variables $(\underset{\sim}{N},\underset{\sim}{Q})$ for the full Hamiltonian such that the new action variables N are constants of the motion. That is

$$H(\underset{\sim}{N},\underset{\sim}{Q}) = H(\underset{\sim}{N}) \equiv E(\underset{\sim}{N}) \quad . \qquad (3.24)$$

The new action variables can be defined by a canonical transformation generated by a function $F(\underset{\sim}{q},\underset{\sim}{N})$ of the F_2-type as described by Goldstein.[64] The transformation is defined by

$$\underset{\sim}{n}(\underset{\sim}{q},\underset{\sim}{N}) = F(\underset{\sim}{q},\underset{\sim}{N})/\partial \underset{\sim}{q} \qquad (3.25a)$$

$$\underset{\sim}{Q}(\underset{\sim}{q},\underset{\sim}{N}) = F(\underset{\sim}{q},\underset{\sim}{N})/\partial \underset{\sim}{N} \quad . \qquad (3.25b)$$

Inserting eq. (3.25a) into eq. (3.22) gives the Hamilton-Jacobi equation in action-angle variables for the generating function $F(\underset{\sim}{q},\underset{\sim}{N})$:[57]

$$H\,\underset{\sim}{q},\left(\frac{\partial F(\underset{\sim}{q},\underset{\sim}{N})}{\partial \underset{\sim}{q}}\right) = H_0\left(\frac{\partial F(\underset{\sim}{q},\underset{\sim}{N})}{\partial \underset{\sim}{q}}\right) + H_1\left(\underset{\sim}{q},\frac{\partial F(\underset{\sim}{q},\underset{\sim}{n})}{\partial \underset{\sim}{q}}\right) = E(\underset{\sim}{N}) \quad . \qquad (3.26)$$

In the case that H_1 is equal to zero, $(\underset{\sim}{n},\underset{\sim}{q})$ are the good action-angle variables; therefore, we want $F(\underset{\sim}{q},\underset{\sim}{N})$ to be the generator of the identify transformation,[65]

$$\underset{\sim}{n}(\underset{\sim}{q},\underset{\sim}{N}) = \underset{\sim}{N} \quad ,$$

$$\underset{\sim}{Q}(\underset{\sim}{q},\underset{\sim}{N}) = \underset{\sim}{q} \quad , \qquad (3.27)$$

therefore

$$F(\underset{\sim}{q},\underset{\sim}{N}) = \underset{\sim}{q} \cdot \underset{\sim}{N} \quad .$$

Thus the generator for the full Hamiltonian can be taken to be of the form

$$F(\underset{\sim}{q},\underset{\sim}{N}) = \underset{\sim}{q} \cdot \underset{\sim}{N} + G(\underset{\sim}{q},\underset{\sim}{N}) \quad . \qquad (3.28)$$

The quantum condition for $F(\underset{\sim}{q},\underset{\sim}{N})$ can be clearly seen by examining the semiclassical approximation to the wavefunction in $\underset{\sim}{q}$-space, $\Psi_{\underset{\sim}{N}}(\underset{\sim}{q})$. The phase of $\Psi_{\underset{\sim}{N}}(\underset{\sim}{q})$ is the generating function,

$$\begin{aligned} \Psi_{\underset{\sim}{N}}(\underset{\sim}{q}) &\sim \exp\,[i\,F(\underset{\sim}{q},\underset{\sim}{N})/\hbar] \\ &\sim \exp\,[i\,\underset{\sim}{q}\cdot\underset{\sim}{N}/\hbar]\,\exp[i\,G(\underset{\sim}{q},\underset{\sim}{N})/\hbar] \quad . \end{aligned} \qquad (3.29)$$

where the angle variables $\underset{\sim}{q}$ have units of $\hbar$. (It is convenient to use atomic units in which $\hbar = 1$. This will be assumed throughout the remainder of this section.) Requiring the wavefunction to be single valued on the interval 0 to 2π restricts the action variables $\underset{\sim}{N}$ to be integers and $G(\underset{\sim}{q},\underset{\sim}{N})$ to be a periodic function of $\underset{\sim}{q}$. Contributions to the phase from the pre-exponential modifies this result to $\underset{\sim}{N}$ being half integers or equivalently, $\underset{\sim}{N}$ is replaced by $(\underset{\sim}{N} + 1/2)$ with $\underset{\sim}{N}$ now taken integer values. At this point the method presented here differs from that of Born, who used classical perturbation theory to solve eq. (3.26) for the generating function $F(\underset{\sim}{q},\underset{\sim}{N})$.

The method presented here is a nonperturbative approach to the solution of eq. (3.26). Since $G(\underset{\sim}{q},\underset{\sim}{N})$ is a periodic function of $\underset{\sim}{q}$ it can be expanded in a Fourier series,

$$G(\underset{\sim}{q},\underset{\sim}{N}) = i \sum_{\underset{\sim}{k}}{}' B_{\underset{\sim}{k}}(\underset{\sim}{N})\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{q}} \tag{3.30}$$

and

$$\underset{\sim}{n} = \frac{\partial F(\underset{\sim}{q},\underset{\sim}{N})}{\partial \underset{\sim}{q}} = \underset{\sim}{N} - \sum_{\underset{\sim}{k}}{}' \underset{\sim}{k}\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{q}}\, B_{\underset{\sim}{k}}(\underset{\sim}{N}) \tag{3.31}$$

where Σ' implies that the constant term $\underset{\sim}{k} = (0,0,\ldots,0) = \underset{\sim}{0}$ is omitted from the sum. Using eq. (3.31) in equation (3.26) gives

$$H\left(\underset{\sim}{q},\underset{\sim}{N} - \sum_{\underset{\sim}{k}}{}' \, \underset{\sim}{k} \, B_{\underset{\sim}{k}} \, e^{i(\underset{\sim}{k}\cdot\underset{\sim}{q})}\right) = E(\underset{\sim}{N}) \tag{3.32}$$

which must be solved for the Fourier coefficients B_k. (The $\underset{\sim}{N}$ dependence of B is omitted for notational convenience.) Multiplying eq. (3.32) by $\exp(-i\underset{\sim}{k}\cdot\underset{\sim}{q})$ and integrating over the angles $\underset{\sim}{q}$ gives the results

$$(2\pi)^{-f} \int_0^{2\pi} d\underset{\sim}{q} \;\; e^{-i\underset{\sim}{k}\cdot\underset{\sim}{q}} \, H(\underset{\sim}{q},\underset{\sim}{n}) = \underset{\sim}{0} \tag{3.33}$$

$$(2\pi)^{-f} \int_0^{2\pi} d\underset{\sim}{q} \, H(\underset{\sim}{q},\underset{\sim}{n}) = E(\underset{\sim}{N}) \quad , \tag{3.34}$$

where $\underset{\sim}{n}$ is given by eq. (3.31).

Equation (3.33) is solved for the Fourier coefficients for a given set of action variables (the N's are parameters in the calculation) and substitution into eq. (3.34) gives the energy eigenvalue.

Equation (3.33) represents an equation for the Fourier coefficients, $B_{\underset{\sim}{k}}$, through $\underset{\sim}{n}$. Although eq. (3.33) cannot be solved directly for $B_{\underset{\sim}{k}}$, iterative schemes can be devised for its solution. By casting eq. (3.33) into the form

$$\underset{\sim}{B}_k = \text{function}\ (\underset{\sim}{B}_k) \quad , \tag{3.35}$$

solution is gained by a direct interative substitution method,

$$\underset{\sim}{B}_k^{(\ell+1)} = \text{function}\ \underset{\sim}{B}_k^{(\ell)} \tag{3.36}$$

$\underset{\sim}{B}_k^{(o)}$ being an initial guess which subsequently generates the sequence $B_k^{(i)}$, $i = 1,2,\ldots,\infty$.

A method for casting eq. (3.33) into the form of eq. (3.35) for a general zeroth order Hamiltonian H_0 is suggested in the case that H_0 is harmonic,

$$H_0(\underset{\sim}{n}) = \underset{\sim}{\omega} \cdot (\underset{\sim}{n} + 1/2) = \sum_{i=1}^{f} \omega_i(n_i + 1/2) \quad . \tag{3.37}$$

In this case the total Hamiltonian becomes

$$H(\underset{\sim}{q},\underset{\sim}{n}) = \underset{\sim}{\omega} \cdot \left(\underset{\sim}{N} - \sum_{\underset{\sim}{k}} \underset{\sim}{k}\, \underset{\sim}{B}_k\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{q}} + 1/2 \right) + H_1(\underset{\sim}{q},\underset{\sim}{n}) \tag{3.38}$$

which gives for eq. (3.33)

$$\underset{\sim}{\omega} \cdot \underset{\sim}{k}\, B_{\underset{\sim}{k}} = (2\pi)^{-f} \int_0^{2\pi} d\underset{\sim}{q}\; e^{-i\underset{\sim}{k}\cdot\underset{\sim}{q}}\, H_1(\underset{\sim}{q},\underset{\sim}{n}) \quad , \qquad (3.39)$$

for $\underset{\sim}{k} \neq 0$.

Introducing $A_{\underset{\sim}{k}} = \underset{\sim}{\omega}\cdot\underset{\sim}{k}\, B_{\underset{\sim}{k}}$ gives

$$A_{\underset{\sim}{k}} = (2\pi)^{-f} \int_0^{2\pi} d\underset{\sim}{q}\; e^{-i\underset{\sim}{k}\cdot\underset{\sim}{q}}\, H_1\left(\underset{\sim}{q},\, \underset{\sim}{N} - {\sum_{\underset{\sim}{k'}}}' \frac{\underset{\sim}{k'}\, e^{i\underset{\sim}{k'}\cdot\underset{\sim}{q}}}{\underset{\sim}{\omega}\cdot\underset{\sim}{k'}}\, A_{\underset{\sim}{k}}\right) \qquad (3.40)$$

and

$$E(\underset{\sim}{N}) = \underset{\sim}{\omega}\cdot(\underset{\sim}{N}+1/2) + (2\pi)^{-f} \int_0^{2\pi} d\underset{\sim}{q}\; H_1\left(\underset{\sim}{q},\, \underset{\sim}{N} - {\sum_{\underset{\sim}{k'}}}' \frac{\underset{\sim}{k'}\, e^{i\underset{\sim}{k'}\cdot\underset{\sim}{q}}}{\underset{\sim}{\omega}\cdot\underset{\sim}{k'}}\, A_{\underset{\sim}{k'}}\right) \qquad (3.41)$$

$$= \underset{\sim}{\omega}\cdot(\underset{\sim}{N} + 1/2) + A_{\underset{\sim}{0}}$$

For a general zeroth order Hamiltonian the same procedure can be applied by adding and subtracting the first two terms of a Taylor series expansion of H_0 to the Hamiltonian inside of the integral in eq. (3.33):

$$(2\pi)^{-f}\int d\underset{\sim}{q}\, e^{-i\underset{\sim}{k}\cdot\underset{\sim}{q}}\Bigg[H\Big(\underset{\sim}{q},\ \underset{\sim}{N}-{\sum_{\underset{\sim}{k'}}}'\underset{\sim}{k'}\, e^{i\underset{\sim}{k'}\cdot\underset{\sim}{q}}B_{\underset{\sim}{k}}\Big)+H_0(\underset{\sim}{N})$$

$$+\underset{\sim}{\omega}(\underset{\sim}{N})\cdot\Big(\underset{\sim}{N}-{\sum_{\underset{\sim}{k'}}}'\underset{\sim}{k'}\, e^{i\underset{\sim}{k'}\cdot\underset{\sim}{q}}B_{\underset{\sim}{k}}\Big)-H_0(\underset{\sim}{N})-\underset{\sim}{\omega}(\underset{\sim}{N})\cdot\Big(\underset{\sim}{N}-\sum_{\underset{\sim}{k'}}\underset{\sim}{k'}\, e^{i\underset{\sim}{k'}\cdot\underset{\sim}{q}}B_{\underset{\sim}{k}}\Big)\Bigg]=\underset{\sim}{0} \qquad (3.42)$$

This in effect adds and substracts harmonic terms of H_0 to the equation, where the frequencies are given by $\omega(N) = \dfrac{\partial H_0(\underset{\sim}{N})}{\partial \underset{\sim}{N}}$. Equation (3.42) rearranges to

$$\underset{\sim}{\omega}\cdot\underset{\sim}{k}\, B_{\underset{\sim}{k}} = \underset{\sim}{\omega}\cdot\underset{\sim}{k}\, B_{\underset{\sim}{k}} + (2\pi)^{-f}\int_0^{2\pi} d\underset{\sim}{q}\, e^{-i\underset{\sim}{k}\cdot\underset{\sim}{q}} H(\underset{\sim}{q},\underset{\sim}{n}) \,, \qquad (3.43)$$

where $\underset{\sim}{n}$ is given by eq. (3.31), or in terms of the $A_{\underset{\sim}{k}}$'s:

$$A_{\underline{k}} = A_{\underline{k}} + (2\pi)^{-f}\int_0^{2\pi} d\underset{\sim}{q}\ e^{-i\underset{\sim}{k}\cdot\underset{\sim}{q}} H\Big(\underset{\sim}{q},\ \underset{\sim}{N} - {\sum_{\underset{\sim}{k'}}}' \frac{\underset{\sim}{k'}\, e^{i\underset{\sim}{k'}\underset{\sim}{q}}}{\underset{\sim}{\omega}\cdot\underset{\sim}{k'}}\ A_{\underset{\sim}{k}}\Big). \qquad (3.44)$$

Equation (3.44) is solved by a direct iterative substitution method as given by eq. (3.36), the final solution being $A_k(\infty)$. In practice one iterates eq. (3.44) until the desired quantity, $E(\tilde{N})$ given by eq. (3.34) converges with respect to the iteration.) If one takes $A_{\underset{\sim}{k}}^{(0)} = \underset{\sim}{0}$ for the initial guess the first iterate is

$$A_{\underset{\sim}{k}}^{(1)} = (2\pi)^{-f} \int d\underset{\sim}{q}\, e^{-i\underset{\sim}{k}\cdot\underset{\sim}{q}}\, H(\underset{\sim}{q},\underset{\sim}{N}) \quad , \tag{3.45}$$

which is equivalent to the result of first order perturbation theory as obtained by Born.[51] The results from a second iteration will not be the same as second order perturbation theory, however, since eq. (3.44) is not linear in $A_{\underset{\sim}{k}}$. Iteration through order infinity is equivalent to infinite order perturbation theory though, giving the exact result. However, this result is dependent upon the convergence of the iteration series, $A_k^{(0)}$, $A_k^{(1)}$, ..., $A_k^{(\infty)}$. Similar to the perturbation series, this series is not guaranteed to converge, which is evident for the case that eq. (3.44) has no solution. For the irregular region of the spectrum there will not be f constants of the motion given by the good action variables N, and eq. (3.44) will have no solution.

There may exist cases in which solutions to eq. (3.44) do exist but the iteration scheme given by eq. (3.36) is not convergent. For these situations an alternate iteration scheme which has better convergence properties is Newton's method. For a one-dimensional system the equation

$$F(x) = 0 \tag{3.46}$$

can be solved by the iteration scheme

$$x^{(\ell+1)} = x^{(\ell)} - \left[\frac{dF\left(x^{(\ell)}\right)}{dx}\right]^{-1} F\left(x^{(\ell)}\right) . \tag{3.47}$$

This is easily extended to a multidimensional system of equations

$$\underset{\sim}{F}(\underset{\sim}{x}) = \underset{\sim}{0} \tag{3.48}$$

by

$$\underset{\sim}{x}^{(\ell+1)} = \underset{\sim}{x}^{(\ell)} - \left[\frac{\partial \underset{\sim}{F}\left(\underset{\sim}{x}^{(\ell)}\right)}{\partial \underset{\sim}{x}}\right]^{-1} \cdot \underset{\sim}{F}\left(\underset{\sim}{x}^{(\ell)}\right) \tag{3.49}$$

where the matrix $\left[\dfrac{\partial F(\underset{\sim}{x})}{\partial \underset{\sim}{x}}\right]$ is defined by

$$\left[\frac{\partial \underset{\sim}{F}(\underset{\sim}{x})}{\partial \underset{\sim}{x}}\right]_{i,j} = \partial F_i(\underset{\sim}{x})/\partial x_j . \tag{3.50}$$

Equation (3.48) is of the form given by eq. (3.33). Application of this scheme to eq. (3.33) gives:

$$\tilde{B}_{k}^{(\ell+1)} = \tilde{B}_{k}^{(\ell)} + \sum_{k'}{}' \, (\tilde{M}^{-1})_{\tilde{k},\tilde{k}'} \, \tilde{W}_{k'} \quad , \tag{3.51a}$$

$$\tilde{M}_{\tilde{k},\tilde{k}'} = (2\pi)^{-f} \int_0^{2\pi} d\tilde{q} \, e^{-i(\tilde{k}-\tilde{k}')\cdot\tilde{q}} \, \tilde{k}' \cdot \left.\frac{\partial H(\tilde{q},\tilde{n})}{\partial \tilde{n}}\right|_{\tilde{n}=\tilde{n}(\tilde{q})} , \tag{3.51b}$$

$$\tilde{W}_{k} = (2\pi)^{-f} \int_0^{2\pi} d\tilde{q} \, e^{-i\tilde{k}\cdot\tilde{q}} \, H(\tilde{q},\tilde{n})\Big|_{\tilde{n}=\tilde{n}(\tilde{q})} \tag{3.51c}$$

and $\tilde{n}$ is given by eq. (3.31). Comparison of equations (3.34) and (3.51) gives the eigenvalue condition

$$E(\tilde{N}) = \tilde{W}_0 \tag{3.52}$$

The major similarity of this method for obtaining semiclassical eigenvalues with the trajectory methods of Section A is that both are concerned with the solution of the Hamilton-Jacobi equation. The trajectory methods solve the Hamilton-Jacobi equation in Cartesian coordinates and as a result have to deal with the multivaluedness of the solution. The solution in action-angle variables obviates the need to know the multivalued nature of the solution by introducing the topology of the system through the zeroth order action-angle variables $(\underset{\sim}{n},\underset{\sim}{q})$. Solutions to eq. (3.33) exist then if the perturbation H_1 is not sufficiently large to alter the topology to where f constants of the motion no longer exist. This is no more rigorous of a restriction than in the trajectory methods since in these approaches one assumes the system is close enough to separability so that quasiperiodic trajectories exist - i.e., one must be in the KAM regime.[58]

The major advantage of the method presented here over the trajectory methods is in the fact that the topology is easily dealt with through the action-angle variables. Also the rhs of eq. (3.44) can be easily computed due to the existence of fast Fourier transform algorithms. However, the number of Fourier coefficients needed to expand the generator $G(\underset{\sim}{q},\underset{\sim}{N})$ increases with the dimensionality of the system while trajectories pose no problem for higher dimensions. This seems to indicate that trajectory methods may prove to be more practical in application for systems of high mathematical dimensions. Finally, a method which blends the approach of trajectory methods to solve the Hamilton-Jacobi equation in action-angle variables has been proposed by Sorbie and Handy[62] and is discussed in section E.

D. Applications

The Hamilton-Jacobi method of obtaining semiclassical eigenvalues described in Section C has been applied to a simple two-dimensional example which has also been treated by trajectory methods[60,61]. The reference Hamiltonian, H_0, is harmonic and for a particle of mass 1:

$$H_0(p,x) = \frac{p_1^2}{2} + \frac{p_2^2}{2} + \frac{1}{2}\omega_1^2 x_1^2 + \frac{1}{2}\omega_2^2 x_2^2 \quad . \tag{3.53}$$

The nonseparable perturbation H_1 is

$$H_1(\underset{\sim}{x}) = \lambda x_1(x_2^2 + \eta x_1^2) \quad . \tag{3.54}$$

From the appendix the action-angle variables for H_0 are given by

$$x_1 = \sqrt{\frac{2n_1+1}{\omega_1}} \cos q_1 \tag{3.55a}$$

$$x_2 = \sqrt{\frac{2n_2+1}{\omega_2}} \cos q_2 \tag{3.55b}$$

where we have made the replacement of $\underset{\sim}{n}$ by $(\underset{\sim}{n} + 1/2)$.

For this harmonic example the Fourier coefficients $A_{\underset{\sim}{k}}$ can be solved for by Eq. (3.40), the energy eigenvalues are given by eq. (3.41). Written out explicity these are

$$A_{k_1k_2} = (2\pi)^{-2} \int_0^{2\pi} dq_1 \int_0^{2\pi} dq_2 \cdot e^{-i(k_1q_1+k_2q_2)} H_1(q_1,q_2,n_1,n_2) \qquad (3.56)$$

$$E(N_1,N_2) = \omega_1 (N_1+1/2) + \omega_2(N_2+1/2) + A_{0,0} \qquad (3.57)$$

$$n_i(q_1,q_2) = N_i - \sum_{k_1,k_2}{}' \frac{k_i\, e^{i(k_1q_1+k_2q_2)}}{\omega_1k_1+\omega_2k_2} A_{k_1,k_2}, i=1,2 \quad . \qquad (3.58)$$

The "good" action variables, $\underset{\sim}{N}$, are fixed parameters in the calculation. The perturbation H_1 is dependent upon $\underset{\sim}{q}$ and $\underset{\sim}{n}$ through the relations given in eq. (3.55). The range of the indices k_1,k_2 should be from $-\infty$ to $+\infty$, however, in practical applications these are truncated, including enough Fourier coefficients to insure convergence of the solution. It should also be noted that since $\underset{\sim}{n}$ as appears in H_1 is a function of the Fourier coefficients A_{k_1,k_2} an iterative solution of eq. (3.56) is desired.

For an easy and efficient means of carrying out the calculation, equations (3.56)-(3.58) are cast into a form amenable to Fourier transform packages already available. This is done by first discretizing the $\underset{\sim}{q}$ integrals in eq. (3.56)

$$q_i = \frac{2\pi\ell_i}{L_i} \quad , \quad \ell = 0,1,\ldots,L_i-1; \quad i = 1,2 \quad . \tag{3.59}$$

The sums over k_1, k_2 in eq. (3.58) must have upper and lower limits such that their differences are (L_1-1) and (L_2-1), respectively. This is done by having the sums go from $\frac{-L_1}{2} \rightarrow \frac{L_1}{2} - 1$ for k_1 and from $\frac{-L_2}{2} \rightarrow \frac{L_2}{2} - 1$ for k_2. It is convenient to have all sums go from 0 to L_i-1, and have the indices of the coefficients A_{k_1,k_2} be in the same range. This is done by shifting the sums up by $L_i/2$ and replacing k_i by $k_i - L_i/2$ in the sums. Using these modifications equations (3.56)-(3.58) become

REDUCE & INSERT (3.60)

$$E(N_1,N_2) = \omega_1(N_1+1/2) + \omega_2(N_2+1/2) + A_{L_{1/2},L_{1/2}} \quad , \tag{3.61}$$

and

$$n_i(\ell_1,\ell_2) = N_i - (-1)^{\ell_1+\ell_2} \sum_{k_1=0}^{L_i-1} \sum_{k_2=0}^{L_2-1} W_1^{k_1\ell_1} \, W_2^{k_2\ell_2} \, \frac{(k_i-L_i/2)\, A_{k_1,k_2}}{\omega_1(k_1-L_1/2) + \omega_2(k_2-L_2/2)} \tag{3.62}$$

for i = 1,2, where

$$W_j = \exp\left[\frac{2\pi i}{L_j}\right] \tag{3.63}$$

The prime in eq. (3.62) indicates that the ($k_1 = L_1/2$, $k_2 = L_2/2$) term is omitted from the sum.

A packaged subroutine for finding the discrete Fourier transform of $(-1)^{\ell_1+\ell_2} H_1(\ell_1, \ell_2)$ and the inverse Fourier transform of $(k_i - \frac{L_i}{2})\ A_{k_1,k_2} / \left(\omega_1\left(k_1 - \frac{L_1}{2}\right) + \omega_2\left(k_2 - \frac{L_2}{2}\right)\right)$ is available at the Lawrence Berkeley Laboratory (complex fast Fourier transform - CFFT). The procedure is first to specify the parameters N_1, N_2 which are set to integers, then n_1, n_2 are calculated by an inverse Fourier transform using the initial guess of A_{k_1,k_2}. The matrix $H_1(l_1,l_2)$ is constructed using these values of $\underline{n}$ with equations (3.55) and (3.54). The Fourier transform of $(-1)^{\ell_1+\ell_2}\ \tilde{H}_1(\ell_1,\ell_2)$ then gives the new iterate of A_{k_1,k_2}. Iteration is continued until eq. (3.61) converges to the energy eigenvalue with respect to the number of iterations.

For a variety of potential parameters ($\omega_1, \omega_2, \lambda, \eta$) convergence to four decimal places was obtained for 64 Fourier coefficients (L_1=L_2=8). Typically 10-15 iterations also produced the same accuracy in the eigenvalue.

First a comparison of these results are made with the trajectory method of Eastes and Marcus[60(a)] and Noid and Marcus[60(b)]. One would expect that the results of the method of Sorbie[61] should be identical to those of Marchus since they both construct solutions to the Hamilton-Jacobi equation in Cartesian coordinates. This is shown to be true in Sorbie's paper to within numerical accuracy of the eigenvalues. It is also argued that the trajectory methods should agree well with the results presented here since the present method also seeks a solution to the Hamilton-Jacobi equation although it is in action-angle variables. This is shown to be the case to within numerical accuracy by the results in Table I.

Comparison with exact quantum mechanical results is also made in Table I, however, the coupling parameter is sufficiently small so that the eigenvalues are only perturbed slightly from the separable limit. As a more rigorous test of the semiclassical eigenvalue condition a study was made of the eigenvalues for a range of coupling parameter, λ. The semiclassical eigenvalues are compared with the quantum results in Table II for $\omega_1 = .7$, $\omega_2 = 1.3$ and $\lambda = -\eta$, with $\lambda = 0 \rightarrow -.2$. The potential for the problem is given by

$$V(x_1,x_2) = \frac{1}{2}\omega_1^2 x_1^2 + \frac{1}{2}\omega_1^2 x_2^2 + \lambda x_1(x_2^2 + x_1^2) , \qquad (3.64)$$

which has a relative maximum (saddle point) at $x_1 = 1/3 \left(\frac{\omega_1}{\lambda}\right)^2$, $x_2=0$, of $V_{max} = \omega_1^6/54\lambda^4$. For energies above V_{max}, eigenvalues no longer exist. The semiclassical eigenvalues are displayed in figure 13 as a function of λ with $V_{max}(\lambda)$ also indicated. The semiclassical values are seen to approach V_{max} fairly closely before breaking off.

As a more graphic display of the agreement between the quantum and semiclassical results, the percent error in the semiclassical level shift, Δ, is graphed in figure 14. The level shift is defined by

$$\Delta(N_1,N_2) \quad = \quad E(N_1,N_2) - \omega_1(N_1+1/2) + \omega_2(N_2+1/2) \qquad (3.65)$$

where QM denotes quantum mechanical and SC denotes semiclassical. The percent error being given by

$$\left| \frac{\Delta_{QM} - \Delta_{SC}}{\Delta_{QM}} \right| \times 100 \quad . \qquad (3.66)$$

As is expected, the lower eigenvalues show a larger error while the higher eigenvalues (here this means all those above the ground state) are within a few percent of the quantum result. This is just the accuracy one expects from the one-dimensional quantization of Bohr-Sommerfeld, eq. (3.1).

The Newton iteration scheme, eq. (3.51), was also applied to this sample potential. The results were identical to four decimal places for a similar number of Fourier coefficients, $L_1 = L_2 = 8$. Although the number of iterations needed for convergence to four decimal places was in general 4-5, no reduction in computational effort was realized over the simple iteration scheme due to the necessity of inverting a large matrix at each iteration.

Finally, it is noted that the Hamilton-Jacobi method (using the simple iterative scheme) has been successfully applied to the vibrational spectra of triatomic molecules by Handy, Colwell and Miller.[66] Agreement with the quantum results was again within 10 percent, this being the worst case of the ground state.

E. Degeneracies

The semiclassical eigenvalue conditions become difficult to apply in the case that the zeroth order Hamiltonian H_0 is degenerate and the perturbation H_1 is small but lifts the degeneracy. In a classical system, degenaracy can be easily described in terms of the action-angle variables. If $(\underset{\sim}{n},\underset{\sim}{q})$ are the action-angle variables for the Hamiltonian of a bound system, H_0, the frequency of the periodicity of each mode is given by

$$\underset{\sim}{\omega} = \dot{\underset{\sim}{q}} = \frac{\partial H_0(\underset{\sim}{n})}{\partial \underset{\sim}{n}} \quad , \tag{3.67}$$

which is a constant in time since $\underset{\sim}{n}$ is a constant of the motion. The system is said to be m-fold degenerate if there exist m relationships of the form

$$\sum_{i=1}^{f} \omega_i \, j_{k,i} = 0 \quad , \quad k = 1,2,\ldots,m \tag{3.68}$$

where $j_{k,i}$ is an integer and f is the dimensionality of the system. If m = f-1 the system is called completely degenerate.

For an f-dimensional system in the regular region of the 2f-dimensional phase space, there are f-topologically independent integrals of the motion which restrict the system to move on a f-dimensional invariant toriod. When the system is m-fold degenerate the motion of the system is further restricted to a (f-m)-dimensional toroid in phase space. In terms of the trajectory methods for quantization, only f-m topologically independent integrals of the type found in eq. (3.6) can be found, therefore only f-m quantum numbers are required to define the energy eigenvalue. This is equivalent to there only being f-m good constants of the motion which are linearly independent. This is true since a canonical transformation can be made from the action-angle variables $(\underset{\sim}{n},\underset{\sim}{q})$ to a new set $(\underset{\sim}{n}',\underset{\sim}{q}')$ such that the Hamiltonian is a function of only f-m of the new action variables, $\underset{\sim}{n}'$:

$$H_0(\underset{\sim}{n}') = H_0(n_1',n_2',\ldots,n_{f-m}') \qquad (3.69)$$

The topology of a degenerate system is very different from a nondegenerate one. This is the basis of the problem encountered in trying to impose a quantization condition on a nondegenerate system which is perturbed slightly from a degenerate one.

In the trajectory methods of section A the degenaracy problem manifests itself through the distortion of the caustic curves. This can be seen for the system studied in section D, given by equations (3.53) and (3.54). If $m_1\ \omega_1 = m_2\ \omega_2$ the zeroth order system described by H_0 is totally degenerate and confined to motion along a single closed curve in phase space. The rapidity with which the trajectory closes on itself depends upon the ratio ω_1/ω_2. If $\omega_1/\omega_2 = 1$ the trajectory will close on itself after one oscillation, whereas if $\omega_1/\omega_2 = 4/3$ it will in general take 12 oscillations for the motion to close on itself. The latter case would cover much more phase space before closing than the former, i.e., it would be a closer approximation to a 2-dimensional toroid in the 4-dimensional phase space. Thus perturbing this degenerate motion to a nondegenerate motion will give a caustic pattern resembling a more normal system in which the zeroth order system is nondegenerate. However, perturbation of the $\omega_1/\omega_2 = 1$ case to nondegeneracy is expected to give more complex caustic curves since the zeroth order motion is very different from a 2-dimensional toroid. For the $\omega_1/\omega_2 = 4/3$ case it is expected that the previously described method of Sorbie[61] might suffice, whereas for $\omega_1/\omega_2 = 1$ the problem will be in identifying 2 topologically independent paths for the path integration. These are exactly the results obtained by Sorbie and Handy.[62] The interested reader is referred to this work for further description and helpful illustrations.

Sorbie and Handy[62] have also given a quantization condition which is capable of handling these more complicated caustic curves. The method is to transform coordinates to the action-angle variables of the zeroth order Hamiltonian H_0, $(\underset{\sim}{n},\underset{\sim}{q})$. The quantum condition is given by

$$\oint n_1(q_1,q_2)\, dq_1 = M_1(m_1 + 1/2)\, 2\pi \quad ,$$
$$\oint n_2(q_1,q_2)\, dq_2 = M_2(m_2 + 1/2)\, 2\pi \quad , \tag{3.70}$$

where m_1,m_2 are integers. The number of circuits around the two topologically independent paths are M_1,M_2, which are given by

$$M_j = \frac{q_j^f - q_j^f}{2\pi} \quad , \; j=1,2, \tag{3.71}$$

where q_j^i q_j^f are the initial and final angle variables. The path chosen for the both integrals is the same, being the trajectory itself which is a combination of the two topologically independent paths. This method includes the topology of the total system correctly through the action-angle variables $(\underset{\sim}{n},\underset{\sim}{q})$. In the limit that the perturbation goes to zero, the system becomes separable and degenerate. Although n_1,n_2 are no longer linearly independent, they both are constants of the motion and describe the zeroth order system.

In Born's[51] perturbative method the degeneracy manifests itself through the small divisor problem. This is equivalent to the problem encountered in applying eq. (3.40) to degenerate system. The $\underset{\sim}{\omega}\cdot\underset{\sim}{k}$ term appearing in the denominator will be zero for some $\underset{\sim}{k}$ vector other than the zero one ($\underset{\sim}{k} = \underset{\sim}{0}$), due to equation (3.68). Attempts to apply the

the Newton iteration method, given by eq. (3.51), to degenerate systems gave very disappointing results, indicating further that the method does not deal properly with the topology of the degenerate systems.

At present a method for including the proper topology into the semi-classical quantization condition given in section C is not obvious. However, an alternate method of formulating the quantization condition which treats degeneracies differently has been given by Miller.[67] The previous approach sought the solution to the Hamilton-Jacobi equation, it being the generator $F(\underset{\sim}{q},\underset{\sim}{N})$, by expansion of the generator in a Fourier series and iterative solution for the Fourier coefficients. The alternate method of Miller derives from the Hamilton-Jacobi equation a Schrodinger-like equation in action-angle variables for the semiclassical wavefunction, $\psi_{\underset{\sim}{N}}(\underset{\sim}{q})$:

$$E\psi_{\underset{\sim}{N}}(\underset{\sim}{q}) = -\left[-i\underset{\sim}{\omega}\cdot\frac{\partial}{\partial\underset{\sim}{q}} + V(\underset{\sim}{q},\underset{\sim}{n})\right]\psi_{\underset{\sim}{N}}(\underset{\sim}{q}) \ , \tag{3.72}$$

where the reference Hamiltonian H_0 has been assumed to be harmonic, and $V(\underset{\sim}{q},\underset{\sim}{n})$ is equal to $H_1(\underset{\sim}{q},\underset{\sim}{n})$ in section C. This is a classical equation, quantization of the energy resulting from the restriction that $\psi_{\underset{\sim}{N}}(\underset{\sim}{q})$ be a single valued function of $\underset{\sim}{q}$. The single valuedness of $\psi_{\underset{\sim}{N}}(\underset{\sim}{q})$ can be imposed by its Fourier series expansion:

$$\psi_{\underset{\sim}{N}}(\underset{\sim}{q}) = \sum_{\underset{\sim}{k}} C_{\underset{\sim}{k}}\left(\underset{\sim}{N}\right) e^{i\underset{\sim}{k}\cdot\underset{\sim}{q}} \ . \tag{3.73}$$

Manipulations similar to those in section C give equations for the iterative solution for the Fourier coefficients. Practical application of this method is impeded by the necessity to solve an eigenvalue problem at each iteration.

This method of semiclassical quantization is very useful in the examination of the degeneracy problem. Quantum mechanical degeneracies are manifested in the equality of energies of two distinct eigenfunctions. For a zeroth order degeneracies in our problem we have

$$\underset{\sim}{N}_1 \cdot \underset{\sim}{\omega} = \underset{\sim}{N}_2 \cdot \underset{\sim}{\omega} \tag{3.74}$$

therefore the zeroth order wavefunction must be a linear combination of the two states:

$$\psi_0(\underset{\sim}{q}) \sim c_1\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{N}_1} + c_2\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{N}_2} \tag{3.75}$$

The zeroth order part of the generator $F(\underset{\sim}{q},\underset{\sim}{N})$ is then proportional to the logarithm of $\psi_0(\underset{\sim}{q})$:

$$F_0(\underset{\sim}{q}) \sim -i\, \ln\left[c_1\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{N}_1} + c_2\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{N}_2}\right] . \tag{3.76}$$

In the case of no degeneracy $c_2 \rightarrow 0$ and $F_0(\underset{\sim}{q}) \sim \underset{\sim}{q}\cdot\underset{\sim}{N}_1$. In the degenerate case it is obvious that the expansion given by equation (3.28) is not correct. The alternate method is not faced with this problem since a solution for the wavefunction is desired, not the solution of the generator.

Finally it is noted that the formalism given by Miller no longer contains the need to define "good" action variables which are then set to integers. Quantization arises solely from requiring the wavefunction to be single valued. For this reason it seems very possible that this method should be extendable to the irregular region of the energy spectrum.

APPENDIX

ACTION-ANGLE VARIABLES FOR ONE-DIMENSIONAL SYSTEMS

Action-angle variables are very useful for describing periodic systems, the action variables being constants of the motion and the angles varying linearly with time. The action-angle variables can be defined by a canonical transformation from Cartesian coordinates (p,x) to (n,q) by a generating function S(x,n) (F_2-type of Goldstein):[68]

$$p = \frac{\partial S(}{\ } , \tag{A.3.1a}$$

$$q = \frac{\partial S(x,n)}{\partial n} . \tag{A3.1b}$$

Replacing p by eq. (A3.1a) in the Hamiltonian gives the Hamilton-Jacobi equation for S(x,n):

$$H\left(x \quad \frac{\partial S(x,n)}{\partial x}\right) = E \tag{A3.2}$$

In Cartesian coordinates this is

$$\frac{1}{2m}\left(\frac{\partial S(x,n)}{\partial x}\right)^2 + V(x) = E , \tag{A3.3}$$

which gives for the generator

$$S(x,n) \;=\; \int_{x_0}^{x} dx' \sqrt{2m\left(E-V(x')\right)} \qquad \text{(A3.4)}$$

The action variable is defined by

$$n = \frac{1}{2\pi\hbar} \oint_{x_<}^{x_>} dx \;\; \frac{\partial S(x,n)}{\partial x} \qquad \text{(A3.5)}$$

the integral being over one period. The angle is defined by eq. (A3.1b). In explicit notation these are given by

$$n \;=\; \frac{1}{2\pi\hbar} \;\; 2\int_{x_0}^{x} dx \sqrt{2m\left(E-V(x)\right)} \qquad \text{(A3.6)}$$

where x , x are the classical turning points, and

$$q(x) \;=\; m\,\frac{\partial E(n)}{\partial n} \int_{x_0}^{x} \frac{dx'}{\sqrt{2m\left(E(n)\;-\;V(x')\right)}}\;, \qquad \text{(A3.7)}$$

where E(n) is defined implicitly by eq. (A3.6). The momenta is defined in terms of the action-angle variables by eq. (A3.1a) where x(q,n) is obtained by inversion of eq.(A3.7). These equations can be solved analytically for a few simple one-dimensional potentials. Three examples are given below:

Harmonic oscillator: $V(x) = 1/2\, m\, \omega^2 x^2 \quad , \quad E \geqslant 0$

$$n = E/\hbar\omega \tag{A3.8}$$

$$q = \hbar \cos^{-1}\left(x \sqrt{\frac{m\omega}{2n\hbar}}\right) \tag{A3.9}$$

which implies that

$$E = n\hbar\omega \tag{A3.10}$$

$$x = \sqrt{\frac{2n\hbar}{m\omega}} \cos(q/\hbar) \tag{A3.11}$$

and the momentum is given by

$$P = \sqrt{2m\, n\, \hbar\omega}\ \ \sin(q/\hbar) \quad . \tag{A3.12}$$

In all these examples x_0 in eq. (A3.7) is chosen conveniently to give a cosine dependence upon q.

Morse oscillator: $V(x) = D\,(e^{-ax} - 1)^2\ - D \quad , \quad -D \leqslant E \leqslant 0$

$$n = \frac{\sqrt{2mD}}{a\hbar}\left[1 - \sqrt{-E/D}\right] \tag{A3.13}$$

$$q = \hbar\cos^{-1}\left[\frac{1}{\sqrt{1 + E/D}}\left(1 + E/D\ e^{ax}\right)\right] \tag{A3.14}$$

which implies

$$E = -D\lambda^2 \quad , \quad \lambda = (1 - 2n/k)$$

$$k = \frac{2}{a}\sqrt{\frac{2mD}{\hbar^2}} \tag{3.15}$$

$$x = \frac{1}{a} \ln \left[\frac{1 - \sqrt{1-\lambda^2} \cos(q/\hbar)}{\lambda^2} \right] \qquad (A3.16)$$

the momenta is given by

$$= \sqrt{2mD} \frac{\lambda \sqrt{1-\lambda^2} \sin(q/\hbar)}{\left(1 - \sqrt{1-\lambda^2} \cos(q/\hbar)\right)^2} \qquad (A3.17)$$

Inverted Eckart barrier: $V(x) - -D \operatorname{sech}^2(ax)$, $-D \leqslant E \leqslant 0$

$$n = \frac{\sqrt{2mD}}{\hbar a} (1 - \sqrt{-E/D}) \qquad (A3.18)$$

$$q = \hbar \cdot \cos^{-1} \sinh(ax) \frac{\lambda}{\sqrt{1-\lambda^2}} \qquad (A3.19)$$

where

$$\lambda = 1 \frac{2n}{k} , \quad k = \frac{2}{a} \sqrt{\frac{2mD}{\hbar^2}} ,$$

which implies

$$E = -D\lambda^2 \qquad \text{(A3.20)}$$

$$x = \frac{1}{a}\ln\left[\frac{\sqrt{1-\lambda^2}}{\lambda}\cos(q/\hbar) + \sqrt{\frac{1-\lambda^2}{\lambda^2}\cos^2(q/\hbar) + 1}\right] \qquad \text{(A3.21)}$$

the momenta is given by

$$= \frac{(\lambda^2-1)\sin^2(q/\hbar)}{1 + \frac{1-\lambda^2}{\lambda^2}\cos^2(q/\hbar)} \qquad \text{(A3.22)}$$

IV. "GOOD" ACTION VARIABLES FOR REACTIVE SYSTEMS

In the previous two chapters it was seen how semiclassical methods could be used for the description of quantum mechanical phenomena: tunneling in molecular collisions and the quantization of bound systems. A unifying aspect of these different semiclassical methods is the applicability of Gutzwiller's periodic orbit theory,[44] to obtain a semiclassical rate constant expression as well as a semiclassical quantization condition.

It was noted earlier in this work that the periodic orbit theory for semiclassical eigenvalues contained dynamical approximation as well as the semiclassical assumptions. However, the Hamilton-Jacobi method for constructing "good" action variables for bound systems provided a more rigorous approach to the semiclassical quantization of nonseparable systems.

The dynamical approximations of periodic orbit theory are also present in the semiclassical rate expression. In an attempt to derive a theory for reactive systems which no longer contains these dynamical approximations, Miller[69] has presented a theory for reaction rates which is based upon the "good" action variables in the saddle point region separating reactants from products. The theory is reviewed in section A, applications to the collinear $H + H_2$ system being presented in section B.

Another system for which this theory is potentially applicable is the splitting of energy eigenvalues in a two-dimensional nonseparable double well potential. The eigenvalue splitting is a consequence of the dynamical effect of tunneling through the barrier separating the two wells. The "good" action variables in the barrier are used to describe this tunneling and its effect upon the eigenvalues. This system is studied in section C. Finally the results of the applications of the theory are discussed in detail in section D.

A. Theory

The thermal rate constant, $k_{b\leftarrow a}(T)$ for a bimolecular reaction can be given in terms of the cummulative reaction probability, N(E), by eq. (2.42). The semiclassical approximation to N(E) as obtained from periodic orbit theory is given by equations (2.82) and (2.83). For a one dimensional system eq. (2.82) reduces to

$$N(E) = \{1 + \exp[2\theta(E)]\}^{-1} \tag{4.1}$$

where θ(E) reduces to the usual barrier penetration integral,

$$\theta(E) = \int_{x_<}^{x_>} \sqrt{\frac{2m}{\hbar^2}\Big(V(x) - E\Big)}\, dx \ . \tag{4.2}$$

The use of "good" action variables can be motivated by noticing that the action variable for this one degree of freedom, which is given by

$$2\pi(n + 1/2) = \int_{x_<}^{x_>} \sqrt{\frac{2m}{\hbar^2}\left(E - V(x)\right)} \qquad (4.3)$$

is related to the barrier penetration integral by

$$2\pi(n + 1/2) = i\theta(E) \qquad (4.4)$$

Therefore in terms of the action variable, the cumulative reaction probability is given by

$$N(E) = [1 + 2\pi \mathrm{Im}\, n(E)]^{-1} \qquad (4.5)$$

For a f-dimensional system which is separable with only one unbound degree of freedom at the saddle point, the action variable for the unbound motion, n_f, is given by

$$2\pi(n_f \;\; 1/2) = \int_{x_<}^{x_>} \sqrt{\frac{2m}{\hbar^2}\left(E - V_f(x)\right)} \qquad (4.6)$$

where $V_f(x)$ is the potential in the f degree of freedom and $E_t = E - \varepsilon(\underset{\sim}{n})$ $n = n_1, n_2, \ldots, n_{f-1}$, is the translational energy for that motion. The cumulative reaction probability for this separable system is

$$N(E) = \sum_{\underset{\sim}{n}=0}^{\infty} \{1 + \exp[2\pi \, \mathrm{Im} \, n_f(E,\underset{\sim}{n})]\}^{-1} \tag{4.7}$$

As an example consider a two-dimensional separable system defined by a particle of mass m moving in a potential

$$V = 1/2 \, m \, \omega_1^2 \, x_1^2 - 1/2 \, m \, \omega_2^2 \, x_2^2 \tag{4.8}$$

The Hamiltonian in the "good" action variables is

$$\begin{aligned} H(n_1,n_2) &= \hbar\omega_1(n_1+1/2) + i\hbar\omega_2(n_2+1/2) \\ &= E(n_1,n_2) \end{aligned} \tag{4.9}$$

Solving for the action variable n_2 as a function of energy and n_1 gives

$$n_2 = -1/2 + i[\hbar\omega_1(n_1 + 1/2) - E]/(\hbar\omega_2) \quad , \tag{4.10}$$

which substituted into eq. (4.7) gives

$$N(E) = \sum_{n_1=0}^{\infty} \left\{ 1 + \exp \frac{2\pi}{\hbar\omega_2} \quad \hbar\omega_1(n_1+1/2)-E \right\}^{-1} \tag{4.11}$$

Using eq. (2.42) one can solve for an analytic expression for the rate constant

$$k(T) = \Gamma(T)\,\frac{kT}{h}\,\frac{Q^{\ddagger}(T)}{Q_0(T)} \quad , \tag{4.12}$$

where

$$Q^{\ddagger}(T) = 1/2\ \hbar\omega_1\beta/\sinh\ (1/2\ \hbar\omega_1\beta) \tag{4.13}$$

$$\Gamma(T) = 1/2\ \hbar\omega_2\beta/\ \sin\ (1/2\hbar\omega_2\beta) \quad . \tag{4.14}$$

These are the correct partition function and tunneling correction factor for a harmonic well and parabolic barrier respectively.

The theory can be extended to multidimensional nonseparable potentials, a rigorous derivation of eq. (4.7) for nonseparable systems being given by Miller[69]. Equation (4.7) is the result for the nonseparable system, however, $n_f(E,n)$ is no longer obtained by solving a one-dimensional problem. The idea then is to use the methods described in Chapter III to construct these "good" action variables for the saddle point region.

The trajectory methods of semiclassical quantization seem inapplicable to regions of phase space which are classical nonaccessible. Although it is known that complex valued trajectorires can be used to describe such tunneling phenomena,[21] such trajectories would not in general form quasi-periodic manifolds with which to construct the action variables.

The periodic orbit theory of Gutzwiller, however, is applicable and in effect has already been used to describe tunneling in the collinear $H + H_2$ reaction. The periodic orbit theory for reaction rates can be obtained by substituting the periodic orbit theory eigenvalue condition in the saddle point, into eq. (4.7). The modified version of the eigenvalue condition, eq. (3.17),

$$\Phi\left(E - \sum_{i=1}^{f-1} \hbar\omega_i(E)\ (n_i+1/2)\right) = 2\pi\hbar(n_f+1/2) \tag{4.15}$$

gives the energy eigenvalue implicitly, where $\Phi(E)$ is the action around the periodic orbit and $\{\omega_i(E)\}$ are the f-1 stability parameters. The proper periodic trajectory is found by running the trajectory in purely imaginary time, corresponding to purely real time on the inverted surface. This gives a purely imaginary value for the action

$$\Phi(E)/\hbar = 2i\theta(E) \quad , \tag{4.16}$$

and thus,

$$2\pi \ \mathrm{Im} \ n_f(E,n_1,\ldots,n_{f-1}) = 2\theta\left(E - \sum_{i=1}^{f-1} \hbar\omega_i(E)(n_i+1/2)\right) \tag{4.17}$$

Substitution of this into eq. (4.7) gives the modified version of the periodic orbit theory for reaction rates, eq. (2.84).

The motivating idea for this chapter was the construction of a reaction rate theory <u>without</u> the approximations of periodic orbit theory. This can be accomplished by the use of the Hamilton-Jacobi approach of chapter III section C. This approach to the construction of "good" action variables for saddle point regions is used in the following sections.

B. Collinear H + H_2 Reaction

The calculations for the collinear H + H_2 reaction were carried out using the Hamiltonian in natural collision coordinates as given by Madden.[70] Madden claims to obtain the same qualitative results as Duff and Truhlar,[71] with the anharmonic potential given below. The Hamiltonian is given by

$$H(p_s,p_\rho,s,\rho) = \frac{{p_s}^2}{2\mu\left(1 + \rho K(s)\right)^2} + \frac{{p_\rho}^2}{2\mu} + V(s,\rho) \qquad (4.18)$$

$$K(s) = 1.6 \ e^{-1.9s^2}$$

$$k(s) = k_{sp} + U_k \tanh^2 (\alpha_k s)$$

$$\mu = \frac{2}{3} m_H, \ m_H = \text{Mass of hydrogen.}$$

Two forms for the potential $V(s,\rho)$ were used, one harmonic in the ρ motion, the other anharmonic in the ρ motion.

$$\text{harmonic:} \quad V(s,\rho) = U_V \operatorname{sech}^2(\alpha_V s) + k(s)\rho^2 \tag{4.19}$$

$$\text{anharmonic:} \quad V(s,\rho) = U_V \operatorname{sech}^2(\alpha_V s) + D\left(1 - e^{-\rho\sqrt{\frac{k(s)}{D}}}\right)^2 \tag{4.20}$$

The coordinate s marks progress along the reaction coordinate with ρ being the bound motion orthogonal to s. The potential in s is a symmetric Eckhart barrier centered at s = 0, the potentials in ρ are oscillators with s dependent parameters.

The construction of "good" action variables for the saddle point region (s = 0) was accomplished using the Hamilton-Jacobi approach. Both the iterative substitution method given by eq. (3.44) and the Newton iteration, eq. (3.51) were used. For both iteration schemes the zeroth order Hamiltonian was taken to be

$$H_0 = \frac{p_s^2}{2\mu} + U_V \operatorname{sech}^2(\alpha_V s) + \frac{p_\rho^2}{2\mu} + V_0(\rho) \tag{4.21}$$

where $V_0(\rho)$ are:

$$k_{sp}\,\rho^2 \qquad \text{- harmonic} \tag{4.22}$$

$$D\left[1 - \exp\left(-\sqrt{\frac{k_{sp}}{D}}\;\rho\right)\right]^2 \qquad \text{- anharmonic} \tag{4.23}$$

For the one-dimensional oscillators the action-angle variables are given in the appendix to chapter III. The action-angle variables for the Eckart barrier are obtained from those given for the inverted barrier in the same appendix. From the transcription D → -D and requiring the energy to be in the range 0 → D, we obtain the desired results. The zeroth order action-angle variables and the energy as a function of the action are given for these three potentials below.

Harmonic oscillator:

$$\begin{aligned} \varepsilon_w(m) &= (m+1/2)\;\hbar\sqrt{\frac{2k_{sp}}{\mu}} \\ \rho(m,q_m) &= \left(\frac{2(m+1/2)\hbar}{\sqrt{2\mu k_{sp}}}\right)^{1/2} \cos(q_m/\hbar) \end{aligned} \tag{4.24}$$

Morse oscillator:

$$\varepsilon_W(m) = -D\lambda_\rho^2 \quad ; \quad \lambda_\rho = 1 - (2m+1)\ \frac{\hbar}{2D}\sqrt{\frac{2\mu}{k_{sp}}} \tag{4.25}$$

$$\rho(m,q_m) = \sqrt{\frac{D}{k_{sp}}}\ \ln\left[\frac{1 - \sqrt{1-\lambda_\rho^2}\cos(q_m/\hbar)}{\lambda_\rho^2}\right]$$

Eckhart barrier:

$$\varepsilon_B(n) = U_V\ \lambda_s^2 \quad ; \quad \lambda_s = 1 + i(2m+1)\ \frac{\alpha_V}{2}\sqrt{\frac{\hbar^2}{2\mu U_V}} \tag{4.26}$$

$$s(n,q_n) = \frac{1}{\alpha_V}\ \ln\left\{\frac{\sqrt{1-\lambda_s^2}}{\lambda_s}\cos q_n + \sqrt{1 + \frac{1-\lambda_s^2}{\lambda_s^2}\cos^2 q_n}\right\}$$

The total Hamiltonian in action angle variables is given by

$$H(q_n, q_m, n, m) = \frac{\varepsilon_\beta(n)}{\left(1+\rho K(s)\right)^2} + \varepsilon_W(m) + V(s;p) - \frac{U_V \operatorname{sech}^2(\alpha_V s)}{\left(1+\rho K(s)\right)^2} \tag{4.27}$$

where $s(n,q_n)$ and $\rho(m,q_m)$ are given above.

The iterative substitution scheme is employed by use of eq. (3.44):

$$A_{k_1k_2}^{(\ell+1)} = A_{k_1k_2}^{(\ell)} + (2\pi)^{-2} \int_0^{2\pi} dq_n \int_0^{2\pi} dq_m \, e^{-i(k_1q_m+k_2q_n)} \, H\Big(q_n, q_m, n(q_n,q_m), m(q_n,q_m)\Big) \qquad (4.28)$$

where

$$m(q_n \; q_m) = M - \sum_{k_1,k_2}{}' \frac{k_1 \, e^{i(k_1q_m+k_2q_n)}}{(k_1\omega_1 + k_2\omega_2)} A_{k_1k_2}^{(\ell)} \qquad (4.29)$$

$$n(q_n \; q_m) = N - \sum_{k_1,k_2}{}' \frac{k_2 \, e^{i(k_1q_m+k_2q_n)}}{(k_1\omega_1 + k_2\omega_2)} A_{k_1k_2}^{(\ell)} \quad . \qquad (4.30)$$

The "good" action variables (N,M) are parameters in the calculation, thus one specifies the set (N,M) and solves for the Fourier coefficients A_{k_1,k_2}. The energy is given by

$$E(M,N) = (2\pi)^{-2} \int_0^{2\pi} dq_n \int_0^{2\pi} dq_m \; H\Big(q_n,q_m,n(q_n,q_m),m(q_n,q_m)\Big) \; . \qquad (4.31)$$

The frequencies (ω_1,ω_2) are given by $\omega(N) = \partial H_o(N)/\partial N$,

$$\omega_1 = \sqrt{\frac{2k_{sp}}{\mu}} \qquad \text{-harmonic}$$

$$= \sqrt{\frac{2k_{sp}}{\mu}}\ \lambda_p \qquad \text{-anharmonic} \tag{4.32}$$

$$\omega_2 = i\ 2\alpha_v\ U_v \sqrt{\frac{\hbar^2}{2\mu U_v}}\ \lambda_s$$

The discretization procedure used in section D of the previous chapter is employed to give the working formulae:

$$A^{(\ell+1)}_{k_1k_2} = A^{(\ell)}_{k_1k_2} + C^{(\ell)}_{k_1k_2}$$

$$C^{(\ell)}_{k_1k_2} = (L_1L_2)^{-1} \sum_{\ell_1=0}^{-1} \sum_{\ell_2=0}^{L_2-1} W_1^{-k_1\ell_1} W_2^{-k_2\ell_2} (-1)^{\ell_1+\ell_2}\ H(\ell_1,\ell_2,m(\ell_1\ell_2),n(\ell_1,\ell_2))$$

$$m(\ell_1,\ell_2) = M - (-1)^{\ell_1+\ell_2} \sum_{k_1=0}^{L_1-1}{}' \sum_{k_2=0}^{L_2-1}{}' \frac{(k_1-L_2/2)\ A^{(\ell)}_{k_1k_2}}{\omega_1(k_1-L_1/2) + \omega_2(k_2-L_2/2)}$$

$$n(\ell_1,\ell_2) = N - (-1)^{\ell_1+\ell_2} \sum_{k_1=0}^{L_1-1} \sum_{k_2=0}^{L_2-1} \frac{(k_2-L_2/2)\ A^{(\ell)}_{k_1k_2}}{\omega_1(k_1-L_1/2) + \omega_2(k_2-L_2/2)}$$

$$q_m(\ell_1) = \frac{2\pi\ell_1}{L_1} \quad , \quad q_n(\ell_2) = \frac{2\pi\ell_2}{L_2}$$

$$E(M\ N) = \lim_{\ell\to\infty} C^{(\ell)}_{L_1/2,L_2/2} \tag{4.33}$$

The Hamiltonian $H(q_m,q_n,m,n)$ is given by eq. (4.27)

Because of convergence problems with this method the Newton iteration scheme was also used. This is given by eq. (3.51) which can be written explicitly as follows:

$$B^{(\ell+1)}_{k_1k_2} = B^{(\ell)}_{k_1k_2} + \sum_{k_1'k_2'}{}' (M^{-1})_{k_1k_2,k_1'k_2'} W_{k_1'k_2'}$$

$$M_{k_1k_2,k_1'k_2'} = M^2_{\Delta k_1\Delta k_2} + M^2_{\Delta k_1\Delta k_2}$$

where $\Delta k_i = (k_i-k_i') \bmod L_i$ and

$$M'_{k_1k_2} = (2\pi)^{-2}\int_0^{2\pi} dq_n \int_0^{2\pi} dq_m\ e^{-i(k_1q_m+k_2q_n)}\ k_1 \frac{\partial H}{\partial m}$$

$$M^2_{k_1k_2} = (2\pi)^{-2}\int_0^{2\pi} dq_n \int_0^{2\pi} dq_m\ e^{-i(k_1q_m+k_2q_n)}\ k_2 \frac{\partial H}{\partial n}$$

$$W_{k_1k_2} = (2\pi)^{-2}\int_0^{2\pi} dq_n \int_0^{2\pi} dq_m\ e^{-i(k_1q_m+k_2q_n)}\ H(q_m,q_n,m,n)$$

$$m(q_n,q_m) = M - \sum_{k_1k_2}{}' k_1\ e^{i(k_1q_m+k_2q_m)}\ B^{(\ell)}_{k_1k_2}$$

$$n(q_{n_1}q_m) = N - \sum_{k_1k_2}{}' k_2\ e^{i(k_1q_m+k_2q_n)}\ B^{(\ell)}_{k_1k_2}$$

$$E(M,N) = W_{0,0}$$

Discretization of this method is similar to the simple iterative scheme and presents no problems.

The procedure then is to specify the good action variables (M,N) and solve for the energy. The action variable M is restricted to be a real integer, however N is chosen a complex number. The cumulative reaction probability $N_R(E)$ is then given by

$$N_R(E) = \sum_{M=0}^{\infty} \left[1 + \exp 2\pi \text{ Im } N\right]^{-1} \tag{4.35}$$

using only the imaginary part of N. The real part of N is chosen such that the energy is purely real. In effect one picks a reaction probability which defines Im(N), and finds the energy for this reaction probability.

The results of this semiclassical calculation were compared with the exact quantum scattering results of Madden and an adiabatic semiclassical calculation. The adiabatic approximation assumes that the energy in the ρ degree of freedom adjusts rapidly to its eigenvalue as one moves along the s coordinate. The tunneling in the s degree of freedom is defined by the barrier penetration integral for an effective potential, $V_{eff}(s)$:

$$\theta(E) = \int_{s_<}^{s_>} \sqrt{\frac{2\mu}{\hbar^2}\left(V_{eff}(s) - E\right)} \tag{4.36}$$

where the effective potential is given by

$$
\begin{aligned}
V_{eff}(s) &= U_V \operatorname{sech}^2(\alpha_V s) + V_\rho(s;M) \\
V_\rho(s;M) &= \hbar\omega(s)\ (M + 1/2) && \text{- harmonic} \\
V_\rho(s;M) &= D\left[1 - \left(1-(M+1/2)\ \frac{\hbar\omega(s)}{D}\right)\right] && \text{- anharmonic}
\end{aligned}
\tag{4.37}
$$

where $\omega(s) = \sqrt{2k(s)/\mu}$. The turning points are defined by $V_{eff}(s) = E$.

The results of these calculations are shown in figures 15 and 16, the reaction probability for $M = 0$ given versus the total energy for the harmonic and anharmonic potentials respectively. The appropriate potential parameters used in the calculations are given in Table III. The contribution to the probability from $M > 0$ is negligible for the energies investigated. Comparison with the exact quantum results is very poor, the results of the Hamilton-Jacobi approach being almost identical to the adiabatic limit. Further discussion of this is delayed until section D, where a detailed discussion of these results and the results of the following example will be presented.

C. Symmetric Double-Well Potential

The semiclassical eigenvalue condition for a one-dimensional double-well potential is well-known[72]. In the case of a symmetric potential as shown in figure 17, the energy eigenvalues are given by

$$(n + 1/2)\pi = \phi(E) \pm 1/2 \tan^{-1}[e^{-\theta(E)}] + Q(\theta) \quad , \qquad (4.38)$$

for energies below the barrier height and integer values of n. The phase integrals ϕ and θ, defined by

$$\phi(E) = \int_a^b \sqrt{\frac{2m}{\hbar^2}\Big(E - V(x)\Big)}\, dx = \int_c^d \sqrt{\frac{2m}{\hbar^2}\Big(E-V(x)\Big)}\, dx \qquad (4.39)$$

$$\theta(E) = \int_d^c \sqrt{\frac{2m}{\hbar^2}\Big(V(x) - E\Big)}\, dx \quad , \qquad (4.40)$$

where a,b,c, and d are classical turning points, can be recognized as the integral one quantizes in the single well potential and the barrier penetration integral, respectively. This is analogous to defining "good" action variables for the well and barrier regions of the potential. The quantity $Q(\theta)$ is a quantum correction function given by

$$Q(\theta) = 1/2 \arg [1/2 + i\theta/\pi] - \frac{\theta}{2\pi} \ln \frac{\theta}{e\pi} \quad . \tag{4.41}$$

In this section an attempt is made to generalize this one-dimensional WKB eigenvalue condition to a two-dimensional symmetric double-well as shown in figure 18. The potential in the x direction is taken to be a symmetric double well and the y direction is simply harmonic with an x dependence in the frequency.

In the spirit of constructing "good" action variables for the saddle point region of a scattering system, we wish to construct the "good" action variables, (N_x^{ii}, N_y^{ii}), for the barrier region of the double-well. The generalized barrier penetration integral is then defined as

$$\theta(E) = \pi \operatorname{Im} N_x^{ii}(E) \tag{4.42}$$

The "good" action variables (N_x^i, N_y^i), are also constructed for the potential well, the generalization of the phase integral $\phi(E)$ is defined by

$$\phi(E) = \pi \; N_x^i + 1/2 \tag{4.43}$$

Quantization is imposed by requiring $N_y^i = N_y^{ii}$ = integer, i.e., motion in the bound degree of freedom y is quantized in the barrier in the same manner as in the well. The quantization condition is completed by requiring $\phi(E)$ and $\theta(E)$ as defined by equations (4.42) and (4.43) to obey the one-dimensional quantization condition, eq. (4.38)

This is our ansatz and we now wish to test it. For this purpose we chose a form for the potential of the type

$$V(x,y) = V_o(x) + V_c(y;x) \quad ,$$

$$\text{where} \quad V_o(x) = 1/2\, ax^2 + 1/2\, bx^4 + V_1\, e^{-cx^2} \quad ,$$

$$\tag{4.44}$$

$$V_c(y;x) = 1/2\, m\omega_y^2(x)\, y^2 \quad ,$$

$$\text{and} \quad \omega_y(x) = \omega_o\left[1 - \lambda \exp\left(-(\alpha x)^n\right)\right] \quad .$$

The form of $V_o(x)$ was suggested by previous work[73] on the one-dimensional double well. The potential V_o has a maximum at x=0 and two minima at $x = \pm\, 1/c\, \ln(2cV_1/a) = \pm\, x_o$.

The calculation in the well was carried out using the Hamilton-Jacobi approach of chapter III section C. The reference Hamiltonian was taken to be a Morse oscillator fit to $V_0(x)$ at $x = -x_0$ in the x direction and a harmonic oscillator in y with frequency $\omega_y(x_0)$. The calculation is very similar to those for the two-dimensional coupled harmonic oscillators treated in the previous chapter and further details of this phase of the calculation are omitted.

The calculation for the "good" action angle variables in the barrier parallels the calculation done in the previous section of this chapter the barrier to reaction in the $H + H_2$ system. The reference potential was taken to be an Eckart barrier in the x direction fit to $V_0(x)$ around $x = 0$, and a harmonic oscillator in y with frequency $\omega_y(x{=}0)$. The close similarity of this calculation to that previously done obviates the necessity to further outline the calculation of the barrier penetration integral.

The procedure then was to find the energy in the well $E_w(N_x^i, N_y^i)$ for the action variables N_x^i, N_y^i. The calculation in the barrier was performed with $N_y^{ii} = N_y^i$ varying N_x^{ii} until the energy in the barrier $E_b(N_x^{ii}, N_y^{ii})$ was equal to that in the well. Thus one constructs the "good" action variables N_x^i, N_x^{ii} for an energy $E \equiv E_w = E_b$. The energy E is an eigenvalue if the phase integrals defined by equations (4.42) and (4.43) obey eq. (4.38).

In the limit that the barrier is infinite, the barrier penetration integral becomes infinite also and $\tan^{-1}(e^{-\theta}) \to 0$. That is, the energy levels in the two wells become degenerate, determined by the eigenvalue condition N_x^i = integer. For a finite barrier the degeneracy is split, the two eigenvalues given by the quantization condition, eq. (4.38). However, if the tunneling probability is small as is the case of the lowest eigenstate of the potential in figure 17, the splitting will be small and N_x^i will be close to an integer. In practice one then does a root search over the variable N_x^i until eq. (4.38) is satisfied. That is we want to solve $F(N_x^i) = 0$, where

$$F\left(N_x^i\right) = \left(N_x^i - n\right) \pm 1/2 \tan^{-1} (e^{-\theta}) + Q(\theta) \tag{4.45}$$

for n = 0,1.... $\theta(E)$ can be thought of as a function of N_x^i through the equation

$$E_w(N_x^i) = E_b(\theta) \equiv E \tag{4.46}$$

which must also be solved for as a root search in θ for a specified N_x^i. It should also be mentioned that eq. (4.45) need be solved for both signs of the $\tan^{-1}$, i.e., for the two eigenvalues. Also eq. (4.45) must be solved for every value of n desired, as long as the resulting eigenvalue is below the barrier height. Finally it should be noted that eq. (4.45) and eq. (4.46) are parameterically dependent upon N_y^i.

Two other calculations were performed upon this system for comparison. A quantum mechanical calculation was performed by diagonalizing the Hamiltonian in a basis of harmonic oscillator states centered at the origin. The basis state was a product of harmonic oscillator states for the x and y degrees of freedom:

$$\Psi_{i,j}\,(x,y) \;=\; \phi_i^x(x)\;\phi_i^y(y) \tag{4.47}$$

where

$$\phi_i^j(y) \;=\; N_i\;H_i(\alpha_j\xi\,)\;e^{-1/2\;\alpha_j^2\;\xi^2};\quad j = x,y \quad .$$

Convergence of the results was checked by using progressively larger basis sets.

The other calculation done was of a semiclassical nature, using an adiabatic approximation. The adiabatic approximation is similar to that used in the reactive H + H_2 system. An effective potential for motion in the x degree of freedom is defined as

$$V_{eff}(x) \;=\; V_o(x) \;+\; h\omega_y(x)\;(N_y + 1/2) \tag{4.48}$$

Thus one has an effective one-dimensional problem which can be solved using equations (4.38) - (4.40) with $V(x)$ replaced by $V_{eff}(x)$.

These calculations were performed for the potential parameters listed in Table IV, the coupling parameter λ was varied from 0 to .3. The effect of the coupling is to relax the vibrational frequency in the y direction as one moves towards the saddle point. Within the adiabatic approximation this will allow more energy to be in the translational degree of freedom, therefore increasing the tunneling probability. The increase in tunneling would cause a greater splitting in the eigenvalues. This qualitative behavior is exhibited in all three of the calculations, which are compared in Table V. The splitting of the lower two eigenvalues is less than .03% of the eigenvalues, due to the small amount of tunneling. Both semiclassical methods give the lowest eigenvalue to less than .2% error, however the splitting is a more rigorous test of the theory and is shown to be between 7% and 8% in error. This is still reasonable agreement for the semiclassical approximation to the lowest eigenvalue.

Comparison of the two semiclassical calculations is meaningless for the lowest pair of energy levels due to the small amount of splitting. However, the second pair of eigenvalues affords a good comparison of the two methods. In the limit of no coupling, $\lambda=0$, the results for the Hamilton-Jacobi approach and the adiabatic approximation are identical as is expected. However it is surprising that they continue to give identical results as the coupling is increased. For the uncoupled case, the results are low by approximately 2%. As the coupling is increased the results for the splitting become higher than the quantum results by a factor of about 7% when $\lambda = .2$. It is expected that the adiabatic results would fail as the coupling becomes large, however it is unclear why the Hamilton-Jacobi method appears to make an adiabatic type of approximation also. This result was not totally unexpected though since we have observed in the previous section that the Hamilton-Jacobi approach to tunneling in the reactive H + H_2 system also gave adiabatic type results. This behavior is discussed in more detail in the following section.

Before leaving this section, one further attempt was made at obtaining an eigenvalue condition for the two-dimensional double well. Although the Hamilton-Jacobi approach to reaction rates proved unsuccessful, the periodic orbit theory for reaction rates gave an adequate description of tunneling in the reactive system. Therefore it was thought that different results for the semiclassical eigenvalues of the double well might be obtained by using periodic orbit theory to construct the good action variables in the well and barrier regions of the potential. The eigenvalue condition for the well is given by eq. (3.17). For this two-dimensional system, there is only one stability frequency and eq. (3.17) defines the phase integral for the well as $\Phi(E_m)$, where

$$E_m = E - (m + 1/2)\ \hbar\omega_w(E_m) \quad , \text{ and } m = N_y^i \ , \tag{4.49}$$

$2\Phi(E)$ is the action along a periodic trajectory of total energy E, and $\omega_w(E)$ is the stability frequency of that trajectory.

The barrier penetration integral is obtained from a trajectory on the inverted potential surface which is periodic and begins at the saddle point. The barrier penetration integral is then given by $\theta(E_m)$, where E_m is given by

$$E_m = E - (m + 1/2)\ \hbar\omega_b(E_m) \quad , \text{ and } m = N_y^{ii} \quad , \tag{4.50}$$

where $2\theta(E)$ is the action along the classical trajectory of total energy E, and $\omega_b(E)$ is the stability parameter of this trajectory. From this point the quantization condition for the two-dimensional double well is the same as in the Hamilton-Jacobi approach. We specify $N_y^i = N_y^{ii} = m$, for m equal to an integer and require that $\phi(E_m)$ and $\theta(E_m)$ as defined above obey equation (4.38).

The pertinent periodic trajectories for both the well and barrier regions are trivial to find, both being along the x-axis. Because y remains equal to zero for the entire trajectory, one can reduce the problem to two coupled differential equations for calculating the trajectory. This also greatly reduces the calculation of the R matrix as defined in the appendix of chapter II. Of the sixteen variables forming the matrix, only eight are nonzero, requiring the integration of only eight additional equations of motion instead of sixteen. The final matrix is also block diagonal, with 2x2 submatrices. These eigenvalues can be evaluated directly without recourse to diagonalization routines. The procedure for the calculation of the stability frequency and the action for both the barrier and the well is outlined in the appendix of chapter II. The equations of motion for the well change by the prescription $V \rightarrow -V$ in eq. (A2.6), i.e., the trajectories are computed on the right-side up potential. Also the eigenvalues of the R matrix for the well calculation will be complex, however, the eigenvalues can be expressed as $\lambda = e^{\pm iv}$, where v are the stability parameters.

The procedure then parallels that in the Hamilton-Jacobi approach, one fixes m at an integer value and calculates $\theta(E_m)$ and $\phi(E_m')$, where E_m and E_m' are given by equations (4.49) and (4.50), respectively, but for the same value of total energy E. If θ and ϕ obey eq. (4.38) then E is an eigenvalue.

The results for this calculation are quite disappointing. The eigenvalue splittings for the lowest two energy levels obtained here are identical to those obtained by the Hamilton-Jacobi approach. The eigenvalues and their splitting for the second pair of energy levels as calculated by these semiclassical methods as well as the correct quantum mechanical results are presented in Table VI. The surprising results are that the periodic orbit theory gives worse agreement with the quantum eigenvalue splitting than does the Hamilton-Jacobi approach. This implies that the periodic orbit theory overestimates the amount of tunneling, more so than adiabatic approximation. This results is puzzling since periodic orbit theory was used quite successfully to describe tunneling in the $H + H_2$ reaction. The use of periodic orbit theory and Hamilton-Jacobi theory to describe tunneling in both these systems, the double well and the reactive molecular collision, are discussed in more detail in the following section.

D. Discussion

The results of the previous two sections, using the Hamilton-Jacobi approach to construct the "good" action variables for the saddle point region, are disappointing. For both systems studied, $H + H_2$ reaction and the eigenvalue splitting in the double-well potential, the Hamilton-Jacobi approach gave nearly adiabatic results. An alternate approach to these problems has been the use of periodic orbit theory to describe the tunneling in the saddle point region. However, periodic orbit theory for reaction rates is entirely equivalent to using eq. (4.7) for the cummulative reaction probability, with the "good" action variables being constructed by periodic orbit theory for eigenvalues. Therefore the only difference between periodic orbit theory and the Hamilton-Jacobi approach to reaction rates is the method by which one constructs the "good" action variables.

A comparison of these two semiclassical methods as used to define an eigenvalue condition has been made in Chapter III. The periodic orbit theory is based upon the semiclassical approximation to the matrix element of the propagator. Hamilton-Jacobi theory is based upon the solutions of the Hamilton-Jacobi equation which gives the phase of the semiclassical wavefunction. The semiclassical approximations made in the two theories are quite different in nature and give quite different results in their applications.

The use of periodic orbit theory to describe reaction rates is justified by the rigorous derivation of the periodic orbit theory of reaction rates as reviewed in chapter II, section C. The validity of the Hamilton-Jacobi method for reaction rates is questionable though. For bound systems the Hamilton-Jacobi approach to eigenvalues gives quantization by requiring the semiclassical wavefunction to be single-valued. For a saddle point region, single-valuedness of the wavefunction restricts the "good" action variables in the bound degrees of freedom to be integers and an attempt has been made to identify the action variable in the tunneling direction as a generalized WKB barrier penetration integral. However, if one examines the derivation of the WKB tunneling probability for the one-dimensional case, one sees that the semiclassical wavefunctions outside of the barrier are also used. One matches these exterior solutions to the solution inside the barrier. The tunneling probability is then given by the square modulus of the ratio of the amplitudes. More explicitly, the WKB wavefunction to the left of the barrier is given by

$$\Psi(x) = \frac{A\, e^{i[\pi/4 + \int_{x_1}^{x} k(x')dx']}}{\sqrt{k(x)}} + \frac{B\, e^{-i[\pi/2 + \int_{x_1}^{x} k(x')\, dx']}}{\sqrt{k(x)}} \qquad (4.51)$$

and to the right of the barrier there is only flux to the right

$$\Psi(x) = \frac{C\, e^{i[\pi/4 + \int_{x_2}^{x} k(x)dx]}}{\sqrt{k(x)}} \quad . \qquad (4.52)$$

These two solutions to Schrodingers equation are matched by assuming the barrier to the parabolic and using parabolic cylinder functions as the solution inside the barrier. The tunneling probability is then given by

$$P = |C/A|^2 = [1 + e^{2\theta}]^{-1} , \qquad (4.53)$$

where

$$\theta(E) = \int_{x_1}^{x_2} \sqrt{\frac{2m}{\hbar 2} \left(V(x)-E\right)} . \qquad (4.54)$$

This entails knowing the solution outside of the barrier, not just the solution through the barrier. The use of Hamilton-Jacobi theory to construct the multidimensional barrier penetration integral does not do this mathcing, it uses only the solution inside the barrier. Therefore, is no surprise that the proposed method of constructing the generalization to the WKB barrier penetration integral is not the correct one. However at this time no alternative method is obvious to correct this discrepancy.

In the application of Hamilton-Jacobi theory to the double well this matching of solutions interior and exterior to the barrier is again the problem. To insure the correct solution to the eigenvalue problem this matching must be done rigorously. The method described in section C attempts to do this matching by requiring the action variable for the bound degree of freedom, y, to be the same in the well and in the barrier. The procedure is completed by use of eq. (4.38) to restrict the action variables in the x direction. Similar to the derivation of the one-dimensional WKB tunneling probability, the derivation of eq. (4.38) is accomplished by matching the WKB solutions to the Schrodinger equation across the barrier and requiring the wavefunctions to be exponentially decaying in the classically forbidden parts of the potential. The results of section C have shown that the method described there does not do this matching properly for a multi-dimensional nonseparable potential.

The application of periodic orbit theory to the double-well potential also gave poor results and again it can be attributed to the improper mathcing of the wavefunctions across the barrier. The same method of quantization of the system was imposed as in the case of the application of Hamilton-Jacobi theory, only the method of constructing the "good" action variables differed. In this light then one would expect that periodic orbit theory would give results that are at least as bad as the Hamilton-Jacobi theory.

This brings to mind the question of why periodic orbit theory works so well for describing reaction rates when it gives poor results for the eigenvalues of the double-well. To get the proper eigenvalue condition for the double well in two-dimensions it is mandatory that the WKB wavefunctions are known exterior to the barrier (in the wells) and that they are matched properly across the barrier. However, in the application of periodic orbit theory to reaction rates this matching is not needed. Indeed, the periodic orbit theory of reaction rates is derived from transition state theory which approximates the dynamics of the system in order to obviate the need for solutions to the full dynamical problem outside the saddle point region. The generalization of the WKB tunneling probability arise naturally out of a rigorous derivation of the theory, therefore obviating the need to derive the proper tunneling probability by the matching of wavefunctions across the barrier, i.e., completing a full dynamical calculation for the system.

It is still desirable to obtain a method by which the "good" action variables at the saddle point could be used to describe the tunneling and give a good estimate of the reaction rate without knowledge of the solutions outside the barrier region. At this time the periodic orbit method is the only method at our disposal and it contains dynamical approximations which are undesirable. It would also be desirable to obtain a method for matching solutions of the Hamilton-Jacobi equation for the regions outside the barrier by the solutions inside the barrier. This would allow a state-to-state description of reactive rates for reactive systems, and would also give a procedure for calculating the eigenvalues of the double well potential in two-dimensions. The classical S-matrix theory of Miller[31] effectively does this for the reactive system by use of complex trajectories which tunnel through the barrier. It would be advantageous however to construct the "good" action variables by the Hamilton-Jacobi method for regions interior and exterior to the barrier and match the solutions properly to give the detailed state-to-state rate expressions. Solution of the Hamilton-Jacobi equation for the "good" action variables could then be constructed by means of the method described in section C of chapter III.

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TABLE I. Semiclassical Eigenvalues[a]

ω_1^2	ω_2^2	λ	η	N_1	N_2	Ref. 11a	Ref. 11b	Present	Exact Quantum
0.29375	2.12581	-.1116	.08414	0	0	.9920	.9922	.9920	0.9916
				1	0	1.5164	1.5164	1.5164	1.5159
				2	0	2.0313	2.0313	2.0313	2.0308
				0	1	2.4196	2.4198	2.4194	2.4188
0.36	1.96	-.1	0.1	0	0	0.9942	0.9942	0.9941	0.9939
				1	0	1.5813	1.5812	1.5812	1.5809
				2	0	2.1615	2.1616	2.1615	2.1612
0.49	1.69	-.1	0.1	0	0	0.9955	0.9954	0.9955	0.9955
				1	0	1.6870	1.6870	1.6870	1.6870
				0	1	2.2780	2.2785	2.2782	2.2781
				2	0	2.3750	2.3751	2.3750	2.3750
				1	1	2.9584	2.9588	2.9584	2.9583
				0	2		3.5480	3.5480	3.5479
0.81	1.21	-.08	0.1	0	0	0.9978	0.9978	0.9978	0.9980
				1	0	1.8941	1.8944	1.8941	1.8944
				0	1	2.0897	2.0889	2.0890	2.0890
				2	0	2.7895	2.7900	2.7896	2.7899

---

[a] These eigenvalues refer to the potential described in Section D.

TABLE II. Semiclassical Eigenvalues: $\omega_1 = 0.7$ and $\omega_2 = 1.3$

λ	$(N_1 = 0, N_2 = 0)$		$(N_1 = 1, N_2 = 0)$		$(N_1 = 0, N_2 = 1)$	
	Semiclassical	Quantum	Semiclassical	Quantum	Semiclassical	Quantum
0	1.	1.	1.7	1.7	2.3	2.3
-.06	.9987	.9988	1.6970	1.6970	2.2932	2.2932
-.08	.9975	.9975	1.6933	1.6933	2.2870	2.2870
-.10	.9955	.9955	1.6870	1.6870	2.2782	2.2781
-.12	.9927	.9926	1.6770	1.6769	2.2661	2.2658
-.14	.9889	.9884	1.6617	1.6612	2.2496	2.2490
-.16	.9836	.9826	1.6382	1.6370	2.2268	2.2257
-.18	.9764	.9743	1.6010	1.5980		
-.20	.9667	.9621				

TABLE III. Parameters for Madden's H_3 Natural Collision Coordinate Hamiltonian[a]

---

k_{sp} = 1.65 eV/a_o^2

U_k = 4.858 eV

α_k = 2.2164 a_o

U_v = .3958 eV

α_v = 2.0473 a_o

D = 4.476 eV

a_o = atomic unit of length

[a] The analytical form for the Hamiltonian is given by equations (4.18) - (4.20).

TABLE IV. Potential Parameters for the Two-dimensional Double Well[a]

$a = 1.6464 \ \mathrm{eV}/a_o^2$

$b = .23003 \ \mathrm{eV}/a_o^4$

$c = 1.1954 \ /a_o^2$

$V_1 = 1.5304 \ \mathrm{eV}$

$\hbar\omega_o = .40818 \ \mathrm{eV}$

$\alpha = 6. \ /a_o$

$n = 2$

$m = 4.250 \times 10^{-24} \mathrm{g}$

---

[a] The potential is given by eq. (4.44).

TABLE V. Double Well Eigenvalues[a]

λ		Hamilton-Jacobi		Adiabatic		Quantum	
0.	0_g	2163.58	(.77)	2163.58	(.77)	2159.28	(.83)
	0_u	2164.35		2164.35		2160.11	
	1_g	3095.0	(35.6)	3095.0	(35.6)	3089.4	(36.4)
	1_u	3130.6		3130.6		3125.8	
.1	0_g	2163.43	(.88)	2163.43	(.88)	2158.93	(.96)
	0_u	2164.31		2164.31		2159.89	
	1_g	3087.7	(44.8)	3087.7	(44.9)	3078.1	(44.4)
	1_u	3132.5		3132.6		3122.5	
.2	0_g	2163.26	(1.02)	2163.26	(1.02)	2158.56	(1.10)
	0_u	2164.28		2164.28		2159.66	
	1_g	3078.4	(58.6)	3078.3	(58.8)	3064.2	(54.9)
	1_u	3137.0		3137.1		3119.1	
.3	0_g	2163.07	(1.18)	2163.07	(1.19)	2158.16	(1.27)
	0_u	2164.25		2164.26		2159.43	
	1_g			3065.3	(86.5)	3047.1	(68.4)
	1_u			3151.8		3115.5	

---

[a] Eigenvalues for potential given by eq. (4.44) using potential parameters of Table IV. All energies are in cm^{-1}, the quantities in parentheses represent the splitting of the eigenvalues.

TABLE VI. Double Well Eigenvalues[a]

λ		Periodic Orbit		Hamilton-Jacobi		Quantum	
0.	1_g	3095.0	(35.6)	3095.0	(35.6)	3089.4	(36.4)
	1_u	3130.6		3130.6		3125.8	
.1	1_g	3087.6	(45.0)	3087.7	(44.8)	3078.1	(44.4)
	1_u	3132.6		3132.5		3122.5	
.2	1_g	3077.6	(60.8)	3078.4	(58.6)	3064.2	(54.9)
	1_u	3138.4		3137.0		3119.1	
.3	1_g	3062.3				3047.1	(68.4)
	1_u					3115.5	

[a] Energy eigenvalues for the potential given by eq. (4.44), potential parameters given in Table IV. All energies in cm^{-1}, the quantities in parentheses are the energy level splittings.

FIGURE CAPTIONS

Fig. 1 Sketch of a collinear potential energy surface for a symmetric atom diatom reaction, A + BA AB + A. x and y are mass weighted, or "skewed", coordinates that diagonalize the kinetic energy: $x = R(\mu/M)^{\frac{1}{2}}$, $y = r(m/M)^{\frac{1}{2}}$, where R and r are the translational and vibrational coordinates, respectively, and m the corresponding reduced masses [$m = BA/(B+A)$, $\mu = A(B+A)/(2A+B)$]. M is any arbitrary mass, and the classical kinetic energy is $\frac{1}{2}M(\dot{x}^2 + \dot{y}^2)$. s and u are the linear combinations of x and y which diagonalize the potential energy at the saddle point. S_1,S_2 and S_3 indicate the "surfaces" which are referred to in the text.

Fig. 2 Reaction probability for the collinear H + H_2 reaction on the Porter-Karplus potential surface from a microcanonical classical trajectory calculation (CL DYN) and microcanonical classical transition state theory (CL TST), as a function of total energy above the barrier height. Results from ref. 12.

Fig. 3 Same as Figure 2, except that $\sigma(E)$ is the microcanonical reactive cross section for the three-dimensional H + H_2 reaction.

Fig. 4 One-dimensional tunneling coefficient for the Eckart barrier [eq. (2.52(b))]; the dimensionless parameters α and u are defined by eq. (2.52(b)). The solid line is the exact quantum mechanical values given in ref. 29, and the broken line the result given by eq. (2.64).

Fig. 5 Rate constant as a function of temperature for the collinear $H + H_2$ reaction, here with the Truhlar-Kuppermann (ref. 34) potential surface. The upper line is the exact quantum result given in ref. 38(a), the lower line the result of conventional transition state theory, eq. (2.65), and the points the results given by eq. (2.61) which is based upon the use of the semiclassical phase space distribution function.

Fig. 6 Same as Fig. 5, except with the Porter-Karplus (ref. 37) potential surface.

Fig. 7 A perspective view of the upside-down H_3 potential surface with the periodic trajectories corresponding to two different energies. The circle shows the position of the saddle point.

Fig. 8 The classical action integral (a generalized barrier penetration integral) along the periodic trajectory on the upside-down H_3 potential surface, as a function of total energy E. V_{sp} is the height of the saddle point.

Fig. 9 The stability frequency for the (unstable) periodic trajectory on the upside-down H_3 potential surface, as a function of total energy E. The quantity plotted is the ratio of the stability frequency of the free H_2 molecule.

Fig. 10 The cumulative reaction probability N(E) as a function of total energy $E \equiv E_0 + \frac{1}{2}\hbar\omega_{H_2}$, here for the collinear $H + H_2$ reaction on the Truhlar-Kuppermann (ref. 34) potential surface. The solid line is the exact quantum mechanical result given in ref. 38(a), and the points connected by the broken line are the values given by the semiclassical limit of quantum transition state theory, eq. (2.82).

Fig. 11 Same as Fig. 10, except with the Porter-Karplus (ref. 37) potential surface.

Fig. 12 Cummulative reaction probability N(E) as a function of total energy $E \equiv E_0 + \frac{1}{2}\hbar\omega_{H_2}$, for the collinear H + H_2 reaction on the Porter-Karplus (ref. 37) potential surface. The pair of lines to the right are reproduced from Fig. 11, the upper being the quantum scattering results of ref. 38(b), the lower the semiclassical results of eq. (2.82). The solid line to the left is the results from periodic orbit theory without the modification, eq. (2.80), and the triangles represent the results of the local approximation given by eq. (2.92).

Fig. 13 Comparison of the exact quantum mechanical (solid line) and semiclassical (broken line) eigenvalues as a function of non-separable coupling. The lowest three eigenvalues — $(N_1,N_2 = (0,0), (1,0)$, and $(0,1)$ — are shown for the system described in Chapter III, with $\omega_1 = 0.7$, $\omega_2 = 1.3$, and $\eta = -\lambda$. (For the top curve the solid and dashed lines are indistinguishable.) The dotted lines show the maximum in the potential energy surface as a function of λ.

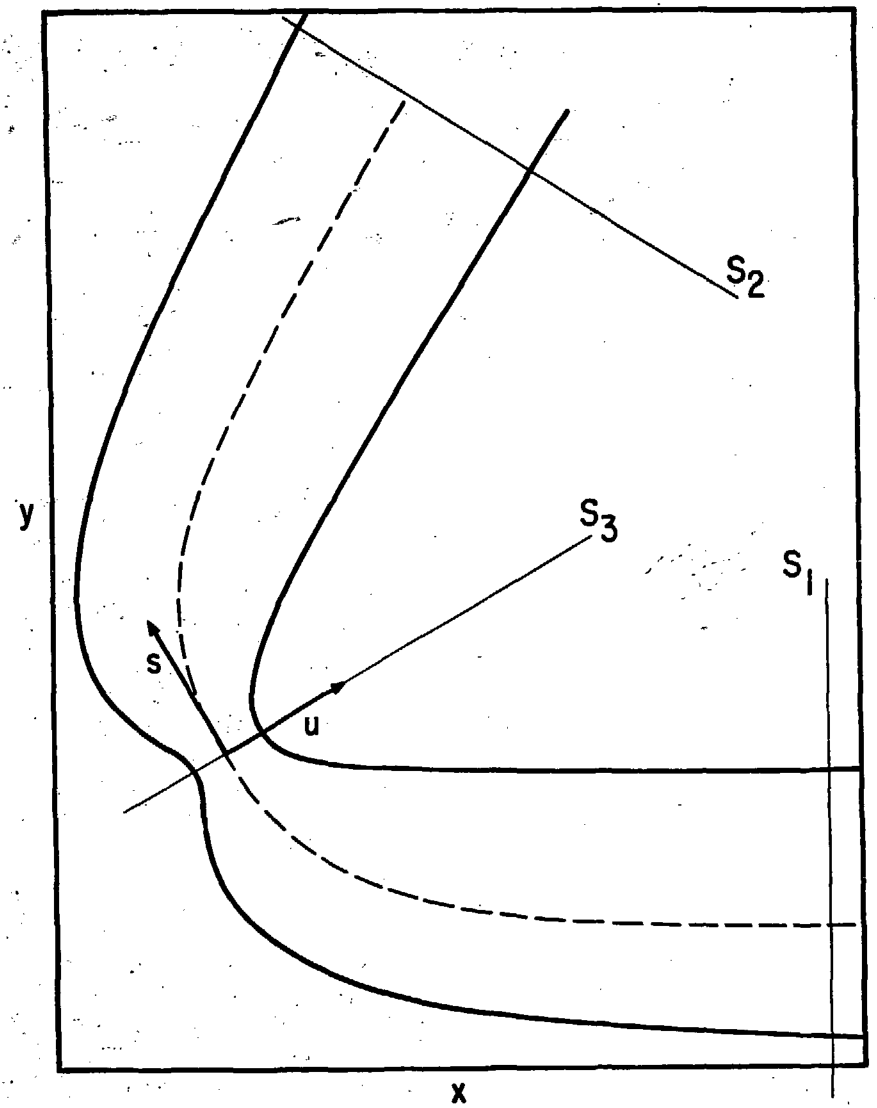
Fig. 14 Percent error in the semiclassical level shift, as a function of the non-separable coupling. The results are those in Table II and Figure 13, and the quantity plotted is $100X|(\Delta_{QM} - \Delta_{SC})/\Delta_{QM}|$, where Δ is defined in Eq. (3.66) and QM = quantum mechanical, SC = semiclassical.

Fig. 15 Cumulative reaction probability versus the total energy for the $H + H_2$ reaction using the Hamiltonian in natural collision coordinates as given in ref. 70. The potential in the coordinate perpendicular to the reaction coordinate is taken to be harmonic. The solid line is the exact quantum mechanical (EQ) result of Madden[70]. The broken line represents the semiclassical approach of constructing "good" action variables for the barrier region by the Hamilton-Jacobi method (HJ). The dotted line is the result of a semiclassical adiabatic (AB) calculation.

Fig. 16 Same as Fig. 15, except the potential perpendicular to the reaction coordinate is taken to be anharmonic (Morse oscillator).

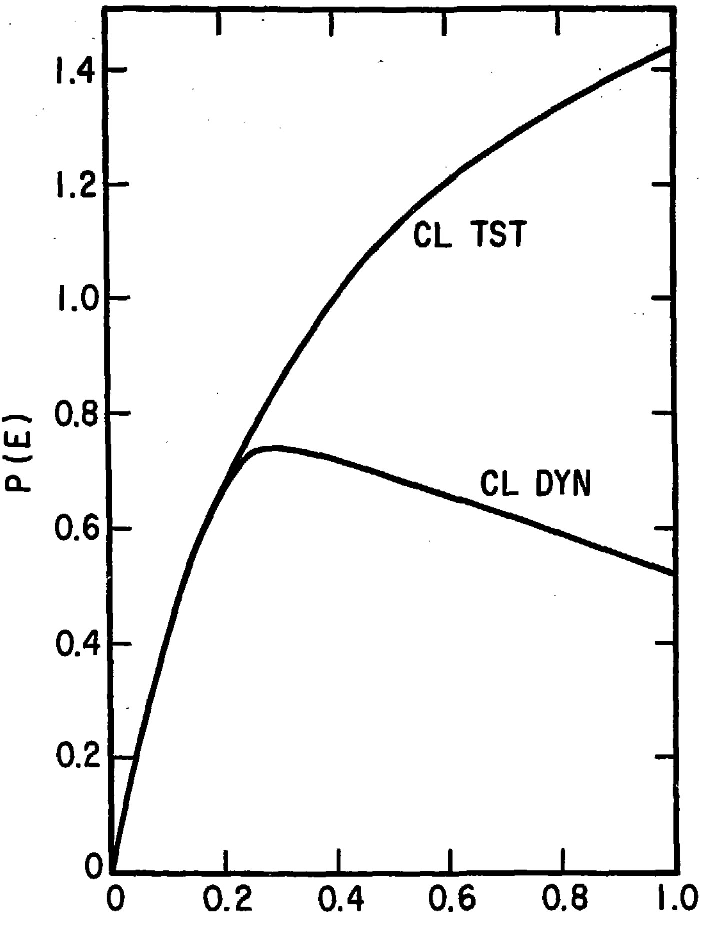
Fig. 17 Symmetric double well potential for a one-dimensional potential of the form given by $V_0(x)$ in eq. (4.44). The exact quantum mechanical energy levels are given, occurring in pairs labeled by g, u for the even and odd states, respectively. The eigenvalues are for the potential $V_0(x)$ with the parameters as given in Table IV. The splitting of the lowest two eigenvalues is smaller than the scale of the figure.

Fig. 18 Two-dimensional double well potential as given by eq. (4.44). This is a contour map of equally spaced equipotential lines in the (x,y) plane. The outer two crosses represent the location of the two minima, the location of the saddle point between the two wells is given by the center cross.



XBL 744-6034

Fig. 1



XBL 744-6105

Fig. 2

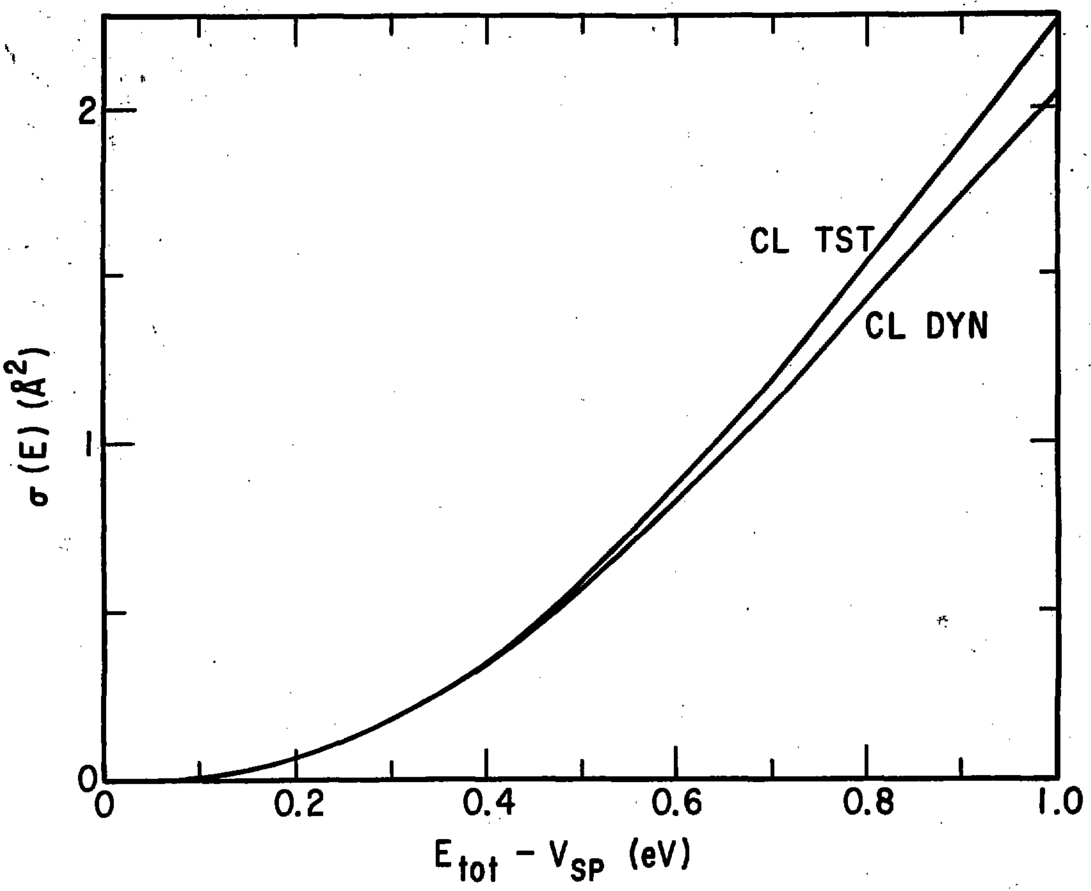
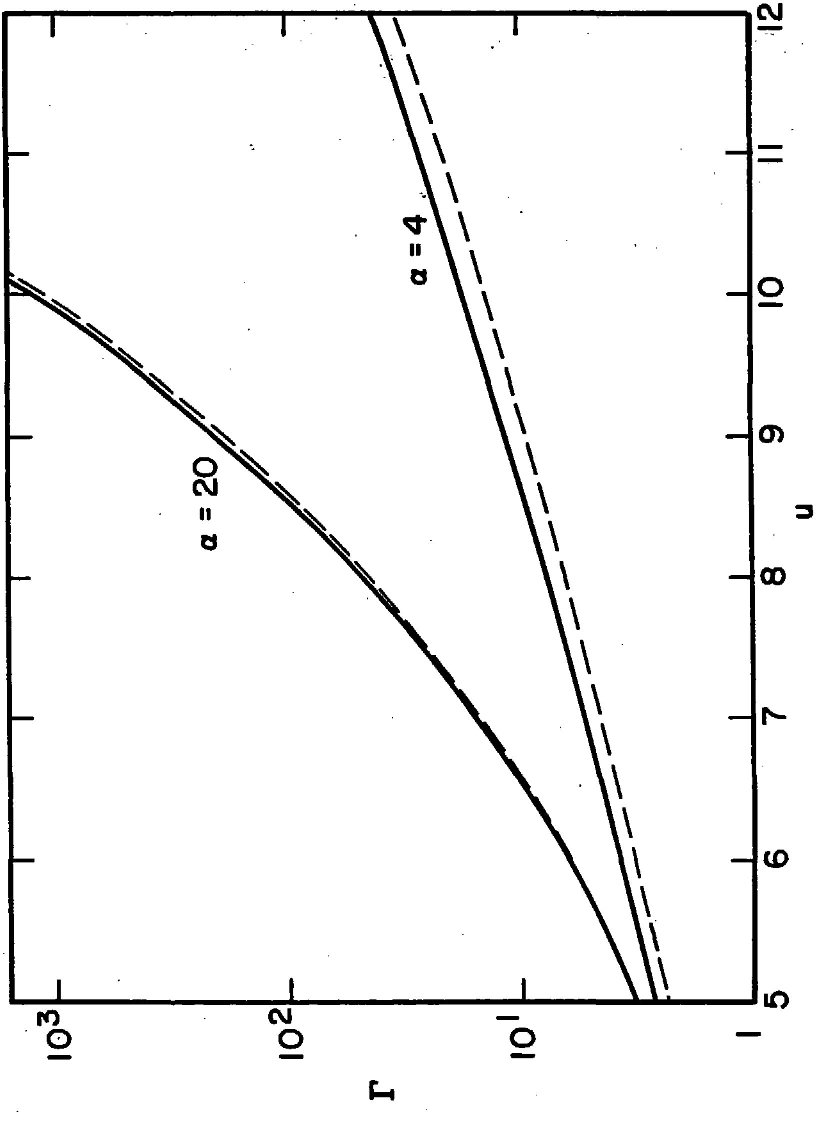


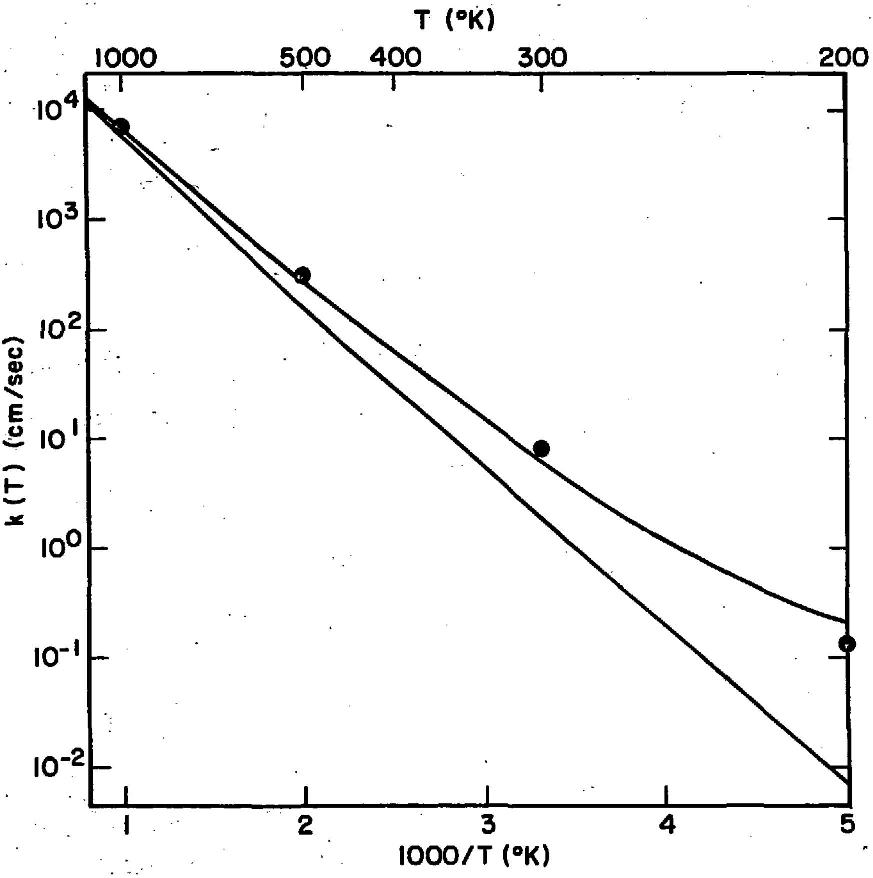
Fig. 3

XBL 7410-7518



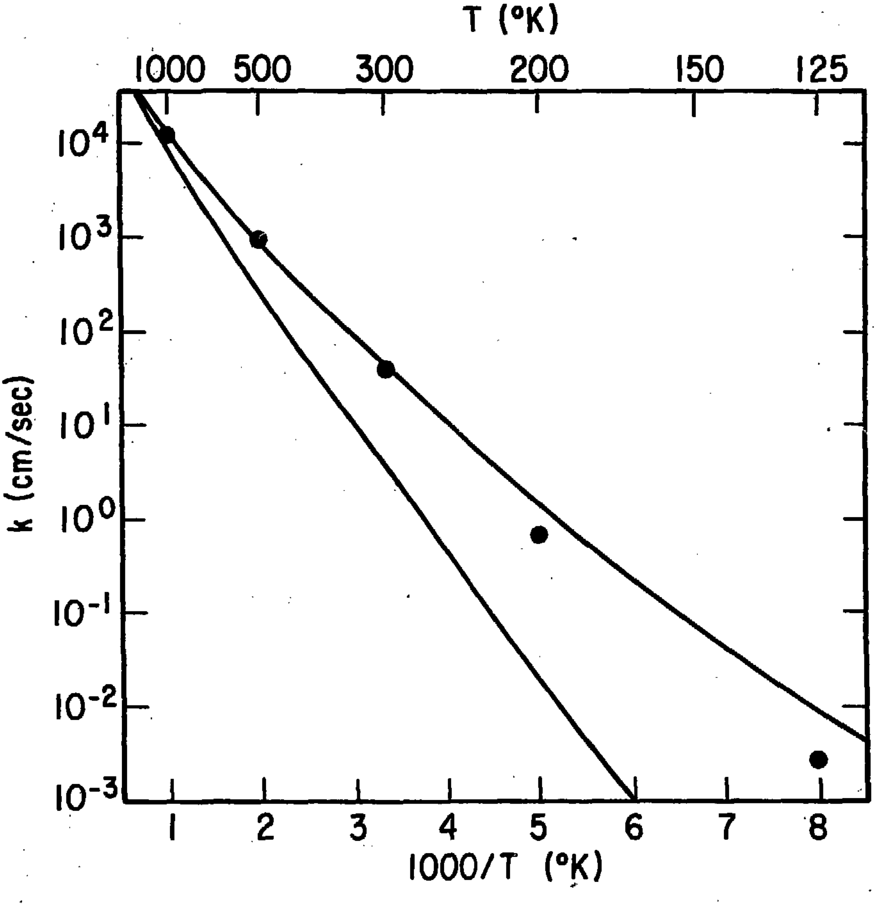
XBL 753-5899

Fig. 4



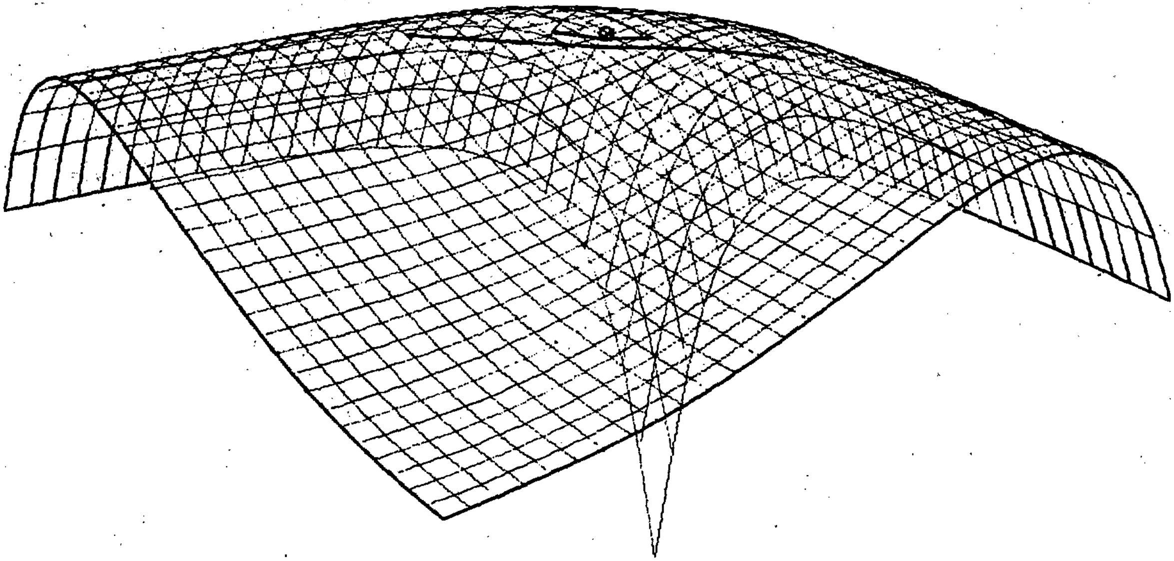
XBL-7411-7555

Fig. 5



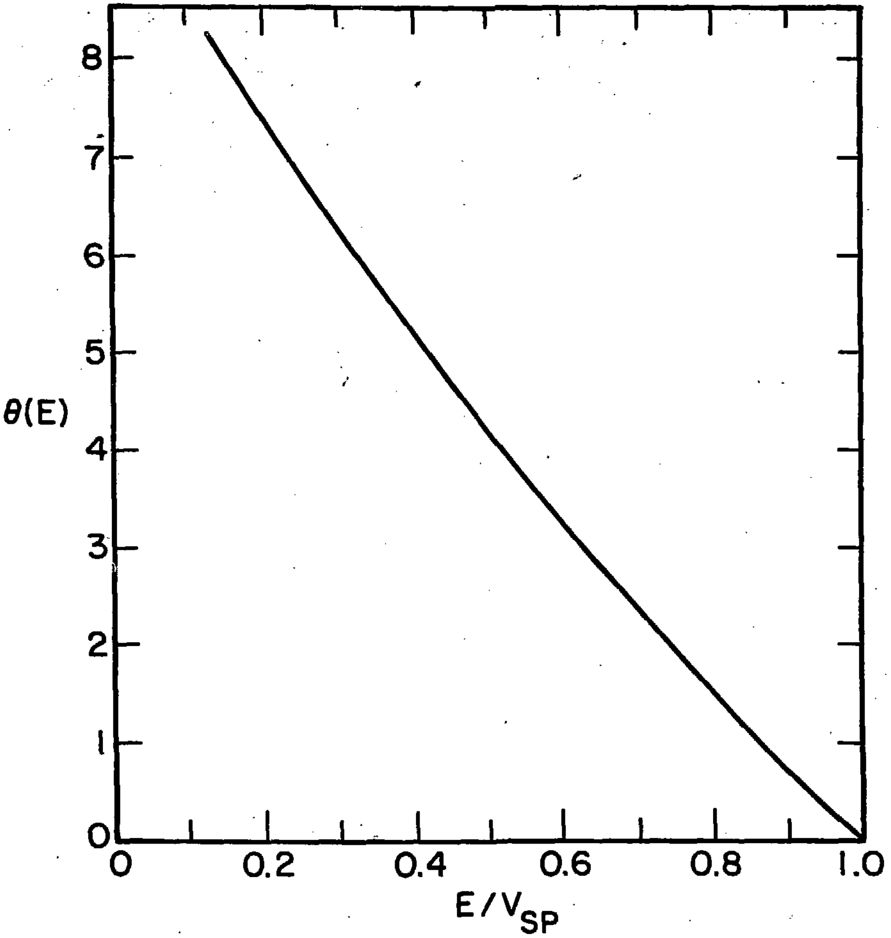
XBL 754-6046

Fig. 6



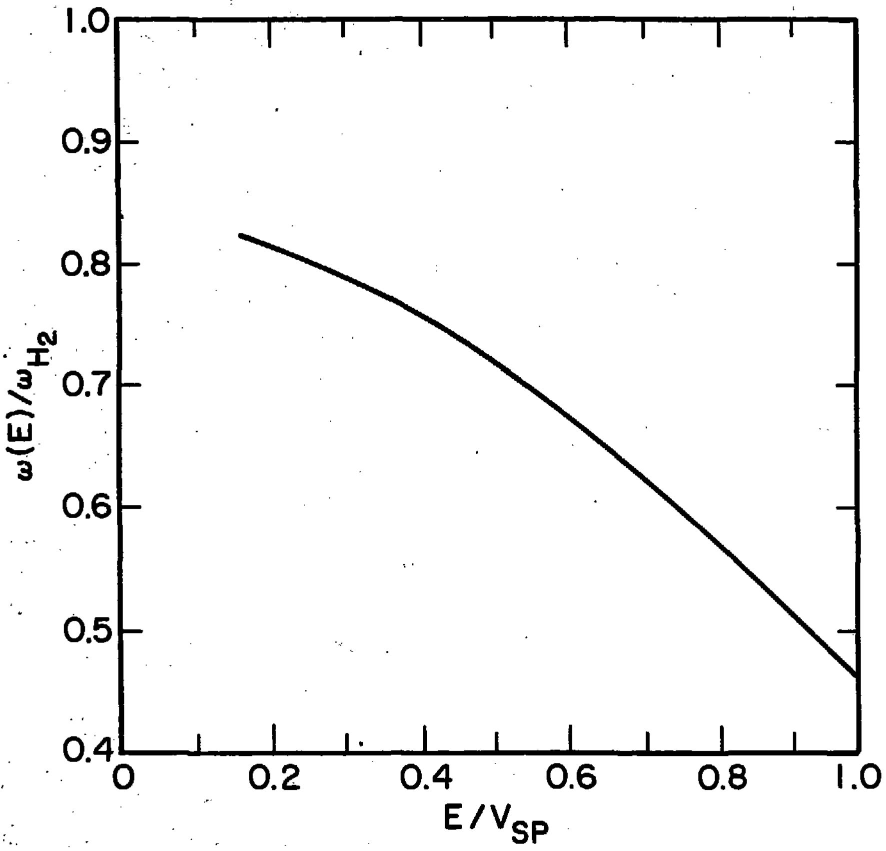
XBL753-693

Fig. 7



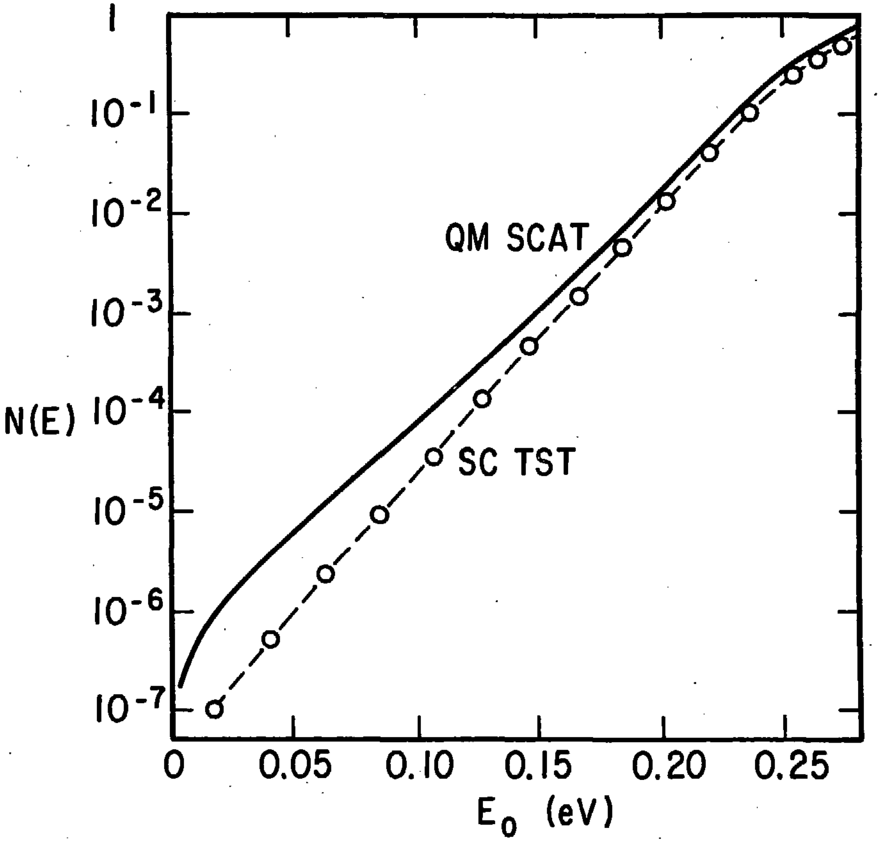
XBL 753-5900

Fig. 8



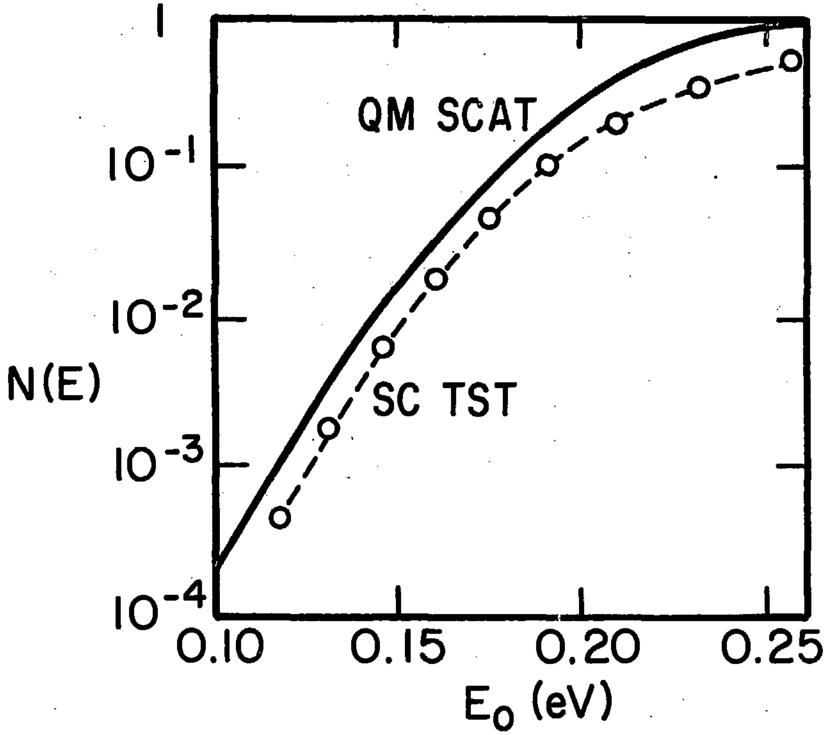
XBL753-5901

Fig. 9



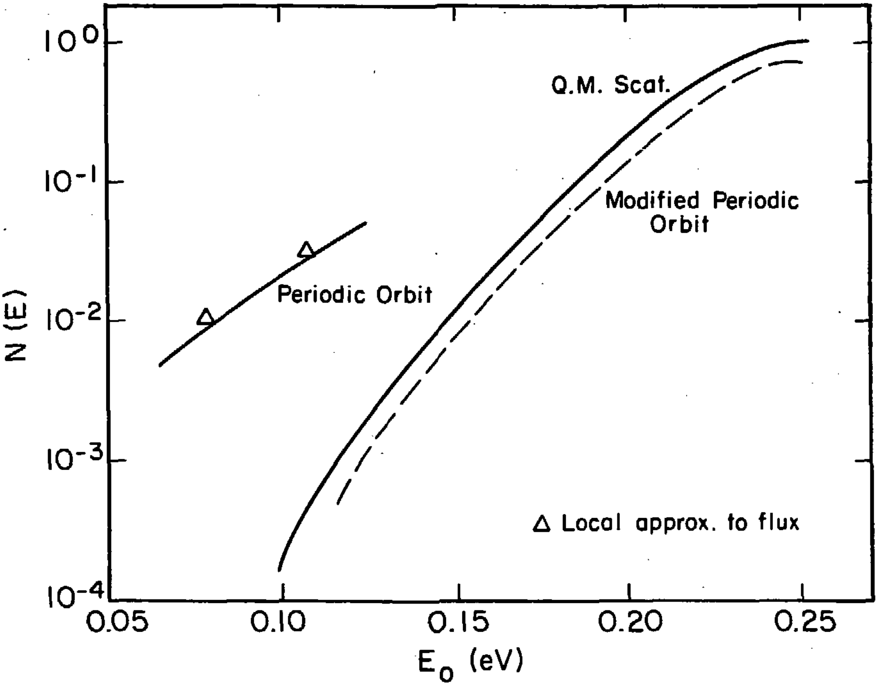
XBL 751-5660

Fig. 10



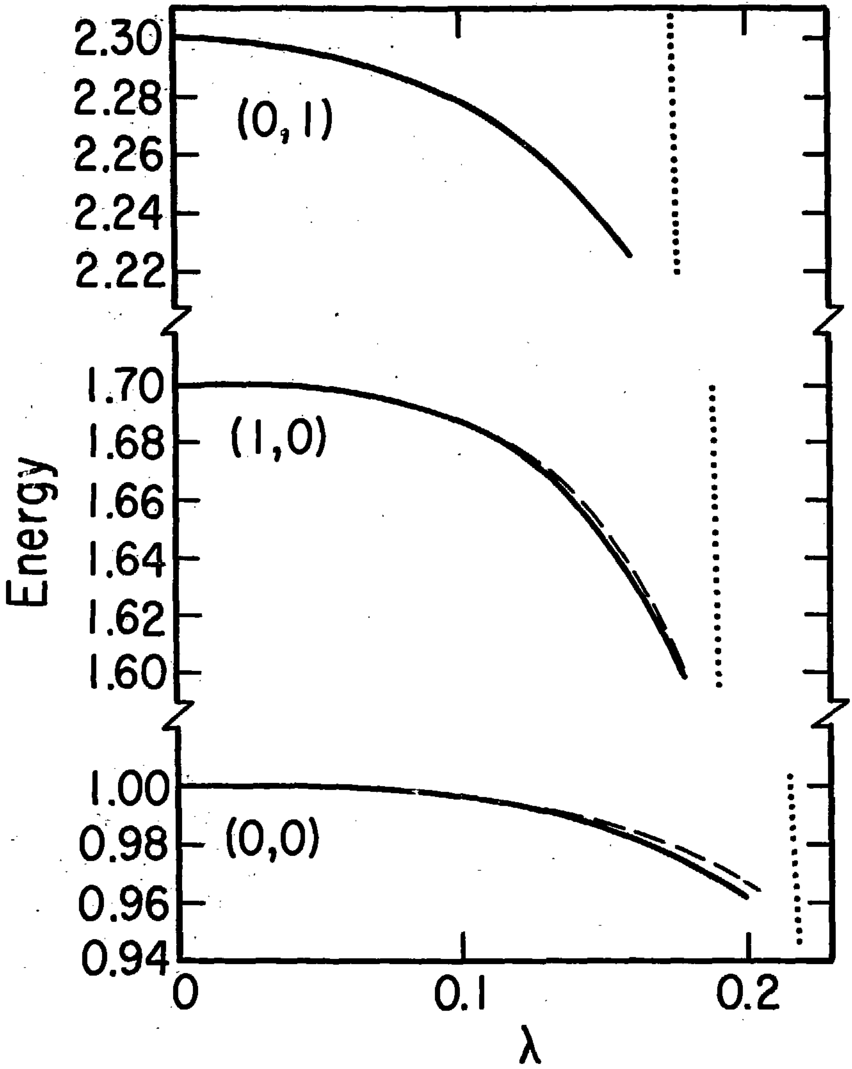
XBL 751-5661

Fig. 11



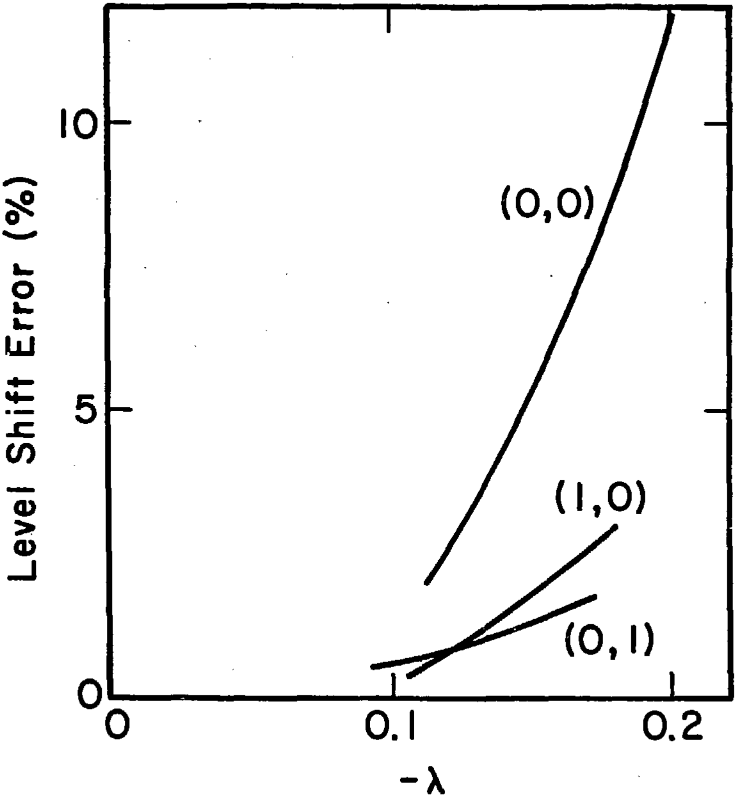
XBL 778-9895

Fig. 12



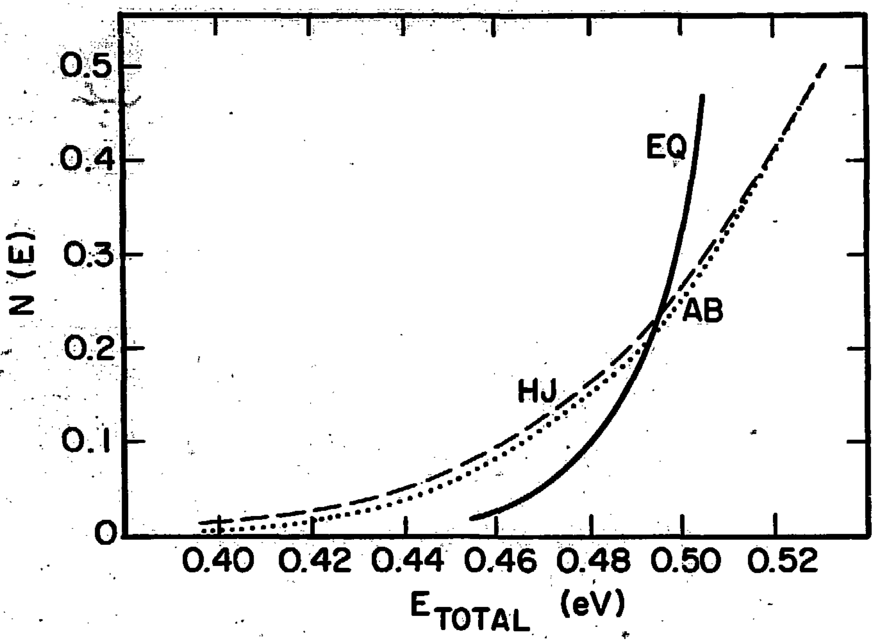
XBL 757-6717

Fig. 13



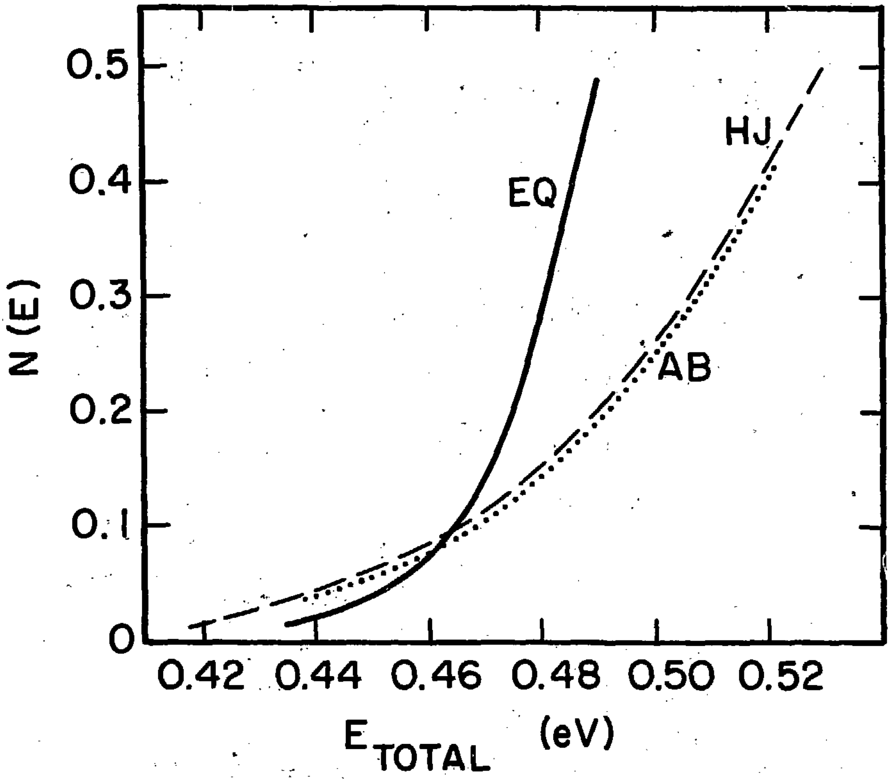
XBL 758-1946

Fig. 14



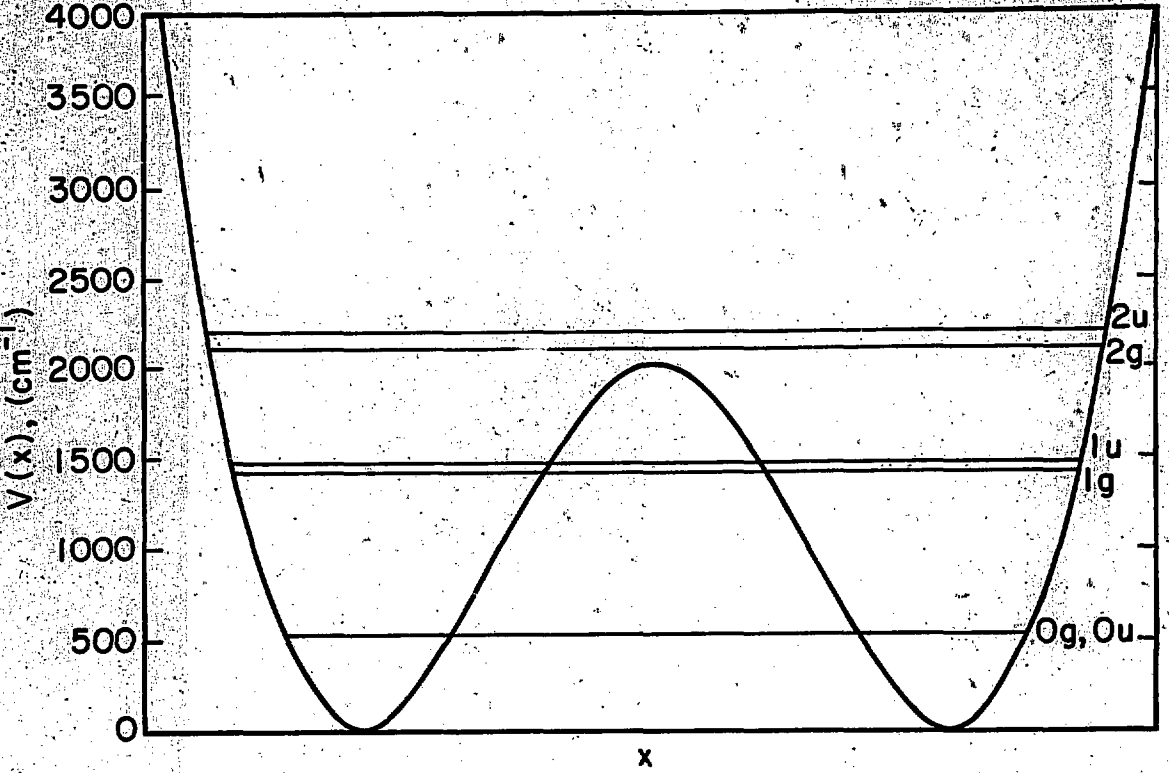
XBL 778-9896

Fig. 15



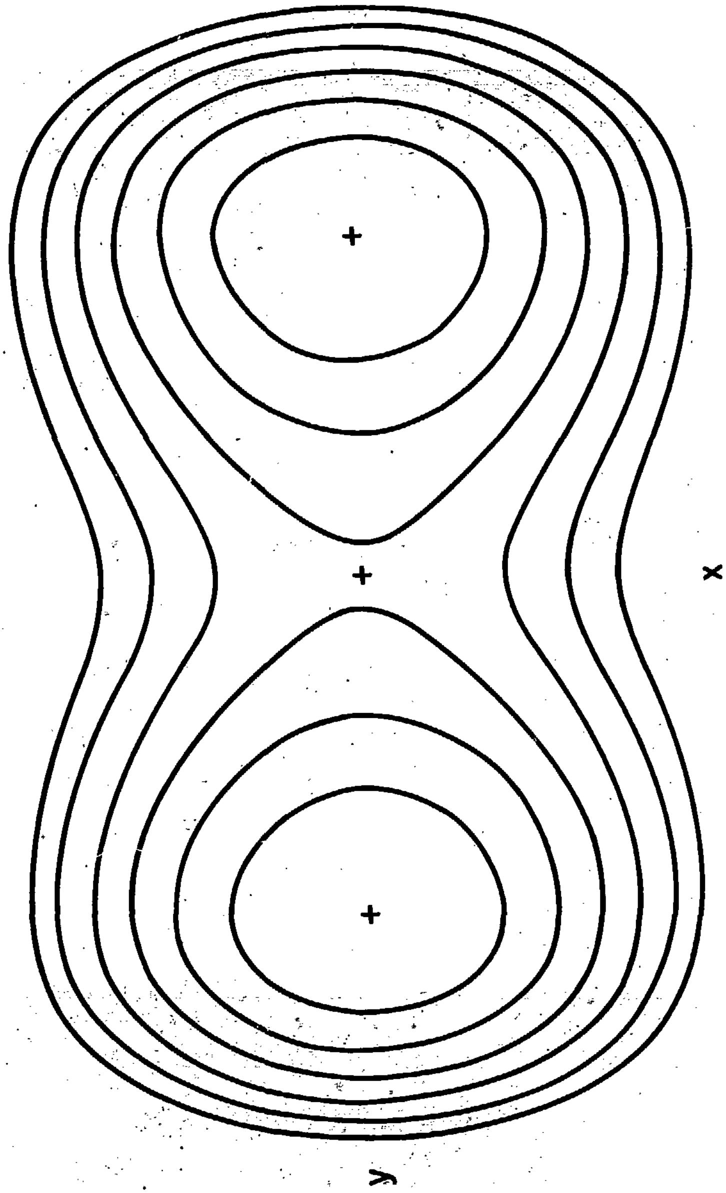
XBL 778-9897

Fig. 16



XBL 778-9898

Fig. 17



XBL 778-9899

Fig. 18