Theory of Semiclassical Transition Probabilities (S Matrix) for Inelastic and Reactive Collisions*

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In the present paper the time-independent Schrödinger equation for inelastic collisions is solved directly in the WKB approximation, using action-angle variables and the method of characteristics. A single wavefunction, consisting of an ingoing and an outgoing term, is thereby derived, describing all collision channels and so avoiding the application of WKB methods to an infinite set of coupled differential equations. An integral is obtained for the S matrix, and asymptotic methods (e.g., steepest descents, stationary phase) are used for its evaluation. The expressions can be calculated using numerical data on classical trajectories or using approximations. To facilitate the latter and to show the connection with approximations in the literature, a canonical perturbation theory is described for the wave phase and amplitude, in a form suited to collisions, and used to relate the theory to those approximations. The topic of collisional selection rules is also considered. The extension of the method employed in the present paper to the direct calculation of differential and total inelastic cross sections, rather than via the S matrix, is briefly described, and the extension to reactive cross sections is also noted. The method can also be used to treat time-dependent problems, and so is not restricted to collisions. These topics and other applications will be described in later papers of this series.

I. INTRODUCTION

Classical action-angle variables were used to treat atomic and molecular structure, as well as absorption and emission of radiation, many years ago.[1] Recently, we have employed them to treat inelastic and certain chemically reactive collisions.[2–5] In the present paper a quantum mechanics in action-angle variables, in the WKB approximation, is used to calculate transition probabilities in collisions. The final expression can be evaluated by integration of a system of ordinary differential equations (the classical equations of motion) or by various approximation techniques.

As before, we use conventional coordinates (R, p_R) to describe the radial motion and employ action-angle variables to describe the other degrees of freedom.[3] The present paper is the one cited as Ref. 2 there.[3b] A method, based on the Feynman propagator, for applying action-angle variables to the S matrix has recently been employed by Miller.[6]

In the present paper we have calculated the S matrix, partly to facilitate comparison both with exact (numerical) computations and with various approximations in the literature. However, the method requires relatively little modification to calculate the observables directly, the differential and total cross sections for inelastic processes. The nature of the modification is indicated briefly, and described more fully in a later paper. The method can also be used to treat problems with time-dependent Hamiltonians, and so is not restricted to scattering phenomena. These results will also be described subsequently.

Usually, WKB treatments of the time-independent Schrödinger equation for inelastic collisions first resolve the equation into coupled equations, one per quantum state.[7] The latter are then solved by a WKB method, with added approximations. In our case, instead, a single WKB solution is found for the entire system rather than using coupled equations. Apart from one restriction[8] the approximation in the present work is the application of an asymptotic (i.e., WKB) argument. The accuracy of WKB arguments for describing quantum mechanical phenomena and interferences in elastic collisions accurately is now well established.[9]

We have employed action-angle variables because of their desirable properties: the action variables are closely related to quantum numbers (WKB, Bohr–Sommerfeld formulas); the initial angle variables each occur randomly in the interval $[0, 1]$; and the angle variables are uniformizing variables, removing the singularities in unperturbed WKB wavefunctions.

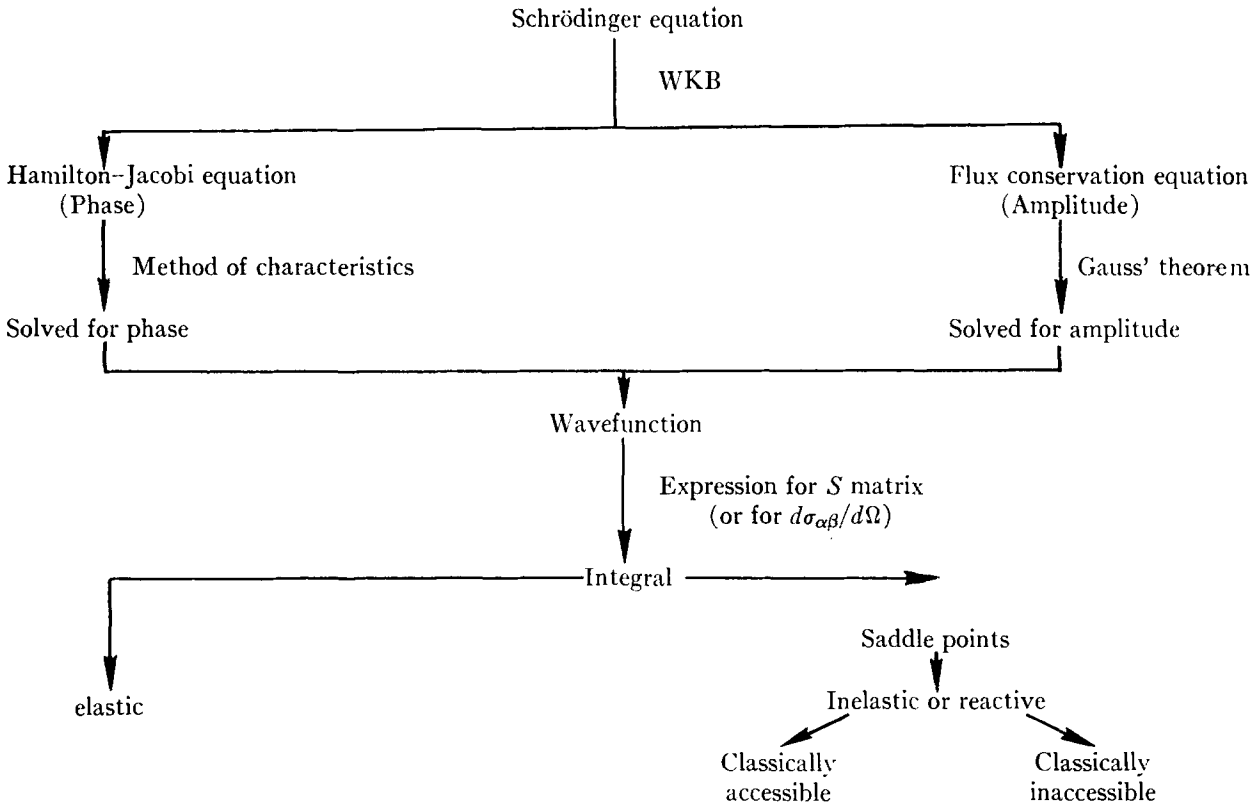
The presentation in the paper has the following format: In Sec. II a simple classical result is given for the transition probabilities, as an illustration of the use of these variables. In Sec. III the unperturbed Schrödinger equation is given, and in Sec. IV the actual equation and its WKB solution are described for the system. Application is made in Sec. V for the elastic case to verify that the phase shift and the solution as a whole reduce to the usual one in that case. An expression for the S matrix is given in Sec. VI and asymptotic methods (steepest descents, stationary phase) are applied to its evaluation in Sec. VII. A canonical perturbation theory for the phase and amplitude, and hence for the S matrix, is derived in Sec. VIII. It is used as a guide in Sec. IX to apply exact and approximate numerical results[3–5] of trajectory calculations to the problem, as a preliminary to a more detailed discussion to be given elsewhere. The topic of collisional selection rules is also noted there. In Sec. X

both the extension from S matrices to differential and total inelastic cross sections, and the extension to chemical reactions, are indicated. The relationship to various approximations in the literature is also described.

The principal equations in the paper are Eqs. (6.5)–(6.7) and (7.17). Others are (7.6), (7.9) [and their asymptotic forms (7.13)–(7.14)], (7.16), (7.27), and (8.15)–(8.18).

The myriad of phenomena associated with inelastic transitions makes clear some of the applications of the method. We shall describe some of these applications in later papers of this series.

A flow sheet of the present procedure is as follows:



The approach in this paper is a direct descendent of the WKB method used for treating the time-independent Schrödinger equation for elastic scattering or eigenvalue problems. Miller's approach[6] is a most interesting one which begins with the classical Feynman propagator. While their starting points and their integral expressions for S_{mn} differ, one can anticipate that future interaction between the two approaches should enrich both. We hope to compare the two, both with respect to phase and amplitude of S_{mn}, in a later paper. The terms in the phase of S_{mn} play a role in phenomena such as line broadening.

II. A SIMPLE CLASSICAL RESULT

An application of a formalism based on action-angle variables is illustrated by calculation of a "classical" transition probability for a classically accessible transition. The angle variables, as already noted, have the convenient property of lying, initially randomly, in the interval [0, 1]. The probability of finding the system in some quantum state m after a collision, if the system was in an initial state n, is denoted by P_{mn}. Corresponding to a unit interval in quantum number m is an interval $\Delta J=h$ in action variable J. [J equals mh or $(m+\frac{1}{2})h$, according to Bohr–Sommerfeld theory, depending on the degree of freedom.] If Δw^0 is the interval in initial angle variable w^0 leading to a J_m lying in $(J_m, J_m+\Delta J)$, then P_{mn} is equal to Δw^0. Since Δw^0 equals $\Delta J/(\partial J_m/\partial w^0)$ for small Δw^0, and since ΔJ is h, we have

$$P_{mn}=h/(\partial J_m/\partial w^0). \tag{2.1}$$

This classical result is immediately generalized to r dimensions: Since

$$\Delta w_1^0\cdots\Delta w_r^0=|\,\partial J_{m_i}/\partial w_j^0\,|^{-1}\Delta J_1\cdots\Delta J_r, \tag{2.2}$$

where $|\ |$ denotes an $r\times r$ determinant, and since $\Delta J_i=h\Delta m_i=h$, we have

$$P_{m_1\ldots m_r n_1\ldots n_r}=h^r/|\,\partial J_{m_i}/\partial w_j^0\,|. \tag{2.3}$$

When several isolated Δw^0 intervals contribute the contributions are added to yield the total P_{mn} in (2.1)

and (2.3). Equation (2.3) can also be derived later from (7.17).

Frequently, one is interested in only one or several of the m_i's, and the corresponding transition probability is obtained by integrating (2.3) over the remaining m_i's (treated as continuous variables).

III. SCHRÖDINGER EQUATION AND WKB SOLUTION IN ACTION-ANGLE VARIABLES

The classical Hamiltonian H_0 in an unperturbed system having $r+1$ degrees of freedom is a function only of the action variables J_i ($i=1$ to r), the radial coordinate R and its conjugate momentum p_R. It can therefore be written as $H_0(J, p_R, R)$, where J denotes $(J_1, \cdots, J_r)$. An approximate action-angle quantum mechanical formalism was introduced many years ago by Dirac[10] and yielded results for the hydrogen atom and for the harmonic oscillator similar to those obtained by WKB theory.[11] The quantum mechanical action variable operators $\mathbf{J}_i$ did not correspond precisely to the action variables J_i, but differed from them by some term, $h\delta_i$, of order h.[10] In the w representation we may write $\mathbf{J}_i$ as $(\hbar/i)\partial/\partial w_i$. The Schrödinger equation for the unperturbed system is then

$$H_0(\mathbf{J}+h\delta, \mathbf{p}_R, R)\psi^0=E\psi^0, \tag{3.1}$$

where H_0 is chosen to be a Hermitian operator, $\mathbf{p}_R$ is the momentum operator $(\hbar/i)\partial/\partial R$ in the R representation, $\mathbf{J}+h\delta$ denotes $(\mathbf{J}_1+h\delta_1, \cdots, \mathbf{J}_r+h\delta_r)$, and E is the total energy. Dirac's paper contains a prescription for finding the operator $\mathbf{J}_i+h\delta_i$. However, for our purpose it suffices to choose the δ_i's to satisfy their WKB values, given below.

The wavefunction ψ^0 is periodic in each w_i, with unit period. Since the w_i are absent in (3.1) the solution $\psi_{mE}{}^0$ to (3.1) for a given state mE is

$$\psi_{mE}{}^0=f_m(R)\exp 2\pi i m w, \tag{3.2}$$

where mw denotes $\sum_i m_i w_i$. The m_i's are integers, because of the periodicity of $\psi_{mE}{}^0$ in the w_i's. $f_m(R)$ is the radial wavefunction, with wavenumber k_m at $R=\infty$; k_m is determined by energy conservation once E and m_i's are specified: If $E_m{}^0$ is the internal energy of the separated collision partners at $R=\infty$ then

$$E=E_m{}^0+k_m{}^2\hbar^2/2\mu, \tag{3.3}$$

where μ is their reduced mass.

According to Eqs. (3.1) and (3.2) and the nature of $\mathbf{J}_i$ in the w representation, the energy of the unperturbed system is the same function of $(m_i+\delta_i)h$ that it is of the classical action variable J_{m_i}. (J_{m_i} is the value of the classical action variable J_i in the m_ith quantum state of the ith degree of freedom.) Thus, in this WKB-type approximation

$$J_{m_i}=(m_i+\delta_i)h. \tag{3.4}$$

The δ_i are known from WKB solutions for the various standard problems. For example, δ_i is 0 for a plane rotator, $\frac{1}{2}$ for an oscillator, $\frac{1}{2}$ for an orbital motion, 0 for the z component of the latter, etc. A prescription due to Keller[12] is illuminating in this connection.

In scattering theory the relative translational motion in the initial state is described by a plane wave, which is usually then decomposed into partial waves, each characterized by an orbital angular momentum and the latter's z component. An analogous decomposition can be made with the present coordinates. Equation (3.2) represents a partial wave for the unperturbed system.

IV. SCHRÖDINGER EQUATION AND WKB SOLUTION FOR THE PERTURBED SYSTEM

The Schrödinger equation for the perturbed system is

$$H(\mathbf{J}+h\delta, \mathbf{p}_R, w, R)\psi=E\psi, \tag{4.1}$$

H being Hermitian.

In the following, $(q_1, \cdots, q_r, q_{r+1})$ denotes $(w_1, \cdots, w_r, R)$, respectively, and $(p_1, \cdots, p_r, p_{r+1})$ denotes the canonically conjugate classical momenta $(J_1, \cdots, J_r, p_R)$.

A partial wave ψ_{nE} in the perturbed system [n denotes the set $(n_1, \cdots, n_r)$] can be expressed as

$$\psi_{nE}=\exp[i\Phi(q, n, E)/\hbar]. \tag{4.2}$$

Following Dirac[13a], the latter can be written as

$$\psi_{nE}\cong A\exp[i\bar{\phi}(q, n, E)/\hbar], \tag{4.3}$$

where A and $\bar{\phi}$ are real and vary slowly as a function of the q_i's. A and $\bar{\phi}$ describe the phase and amplitude of ψ_{nE}. The pre-exponential factor A satisfies an equation of conservation of probability flux, which for the time-independent Schrödinger equation, after some manipulation[13b], is

$$\nabla\cdot(A^2\dot{\mathbf{q}})\equiv\sum_i(\partial/\partial w_i)(A^2\dot{w}_i) + R^{-2}(\partial/\partial R)R^2A^2\dot{R}=0, \tag{4.4}$$

where the velocity component $\dot{q}_i$ denotes $\partial H/\partial p_i$. The n-dimensional divergence ∇ and vector $\dot{\mathbf{q}}$ have components $(\partial/\partial w_1, \cdots, \partial/\partial w_r, R^{-2}(\partial/\partial R)R^2)$, and $(\dot{w}_1, \cdots, \dot{w}_r, \dot{R})$, respectively. A is determined later from Eq. (4.4). The latter can be rewritten in terms of the probability current density $\mathbf{i}$:

$$\nabla\cdot\mathbf{i}=0, \quad \mathbf{i}=A^2\dot{\mathbf{q}}. \tag{4.4'}$$

ϕ is found from (4.1) and (4.3) to satisfy[13a]

$$H(\partial\bar{\phi}/\partial q+h\delta, q)=E, \tag{4.5}$$

where δ_R is zero. It is useful to define a function ϕ;

$$\phi(q, \alpha)=\bar{\phi}(q, n, E)+2\pi w\delta\hbar, \tag{4.6}$$

where $w\delta$ denotes $\sum_i w_i\delta_i$ and where α denotes

$$\alpha_i=J_{n_i}(i\leq r), \qquad \alpha_{r+1}=E. \tag{4.7}$$

Here, J_{n_i} is the value of J_i for the initial quantum state $(n_1, \cdots, n_r)$. Equations (4.3) and (4.5) then become

$$\psi_{nE}=A\exp[i(\phi-2\pi w\delta\hbar)/\hbar], \tag{4.8}$$

$$H(\partial\phi/\partial q, q)=E. \tag{4.9}$$

Equation (4.9) is a Hamilton–Jacobi type equation for a generating function[14] ϕ for a canonical transformation. The transformation is from old variables (p, q) and a Hamiltonian H to new variables (α, β) and to a Hamiltonian E. Thereby,

$$p_i=\partial\phi/\partial q_i, \qquad \beta_i=\partial\phi/\partial\alpha_i. \tag{4.10}$$

The new equations of motion are

$$\dot{\alpha}_i=-\partial E/\partial\beta_i=0, \qquad \dot{\beta}_i=\partial E/\partial\alpha_i=\delta_{i,r+1}. \tag{4.11}$$

They show that $\alpha_1, \cdots, \alpha_{r+1}, \beta_1, \cdots, \beta_r$ are all constants and that, since α_{r+1} has been chosen to be E, β_{r+1} is $t-t_0$, where t_0 is some arbitrary constant. As β_i we choose

$$\beta_i=w_i^0 \qquad (1\leq i\leq r), \qquad \beta_{r+1}=t-t_0, \tag{4.12}$$

where w_i^0 is the initial value of w_i at some specified separation distance R_0 before collision. The choice (4.12) for $(\beta_1, \cdots, \beta_r)$ is dictated by the fact that according to (4.7) α_i is J_{n_i} the initial value of J_i, and that β_i is canonically conjugate to α_i.

Equation (4.9) may be integrated by the method of characteristics. The characteristics satisfy[15]

$$\begin{aligned} dq_1/(\partial H/\partial p_1)=\cdots=dq_{r+1}/(\partial H/\partial p_{r+1}) \\ =dp_1/(-\partial H/\partial q_1)=\cdots \\ =dp_{r+1}/(-\partial H/\partial q_{r+1}) \\ =d\phi/\sum_i(\partial\phi/\partial q_i)(\partial H/\partial p_i). \end{aligned} \tag{4.13}$$

The expression for $d\phi$ along the characteristics is then found to be[15]

$$d\phi=\sum_i p_i dq_i. \tag{4.14}$$

For purposes of evaluating the ϕ and A in Eq. (4.8) the integration in (4.14) is to be performed from an initial configuration $(w_1^0, \cdots, w_r^0, R_0)$ to some large post-collision value of R, and so to some configuration $(w_1, \cdots w_r, R)$. If the right-hand side of (4.13) is written as an infinitesimal parameter, $d\tau$, and if we now use a dot to denote $d/d\tau$, then Eq. (4.13) for the characteristics becomes

$$\begin{aligned} \dot{w}_i=\partial H/\partial J_i, \qquad \dot{R}=\partial H/\partial p_R \\ \dot{J}_i=-\partial H/\partial w_i, \qquad \dot{p}_R=-\partial H/\partial R. \end{aligned} \tag{4.15}$$

Since these equations are the equations of motion along the characteristics, τ is the "time." The final time of integration will, incidentally, be different for different values of $(w_1^0, \cdots, w_r^0)$ since the time to reach the final R will vary.

In integrating (4.14) along the characteristics (4.15) there are several boundary conditions to be satisfied:

(i) Initially, R is R_0 and p_R is negative. In the precollision region ϕ should be the unperturbed ϕ, which is seen from (4.14) to be

$$\phi(q, \alpha)=\sum_{i=1}^{r} J_{n_i}w_i+p_R^0R \qquad (p_R^0<0, R>R_0), \tag{4.16}$$

where p_R^0, the initial p_R, is expressible in terms of the α_i's by energy conservation.

(ii) At the turning point of the radial motion p_R changes from negative value to positive and, by WKB theory, the phase $\phi/\hbar$ decreases by $\pi/2$ there.[12] (When there are several turning points in the R motion the $\pi/2$ in (4.17b) is modified. We reserve until a later paper any discussion of such topics.)

The $\phi(q, \alpha)$ satisfying (4.14) and these boundary conditions is

$$\begin{aligned} \phi(q, \alpha)=\sum_{i=1}^{r}\left(\int_{w_i^0}^{w_i} J_i dw_i+J_{n_i}w_i^0\right) \\ +\left(\int_{R_0}^{R} p_R dR+p_R^0R_0\right) \qquad (p_R<0), \end{aligned} \tag{4.17a}$$

$$\begin{aligned} \phi(q, \alpha)=\sum_{i=1}^{r}\left(\int_{w_i^0}^{w_i} J_i dw_i+J_{n_i}w_i^0\right) \\ +\left(\int_{R_0}^{R} p_R dR+p_R^0R_0\right)-\tfrac{1}{2}\pi\hbar \ (p_R>0), \end{aligned} \tag{4.17b}$$

where the integrals are line integrals, i.e., the integration is performed along the characteristics (Fig. 1). The dependence of (4.17) on the initial coordinates is only an apparent one, since partial differentiation of (4.17) shows that $\partial\phi/\partial w_i^0$ and $\partial\phi/\partial R_0$ vanish. Numerical integration along the characteristics (15) to some final R, for various initial values of the w_i^0's,

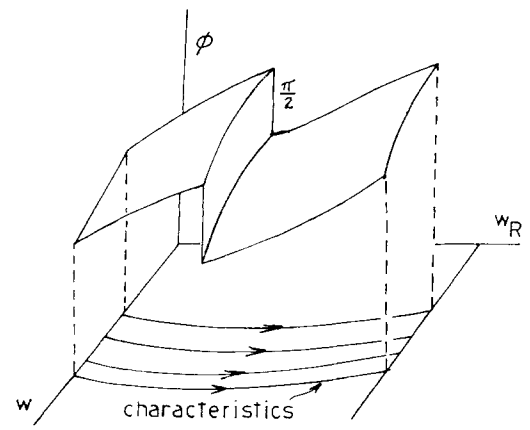


FIG. 1. Plot of the phase function ϕ vs a w_i and a uniformized R variable, w_R, indicating the characteristics (the streamlines of the motion), and the decrease in phase by $\pi/2$ at a w_R corresponding to the turning point of the R motion.

provides the desired set of numerical values of $\phi(w, R, J_{n_i}, E)$.

The phase ϕ given by (4.17) is plotted schematically in Fig. 1. The characteristics and the change in phase of ϕ at the turning point are both depicted. Purely for convenience of drawing we have used a uniformizing variable w_R based on a line integral,

$$w_R = \frac{\partial}{\partial p_R{}^0} \int_{R_0}^{R} p_R dR. \tag{4.18}$$

This w_R increases monotonically during the collision since p_R is negative when dR is negative, and p_R is positive when dR is positive. At very large separation distances, the integral is initially $p_R{}^0(\mathcal{R}-R_0)$ and so initially w_R is simply R. At large final separations it is a linear function of R.

It remains to evaluate A using Eq. (4.4). A schematic diagram of the probability flow in w-R space is given in Fig. 2. An initial region $\prod_i dw_i{}^0$ at some initial R_0 has a cross-sectional area $R_0{}^2\prod_i dw_i{}^0$ normal to the R coordinate. (The volume element in w-R space is $R_0{}^2 dR \prod_i dw_i{}^0$.) The streamlines (the characteristics) are also indicated in Fig. 2. At some final R the $w_i{}^0$ have evolved to w_i and the final cross-sectional area normal to the R coordinate is $R^2\prod_i dw_i$. Since the flow is divergenceless, according to (4.4), application of Gauss' theorem to this $r+1$ dimensional space shows that the net flow out of the region enclosed by the heavy solid lines in Fig. 2 is zero. Since there is no flow across the sides (the streamlines) of the tube, the only flow is across the ends. Considering the volume enclosed by a dark outline in Fig. 2 it follows from (4.4), (4.4′), and Gauss' theorem therefore, that

$$i_R{}^0 R_0{}^2 \prod_i dw_i{}^0 + i_R R^2 \prod_i dw_i = 0, \tag{4.19}$$

where i_R is the R component of the probability current, and, by (4.4′), is given by (4.20); $i_R{}^0$ is its initial value at the initial R_0 and

$$i_R = A^2 \dot{R} = A^2 p_R/\mu. \tag{4.20}$$

Here μ denotes the reduced mass of the collision partners

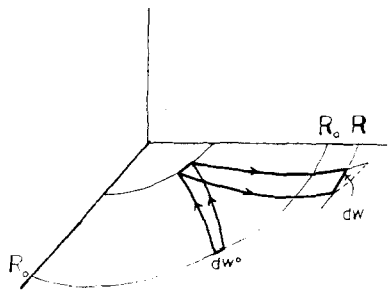


FIG. 2. Plot of the characteristics in an $R-w$ space ($w/2\pi$ is the angular variable) showing the relation between the initial dw^0 and the final (postcollision) dw, indicating the dependence of the surface area ($R^2 dw$ in the actual $r+1$ dimensional system) for any given R and showing the reflection of the R motion. The characteristics are indicate by arrows, and the final wave front by a dotted line. ϕ could be plotted as the vertical coordinate.

in the given channel. The incoming wave has a preexponential factor which we can denote by A_0.

Equations (4.19) and (4.20) yield

$$A_0{}^2 R_0{}^2 v_n \prod_i dw_i{}^0 - A^2 R^2 v \prod_i dw_i = 0, \tag{4.21}$$

where v is the magnitude of the final R component of velocity, $|p_R|/\mu$, in the outgoing channel and v_n is the corresponding component, $-p_R{}^0/\mu_n$ in the incoming one, n ($p_R{}^0$ is negative). When chemical reaction occurs[16] certain $\prod_i dw_i{}^0$ intervals in (4.21) lead eventually to a product channel, for the given α_i's; other $\prod_i dw_i{}^0$ intervals at these α_i's lead only to the original reactants.

$\prod_i dw_i$ and $\prod_i dw_i{}^0$ are related by a Jacobian,

$$\prod_i dw_i = |\partial w_i/\partial w_j{}^0| \prod_i dw_i{}^0, \tag{4.22}$$

where $||$ denotes an $r\times r$ determinant. Equations (4.21) and (4.22) yield the final result,

$$A = A_0 (R_0/R)(v_n/v)^{1/2} |\partial w_i/\partial w_j{}^0|^{-1/2}. \tag{4.23}$$

We shall choose A_0 so that the incident R flux of the partial wave, integrated over all $w_i{}^0$ (namely, $A_0{}^2 R_0{}^2 v_n$ for $R=R_0$) is unity. Thereby,

$$A_0 = (R_0 v_n{}^{1/2})^{-1}. \tag{4.24}$$

For later notational convenience, and without loss of generality, we shall multiply both incoming and outgoing portions of the above wavefunction by $\exp(in_1\pi/2)$. (Throughout this paper n_1 (and m_1) will denote the principal orbital quantum number, usually denoted by l.) R_0 is now chosen to equal R, so as to evaluate $\psi_{nE}{}^{(+)}$ at this R.

If the wavefunction of the complete partial wave is denoted by $\psi_{nE}{}^{(+)}$, its form at large R is, from (4.8), (4.16), (4.17b), (4.23), (4.24), and the preceding discussion, seen to be

$$\psi_{nE}{}^{(+)} \underset{R\to\infty}{\sim} (R v_n{}^{1/2})^{-1} \psi_{nw}{}^0 \exp(-ik_n R + in_1\pi/2) - (R v^{1/2})^{-1} |\partial w_i/\partial w_j{}^0|^{-1/2} \exp[i\phi^*(q,\alpha)/\hbar], \tag{4.25}$$

where $\psi_{nw}{}^0$ is $\exp(2\pi i \sum_i n_i w_i)$, and where

$$\phi^*(q,\alpha)/\hbar = (\phi/\hbar) + \tfrac{1}{2} n_1\pi + \pi - 2\pi \sum_i w_i \delta_i. \tag{4.26}$$

Here the π compensates for the minus sign of the last term in (4.25), and ϕ is given by (4.17b). These equations yield

$$\phi^*(q,\alpha) = \sum_{i=1}^{r} \left[\int_{w_i{}^0}^{w_i} J_i dw_i + J_{n_i} w_i{}^0 \right] + \int_{R_0}^{R} p_R dR + p_R{}^0 R_0 + [(n_1+1)\hbar\pi/2] - 2\pi \sum_i w_i \delta_i \hbar. \tag{4.26′}$$

The integrals in (4.26′) are line integrals along the characteristics defined by (4.15).

It is useful to define a continuous variable $\bar{n}_i$ by

$$(\bar{n}_i + \delta_i)h = J_i. \tag{4.27}$$

On introducing this result into (4.26′), using (3.4), and rearranging the terms, Eq. (4.26′) becomes

$$\frac{\phi^*(q,\alpha)}{\hbar} = 2\pi \sum_{i=1}^{r} \int_{w_i^0}^{w_i} (\bar{n}_i - n_i) dw_i + \int_{R_0}^{R} k dR + 2\pi \sum_i n_i w_i - k_n R_0 + (n_1+1)\tfrac{1}{2}\pi, \quad (4.28)$$

where k is $p_R/\hbar$, a function of R, and k_n is the magnitude of $p_R^0/\hbar$ (p_R^0 is negative; hence $k_n = -p_R^0/\hbar$). Since initially $\bar{n}_i$ equals n_i and $-k$ equals k_n, the expression is independent of the lower limits on the integrals (as differentiation with respect to w_i^0 or R_0 shows). In (4.28), as in all preceding and all subsequent expressions, the integrals are to be evaluated along the characteristics, i.e., along the trajectories.

V. ELASTIC COLLISION

We verify in this section that (4.25) reduces to the usual WKB expression when the collision is elastic, i.e., when all J_i equal their initial values J_{n_i}. The Jacobian $|\partial w_i/\partial w_j^0|$ is unity since w_i in this case equals $w_i^0 + \nu_i^0(t-t_0)$, where ν_i^0 is the i'th unperturbed frequency. The first term in (4.28) is zero, and k in the next term now satisfies the equation

$$(k^2\hbar^2/2\mu) + (J_{n_1}^2/8\pi^2\mu R^2) + V(R) = k_n^2\hbar^2/2\mu, \quad (5.1)$$

where $J_{n_1}/2\pi$ is the orbital angular momentum and $V(R)$ is the interaction potential. On introducing (5.1) into (4.28), and relating this integral to its value when $V=0$, one obtains, on letting R (and R_0) become large,

$$\phi^*(q,\alpha)/\hbar = k_n R - (n_1\pi/2) + 2\delta_l + 2\pi \sum_i n_i w_i, \quad (5.2)$$

where

$$\delta_l = \int_{r_0}^{\infty} (k - k_n) dR - k_n r_0 + (n_1 + \tfrac{1}{2})\tfrac{1}{2}\pi. \quad (5.3)$$

Here, r_0 is the classical turning point of the R motion in (5.1).

Thus, $\psi_{nE}^{(+)}$ for this case, obtained from (4.25), is

$$\psi_{nE}^{(+)} \underset{R\to\infty}{\sim} (Rv_n^{1/2})^{-1}\psi_{nw}^0 \{\exp[-i(k_n R - n_1\pi/2)] - \exp[i(k_n R - (n_1\pi/2) + 2\delta_l)]\}. \quad (5.4)$$

The δ_l given by (5.3) is the standard WKB expression for the phase shift in an elastic collision.[17a]

In the absence of the interaction potential $V(R)$, δ_l vanishes and $\psi_{nE}^{(+)}$ becomes ψ_{nE}^0, the unperturbed wavefunction. Replacing the n by m, we have

$$\psi_{mE}^0 \underset{R\to\infty}{\sim} (Rv_m^{1/2})^{-1}\psi_{mw}^0 \{\exp[-i(k_m R - m_1\pi/2)] - \exp[i(k_m R - m_1\pi/2)]\}. \quad (5.5)$$

VI. CALCULATION OF S MATRIX

Once the S matrix is known the other properties, such as differential and total cross sections, for inelastic and reactive collisions are known. The on-the-energy shell S matrix is defined by the asymptotic form of the exact wavefunction[17b]:

$$\psi_{nE}^{(+)} \underset{R\to\infty}{\sim} R^{-1} \sum_{m'} v_{m'}^{-1/2}\psi_{m'w'}^0 \{\delta_{m'n}\exp(-ik_{m'}R + im_1'\pi/2) - S_{m'n}\exp(ik_{m'}R - im_1'\pi/2)\}. \quad (6.1)$$

Equation (6.1) applies both to reactive and nonreactive collisions. In the case of a reactive collision the reduced mass μ_m used to calculate the velocity v_m from the wavenumber k_m ($v_m = k_m\hbar/\mu_m$) will normally be different from μ_n, when m refers to a quantum state of the reaction products.

Integration by parts (Green's theorem) shows that[18]

$$\int_{w,R} \psi_{mE}^{0*}(H - H_m)\psi_{nE}^{(+)} R^2 dR \prod_i dw_i = \frac{\hbar^2}{2\mu_m} \lim_{R\to\infty} R^2 \int_{w=0}^{1} \left(\psi_{mE}^{0*}\frac{\partial\psi_{nE}^{(+)}}{\partial R} - \psi_{nE}^{(+)}\frac{\partial\psi_{mE}^{0*}}{\partial R}\right)\prod_i dw_i, \quad (6.2)$$

where H_m is the unperturbed Hamiltonian in the outgoing channel m and R is the separation distance in that channel. Like Eq. (6.1), Eq. (6.2) applies to elastic ($m=n$), inelastic ($m\neq n$, $H_m = H_n$) and reactive ($H_m \neq H_n$) collisions.

Introducing (6.1) into the right-hand side of (6.2) shows that

$$S_{mn} = \delta_{mn} - \frac{i}{\hbar}\int_{w,R} \psi_{mE}^{0*}(H - H_m)\psi_{nE}^{(+)} R^2 dR \prod_i dw_i \quad (6.3)$$

Equations (6.2) and (6.3) then yield

$$S_{mn} = \delta_{mn} - \frac{i\hbar}{2\mu_m} \lim_{R\to\infty} R^2 \int_{w=0}^{1} \left(\psi_{mE}^{0*}\frac{\partial\psi_{nE}^{(+)}}{\partial R} - \psi_{nE}^{(+)}\frac{\partial\psi_{mE}^{0*}}{\partial R}\right)\prod_i dw_i. \quad (6.4)$$

When Eqs. (4.25) and (4.28) for $\psi_{nE}^{(+)}$ and Eq. (5.5) for ψ_{mE}^0 are introduced into (6.4), one obtains[19]

$$S_{mn} = \lim_{R\to\infty} \int_0^1 \left|\frac{\partial w_i}{\partial w_j^0}\right|^{-1/2} \left(\frac{(v+v_m)}{2(v_m v)^{1/2}}\right)(\exp i\Delta)\prod_i dw_i, \quad (6.5)$$

where v is the postcollision velocity at large R, as before, and is a function of w. Δ is given by

$$\Delta = [\phi^*(q,\alpha)/\hbar] - k_m R - 2\pi \sum_i m_i w_i + \tfrac{1}{2} m_1 \pi. \quad (6.5')$$

That is,

$$\Delta = 2\pi \sum_{i=1}^{r} \int_{w_i^0}^{w_i} (\bar{n}_i - n_i) dw_i + \int_{R_0}^{R} k dR - k_n R_0 - k_m R + 2\pi \sum_i (n_i - m_i) w_i + (n_1 + m_1 + 1)\tfrac{1}{2}\pi. \quad (6.6)$$

In (6.6), as noted earlier, the expression is independent of the lower limits, w_i^0 and R_0. Incidentally, if the value of $\phi^*(q,\alpha)$ for the unperturbed system in the mth state is denoted by $\phi_m{}^{*0}$, then inspection of (6.5′) and evaluation of (4.28) for the unperturbed problem shows that

$$\Delta=\phi^*-\phi_m{}^{*0}. \tag{6.6′}$$

In the case of an elastic collision Δ can readily be shown to reduce to

$$2\delta_l+2\pi\sum_i (n_i-m_i)w_i+(k_n-k_m)R-(n_1-m_1)\tfrac{1}{2}\pi,$$

where δ_l is given by (5.3). The pre-exponential factor in (6.5) becomes unity, and S_{mn} becomes its well-known value, $[\exp(2i\delta_l)]\delta_{mn}$.

When, as in the application of a steepest descents method (discussed later), the final value of $\bar{n}_i$ at a saddle point w' is (for each i) m_i, integration of (6.6) by parts yields for Δ', the value of Δ at w',

$$\Delta'=-2\pi\sum_{i=1}^{r}\int_{n_i}^{m_i} w_i d\bar{n}_i-\int_{-k_n}^{k_m} R dk+(n_1+m_1+1)\tfrac{1}{2}\pi, \tag{6.7}$$

since the initial value of $\bar{n}_i$ is n_i, and that of k is $p_R{}^0/\hbar$, i.e., $-k_n$.

From a numerical point of view, different values of $(w_1,\cdots,w_r{}^0)$ can be chosen at some R_0 and used to evaluate Δ and $(w_1,\cdots,w_r)$, using (6.6) and an integration of (4.15), respectively. Thereby, known values of $(\Delta, w_1,\cdots,w_r)$ are generated and can be employed to calculate (6.5)–(6.7) and the subsequent equations of Sec. VII.

In an examination of the behavior of (6.5) as $R\to\infty$ we have noted the following: In the case of $m=n$, i.e., of S_{nn}, Δ consists of an unperturbed term which vanishes and of a perturbed term which, by a simple change of variable w_i, can be made independent of R. In the case of $m\neq n$, the steepest descents method becomes applicable, as noted in the following section, and the integration by parts leading to (6.7) converts Δ to Δ', which is independent of R at large R, as already noted. Examples illustrating these different features for $m=n$ and for $m\neq n$, as well as those in Sec. VII, will be given in a later paper.

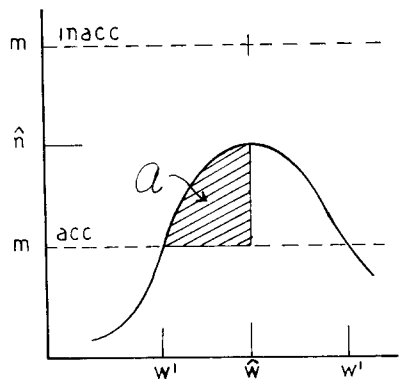


FIG. 3. Plot of number variable $\bar{n}[=(J/\hbar)-\delta]$ vs w in the vicinity of a maximum. The straight lines for $n=m$, an integer, are indicated for the classically accessible (acc.) and inaccessible (inacc) cases. The w' are saddle points. $\hat{n}$ is the curve maximum. The shaded area a appears in the final expressions for S_{mn}.

VII. EVALUATION OF S_{mn} USING EQ. (6.5)

The principal contribution to an integral of the type in (6.5) normally comes from the saddle points[20] or when there are none, from the integrand as a whole. Since an asymptotic method (WKB) was used to derive (6.5), grounds of consistency suggest that only the leading term (or terms) in the evaluation will be significant.

An example of an integral in (6.5) having no saddle points is that for the elastic collision. Here, the integral can be evaluated exactly, as in Sec. VI, to yield

$$S_{mn}=(\exp 2i\delta_l)\delta_{mn}. \tag{7.1a}$$

When in an inelastic collision system the "elastic case" of $m=n$ is considered, the steepest descents method will still not be suitable when S_{nn} is close to unity, and the integrand as a whole must be treated.

In an inelastic collision, for S_{mn} with $m\neq n$ or, when S_{nn} is small, for $m=n$, the integral in (6.5) will be the sum of its saddle-point contributions. In the remaining portion of this section we investigate this case.

The saddle points of Δ will be denoted by $(w_1',\cdots,w_r')$. Regarding each w_i as a complex variable, this w' is the solution of

$$0=\partial\Delta/\partial w_i=2\pi(\bar{n}_i-m_i)\qquad(w=w'). \tag{7.1b}$$

w' is real when the transition is classically accessible, and contains an imaginary component when the transition is classically inaccessible. We shall use the method of steepest descents (or that of stationary phase, when natural) to evaluate (6.5).

To illustrate some of the points and to serve as a check on our more general calculations we first consider in (i) and (ii) a more restricted case, a system having one w and a parabolic approximation to the usual $\bar{n}$ vs w plot in Fig. 3.[21] The actual curve in that figure is represented by

$$\bar{n}=\hat{n}-(w-\hat{w})^2 a(w)/2\pi, \tag{7.2}$$

where $a(w)$ is a function of w having zeros distant from $w=\hat{w}$, the position of the local maximum in Fig. 3; $\hat{n}$ is the value of $\bar{n}$ at $\hat{w}$. In the parabolic approximation $a(w)$ is a constant, a. The factor of 2π is introduced to simplify later notation. In Secs. VII.A and VII.B we consider the case where $\hat{n}$ is a local maximum at $\hat{w}$, while in Sec. VII.F the case where it is a local minimum is treated.

A. Parabolic Approximation; Classically Accessible Case

In the classically accessible case, m is less than $\hat{n}$ and the solutions of (7.1b) and (7.2) are

$$w'-\hat{w}=\pm[2\pi\mid\hat{n}-m\mid/a]^{1/2} \tag{7.3}$$

where the magnitude symbols about $\hat{n}-m$ are added for later notational convenience. The path of integration is along the real axis. The phase Δ in (6.5) is stationary at the points defined by Eq. (7.1b), leading to excessive cancellation of the integrand at all other regions but these, whenever the asymptotic method is appropriate. Hence, the pre-exponential factor in (6.5) can be replaced by its value at the saddle points (7.3) (Singularities or zeros of the pre-exponential factor near the saddle point appear to be rare,[22a] and throughout Sec. VII we shall suppose them to be absent. Should they arise, a modified treatment can be given.) Thereby, by (7.1b) and energy conservation, v equals v_m in the pre-exponential factor. We now have

$$S_{mn}=\mid\partial w/\partial w^0\mid^{-1/2}\int\exp i\Delta dw. \tag{7.4}$$

The original integration region over w of $[0, 1]$ can be changed to $(-\infty, +\infty)$. $\Delta(w)$ is expressed in terms of its value at $w=\hat{w}$, by integrating (7.2) [with $a(w)=a$ in the parabolic case]. This integration of (7.2), from $\hat{w}$ to w, yields

$$\Delta(w)=\Delta(\hat{w})+2\pi\mid\hat{n}-m\mid(w-\hat{w})-(a/3)(w-\hat{w})^3, \tag{7.5}$$

where the "magnitude symbols" about $\hat{n}-m$ are again added. Letting s denote $-a^{1/3}(w-\hat{w})$, Eqs. (7.4) and (7.5) now yield

$$S_{mn}=a^{-1/3}\mid\partial w/\partial w^0\mid^{-1/2}[\exp i\Delta(\hat{w})]\times\int_{-\infty}^{\infty}\exp[-ibs+\tfrac{1}{3}(is^3)]ds, \tag{7.6}$$

where

$$b=2\pi\mid\hat{n}-m\mid a^{-1/3}. \tag{7.7}$$

The integral in (7.6) is 2π times the Airy function $Ai(-b)$.[23] For later purposes it is useful to relate this argument b to the shaded area $\mathfrak{A}$ in Fig. 3: For the present parabolic case the area $\mathfrak{A}$ is the integral of $(n-m)dw$ from w' to $\hat{n}$ and so, from (7.3) and (7.5), is $[\Delta(\hat{w})-\Delta(w')]/2\pi$, where w' is the negative square root in (7.3). Using Eq. (7.5) one finds

$$\mathfrak{A}=[\Delta(\hat{w})-\Delta(w')]/2\pi=(2/3)\mid\hat{n}-m\mid^{3/2}(2\pi/a)^{1/2}. \tag{7.8}$$

According to (7.7) and (7.8) the argument of the Airy function equals $(-3\pi\mathfrak{A})^{2/3}$, and we have

$$S_{mn}=2\pi a^{-1/3}\mid\partial w/\partial w^0\mid^{-1/2}\times[\exp(i\Delta'+2\pi i\mathfrak{A})]Ai(-[3\pi\mathfrak{A}]^{2/3}), \tag{7.9}$$

Both Δ', given by (6.7), and $\mathfrak{A}$ can be calculated from the data on classical trajectories.

B. Parabolic Approximation; Classically Inaccessible Case

When the transition is classically inaccessible in Fig. 3, $\bar{n}-m$ is negative, the roots of (7.1b) are imaginary, and so the saddle points in the $w-\hat{w}$ complex plane lie on the imaginary axis. As noted later for a related integral, the present integration path along the real axis can be deformed in the complex plane without changing the value of the integral, and be made to lie along the line of steepest descents passing through the saddle point at $w'-\hat{w}=-i[2\pi\mid\hat{n}-m\mid/a]^{1/2}$. The pre-exponential factor in (6.5) can now be set equal to its value at this point, placed outside the integrand, and the integration path deformed back to its original position along the real axis. One then has

$$S_{mn}=a^{-1/3}\mid\partial w/\partial w^0\mid^{-1/2}[\exp i\Delta(\hat{w})]\times\int_{-\infty}^{\infty}\exp(ibs+\tfrac{1}{3}is^3)ds, \tag{7.10}$$

where b is given by (7.7), and where $\mid\partial w/\partial w^0\mid^{-1/2}$ is evaluated at the saddle point on the negative imaginary axis in the $w-\hat{w}$ complex plane. The new integral is 2π times the Airy function $Ai(b)$, where b is related to the area $\mathfrak{A}$ in Fig. 3 as discussed previously. Equation (7.10) becomes

$$S_{mn}=2\pi a^{-1/3}\mid\partial w/\partial w^0\mid^{-1/2}[\exp i\Delta(\hat{w})]Ai[(3\pi\mathfrak{A})^{2/3}], \tag{7.11}$$

where $\mid\partial w/\partial w^0\mid^{-1/2}$ is evaluated at the saddle point on the negative imaginary axis.

The question arises as to whether the $\Delta(\hat{w})$ in (7.11) is a collisional "invariant," in the sense of being independent of R once R becomes large. Letting Δ' now denote the value of Δ at the saddle point on the negative imaginary axis in the complex $w-\hat{w}$ plane, Eq. (7.5) shows that

$$\Delta'=\Delta(\hat{w})+2\pi i\mathfrak{A}\qquad\text{(classically inaccessible }\Delta'\text{)}, \tag{7.12}$$

where $\mathfrak{A}$ is given by (7.8) and is again the shaded area in Fig. 3. Equation (6.7) showed that Δ' is an invariant. Since $\mathfrak{A}$ is also an invariant, Eq. (7.12) shows that $\Delta(\hat{w})$ is. Both $\Delta(\hat{w})$ and $\mathfrak{A}$ are obtained from the trajectory data. If one wished, Δ' could then be obtained from the latter, even though w' is now classically inaccessible, by using (7.12).

The asymptotic forms[23] of (7.9) and (7.11), useful only when $\mathfrak{A}$ is not too small, illustrate the various features of those expressions, such as the oscillatory dependence of one on $\mathfrak{A}$ and the exponential dependence

of the other:

(accessible)

$$S_{mn}=C\{\exp[i\Delta'+(i\pi/4)]+\exp[i\Delta'+4\pi i\mathfrak{A}-(i\pi/4)]\} \tag{7.13}$$

(inaccessible)

$$S_{mn}=C\exp[-2\pi\mathfrak{A}+i\Delta(\hat{w})], \tag{7.14}$$

where

$$C=\pi^{1/2}a^{-1/3}(3\pi\mathfrak{A})^{-1/6}\,|\,\partial w/\partial w^0\,|^{-1/2}. \tag{7.15}$$

In (7.14), $|\,\partial w/\partial w^0\,|^{-1/2}$ is evaluated at the relevant saddle point; in (7.13) it can be evaluated at either saddle point[22b]; the Δ' in (7.13) is given by (6.7) and refers to the saddle point on the negative real axis of the $w-\hat{w}$ complex plane. The "$\Delta'/2\pi$" for the second saddle point, the one on the positive real axis, is that for the first plus the area difference $2\mathfrak{A}$, as one sees from Fig. 3, thus providing an insight into the second exponent in (7.13).

Finally, both here and in later sections one should distinguish between classical inaccessibility and energetic feasibility. Some classically inaccessible transitions involve so much energy expenditure that the k_m at $R=\infty$ would be imaginary. Their partial wave is exponentially damped there and such channels are "closed."

C. More General Case, Introduction

We turn now to the more general case. In the case of classically inaccessible transitions, with their inverse exponential dependence on the area $\mathfrak{A}$, the parabolic approximation will sometimes be too restrictive. The error is of course much less for the classically accessible transition. However, in this case there is another reason for treating a more general $\bar{n}$ vs w plot: In several dimensions quadratic expansions of Δ about the saddle points are usually acceptable, but independent cubic expansions of the type in (7.5), one per degree of freedom, may be less realistic when those degrees of freedom are significantly coupled.

When the saddle points in (6.5) are fairly isolated the leading term in the asymptotic expansion is obtained by expanding the exponent, Δ, in a power series about the saddle point $(w_1', \cdots, w_r')$ and omitting powers of w_i-w_i' higher than the second. Diagonalization of the resulting quadratic serves to locate the initial direction of the path of steepest descents. (When further terms in the asymptotic expansion are needed more data than the initial direction is used.) After expansion of the exponent the integrand is Gaussian-like and the integration interval can be made infinite.[24] There are frequently a number of saddle points w' and the integral becomes the sum over the saddle points. Equation (6.5) thus yields

$$S_{mn}=\sum_{w'}(\exp i\Delta')\int_{-\infty}^{\infty}\left|\frac{\partial w_i}{\partial w_j^0}\right|^{-1/2}\times\exp\left[\frac{i}{2\hbar}\sum_{i,j}\left(\frac{\partial^2\phi}{\partial w_i\partial w_j}\right)_{w=w'}(w-w_i')(w-w_j')\right]\prod_i dw_i$$

$$=\sum_{w'}\left|\frac{\partial w_i}{\partial w_j^0}\right|^{-1/2}\hbar^{r/2}\left|\frac{-i\partial^2\phi}{\partial w_i\partial w_j}\right|^{-1/2}\exp i\Delta', \tag{7.16}$$

where the absolute value is not intended in the $r\times r$ determinant

$$|\,-i\partial^2\phi/\partial w_i\partial w_j\,|^{-1/2},$$

but rather due account of the phase of each factor is to be taken. For example, in the case of a real $\partial^2\phi/\partial w^2$, $|\,-i\partial^2\phi/\partial w_i\partial w_j\,|^{-1/2}$ has a phase of $(-\pi/2)(-1/2)$ or $(+\pi/2)(-1/2)$, i.e., $\pi/4$ or $-\pi/4$, according as $\partial^2\phi/\partial w^2$ is positive or negative. In the case of two dimensions we may suppose for illustration that the axes in $(w-w')$ space have been rotated so that $\partial^2\phi/\partial w_1\partial w_2$ vanishes and, hence, so that $\partial^2\phi/\partial w_1^2$ and $\partial^2\phi/\partial w_2^2$ become the principal curvatures of the ϕ vs (w_1, w_2) surface at the saddle point. (Since $\partial\phi/\partial w_1=\partial\phi/\partial w_2=0$ there, the usual formula for curvatures of a surface contains only second derivatives.) According as the two curvatures are both positive, both negative, or of opposite sign the phase of $|\,-i\partial^2\phi/\partial w_i\partial w_j\,|^{-1/2}$ is $[(-\pi/2)+(-\pi/2)](-1/2)$, $[(\pi/2)+(\pi/2)](-1/2)$, or $[(-\pi/2)+(\pi/2)](-1/2)$, i.e., $\pi/2$, $-\pi/2$, or 0, respectively.

The value of $\partial\phi/\partial w_i$ is $(\bar{n}_i+\delta_i)h$ so that the $\partial^2\phi/\partial w_i\partial w_j$ equals $h\partial\bar{n}_i/\partial w_j$. Since the product $|\,\partial w_i/\partial w_j^0\,|^{-1/2}\,|\,-i\partial\bar{n}_i/\partial w_j\,|^{-1/2}$ in (7.16) equals $|\,-i\partial\bar{n}_i/\partial w_j^0\,|^{-1/2}$, with the precautions referred to regarding phase of $\partial^2\phi/\partial w_i\partial w_j$ being again understood, Eq. (7.16) becomes

$$S_{mn}=\sum_{w'}|\,-i\partial\bar{n}_i/\partial w_j^0\,|^{-1/2}\exp i\Delta'. \tag{7.17}$$

D. Application of Eq. (7.17) to Classically Accessible Case

Equation (7.17) can be shown to reduce to (7.13) when the special assumptions of the latter are introduced.

The simple classical Eq. (2.3) also follows from (7.17): one first notes that Δ' for a classically accessible transition is real since the saddle- points in (6.7) are real. $S_{mn}{}^*S_{mn}$ may be computed from (7.17) to obtain the transition probability. If interferences (i.e., cross terms) between different saddle points are ignored, a permissible step when they are sufficiently far apart that their average over a small range of initial translational kinetic energies is zero, one obtains (2.3), summed over all contributing saddle points.

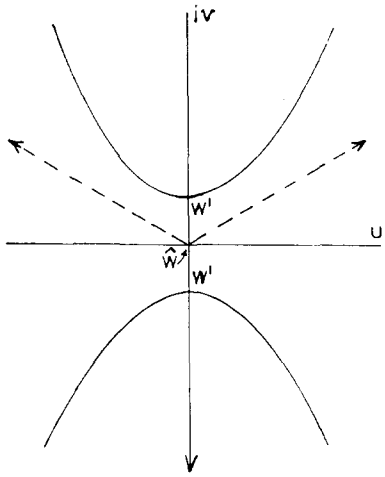


FIG. 4. Plot of the $w-\hat{w}$ complex plane, indicating the saddle points w' and curves of steepest descent for the classically inaccessible case. The three directions on which $\exp i\Delta$ becomes infinite at infinity are indicated by arrows. The original path of integration is the real axis and the deformed path coincides with the lower hyperboliclike curve, or, in the saddle-point approximation, with a straight line tangent to it at w'. Various curves (solid and dotted) for the classically accessible case are obtained by clockwise rotation of the curves through 90°.

E. Application of Eq. (7.17) to Classically Inaccessible Case

In this illustration of (7.17) the one-dimensional case based on (7.2) will be treated. (The arguments are also readily extended to the case of a local minimum.) The function $a(w)$ will be chosen so as not to distort the parabolic shape of (7.2) in the immediate vicinity of the maximum. Thereby, its zeros are appreciably removed from $\hat{w}$ and so the first few derivatives of $a(w)$ are small near $\hat{w}$ or near the saddle point. It is also supposed, as is frequently done in phase integral treatments[25] involving an analogous quantity, that $a(w)$ is such that the roots of (7.1b) for negative $\hat{n}-m$ are obtained from those for positive $\hat{n}-m$ by multiplying the latter by i. [An exact example occurs when $a(w)$ can be expanded as $1+c_1(w-\hat{w})^4+\cdots$]. Thus, for this classically inaccessible case the saddle points w' are given by (for a symmetrical $\bar{n}$ vs w curve, for illustration)

$$w'-\hat{w}=\pm i[2\pi\,|\,\hat{n}-m\,|/a(w')]^{1/2}, \tag{7.18}$$

where $a(w')$ is the same for both roots, and equals $a(\bar{w}')$, where $\bar{w}'$ denotes the known (real) roots for the classically accessible case with the same $|\,\hat{n}-m\,|$. Thus,

$$w'-\hat{w}=i(\bar{w}'-\hat{w}). \tag{7.19}$$

Curves of steepest descents have constant phase, Δ, and pass through one or more saddle points.[20] Some insight into their position near the saddle point is obtained by setting $a(w)$ in (7.2) equal to its value there $a(w')$, and hence to $a(\bar{w}')$, and noting that $a(\bar{w}')$ is real. The expression for Δ is now a cubic in $w-\hat{w}$. When $w-\hat{w}$ is written as $u+iv$, and introduced into the integrated expression, the phase of Δ may be computed and equated to its value at a saddle point. The curves of steepest descents are found to satisfy the equation[26]

$$u(3v^2-u^2-3x)=0, \tag{7.20}$$

where

$$x=2\pi\,|\,\hat{n}-m\,|/a(\bar{w}'). \tag{7.21}$$

The second saddle point satisfies a similar equation, and the three solutions to (7.20) are two branches of a hyperbola, each of which passes through one saddle point, and the imaginary axis, which passes through both, as in Fig. 4. The original path of integration in (6.5), which was along the real axis, is next deformed to one of these curves of steepest descents. To avoid changing the value of the integral in the process, the deformation of the path should involve no crossing of singularities, and the value of the integral along the path completing the contour at ∞ should be zero. The general location of the singularities is readily determined and shows how to deform the path:

When $w-\hat{w}$ is small, $a(w)$ may be set equal to $a(\hat{w})$ in (7.2) and the result integrated to obtain Δ. The integrated expression shows that $\exp(i\Delta)$ would tend to infinity along the radii $\infty\ \exp i\pi/6$, $\infty\ \exp(5i\pi/6)$ and $\infty\ \exp(-i\pi/2)$ (Fig. 4). The presence of a nonconstant $a(w)$ distorts such curves but their general location with respect to the saddle points w' and the lines of steepest descents is largely unchanged. The (undistorted) curves are indicated schematically by dotted lines in Fig. 4. From this figure it is seen that if the saddle point on the negative imaginary axis is selected, the original path of integration in Eq. (6.5) may be deformed to coincide with the hyperbola (the curve of steepest descent) passing through that saddle point or be tangent to it there, without crossing singularities and with having a zero contribution from the path completing the contour at ∞.

Integration of (6.5) using the method of steepest descents and leading to (7.16) can thus be performed. In (7.16) $\exp(i\Delta')$ is to be evaluated from the trajectory data, even though it has imaginary components, as in (7.26) below. Integrating Eq. (7.2) for this purpose, from $w=\hat{w}$ to $w=w'$ we have (since $m>\hat{n}$)

$$\Delta'-\Delta(\hat{w})=\int_{\hat{w}}^{w'}[-2\pi\,|\,\hat{n}-m\,|-(w-\hat{w})^2a(w)]dw. \tag{7.22}$$

Setting $w-\hat{w}$ equal to $(-is)$, then using (7.19) and the equality of $a(\hat{w}-is)$ and $a(\hat{w}-s)$ discussed earlier, Eq. (7.22) yields

$$\Delta'-\Delta(\hat{w})=i\int_0^{-(\bar{w}'-\hat{w})}[2\pi\,|\,\hat{n}-m\,|-s^2a(\hat{w}-s)]ds, \tag{7.23}$$

where $\bar{w}'$ is on the negative real axis in the $w-\hat{w}$ complex plane.

Equation (7.23) may be compared with the change in Δ in the classically accessible case, where w changed from $\bar{w}'$ to $\hat{w}$, along the real axis. The change in Δ for this case is the shaded area under the curve in Fig. 3, and is again denoted by $\mathfrak{A}$ though now without any parabolic approximation to the curve in Fig. 3. Integration of Eq. (7.2) yields, for this classically accessible case,

$$\mathfrak{A}=\int_{\bar{w}'}^{\hat{w}}[|\hat{n}-m|-(w-\hat{w})^2a(w)(2\pi)^{-1}]dw. \quad (7.24)$$

Setting $w-\hat{w}$ equal to $-s$ we have

$$\mathfrak{A}=\int_0^{-(\bar{w}'-\hat{w})}[|\hat{n}-m|-s^2a(\hat{w}-s)(2\pi)^{-1}]ds. \quad (7.25)$$

Equations (7.23) and (7.25) show that

$$\Delta'=\Delta(\hat{w})+2\pi i\mathfrak{A}, \quad (7.26)$$

and so Eq. (7.17) becomes

$$S_{mn}=\sum_{w'}|-i\partial\bar{n}_i/\partial w_j^0|^{-1/2}\exp(-2\pi\mathfrak{A}+i\Delta(\hat{w})). \quad (7.27)$$

Since $\Delta(\hat{w})$ can be calculated from the trajectory calculations, because $\hat{w}$ is classically accessible, and since the area $\mathfrak{A}$ is also known, Δ' can be calculated from (7.26). The exponent in (7.27) is identical with that in Eq. (7.14), but is no longer restricted to the parabolic case; $\mathfrak{A}$ is now the shaded area under the actual curve in Fig. 3.

For further comparison of (7.14) and (7.27) one writes $|-i\partial\bar{n}_i/\partial w_j^0|^{-1/2}$ at the saddle point in its original form in (7.16), $|\partial w_i/\partial w_j^0|^{-1/2}|-i\partial\bar{n}_i/\partial w_j|^{-1/2}$. Using Eq. (7.2) and neglecting the derivative of $a(w)$, as discussed earlier, $\partial\bar{n}/\partial w$ is found to be $-(w'-\hat{w})a(w')/\pi$. If, for the comparison, $a(w)$ in (7.25) is written as $a(w')$ and the integration performed, $\mathfrak{A}$ can be computed. In this way $\partial\bar{n}/\partial w$ can be expressed in terms of $\mathfrak{A}$. One finds thereby that (7.4) can be obtained from (7.27).

Similarly, for the classically accessible case, Eq. (7.13) can be deduced from (7.17) without the parabolic restriction. This result and the preceding one indicates that Eqs. (7.9) and (7.11) are also applicable without the parabolic restriction.

F. Case Where Curve (7.2) Refers to a Local Minimum

In this case $a(w)$ is negative and classical accessibility implies that $m>\hat{n}$, $\hat{n}$ being the local minimum of n. In Eq. (7.5) the sign of the two last terms are altered. If s now denotes $|a|^{1/3}(w-\hat{w})$, Eq. (7.6) is again obtained, with a in (7.7) now replaced by $|a|$. The integral is again $2\pi Ai(-b)$. The half-area enclosed between $n(w)$ curve and the $\bar{n}=m$ horizonal line (the shaded area in Fig. 3) is seen by inverting Fig. 3 to be "negative." If it is denoted by $-\mathfrak{A}$, where $\mathfrak{A}$ is positive, then (7.8) is replaced by

$$-\mathfrak{A}=[\Delta(\hat{w})-\Delta(w')]/2\pi \quad (7.28)$$

and Eq. (7.9) is again obtained, but with $2\pi i\mathfrak{A}$ replaced by $-2\pi i\mathfrak{A}$.

In a classically inaccessible transition we now have $\hat{n}>m$. Eq. (7.10) would again follow, with b given by (7.7) and a now denoting $|a|$. Eq. (7.27) would also follow. The desired saddle point is now on the positive imaginary axis and the details of the discussion leading to (7.27) would be modified accordingly.

VIII. CANONICAL PERTURBATION THEORY

To gain some insight into the ϕ in (4.17b) and hence into the ϕ^* of (4.28) and the Δ of (6.6), as well as to relate its properties to previous studies[2-5] it is useful to develop here a canonical perturbation theory for the time-independent Hamiltonian–Jacobi equation (4.9).[27] Normally, the canonical perturbation theory for the latter equation has been one which is appropriate to bound state problems, rather than collisions. The one derived below is suitable for collisions.

The Hamiltonian H, written in terms of a perturbation parameter λ, is

$$H(q,\partial\phi/\partial q)=H_0(q,\partial\phi/\partial q)+\lambda H_1(q,\partial\phi/\partial q)=E, \quad (8.1)$$

where E is α_{r+1} as before. The generating function ϕ, expanded in powers of λ, is

$$\phi(q,\alpha)=\sum_{N=0}^{\infty}\phi_N(q,\alpha)\lambda^N. \quad (8.2)$$

When (8.2) is introduced into (8.1), and both H_0 and H_1 are then expanded in powers of λ, one obtains

$$H_0(q,p^{(0)})+\lambda H_1(q,p^{(0)})+\sum_{\text{all }n_i=1}^{\infty}\prod_{i=1}^{r+1}\left(\frac{\partial^{n_i}}{\partial p_i^{(0)n_i}}H_0(q,p^{(0)})+\lambda H_1(q,p^{(0)})\right)\times\left[\lambda^{n_i}\left(\frac{\partial\phi_N}{\partial q_i}\right)^{n_i}\Big/n_i!\right]=E, \quad (8.3)$$

where

$$p^{(0)}=\partial\phi_0(q,\alpha)/\partial q. \quad (8.4)$$

Equating equal powers of λ one obtains

$$H_0(q,p^{(0)})=E, \quad (8.5)$$

$$\sum_{i=1}^{r+1}\frac{\partial H_0}{\partial p_i^{(0)}}\frac{\partial\phi_N}{\partial q_i}=-K_N(q,\alpha)\qquad(N=1,2,\cdots), \quad (8.6)$$

where the first several terms are

$$K_1(q,\alpha)=-H_1(q,p^{(0)}), \quad (8.7)$$

$$K_2(q,\alpha)=\{\phi_1,H_1\}+(1/2!)\{\phi_1,\{\phi_1,H_0\}\}, \quad (8.8)$$

$$K_3(q,\alpha)=\{\phi_2,H_1\}+(1/2!)\{\phi_1,\{\phi_1,H_1\}\}+(1/3!)\{\phi_1,\{\phi_1,\{\phi_1,H_0\}\}\}, \quad (8.9)$$

and $\{X,Y\}$ denotes

$$\{X,Y\}=\sum_{i=1}^{r+1}\left(\frac{\partial X}{\partial q_i}\frac{\partial Y}{\partial p_i^{(0)}}-\frac{\partial X}{\partial p_i^{(0)}}\frac{\partial Y}{\partial q_i}\right). \quad (8.10)$$

Equations (8.8)–(8.10) employ a compact notation which distinguishes α_i from $p_i^{(0)}$, i.e., the $\partial\phi_N(q,\alpha)/\partial p_i^{(0)}$ are zero there.

The sequence of equations (8.6) can be solved for the ϕ_N's by the method of characteristics.[15] The latter yields

$$\frac{dq_i}{\partial H_0/\partial p_i^{(0)}} = \frac{d\phi_N}{\sum_i (\partial\phi_N/\partial q^i)(\partial H_0/\partial p_i^{(0)})} \cdot$$

$$= \frac{d(\partial\phi_N/\partial q_i)}{-\partial K_N/\partial q_i} \cdot \tag{8.11}$$

Setting (8.11) equal to an infinitesimal parameter "dt" and using a dot to denote d/dt, we have

$$\dot{q}_i = \partial H_0/\partial p_i^{(0)}, \tag{8.12}$$

which, for the w_i, yields

$$w_i = w_i^0 + \nu_i^0(t-t_0), \tag{8.13}$$

where ν_i^0 is the i'th unperturbed frequency, $\partial H_0/\partial p_i^{(0)}$. For R, Eq. (8.12) yields

$$R-R_0 = \int_{t_0}^{t}\left[2\left(\epsilon - V(R') - \frac{J_{n_1}^2}{8\pi^2\mu R'^2}\right)\Big/\mu\right]^{1/2} dt', \tag{8.14}$$

where R' denotes $R(t')$, and where ϵ is $k_n^2\hbar^2/2\mu$. Hence, the parameter t is uniquely specified by R and the sign of p_R, and can be understood as $t(R, \mathrm{sgn}p_R)$ and abbreviated as $t(R)$. Since $d\phi_N$ is seen from (8.6) and (8.11) to be $-K_N(q,\alpha)dt$ along the characteristics, integration yields

$$\phi_N = -\int_{-\infty}^{t(R)} K_N(\tilde{q}(\tau),\alpha)d\tau \qquad (N=1, 2, \cdots), \tag{8.15}$$

where $\tilde{q}(\tau)$ is the q evolving with τ according to (8.12), and hence with (8.13)–(8.14). In (8.15) the $\tilde{q}_i(\tau)$ must be chosen so that

$$\tilde{q}_i(\tau) = q_i \quad \text{at} \quad \tau = t(R), \tag{8.16}$$

i.e., $\tilde{w}_i$ and $\tilde{R}$ are given by (8.13)–(8.14) with w_i^0, t_0, and R_0 replaced by $\tilde{w}_i$, τ, and $\tilde{R}$. ϕ is obtained from (8.2) by setting $\lambda=1$. Examination of (8.7)–(8.10) and (8.15) shows that, when present in the integrand of (8.15), $\{X, V\}$ becomes a Poisson-Bracket: it becomes expressed in terms of variables $\tilde{q}_i$ and $p_i^{(0)}$, variables which are canonically conjugate in the unperturbed problem.

$$\phi(q,\alpha) = \sum_{N=0}^{\infty} \phi_N(q,\alpha), \tag{8.17}$$

where ϕ_N is given by (8.15).

In (8.15) ϕ_N depends on R, both directly and (implicitly) via the presence of a $t(R)$ in the integration limit, and in the integrand in the expression for the $\tilde{q}_i(\tau)$, which conforms to (8.16). Illustrations and applications of the formalism based on (8.6)–(8.17) will be given in subsequent papers.

In a previous paper, we have tested an expression equivalent to the first-order approximation, $\phi_0+\phi_1$, and in certain respects have tested one equivalent to $\phi_0+\phi_1+\phi_2$ by comparing the exact (numerical) and approximate values of the action variable after the collision.[3b] ($J_i=\partial\phi/\partial w_i$, i.e., $J_{n_i}+\partial\phi_1/\partial w_i$ in the first approximation and $J_{n_i}+\partial\phi_1/\partial w_i+\partial\phi_2/\partial w_i$ in the second.) The agreement was encouraging and the range of validity was ascertained for various molecular parameters. The results are used in the Discussion section, to consider Eq. (6.5)–(6.6) for S_{mn}. The ϕ_N terms can be introduced via (4.26) and (6.5)–(6.6) or via the relations

$$\bar{n}_i = n_i + n_i^{(1)} + n_i^{(2)} + \cdots,$$

$$w_i^0 = \tilde{w}_i^0 + w_i^{0(1)} + w_i^{0(2)} + \cdots$$

$$k = k_n + k^{(1)} + k^{(2)} + \cdots, \qquad v = k\hbar/\mu_n, \tag{8.18}$$

where

$$n_i^{(N)} = \hbar^{-1}\partial\phi_N/\partial w_i, \qquad w_i^{0(N)} = \partial\phi_N/\partial J_{n_i},$$

$$k^{(N)} = \hbar^{-1}\partial\phi_N/\partial R, \tag{8.19}$$

and $n_i+\delta_i$, $\tilde{w}_i^0$ and k_n are $\hbar^{-1}\partial\phi_0/\partial w_i$, $\partial\phi_0/\partial J_{n_i}$, and $\hbar^{-1}\partial\phi_0/\partial R$, respectively. We note for (8.19) that $\partial/\partial w_i$ and $\partial/\partial J_{n_i}$ are commutative with the integral sign in (8.15).

These equations can also be applied to the pre-exponential factor in (4.23), (6.5), and (7.17).

IX. REMARKS ON SEC. VIII AND ON COLLISIONAL SELECTION RULES

The approximations, $\phi_0+\phi_1$ and $\phi_0+\phi_1+\phi_2$, have been tested, in part, for several collisions,[3b,28] and the results may be applied to (6.5) or (7.16). We reserve for a later communication a more detailed discussion of them. For certain fairly wide ranges of molecular parameters, $\phi_0+\phi_1$ provided an excellent approximation. (This approximation was referred to as $\Delta j^{||}$ in Ref. 3b, and many curves are given there relating $\Delta j^{||}$ to the exact change of rotational angular momentum of the molecule as a result of collision.)

The value of $\bar{n}_i-n_i$ at any w_j always equals that at w_j+1 since H is periodic in the w_i's, with unit period. In addition, because of some suitable symmetry in H, H may have a higher periodicity in w_i, with period $1/M_i$, where M_i is an integer. Then, $\bar{n}_i-n_i$ for the family of characteristics passing through w_i is the same as $\bar{n}_i-n_i$ for the family passing through $w_i+M_i^{-1}$. Thus, in an $\bar{n}_i$ vs w_i plot for this case there are M_i oscillations in the unit interval of w_i. In this case, for a classically accessible transition, there are $2M_i$ saddle points. For a classically inaccessible transition, there would be M_i saddle points for the (M_i) maxima in the $\bar{n}_i$ vs w_i plot and M_i for the (M_i) minima.

The above result has immediate implications for selection rules as well. If one integrates (6.5) first over w_i, one finds that the integral will now vanish unless

$n_i - m_i = 0, \pm M_i, \pm 2M_i, \cdots$, etc.[29] For the case where Δ has a simple cosine or sine dependence on w_i then if the exponent in (6.5) is expanded and only the first two terms are retained, (6.5) would give $n_i - m_i = 0, \pm M_i$, while if the third term in the expansion is also retained one would have $0, \pm M_i, \pm 2M_i$, and so on. (Other selection rules, based on other symmetries in H, when they exist, will be considered in a later paper.)

Thus, application of group theoretic considerations prior to application of asymptotic methods simplifies the problem by reducing the w_i domain of integration. (However, asymptotic methods could be applied first. There would be cancellations from various saddle-point contributions, giving rise to the same selection rules as those obtained above.)[30]

An example of the selection rules occurs in the collision of an atom with a symmetric top molecule such as NH_3; the component of the interaction force acting on the rotation about the symmetry axis has mainly a Fourier component of 3 times the corresponding rotational frequency. Hence, selection rules for the change of $K\hbar$, the component of the rotational angular momentum along the symmetry axis is $0, \pm 3$ in lowest-order quantum mechanical perturbation theory and $0, \pm 3, \pm 6, \cdots$ in higher orders. Similarly, in the case of a collision of an atom with a homonuclear diatomic rigid rotor M is 2 and the selection rule should be $j = 0, \pm 2, \cdots$. The two oscillations per unit w interval in an $\bar{n}_i$ vs w_i plot here may be seen in Figs. 4 and 5 of Ref. 4b (where only one-half the w interval was plotted to avoid repetition).

The true saddle points are those for which Eq. (7.1b) is fulfilled for all i simultaneously. While coalescence of saddle points is common in the case of one dimension, our impression on examining the results in Ref. 3b is that it is rarer in the case of interacting degrees of freedom (varying in probability of occurrence as p^N, where N is the number of interacting degrees of freedom, and p is the probability for one). For example, one finds from the equations in Ref. 3b that when the saddle points for the j vs w plot tend to coalesce, (j is the rotational angular momentum quantum number), those for the m_j vs w plot do not (at least usually do not).

X. CONCLUDING REMARKS

In the present paper we have attempted to show how the Hamilton–Jacobi equation for collision problems, solved with the aid of the method of characteristics, can be used to obtain the WKB solution and the S matrix for inelastic collisions. In the process the relation to our previous action-angle variable studies of the classical mechanics of collisions has been noted, as has the application of a canonical perturbation treatment of collisions. The application of complex variable techniques, particularly in the form of steepest descents or stationary phase, has also been described.

One approximation which has been employed in the literature of inelastic collisions, the sudden approximation,[31] corresponds to setting all $v_i^0 = 0$ and $R = \tilde{R}$ in Eq. (9.1) [K_N for $N \geq 2$ then vanish in (8.15)], and then introducing the result into (6.5). The eikonal approximation[32] corresponds in part to replacing the relative translational motion (R and the two orbital w_i's) by a straight line trajectory. The usual first-order distorted wave approximation corresponds to expanding the exponential in (6.5) and retaining only the first two terms, while second-order distorted wave theory corresponds to retaining the next term. In the sometimes termed "semiclassical approximation,"[33] the relative translational motion (R and the two orbital w_i's) is treated classically (and sometimes in the rectilinear path approximation); the other motions are treated in terms of the $\phi_0 + \phi_1$ or $\phi_0 + \phi_1 + \phi_2$, approximations, or sometimes by numerical solution of the coupled equations for the wavefunctions of these remaining $r - 2$ degrees of freedom.

The final equations of the present paper should also apply to chemical reactions, with certain restrictions dealing with the change of phase in the radial contribution in a partial wave when the system is reflected from the incoming into the outgoing channel. This problem will be treated subsequently.

While the principal equations refer to the S matrix, the method requires relatively little modification, as mentioned earlier, to treat differential and total inelastic cross sections directly. In (4.16) the boundary condition is modified so that the incident $\phi(q, \alpha)$ is of the form

$$\mathbf{k}_n \cdot \mathbf{r}_\alpha + 2\pi \sum_{i=3}^{r} n_i w_i,$$

where the summation is over the $r - 3$ internal coordinates of the collision partners and where α defines the incident direction. Equations (4.19)–(4.21) for the flux conservation are modified to include the new geometry.[34] Finally, in the treatment of (4.25)–(4.28) and (6.1)–(6.7) leading to the S and T matrices, the wavefunction $\psi_{nE}^{(+)}$ is replaced by the expression for the full (incident plane wave plus scattered wave) wavefunction in terms of scattering amplitudes. The analog of (6.3) based on an integration of the new (6.2)[19] by parts is then applied to calculate the scattering amplitude. The formal details are given in a subsequent communication.

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research. This paper was presented at the Conference on Potential Energy Surfaces, University of California, Santa Cruz, California, 10–13 August 1970, and is described in the proceedings of that conference [W. A. Lester, Jr. (Ed.), IBM, San Jose, Calif. 1970]. Compare, R. A. Marcus, Chem. Phys. Letters **7,** 525 (1970), for that summary and introduction to the present article.

[1] See, for example, M. Born, *The Mechanics of the Atom* (Ungar, New York, 1960) (English translation).

[2] R. A. Marcus, J. Chem. Phys. **45,** 4500 (1966); **49,** 2617 (1968).

[3] (a) A. O. Cohen and R. A. Marcus. J. Chem. Phys. **49,** 4509 (1968); (b) **52,** 3140 (1970).

[4] M. Attermeyer and R. A. Marcus, J. Chem. Phys. **52,** 393 (1970).

[5] S.-f. Wu and R. A. Marcus, J. Chem. Phys. **53,** 4026 (1970).

[6] (a) W. H. Miller, J. Chem. Phys. **53,** 1949 (1970); (b) J. Chem. Phys. **53,** 3578 (1970). The Feynman propagator has also been applied by P. Pechukas to elastic collisions [Phys. Rev. **181,** 166 (1969)] and to atomic excitation [*ibid.* **181,** 174 (1969)].

[7] See, for example, L. D. Landau and E. M. Lifshitz, *Quantum Mechanics,* (Addison-Wesley, Reading, Mass. 1958).

[8] In the present paper, complications in the R motion, such as tunneling through centrifugal barriers, are omitted for simplicity. It is planned later to blend WKB treatments of the latter [e.g., J. N. L. Connor, Mol. Phys. **16,** 525 (1969)] with the present one.

[9] See, for example, K. W. Ford and J. A. Wheeler, Ann. Phys. **7,** 259 (1959); R. B. Bernstein, Advan. Chem. Phys. **10,** 75 (1966); M. V. Berry, Proc. Phys. Soc. (London) **89,** 479 (1966); W. H. Miller, J. Chem. Phys. **48,** 464 (1968); M. V. Berry, J. Phys. B **2,** 381 (1969); A. S. Dickinson, Mol. Phys. **18,** 441 (1970).

[10] P. A. M. Dirac, Proc. Roy. Soc. (London) **A111,** 281 (1926); **A114,** 243 (1927). Dirac's prescription for the J_i led to WKB-type results for the orbital motion. [Angular momentum $=(l+1/2)\hbar$]. Unless considerable care is taken, e.g., as in B. Leaf [J. Math. Phys. **10,** 1980 (1969)] for the harmonic oscillator, action-angle variable mechanics would not yield results better than WKB. For our present purpose, this shortcoming does not matter.

[11] P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford U. P., New York, 1958), 4th ed. We have used the prescription given here (p. 92) for any momentum operator p_i in a coordinate representation. As noted there (p. 93), addition of a function of coordinates to the definition is equivalent to a coordinate-dependent phase shift in the eigenfunctions. Dirac himself used commutation relations rather than a w representation in Ref. 10. For an action-angle quantum mechanics see also P. Jordan, Z. Physik **40,** 809 (1927); **44,** 1 (1927). Action-angle aspects of the oscillator problem are considered by B. Leaf[10] and of the rotational problem by L. C. Biedenbarn and P. J. Brussard, Ann. Phys. **16,** 1 (1961).

[12] J. B. Keller, Ann. Phys. **4,** 180 (1958). For an application of the latter to wave functions and eigenvalues of a three-body problem see D. J. Vezzetti and S. I. Rubinow, *ibid.* **35,** 373 (1965).

[13] (a) Dirac, Ref. 11, pp. 121–123. In that treatment the q_i's were general, and the detailed form of H was not specified for the case where some of the q_i's were angle variables. Thereby, that equation did not contain the δ_i's used in (3.1) [and (4.1)] to match WKB eigenvalues for the unperturbed problem. In the step corresponding to an expansion of Dirac's Eq. (37) in powers of $\hbar$, we retain the $\hbar\delta_i$ with the $\partial\Phi/\partial q_i$, rather than expanding the former, to fulfill the purpose of the δ_i's.

The Hermitian $\mathbf{p}_R$-dependent term in H_0 and H is

$$(1/2\mu R^2)\mathbf{p}_R R^2 \mathbf{p}_R.$$

(b) The derivation in Ref. 13a, as well as those in Ref. 12 and in J. H. Van Vleck, Proc. Natl. Acad. Sci., **14,** 178 (1928), employ a formalism based on the unit weight function in the volume element. However, the results are readily transformed to some with weight function ρ (our ρ is R^2), as follows [for related manipulations of Hamiltonians, see E. C. Kemble, *The Fundamental Principles of Quantum Mechanics* (Dover, New York, 1958), p. 239]: If primes are used to denote properties in the system with unit weight function then the volume element dV' is $\Pi_i dq_i$, dV is $\rho\Pi_i dq_i$, and so $dV=\rho dV'$. Here $|\psi|^2 dV$ is an invariant and so equals $|\psi'|^2 dV'$, whence $|\psi'|^2=\rho|\psi|^2$, i.e., the amplitude A' equals $\rho^{1/2}A$. If $\mathbf{i}$ denotes a probability current density, i.e., if $\mathbf{i}=|\psi|^2\dot{\mathbf{q}}$, where $\dot{q}$ has velocity components $\dot{q}_i(=\partial H/\partial p_i)$, $\dot{\mathbf{q}}$ is the same in the two systems since the classical H is the same, and thus $\mathbf{i}'=\mathbf{i}'\rho$.

Here $(\nabla\cdot\mathbf{i})dV$ is an invariant, and so equals $(\nabla'\cdot\mathbf{i}')dV'$. Since ∇' has components $\partial/\partial q_i$, one finds using the above ratios of $\mathbf{i}'/\mathbf{i}$, and dV'/dV that ∇ has components $\rho^{-1}(\partial/\partial q_i)\rho$. In Ref. 13a it was shown that $\nabla'\cdot(A'^2\dot{\mathbf{q}})=0$, i.e., $\nabla'\cdot\mathbf{i}'=0$. Since $\nabla\cdot\mathbf{i}$ equals $(\nabla'\cdot\mathbf{i}')\ (dV')/dV$, $\nabla\cdot\mathbf{i}=0$. Using the components for $\nabla\cdot$ and $\mathbf{i}$ given above, and Eq. 42 of Ref. 13a, Eq. (4.4) of the present paper is obtained.

In the preceding argument, incidentally, it has not been assumed that the Hamiltonian contains an operator ∇^2, and indeed such an assumption would be inappropriate for action-angle variables. The value obtained above for the divergence vector nevertheless coincides with that found for curvilinear coordinates for which the Hamiltonian does contain ∇^2.

[14] See, for example, H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, Mass., 1950), p. 241.

[15] Setting each term in (4.13) equal to a parameter λ, we have

$$d\phi=\lambda\sum_i(\partial\phi/\partial q_i)(\partial H/\partial p_i)$$
$$=\sum_i(\partial\phi/\partial q_i)dq_i=\sum_i p_i dq_i,$$

e.g., I. N. Sneddon, *Elements of Partial Differential Equations* (McGraw-Hill, New York, 1957), p. 64.

[16] In certain chemical reactions quantum mechanical interferences arising from indistinguishability of reactant and product channels can occur, just as in electron scattering (Ref. 17), but this effect is omitted for brevity in the present paper.

[17] (a) E.g., N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions,* (Oxford U. P., London, 1965), p. 99; (b) p. 436.

[18] A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1961), Vol. 2, p. 838. Equation (6.2) also utilizes the fact that $\psi_{mE}{}^0$ is exponentially vanishing when any channel distance R, other than R_m, is large.

[19] In Eq. (6.5) a term has been omitted which vanishes in the elastic case, and which can be shown by the Riemann–Lebesque lemma, to vanish in the inelastic case, when a steepest decents method is valid. The omitted term, which would be added to (6.5), has an integrand the same as that in (6.5), but with the $v+v_m$ and $k_mR-(m_1\pi/2)$ replaced by v_m-v and $-k_mR+(m_1\pi/2)$.

[20] See, for example, (a) E. T. Copson, *Asymptotic Expansions* (Cambridge U. P., Cambridge, England, 1965) for a discussion of stationary phase, steepest descents, the latter's saddle-point version, and Airy's integral. (b) M. Born and E. Wolf, *Principles of Optics* (Macmillan, New York, 1954), Appendix III.

[21] Another treatment of the parabolic case, based on a discussion in G. F. Carrier, J. Fluid Mech. **24,** 641 (1966), is by W. H. Miller, Ref. 6b.

[22] (a) We note that

$$|\partial w_i/\partial w_j{}^0| = |\partial w_i{}^0/\partial w_j|^{-1} = |\partial^2\phi/\partial J_{n_i}\partial w_j|^{-1} = |\partial J_j/\partial J_{n_i}|^{-1}.$$

Thus, considering the one-dimensional case for illustration, $\partial w/\partial w^0$ becomes infinite at the saddle point when $\partial J/\partial J_n$ vanishes there. An example of a minimum where J and J_n are the final and initial rotational angular momentum appears in Fig. 10 of Ref. 3b, but this is extremely rare. It is undoubtedly even rarer when a full plot in r dimensions, rather than merely a profile is examined, in other words, when $|\partial J_j/\partial J_{n_i}|$ is investigated rather than $\partial J_j/\partial J_{n_i}$. Certain singularities are readily treated. See, for example, B. L. van der Waerden, Appl. Sci. Res. **B2,** 33 (1952). (b) The pre-exponential velocity factor in (6.5) is always the same at each saddle point because of Eq. (7.1b) and energy conservation. The other factor, $\partial w/\partial w^0$, is also the same under certain circumstances, which we shall suppose for (7.4) and (7.10) but not necessarily for (7.17): According to (a), $\partial w/\partial w^0$ equals $(\partial J/\partial J_n)^{-1}$. Plots of $\bar{n}$, and hence of J, vs w are periodic in w. When the main effect of variation in J_n, in the case of a symmetrical periodic curve, is to change the amplitude of the plot rather than to shift it (e.g., colinear vibrational–translational energy transfer), $\partial J/\partial J_n$, and hence $(\partial w/\partial w^0)^{-1}$, will be the same at the two saddle points.

[23] See, for example, M. A. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1964), p. 447.

[24] An example for two dimensions is given in M. Born and E. Wolf, Ref. 20b, p., 754. The case of n dimensions (real variables)

is treated in L. C. Hsu, Am. J. Math. **73,** 625 (1951). n dimensions (complex variable exponent) is treated by N. Chako, J. Inst. Math. Appl. **1,** 372 (1965), Sec. VII (but note an error in sign in the i factor).

[25] See, for example, J. Heading, *An Introduction to Phase Integral Methods* (Wiley, New York, 1962).

[26] A nice discussion of the pure parabolic case is given in Ref. 20.

[27] For a time-dependent perturbation theory [without deriving the analog of (15)] see, H. C. Corben and P. Stehle, *Classical Mechanics* (Wiley, New York, 1950), p. 252.

[28] In Refs. 4 and 5 the formalism corresponded to an adiabatic basis rather than, as with $\psi_{mw}{}^0$, a basis set for the noninteracting system. However, the present results can, in certain respects, be extended to an adiabatic basis set and the application of Refs. 4 and 5 made. In J. D. Kelley and M. Wolfsberg [J. Chem. Phys. **44,** 324 (1966)], the zeroth-order classical approximation does correspond to an unperturbed basis set and their numerical results can be used to test, in part, $\phi_0+\phi_1+\phi_2$.

[29] The family of characteristics passing through w_i and, at R_0 through $w_i{}^0$, has the same properties, including the same Δ, as the family passing through $w_i+M_i{}^{-1}$. The pre-exponential factor is also the same for these two w_i's. Thus, the $[0, 1]$ domain of w_i in the integral in (6.5) can be decomposed into M_i domains, each of length $M_i{}^{-1}$. If the value of the integral in the first domain is I_{mn}, that in the next is $I_{mn}\exp[2\pi i(n_i-m_i)/M_i]$ (as one sees by a change of variable w_i), that in the next is $I_{mn}\exp(2\pi i 2(n_i-m_i)/M_i]$, and so forth. Thus, we have

$$S_{mn}=(1+x+x^2+\cdots+x^{M_i-1})I_{mn}=(1-x^{M_i})I_{mn}/(1-x),$$

where x is $\exp[2\pi i(n_i-m_i)/M_i]$. One readily verifies from this result that S_{mn} vanishes unless n_i-m_i is a multiple of M_i. In the latter case, the first half of the above equation shows that S_{mn} equals M_iI_{mn}.

[30] If the steepest descents' value of the integral in the w_i-interval $(0, M_i{}^{-1})$ is denoted by I_{mn}, one finds that since Δ at w_i equals that at $w_i+M_i{}^{-1}$, the steepest descents' value of the integral in the w_i domain of $M_i{}^{-1}$ to $2M_i{}^{-1}$ is $I_{mn}\exp[2\pi i(n_i-m_i)/M_i]$, and so forth. The equation in Ref. 29 now applies, as do the conclusions there.

[31] See, R. W. Fenstermaker and R. B. Bernstein, J. Chem. Phys. **37,** 4417 (1967), and references cited therein.

[32] See, e.g., for *atomic* collisions, L. Wilets and S. J. Wallace, Phys. Rev. **169,** 84 (1968); J. C. Y. Chen and K. M. Watson, *ibid.* **174,** 152 (1968). (while our use of action-angle variables is legitimate for molecular motions, it would be much less so for atomic collisions, however.)

[33] See, for example, K. Takayanagi, Progr. Theoret. Phys. (Kyoto), Suppl. **25,** 1 (1963); D. Rapp and T. Kassal, Chem. Rev. **69,** 61 (1969); K. P. Lawley and J. Ross, **43,** 2930 (1965).

[34] See, for example, A. B. Midgal and V. P. Krainov, *Approximation Methods in Quantum Mechanics* (Benjamin, New York, 1969), p. 140, ff.

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Inelastic Neutron Scattering Spectra from Lanthanum Dihydride and Lanthanum Trihydride

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The optical hydrogen vibrations in lanthanum dihydride and lanthanum trihydride have been investigated by the energy-gain scattering of cold neutrons. The approximate frequency distributions, derived from the observed time-of-flight spectra, show peaks which correlate well with the known crystal structures. In fcc lanthanum trihydride the optical bands are peaked at 940 and 515 cm^{-1} corresponding to hydrogen vibrating at tetrahedral and octahedral sites, respectively, and in lanthanum dihydride there is a single peak at 825 cm^{-1} due to tetrahedral hydrogen. Other weak peaks have been observed and are thought to be due to vibrations of hydrogen atoms dissolved in the metal phase; this phase was identified by x rays in both samples. A large width of the optical levels, a common feature in all metallic hydrides, was also observed for LaH_2 and LaH_3.

INTRODUCTION

The inelastic scattering of neutrons has become a useful technique for studying atomic and molecular motions in liquids and solids. In the scattering process, lattice vibrational quanta (phonons) are exchanged between the sample and the incident neutrons and by analyzing the scattered neutron beam one obtains a spectrum from which an approximate frequency distribution for the scattering sample can be derived. The technique is particularly suited to the study of hydrogen-containing compounds, because of the large incoherent scattering cross section of hydrogen.

The vibrational properties of a number of hydrides have in the past been studied by inelastic neutron scattering methods.[1-10] The early work was mostly directed towards the study of metallic hydrides where infrared spectroscopy is useless because of the interactions between the infrared radiation and the conduction electrons. The present study deals with such hydrides. We have investigated the vibration spectra of LaH_2 and LaH_3 by the inelastic scattering of cold neutrons. In this type of experiment phonons are transferred from the sample to the incident neutrons. The time-of-flight technique is used to obtain an energy analysis of the scattered neutrons. The probability that a phonon exists is given by the Boltzmann population term, and the cross section for the scattering process (which is a measure of the probability of observation of a vibrational band) is therefore proportional to the Boltzmann factor. Peaks in the derived neutron spectra are correlated with the vibrational motions of hydrogens in their lattice sites.

EXPERIMENTAL

Lanthanum trihydride was prepared as follows: Lanthanum metal, obtained from Ronson Metal Cor-