EXTENSION OF THE WKB METHOD TO WAVE FUNCTIONS AND TRANSITION PROBABILITY AMPLITUDES (*S*-MATRIX) FOR INELASTIC OR REACTIVE COLLISIONS ‡

R. A. MARCUS
Department of Chemistry, University of Illinois, Urbana, Illinois 61801, *USA*

Received 5 October 1970

A WKB-type method is used to calculate the wave function and *S*-matrix for these collisions directly, instead of applying WKB to the customary infinite set of coupled differential equations. Action-angle variables and exact or approximate classical trajectories are used.

1. OUTLINE OF PROCEDURE

The WKB treatment of the time-independent Schrödinger equation for inelastic collisions has usually first involved writing the latter in the form of an infinite set of coupled differential equations. A WKB method is then applied to each of the latter, normally with added approximations [1].

In the present paper‡‡, we apply instead the WKB method directly to the original Schrödinger equation itself, obtaining a single wave function consisting of an ingoing and an outgoing term. The phase is found to satisfy the Hamilton-Jacobi equation, while the amplitude satisfies an equation for the conservation of probability flux. The former, a nonlinear partial differential equation, is solved by the method of characteristics [3]. These characteristics are readily shown to be the trajectories associated with the classical equations of motion. The equation for the amplitude is solvable with Gauss' theorem [4]‡‡‡

When the boundary conditions are such that the wave function describes a partial wave, the latter can be introduced into an integral expression to yield the *S*-matrix elements [2]. When instead the wave function describes an incoming plane wave plus scattered wave one obtains [4] an integral expression for the differential cross section for scattering into some internal state and solid angle [2] $d\sigma_{\alpha\beta}/d\Omega$. These equations are not restricted to inelastic scattering. Under a certain restriction regarding the motion along the reaction coordinate they apply to chemical reactions also. Further work on this restriction is planned.

In the case of pure elastic scattering the integral expression for the *S*-matrix elements can be shown [2] to reduce to the standard one, $\delta_{mn} \exp 2i\delta_l$, for elastic scattering, where δ_l is the usual WKB phase shift. In other cases the integral can be evaluated by asymptotic methods [2]. Indeed, since an asymptotic (i.e., short wavelength) method (the WKB method) was used initially, consistency suggests that only the leading term, or terms, in an asymptotic expression for the final integral will be meaningful.

With integrals of the type obtained in the present paper, the principal contributions come from the saddle-points of the exponent of the integrand (regarded as a complex variable) and, in some cases, from the boundary points. Most commonly, the former contribution dominates, except perhaps for the elastically scattered term. An example where the boundary point contribution dominates, however, is the case of pure elastic scattering. Here, there are no saddle-points, and the integral can either be evaluated exactly or, in an asymptotic way, from its boundary-point contributions [2].

Fig. 1 summarizes the present procedure [2].

‡ Acknowledgement is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research. This paper was presented at the Conference on Potential Energy Surfaces, University of California, Santa Cruz, California (1970), and is also available as an IBM report (proceedings of the above Conference) on request by writing Librarian, IBM Research Laboratory, San José, California 95114, USA.

‡‡ This paper summarizes and elaborates on an article scheduled to appear in January 1971 [2].

‡‡‡ For an application of the latter to wave functions and eigenvalues of a three-body problem see ref. [5].

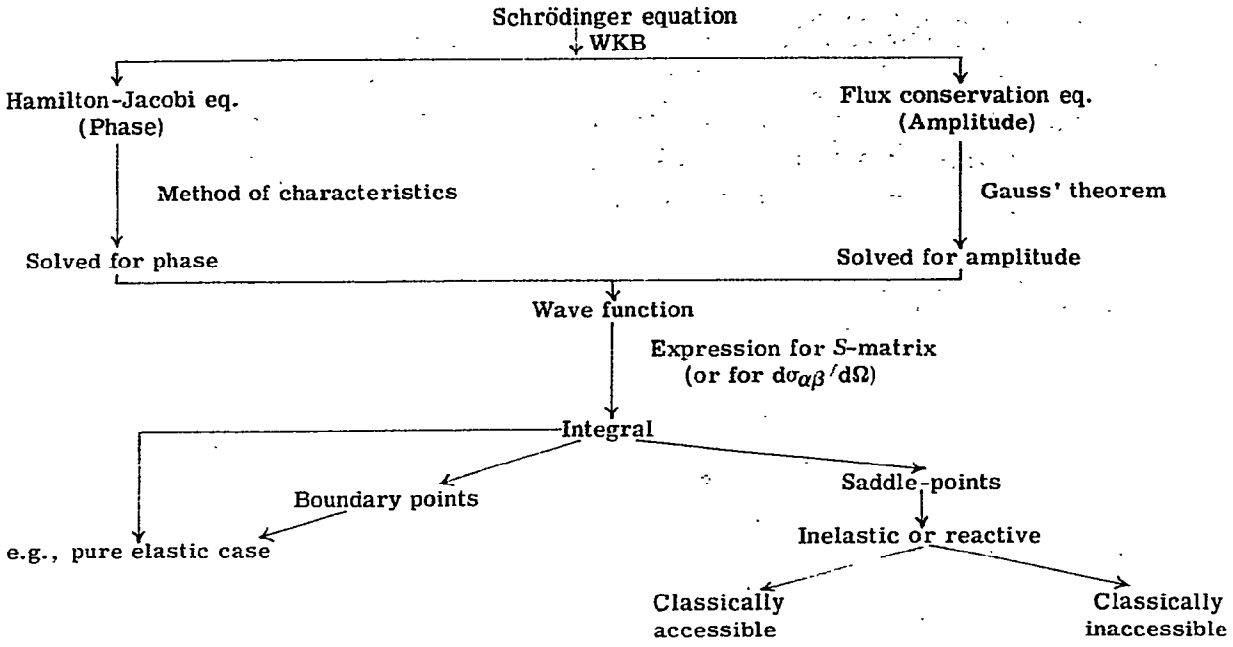

Fig. 1. Flow sheet of the present procedure.

Inasmuch as a detailed description of the method will be published elsewhere [2] only a brief description of the equations will be given in the present letter. The present approach can be compared with others: Keller [4] has treated the application of WKB methods to nonseparable problems - thus making a major step forward - though did not treat inelastic transitions. Miller has computed matrix elements of the Feynmann propagator for inelastic collisions, in various representations [6]. Both of these papers are highly illuminating and related to the present study, and helped expedite our own work in this field.

2. REMARKS ON ACTION-ANGLE VARIABLES

The present approach continues our earlier (classical) work in the application of action-angle variables (J, w) to molecular collisions [7]. These variables have several convenient features: the action variables bear a simple (WKB) relation to quantum numbers, the initial angle variables are random in the interval [0,1], and the use of these variables removes singularities in the unperturbed WKB wave function. The usual one dimensional WKB wave function in conventional cartesian coordinates q and momenta p is $p^{-1/4} \exp[(i/\hbar) \int p\, dq]$. The singularity at $p = 0$ implies a large probability amplitude in that neighborhood. It reflects the long time spent by the classical particle at the classical turning points of the motion (i.e., at $p = 0$). There are no turning points for the angle variable w in an action-angle description of the unperturbed motion, i.e., no points where $dw/dt = 0$. Thus, the unperturbed wave function has no singularities when expressed in terms of these variables. Quantum mechanics in action-angle variables dates back to 1926-1927 and was first introduced by Dirac and slightly later by Jordan [8]‡. Unless particular care is taken only results of WKB accuracy are obtained, but this accuracy is all that is desired in the present procedure.

Quantum mechanics in action-angle variables, when used within the above (WKB) approximation, has a considerable simplicity for separable systems. For example, if a classical hamiltonian is $H_0(J)$, where J is the action variable, a quantum hamiltonian yielding the usual WKB expressions for the eigenvalues is $H_0(J + \hbar\delta)$, where $\delta = \frac{1}{2}$ for a harmonic oscillator, 0 for a plane rotator or a particle in a box,

‡ For a careful analysis of the harmonic oscillator case see ref. [9].

$\frac{1}{2}$ for a principal rotational or orbital angular momentum, 0 for their z-components, etc. $\boldsymbol{J}$ is the operator $(\hbar/\mathrm{i})\,\partial/\partial w$ in the angle variable representation. For γ degrees of freedom one has

$$H_0(J_1, \ldots, J_\gamma) = E \qquad \text{(classical)} \ ; \tag{1}$$

$$H_0(\boldsymbol{J}_1 + \hbar\delta_1, \ldots, \boldsymbol{J}_\gamma + \hbar\delta_\gamma)\psi^0 = E\psi^0 \qquad \text{(quantum)} \ . \tag{2}$$

where $\boldsymbol{J}_i$ is $(\hbar/\mathrm{i})\,\partial/\partial w_i$. The solution of the Schrödinger equation (2) has a corresponding simplicity; the normalized solution is

$$\psi^0_m = \exp\Big(2\pi\mathrm{i}\sum_{k=1}^{\gamma} m_k w_k\Big) \ . \tag{3}$$

where m denotes $(m_1, \ldots, m_\gamma)$ and where the m_i's are integers. The absence of a coordinate-dependent pre-exponential factor reflects the constancy of the $\mathrm{d}w_k/\mathrm{d}t$ in the unperturbed classical case. ($\dot{w}_k = \partial H_0/\partial J_k$ = constant, the dot denoting $\mathrm{d}/\mathrm{d}t$).

Examples of H_0 in eq. (2) are $(\boldsymbol{J} + \frac{1}{2}\hbar)\nu$, $\boldsymbol{J}^2/8\pi^2 I$ and $(\boldsymbol{J} + \frac{1}{2}\hbar)^2/8\pi^2 I$ for the harmonic oscillator, the plane diatomic rotor and the spatial rotor, respectively. Their eigenvalues, obtained from eqs. (2) and (3), are $(m + \frac{1}{2})\hbar\nu$, $m^2\hbar^2/2I$ and $(m + \frac{1}{2})^2\hbar^2/2I$, respectively, and are the well-known WKB eigenvalues.

3. THE COLLISION PROBLEM

Turning now to the collision problem, there is an additional variable, the radial coordinate R, which does not execute a periodic motion in the unperturbed problem. One could still define an "angle" variable w_R related to R, one having some of the properties of action-angle variables, e.g., having $\dot{w}_R \neq 0$ and thus avoiding the singularity in the wave function at the classical turning point of the R-motion. However for the present paper at least we simply use R itself. Instead of eqs. (1) and (2) we can write

$$H_0(J, p_R, R) = E \qquad \text{(classical)} \ ; \tag{4}$$

$$H_0(\boldsymbol{J} + \hbar\delta, \boldsymbol{p}_R, R)\psi^0 = E\psi^0 \qquad \text{(quantum)} \ , \tag{5}$$

where J denotes $(J_1, \ldots, J_\gamma)$, $\boldsymbol{J} + \hbar\delta$ denotes $(\boldsymbol{J}_1 + \hbar\delta_1, \ldots, \boldsymbol{J}_\gamma + \hbar\delta_\gamma)$, and the operator $\boldsymbol{p}_R$ is $(\hbar/\mathrm{i})\,\partial/\partial R$ in the coordinate representation. The unperturbed wave function ψ^0, denoted now by ψ^0_{mE}, is

$$\psi^0_{mE} = f_{mE}(R)\exp\sum_{k=1}^{\gamma} 2\pi\mathrm{i}\, m_k w_k \ . \tag{6}$$

where $f_{mE}(R)$ is the radial wave function, one which may depend on some or all of the m_k's, as well as on E.

The perturbed problem has a classical hamiltonian H.

$$H(J, p_R, w, R) = H_0(J, p_R, R) + H_1(J, p_R, w, R) \ , \tag{7}$$

where H_1 is the perturbation. The Schrödinger equation now reads

$$H(\boldsymbol{J} + \hbar\delta, \boldsymbol{p}_R, w, R)\,\psi = E\psi \ . \tag{8}$$

The asymptotic (i.e., short wavelength, WKB) approximation is made in the usual way by introducing an expansion for ψ into (8) [10],

$$\psi = \exp\left[(\mathrm{i}/\hbar)(\varpi + \hbar\varpi_1 + \hbar^2\varpi_2 + \ldots)\right] \ , \tag{9}$$

applying the operator H, equating equal powers of $\hbar$, so solving for $\varpi, \varpi_1, \varpi_2, \ldots$, and finally retaining only the first two terms in the expansion. In this way, one finds [2] that ϖ is given by

$$\varpi = \varphi - 2\pi\sum_{k=1}^{\gamma} w_k\,\delta_k\hbar \ , \tag{10}$$

where φ satisfies the classical Hamilton-Jacobi equation,

$$H(\partial\varphi/\partial w, \partial\varphi/\partial R, w, R) = E \ . \tag{11}$$

$\bar{\varphi}_1$ is found to be a pure imaginary. Writing exp i$\bar{\varphi}_1$ as A, the new expression for ψ (neglecting $\bar{\varphi}_2$ and higher terms, in the usual WKB manner) is

$$\psi = A \exp[\mathrm{i}(\varphi - 2\pi \sum_{k=1}^{r} w_k \delta_k \hbar)/\hbar] \ . \tag{12}$$

The pre-exponential factor A is found to satisfy an equation for conservation of probability flux (cf. also Keller [4]).

$$\nabla\cdot(A^2 \boldsymbol{q}) = 0 \ , \tag{13}$$

where $\boldsymbol{q}$ is a vector with velocity components along the $r+1$ coordinate axes and where ∇ is also expressed in terms of components along those coordinates.

4. S-MATRIX

The S-matrix elements can be defined in terms of the coefficients of outgoing scattered waves, at large R [1]:

$$\psi^{(+)}_{nE} \sim R^{-1}\left(v_n^{-1/2}\psi^0_{nw} \exp[-\mathrm{i}k_n R + \tfrac{1}{2}\pi \mathrm{i} l_n] - \sum_m S_{mn} v_m^{-1/2} \psi^0_{mw} \exp[\mathrm{i}k_m R - \tfrac{1}{2}\pi \mathrm{i} l_m]\right), \tag{14}$$

where l_n and l_m are incident and final orbital angular momenta and represent one of the n_i's and m_i's respectively (e.g., $l_n \equiv n_1, l_m \equiv m_1$).

When an incident wave of the form of the first term in (14) is used for an ingoing wave, the outgoing wave can be determined by solving eqs.(11) and (13) for φ and A. We found, in this way [2], that

$$\psi^{(+)}_{nE} \sim R^{-1}\left(v_n^{-1/2}\psi^0_{nw} \exp[-\mathrm{i}k_n R + \tfrac{1}{2}\pi \mathrm{i} l_n] - v^{-1/2}\left|\partial w_i/\partial w_j^0\right|^{-1/2} \exp[\mathrm{i}\varphi^*/\hbar]\right) , \tag{15}$$

where $|\partial w_i/\partial w_j^0|$ is an $r \times r$ determinant and where φ^* is

$$\varphi^* = \sum_{i=1}^{r}\left[\int_{w_i^0}^{w_i} J_i \, \mathrm{d}w_i + J_{n_i} w_i^0\right] + \int_{R_0}^{R} p_R \, \mathrm{d}R + p_R^0 R_0 + \tfrac{1}{2}\pi(l_n+1)\hbar - 2\pi\sum_{i=1}^{r} w_i \delta_i \hbar \ . \tag{16}$$

(φ^* is $\varphi - 2\pi \sum_i w_i \delta_i \hbar + \tfrac{1}{2}\pi(l_n+1)\hbar$.)

In eq. (16) w_i^0, J_{n_i}, R_0 and p_R^0 are initial values of w_i, J_i, R and p_R on the trajectory; the integrals are along the characteristics. The equations of the characteristics are the solutions of Hamilton's equations of motion,

$$\dot{w}_i = \partial H/\partial J_i \ , \quad \dot{R} = \partial H/\partial p_R \ , \quad \dot{J}_i = -\partial H/\partial w_i \ , \quad \dot{p}_R = -\partial H/\partial R \ . \tag{17}$$

A schematic example of the characteristics and of the behavior of φ as a function of a uniformized R-variable w_R is given in figs. 2 and 3, respectively‡.

‡ Gauss' theorem was applied in ref. [2] to the heavy solid-line enclosure in fig. 2, to solve eq. (13) and obtain eq. (15). The w_R in fig. 3, defined [2] in terms of an integral along the classical trajectory,

$$w_R = (\partial/\partial p_R^0) \int_{R_0}^{R} p_R \mathrm{d}R \ .$$

by analogy with the usual angle variables, is used only for convenience of illustration of fig. 3. The decrease of φ by an amount $\pi/2$, indicated in fig. 3, reflects a typical change in phase at the turning-point of the radial motion.

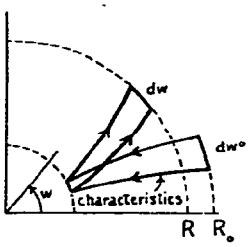

Fig. 2. Plot of characteristics describing collision using (w,R) coordinates.

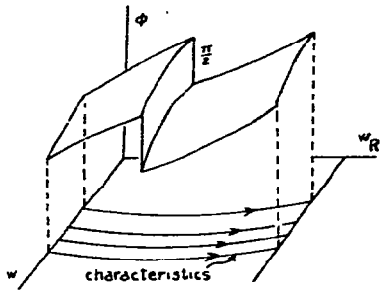

Fig. 3. Plot of phase ϕ versus angle variables (w,w_R).

One can extract an expression for the S-matrix elements from (14) and (15). To this end, one may use the following identity, proven by integration by parts (Green's theorem) [12]:

$$\int\limits_{w,R}\!\!\cdots\!\int \psi^{0*}_{mE}(H-H_0)\psi^{(+)}_{nE}R^2\,\mathrm{d}R\prod_i \mathrm{d}w_i = (\hbar^2/2\mu)\lim_{R\to\infty}\int\limits_{w}\!\cdots\!\int [\psi^{0*}_{mE}(\partial\psi^{(+)}_{nE}/\partial R) - \psi^{(+)}_{nE}(\partial\psi^{*}_{mE}/\partial R)]\prod_i \mathrm{d}w_i\ , \quad (18)$$

where μ is the reduced mass of the collision partners. Introduction of (14) into (18) leads to

$$S_{mn} = \delta_{mn} - (\mathrm{i}\hbar/2\mu)\lim_{R\to\infty} R^2 \int\limits_{w_i=0}^{1}\!\cdots\!\int [\psi^{0*}_{mE}(\partial\psi^{(+)}_{nE}/\partial R)\ldots\psi^{(+)}_{nE}(\partial\psi^{0*}_{mE}/\partial R)]\prod_i \mathrm{d}w_i\ . \quad (19)$$

and introduction of (15) into (19) leads to

$$S_{mn} = \lim_{R\to\infty}\int\limits_{w_1=0}^{1}\!\cdots\!\int |\partial\omega_i/\partial\omega^0_j|^{-1/2}[(v+v_m)/2(v_m v)^{1/2}](\exp \mathrm{i}\Delta)\prod_{i=1}\mathrm{d}w_i\ . \quad (20)$$

where the velocity v is p_R/μ and v_m is $k_m\hbar/\mu$. Δ is

$$\Delta = 2\pi\sum_{i=1}^{r}\int_{w_i^0}^{w_i}(\bar{n}_i - n_i)\,\mathrm{d}w_i + \int_{R_0}^{R} k\,\mathrm{d}R - k_n R_0 - k_m R + 2\pi\sum_i (n_i - m_i)w_i + \tfrac{1}{2}\pi(l_n + l_m + 1)\ , \quad (21)$$

where $\bar{n}_i$ is a continuously varying quantity, defined in terms of J_i by

$$(\bar{n}_i + \delta_i)h = J_i. \quad (22)$$

So defined, $\bar{n}_i$ equals n_i initially.

In (21) k is defined as $p_R/\hbar$ and so has both a sign and a magnitude; k_n is the magnitude of $p^0_R/\hbar$ and, since p^0_R is negative, k_n equals $-p^0_R/\hbar$. Initially, k equals $-k_n$. As in (16), the integration path in (21) is along the characteristics of the motion.

5. SOME APPLICATIONS

In the case of a purely elastic collisional system the integral in (20) is readily evaluated and this S_{mn} can be shown to reduce to the standard WKB expression for elastic collisions [2]. In the inelastic case $(n_i - m_i)$, an asymptotic method may be used to evaluate the integral in (20). The latter's integrand has saddle-points, $(w'_1,\ldots,w'_r)$, which occur at values of $(w_1,\ldots,w_r)$ where $\partial\Delta/\partial w_i$ vanishes, and hence where, according to (21),

$$\bar{n}_i = m_i \quad \text{(at a saddle-point)}\ . \quad (23)$$

At this point, too, the velocity v equals v_m (i.e., $k_m \hbar/\mu$), by energy conservation. Usually there are several saddle-points for a given final state $(m_1, \ldots, m_\gamma)$ and given initial state $(n_1, \ldots, n_\gamma)$. When the saddle-points are not too close to each other, application of the method of steepest descents to (20) yields [2]

$$S_{mn} = \sum_{w'} |\partial w_i/\partial w_j^0|^{-1/2} h^{\gamma/2} |-i\partial^2 \omega/\partial w_i \partial w_j|^{-1/2} \exp i\Delta' \ . \tag{24}$$

where Δ', the value of the Δ in (20) at a saddle-point w', is found to be

$$\Delta' = -2\pi \sum_i \int_{n_i}^{m_i} w_i \, d\bar{n}_i - \int_{k_n}^{k_m} R \, dk + \tfrac{1}{2}\pi(l_n + l_m + 1) \ . \tag{25}$$

the integration path once again being along the characteristic. The summation over w' in (25) is over all saddle-points satisfying (23), i.e., contributing to the transition $n_i \to m_i$.

When the transition is classically accessible, the saddle-point $(w_1', \ldots, w_\gamma')$ lies on the real axis of each w_i variable (regarding each w_i variable as a complex variable). When the transition is classically inaccessible, w' has an imaginary component [2,6]. The S-matrix element is found to depend exponentially on the area $\mathcal{A}$ enclosed between an $\bar{n}$ versus w plot and the straight line $\bar{n} = m$, with a closely related result for the case where these two plots do not intersect [2]. The latter case is the classically inaccessible one. In this case a simple geometric construction was possible and permitted the definition of a related area, $\mathcal{A}$, but now S_{mn} depends exponentially on $i\mathcal{A}$.

When two saddle-points appropriate to $n \to m$ are near each other, cognizance must be taken of their proximity in evaluating (20) by the steepest-descents method, and (24) becomes inadequate. For the case of a single w_i, this proximity when it occurs, is fairly readily treated [2,6].

Detailed equations for S_{mn} may be found in ref. [2], eqs. (7.9), (7.11), (7.13), (7.14) and (7.27).

6. CANONICAL PERTURBATION THEORY

To relate eqs. (20) and (24) to common approximations for transition probabilities in the literature a canonical perturbation theory was also formulated in ref. [2] for the phase ω, yielding

$$\omega(q, a) = \sum_{N=0}^{\infty} \omega_N(q, a) \ , \tag{26}$$

where ω_0 is the solution for the unperturbed Hamilton-Jacobi equation, and where the other terms are defined in appendix I. Various terms in eq. (26) have been tested in part in recent publications from our laboratory, by numerically comparing exact and approximate classical mechanical results for various molecular collisions [7]. An example is given by the plots in ref. [13].

Eq. (26) can also be used to obtain information on the position of the saddle-points in several-dimensional systems and on the chance of their being close to each other [2]. In conjunction with eq. (20) eq. (26) provides insight into the topic of collisional selection rules and into the usefulness of symmetry arguments in reducing the number of saddle-points about which detailed separate calculations need be made in evaluating (20) or (24) [2].

7. EXTENSIONS AND CONCLUDING REMARKS

To obtain the S-matrix elements a partial wave was employed for $\psi_{nE}^{(+)}$, as in eq. (15). Had an incident plane wave been used instead, one would have obtained the differential cross section for the transition, instead of the S-matrix elements. The procedure of so obtaining $d\sigma_{\alpha\beta'}/d\Omega$ is outlined in ref. [2], and the detailed equations will appear in a subsequent paper.

The identity in eq. (18) is applicable not only to inelastic collisions but also to reactive ones as well [2]. In this case H_0 and μ will vary with the chemical constitution in the products channel. Apart from a restriction regarding the nature of the motion along the radial coordinate in each channel, the subsequent equations are also applicable to reactions, but further investigation into the restriction is needed.

A variety of approximations for treating collisions in the literature (e.g., sudden, eikonal, and others)

can be discussed [2] in terms of eq. (20) for S_{mn}, using the canonical perturbation theory expressed by eq. (26).

There is considerable scope for applying the present WKB formalism to a wide variety of differential cross sections which have appeared in many phenomena and have been admirably summarized recently [14]. The now-extended WKB formalism has a broad potentiality for applying various asymptotic methods to the integral expressions for S_{mn} or $d\sigma_{\alpha\beta}/d\Omega$. The richness of the complex variable field offers much promise in this connection.

APPENDIX I

Definition of terms in eq. (26).

In eq. (26) φ_0 is the solution of the unperturbed Hamilton-Jacobi equation,

$$H(p^{(0)}, q) = E \ , \tag{27}$$

where $p_i^{(0)}$ is $\partial\varphi_0(q,\alpha)/\partial q_i$, the α being the constants of the motion; φ_N for $N \geq 1$ is

$$\varphi_N(q,\alpha) = -\int_{-\infty}^{t} K_N(\tilde{q}(\tau),\alpha)\,d\tau \ , \tag{28}$$

where $\tilde{q}_i(\tau)$ satisfies the unperturbed Hamilton equation of motion

$$\dot{\tilde{q}}_i = \partial H_0/\partial p_i^{(0)} \ , \quad \dot{p}^{(0)} = \partial H_0/\partial \tilde{q}_i \ , \tag{29}$$

The $\tilde{q}_i(\tau)$ in (27) must be chosen so as to equal q_i at $\tau = t$; the first few K_N's are

$$K_1(q,\alpha) = -H_1(q, p^{(0)}) \ , \tag{30}$$

$$K_2(q,\alpha) = \{\varphi_1, H_1\} + (1/2!)\{\varphi_1,\{\varphi_1, H_0\}\} \ , \tag{31}$$

where

$$\{X, Y\} = \sum_{i=1}^{r+1} [(\partial X/\partial q_i)(\partial Y/\partial p_i^{(0)}) - (\partial X/\partial p_i^{(0)})(\partial Y/\partial q_i)] \ . \tag{32}$$

The q's in these equations denote all the w_i's and the R. The Δ in eq. (20) is related to the phase φ by the equation

$$\Delta = (\varphi/\hbar) - 2\pi \sum_{i=1}^{r} (m_i + \delta_i) w_i - k_m R + \tfrac{1}{2}\pi(l_m + l_n + 1) \ . \tag{33}$$

REFERENCES

[1] L. D. Landau and E. M. Lifshitz, Quantum mechanics (Addison-Wesley, Reading, Mass., 1958).
[2] R.A. Marcus, J. Chem. Phys., to be published.
[3] I. N. Sneddon, Elements of partial differential equations (McGraw-Hill, New York, 1957) p. 64.
[4] J. B. Keller, Ann. Phys. 9 (1960) 24.
[5] D. J. Vezzetti and S. I. Rubinow, Ann. Phys. 35 (1965) 373.
[6] W.H. Miller, J. Chem. Phys. 53 (1970) 1949; and to be published.
[7] R. A. Marcus, J. Chem. Phys. 45 (1966) 4500; 49 (1968) 2617;
A. O. Cohen and R.A. Marcus, J. Chem. Phys. 49 (1968) 4509; 52 (1970) 3140;
M. Attermeyer and R. A. Marcus, J. Chem. Phys. 52 (1970) 393;
Shiou-fu Wu and R. A. Marcus, J. Chem. Phys., to be published.
[8] P. A. M. Dirac, Proc. Roy. Soc. A111 (1926) 281; A114 (1927) 243.
P. Jordan, Z. Physik 40 (1927) 809; 44 (1927) 1.

[9] B. Leaf, J. Math. Phys. 10 (1969) 1980.
[10] P. A. M. Dirac, The principles of quantum mechanics, 4th Ed. (Oxford Univ. Press, New York, 1958) p. 121.
[11] N. F. Mott and H. S. W. Massey, Theory of atomic collisions (Oxford Univ. Press, London, 1965) p. 436.
[12] A. Messiah, Quantum mechanics, vol. II (North-Holland, Amsterdam, 1961) p. 838.
[13] A. O. Cohen and R. A. Marcus, J. Chem. Phys. 52 (1970) 3140.
[14] R. G. Gordon, in: Advances in magnetic resonance, Vol. 3, ed. J. S. Waugh (Academic Press, New York, 1968) p. 1
R. G. Gordon, W. Klemperer and J. I. Steinfeld, Ann. Phys. Chem. 19 (1968) 215.