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On the Stokes Phenomenon for the Differential Equations Which Arise in the Problem of Inelastic Atomic Collisions

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The problem of inelastic atomic collisions, involving exchange of energy between the atoms, depends upon the solution of a pair of coupled differential equations equivalent to a single differential equation of the fourth order, in which the independent variable is the distance, r, between the two atoms. Asymptotic forms for the solutions of this pair of equations may be found. The probability of energy exchange may be shown to depend upon the connections between the solutions for values of r which correspond to regions of space where the relative kinetic energy of the two atoms is positive and the solutions for values of r corresponding to regions where the kinetic energy is negative. The finding of these connections involves a study of the asymptotic forms of the solutions when these forms are considered as functions of a complex variable. Such a study has been made in this paper, and the corresponding Stokes phenomenon investigated. The desired end was not achieved, but results of interest have nevertheless been obtained. A brief discussion is given of the previous work of Stueckelberg.

§1. INTRODUCTION

THE theoretical calculation of the probability of exchange of energy by two atoms on collision is a problem of considerable interest. It may be best treated by considering that the two atoms form an unstable molecule. The problem then resolves itself into the determination of the probability of a radiationless transition, whereby the molecule passes from one repulsive potential energy curve to another without change in total energy.

It may be formulated mathematically as follows. We let Φ_i be the composite eigenfunction, representing the internal state of the system (that is, the electronic states of the two atoms and the rotational state of the unstable molecule which the two atoms are assumed to form), neglecting any interation between them. Φ_i obeys the wave equation

$$(H_0-U_i)\Phi_i=0, \tag{1}$$

where U_i is the eigenvalue and H_0 is the Hamiltonian for the pair of atoms, neglecting any terms in the potential due to interaction of one atom with the other. H_0 depends upon the electronic coordinates and the angles giving the relative orientation of the two atoms, but the distance, r, between the atoms does not enter H_0 at all. U_i, which gives the potential energy of the unstable molecule is, in this approximation, independent of r. Only when the interaction between the two atoms is taken into account do we get the proper potential energy curves.

We shall assume that only two states of the unstable molecule need to be taken into account. These two states we distinguish by letting i be replaced by 1 or 2, respectively. We shall further assume that a selection rule operates so that its rotational quantum numbers do not change in the transition. This would seem really not to be an additional assumption, but rather a necessary restriction required by the first assumption, since each set of rotational quantum numbers defines what is effectively a separate internal state of the system with its own potential-energy curve. If any other selection rule holds we should thus be compelled to consider transitions involving more than two internal states.

The complete Hamiltonian for the system, which takes into account the mutual interaction of the two atoms, as well as their motion with respect to each other, may be written

$$H=H_0+V+H_r, \tag{2}$$

where V consists of the previously neglected potential energy terms giving the mutual interaction, and

$$H_r=-\frac{1}{\kappa^2}\left(\frac{\partial}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right), \tag{3}$$

where $\kappa^2=8\pi M/h^2$, where M is the reduced mass of the system and h is Planck's constant. If we let ψ be the eigenfunction corresponding to the Hamiltonian (2) we have

$$(H_0+V+H_r-E)\psi=0, \tag{4}$$

where E is the energy of the system. Now, if, as we have assumed, only two states of the system need to be taken into account, then we may write

$$\psi = F_1\Phi_1/r + F_2\Phi_2/r, \qquad (5)$$

where F_1 and F_2 are functions of r. If we substitute (5) into (4), multiply through by Φ_1 and integrate over all values of the internal coordinates, remembering (1) and the orthogonal properties of Φ_1 and Φ_2, and noting that $H_r(F_i/r) = -\kappa^{-2}r^{-1}d^2F_i/dr^2$, we get

$$U_1F_1 + v_{11}F_1 + v_{12}F_2 - \kappa^{-2}d^2F_1/dr^2 - EF_1 = 0, \qquad (6)$$

where[1]

$$v_{11} = \int \Phi_1 V \Phi_1 d\tau \qquad (7)$$

and

$$v_{12} = \int \Phi_1 V \Phi_2 d\tau, \qquad (8)$$

where $d\tau$ represents the volume element for all the coordinates except r and the integrals are taken over all allowable values of these coordinates. We now let $V_1 = v_{11} + U_1$. It will be seen that V_1 is the quantity which gives the potential energy of the unstable molecule. By rearranging Eq. (6) slightly it becomes

$$d^2F_1/dr^2 + \kappa^2(E - V_1)F_1 = \kappa^2 v_{12}F_2. \qquad (9a)$$

Similarly

$$d^2F_2/dr^2 + \kappa^2(E - V_2)F_2 = \kappa^2 v_{12}F_1, \qquad (9b)$$

since $v_{21} = v_{12}$. This pair of coupled differential equations, which are to be solved simultaneously, was originally obtained by London.[2]

The most interesting case arises when the potential energy curves V_1 and V_2 intersect, as shown in Fig. 1, and the point of intersection is of especial importance in the solution of the equations. We shall, in fact, find it convenient to set $\rho = r - r_0$, where r_0 is the value of r at which the intersection occurs, and to let the arbitrary zero of energy coincide with the energy of the intersection.

The pair of coupled differential equations, (9a) and (9b), is equivalent to a single differential equation of the fourth order. For large positive values of ρ, it may be shown that the four independent solutions represent, respectively, a stream of particles (really pairs of particles) going out (toward larger ρ's) on V_1, a stream coming in on V_1, a stream going out on V_2, and a stream coming in on V_2. Now these solutions connect with the solutions for negative values of ρ, two of which decrease exponentially as ρ goes to greater negative values, while two increase exponentially. The latter two solutions are excluded as having no physical significance, which is equivalent to placing certain conditions on the coefficients of the solutions for positive values of ρ. This enables us to find the transition probability, as we shall see, provided we are able to connect the asymptotic solutions for ρ positive with those for ρ negative. Now Stueckelberg[3] has attempted to find this connection by Stokes' method of tracing the changes in the asymptotic solutions as they are carried over a large circle in the complex plane.[4] Stueckelberg's work, however, was confined to the case in which the energy, E, was very different from the energy of intersection of the two curves. But the workings of the Franck-Condon principle, as well as the important role which the intersection of the two curves plays in Stueckelberg's analysis, would lead us to expect that the most interesting case would be just that which Stueckelberg's work excludes.[5] I have, therefore, attempted, by extending the method used by Stueckelberg, to solve the problem for the general case in which E is allowed to have any value whatsoever, specializing, however, the form of V_1 and V_2, in fact setting

$$V_1 = -\alpha_1\rho \quad \text{and} \quad V_2 = -\alpha_2\rho, \qquad (10)$$

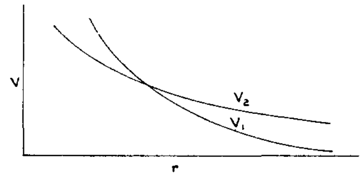

FIG. 1.

[1] We assume Φ_1 and Φ_2 are real. If this is not the case the necessary modifications can readily be made.

[2] London, Zeits. f. Physik **74**, 143 (1932).

[3] Stueckelberg, Helv. Phys. Acta **5**, 369 (1932). For other approaches to the problem see Rice, Phys. Rev. **38**, 1943 (1931); Landau, Physik. Zeits. Sowjetunion **1**, 46, 88 (1932); Zener, Proc. Roy. Soc. **A137**, 696 (1932).

[4] Stokes, Mathematical and Physical Papers **4**, 77, 283, **5**, 221, 283 (or Trans. Camb. Phil. Soc. **10**, 105 (1857), **11**, 412 (1868), Proc. Camb. Phil. Soc. **6**, 362 (1889); Acta Math. **26**, 393 (1902)).

[5] Rice, Phys. Rev. **37**, 1187, 1551 (1931); Jablonski, Zeits. f. Physik **70**, 723 (1931).

where α_1 and α_2 are constants. It was believed that this specialization in the form of the potential energy curves would be a less important restriction than that found necessary by Stueckelberg. It was found, however, that even with the restriction expressed by Eq. (10) it was not possible to solve the problem by means of the method used. In fact, during the course of the work, I have become convinced that Stueckelberg's results, while they appear extremely reasonable, are really open to grave objections. But in spite of the failure to attain the desired end and the generally negative character of the results, it has seemed to me that the considerations developed are of considerable interest mathematically, and should contribute to the understanding of this important problem, if not to its solution.

§2. Solution of the Equations

The first step which must be taken is to find approximate forms of an asymptotic character for the solutions of Eqs. (9a) and (9b). Stueckelberg has accomplished this by eliminating one of the F's, let us say F_2, and substituting a solution of the form

$$F_1 = e^{(S_0 + hS_1 + h^2 S_2 + \cdots)/h} \tag{11}$$

into the resulting fourth order equation, and equating separately to zero the coefficients of the various powers of h. As Stueckelberg gives the merest outline of this procedure, we shall show how it is done. There seems, however, to be some advantage to be gained by simply using the similar expression for F_2,

$$F_2 = e^{(T_0 + hT_1 + h^2 T_2 + \cdots)/h} \tag{12}$$

and substituting them together into Eqs. (9). Now if we are to set the coefficients of the various powers of h which occur on the two sides of each of the resulting equations equal to each other we must expand the exponentials. This at once leads us into difficulties on account of the negative power of h. We shall, therefore, substitute the almost equivalent condition, that the solution given by Eqs. (11) and (12) must remain valid for all values of h. By letting h go to zero we see that we must have $S_0 = T_0$, a fact of some importance, as we shall see, which was not brought out in Stueckelberg's work. We now divide $e^{S_0/h} = e^{T_0/h}$ out of the equations and expand the exponentials, letting primes indicate differentiation with respect to ρ. We obtain

$$\begin{aligned}
&[(1/h^2)(S_0' + hS_1' + h^2 S_2' + \cdots)^2 \\
&\quad + (1/h)(S_0'' + hS_1'' + h^2 S_2'' + \cdots) \\
&\quad + (8\pi^2 M/h^2)(E - V_1)]e^{S_1}(1 + hS_2 + \cdots) \\
&\qquad = (8\pi^2 M/h^2) v_{12} e^{T_1}(1 + hT_2 + \cdots)
\end{aligned} \tag{13_1}$$

and a similar equation in which T's and S's are interchanged and V_2 occurs in place of V_1. This latter we shall denote as Eq. (13_2), and we shall use this subscript notation several times in the next few lines to designate equations related in this way in order to avoid having to write down both of them. The term in $1/h^2$ gives us (dividing (13_1) through by e^{S_1})

$$S_0'^2 + 8\pi^2 M(E - V_1) = 8\pi^2 M v_{12} e^{T_1 - S_1}. \tag{14_1}$$

Remembering now that $T_0 = S_0$ and letting $V = (V_1 + V_2)/2$, the average of the two potentials, we see by adding (14_1) and (14_2)

$$\begin{aligned}
S_0'^2/h^2 &= T_0'^2/h^2 \\
&= \kappa^2 [v_{12} \cosh (T_1 - S_1) - (E - V)].
\end{aligned} \tag{15}$$

Subtracting (14_2) from (14_1) we get

$$V_2 - V_1 = 2v_{12} \sinh (T_1 - S_1). \tag{16}$$

Using the relation between cosh and sinh we get from (15) and (16)

$$\begin{aligned}
S_0'/h &= T_0'/h \\
&= \pm\kappa[\pm\{v_{12}^2 + \tfrac{1}{4}(V_2 - V_1)^2\}^{\frac{1}{2}} - (E - V)]^{\frac{1}{2}}.
\end{aligned} \tag{17}$$

Now, returning to Eq. (13_1), the term in $1/h$ gives

$$\begin{aligned}
2S_0'S_1' + S_0'' + S_0'^2 S_2 + 8\pi^2 M(E - V_1)S_2 \\
= 8\pi^2 M v_{12} T_2 e^{T_1 - S_1}.
\end{aligned} \tag{18_1}$$

Using Eq. (14_1) we find

$$2S_0'S_1' + S_0'' = 8\pi^2 M v_{12}(T_2 - S_2)e^{T_1 - S_1}. \tag{19_1}$$

Adding (19_1) and (19_2), remembering $S_0 = T_0$, and using (16) we get

$$\begin{aligned}
2S_0'(S_1' + T_1') + 2S_0'' \\
= 8\pi^2 M(T_2 - S_2)(V_2 - V_1).
\end{aligned} \tag{20}$$

Subtracting (19_2) from (19_1) we get

$$S_0'(S_1'-T_1')=8\pi^2 M v_{12}(T_2-S_2)\cosh(T_1-S_1). \quad (21)$$

From (16) $(V_2-V_1)/2v_{12}=\sinh(T_1-S_1)$. By differentiating both sides,

$$[(V_2-V_1)/2v_{12}]'=(T_1'-S_1')\cosh(T_1-S_1).$$

From this we can solve for $S_1'-T_1'$. Substituting for $S_1'-T_1'$ and $\cosh(T_1-S_1)$(obtained from Eq. (16)) in Eq. (21) we get

$$8\pi^2 M(T_2-S_2)=-2v_{12}S_0'[(V_2-V_1)/v_{12}]'\times[4v_{12}^2+(V_2-V_1)^2]^{-1}. \quad (22)$$

Substituting (22) into (20) and making some reductions we get

$$(S_1'+T_1')=-S_0''/S_0'-\tfrac{1}{2}[(V_2-V_1)^2/4v_{12}^2]'[(V_2-V_1)^2/4v_{12}^2+1]^{-1}. \quad (23)$$

Integrating,

$$(S_1+T_1)=-\log S_0'-\log[(V_2-V_1)^2/4v_{12}^2+1]^{\frac{1}{2}}+C, \quad (24)$$

where C is the constant of integration.

From (16) we have

$$T_1-S_1=\sinh^{-1}\{(V_2-V_1)/2v_{12}\}=\log\{(V_2-V_1)/2v_{12}+[(V_2-V_1)^2/4v_{12}^2+1]^{\frac{1}{2}}\}=\log\mu, \quad (25)$$

(where μ is defined by the equation) provided the sign of the inner square root of (17) is positive.[6] If the inner square root is negative[7]

$$T_1-S_1=-\log\mu+i\pi \quad (26)$$

where μ has the same definition as before (positive sign in front of the square root).

With Eqs. (17), (24), (25) and (26) we now have sufficient material to evaluate the expressions (11) and (12) for F_1 and F_2, respectively, as far as the second term in the exponential. Before doing this, it will repay us to establish a nomenclature which will distinguish the four different solutions and which we can use throughout the rest of the paper. In order to do this most effectively we shall proceed at once to use the approximation indicated in Eqs. (10), writing $V_1=-\alpha_1\rho$ and $V_2=-\alpha_2\rho$. As in Fig. 1, we shall assume that $V_2>V_1$ for ρ real and positive, hence we see that we must have

$$\alpha_1>\alpha_2. \quad (27)$$

Since we shall desire to consider the solutions, F_1 and F_2, as functions of a complex variable we shall write $\rho=\rho_0 e^{i\theta}$, and using Eqs. (10) we may substitute into Eq. (17). We shall write

$$\nu_1=[-\{v_{12}^2+\tfrac{1}{4}(\alpha_1-\alpha_2)^2\rho_0^2e^{2i\theta}\}^{\frac{1}{2}}-E-\tfrac{1}{2}(\alpha_1+\alpha_2)\rho_0e^{i\theta}]^{\frac{1}{2}} \quad (28)$$

and

$$\nu_2=[+\{v_{12}^2+\tfrac{1}{4}(\alpha_1-\alpha_2)^2\rho_0^2e^{2i\theta}\}^{\frac{1}{2}}-E-\tfrac{1}{2}(\alpha_1+\alpha_2)\rho_0e^{i\theta}]^{\frac{1}{2}}. \quad (29)$$

The reason for the particular choice of subscripts for the ν's is readily understood if we consider these expressions when ρ_0 is very great. Remembering (27) we readily find

$$\lim_{\rho_0=\infty}\nu_1=\alpha_1^{\frac{1}{2}}\rho_0^{\frac{1}{2}}e^{i\theta/2+i\pi/2} \quad (30)$$

and

$$\lim_{\rho_0=\infty}\nu_2=\alpha_2^{\frac{1}{2}}\rho_0^{\frac{1}{2}}e^{i\theta/2+i\pi/2}. \quad (31)$$

In these expressions $\alpha_1^{\frac{1}{2}}$, $\alpha_2^{\frac{1}{2}}$ and $\rho_0^{\frac{1}{2}}$ are to be taken as positive. It is thus seen that ν_1^2 approaches V_1 and ν_2^2 approaches V_2, when $\theta\to 0$, since E is negligible if ρ_0 is large.

Remembering now that Eqs. (25) and (26) are to be used with ν_2 or ν_1, respectively, we see that on substituting them, together with (17) and (24), into (11) and (12) we get four independent solutions of the differential equation. The four independent pairs of functions we shall write as $F_{1,i}$ and $F_{2,i}$ $(i=1, 2, 3, \text{or } 4)$. The expressions for the $F_{1,i}$ are given below. (The $F_{2,i}$ are obtained from these merely by changing the sign of the exponent on μ.)

[6] See Peirce, *A Short Table of Integrals*, formula 679, which follows from the relation $x=\log(\sinh x+\cosh x)$.

[7] This inner square root is simply $\cosh(T_1-S_1)$, and if this is negative then T_1-S_1 is to be obtained by putting a minus sign before the square root in the logarithmic expression, which yields Eq. (26).

$$F_{1,\,4}=A_4\nu_1^{-\frac{1}{2}}\lambda^{-\frac{1}{4}}\mu^{\frac{1}{2}}e^{-\kappa\int\nu_1 d\rho}=A_4\eta_4\mu^{\frac{1}{2}}f_1, \quad (32)$$

$$F_{1,\,1}=A_1\nu_1^{-\frac{1}{2}}\lambda^{-\frac{1}{4}}\mu^{\frac{1}{2}}e^{\kappa\int\nu_1 d\rho}=A_1\eta_1\mu^{\frac{1}{2}}f_1, \quad (33)$$

$$F_{1,\,3}=A_3\nu_2^{-\frac{1}{2}}\lambda^{-\frac{1}{4}}\mu^{-\frac{1}{2}}e^{-\kappa\int\nu_2 d\rho}=A_3\eta_3\mu^{-\frac{1}{2}}f_2, \quad (34)$$

$$F_{1,\,2}=A_2\nu_2^{-\frac{1}{2}}\lambda^{-\frac{1}{4}}\mu^{-\frac{1}{2}}e^{\kappa\int\nu_2 d\rho}=A_2\eta_2\mu^{-\frac{1}{2}}f_2 \quad (35)$$

where $\lambda=[(V_2-V_1)/2v_{12}]^2+1$, where the A's are arbitrary constants, and where the η's are abbreviations for the exponential parts of the solutions, and the f's for the rest of the variable part, excluding the power of μ. The general solution may therefore be written

$$\begin{aligned} F_1&=A_1\eta_1\mu^{\frac{1}{2}}f_1+A_2\eta_2\mu^{-\frac{1}{2}}f_2\\ &\qquad+A_3\eta_3\mu^{-\frac{1}{2}}f_2+A_4\eta_4\mu^{\frac{1}{2}}f_1,\\ F_2&=A_1\eta_1\mu^{-\frac{1}{2}}f_1+A_2\eta_2\mu^{\frac{1}{2}}f_2\\ &\qquad+A_3\eta_3\mu^{\frac{1}{2}}f_2+A_4\eta_4\mu^{-\frac{1}{2}}f_1. \end{aligned} \quad (36)$$

§3. The Transition Probability

It is readily seen that the limit of $\mu^{\frac{1}{2}}f_1$ as ρ becomes infinite is $2^{\frac{1}{2}}\nu_1^{-\frac{1}{2}}$, that of $\mu^{\frac{1}{2}}f_2$ is $2^{\frac{1}{2}}\nu_2^{-\frac{1}{2}}$, while $\mu^{-\frac{1}{2}}f_1$ and $\mu^{-\frac{1}{2}}f_2$ become zero more rapidly than $\nu_1^{-\frac{1}{2}}$ or $\nu_2^{-\frac{1}{2}}$. Hence to a first approximation we may write for ρ real and positive

$$\lim_{\rho=\infty} F_1(0) =2^{\frac{1}{2}}\nu_1^{-\frac{1}{2}}(0)(A_1(0)\eta_1(0)+A_4(0)\eta_4(0)), \quad (37a)$$

$$\lim_{\rho=\infty} F_2(0) =2^{\frac{1}{2}}\nu_2^{-\frac{1}{2}}(0)(A_2(0)\eta_2(0)+A_3(0)\eta_3(0)). \quad (37b)$$

We introduce here a notation of which we shall hereafter make much use, whereby we insert in parentheses the value of θ. It is necessary to designate the value of θ even in the case of the A's, for they are not the same for all values of θ, this being, in fact, the essence of the Stokes phenomenon.

Now $A_1(0)\nu_1^{-\frac{1}{2}}(0)\eta_1(0)$ represents a stream of particles going from right to left on the curve V_1 with a velocity always proportional to $|\nu_1(0)|$ and $A_4(0)\nu_1^{-\frac{1}{2}}(0)\eta_4(0)$ represents a stream going from left to right on the same curve with the same velocity.[8] In the same way $A_2(0)\nu_2^{-\frac{1}{2}}(0)\eta_2(0)$ and $A_3(0)\nu_2^{-\frac{1}{2}}(0)\eta_3(0)$ represent streams of particles going respectively from right to left and from left to right on the other curve. The densities of these streams of particles will be found by multiplying these expressions by their conjugate complexes and will be, respectively, $2|A_1(0)|^2\nu_1(0)^{-1}$, $2|A_4(0)|^2\nu_1(0)^{-1}$, $2|A_2(0)|^2\nu_2(0)^{-1}$, and $2|A_3(0)|^2\times\nu_2(0)^{-1}$. Since $\nu_1(0)$ and $\nu_2(0)$ are proportional to the respective velocities we see that $|A_1(0)|^2$, $|A_4(0)|^2$, $|A_2(0)|^2$ and $|A_3(0)|^2$ are proportional to the currents (particles per unit time crossing a given point) in the various streams of particles. Now if we let $A_2(0)=0$, then we see that all the incident particles coming from right to left are on the curve V_1. After the collision they are traveling from left to right and a certain number have gone over to the curve V_2. The proportion which go over, on collision, to the curve V_2 is the transition probability; we shall designate it as P (P_1 or P_2 in the two cases considered below). We thus may write:

If $A_2(0)=0$,

$$P_1=|A_3(0)|^2/|A_1(0)|^2, \quad (38)$$

and
$$|A_1(0)|^2=|A_3(0)|^2+|A_4(0)|^2, \quad (39)$$

the last so that we may have conservation of the number of particles. On the other hand, we have:

If $A_1(0)=0$,

$$P_2=|A_4(0)|^2/|A_2(0)|^2, \quad (40)$$

and
$$|A_2(0)|^2=|A_3(0)|^2+|A_4(0)|^2, \quad (41)$$

in this case the transitions being from the curve V_2 to the curve V_1.

Now it will be observed that of our solutions η_1 and η_2 become exponentially infinite and η_3 and η_4 become exponentially zero as ρ goes to $-\infty$. In order, therefore, that F_1 and F_2 should satisfy the necessary conditions for a wave function we must have $A_1(\pi)$ and $A_2(\pi)$ equal to zero. This is sufficient to determine the value of P, and the problem resolves itself into finding the relation between $A_1(0)$ and $A_1(\pi)$, etc.

§4. Character of the Approximate Solutions

The approximate solutions which we have found have an asymptotic validity with respect to variation of ρ. This is roughly seen if we try

[8] It is really quite arbitrary which expression should represent which stream of particles, but we must have a given sign of the integral in the exponential correspond to a particular direction of motion in both (37a) and (37b). (By the term "stream of particles" we really mean stream of pairs of particles. When we say the stream is "going to the right" we mean that the distance ρ is increasing.)

to find S_2 and T_2. If we take the coefficient of h^0 in Eq. (13_1) neglecting S_3 and T_3 where they occur and set it equal to zero, we get

$$2S_0'S_2'+(S_0''+2S_0'S_1')S_2+S_1'^2+S_1''=0. \quad (42)$$

Now it will be observed that, as ρ_0 goes to ∞, the coefficient of S_2' changes as $\rho_0^{\frac{1}{2}}$, the coefficient of S_2 changes as $\rho_0^{-\frac{1}{2}}$, and the other term changes as ρ_0^{-2}. Therefore S_2 itself will change as $\rho_0^{-\frac{3}{2}}$. The same will be true of T_2. Therefore, the approximate solution we have found, will, in the particular case we are considering, become a better and better approximation as ρ_0 goes to ∞. To make this rigorous, we should, of course, consider S_3, T_3, S_4, T_4, etc., but we may confidently accept the conclusion as correct.

Now S_2 and T_2 come into the expression for the solutions of the equation as exponentials, e^{S_2} or e^{T_2}, as the case may be, which multiply the rest of the expression. We see that this factor differs from 1 by an amount which goes to zero as $1/\rho_0^{\frac{3}{2}}$ as ρ_0 goes to ∞, while θ remains constant, and the errors in a special solution, for example $F_{1,\,1}$ will approach $F_{1,\,1}\times O(\rho_0^{-\frac{3}{2}})$.

§5. The Stokes Phenomenon

The problem of the asymptotic representation of the solution of the uncoupled differential equation

$$\partial^2 G/\partial x^2-\kappa^2 VG=0, \quad (43)$$

where $V=-\alpha x$, has been considered in great detail by Stokes. The solution of this equation can be written in the form

$$G=B_1G_1+B_2G_2$$
$$=B_1x^{-\frac{1}{4}}e^{\frac{2}{3}i\alpha^{\frac{1}{2}}\kappa x^{\frac{3}{2}}}+B_2x^{-\frac{1}{4}}e^{-\frac{2}{3}i\alpha^{\frac{1}{2}}\kappa x^{\frac{3}{2}}}; \quad (44)$$

this expression has the same sort of asymptotic validity as the solutions (36) of Eqs. (9). However, in this simple case, it is possible to obtain a complete asymptotic expansion for each of the solutions, which, of course, enables one to get a much better approximation than is given by (44). But even by using these asymptotic expansions, it is found that, in a certain region near those lines in the complex plane for which the exponents of the expressions in Eq. (44) are real (the solid lines of Fig. 2), the error in the asymptotic representation of the large solution becomes greater than the entire magnitude of the small solution. These regions become narrower and narrower as one goes out to $|x|=\infty$, but along the lines themselves it is always true that the error of one solution becomes greater than the other solution. If now we cross this region, then, to use the words of Stokes, unless the coefficient of the large solution is zero the small solution becomes lost in a mist, and on emerging we will find that the arbitrary constant of the small solution will have changed. The change, as Stokes has shown, will be proportional to the coefficient of the large solution.[9] The constant of proportionality we shall call the Stokes coefficient.

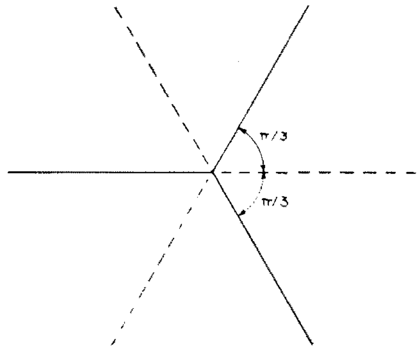

Fig. 2.

Now if we do not use the asymptotic expansion but instead the much rougher solution (44) then the misty region becomes much larger. As $|x|$ approaches infinity it is seen that one solution becomes infinitely large and the other infinitely small. The order of the errors is just the same as in the case of the coupled equations, discussed in §4. Thus the error of one solution becomes

[9] Although implicitly contained in the work of Stokes, this proposition is not very clearly stated there. It may be easily seen as follows. If the coefficient of the large solution is zero, then the small solution does *not* get lost in a mist, and its coefficient remains unchanged as the critical region is crossed. Thus the small asymptotic solution alone represents one solution of the differential equation on both sides of the critical region. On the other hand, if the coefficient of the small asymptotic solution starts at zero and the coefficient of the large asymptotic solution is finite, then the coefficient of the small one changes by a definite amount as the critical region is crossed, and this gives us the representation of another solution of the differential equation on both sides of the critical region. A general solution is a linear combination of the solutions described, and it will be observed that the change in the coefficient of the small asymptotic solution in any such linear combination is proportional to the coefficient of the large solution.

infinitely great as $|x|$ goes to infinity, compared to the entire other solution, over the whole region of the complex plane except certain regions near the dotted lines of Fig. 2, which are midway between the solid lines. As one goes from one of the dotted lines to the other the smaller solution will be lost in a mist nearly the whole way, but exactly the same argument used by Stokes[9] will suffice to show that it changes by an amount proportional to the coefficient of the large solution. We may formulate this as follows. Between $\theta=0$ and $\theta=2\pi/3$ the second solution is large. We therefore have

$$B_1(2\pi/3)=B_1(0)-aB_2(0), \tag{45}$$

where $-a$ is the Stokes coefficient. Similarly

$$B_2(4\pi/3)=B_2(2\pi/3)+bB_1(2\pi/3), \tag{46}$$

where b is the Stokes coefficient, and

$$B_1(2\pi)=B_1(4\pi/3)+cB_2(4\pi/3), \tag{47}$$

where c is the Stokes coefficient.

Now if we carry the expression $\exp\left(\frac{2}{3}i\alpha^{\frac{1}{2}}\kappa x^{\frac{3}{2}}\right)$ around the complex plane, letting θ go from 0 to 2π, it will change into $\exp\left(-\frac{2}{3}i\alpha^{\frac{1}{2}}\kappa x^{\frac{3}{2}}\right)$, and *vice versa*. And as θ goes from 0 to 2π we see that $x^{-\frac{1}{4}}$ changes to $-ix^{-\frac{1}{4}}$. Therefore $G_1(2\pi)=-iG_2(0)$ and $G_2(2\pi)=-iG_1(0)$. But, as the differential equation has no singularities in the finite part of the complex plane, we must have $G(2\pi)=G(0)$. Hence $B_1(2\pi)=iB_2(0)$ and $B_2(2\pi)=iB_1(0)$. Successive use of (45), (46) and (47) together with the last two equations gives us[10] $-a=b=c=i$.

It is thus possible to evaluate the Stokes coefficients for this simple problem. A similar method may be applied to the more complicated case of the coupled differential Eqs. (9). Before we can do this, however, we need to consider in more detail the nature and properties of the solutions of these equations.

§6. Properties of the Approximate Solutions of the Coupled Differential Equations

The properties of the approximate solutions of the coupled equations will be largely determined by the properties of ν_1 and ν_2. To determine these properties we examine Eqs. (28) and (29). The situation can be best visualized by considering $E+\nu_1^2$ and $E+\nu_2^2$ as functions of the real variable $\rho(\rho=\rho_0e^{i\theta}$, the value of ρ_0 being always positive, while θ is 0 if ρ is positive and π if ρ is negative). The straight lines of Fig. 3 represent the original potential energy curves, while one of the dotted curves is $E+\nu_1^2$ and the other $E+\nu_2^2$; these curves represent what may be called perturbed potential energy curves. Just which one of the dotted curves is to be associated with ν_1 and which with ν_2 is indeterminate and depends, in fact, on ρ in a manner which may be arbitrarily fixed, except that, by (30) and (31), for very great positive values of ρ the upper dotted curve is $E+\nu_2^2$ and the lower $E+\nu_1^2$, while if ρ has a very great negative value the reverse is true. At some intermediate point the identification changes. That this must be the case is obvious by inspection of (28) and (29). When $\rho=\pm 2iv_{12}/(\alpha_1-\alpha_2)$ the inner square roots of ν_1 and ν_2 vanish. If we start from a point on the real axis, follow a path which encloses either one of these values of ρ, and return to the original point on the real axis ν_1 will have changed into ν_2 and *vice versa*. Now the two paths shown in Fig. 4 are obviously equivalent; therefore in going from A to B the identification of the dotted curves in Fig. 3 will have changed; but the large semicircle is just the path implied in the case of Eqs. (30) and (31). However, if we take the path along the real axis, the point at which we depart and go around the branch point, and so the point at which the identification of the dotted curves of Fig. 3 changes, is quite arbitrary. This being the case, we shall find it convenient to let this point of change be far to the left of the point ρ_1 of Fig. 3. Then we may evaluate the constants of integration for the integrals $\int\nu_1d\rho$ and $\int\nu_2d\rho$ by writing them as definite integrals, $\int_{\rho_1}^{\rho}\nu_1d\rho$ and $\int_{\rho_2}^{\rho}\nu_2d\rho$. In order to find the value of the first, let us say, of these integrals, at a point ρ whose ρ_0 is large, we may break the integral in two parts, the first part being along the real axis from ρ_1 to ρ_0, the second part along the arc of a large circle with center at the origin and radius ρ_0. We may thus write

$$\int_{\rho_1}^{\rho}\nu_1d\rho=\int_{\rho_1}^{\rho_0}\nu_1d\rho+\int_{\rho_0}^{\rho}\nu_1d\rho. \tag{48}$$

[10] This method of treatment is due to Zwaan, Utrecht Diss. (1929), who considered it in connection with a discussion of the Wentzel-Kramers-Brillouin approximation method.

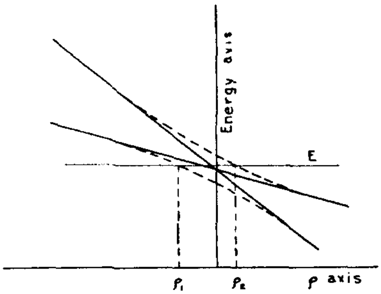

FIG. 3.

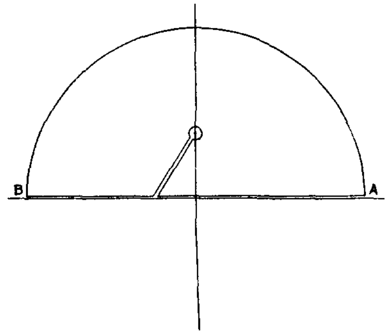

FIG. 4.

We may evaluate the second integral on the right of (48) if we use the binomial theorem first to expand the inner square root of Eq. (28) and then to expand the entire right-hand expression of (28). In this way we find

$$\begin{aligned}\int_{\rho_0}^{\rho}\nu_1 d\rho &= i\alpha_1^{\frac{1}{2}}\rho_0^{\frac{3}{2}}\int_{\theta=0}^{\theta=\theta}\left(e^{i\theta/2}+\frac{E}{2\alpha_1\rho_0 e^{i\theta/2}}+\cdots\right)de^{i\theta}\\ &= i\alpha_1^{\frac{1}{2}}\rho_0^{\frac{3}{2}}[(\tfrac{2}{3}e^{3i\theta/2}+(E/\alpha_1\rho_0)e^{i\theta/2}+\cdots)\\ &\qquad -(\tfrac{2}{3}+(E/\alpha_1\rho_0)+\cdots)]\\ &= i\alpha_1^{\frac{1}{2}}[(\tfrac{2}{3}\rho^{\frac{3}{2}}+(E/\alpha_1)\rho^{\frac{1}{2}}+\cdots)\\ &\qquad -(\tfrac{2}{3}\rho_0^{\frac{3}{2}}+(E/\alpha_1)\rho_0^{\frac{1}{2}}+\cdots)]. \quad (49)\end{aligned}$$

Let us now set $z=\rho+E/\alpha_1$. Then in the limiting case where ρ is very large we see that

$$z^{\frac{3}{2}}=\rho^{\frac{3}{2}}+\frac{3}{2}\frac{E}{\alpha_1}\rho^{\frac{1}{2}}. \quad (50)$$

Thus from (48), (49) and (50)

$$\begin{aligned}\lim_{\rho_0\to\infty}\int_{\rho_1}^{\rho}\nu_1 d\rho &= \int_{\rho_1}^{\rho_0}\nu_1 d\rho-\tfrac{2}{3}i\alpha_1^{\frac{1}{2}}z_0^{\frac{3}{2}}+\tfrac{2}{3}i\alpha_1^{\frac{1}{2}}z^{\frac{3}{2}}\\ &= \delta/2+\tfrac{2}{3}i\alpha_1^{\frac{1}{2}}z^{\frac{3}{2}}, \quad (51)\end{aligned}$$

where z_0 is the absolute value of z and

$$\delta/2=\lim_{\rho_0\to\infty}\left(\int_{\rho_1}^{\rho_0}\nu_1 d\rho-\tfrac{2}{3}i\alpha_1^{\frac{1}{2}}z_0^{\frac{3}{2}}\right). \quad (52)$$

It is readily seen from (30) that the expression on the right-hand side of (52) approaches a finite limit. It is pure imaginary since ν_1 is pure imaginary on the real axis. It would be zero were $E+\nu_1^2$ a straight line coinciding with V_1.

In the same way

$$\lim_{\rho_0\to\infty}\int_{\rho_2}^{\rho}\nu_2 d\rho=\delta'/2+\tfrac{2}{3}i\alpha_2^{\frac{1}{2}}y^{\frac{3}{2}}, \quad (53)$$

where $y=\rho+E/\alpha_2$ and

$$\delta'/2=\lim_{\rho_0\to\infty}\left(\int_{\rho_2}^{\rho_0}\nu_2 d\rho-\tfrac{2}{3}i\alpha_2^{\frac{1}{2}}y_0^{\frac{3}{2}}\right). \quad (54)$$

It can be shown that $\delta'=-\delta$ in the following way. δ is equal to $\oint_{\rho_1}\nu_1 d\rho$ where $\oint_{\rho_1}$ indicates a path starting at ρ_1, going along the real axis to ρ_0, then going clear around the large circle to ρ_0 again, and finally coming back to ρ_1. For if ν_1 is carried clear around the large circle from ρ_0 back to ρ_0 it changes sign, by (30), that is to say

$$\nu_1(2\pi)=-\nu_1(0); \quad (55)$$

hence, remembering that $z=z_0e^{i\theta}$ and that, when we have gone clear around the large circle, $\theta=2\pi$, we see by (51) that

$$\begin{aligned}\oint_{\rho_1}\nu_1 d\rho &= \delta/2+\tfrac{2}{3}i\alpha_1^{\frac{1}{2}}z_0^{\frac{3}{2}}e^{3i\pi}+\int_{\rho_0}^{\rho_1}\nu_1(2\pi)d\rho\\ &= \delta/2-\tfrac{2}{3}i\alpha_1^{\frac{1}{2}}z_0^{\frac{3}{2}}+\int_{\rho_1}^{\rho_0}\nu_1(0)d\rho\end{aligned}$$

and from (52) we see that we may write

$$\oint_{\rho_1}\nu_1 d\rho=\delta. \quad (56)$$

Similarly $$\oint_{\rho_2}\nu_2 d\rho=\delta'. \quad (57)$$

In Fig. 5 we show the paths indicated by $\oint_{\rho_1}$ and $\oint_{\rho_2}$. The path of $\oint_{\rho_2}$ is $EMNH$, while the path for $\oint_{\rho_1}$ is shown, rather distorted, by

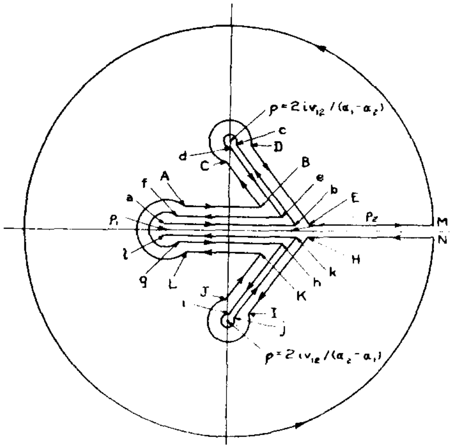

FIG. 5.

abcdefghijkl. Now the value of the integral taken about the closed path *EMNHIJKLABCDE* is zero, so the integral of ν_2 taken about *HIJKLABCDE* is $-\delta'$. But the value of the integral ν_1 taken about *abcdefghijkl*, that is δ, is easily seen to be equal to the integral of ν_2 taken about *HIJKLABCDE*, or $-\delta'$. This appears if we remember that carrying ν_1 or ν_2 around one of the branch points on the imaginary axis changes the sign of the inner square root and so effectively converts one of these quantities into the other. If we start with ν_2 at E and ν_1 at a, then the integrals along the segments marked with capital letters are equal to those along the segments marked with the corresponding small letters. Furthermore, the integral along *ef* cancels that along *gh* since ρ_1 is not a branch point after ν_1 has been carried about the branch point on the imaginary axis.

We shall find it necessary for our subsequent calculations to know how our different solutions change when we go around a large circle in the complex plane from a point where $\theta=0$ back to the same point but with $\theta=2\pi$. It is easy to see from (51), (55), (56), and the original definitions of η_1 and η_4 that

$$\eta_1(2\pi)=\eta_4(0)e^{\kappa\delta} \quad \text{and} \quad \eta_4(2\pi)=\eta_1(0)e^{-\kappa\delta}, \quad (58)$$

while, similarly, since $\delta'=-\delta$,

$$\eta_2(2\pi)=\eta_3(0)e^{-\kappa\delta}; \quad \text{and} \quad \eta_3(2\pi)=\eta_2(0)e^{\kappa\delta}. \quad (59)$$

It is also easy to show that $\mu^{\frac{1}{4}}(2\pi)=-\mu^{\frac{1}{4}}(0)$, and that $f_1(2\pi)=if_1(0)$ and $f_2(2\pi)=if_2(0)$. From these we get

$$F_{1,\,1}(2\pi)=-ie^{\kappa\delta}F_{1,\,4}(0), \quad \text{etc.} \quad (60)$$

and

$$F_{2,\,1}(2\pi)=-ie^{\kappa\delta}F_{2,\,4}(0), \quad \text{etc.} \quad (61)$$

§7. THE STOKES PHENOMENON FOR THE COUPLED EQUATIONS

We now have sufficient information at hand to consider the Stokes phenomenon for the coupled differential equations. We consider again Fig. 2, letting now the origin of the figure, from which the various lines radiate, be the point $\rho=0$. It is readily seen from (51) and (53), remembering that δ and δ' are pure imaginary, that, in the limit of large ρ_0, the integrals $\int_{\rho_1}{}^{\rho}\nu_1 d\rho$ and $\int_{\rho_2}{}^{\rho}\nu_2 d\rho$ are pure imaginary along lines parallel to the dotted lines of Fig. 2. There will be certain small regions near the lines defined by the conditions $\theta=0$, $\theta=2\pi/3$, $\theta=4\pi/3$, $\cdots$, where the ratios of the four solutions of the coupled equations will be finite, and where the errors in the asymptotic forms will be small. In these regions all four arbitrary coefficients, A_1, A_2, A_3 and A_4, are significant. In all other regions the error in the asymptotic form of any solution is larger than the entire value of all smaller solutions. Thus, unless the coefficient of the largest solution is zero, all other solutions become lost in a mist throughout nearly the whole region between two of the dotted lines. It can be shown by a simple extension of Stokes' reasoning[9] that on passing through the misty region each coefficient will have changed by an amount which can be separated into several parts, the number of parts being equal to the number of solutions whose magnitudes are greater than the solution in question, and each part being proportional to the coefficient of one of the solutions of greater magnitude. The order of size of the solutions is entirely determined by the relative sizes of η_1, η_2, η_3 and η_4 since the ratios of these quantities become exponentially infinite if one approaches $\rho_0=\infty$ in any other direction than those indicated by the dotted lines in Fig. 2. Since

$$\eta_4>\eta_3>\eta_2>\eta_1 \text{ if } 0<\theta<2\pi/3 \text{ or if } 4\pi/3<\theta<2\pi$$

and

$$\eta_1>\eta_2>\eta_3>\eta_4 \text{ if } 2\pi/3<\theta<4\pi/3$$

we may write, assuming that we begin with $\theta=2\pi/3$,

$$\begin{aligned}
A_1(0)&=A_1(2\pi/3)+a_{12}A_2(2\pi/3)+a_{13}A_3(2\pi/3)+a_{14}A_4(2\pi/3)\\
A_2(0)&=\qquad\qquad A_2(2\pi/3)+a_{23}A_3(2\pi/3)+a_{24}A_4(2\pi/3)\\
A_3(0)&=\qquad\qquad\qquad\qquad A_3(2\pi/3)+a_{34}A_4(2\pi/3)\\
A_4(0)&=\qquad\qquad\qquad\qquad\qquad\qquad A_4(2\pi/3)
\end{aligned}\tag{62}$$

$$\begin{aligned}
A_1(4\pi/3)&=A_1(2\pi/3)\\
A_2(4\pi/3)&=b_{21}A_1(2\pi/3)+A_2(2\pi/3)\\
A_3(4\pi/3)&=b_{31}A_1(2\pi/3)+b_{32}A_2(2\pi/3)+A_3(2\pi/3)\\
A_4(4\pi/3)&=b_{41}A_1(2\pi/3)+b_{42}A_2(2\pi/3)+b_{43}A_3(2\pi/3)+A_4(2\pi/3)
\end{aligned}\tag{63}$$

$$\begin{aligned}
A_1(2\pi)&=A_1(4\pi/3)+c_{12}A_2(4\pi/3)+c_{13}A_3(4\pi/3)+c_{14}A_4(4\pi/3)\\
A_2(2\pi)&=\qquad\qquad A_2(4\pi/3)+c_{23}A_3(4\pi/3)+c_{24}A_4(4\pi/3)\\
A_3(2\pi)&=\qquad\qquad\qquad\qquad A_3(4\pi/3)+c_{34}A_4(4\pi/3)\\
A_4(2\pi)&=\qquad\qquad\qquad\qquad\qquad\qquad A_4(4\pi/3)
\end{aligned}\tag{64}$$

where the a's, b's and c's are the Stokes coefficients.

But since the coupled differential equations have no singularities in the finite part of the complex plane, we know, as in §5, that $F_i(2\pi) = F_i(0)$, which leads, in conjunction with (60) and (61) to the conditions

$$\begin{aligned}
A_1(2\pi)&=ie^{-\kappa\delta}A_4(0),\quad A_3(2\pi)=ie^{-\kappa\delta}A_2(0),\\
A_2(2\pi)&=ie^{\kappa\delta}A_3(0),\quad A_4(2\pi)=ie^{\kappa\delta}A_1(0).
\end{aligned}\tag{65}$$

By use of (62), (63) and (64) it is possible to express all the A's in (65) in terms of $A_1(2\pi/3)$, $A_2(2\pi/3)$, $A_3(2\pi/3)$ and $A_4(2\pi/3)$. Since the latter are completely arbitrary the multiplier of *each* one of them on the right-hand side of the resulting equations must be set equal to its multiplier on the other side. We thus obtain sixteen equations in the a's, b's and c's, which are as follows:

$$1+c_{12}b_{21}+c_{13}b_{31}+c_{14}b_{41}=0,\tag{66.1}$$

$$c_{12}+c_{13}b_{32}+c_{14}b_{42}=0,\tag{66.2}$$

$$c_{13}+c_{14}b_{43}=0,\tag{66.3}$$

$$c_{14}=ie^{-\kappa\delta},\tag{66.4}$$

$$b_{21}+c_{23}b_{31}+c_{24}b_{41}=0,\tag{66.5}$$

$$1+c_{23}b_{32}+c_{24}b_{42}=0,\tag{66.6}$$

$$c_{23}+c_{24}b_{43}=ie^{\kappa\delta},\tag{66.7}$$

$$c_{24}=ie^{\kappa\delta}a_{34},\tag{66.8}$$

$$b_{31}+c_{34}b_{41}=0,\tag{66.9}$$

$$b_{32}+c_{34}b_{42}=ie^{-\kappa\delta},\tag{66.10}$$

$$1+c_{34}b_{43}=ie^{-\kappa\delta}a_{23},\tag{66.11}$$

$$c_{34}=ie^{-\kappa\delta}a_{24},\tag{66.12}$$

$$b_{41}=ie^{\kappa\delta},\tag{66.13}$$

$$b_{42}=ie^{\kappa\delta}a_{12},\tag{66.14}$$

$$b_{43}=ie^{\kappa\delta}a_{13},\tag{66.15}$$

$$1=ie^{\kappa\delta}a_{14}.\tag{66.16}$$

It turns out that of these 16 equations only 15 are independent. They enable us to express the b's and the c's in terms of the a's, and to get three relations between the a's themselves. First of all we see that (66.16) gives us

$$a_{14}=-ie^{-\kappa\delta}.\tag{67.1}$$

From (66.15), (66.12) and (66.11) we obtain

$$1-a_{13}a_{24}=ie^{-\kappa\delta}a_{23}.\tag{67.2}$$

Substituting for c_{23} from (66.7) and for b_{32} from (66.10) in (66.6), using (66.12), (66.14), (66.8) and (66.15) to evaluate the rest of the quantities in terms of the a's, and finally simplifying with the aid of (67.2) we get

$$a_{12}a_{24}+a_{13}a_{34}-a_{12}a_{34}a_{23}=0.\tag{67.3}$$

It is obvious that further conditions will need to be found before we can evaluate the a's and complete the solution of the Stokes problem. Before considering how other conditions may be discovered, however, we shall show how the transition probabilities may be evaluated in terms of the a's.

§8. Evaluation of the Transition Probabilities in Terms of the Stokes Coefficients

As we have noted at the end of §3 it is necessary to have $A_1(\pi)$ and $A_2(\pi)$ equal to zero. We have preferred in the later sections to consider the values of the A's only for the directions of the dotted lines of Fig. 2; we can continue to do this, for it is readily seen that $A_1(\pi)$ and $A_2(\pi)$ are zero if $A_1(2\pi/3)$ and $A_2(2\pi/3)$ are zero. This condition, it is seen, simplifies Eqs. (62) to a considerable extent. Now to calculate the transition probability P_1 we further set $A_2(0)=0$, so that the second equation of (62) becomes

$$0=a_{23}A_3(2\pi/3)+a_{24}A_4(2\pi/3) \qquad (68)$$

which enables us to express all the $A(0)$'s in terms of $A_3(2\pi/3)$ and the a's. We then get from (38)

$$P_1=\frac{|1-a_{34}a_{23}/a_{24}|^2}{|a_{13}-a_{14}a_{23}/a_{24}|^2} \qquad (69)$$

and (39) gives the equation

$$|a_{13}-a_{14}a_{23}/a_{24}|^2 = |1-a_{34}a_{23}/a_{24}|^2+|a_{23}/a_{24}|^2. \qquad (70)$$

Similarly from (40) and (41)

$$P_2=\frac{|a_{13}/a_{14}|^2}{|a_{23}-a_{13}a_{24}/a_{14}|^2} \qquad (71)$$

and

$$|a_{23}-a_{24}a_{13}/a_{14}|^2 = |1-a_{13}a_{34}/a_{14}|^2+|a_{13}/a_{14}|^2. \qquad (72)$$

§9. Other Relations Between the Stokes Coefficients

Other relations between the a's may be obtained by considering the properties of the solutions when only partial circuits are made. If we start on the positive real axis with any solution or combination of solutions which is real, then it is obvious that on carrying this solution to some particular θ the result will be the conjugate complex of that which would be obtained by carrying the same solution to $-\theta$ and the same ρ_0. Now suppose we set up the expressions

$$F_1(\pi)=A_1(\pi)F_{1,1}(\pi)+A_2(\pi)F_{1,2}(\pi) +A_3(\pi)F_{1,3}(\pi)+A_4(\pi)F_{1,4}(\pi) \qquad (73a)$$

and

$$F_2(\pi)=A_1(\pi)F_{2,1}(\pi)+A_2(\pi)F_{2,2}(\pi) +A_3(\pi)F_{2,3}(\pi)+A_4(\pi)F_{2,4}(\pi), \qquad (73b)$$

where

$$\begin{aligned}
&A_1(\pi)=A_1(3\pi/2),\\
&A_2(\pi)=(b_{21}/2)A_1(3\pi/2)+A_2(3\pi/2),\\
&A_3(\pi)=(b_{31}/2)A_1(3\pi/2) +(b_{32}/2)A_2(3\pi/2)+A_3(3\pi/2),\\
&A_4(\pi)=(b_{41}/2)A_1(3\pi/2)+(b_{42}/2)A_2(3\pi/2) +(b_{43}/2)A_3(3\pi/2)+A_4(3\pi/2).
\end{aligned} \qquad (74)$$

Now if and only if the expressions $F_1(\pi)$ and $F_2(\pi)$ are real (quite regardless of whether the $A(\pi)$'s for the small solutions have any significance when $F_1(\pi)$ and $F_2(\pi)$ are considered as approximate solutions of the differential equations) we see that $F_1(4\pi/3)=F_1^*(2\pi/3)$ (where the asterisk means conjugate complex) and $F_2(4\pi/3)=F_2^*(2\pi/3)$. Therefore, if $F_1(0)$ and $F_2(0)$ are real it follows that $F_1(\pi)$ and $F_2(\pi)$ (as given by (73a) and (73b)) are also real.

Now since $\mu^{\frac{1}{2}}$, f_1 and f_2 start out by being real when $\theta=0$, and since $\eta_1(0)=\eta_4^*(0)$ and $\eta_2(0)=\eta_3^*(0)$, it is readily seen that the conditions that $F_1(0)$ and $F_2(0)$ shall be real are

$$A_1^*(0)=A_4(0) \quad \text{and} \quad A_2^*(0)=A_3(0). \qquad (75)$$

To find the conditions which must be fulfilled in order for $F_1(\pi)$ and $F_2(\pi)$ to be real we first note that, ρ_0 being large and fixed,

$$\mu^{\frac{1}{2}}(\pi)f_1(\pi)=e^{-i\pi/4}\mu^{\frac{1}{2}}(0)f_1(0) \qquad (76a)$$

and

$$\mu^{-\frac{1}{2}}(\pi)f_1(\pi)=e^{-5i\pi/4}\mu^{-\frac{1}{2}}(0)f_1(0) = -e^{-i\pi/4}\mu^{-\frac{1}{2}}(0)f_1(0), \qquad (76b)$$

while exactly the same relations hold with f_2 substituted for f_1. From (51) the imaginary part of $\int_{\rho_1}{}^{\rho(\pi)}\nu_1 d\rho$ is $\delta/2$ and from (53) the imaginary part of $\int_{\rho_2}{}^{\rho(\pi)}\nu_2 d\rho$ is $\delta'/2=-\delta/2$. We therefore see that in order for $F_1(\pi)$ and $F_1(\pi)$ to be real the following relations must hold.

$$\begin{aligned} A_1(\pi)&=e^{i\pi/4}e^{-\kappa\delta/2}\mathfrak{a}_1, & A_3(\pi)&=e^{i\pi/4}e^{-\kappa\delta/2}\mathfrak{a}_3, \\ A_2(\pi)&=e^{i\pi/4}e^{\kappa\delta/2}\mathfrak{a}_2, & A_4(\pi)&=e^{i\pi/4}e^{\kappa\delta/2}\mathfrak{a}_4, \end{aligned} \tag{77}$$

where $\mathfrak{a}_1$, $\mathfrak{a}_2$, $\mathfrak{a}_3$ and $\mathfrak{a}_4$ are real, the quantities which multiply these $\mathfrak{a}$'s being just what is necessary to counteract those factors of the particular solutions which are not real.

Now, as we have said, if one of the sets of equations, (75) or (77), holds the other must hold also. This gives us further conditions on the a's. We evaluate the $A(0)$'s in terms of the $A(3\pi/2)$'s from (62) and substitute into (75). We thus get a pair of equations we shall call (75A). Then we may evaluate the $A(\pi)$'s in terms of the $A(3\pi/2)$'s from (74) and substitute into (77) getting a set of four equations which we designate as (77A). Eliminating the $A(3\pi/2)$'s from (75A) and (77A) we are finally left with two equations involving the $\mathfrak{a}$'s and also, of course, various combinations of the a's and b's. This final pair of equations we designate as (75B). Since the $\mathfrak{a}$'s are arbitrary, the quantity which multiplies any one of them on the left of one of the pair of equations (75B) must be equal to the corresponding multiplier on the right. We thus see that the two equations (75B) actually furnish eight relations between the a's and b's, which with the use of Eqs. (66) may be reduced to relations involving the a's alone. Equating the multipliers of $\mathfrak{a}_4$ on both sides of one of the pair of equations (75B) gives Eq. (67.1) again; the same procedure on the other equation gives

$$a_{34}=-ia_{24}{}^*e^{-\kappa\delta}. \tag{78}$$

Equating the multipliers of $\mathfrak{a}_3$ in the pair of equations (75B) gives

$$a_{13}=a_{13}{}^* \tag{79}$$

and another relation which is not independent of Eqs. (67), Eq. (78) and Eq. (79). The coefficients of $\mathfrak{a}_2$ and $\mathfrak{a}_1$ give relations which are too complicated to handle directly. This being the case, further relations were sought, as shown in the next paragraph, by invoking the law of conservation of particles, as expressed, in part, by Eqs. (70) and (72). This enables one to express five of the a's in terms of the other one, and it may then readily be shown that the equations resulting from the coefficients of $\mathfrak{a}_2$ and $\mathfrak{a}_1$ are satisfied.

Multiplying (70) through by $|a_{24}|^2$ and (72) by $|a_{14}|^2$ and noting that, by (67.1) and (67.2) we have $|a_{23}a_{14}-a_{24}a_{13}|^2=1$, we see that

$$|a_{24}-a_{34}a_{23}|^2+|a_{23}|^2=1 \tag{80}$$

and

$$|a_{14}-a_{13}a_{34}|^2+|a_{13}|^2=1. \tag{81}$$

Now by (67.1), (78) and (79),

$$\begin{aligned}|a_{14}-a_{13}a_{34}|^2&=|-ie^{-\kappa\delta}+a_{13}a_{24}{}^*ie^{-\kappa\delta}|^2\\ &=1-a_{13}a_{24}{}^*-a_{13}a_{24}+a_{13}{}^2a_{24}{}^*a_{24}\end{aligned}$$

which, by (81) is equal to $1-a_{13}{}^2$. It is thus seen that, since a_{13} is not to be zero, we must have

$$a_{13}=(a_{24}+a_{24}{}^*)(1+a_{24}a_{24}{}^*)^{-1}. \tag{82}$$

It is now readily possible from (82), (67.2), (78) and (67.3) to get a_{23}, a_{34} and a_{12} in terms of a_{24}. We have

$$a_{23}=-ie^{\kappa\delta}(1-a_{24}{}^2)(1+a_{24}a_{24}{}^*)^{-1} \tag{83}$$

and

$$a_{12}=-a_{34}=ia_{24}{}^*e^{-\kappa\delta}, \tag{84}$$

whence

$$P_1=P_2=P=(a_{24}+a_{24}{}^*)^2(1+a_{24}a_{24}{}^*)^{-2}. \tag{85}$$

The expression on the right-hand side of (85) has all the characteristic properties of a probability, inasmuch as it may be seen to be real and lie always between 0 and 1. Unfortunately, however, it has thus far proved impossible to find one more relation among the a's which would permit the final evaluation of P. This failure, nevertheless, is in itself rather interesting, inasmuch as it shows what may happen when one attempts to apply Zwaan's adaptation of Stokes' method to more complicated differential equations. In the case of the simple second order differential Eq. (43) the problem is solved by taking the asymptotic solutions once around the complex plane. However, in the case of the coupled differential equations, which are equivalent to a fourth order differential equation, even the more stringent conditions applied in this section, which result from what may be roughly described as taking the solutions halfway around the plane, do not suffice to determine the Stokes coefficients. If we could find conditions to apply when the solutions are carried some smaller part of the way, say one-third of the way around, then we might hope to solve the problem. But the discovery and application of such conditions promises to be so complicated that nothing would be gained over solving the differential equations by series, a process which, theoretically at least, may always be carried out, but is actually forbiddingly involved.

§10. Critique of Stueckelberg's Work

It seems, at first, rather strange, in view of the above, that Stueckelberg should have been able to get definite results even for the special values of the total energy E to which he confined himself. It appears to me, however, that he was able to do this only by using a scheme which implicitly but quite arbitrarily introduces the extra condition which in the present investigation it has not been possible to find. Stueckelberg assumes that the discontinuity in the coefficients of the solutions must always occur along lines where the ratio between two of the solutions is a maximum or minimum. For example, suppose we consider solution 1 and solution 2; then we find the locus in the complex plane where $\log(\eta_1/\eta_2)$ is real—such a locus will, at least in the limiting case, be the locus along which either η_1/η_2 or η_2/η_1, as the case may be, increases most rapidly as we go out in the complex plane away from the origin. Such a line naturally can be considered to begin at a point where the logarithm of the ratio of the η's in question is zero; the branch points considered above are such points. Stueckelberg's analysis is based on the assumption that the ratio of two η's has acquired its asymptotic properties at a distance from its particular branch point which is small compared to the distance between branch points—this is what confines him to the case where E is far from the intersection of the potential energy curves. However, it seems to me that one is not allowed to make assumptions about the lines at which or the regions within which the jumps in the coefficients will take place, nor to decide whether a given solution causes the coefficients of *one* or *more* than one of the other solutions to jump, without a detailed investigation of the asymptotic series and the errors involved therein, and the limits of the regions in which these errors are large. In the simple case we considered in §5 we showed that it was possible to do as much with the rough asymptotic forms as with the more exact asymptotic expansions, but this is by no means necessarily true for a more complicated case. Stueckelberg, furthermore, has not considered all possible pairs of solutions, but only those the logarithms of whose ratios become zero at one of the branch points. It is, again, not certain that this is justified. It is entirely possible that Stueckelberg's analysis is correct; I do not believe, however, that it has been proved to be correct. It might not be impossible to find out whether it is correct, or if it is not exactly but nearly correct how good an approximation it is under various circumstances, but this will require a detailed discussion of the asymptotic *expansions* which promises to be very tedious.