

the electrons has been attempted, since no data are available for such a computation. Furthermore it is not known to what extent these metastable atoms are produced locally by recombination and to what extent they are swept down by the vapor from the region of the arc. Webb and Wang<sup>2</sup> found that both factors are important. They further showed that if into a moving plasma similar to that studied here, they introduced sodium vapor, a marked drop in electron temperature immediately resulted; in the case cited from 2300° to 800°K. The most important action of the sodium on the flowing vapor was to eliminate the metastable atoms by excitation of the sodium, and the most probable explanation of the temperature drop is that the elimination of the metastable atoms removed a source of electron energy, resulting in lowered electron temperature.

Webb and Sinclair<sup>2</sup> found that the rate of recombination depended to a large extent on the electron temperature, and came to the conclusion that a somewhat complex interaction between ions and fast and slow electrons was involved in the recombination process. Furthermore, a study

of the intensity distribution in the afterglow spectrum leads to the conclusion that considerable kinetic energy may be freed by the process. It therefore seems probable that the recombination process is largely responsible for the energy supply which tends to hold up the electron temperature, either through some process involving many-body collisions, or by the metastable atoms which constitute a large part of the atoms formed by recombination. It may be noted that the recombination has been found by Webb and Sinclair and by Mohler and Boeckner<sup>7</sup> to increase with the pressure, which corresponds to the increase in the final electron temperature level with increase in pressure found here. On the other hand, for a given rate of production, the concentration of metastable atoms also tends to increase with increased pressure, as under these conditions the life of these atoms is practically determined by the diffusion to the wall.

The authors wish to express their appreciation to Mr. T. C. Hardy for his assistance in the taking of the measurements.

<sup>7</sup> Mohler and Boeckner, *Bur. Standards J. Research* **2**, 489 (1929).

## A Contribution to the Theory of the B. W. K. Method

EDWIN C. KEMBLE, *Research Laboratory of Physics, Harvard University*

(Received April 16, 1935)

In order to put Zwaan's scheme for deriving the Kramers connection formulas on a rigorous basis, differential equations are set up governing the variation in the coefficients used to fit a linear combination of the B. W. K. type approximation functions to an exact solution of Schrödinger's equation in one dimension. Approximate solutions of the differential equations are worked out which lend themselves to the setting up of the connection formulas and

give definite upper bounds to the errors involved in their use. The method is also used to set up the Sommerfeld phase integral quantum condition independently of the connection formulas. An upper limit to the error in the energy is worked out. A similar treatment of the problem of the transmission of matter waves through rounded potential barriers is formulated.

### 1. INTRODUCTION

Zwaan's<sup>1</sup> scheme for deriving the Kramers connection formulas<sup>2</sup> used in the Brillouin-Wentzel-Kramers (B. W. K.) method is simple and illuminating, but not entirely rigorous. In

the attempt to put Zwaan's argument on a rigorous basis the author has developed a new way of studying the relation of the Stokes phenomenon to the B. W. K. method whose value extends beyond the scope of the connection formulas themselves.

Consider a one-dimensional problem in wave mechanics with the potential energy  $V(z)$  and the classical local momentum

<sup>1</sup> A. Zwaan, *Intensitäten im Ca-Funkenspektrum*, Dissertation, Utrecht, 1929.

<sup>2</sup> H. A. Kramers, *Zeits. f. Physik* **39**, 828 (1926); H. A. Kramers and G. P. Ittman, *Zeits. f. Physik* **58**, 217 (1929).

$$p(z, E) = \{2\mu[E - V(z)]\}^{\frac{1}{2}}.$$

The Schrödinger equation takes the form

$$\psi'' + \lambda^2 p^2 \psi = 0 \quad (1)$$

with  $\lambda$  set equal to  $2\pi/h$ . The basic approximation functions of the B. W. K. method are

$$f_i(z, E) = p(z, E)^{-\frac{1}{2}} e^{i w(z, E)}; \quad (2)$$

$$f_v(z, E) = p(z, E)^{-\frac{1}{2}} e^{-i w(z, E)};$$

$$w(z, E) = \lambda \int_{z_0}^z p(\zeta, E) d\zeta. \quad (3)$$

Here  $i$  denotes  $\sqrt{-1}$ . The point  $z_0$  can be chosen at pleasure but is ordinarily placed on the axis of reals.  $f_i$  and  $f_v$  are readily shown to be solutions of the differential equation

$$f'' + [\lambda^2 p^2 - Q]f = 0, \quad (4)$$

where  $Q$  denotes the function

$$Q = -\frac{3}{4} \left( \frac{p'}{p} \right)^2 - \frac{p''}{2p} \equiv \frac{1}{4} \left[ \frac{5}{4} \left( \frac{V'}{E-V} \right)^2 + \frac{V''}{E-V} \right]. \quad (5)$$

Wherever  $|Q| \ll \lambda^2 p^2$ , Eq. (4) is very nearly the same as (1) and  $f_i, f_v$  may be said to be good approximate solutions of (1).

Let  $z'$  denote a simple real zero point of the function  $E - V(z)$  (primes and double primes denote differentiation *except* when applied to the symbol  $z$  itself). For definiteness, we assume that  $E - V$  is negative to the left of  $z'$  and positive to the right (cf. Fig. 1). At  $z'$ ,  $f_i, f_v$  and  $Q$  all become infinite. Hence  $f_i, f_v$  have no value as approximate solutions of (1) in the neighborhood of  $z'$ . We shall suppose, however, that there exist regions I and II to the left and right of  $z'$ , respectively, where  $|Q| \ll \lambda^2 p^2$  and where the  $f$ 's are good approximate solutions. Then if  $\psi(z)$  is an exact solution of (1), we may reasonably assume that in any not too large portion of I,  $\psi(z)$  is approximately equal to some suitable linear combination of  $f_i$  and  $f_v$ . Thus, if  $\alpha_i$  and  $\alpha_v$  are suitably chosen constants,

$$\alpha_i f_i + \alpha_v f_v = \psi(z) \quad \text{in region I.}$$

Similarly

$$\beta_i f_i + \beta_v f_v = \psi(z) \quad \text{in region II.}$$

It is well known that the coefficients  $\beta_i, \beta_v$  are not equal to  $\alpha_i, \alpha_v$ , respectively. The shift in the

values of the coefficients is called the Stokes phenomenon and the problem is to determine the magnitude of this shift in terms of the values on one side of  $z'$ , say in I.

Kramers method of attack is based on the assumption that  $V(z)$  is sensibly linear in the interval between I and II. Under these circumstances  $\psi(z)$  can be approximated by a suitable Bessel's function over the interval in question and this function constitutes a bridge between the B. W. K. approximations in I and II. Langer<sup>3</sup> has introduced a different type of approximation function involving a Bessel's function of the argument  $w(x)$  defined in Eq. (3). The Langer approximation function degenerates into the B. W. K. type in I and II, but does not go to pieces near  $z'$ . This method is very powerful, but has some disadvantages with respect to that developed in the present article.

Zwaan's derivation of the connection formulas follows closely a line of thought previously developed by Stokes.<sup>4</sup> It is based on the introduction of complex values of the independent variable and the existence of a path  $\Gamma$  joining I and II, but passing around  $z'$  in the complex plane so that the inequality  $|Q| \ll \lambda^2 p^2$  is good along its entire length. If  $V(z)$  is analytic on the axis of reals between I and II, and if its analytic extension into the upper half plane yields no roots of  $V(z) - E$  near  $z'$ , we may assume that such a path can be found.<sup>5</sup>

The essential feature of the situation to which Zwaan calls attention is that along a portion of any such path  $\Gamma$  the approximation  $f_i$  becomes

<sup>3</sup> R. E. Langer, *Trans. Am. Math. Soc.* **33**, 23 (1931); **34**, 447 (1932); *Bull. Am. Math. Soc.* **40**, 545 (1934).

<sup>4</sup> Sir George Gabriel Stokes, *Math. and Phys. Papers*, Vol. 4, pp. 77-109 and 283-298.

<sup>5</sup> Let us assume that  $V(z) - E$  is a polynomial of degree  $n$ , or can be accurately represented by such a polynomial in the interval between I and II. Then, if  $z_k$  denotes the  $k$ th root,  $E - V = C \prod_{k=1}^n (z - z_k)$ . It follows that

$$(E - V)' / (E - V) = \sum_{k=1}^n \frac{1}{z - z_k};$$

$$(E - V)'' / (E - V) = \left( \frac{E - V'}{E - V} \right)^2 - \sum_{k=1}^n \frac{1}{(z - z_k)^2}.$$

Hence

$$\frac{Q}{p^2} = \frac{1}{8\mu C \prod_k (z - z_k)} \left[ \frac{1}{4} \left( \sum_{k=1}^n \frac{1}{z - z_k} \right)^2 + \sum_k \frac{1}{(z - z_k)^2} \right].$$

Inspection of this expression for  $Q/p^2$  proves the above statement for the case that  $n$  is small.

very small, while  $f_v$  becomes very large. Hence  $f_v$  and  $f_i$  are said to be *dominant* and *subdominant*, respectively, in the region in question. Where this is true changes in the subdominant coefficient can take place even when  $|Q| \ll \lambda^2 p^2$ . On the other hand the coefficient of the dominant approximation function cannot change much, since a small change in this coefficient makes a very large difference in the function. Zwaan assumes that the latter coefficient is constant.

## 2. THE DIFFERENTIAL EQUATIONS FOR THE COEFFICIENTS

Granted that the changes do take place, we propose here to investigate them by setting up explicit differential equations for the variation in the coefficients. The formulation of these equations, which forms the essential contribution of the present paper, is reminiscent of a method of attack on one-dimensional problems in quantum mechanics due to Hill.<sup>6</sup>

Let  $\psi(z)$  be an exact solution of (1). Let  $u = a_i f_i + a_v f_v$  be a linear combination of  $f_i$  and  $f_v$  which is fitted to  $\psi$  at the arbitrary point  $z = z_1$ . The best fit will evidently be obtained if  $u$  and  $du/dz$  are made equal to  $\psi$  and  $d\psi/dz$ , respectively, at the point  $z_1$ . In that case

$$a_i f_i(z_1) + a_v f_v(z_1) = \psi(z_1); \quad (6)$$

$$a_i f_i'(z_1) + a_v f_v'(z_1) = \psi'(z_1). \quad (7)$$

As the Wronskian determinant  $f_i f_v' - f_v f_i'$  does not vanish (it has the constant value  $-4\pi i/h = -2\lambda i$ ) it is possible to choose  $a_i$  and  $a_v$  so as to satisfy these equations at an arbitrary point  $z_1$  where  $f_i$  and  $f_v$  are uniquely defined. The coefficients so obtained will then vary *continuously* as  $z_1$  moves around the path  $\Gamma$ , reducing to  $\alpha_i$  and  $\alpha_v$  where  $\Gamma$  meets the axis of reals in I and to  $\beta_i$ ,  $\beta_v$  where  $\Gamma$  meets the axis of reals in II.

Dropping the subscript 1 in Eqs. (6) and (7), solving for  $a_i$ , and differentiating with respect to  $z$ , we obtain

$$\frac{da_i}{dz} = \frac{i}{2\lambda} (f_v'' \psi - f_v \psi''). \quad (8)$$

On reduction with the aid of Eqs. (1) and (4)

$$\frac{da_i}{dz} = \frac{i}{2\lambda} Q f_v \psi = \frac{i}{2\lambda} \frac{Q}{p} [a_i + e^{-2iw} a_v]. \quad (9)$$

Similarly

$$\frac{da_v}{dz} = -\frac{i}{2\lambda} Q f_i \psi = -\frac{i}{2\lambda} \frac{Q}{p} [a_v + e^{2iw} a_i]. \quad (10)$$

These differential equations are *exact*. Their integration is equivalent to the integration of Eq. (1), although they blow up at the zeros of  $p(z, E)$ . If an exact integration were possible, it would be a simple matter to work out the exact eigenfunctions and eigenvalues of (1). The primary usefulness of Eqs. (9) and (10), however, lies in the possibility of deriving useful approximations from them.

## 3. THE APPROXIMATE INTEGRATION OF EQS. (9) AND (10)

Introducing a fixed point  $\xi$ , let us make the transformation

$$b_i(z, \xi) = a_i(z) e^{-iF(z, \xi)}; \quad (11)$$

$$b_v(z, \xi) = a_v(z) e^{+iF(z, \xi)},$$

where

$$F(z, \xi) = \frac{1}{2\lambda} \int_{\xi}^z \frac{Q}{p} dz. \quad (11a)$$

This change of variables leads to the following simpler system of differential equations:

$$\frac{db_i}{dz} = \frac{i}{2\lambda} \frac{Q}{p} e^{-2i(F+w)} b_v; \quad (12)$$

$$\frac{db_v}{dz} = -\frac{i}{2\lambda} \frac{Q}{p} e^{2i(F+w)} b_i.$$

Clearly  $b_i$  and  $b_v$  will be sensibly equal to  $a_i$  and  $a_v$ , respectively, at any point  $z$  which can be connected with  $\xi$  by a path along which  $|Q/p|$  is small enough. It is convenient to define an index of quality  $\mu_{\Lambda}$  for a path  $\Lambda$  in the complex plane by the equation

$$\mu_{\Lambda} = \frac{1}{\lambda} \int_{\Lambda} \left| \frac{Q}{p} \right| ds = \frac{1}{\lambda^2} \int_{\Lambda} \left| \frac{Q}{p^2} \right| |dw|. \quad (13)$$

We shall hereafter refer to a path as *good*, provided that its index of quality is much less than unity. Any short path which gives a wide berth to the

<sup>6</sup> E. L. Hill, Phys. Rev. **38**, 1258 (1931).

zeros of  $p(z, E)$  can ordinarily be assumed to be "good" in this sense. Since

$$\left| \frac{1}{\lambda} \int_{\Lambda} \frac{Q}{p} dz \right| \leq \mu_{\Lambda},$$

it follows that  $|F(z, \xi)| \leq \frac{1}{2}\mu_{\Lambda}$  if  $z$  and  $\xi$  are any two points on  $\Lambda$ .  $b_i$  and  $b_v$  are thus sensibly equal to  $a_i$  and  $a_v$  at any point  $z$  which can be connected with  $\xi$  by a good path.

It will simplify the discussion of the integration of Eqs. (12) if we assume at first a definite path of integration  $\Lambda$ , of total length  $l$ , leading from an initial point  $Z_0$  to a final point  $Z_1$ , and having the property that the imaginary part of  $w$  is a monotonically decreasing function of the path length  $s$  measured from  $Z_0$ . In other words, we

assume that  $|e^{iw}|$  increases monotonically as we move from  $Z_0$  to  $Z_1$  along  $\Lambda$ . With these restrictions we introduce the real variable of integration  $s$  and the notation

$$w(z) = \omega(s), \quad iQ(z)/2\lambda p(z) = \Sigma(s), \tag{14}$$

$$dz/ds = \varphi(s), \quad F(z, \xi) = \theta(s, \xi).$$

Eqs. (12) take the form

$$db_i/ds = \Sigma(s) \varphi(s) e^{-2i(\theta+\omega)} b_v, \tag{15}$$

$$db_v/ds = -\Sigma(s) \varphi(s) e^{2i(\theta+\omega)} b_i. \tag{16}$$

Under favorable circumstances  $b_i$  can be computed approximately for points on  $\Lambda$  by replacing  $b_v$  in (15) by its initial value  $b_v^0 \equiv b_v(Z_0)$ . Let  $\tilde{b}_i(z)$  denote the corresponding approximation for  $b_i(z)$ . Then

$$\tilde{b}_i(s) = b_i^0 + b_v^0 \int_0^s \Sigma(s_1) \varphi(s_1) e^{-2i[\theta(s_1)+\omega(s_1)]} ds_1. \tag{17}$$

This approximation can be tested by computing an upper bound on  $|b_i(Z_1) - \tilde{b}_i(Z_1)|$ . We have

$$b_i(Z_1) - \tilde{b}_i(Z_1) = \int_0^l [b_v(s) - b_v^0] \Sigma(s) \varphi(s) e^{-2i(\theta+\omega)} ds. \tag{18}$$

But from (16)

$$b_v(s) - b_v^0 = - \int_0^s b_i(s_1) \Sigma(s_1) \varphi(s_1) e^{2i[\theta(s_1)+\omega(s_1)]} ds_1. \tag{19}$$

Hence

$$\begin{aligned} b_i(Z_1) - \tilde{b}_i(Z_1) &= - \int_0^l ds \{ \Sigma(s) \varphi(s) e^{-2i[\theta(s)+\omega(s)]} \int_0^s b_i(s_1) \Sigma(s_1) \varphi(s_1) e^{-2i[\theta(s_1)+\omega(s_1)]} ds_1 \} \\ &= - \iint_T b_i(s_1) \Sigma(s_1) \Sigma(s) \varphi(s_1) \varphi(s) e^{-2i[\theta(s)-\theta(s_1)+\omega(s)-\omega(s_1)]} ds_1 ds, \end{aligned} \tag{20}$$

where  $T$  is a triangle in the  $s, s_1$  plane defined by the inequalities  $0 \leq s_1 \leq s; 0 \leq s \leq 1$ . Since  $|e^{iw}|$  increases monotonically along  $\Lambda$ ,  $|e^{-2i[\omega(s)-\omega(s_1)]}| \leq 1$  at every point in  $T$ .  $\varphi(s)$  is of unit absolute value and

$$|e^{-2i[\theta(s)-\theta(s_1)]}| = |e^{-(i/\lambda) \int_{s_1}^s [Q(s')/p(s')] \varphi(s') ds'}| \leq e^{\mu_{\Lambda}}.$$

Introducing the symbol  $M_i$  for the maximum value of  $|b_i|$  on  $\Lambda$ , we readily derive the inequality

$$|b_i(Z_1) - \tilde{b}_i(Z_1)| < M_i e^{\mu_{\Lambda}} \iint_T |\Sigma(s_1)| |\Sigma(s)| ds_1 ds. \tag{21}$$

The function  $|\Sigma(s)| |\Sigma(s_1)|$  being symmetrical with respect to its arguments, the above integral over  $T$  is half the corresponding integral over the complete square  $0 \leq s \leq 1; 0 \leq s_1 \leq 1$ . Thus

$$|b_i(Z_1) - \tilde{b}_i(Z_1)| < \frac{1}{2} M_i e^{\mu_{\Lambda}} \{ \int_0^1 |\Sigma(s)| ds \}^2 = \mu_{\Lambda}^2 e^{\mu_{\Lambda}} (M_i/8). \tag{22}$$

We conclude that in the case of a good path leading uphill with respect to  $|e^{iw}|$  the approximation (17) will lead to an error which is small in comparison with the maximum value of  $|b_i|$  on the path.

Let  $w_0$  denote the value of  $w$  at the point  $Z_0$ . The maximum absolute value of the factor  $e^{-2i\omega(s_1)}$  of the integrand of Eq. (17) is  $|e^{-2iw_0}|$ . Furthermore on the path  $\Lambda$   $|e^{-2i\theta}| \leq e^{2|\theta|} < e^{\mu_0 + \mu_{\Lambda}}$  where  $\mu_0$  denotes the index of quality of the best path leading from  $\xi$  to  $Z_0$ . We assume that  $\mu_0$  is a small quantity of the order of  $\mu_{\Lambda}$ . Eq. (17) yields

$$|\tilde{b}_i(Z_1) - b_i^0| < \frac{1}{2} \mu_{\Lambda} e^{\mu_0 + \mu_{\Lambda}} |b_v^0| |e^{-2iw_0}|.$$

Combining this inequality with (22), we obtain

$$|b_i(Z_1)| < |b_i^0| + \frac{1}{2}\mu_\Lambda e^{\mu_0 + \mu_\Lambda} |b_v^0| |e^{-2i\nu_0}| + \mu_\Lambda^2 e^{\mu_\Lambda} (M_i/8). \tag{23}$$

Let  $Z_m$  denote the point on  $\Lambda$  where  $b_i(z)$  becomes equal to  $M_i$ , and let  $\mu_\Lambda'$  denote the quantity  $1/\lambda \int_{Z_0}^{Z_m} |Q/p| ds$ , where the integration is carried out along  $\Lambda$ . Then  $\mu_\Lambda' \leq \mu_\Lambda$ . Clearly an equation similar to (23) applies to the point  $Z_m$ . Thus

$$M_i < |b_i^0| + (\mu_\Lambda'/2) e^{\mu_0 + \mu_\Lambda'} |b_v^0| |e^{-2i\nu_0}| + \mu_\Lambda'^2 e^{\mu_\Lambda'} (M_i/8).$$

Transposing and neglecting terms of higher power in the small quantities  $\mu_0, \mu_\Lambda$ , we obtain  $M_i < |b_i^0| + \frac{1}{2}\mu_\Lambda |b_v^0| |e^{-2i\nu_0}|$ . It follows that in this approximation

$$|b_i(Z_1) - b_i^0| < |b_i(Z_1) - \tilde{b}_i(Z_1)| + |\tilde{b}_i(Z_1) - b_i^0| < \frac{1}{2}\mu_\Lambda |b_v^0| |e^{-2i\nu_0}| + \frac{1}{8}\mu_\Lambda^2 |b_i^0|. \tag{24}$$

Consider next the change in  $a_i$ . We have

$$|a_i(Z_1) - a_i^0| = |e^{iF(Z_0, \xi)}| |b_i(Z_1) e^{i/2\lambda \int_\Lambda (Q/p) dz} - b_i^0|,$$

where

$$|F(Z_0, \xi)| < \frac{1}{2}\mu_0 \quad \text{and} \quad \left| \frac{1}{2\lambda} \int_\Lambda \frac{Q}{p} dz \right| < \frac{1}{2}\mu_\Lambda.$$

Hence, neglecting small quantities of higher order,

$$|a_i(Z_1) - a_i^0| < e^{\mu_0/2} \{ e^{\mu_\Lambda/2} |b_i(Z_1) - b_i^0| + |b_i^0| (\mu_\Lambda/2) \} < \frac{1}{2}\mu_\Lambda [ |b_i^0| + |b_v^0| |e^{-2i\nu_0}| ].$$

Finally, it follows from (11) that to this same approximation  $|b_i^0| - |a_i^0| < |a_i^0| (\mu_0/2)$ . Consequently

$$|a_i(Z_1) - a_i^0| < \frac{1}{2}\mu_\Lambda [ |a_i^0| + |a_v^0| |e^{-2i\nu_0}| ]. \tag{25}$$

We conclude that the variation in  $a_i$  is small in comparison with the larger of the two quantities  $|a_i^0|$  and  $|a_v^0| |e^{-2i\nu_0}|$ .

In applying the above result two special cases are to be considered. The first is that of a good uphill path restricted by the additional requirement that  $|e^{i\nu}| \geq 1$  along its entire length. (It will be convenient to refer to regions in which  $|e^{i\nu}| > 1$  as *mountains*, and to regions in which  $|e^{i\nu}| < 1$  as *valleys*. Clearly  $f_i$  is dominant and  $f_v$  subdominant on the upper levels of the mountains. These roles are reversed for the lower levels of the valleys.) In this case  $|e^{-2i\nu_0}| < 1$  and  $|a_i(Z_1) - a_i^0|$  is small compared with the average of the quantities  $|a_i^0|$  and  $|a_v^0|$ . Under these circumstances we shall say that  $a_i$  is sensibly constant along the path, although if  $|a_i^0| \ll |a_v^0|$ , it may vary by a large percentage of its initial absolute value.

In order to deal with the variation in  $a_i$  along a good path leading from  $Z_0$  clear over a mountain to  $Z_1$ , but not entering the adjacent valleys,

it is convenient to think of the path as made up of two parts leading to the crest from opposite sides. Applying the above argument to each part of the path we come to the conclusion that  $a_i$  is *sensibly constant* over the entire path in comparison with the largest of the four quantities  $|a_i^0|, |a_v^0|, |a_i(Z_1)|, |a_v(Z_1)|$ .

A second important case of the application of Eq. (25) is that of a good path leading uphill, but beginning in a valley, where  $|e^{i\nu}| < 1$  and  $f_v$  is dominant. If the valley is deep  $|e^{-2i\nu_0}|$  is a very large number, but if  $|a_v^0| |e^{-2i\nu_0}| \leq |a_i^0|$ , we have the inequality

$$|a_i(Z_1) - a_i^0| < \mu_\Lambda |a_i^0| \tag{26}$$

and can say that  $a_i(z)$  is sensibly constant along the good path  $\Lambda$ . Evidently  $a_i(z)$  will also be sensibly constant along a good path  $\Lambda$  extending

across a valley from one mountain to another, provided that  $|a_v(z)| |e^{-2iw(z)}| \leq |a_i(z)|$  at the lowest point of the path.

Turning to  $a_v(z)$ , we readily derive formulas parallel to those for  $a_i(z)$  provided that we perform the integrations in the opposite direction on  $\Lambda$ , i.e., downhill with respect to  $|e^{iw}|$ . Thus, if we take  $a_i^0$  and  $a_v^0$  as the values of  $a_i$  and  $a_v$  at the upper end of the path, we obtain instead of (25) the inequality

$$|a_v(Z_1) - a_v^0| < \frac{1}{2} \mu_\Lambda \{ |a_v^0| + |a_i^0| |e^{2iw_0}| \}. \quad (27)$$

In general the coefficient of the dominant approximation  $f_i$  or  $f_v$  is sensibly constant over a good path  $\Lambda$  on which  $|e^{iw}| - 1$  does not change sign. The coefficient of the subdominant term is also sensibly constant over such a path provided that the absolute value of the dominant term at the point of maximum dominance is zero, or smaller than the product (evaluated at the same point) of the absolute value of the coefficient of the subdominant term multiplied by the smaller of the two quantities  $|e^{\pm 2iw}|$ . However, since we have defined the phrase "sensibly constant" somewhat loosely, it is perhaps best to base all rigorous arguments directly on the inequalities (25) and (27).

4. DERIVATION OF THE CONNECTION FORMULAS

We assume that the potential function in the neighborhood of the classical turning point  $z'$  has the form indicated in Fig. 1. Introducing polar coordinates  $r, \theta$  with the origin at  $z'$ , we write  $p^2$  in the form

$$p^2 = 2\mu(E - V) = re^{i\theta} \varphi(z),$$

where  $\varphi(z)$  is assumed to be bounded from zero in a wide region of the complex plane about  $z'$ . We further assume the existence of a path passing around  $z'$  in the upper half plane (cf. Fig. 3) enclosing no complex zeros of  $p^2$  and good in the technical sense that  $\mu_\Lambda \ll 1$ . Let  $P_1$  and

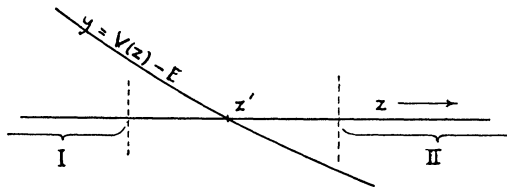


FIG. 1.

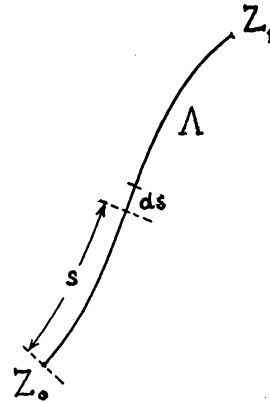


FIG. 2.

$P_2$  denote the end points of  $\Lambda$  located in regions I and II, respectively.

To avoid ambiguity due to the multiple-valued character of  $p, p^{\frac{1}{2}}$ , and  $w$ , we restrict the angle  $\theta$  to the range  $0 \leq \theta \leq 2\pi$  and define  $p$  and  $p^{\frac{1}{2}}$  by the equations

$$p = r^{\frac{1}{2}} e^{i\theta/2} \varphi^{\frac{1}{2}}; \quad p^{\frac{1}{2}} = r^{\frac{1}{4}} e^{i\theta/4} \varphi^{\frac{1}{4}}.$$

$\varphi^{\frac{1}{2}}$  can be treated as single-valued. Let the point  $z_0$  [Eq. (3)] be identified with  $z'$ . Then in the region I we have

$$p = i |p|; \quad p^{\frac{1}{2}} = e^{i\pi/4} |p|^{\frac{1}{2}}; \quad w = -i \lambda \int_{z_0}^{z'} |p| d\zeta. \quad (28)$$

In the region II to the right of  $z'$

$$p = |p|; \quad p^{\frac{1}{2}} = |p|^{\frac{1}{2}}; \quad w = \lambda \int_{z_0}^{z'} |p| d\zeta. \quad (29)$$

A cut extending from  $z'$  to the right along the axis of reals insures that we have a single branch of  $w(z)$  to deal with.

In order to visualize the problem it is convenient to map the level lines of  $|e^{iw}|$ . Eqs. (28) and (29) show directly that the axis of reals passes through a mountain to the left of  $z'$ , but that the portion of the axis of reals to the right of  $z'$  is a level line with  $|e^{iw}| = 1$ . Writing  $z = x + iy$ ;  $p = |p| e^{i\chi}$ , the differential equation for the level lines is seen to be

$$dy/dx = i \frac{(p - p^*)}{(p + p^*)} = -\tan \chi, \quad (30)$$

where  $p^*$  is the complex conjugate of  $p$ . Treating  $\varphi$  in first approximation as constant over the

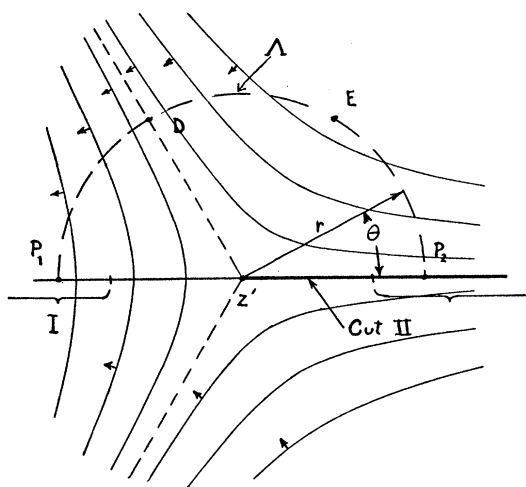


FIG. 3. Level lines of  $|e^{i\omega}|$  for linear potential function.  $|e^{i\omega}|$  is unity along cut and dotted lines radiating from  $z'$ . Arrows indicate the uphill direction.

neighborhood of  $z'$  we obtain the equation  $dy/dx = -\tan \frac{1}{2}\theta$  for the neighborhood in question. Fig. 3 shows the approximate form of the level lines derived from the above differential equation. Three lines radiate from the branch point  $z'$  and from every other simple zero point of  $E - V(z)$ . The exact forms of the contour lines will, of course, depend on  $\varphi(z)$ , but the distortion produced by  $\varphi$  is sure to be small if  $\varphi$  is smooth in the neighborhood of  $z'$ .

We identify the point  $\xi$  of Eqs. (11) with  $P_1$ , thus insuring that the  $a$ 's and  $b$ 's are sensibly equal on  $\Lambda$ . Let  $D$  denote the point where  $\Lambda$  crosses the line  $|e^{i\omega}| = 1$  which extends into the

upper half plane. Then  $a_v$  will be sensibly constant between  $D$  and  $P_2$  because  $f_v$  is dominant over this portion of  $\Lambda$ . It will also be constant over  $P_1D$  if  $a_i$  vanishes, or is very small, at  $P_1$ . It follows that if  $\alpha_i \equiv a_i(P_1) = 0$ ,  $\alpha_v \cong \beta_v$ . This fact, together with the reality condition gives the first connection formula.

Let us cast the argument in rigorous form. Denoting the point on  $\Lambda$  where  $|e^{i\omega}|$  has its minimum value by  $E$  and the corresponding values of  $a_i$  and  $a_v$  by  $\gamma_i$  and  $\gamma_v$ , respectively, we apply Eq. (27) first to the arc  $P_1E$  and then to  $P_2E$ . Let  $\mu_1$  and  $\mu_2$  be the values of  $\mu$  for these two sections of the path  $\Lambda$ . Then

$$\begin{aligned} |\gamma_v - \alpha_v| &< \frac{1}{2}\mu_1 \{ |\alpha_v| + |\alpha_i| |e^{2i\omega(P_1)}| \}, \\ |\gamma_v - \beta_v| &< \frac{1}{2}\mu_2 \{ |\beta_v| + |\beta_i| \}. \end{aligned} \tag{31}$$

Consider the application of these equations to a solution of Eq. (1) which is real on the axis of reals and which is of the  $f_v$  type at  $P_1$ . From the reality condition it follows that  $\beta_i = \beta_v^*$  and  $|\beta_i| = |\beta_v|$ . If the function is to be of  $f_v$  type at  $P_1$  we may assume that  $|\alpha_i| |e^{2i\omega(P_1)}| \leq |\alpha_v|$ . Hence

$$\begin{aligned} |\alpha_v - \beta_v| &< |\gamma_v - \alpha_v| + |\gamma_v - \beta_v| \\ &< \mu_1 |\alpha_v| + \mu_2 |\beta_v| < \mu_\Lambda \{ |\alpha_v| + |\beta_v| \}. \end{aligned}$$

We can accordingly identify  $\alpha_v$  and  $\beta_v$  in first approximation.

It follows from (28) that if  $\alpha_v$  is given the value  $e^{i\pi/4}$  the product  $\alpha_v f_v$  is real in I and describes a real  $\psi$  function. Then  $\beta_v = \beta_i^* = e^{i\pi/4}$ . Thus the connection formula

$$\underbrace{e^{i\pi/4} f_v \equiv |p|^{-\frac{1}{2}} e^{-\lambda \int_{z'}^z |p| d\zeta}}_{\text{Region I}} \rightarrow \underbrace{2p^{-\frac{1}{2}} \cos \left[ \lambda \int_{z'}^z p d\zeta - \frac{\pi}{4} \right]}_{\text{Region II}} \tag{32}$$

is established.

In this formula, following Langer, we draw the arrow from left to right to indicate that the approximate validity of the left-hand member implies that of the right, but that the converse statement is not true. In order to make clear the justification of this one-way street sign and to prepare the way for the derivation of the second connection formula, we observe that in virtue of the homogeneous linear character of Eqs. (9) and (10), the functions  $a_i(z)$ ,  $a_v(z)$  must be homo-

geneous linear in the constants of integration  $\alpha_i$ ,  $\alpha_v$ . Hence  $\beta_i$  and  $\beta_v$  must be homogeneous linear functions of  $\alpha_i$  and  $\alpha_v$ . Thus a complete exact solution of the whole connection problem would involve a complete and exact determination of the matrix  $\|g\|$  of the equations

$$\beta_i = g_{ii}\alpha_i + g_{iv}\alpha_v, \quad \beta_v = g_{vi}\alpha_i + g_{vv}\alpha_v. \tag{33}$$

Our approximate solution of Eqs. (9) and (10) for the special case that  $\alpha_i = 0$  shows that

$$g_{vv} = 1 + \delta; \quad g_{iv} = -i(1 + \delta^*), \tag{34}$$

where  $\delta$  is a small quantity of the order of magnitude of  $\mu_\Lambda$  which we have neglected in (32).

Additional information regarding the matrix  $\|g\|$  is obtainable from the fact that the Wronskian of any two exact solutions of the Schrödinger equation, say  $\psi$  and  $\bar{\psi}$ , is constant along the axis of reals.<sup>7</sup> Thus if

$$\psi = \alpha_i f_i + \alpha_v f_v; \quad \bar{\psi} = \bar{\alpha}_i f_i + \bar{\alpha}_v f_v$$

in  $I$ , it follows that in  $\bar{I}$

$$W[\psi, \bar{\psi}] \equiv \psi \frac{\partial \bar{\psi}}{\partial z} - \bar{\psi} \frac{\partial \psi}{\partial z} = 2i\lambda(\alpha_v \bar{\alpha}_i - \alpha_i \bar{\alpha}_v) = \text{constant.}$$

The Wronskian of the same pair of solutions in  $II$  takes the form

$$W[\psi, \bar{\psi}] = 2i\lambda(\alpha_v \bar{\alpha}_i - \alpha_i \bar{\alpha}_v)(g_{vv} g_{ii} - g_{iv} g_{vi}).$$

Equating these two expressions for the Wronskian, we see that *the determinant of  $\|g\|$  is unity*. Hence the inverse equations to (33) are

$$\alpha_i = g_{vv} \beta_i - g_{iv} \beta_v, \quad \alpha_v = -g_{vi} \beta_i + g_{ii} \beta_v. \quad (35)$$

It follows from the reality condition that if  $\beta_i = \beta_v^*$ , the quantities  $\alpha_i e^{i\pi/4}$  and  $\alpha_v e^{i\pi/4}$  are real. Hence

$$g_{vi} = -i g_{ii}^*; \quad g_{iv} = -i g_{vv}^*. \quad (36)$$

Combining the last relation with the requirement that  $|g|$  be equal to unity, we obtain the following relation between  $g_{ii}$  and  $\delta$ :

$$g_{ii}(1+\delta) + g_{ii}^*(1+\delta^*) = 1. \quad (37)$$

If we neglect small quantities of the order of  $\mu_\Lambda$  in comparison with unity, we may conclude that the real part of  $g_{ii}$  is  $\frac{1}{2}$ . The imaginary part of  $g_{ii}$  cannot be determined even approximately without an explicit evaluation of an integral of the form given in Eq. (17) over a path on which the exponential factor is very large. However, if we apply the inequalities (31) to the evaluation of  $|\beta_v|$  when  $\alpha_v = 0$  we can derive the upper bound

$$|g_{ii}| = |g_{vi}| < \mu_\Lambda |e^{2i\omega(P_1)}| = \mu_\Lambda \exp \left[ 2\lambda \int_{P_1}^{z'} |p| d\xi \right].$$

<sup>7</sup> The writer is indebted to Dr. Eugene Feenberg for the observation that the second connection formula can be derived from the first by means of the properties of the Wronskian.

It does not seem necessary to include the details of this simple proof here.

Let us now consider the validity of the inverse of Eq. (32). If the relation in question were exact, we could, of course, invert it; but it is actually only approximate. We know from the derivation that if the left-hand member fits the function  $\psi(z)$  exactly at  $P_1$ , the right-hand member fits the same function approximately at  $P_2$  and along the neighboring portion of the axis of reals. The inverse relation would be the statement that if the right-hand member fits  $\psi(z)$  exactly at  $P_2$ , the left-hand member is approximately correct at  $P_1$ . With the aid of our partial determination of the matrix  $\|g\|$  we can test the validity of this statement. We accordingly assume as in the right-hand member of (32) that  $\beta_i = i\beta_v = e^{i\pi/4}$ . It follows that the corresponding values of  $\alpha_v$  and  $\alpha_i$  are not  $e^{i\pi/4}$  and 0, but  $e^{i\pi/4}[1 - \delta^* + g_{ii}(\delta^* - \delta)]$  and  $(\delta - \delta^*)e^{-i\pi/4}$ . Although the correction to the value of  $\alpha_i$  is small, its product by the dominant approximation function  $f_i$  is not necessarily small. Hence the left-hand member of (32) may be entirely incorrect if the right-hand member is exact.

The *second connection formula* is a direct consequence of (35) and our information regarding  $\|g\|$ . Consider an exact solution of (1) which has the form

$$\psi(x) = 2p^{-\frac{1}{2}} \cos(w + \gamma) = e^{i\gamma} f_i + e^{-i\gamma} f_v$$

in the neighborhood of  $P_2$ . By (35) the corresponding values of  $\alpha_i$  and  $\alpha_v$  are, if we neglect small quantities of the order of  $\mu_\Lambda$ ,

$$\alpha_i = 2e^{i\pi/4} \cos\left(\gamma - \frac{\pi}{4}\right);$$

$$\alpha_v = e^{i\pi/4} \left[ 2x \cos\left(\gamma - \frac{\pi}{4}\right) - \sin\left(\gamma - \frac{\pi}{4}\right) \right].$$

Here we have introduced the symbol  $x$ , for the unknown, but finite, imaginary part of  $g_{ii}$ . If  $\gamma$  is not too close to the critical value  $-\pi/4$  (cf. the *first* connection formula) so that  $|\cos(\gamma - \pi/4)|$  is not *much* smaller than  $|\sin(\gamma - \pi/4)|$ , the product  $\alpha_v f_v$  is small compared with  $\alpha_i f_i$ . Hence we have the connection formula



$$\underbrace{\cos\left(\gamma - \frac{\pi}{4}\right) |p|^{-\frac{1}{2}} e^{+\lambda \int_{z'}^z |p| dz}}_{\text{Region I}} \leftarrow p^{-\frac{1}{2}} \underbrace{\cos\left[\lambda \int_{z'}^z p d\xi + \gamma\right]}_{\text{Region II}}. \tag{38}$$

This is usually specialized by writing  $\gamma = \pi/4$ , but the possibility of a generalization has been indicated by Langer (last reference, Note 3).

In addition to the restriction on  $\gamma$ , the only condition for the validity of (32) and (38) is that there shall exist a path  $\Lambda$  in the upper half plane connecting  $P_1$  with  $P_2$ , enclosing no complex zeros of  $p^2$  and having the property that  $\mu_\Lambda \ll 1$ .

Both connection formulas in the form given above presuppose that the slope of the real curve  $y = V(z)$  is negative at  $z'$ . In order to obtain the connection formulas for the case in which  $V(z)$  has a positive slope at the classical turning point  $z'$  it is only necessary to make the transformation  $z \rightarrow -z$  in (32) and (38) and to interchange the roles of the regions I and II.

5. LIMITING CASE WHERE ONE OF THE CONNECTED POINTS IS AT INFINITY

So far we have assumed that the points  $P_1$  and  $P_2$  are located at finite distances from  $z'$  and can be connected by a good path  $\Lambda$  of finite length. In applying the B. W. K. method to energy level problems, however, we frequently wish to assume that  $\psi(z)$  vanishes at  $z = \pm \infty$ . In this case it becomes necessary to discuss the changes in the coefficients  $a_i, a_v$  which occur in a path which extends to infinity along the axis of reals. Consider, for example, a case in which  $p(z)$  is imaginary and bounded from zero for all real values of  $z$  to the left of the turning point  $z'$  of Fig. 1. Let it be required to find the values of  $\beta_i, \beta_v$  appropriate to  $P_2$  when  $a_i$  is known to vanish at  $z = -\infty$ . The required transformation of the  $a$ 's can be thought of as made in two steps, of which the first gives the values at  $P_1$  in terms of those at  $-\infty$  and the second is the one already studied giving the values at  $P_2$  in terms of those at  $P_1$ .

Consider first the value of  $a_i$  at  $P_1$ , which as before we shall call  $\alpha_i$ . It follows from Eq. (9) that

$$\alpha_i = \frac{i}{2\lambda} \int_{-\infty}^{P_1} Q f_v \psi dz. \tag{39}$$

As both  $f_v$  and  $\psi$  approach zero exponentially for large negative values of  $z$ ,  $|\alpha_i|$  is clearly very small. We compute an upper limit. Let  $z_1$  denote the value of  $z$  at  $P_1$ . Eq. (39) is equivalent to

$$\alpha_i = \frac{i}{2\lambda^2} \int_{w(-\infty)}^{w(z_1)} \frac{Q e^{-i w}}{p^{\frac{1}{2}}} \psi dw.$$

Hence

$$|\alpha_i| < \frac{1}{2} \int_{w(-\infty)}^{w(z_1)} \left| \frac{Q}{\lambda^2 p^{\frac{1}{2}}} e^{-|w|} |\psi| \right| dw.$$

Let  $m$  denote the maximum value of  $|Q/\lambda^2 p^{\frac{1}{2}}|$  in the range of integration. This we may assume to be small. Since  $|\psi(z)|$  decreases monotonically as we pass from  $z_1$  out to  $-\infty$  along the axis of reals,

$$\begin{aligned} |\alpha_i| &< \frac{m}{2} |\psi(z_1)| \int_{w(z_1)}^{w(-\infty)} e^{-|w|} d|w| \\ &< \frac{m}{2} |\psi(z_1)| e^{-|w(z_1)|} \\ &< \frac{m}{2 |p(z_1)^{\frac{1}{2}}|} [|\alpha_i| + |\alpha_v| e^{-2|w(z_1)|}]. \end{aligned} \tag{39a}$$

If  $m/|p(z_1)^{\frac{1}{2}}|$  is much less than unity,  $|\alpha_i| \ll |\alpha_v| e^{-2|w(z_1)|}$ .

By analogy with the corresponding problem for a finite path one expects that  $\alpha_v$  is sensibly equal to the limiting value of  $a_v(z)$  as  $z$  moves out to  $-\infty$ . It is not necessary, however, to investigate this point in order to deal with the eigenvalue-eigenfunction problem.

Consider the application of Eqs. (33) to the determination of  $\beta_i$  and  $\beta_v$  when  $a_i(z)$  vanishes at the negative end of the axis of reals. In view of the upper bounds on  $|\alpha_i|$  and  $|g_{vi}|$

$$|g_{vi} \alpha_i| < \frac{m}{2 |p(z_1)^{\frac{1}{2}}|} \mu_\Lambda |\alpha_v g_{vv}|.$$

Thus, by Eqs. (33), if  $P_1$  is connected with  $P_2$

by a good path, and if  $|Q(z)/\lambda^2 p(z)^{3/2} p(z_1)^{1/2}|$  is small between  $P_1$  and  $-\infty$ ,  $\beta_v$  has sensibly the same value as if  $\alpha_i$  were zero, i.e.,  $\beta_v$  is sensibly equal to  $\alpha_v$ . We conclude that the connection formula (32) remains valid when the point  $P_1$  is moved out to infinity along the negative axis of reals, provided that  $m/|p(z_1)^{1/2}| \ll 1$ .

#### 6. EVALUATION OF THE LOW ENERGY LEVELS OF A ONE-DIMENSIONAL OSCILLATOR

The usual wave mechanics derivation of the Sommerfeld "phase integral" quantum condition (with half-integral quantum numbers) is based on the use of the connection formulas and loses its validity when applied to the lower energy levels. Thus in the case of the Planck ideal linear oscillator, where  $V(z) = \frac{1}{2}kx^2$ , we have

$$Q = k(E + 6V)/(E - V)^2. \quad (40)$$

The minimum value of  $|Q/\lambda^2 p^2|$  consistent with the reality of  $p$  occurs at the origin and is  $k/(8\lambda^2 \mu E^2)$ . In the case of the lowest energy level the value is  $\frac{1}{2}$  and the corresponding minimum value of  $\lambda^{-1} \int |Q/p| ds$  for any path joining the region of classical vibration with any point outside this region is  $\frac{1}{3}$ . As this is of the order of unity, appreciable departures from the connection formulas are to be expected for this lowest energy level, and it is surprising to note that the value of  $E$  given by the phase integral formula is in *exact* agreement with the rigorous value obtained by other methods. Thus one is

led to inquire whether there is not some way of validating the Sommerfeld formula without assuming the existence of good paths joining the region of classical vibration with the regions of imaginary momentum on the axis of reals.

Birkhoff<sup>8</sup> has recently sketched a proof of the phase integral formula applicable to the lower energy levels. Partly, however, due to the fact that Birkhoff's technique is unfamiliar to physicists, and partly because his proof rests on a plausible, but as yet unverified assumption, it seems worth while to give an independent derivation here.

Let the problem under discussion be that of finding the discrete energy levels of a one-dimensional oscillator with the fundamental interval  $-\infty < z < +\infty$  and a single potential valley in which the classical local momentum  $p(z, E)$  takes on real values. We shall assume at first that  $V(z)$  has the special parabolic form  $V = \frac{1}{2}kz^2$  and consider later on the modification of the argument for an anharmonic oscillator.

Let the complex  $z$  plane have a cut extending from the left-hand classical turning point  $z'$  through the right-hand turning point  $z''$  to  $+\infty$  along the axis of reals. The functions  $p$ ,  $p^{\frac{1}{2}}$  and  $w$  are uniquely defined over the cut plane by the requirement that they conform to Eqs. (28) for all negative real values of  $z - z'$ . They will then conform to Eqs. (29) on the upper lip of the cut between  $z'$  and  $z''$ . For positive real values of  $z - z''$  we have

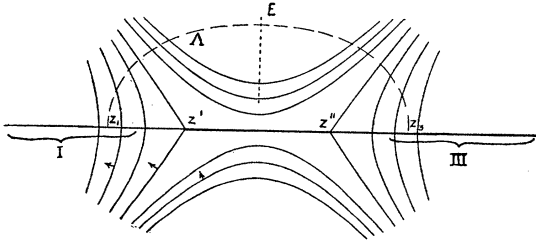
$$\begin{aligned} \text{Upper lip: } p &= -i|p|; & p^{\frac{1}{2}} &= e^{-i\pi/4}|p^{\frac{1}{2}}|; & w &= \lambda \int_{z'}^{z''} |p| d\zeta - i\lambda \int_{z''}^z |p| d\zeta; \\ \text{Lower lip: } p &= -i|p|; & p^{\frac{1}{2}} &= -e^{-i\pi/4}|p^{\frac{1}{2}}|; & w &= -\lambda \int_{z'}^{z''} |p| d\zeta - i\lambda \int_{z''}^z |p| d\zeta. \end{aligned} \quad (41)$$

We designate by III that portion of the region of imaginary momentum on the axis of reals to the right of  $z''$  where  $|Q/\lambda^2 p^2| \ll 1$  (cf. Fig. 4). It follows from Eqs. (41) that  $|e^{iw}|$  is very large in both of the regions I and III. The level lines of  $|e^{iw}|$  are readily sketched in and show that any path connecting I with III and avoiding the classical portion of the axis of reals must cross a single valley between the ridges on which it

terminates. This is true whether the path lies in the upper or lower half plane.

Let  $z_1$  and  $z_3$  be any two points on the axis of reals in I and III, respectively. It follows from (40) that in the case of the parabolic potential function under consideration it is always possible to join  $z_1$  and  $z_3$  by a path  $\Lambda$  for which  $\mu_\Lambda \ll 1$ . In more general cases such a path will exist provided

<sup>8</sup> G. D. Birkhoff, Bull. Am. Math. Soc. 39, 696 (1933).

FIG. 4. Level lines of  $|e^{iw}|$  for harmonic oscillator.

there are no complex zeros of  $V-E$  near to  $z'$  and  $z''$ .

Let us now assume that we have to do with an eigenvalue of the energy  $E=E_n$  and a corresponding eigenfunction  $\psi_n(z)$ . Then  $\psi_n$  vanishes at both ends of the axis of reals. Since  $f_i(z)$  becomes infinite at both ends of this axis,  $a_i$  must vanish there. It follows from our previous analysis that  $a_i$  is very small at both of the points  $z_1$  and  $z_3$ . Let  $E$  denote the point where the path  $\Lambda$  crosses the bottom of the valley, i.e., the point on  $\Lambda$  where  $|e^{iw}|$  takes on its minimum value. Integration from  $z_1$  to  $E$  shows that  $a_v$  is sensibly constant along the corresponding portion of  $\Lambda$ . Similarly integration from  $z_3$  to  $E$  shows that it is constant along the rest of  $\Lambda$ . If we reflect the path  $\Lambda$  in the axis of reals we get a second path connecting  $z_1$  with  $z_3$  along which  $a_v$  is constant neglecting small quantities of the order of  $\mu_\Lambda a_v(z_1)$ . The existence of these two paths shows that  $a_v$  takes on the same values on the upper and lower edges of the cut at  $z_1$ .  $\psi_n$  is, of course, single-valued along the entire axis of reals. Hence  $f_v(z)$  must have the same value on the upper and lower edges of the cut at  $z_3$ . Equating the two values of  $f_v$  in question and using the corresponding values of  $p^\dagger$  and  $w$  given in Eqs. (41), we obtain

$$\exp \{ \lambda \int_{z'}^{z''} |p| d\zeta \} = - \exp \{ - \lambda \int_{z'}^{z''} |p| d\zeta \},$$

or the familiar equation

$$\oint p dz = (n + \frac{1}{2})h. \quad (42)$$

The accuracy of the result is limited only by the quality of the path  $\Lambda$ . But in the case of the ideal linear oscillator it is possible to reduce the value of  $\mu_\Lambda$  below any assignable quantity by choosing the path  $\Lambda$  as a semicircle of sufficiently large radius with the origin as its center. Hence the above equation is *exact* for the case under discussion.

Turning now to the problem of the *anharmonic oscillator*, we observe that in order to secure single-valued functions  $f_i, f_v$  it is necessary to introduce cuts extending from the complex roots of  $E-V$  to infinity. The argument then goes through exactly as in the case of the harmonic oscillator except that the path  $\Lambda$  must lie inside all the roots above mentioned in order to avoid crossing the cuts. Consequently it is not possible to reduce the value of  $\mu_\Lambda$  below a certain minimum determined by the location of the roots of  $E-V$ . The formula (42) is essentially inexact for anharmonic oscillators.

The uncertainty  $\delta E$  in the energy due to the fact that  $\mu_\Lambda$  and  $m$  do not actually vanish is readily calculated if we retain terms of the first order in these two infinitesimals. Let  $\tilde{a}_i(z_3)$  and  $\tilde{a}_v(z_3)$  denote the values of  $a_i(z)$  and  $a_v(z)$  on the lower edge of the cut at  $z_3$ . Equating the approximate expressions for  $\psi$  on the two edges of the cut at  $z_3$  in terms of  $f_i, f_v$  we obtain

$$e^{i(\pi + \lambda J)} = \frac{a_v(z_3) + e^{2\lambda \int_{z'}^{z_3} |p| d\zeta} \tilde{a}_i(z_3)}{\tilde{a}_v(z_3) + e^{2\lambda \int_{z'}^{z_3} |p| d\zeta} a_i(z_3)}.$$

Let  $\epsilon_v$  and  $\tilde{\epsilon}_v$  denote the small quantities  $a_v(z_3) - a_v(z_1)$ ,  $\tilde{a}_v(z_3) - a_v(z_1)$ , respectively. To a first approximation

$$i(\pi + \lambda J) = \log_e \left\{ 1 + \frac{\epsilon_v - \tilde{\epsilon}_v + [\tilde{a}_i(z_3) - a_i(z_3)] e^{2\lambda \int_{z'}^{z_3} |p| d\zeta}}{a_v(z_1)} \right\}.$$

Introducing appropriate upper bounds for  $\epsilon_v, \tilde{\epsilon}_v, |a_i(z_3)|, |\tilde{a}_i(z_3)|$  from the inequalities (27) and (39a), we obtain

$$|\pi + \lambda J - 2\pi k| < \mu_\Lambda + m / |p(z_3)^{\frac{1}{2}}|, \quad k=0, 1, 2, \dots,$$

where  $m$  is the maximum value of  $|Q/\lambda^2 p^{\frac{1}{2}}|$  between  $z_3$  and  $+\infty$ . Let  $\Delta E$  denote the quantity  $\hbar \partial E / \partial J$  which measures the approximate spacing of the energy levels given by the Sommerfeld formula. Then

$$\frac{\delta E}{\Delta E} = \frac{1}{2\pi} \left( \mu_\Lambda + \frac{m}{|p(z_3)^{\frac{1}{2}}|} \right).$$

The writer has carried through a calculation of  $\mu_\Lambda$  and  $m/|p(z_3)^{\frac{1}{2}}|$  for the Morse curve potential function corresponding to the normal state of the

$H_2$  molecule. For simplicity of computation the energy  $E$  was so chosen as to bring the classical turning points  $z'$  and  $z''$  together.  $\Lambda$  was taken to be a semicircle with radius equal to half the distance from  $z'$  to the nearest complex root of  $p^2(E, z)$ . Under these circumstances  $\mu_A$  is approximately 0.015 and  $m/|p(z_3)^{3/2}|$  is  $7.5 \times 10^{-5}$ . The corresponding value of  $\delta E/\Delta E$  is 0.0025, showing that the B. W. K. approximation should give the energy correct to at least two or three tenths of a percent of the spacing of adjacent levels. Of course the actual error involved should be appreciably less than this upper limit.

### 7. HIGHER ORDER APPROXIMATIONS

It is well known that our functions  $f_i, f_v$  can be obtained from (1) by making the transformation  $\psi = e^{i\lambda \int y dz}$ , expanding  $y$  formally in powers of  $h$ , or  $1/\lambda$ , and taking only the first two terms of the series. By taking  $n$  terms of the series, one obtains functions  $f_i^{(n)}, f_v^{(n)}$  having properties similar to those of  $f_i$  and  $f_v$ . The series are semiconvergent and hence the  $f^{(n)}$ 's, regarded as approximate solutions of (1), at first improve in quality as  $n$  increases, and then grow worse. They obey equations of the form

$$\frac{d^2 f^{(n)}}{dz^2} + [\lambda^2 p^2 - Q^{(n)}] f^{(n)} = 0,$$

where  $Q^{(n)}(z, E)$  is a polynomial in  $1/\lambda$  beginning with a term of degree  $n-2$ . If  $Q \equiv Q^{(2)}$  is small at any point of the complex plane,  $|Q^{(n)}|$  will be smaller than  $|Q|$  provided that  $n > 2$ , but not too large. Thus if  $|Q/p^2|$  is small along a path  $\Lambda$  joining  $z_1$  and  $z_3$ ,  $|Q^{(n)}/p^2|$  will be still smaller. We infer that the argument used to prove that, in the case of an anharmonic oscillator and an eigenvalue of  $E$ , the function  $f_v$  has sensibly the same values on the upper and lower edges of the cut in the region *III*, is applicable with a higher degree of precision to  $f_v^{(n)}$ . It follows at once that the energy level condition<sup>9</sup>

$$\oint y_v^{(n)} dz = mh, \quad m = 0, 1, 2, \dots \quad (43)$$

is even more accurate than (42) for small values of  $n$  greater than 2.

<sup>9</sup> Cf. J. L. Dunham, Phys. Rev. **41**, 713 (1932). Dunham's derivation of (43) is fundamentally sound, though no more rigorous than Zwaan's proof of the connection formulas.

### 8. MODIFICATION OF THE B. W. K. METHOD FOR THE RADIAL EQUATION IN THE TWO-BODY PROBLEM

In applying the B. W. K. method to the radial equation of the two-particle problem one meets with an apparent difficulty in that the B. W. K. approximations do not have the right character to fit the exact solutions of the differential equation at the left-hand boundary point  $r=0$ . As Kramers has pointed out, however, it is possible to fit the boundary conditions at both ends of the fundamental region if we modify the approximation formulas by the addition of the term  $h^2/32\pi^2\mu r^2$  to the potential energy. The added term is negligible except in the immediate neighborhood of the origin, and it is ordinarily possible to find a good path  $\Lambda$  leading from the origin around the classical turning points (there is only one when the angular momentum is zero) in the complex plane to a point on the axis of reals outside the region of classical motion where the approximation function is good. In this manner it is possible to apply to the two-particle problem essentially the same reasoning as we have used above for the anharmonic oscillator in the interval  $-\infty < z < +\infty$ . One obtains the energy level formula (42) with  $p(r, E)$  modified by the substitution of  $(l+\frac{1}{2})^2$  for  $l(l+1)$  in the term which gives the contribution of centrifugal force to the effective potential energy of the radial vibration. Further details regarding this application of our technique will be published elsewhere.<sup>10</sup>

### 9. THE TRANSMISSION OF PROGRESSIVE MATTER WAVES THROUGH A POTENTIAL BARRIER

The transmission of matter waves through potential barriers has been the subject of much discussion,<sup>11</sup> but so far as the writer has been able to discover there has been no application of the B. W. K. method to this problem that is properly applicable to cases in which the energy of the incident particles is not very different from the maximum potential energy of the barrier.

Let us assume a rounded potential hill of approximately parabolic form. Consider first the

<sup>10</sup> In a book on the general principles of quantum mechanics now in preparation.

<sup>11</sup> Cf., e.g., N. H. Frank and L. A. Young, Phys. Rev. **38**, 80 (1931).

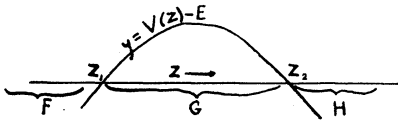


FIG. 5.

case in which the top of the hill projects above the energy level of the incident particles. We divide the axis of reals of the complex  $z$  plane into three parts  $F$ ,  $G$ ,  $H$ , separated by the classical turning points  $z_1$ ,  $z_2$  as indicated in Fig. 5. Single-valued functions  $f_i$ ,  $f_v$  are obtained by introducing a cut along the axis of reals from  $z_1$  to  $+\infty$  and by choosing those branches of  $p$  and  $p^{\frac{1}{2}}$  which are negative real and negative imaginary, respectively, in  $F$ .  $p$ ,  $p^{\frac{1}{2}}$ , and  $w$  are to be analytic over the cut plane.  $p$  is then real and positive in  $H$  and positive imaginary in  $G$ . On both sides of the hill the function

$$f_i e^{-2\pi i E t/h} = p^{-\frac{1}{2}} \exp \left\{ \frac{2\pi i}{h} \left[ \int_{z'}^z p d\zeta - Et \right] \right\}$$

describes an outgoing wave, while  $f_v e^{-2\pi i E t/h}$  describes an incoming wave. The level lines of  $|e^{iw}|$  for a parabolic potential function are shown in the figure.  $f_v$  is dominant in most of the first and third quadrants, while  $f_i$  is dominant in most of the second and fourth quadrants.

Let us assume that progressive waves are incident on the potential hill from the left side only. There will then be reflected as well as incident waves in  $F$ , but only transmitted waves in  $H$ . We accordingly assume that  $a_v$  vanishes in the first quadrant where  $f_v$  is dominant. Let the regions  $F$  and  $H$  be connected by a good path  $\Lambda$ . Then  $a_i$  will be sensibly constant along this path. Thus we have a connection formula of the type

$$f_i + c f_v \rightarrow f_i, \quad (44)$$

where  $c$  is a constant whose value has yet to be determined. As a matter of fact we can evaluate

only the modulus of  $c$ . This is done by using the constancy of the current density

$$D[\psi] = \frac{h}{4\pi i} \left( \psi^* \frac{d\psi}{dz} - \psi \frac{d\psi^*}{dz} \right)$$

on the axis of reals. Choosing  $z_1$  as the origin of the integral  $w$ , we give  $e^{iw}$  the absolute value 1 in the region  $F$  and the absolute value  $e^{-K}$  in  $H$  where  $K$  denotes the integral  $(2\pi/h) \int_{z_1}^{z_2} |p| d\zeta$ . The right-hand member of (40) now represents a current of density  $e^{-2K}$  in the direction of the positive  $z$  axis, while the left-hand member represents a current with the density  $cc^* - 1$  in the same direction. Equating these two currents, we find that  $cc^* = 1 + e^{-2K}$ . The corresponding transmission coefficient is

$$T = e^{-2K}/cc^* = 1/(1 + e^{2K}). \quad (45)$$

This formula is free from all restrictions depending on the height of the hill provided that  $E - V_{\max} < 0$ . Like Eq. (42) it is easily seen to hold for any analytic potential hill which yields no zeros of  $E - V$  near  $z_1$  and  $z_2$  and hence permits a good path  $\Lambda$  joining the regions  $F$  and  $H$ .

If the maximum potential energy is less than the energy of the incident particles, a parabolic potential function yields two imaginary roots of  $E - V(z)$ ,  $z = \pm i \{ 2(E - V_{\max})/k \}^{\frac{1}{2}}$ , where  $k$  denotes the negative of  $V''$ . Denoting these roots by  $z_1$  and  $z_2$  and the integral  $(2\pi/h) \int_{z_1}^{z_2} |p| |d\zeta|$  by  $K'$ , it is not difficult to prove that the transmission coefficient is

$$T = 1/(1 + e^{-2K'}). \quad (46)$$

The reader will observe that the formulas (45) and (46) join continuously in the limiting case where  $z_1 = z_2 = 0$ , giving the common value  $\frac{1}{2}$  for  $T$ .

The writer is greatly indebted to Dr. Eugene Feenberg, Professor G. D. Birkhoff and Professor J. H. Van Vleck for helpful suggestions.