A CONTRIBUTION TO THE QUANTUM MECHANICAL THEORY OF RADIOACTIVITY AND THE DISSOCIATION BY ROTATION OF DIATOMIC MOLECULES

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(Received February 26, 1930)

Abstract

In the recent theory of radioactive decay, and also, as is shown, in the theory of dissociation of a diatomic molecule by the acquisition of rotational energy, there occurs a potential energy curve which has the following shape, as we go, say, from left to right. At the left the potential energy is very high, it then comes down to a minimum, increases to a maximum, and again falls off to an asymptotic value. The problems connected with such a curve are of two types. First, we may be given a particle in the region near the minimum, in an energy level which lies below the maximum, and wish to find the chance that it appear by a quantum mechanical process in the region on the other side of the maximum. Second, we wish to find how the "discrete states" in the neighborhood of the minimum are "broadened" by the continuum on the other side of the maximum. To solve these problems we first find the stationary eigenfunctions. By means of them the width and shape of the "broadened discrete levels" are found immediately. We then use these eigenfunctions to set up a wave packet, or, rather, we show how nature may set up a wave packet, which enables us to solve the first of the problems mentioned. The result justifies the use of complex eigenvalues for the solution of the problem.

Introduction

The theory of radioactive decay, recently proposed by Gurney and Condon,[2] and independently by Gamow[3] makes use of a potential energy curve of the type shown in Fig. 1 (solid curve), the wave equation being of the form

$$d^2\psi/dx^2 + (8\pi^2 M/h^2)(E - U)\psi = 0. \quad (1)$$

The alpha-particle is supposed to be originally in some energy level such as E between x_2 and x_3. There is then a finite probability of its appearing to the right of x_1 which gives the chance of disintegration of the radioactive atom.

Curves of much the same general characteristics also occur in the case of molecules, and can be used to explain the phenomenon of dissociation by rotation; i.e. one can use them to show how rotational energy can cause a diatomic molecule to dissociate. This explanation was given by Oldenberg,[4] but as his work was not put into quantum mechanical form, and as a little more information may be obtained when this is done, it seems worth while to devote a paragraph to indicating how this may be done.

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[2] Gurney and Condon, Nature **122,** 439 (1928); Phys. Rev. **33,** 127 (1929).

[3] Gamow, Zeits. f. Physik **51,** 204 (1928).

[4] Oldenberg, Zeits. f. Physik **56,** 563 (1929).

One begins with the wave equation of a rotating and oscillating diatomic molecule, and, in the usual way, separates out the variables which give the orientation of the molecule. One thus obtains a wave equation in r, the dis-

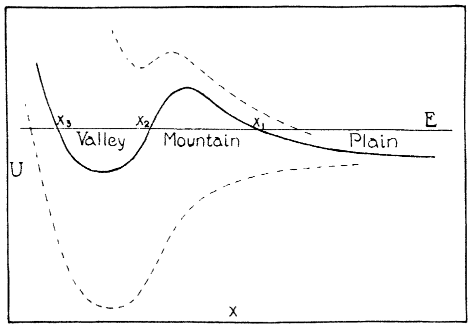

Fig. 1.

tance between the two nuclei. If we let $F = rR$, where R is the part of the eigenfunction which depends on r, this equation is[5]

$$d^2F/dr^2 - j(j+1)F/r^2 + (8\pi^2 M/h^2)(E - U_0)F = 0$$

where j is the rotational quantum number, M the reduced mass, E the eigenvalue, and U_0 the potential energy, which is a function of r. The term $j\,(j+1)/r^2$ when multiplied by $h^2/8\pi^2 M$ acts exactly like an addition to the potential energy[6] and we may replace $U_0 + (h^2/8\pi^2 M)j(j+1)/r^2$ by an effective potential energy U, getting an equation like (1). When $j = 0$ the curve has the usual form of the potential energy curve for a molecule (lower dotted curve in Fig. 1). As j increases the curves become like the solid curve of Fig. 1, and finally when j is quite large they are like the upper dotted curve of Fig. 1, the valley becoming shallower and finally disappearing altogether.[7] Now, as we shall see, we can in a certain sense speak of discrete states in the valley, corresponding to an oscillation of the molecule in this region, and we see that the number of discrete states in the valley grows less and less until at last there are no more. Thus if a molecule is in a certain vibrational state, this state will disappear, and the molecule will dissociate, if j exceeds a certain value. This is the phenomenon observed in the case of mercury hydride, and the explanation does not differ greatly from that given by Oldenberg.

For energy levels such as E between the top of the mountain and the level of the plain, the problems which occur in the case of radioactivity will have an analog in the case of molecules. In the case of radioactivity what we observe is that a system starting in the valley goes through the mountain and appears in the plain. In the case of molecular spectra we actually observe another phenomenon. We find that the discrete states in the valley will be broadened

[5] Fues, Ann. d. Physik **80,** 371 (1926).

[6] See Gamow and Houtermans, Zeits. f. Physik **52,** 509 (1928).

[7] The curves of Fig. 1 are quite schematic. For curves drawn to scale see Oldenberg, l.c.

in the same sense as in the case of predissociation,[8] and one in fact observes diffuse rotation lines.

The problem which concerns the rate at which particles appear on the plain, and which, as noted, is of particular interest in the case of radioactivity, has been considered by a number of investigators. In the original papers of Gurney and Condon, and Gamow, no attempt was made to put this calculation on a rigorous basis. Numerous articles have appeared since, attempting to do this.[9] Among the various methods used the introduction of complex eigenvalues offers to my mind the most elegant solution of this problem which has appeared so far. This very ingenious procedure gives very reasonable results. Still the idea of a complex eigenvalue is a rather unusual one. The method also includes the assumption that the decomposition is proceeding in just the same way as if it had been going on for an infinite length of time. This is also not an unreasonable assumption but it can be avoided; at the same time the use of complex eigenfunctions can be justified, and new light thrown on the significance of the whole process by the method we propose to use.

Method of Attack

First of all we shall consider the entire system to be enclosed in a large box, to avoid the necessity of considering a continuum. Then we shall find the stationary eigenfunctions. In general it will be found that the part of the eigenfunction on the plain will be great compared to that in the valley. As we pass through certain energies, however, the relative size of the part inside will increase, reach a maximum and fall off again. To avoid circumlocution we shall refer to these energies as "discrete levels." They will in general occur near an energy where we would expect a discrete level to be if the curve rose continuously to the right of the valley. Since there is a finite energy range over which the part of the eigenfunction in the valley has a relatively large size these discrete levels are "broadened."

We wish now to investigate how our system can appear in a "discrete state," and what it means to say that we start out with our system in the valley, and calculate the probability that it will get out on the plain. To do this we suppose that the system was originally in some real discrete state which might or might not be part of the system of states belonging to the potential energy curve of Fig. 1, but from which no escape from the valley into the plain is possible. We will call the eigenfunction of this state ψ_0 and its energy E_0. Now our system is subjected to a perturbation which causes it to appear in one of the states belonging to the curve of Fig. 1. There is a cer-

[8] Rice, Phys. Rev. **33,** 748 (1929). And see Schrödinger, Sitzungsber. Preuss. Akad. Wiss., (1929) 668.

[9] Kudar, Zeits. f. Physik **53,** 61, 95, 134 (1929); **54,** 297 (1929); Gamow and Houtermans, Zeits. f. Physik **52,** 496 (1928); Gamow, Zeits. f. Physik **53,** 601 (1929); Fowler and Wilson, Proc. Roy. Soc. **A124,** 493 (1929). See also v. Laue, Zeits. f. Physik, **52,** 726 (1928); Sexl, Zeits. f. Physik **54,** 445 (1929); **56,** 62, 72 (1929); Born, Zeits. f. Physik, **58,** 306 (1929); Atkinson and Houtermans, Zeits. f. Physik **58,** 478 (1929); Sexl, Zeits. f. Physik **59,** 579 (1930). Relativity treatment, Møller, Zeits. f. Physik, **55,** 451 (1929).

tain probability that it will land in some one of these states, of energy E, say, which is near some discrete energy, E_d. The eigenfunction of energy E (not including the exponential time factor) will be called $\psi(E)$. The wave packet which is formed by systems jumping from the state to the states $\psi(E)$ will be of the form

$$\psi = \sum a(E)\psi(E) \exp(-2\pi iEt/h)$$

where $a(E)$ is a constant coefficient for any E, and the sum is taken over all allowable values of E, which form a continuous set within the limits allowed by the box.

As a typical example, we shall consider the case where the perturbation which sets up the wave packet ψ for us is due to the action of monochromatic light,[10] of a frequency somewhere near $E_d - E_0$ which difference we will suppose great[11] compared to the "breadth" of the discrete state at E_d. Now we have said that we will have the wave packet produced by monochromatic light. But if light is to be strictly monochromatic we have to shine it in for an infinitely long time. There would be no sense in making any calculation for a process which occurs after such an excitation. In fact there would be no process to calculate. The system after the excitation by light would simply be in one of the stationary states $\psi(E)$. We can, however, shine in light of a given frequency for a short time. It is of particular interest to have it shine in for so short a time that any of the states $\psi(E)$ over a considerable range of energies in the neighborhood of E_d may be excited, and short enough so that no appreciable difference in phase of the exponential factor for the various states $\psi(E)$ in the expression for ψ can arise.[12] The matrix component of the perturbation for the excitation by light from state ψ_0 to a state $\psi(E)$ is proportional to the matrix component,[13] $P_{0E} = \int_0^\infty \psi_0 P \psi(E) dx$, where P is the electrical polarization expressed as a function of x. The $\psi(E)$ must be normalized. $a(E)$ will be proportional to P_{0E} and to find out how P_{0E} depends on E we must make a certain assumption regarding the integral which gives it. We assume that all appreciable contributions to this integral come from the range

[10] Rice, Phys. Rev. **34**, 1454 (1929).

[11] The assumption that $E_d - E_1$ should be great compared to the width of the discrete state at E_d was also made in the previous work, Ref. 9, but it was forgotten to mention it explicitly there. This assumption was necessary to show that a_n in Eq. (5) of that article is proportional to P_{no}; it makes $E_n' - E_o$ practically independent of E_n' over the important range of E_n'.

[12] As in the case previously considered (Ref. 10, see p. 1458) it seems safe to replace this condition by the statement that the time of illumination must be short compared to the time of decomposition, i.e. in this case the average life of a particle in the valley before it escapes into the plain. If the time of illumination is so short that more than one discrete state is excited the various decompositions from the various states may all be treated separately provided the energy between two discrete states is great compared to the breadth of a discrete state, a condition which must be fulfilled anyhow. This will also presumely be the case, if the perturbation is due to any other cause, provided it lasts for such a short time that no appreciable decomposition takes place in this time. The point is, as we shall see, that the wave packet starts in the neighborhood of the valley, and if the time of the perturbation is short enough, it will not, during that time, get out of the valley.

[13] Dirac, Proc. Roy. Soc. **A112**, 674 (1926).

of x in the valley, because ψ_0 is supposed to have appreciable values only in the valley. In the immediate neighborhood of any given discrete level in the valley, the shape of the part of $\psi(E)$ which is in the valley or the amplitude of the part in the plain will not vary greatly with the energy over a small energy range, but the ratio which we call B, of the magnitude of the valley part of $\psi(E)$ (for some definite value of x, say x^1) to the amplitude of the plain part will vary greatly with the energy. Let us designate the maximum of B as B_1. Then B/B_1 (which does not depend on x^1) is equal to the ratio[14] P_{0E}/P_{0E_1} because the normalization makes all $\psi(E)$ alike in the plain.[14a] The coefficient $a(E)$ is proportional to P_{0E} hence to P_{0E}/P_{0E_1}, hence to B/B_1. Therefore, neglecting a constant factor, ψ becomes

$$\psi = \sum (B/B_1)\psi(E) \exp(-2\pi i E t/h) \tag{2}$$

where the summation is over all allowable values of E. Now it will later be seen that this equation results in the total amount of material in the plain at $t=0$ being zero or almost so, but as time goes on, matter appears in the plain, and the amount of material in the valley suffers an exponential decrease.

If E_0 is greater than E_d so that the wave packet is set up by emission of light the above will also hold.

Calculation of the Stationary Eigenfunction

If ψ now is the stationary eigenfunction for some definite energy E, it has been shown that for regions when $|E-U|$ is not too small, and the slope of the U vs. x curve not too great, that the solutions of the wave equation can be written in the form[15] (disregarding constant factors)

$$\psi = (E-U)^{-1/4} \begin{matrix}\sin\\ \text{or}\\ \cos\end{matrix} \left\{ \kappa \int (E-U)^{1/2} dx \right\} \tag{3}$$

for $U<E$, and

$$\psi = (U-E)^{-1/4} \exp\left\{ \pm\kappa \int (U-E)^{1/2} dx \right\} \tag{4}$$

for $U>E$, where $\kappa=(8\pi^2 M/h^2)^{1/2}$.

In the immediate neighborhood of such a point as x_1 these solutions do not hold. The question now arises as to what happens if we start with some given solution in the mountain to the left of x_1, and go through x_1 into the plain. On the assumption that the side of the mountain is long and straight, Kramers[16] has shown that, if we start with the solution

$$(U-E)^{-1/4}\exp\left\{-\kappa\int_x^{x_1}(U-E)^{1/2}dx\right\}$$

far to the left of x_1, after going through x_1 and getting far to the right the solution has become

[14] E_d is not a well defined energy and we could take it as that value of the energy for which B is a maximum. We prefer, however, to designate the latter energy as E_1.

[14a] The matter of normalization is explained in more detail after Eq. (17). See also Ref. 8, p. 749.

[15] See, e.g., Nordheim, Zeits. f. Physik **46**, 842 (1927).

[16] Kramers, Zeits. f. Physik **39**, 828 (1926).

$$2(E-U)^{-1/4}\cos\left\{\kappa\int_{x_1}^{x}(E-U)^{1/2}dx-\pi/4\right\}.$$

This means that the particular solution of the differential equation which has the one form to the left of x_1 has the other form to the right. We express this by using the following notation:

$$(U-E)^{-1/4}\exp\left\{-\kappa\int_{x}^{x_1}(U-E)^{1/2}dx\right\}$$
$$\overset{x_1}{\longleftrightarrow} 2(E-U)^{-1/4}\cos\left\{\kappa\int_{x_1}^{x}(E-U)^{1/2}dx-\frac{\pi}{4}\right\} \quad (5)$$

Putting in the limits is equivalent to evaluating the constant of integration, the integral being a function of x. Kramers and Ittman[17] also point out that

$$(U-E)^{-1/4}\exp\left\{\kappa\int_{x}^{x_1}(U-E)^{1/2}dx\right\}$$
$$\overset{x_1}{\longleftrightarrow} -(E-U)^{-1/4}\sin\left\{\kappa\int_{x_1}^{x}(E-U)^{1/2}dx-\frac{\pi}{4}\right\} \quad (6)$$

Zwaan[18] points out that the relation (5) holds whether the side of mountain is long and straight or not, if we can go from a region where the approximations of the type (4) hold to a region where the approximations of the type (3) hold, *via* a path in the complex plane along which the solutions are of the general type $(E-U)^{-1/4}\exp\{i\kappa\int_{x_1}^{x}(E-U)^{1/2}dx\}$ and which crosses the curve along which argument of $\int_{x_1}^{x}(E-U)^{1/2}dx$ is $\pi/2$ at a point where the absolute value of $\int_{x_1}^{x}(E-U)^{1/2}dx$ is large.[19]

In similar manner we also have

$$2(E-U)^{-1/4}\cos\left\{\kappa\int_{x}^{x_2}(E-U)^{1/2}dx-\frac{\pi}{4}\right\}$$
$$\overset{x_2}{\longleftrightarrow}(U-E)^{-1/4}\exp\left\{-\kappa\int_{x_0}^{x}(U-E)^{1/2}dx\right\} \quad (7)$$

and

$$-(E-U)^{-1/4}\sin\left\{\kappa\int_{x}^{x_2}(E-U)^{1/2}dx-\frac{\pi}{4}\right\}$$
$$\overset{x_2}{\longleftrightarrow}(U-E)^{-1/4}\exp\left\{\kappa\int_{x_2}^{x}(U-E)^{1/2}dx\right\}. \quad (8)$$

Now if we multiply the left hand side of expression (5) by the factor exp $\{\kappa\int_{x_2}^{x_1}(U-E)^{1/2}dx\}$ which we will call $\theta/2$ we see that it coincides exactly with the right hand side of expression (8). Likewise if we multiply the left

[17] Kramers and Ittman, Zeits f. Physik **58** 222 (1929)

[18] Zwaan: Intensitäten im Ca-Funkenspektrum, Thesis, Utrecht (1929), p. 35. I am indebted to Dr. F. Bloch for calling my attention to this work.

[19] Kramers and Ittman state that (6) can be derived in the same way.

hand side of (6) by $2\theta^{-1}$ it coincides with the right hand side of (7). Thus we have established a connection between the solutions to the left of x_2 and to the right of x_1. We see, in fact, that

$$-(E-U)^{-1/4}\sin\left\{\kappa\int_x^{x_2}(E-U)^{1/2}dx-\frac{\pi}{4}\right\} \xleftrightarrow{x_2 \text{ and } x_1} \theta(E-U)^{-1/4}\cos\left\{\kappa\int_{x_1}^{x}(E-U)^{1/2}dx-\frac{\pi}{4}\right\} \quad (9)$$

and

$$(E-U)^{-1/4}\cos\left\{\kappa\int_x^{x_2}(E-U)^{1/2}dx-\frac{\pi}{4}\right\} \xleftrightarrow{x_2 \text{ and } x_1} -\theta^{-1}(E-U)^{-1/4}\sin\left\{\kappa\int_{x_1}^{x}(E-U)^{1/2}dx-\frac{\pi}{4}\right\}. \quad (10)$$

The actual eigenfunction in the valley must consist of a linear combination of the left hand sides of (9) and (10). If the eigenfunction in the valley is

$$(E-U)^{-1/4}\left[\cos\left\{\kappa\int_x^{x_2}(E-U)^{1/2}dx-\frac{\pi}{4}\right\} + b\sin\left\{\kappa\int_x^{x_2}(E-U)^{1/2}dx-\frac{\pi}{4}\right\}\right] \quad (11)$$

the same eigenfunction in the plain is

$$-(E-U)^{-1/4}\left[\theta^{-1}\sin\left\{\kappa\int_{x_1}^{x}(E-U)^{1/2}dx-\frac{\pi}{4}\right\} + b\,\theta\cos\left\{\kappa\int_{x_1}^{x}(E-U)^{1/2}dx-\frac{\pi}{4}\right\}\right] \quad (12)$$

THE SHAPE OF THE BROADENED DISCRETE STATE

In order that the solution of the wave equation should be an eigenfunction it must satisfy a certain condition to the left of x_3. It is probably good enough to assume that to the left of x_3 the solution must decrease exponentially in absolute value as we go to the left,[16] and the solution to the left of x_3 will therefore be of the form $(U-E)^{-1/4}\exp\{-\kappa\int_x^{x_3}(U-E)^{1/2}dx\}$. Now

$$(U-E)^{-1/4}\exp\left\{-\kappa\int_x^{x_3}(U-E)^{1/2}dx\right\} \xleftrightarrow{x_3} 2(E-U)^{-1/4}\cos\left\{\kappa\int_{x_3}^{x}(E-U)^{1/2}dx-\frac{\pi}{4}\right\} \quad (13)$$

(11) must be the same as the right hand side of (13), and it can be made the same as follows. We can easily at any time adjust the amplitude of (11) or (13) so that they will be the same. But we have to adjust the phase of (11)

so that it will coincide with (13). This is done by choosing the value of b. At some energy, say for example at E_1, the value of b will be zero. Then under the mountain we have only the decreasing exponential. The value E_1 will therefore be approximately the same as an eigenvalue of the wave equation if the curve for U increased indefinitely to the right. Kramers[16] has shown that the condition that E_1 should be the energy of such a discrete state is

$$\kappa\int_{x}^{x_2}(E_1 - U)^{1/2}dx = n\pi \tag{14}$$

when $n=1/2,\ 3/2,\ 5/2,\ \cdots$. The phase of the right hand side of (13) (starting from $x_.$) is less than that of the first term of (11), at some E not too distant from E_1, by

$$\kappa\int_{x_3}^{x_2}(E - U)^{1/2}dx - \kappa\int_{x_3}^{x_2}(E_1 - U)^{1/2}dx. \tag{15}$$

The amount that the phase of (11) is less than that of its first term is $\tan^{-1}b$. Thus, since (13) and (11) must be alike,

$$b = \tan\left\{\kappa\int_{x_3}^{x_2}(E - U)^{1/2}dx - \kappa\int_{x_3}^{x_2}(E_1 - U)^{1/2}dx\right\}. \tag{16}$$

Now if the breadth of the "broadened discrete state" is to be narrow compared to the distance between two discrete states, it means that over the "width" of the discrete state (15) must be small compared to π. We assume it so small that we may write

$$\begin{aligned} b &= \kappa\int_{x_3}^{x_2}(E - U)^{1/2}dx - \kappa\int_{x_3}^{x_2}(E_1 - U)^{1/2}dx \\ &= (E - E_1)\frac{\partial}{\partial E}\kappa\int_{x_3}^{x_2}(E - U)^{1/2}dx \end{aligned} \tag{17}$$

which we set $=b'(E-E_1)$. The derivative is taken for $E=E_1$. It is important to note that b' is positive.

We now wish to find how the value of b affects the relative size of the eigenfunction in the valley and on the plain. For large values of x we know that U takes on some asymptotic value, which we can without loss of generality take as 0. Then (12) also has an asymptotic form. In the limiting case when the box is large this part of (12) will determine the normalization, as the integral of ψ^2 over the plain can always, by taking the plain long enough, be made large compared to the integral across the valley. We make $\int_0^\infty\psi^2dx=1$. The amplitude of the sinusoidal function represented by (12) is (for large values of x where $U=0$) equal to $(\theta^{-2}+b^2\theta^2)^{1/2}E^{-1/4}$. To satisfy the normalization conditions the amplitude must be $(2/x_\infty)^{1/2}$ where x_∞ is the largest possible value[20] of x. To normalize we therefore multiply (12) by $(\theta^{-2}+b^2\theta^2)^{-1/2}E^{1/4}$

[20] Giving x a largest value allows in an idealized way for the fact that the system is in a box.

$(2/x_\infty)^{1/2}$. Now (11) must also be multiplied by the same thing, so its amplitude becomes $(1+b^2)^{1/2}(E-U)^{-1/4}(\theta^{-2}+b^2\theta^2)^{-1/2}E^{1/4}(2/x_\infty)^{1/2}$. But if b is small so that (17) holds, then it will also be negligible compared to 1. So the amplitude of (11) becomes

$$(E-U)^{-1/4}(\theta^{-2}+b^2\theta^2)^{-1/2}E^{1/4}(2/x_\infty)^{1/2}.$$

If we divide this expression by its value when $E=E_1$, and hence $b=0$, we get an expression which will no longer depend on the particular value of x between x_2 and x_3, and which will in fact be just equal to the quantity B/B_1 which appeared in Eq. (2). We thus find (assuming that E and θ do not vary appreciably over the range of E included in a broadened discrete state):

$$B/B_1 = (1 + b^2\theta^4)^{-1/2} = [1 + b'^2(E - E_1)^2\theta^4]^{-1/2}. \tag{18}$$

The shape of the broadened discrete state is found by plotting

$$(B/B_1)^2 = [1 + b'^2(E - E_1)^2\theta^4]^{-1} \tag{19}$$

against E. The width w of the state we may define as the energy over which $(B/B_1)^2$ has the value $\frac{1}{2}$ or greater, or twice the absolute value of $E-E_1$ for which $(B/B_1)^2=\frac{1}{2}$. Thus

$$w = 2/b'\theta^2. \tag{20}$$

The Setting-up of the Wave Packet; the Rate of Decay; Proof of Assumption of Complex Eigenvalues

For a very large box the summation in Eq. (2) can be replaced by an integration, which is surely allowable, as it will be seen that the integrand has no singular points. Eq. (2) thus becomes

$$\psi = \int_{-\infty}^{\infty}(B/B_1)\psi(E)\exp(-2\pi iEt/h)dE/\epsilon \tag{21}$$

where ϵ is the distance between energy levels, and is equal to $2\pi E^{1/2}/\kappa x_\infty$ where x_∞ is the largest possible value of x. It is only possible to integrate thus from ∞ to $-\infty$ because only a small range of E's contributes appreciably. To find ψ for $x\gg x_1$ we substitute for $\psi(E)$ in (21) the expression (12) with $U=0$ which must however be multiplied, as noted, by $(\theta^{-2}+b^2\theta^2)^{-1/2}E^{1/4}(2/x_\infty)^{1/2}=\theta(B/B_1)E^{1/4}(2/x_\infty)^{1/2}$. To find $\psi(E)$ for $x_3<x<x_2$ we use (11) multiplied by the same thing. We will, however, find it convenient to multiply (11) and (12) through by $-\theta(B/B_1)E^{1/4}\epsilon$, instead, which is permissible for the following reasons: ψ itself is not normalized, and we can always further multiply or divide (11) and (12) by any factor which does not depend on E. And in the range of values of E which contribute importantly in the integral (21) we may regard ϵ as constant. $E^{1/4}$, $(E-U)^{1/4}$, and θ are also practically constant. So (11) gives, when thus multiplied and substituted in (21) remembering (17) and (19):

$$\psi = -\frac{E_1^{1/4}\,\theta}{(E_1-U)^{1/4}}\left[\int_{-\infty}^{\infty}\frac{\cos\left\{\kappa\int_x^{x_2}(E-U)^{1/2}dx-\frac{\pi}{4}\right\}\exp(-2\pi iEt/h)}{1+b'^2\theta^4(E-E_1)^2}dE\right.$$

$$\left.+\int_{-\infty}^{\infty}\frac{b'(E-E_1)\sin\left\{\kappa\int_x^{x_2}(E-U)^{1/2}dx-\frac{\pi}{4}\right\}\exp(-2\pi iEt/h)}{1+b'^2\theta^4(E-E_1)^2}dE\right] \quad (22)$$

For great values of x we can substitute $\kappa E^{1/2}x+\zeta$ for $\kappa\int_{x_1}^{x}(E-U)^{1/2}dx-\pi/4$ in (12). We simply let ζ be the difference between these two expressions, this difference being constant for large values of x. Then we multiply (12) by the same expression as we multiplied (11) by, and get

$$\psi = \int_{-\infty}^{\infty}\frac{[\sin\{\kappa E^{1/2}x+\zeta\}+\theta^2 b'(E-E_1)\cos\{\kappa E^{1/2}x+\zeta\}]\exp(-2\pi iEt/h)}{1+b'^2\theta^4(E-E_1)^2}dE \quad (23)$$

We assume that the important range of E in this integral is so small that ζ is the same for all the states in this range. We now proceed to evaluate (23).

We substitute $(E-E_1)+E_1$ for E, and $E_1^{1/2}+(E-E_1)/2E_1^{1/2}$ for $E^{1/2}$, as this is allowable for the small values of $E-E_1$ which contribute to the integral. The latter substitution gives the cosine and the sine of the sum of the two angles $\kappa E_1^{1/2}x+\zeta$ and $(\kappa/2E_1^{1/2})\,(E-E_1)x$. These are reduced by the usual trigonometric formulas. We also write $\exp\,(-2\pi iEt/h)=\exp\,(-2\pi iE_1t/h)$ $[\cos\,\{2\pi(E-E_1)t/h\}-i\,\sin\,\{2\pi(E-E_1t/h\}]$. One thus gets a number of parts of the integral which drop out because they are antisymmetrical about the point $E-E_1=0$. The rest of the expression becomes

$$\psi = \exp(-2\pi iE_1t/h)$$

$$\left[\int_{-\infty}^{\infty}\frac{\sin\{\kappa E_1^{1/2}x+\zeta\}\cos\{(\kappa/2E_1^{1/2})(E-E_1)x\}\cos\{2\pi(E-E_1)t/h\}}{1+b'^2\theta^4(E-E_1)^2}d(E-E_1)\right.$$

$$-\,b'\theta^2\int_{-\infty}^{\infty}\frac{(E-E_1)\sin\{\kappa E_1^{1/2}x+\zeta\}\sin\{(\kappa/2E_1^{1/2})(E-E_1)x\}\cos\{2\pi(E-E_1)t/h\}}{1+b'^2\theta^4(E-E_1)^2}d(E-E_1)$$

$$-\,i\int_{-\infty}^{\infty}\frac{\cos\{\kappa E_1^{1/2}x+\zeta\}\sin\{(\kappa/2E_1^{1/2})(E-E_1)x\}\sin\{2\pi(E-E_1)t/h\}}{1+b'^2\theta^4(E-E_1)^2}d(E-E_1)$$

$$\left.-\,ib'\theta^2\int_{-\infty}^{\infty}\frac{(E-E_1)\cos\{\kappa E_1^{1/2}x+\zeta\}\cos\{(\kappa/2E_1^{1/2})(E-E_1)x\}\sin\{2\pi(E-E_1)t/h\}}{1+b'^2\theta^4(E-E_1)^2}d(E-E_1)\right]$$

The four integrals we shall designate respectively as I_1, I_2, I_3, I_4. Another trigonometric reduction gives $I_1=\frac{1}{2}[\sin\{\kappa E_1^{1/2}x+\zeta\}]\;(I_1^{+}+I_1^{-})$ and $I_2=\frac{1}{2}[\sin\{\kappa E_1^{1/2}x+\zeta\}]\;(I_2^{+}+I_2^{-})$, where

$$I_1^{\pm} = \int_{-\infty}^{\infty}\frac{\cos\{[(\kappa/2E_1^{1/2})x\pm 2\pi t/h](E-E_1)\}}{1+b'^2\theta^4(E-E_1)^2}d(E-E_1)$$

and

$$I_2^{\pm} = \int_{-\infty}^{\infty}\frac{(E-E_1)\sin\{[(\kappa/2E_1^{1/2})x\pm 2\pi t/h](E-E_1)\}}{1+b'^2\theta^4(E-E_1)^2}d(E-E_1)$$

I_1^+ and I_1^- are to be found from Pierce's Tables[21] and I_2^+ and I_2^- can readily be found by differentiating I_1^+ and I_1^- with respect to the proper parameter $(\kappa/2E_1)^{1/2}x \pm 2\pi t/h$. Now it will be found (as b' is positive) that the contributions from I_1^+ and I_2^+ cancel each other in the expression for ψ, as do also the contributions from I_1^- and I_2^- when $(\kappa/2E_1^{1/2})x > 2\pi h/t$. When, however, $(\kappa/2E_1^{1/2})x < 2\pi h/t$ the latter add. We can treat I_3 and I_4 in a similar way. So ψ is zero for $(\kappa/2E_1^{1/2})x > 2\pi h/t$ and for $(\kappa/2E_1^{1/2})x < 2\pi h/t$ we have

$$\begin{aligned}\psi &= (\pi/b'\theta^2)[\sin(\kappa E_1^{1/2}x + \zeta) - i\cos(\kappa E_1^{1/2}x + \zeta)] \\ &\quad \exp\{[(\kappa/2E_1^{1/2})x - 2\pi t/h]/b'\theta^2\} \exp(-2\pi i E_1 t/h) \qquad (24) \\ &= (\pi/b'\theta^2)\exp\{i(\kappa E_1^{1/2}x - 2\pi E_1 t/h - \pi/2 + \zeta)\}\exp\{[(\kappa/2E_1^{1/2})x - 2\pi t/h]/b'\theta^2\}\end{aligned}$$

We see that this represents a wave going in the positive direction with the particle velocity $(2E_1/M)^{1/2}$, and with an amplitude determined by the second exponential factor for values of x up to the place where $(\kappa/2E_1^{1/2})x = 2\pi t/h$ after which it breaks off. The wave shows an exponential decrease with time and just the proper exponential increase with distance to insure that the amount of matter in the wave is conserved. This is exactly like the outward going wave of Kudar's,[9] which resulted from the use of complex eigenvalues, except that his did not break off, but continued out to infinity in space and negative infinity in time.

We shall now evaluate (22). The sine and cosine of $\kappa\int_x^{x_2}(E-U)^{1/2}dx - \pi/4$ are roughly periodic functions of E, but we know that in the important range of E the functions have gone through a small fraction of a period, as we are considering a discrete state that is narrow compared to the distance between two discrete states We can therefore consider the sine and cosine terms as constant factors in the integration of (22). We write $\exp(-2\pi i Et/h)$ in sine and cosine form, as before, substitute in (22), note that some of the parts of the resulting integral drop out because of antisymmetry of the part of the integrand about $E - E_1 = 0$, integrate the remaining terms, which involve integrals of the type already met with, and get

$$\begin{aligned}\psi = &- [\exp(-2\pi i E_1 t/h)][(E_1^{1/4}\theta)/(E_1 - U)^{1/4}] \\ &[(\pi/b'\theta^2)\cos\left\{\kappa\int_x^{x_2}(E_1 - U)^{1/2}dx - \pi/4\right\}\exp(-2\pi t/hb'\theta^2) \\ &- i(\pi/b'\theta^4)\sin\left\{\kappa\int_x^{x_2}(E_1 - U)^{1/2}dx - \pi/4\right\}\exp(-2\pi t/hb'\theta^2)].\end{aligned} \qquad (25)$$

Since the distance between two discrete states is by (17) and (14) of the order of $1/b'$ and since, if w is to be small compared with this, θ^2 must, by (20), be large compared to 1, the last term in the expression (25) is negligible, and we are left with

$$\begin{aligned}\psi = &- [\exp(-2\pi i E_1 t/h)]E_1^{1/4}\theta(E_1 - U)^{-1/4}(\pi/b'\theta^2) \\ &\cos\left\{\kappa\int_x^{x_2}(E_1 - U)^{1/2}dx - \pi/4\right\}\exp(-2\pi t/hb'\theta^2),\end{aligned} \qquad (26)$$

[21] Pierce, "A short Table of Integrals," Ginn and Co., Formula 490.

a standing wave, except for the exponential decrement with time. Actually, if we consider terms of higher order, the wave function in the valley will not be expected to be merely a standing wave with exponential decrement with time.

Now if the mountain is not too thick through (i.e. if x_1-x_2 is not too great)[22] we may find the expression for ψ in the mountain the same way as we found it for ψ in the valley. We simply assume that $\exp\{\kappa\int_{x_2}^{x}(U-E)^{1/2}dx\}$ does not vary over the effective range of $E-E_1$, and this is, in fact included in the assumption we have already made that θ does not vary appreciably over this range. The integrations are then readily performed. We get an expression which again contains the factor $\exp(-2\pi iE_1t/h-2\pi t/hb'\theta^2)$. Also just to the right of x_1, (23) does not give an exact expression for ψ. The difference between the true value of ψ and that given by (23) will, however, not be appreciably different from 0 for any great distance to the right of x_1, and for this range we may also assume that $\kappa\int_{x_1}^{x}(E-U)^{1/2}dx$ does not vary appreciably with E over the range w, or at least that it is a linear function of $E-E_1$. In either case it is easily seen that the expression for ψ will contain the factor $\exp(-2\pi iE_1t/h-2\pi t/hb'\theta^2)$. Thus we see that the assumption of a complex eigenvalue is at least approximately correct, and that the smaller w is the better the approximation is. It also depends on the relations (9) and (10). It is also, of course, necessary that t should not be too small.

The rate of decay, γ, of ψ^2 is of course given by twice the real factor of t in this exponential time factor. We have[23]

$$\begin{aligned}\gamma &= 4\pi/hb'\theta^2 \\ &= \frac{\pi}{h}\left(\frac{\partial}{\partial E}\,\kappa\int_{x_3}^{x_2}(E-U)^{1/2}dx\right)^{-1}\exp\left\{-2\kappa\int_{x_2}^{x_1}(U-E)^{1/2}dx\right\}\,.\end{aligned}\tag{27}$$

It is seen from (20) that

$$w/\gamma = h/2\pi \tag{28}$$

the same relation that held in the case of predissociation, where we have a different type of interaction between discrete and continuous states.[24]

Generalization of the Results

Our results so far are somewhat unsatisfactory inasmuch as the general validity of the relations (5), (6), (7) and (8) depends upon the properties of $E-U$ considered a function of x when x is a complex variable, which are a little hard to investigate in a general way, or upon the assumption that the

[22] In order for the discrete state not to be too broad, θ must be great. The condition just cited states that a sufficient portion of this greatness must be caused by the height rather than the breadth of the mountain. If the mountain and the valley are of somewhat the same width the required condition will be sufficiently well fulfilled.

[23] This expression agrees with that of Kudar, Zeits. f. Physik **53**, 99 (1929) also that of Fowler and Wilson, l.c., in the exponential part, but not in the factor. The difference is probably due to the fact that Kudar and Fowler and Wilson considered a type of potential energy curve to which Kramer's approximation method could hardly apply.

[24] Ref. 10, p. 1457.

mountain-sides are long and straight. We may, however, show that the general character of the results depends only on the broadening of the discrete state being sufficiently small so that any given solution of the wave equation does not change its general character in that range. For then we may assume that a particular solution in the plain (far to the right of x_1) is connected with a particular type of solution in the mountain and in the valley. Thus the two solutions $E^{-1/4}\substack{\cos \\ \sin}(\kappa E^{1/2}x+\zeta)$ are connected with solutions in the mountain and valley which do not change much over the range of energies in the width of the discrete state. This will be true no matter what value we choose for ζ. Let us choose ζ so that if $E=E_1$ the eigenfunction in the plain becomes $E^{-1/4}\sin(\kappa E^{1/2}x+\zeta)$. For any other value of E the eigenfunction in the plain is

$$[E^{-1/4}\sin(\kappa E^{1/2}x+\zeta)+gE^{-1/4}\cos(\kappa E^{1/2}x+\zeta)]/(1+g^2)^{1/2}. \tag{29}$$

If $E-E_1$ is small enough g can be written as a linear function of $E-E_1$ say $g'(E-E_1)$ and in general it may be expected to be of the order of $b'\theta^2(E-E_1)$ as before, but the general character of the results, and the possibility of the use of complex eigenvalues do not depend on this. (The sign of g' is important but is surely the same as that of $b'\theta^2$.) Since we assume that the range of $E-E_1$ is so small that the shape of the eigenfunction in the valley is not affected we see that $(B/B_1)^2$ is given by $1/[1+g'^2(E-E_1)^2]$, hence all our previous results follow with g' substituted for $b'\theta^2$. Except, therefore, for this substitution we see that our results depend only on general properties of the solutions of the wave function, and not on their specific form.

I wish to thank Professor W. Heisenberg and Dr. F. Bloch for discussing this problem with me. I am informed by Dr. Bloch that much the same thing has been worked out independently by Professor Kramers, though without indicating, as is done here, how the wave packet is probably formed in nature.