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The Decay of Resonance Radiation by Spontaneous Emission

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A critical examination of the theory of resonance radiation has been carried through, employing the mathematical technique of Laplace and Stieltjes transforms. Particular attention has been devoted to the question of the temporal behavior of the excited state. With no restrictions on the interaction between atom and radiation field other than that it be real, and that processes of sufficiently high frequency contribute only negligible effects, one can prove that the probability amplitude of the excited state cannot decay according to the general law

$$\Sigma_{\mu,\nu} C_{\mu\nu} t^{\lambda_\mu} e^{-\beta_\nu t},$$

where the λ_μ and β_ν are complex constants lying in the right half-plane and the $C_{\mu\nu}$ are arbitrary complex coefficients. The deviation from the law just cited can be termed a straggling phenomenon since exact analysis shows that the probability amplitude, for sufficiently long times, is greater than that defined according to the radioactive decay law.

Rigorous analysis of the source of this apparently anomalous behavior reveals the following explanation. Although the probability amplitude of the excited state is, strictly speaking, a functional of the interaction between the transition current in the atom and the photon states of the electromagnetic field, the essential features are determined principally by those states lying near the resonance frequency. Three elementary observations are immediately apparent. First, a particularly tractable analytical approximation for the interaction can be made such that the value of the actual interaction is reproduced at the resonance frequency and such that the behavior for high and low frequency photon states is at least qualitatively correct. Exact solutions in closed form can be obtained for this interaction. Second, in terms of the preceding representation it is possible to show that, associated with the transition between two atomic states, one is presented with a concomitant picture of a damped oscillation of charge describable in purely classical terms. Third, this classical motion can be interpreted as forming a source function for a continuous stochastic process in terms of which one finally derives the representation of the probability amplitude of the excited state. The straggling phenomenon previously cited is therefore that associated with all diffusion processes. The consideration of the exact interaction leads to more involved diffusion phenomena but does not in any case permit a radioactive decay law.

INTRODUCTION

A CLASSIC investigation on the theory of natural line breadth[1] is that of Weisskopf and Wigner. Their analysis is concerned with the reaction of the emitted radiation on the atomic electrons.

The quantum-mechanical description of the behavior of an atom in the presence of the ambient electromagnetic field, according to Dirac, is contained in the following equation of motion:[2]

$$\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = (E_Q + 2\pi\hbar\textstyle\sum_\rho \nu_\rho N_\rho)\psi(Q; N_1, N_2, \cdots)$$
$$+\textstyle\sum \omega_{QU^\rho}[(N_\rho+1)^{\frac{1}{2}}\psi(U; N_1, N_2, \cdots N_\rho+1, \cdots)$$
$$+N_\rho{}^{\frac{1}{2}}\psi(U; N_1, N_2, \cdots N_\rho-1, \cdots)], \quad (1)$$

where Ψ is the Schrödinger probability amplitude for the system of atom plus photons; Q, U the designation of atom states; N_1, N_2, $\cdots$ the occupation numbers of the photon states; and, where ω_{UQ^ρ} denotes the matrix element of the interaction between the electromagnetic field and the atomic electric current associated with the transition between the two states Q and U. The symbol ρ serves to label the direction of emission of the photon, its polarization, and, finally, its energy.

Weisskopf and Wigner have applied Eq. (1) to the case of resonance radiation, assuming that in the notation of the preceding section the physical system could be described completely in the Hilbert space having for basis vectors

$$\Psi(A, 0), \quad \Psi(B, 1_\rho), \quad (2)$$

where A denotes the excited atomic state and 0 the absence of any photons in the field. B then denotes the ground state of the atom, and 1_ρ a photon in the state labeled by ρ.

[1] V. Weisskopf and E. Wigner, Z. Physik **63**, 54 (1930); **65**, 19 (1930).
[2] W. Heitler, *Quantum Theory of Radiation* (Clarendon Press, Oxford, 1936), first edition, Chap. III.

PRELIMINARY ANALYSIS

The objective confronting us is the specialization of Eq. (1) to the problem at hand. We shall begin by working with the theory reduced to its simplest basis; that is, we shall at first make no specific assumption about the form of the matrix elements ω_{QU^ρ}, avoiding in this way reference to a particular atomic model. The excited state, further, is assumed to be "oriented at random." The probability of emission is then isotropic with respect to direction and polarization. We shall also assume that the "hohlraum" is large enough to go from the sums employed in Eq. (1) to integrals by using the Jeans formula

$$\sum_\rho \cdots \equiv \int_0^\infty \cdots \frac{8\pi\nu^2 V}{c^3} d\nu, \tag{3}$$

where V designates the volume of configuration space and c the velocity of light. We shall introduce the notation that

$$\omega_{AB^\rho} \equiv \hbar W(\nu). \tag{4}$$

The replacement of ρ as a label by ν accords with the picture of isotropic emission. The dropping of A, B is permissible because no other states participate in the emission. Finally, we adopt the following symbols for the various probability amplitudes

$$\Psi(A, 0) \equiv a(t), \quad \Psi(B, 1_\rho) \equiv b(\nu, t). \tag{5}$$

Selecting our energy scale so that $E_A = 0$, we find that Eqs. (1) become

$$\begin{aligned} -i\frac{\partial a}{\partial t} &= \int_0^\infty W(\nu) b(\nu, t) S(\nu) d\nu, \\ -i\frac{\partial b}{\partial t} &= 2\pi(\nu - \nu_B{}^A) b + W^* a, \end{aligned} \tag{6}$$

where $S(\nu)$ represents

$$S(\nu) \equiv 8\pi\nu^2 V/c^3. \tag{7}$$

One can readily verify that

$$aa^* + \int_0^\infty bb^* S(\nu) d\nu = 1 \tag{8}$$

for all t, if the relation is satisfied at $t = 0$.

The implication that processes involving frequencies much greater than $\nu_B{}^A$ do not contribute appreciably to the decay of the excited state is expressed mathematically by the assignment of the property of uniform convergence to the integral occurring in the first of Eqs. (6). It is not difficult to establish that $W(\nu)$ does actually have the requisite behavior when calculated for an actual atomic model. For sufficiently large values of ν, the Fourier components of the vector potential oscillate rapidly over the atomic domain, thus forcing ω_{AB^ρ} to cut off sharply in this limit.

Equations (6) are now to be solved subject to the following boundary conditions:

$$a(0) = 1, \quad b(\nu, 0) = 0. \tag{9}$$

Taking the Laplace transforms[3] of Eqs. (6), with z as the transform parameter, and solving them, we obtain

$$\begin{aligned} \bar{a}(z) &= 1 \Big/ \left[z + g\left(\frac{zi}{2\pi} - \nu_B{}^A \right) \right], \\ \bar{b}(\nu, z) &= -W^*(\nu)\bar{a}(z) / [zi + 2\pi(\nu - \nu_B{}^A)], \end{aligned} \tag{10}$$

where

$$g(z) = \frac{i}{2\pi} \int_0^\infty \frac{f(\nu)}{z + \nu} d\nu \tag{11}$$

and

$$f(\nu) = |W(\nu)|^2 S(\nu). \tag{12}$$

The bar above a or b denotes the transform in all subsequent analysis.

INTRODUCTION OF ELECTROSTATIC ANALOG

Clearly, if one is to ascertain the properties of $\bar{a}(z)$ and hence $a(t)$, it is necessary to determine first the properties of the function g. The latter represents the Stieltjes transform[4] of $f(\nu)$, and one could simply draw upon the available store of representation theorems to establish the functional properties of g. However, the content of these theorems can be obtained directly by noting that g can be taken as representing a conformal representation of potential[5] and field lines of a double layer of electric charge placed along the imaginary axis in the z plane from $-2\pi i\nu_B{}^A$ to $+i\infty$. This is made clearer by writing

$$g\left(\frac{zi}{2\pi} - \nu_B{}^A \right) = \frac{1}{2\pi} \int_{-2\pi\nu_B{}^A}^{+\infty} \frac{f(\eta/2\pi + \nu_B{}^A)}{z - i\eta} d\eta, \tag{13}$$

where

$$\eta = 2\pi(\nu - \nu_B{}^A).$$

The "moment density" is evidently to be taken as $(1/2\pi) f(\eta/2\pi + \nu_B{}^A)$ and directed so that the "potential" is positive in the right half-plane and negative in the left half-plane. The field lines are clearly symmetrical with respect to the imaginary axis. Using the terminology of the electrostatic analog, we can rewrite the first of Eqs. (10) in the more useful form

$$\bar{a}(z) = [z + V(x, y) + iU(x, y)]^{-1}, \tag{14}$$

where V and U now denote the "potential" and "field."

[3] This method is particularly advantageous. Compare the treatment of internal conversion by N. Tralli and G. Goertzel, Phys. Rev. 83, 399 (1951).

[4] D. V. Widder, *The Laplace Transform* (Princeton University Press, Princeton, 1946), first edition, Chap. VIII.

[5] For example the so-called complex inversion theorem for the Stieltjes transform becomes the well-known theorem of electrostatics that the potential is discontinuous at a double layer by an amount equal to 2π times the moment density.

An immediate consequence of the properties of V and U is that the $\bar{a}(z)$ can have no singularities in the entire z plane[6] with the possible exception of the imaginary axis. It is, therefore, impossible to expand $a(t)$ in a finite series of the form[7]

$$a(t)=\sum_{\mu,\nu} C_{\mu\nu} t^{\lambda_\mu} e^{-\beta_\nu t}, \tag{15}$$

where

$$\mathrm{Re}(\lambda_\mu)\geqslant 0, \quad \mathrm{Re}(\beta_\nu)>0, \tag{16}$$

with $C_{\mu\nu}$ arbitrary. It will be noted that the conclusion is valid with no other restrictions on $W(\nu)$ than that it be of such a form as to make the integral in Eqs. (6) converge uniformly. The Hermitean nature of the interaction has, of course, already been exploited in writing $\omega_{AB^\rho}=\omega_{BA^\rho}{}^*$ and in effect forces the moment density to be real.

Reverting to the second of Eqs. (10), one can prove by elementary means that the spectrum of emitted radiation is given by[2]

$$\lim_{t\to\infty}|b(\nu,t)| = \left|\frac{W^*(\nu)}{\{2\pi(\nu-\nu_B{}^A)+U[0,2\pi(\nu-\nu_B{}^A)]+iV[0,2\pi(\nu-\nu_B{}^A)]}\right|. \tag{17}$$

One sees that the line shape is necessarily asymmetric

INTRODUCTION OF PARTICLE OSCILLATOR

While the rejection of Eq. (15) is somewhat disturbing, no "model" has been presented in terms of which this result could have been foreseen.

It is perhaps of some interest to point out that such a model can be derived on the basis of elementary concepts. One simply retains the picture that the emission of radiation is associated with an actual oscillation of charge. This oscillation must be damped, in accordance with energy conservation. The reaction force, representing this damping action, should, of course, be derivable from Eqs. (10) as a functional of the interaction matrix. The precise form of the reaction force clearly cannot be assumed *a priori*. However, one point of primary importance emerges from this picturization. The reaction force represents the *integrated* effect of all modes of oscillation of the radiation field in retarding the charge vibration. In terms of the *electrostatic analog* one must therefore anticipate the replacement of the "moment density" along the imaginary axis by an "equivalent dipole," in the simplest possible case. This "dipole" is, schematically, the origin of the reaction force causing the decay of the classical vibration. The preceding discussion, it will be shown, provides a framework adequate to define the mathematical procedure which must now be followed.

We note first that the z plane is not sufficient to map $\bar{a}(z)$ completely. One must employ the concept of a multisheeted Riemannian surface of which one sheet is the z plane. The remaining sheets are entered through the cut in the z plane along the imaginary axis from $-2\pi i\nu_B{}^A$ to $+i\infty$. The simplest space of this type would be one of two sheets. For an arbitrary assumption as to the matrix elements $W(\nu)$ one would require an infinite number of sheets to map $\bar{a}(z)$ uniquely.

From the appearance of the spectrum of emitted photons, as given by Eq. (17), we see, however, that only frequencies near the resonance frequency $\nu_B{}^A$ are important in causing the excited state to decay. In seeking to replace the actual interaction matrix ω_{AB^ρ} by an equivalent form more amenable to calculation, one must, therefore, match the magnitude of ω_{AB^ρ} for $\nu\sim\nu_B{}^A$ and merely achieve a qualitative fit in the regions $\nu\ll\nu_B{}^A$ and $\nu\gg\nu_B{}^A$. By way of comparison, it may be mentioned that Weisskopf and Wigner considered that ω_{AB^ρ} could be replaced in the final formulas by its value at $\nu=\nu_B{}^A$. The approximation is good because of the smallness of the natural widths.

It will now be demonstrated that the equivalent form can be selected in such a way that $\bar{a}(z)$ will then be mapped on a two-sheeted Riemannian surface. The dipole previously described as replacing the continuous "moment density" will appear on the second sheet. If one then maps the points of this surface upon a ζ-plane, with ζ taken to mean the transform parameter for the classical damped oscillations, the prescription is complete.

The "model" interaction permitting a solution for $a(t)$ in terms of elementary functions is

$$f(\nu)=\frac{A\nu^{\frac{1}{2}}}{\pi(\nu+B^2)}, \tag{18}$$

where A and B are constants to be determined by comparison with the actual matrix ω_{AB^ρ}.

With $f(\nu)$ defined according to Eq. (18), g can be evaluated by elementary methods and is found to be[9]

$$g\left(\frac{zi}{2\pi}-\nu_B{}^A\right)=\frac{Ai}{2\pi[(zi/2\pi-\nu_B{}^A)^{\frac{1}{2}}+B]}. \tag{19}$$

The ζ-plane (representation) is obtained by pulling this dipole through the cut along the imaginary axis by means of the transformation

$$\zeta^2=2\pi i\nu_B{}^A(z+2\pi i\nu_B{}^A). \tag{20}$$

The meaning of the various terms of Eq. (20) follows. The factor $z+2\pi i\nu_B{}^A$ merely expresses the fact that the

[6] Derivation of an exponential decay results from an approximation which creates a singularity in the left half z plane [M. F. Ripelle, Compt. rend. **232**, 2403 (1951)].

[7] The class of functions excluded is broader than that indicated by Eq. (15).

[8] G. Doetsch, *Laplace Transformation* (Dover Publications, New York, 1943), first edition, Part III.

[9] The insertion of this result into Eq. (10) can be shown to lead to the expression of $a(t)$ in terms of three error functions of complex argument. Owing to the lack of complete tables, the result is not of practical interest.

cut in the z plane extends to $-2\pi i\nu_B{}^A$. The factor "i" outside guarantees that the axis of imaginaries in the ζ plane corresponds to the cut in the z plane. The factor $2\pi\nu_B{}^A$ insures that the classical vibration "keeps correct time."

By transformation (20), g becomes

$$g=\frac{iA(\nu_B{}^A)^{\frac{1}{2}}}{\zeta+2\pi B(\nu_B{}^A)^{\frac{1}{2}}}. \tag{21}$$

The "dipole" accordingly is found in the ζ-plane at $\zeta=-2\pi(\nu_B{}^A)^{\frac{1}{2}}B$ and has a "moment" equal to $A(\nu_B{}^A)^{\frac{1}{2}}$. The transform derived by the insertion of the value of g given by Eq. (21) into the first of Eqs. (10) must be understood as the Laplace transform image, not of $a(t)$ but of a motion, say $R(t)$.[10]

Using the same symbolism for this function, we have

$$\bar{R}(\zeta)=\frac{2\pi i\nu_B{}^A}{\zeta^2+(2\pi\nu_B{}^A)^2-2\pi(\nu_B{}^A)^{\frac{1}{2}}A/[\zeta+2\pi(\nu_B{}^A)^{\frac{1}{2}}B]}. \tag{22}$$

The last term in the denominator represents the damping of the harmonic oscillation $\zeta^2+2\pi(\nu_B{}^A)^2$. Actually all three poles of $\bar{R}(\zeta)$ lie in the left half-plane. $R(t)$ therefore contains only retarded effects.[11] In fact, the damping force is a memory term of the form

$$2\pi m(\nu_B{}^A)^{\frac{1}{2}}A\int_0^t \exp[-2\pi(\nu_B{}^A)^{\frac{1}{2}}B(t-\tau)]R(\tau)d\tau. \tag{23}$$

The equation of motion of such a particle oscillator is thus

$$m\frac{d^2R}{dt^2}+4\pi^2m(\nu_B{}^A)^2R-2\pi m(\nu_B{}^A)^{\frac{1}{2}}A\times\int_0^t \exp[-2\pi(\nu_B{}^A)^{\frac{1}{2}}B(t-\tau)]R(\tau)d\tau=0. \tag{24}$$

Generally,[12]

$$m\frac{d^2R}{dt^2}+4\pi^2m(\nu_B{}^A)^2R-4\pi m\nu_B{}^A\times\int_0^t\int_0^\infty f(\nu^2/\nu_B{}^A)e^{-2\pi\nu(t-\tau)}d\nu R(\tau)d\tau=0. \tag{25}$$

[10] The transformation of $R(t)$ into $a(t)$ can be considered as representing a perturbation in the equation of motion governing $R(t)$. One may consider the stochastic perturbation of a harmonic oscillator as illustrative of this point of view [W. R. van Wijk, Physica **3**, 1111 (1936)].

[11] Compare F. Bopp, Naturforsch. **1**, 53 (1946).

[12] Assuming that $f(\nu)$ is single values and that $f(\nu)\nu^{-\frac{1}{2}}$ is expressible as a Stieltjes transform.

One can easily show that $R(t)$ defined by Eq. (24) has two decay periods. The "fast" decay, which is non-oscillatory, is important only for very short times.

Finally, we note that $a(t)$ can be expressed directly in terms of $R(t)$.[13]

$$|a(t)|=\left|\frac{1}{4\pi D^{\frac{3}{2}}t^{\frac{3}{2}}}\int_0^\infty R'(\tau)\tau\exp(-\tau^2/4Dt)d\tau\right|, \tag{26}$$

where

$$D=(2\pi i\nu_B{}^A)^{-1} \tag{27}$$

and

$$R'=2\pi^{\frac{1}{2}}DR. \tag{28}$$

This relation between $R(t)$ and $a(t)$ can be expressed most conveniently in terms of an auxiliary function $\varphi(t,\tau)$ satisfying the following equation,

$$\frac{\hbar}{i}\frac{\partial\varphi}{\partial t}=\frac{1}{2M_B{}^A}\left[\left(i\hbar\frac{\partial}{\partial c\tau_1}\right)^2+\left(i\hbar\frac{\partial}{\partial c\tau_2}\right)^2+\left(i\hbar\frac{\partial}{\partial c\tau_3}\right)^2\right]\varphi, \tag{29}$$

where

$$\tau^2=\tau_1{}^2+\tau_2{}^2+\tau_3{}^2, \tag{30}$$

$$M_B{}^A=\tfrac{1}{2}h\nu_B{}^A/c^2, \tag{31}$$

with the "initial" condition,

$$4\pi\tau^2|\varphi(0,\tau)|^2=|R'|^2. \tag{32}$$

One finds then that Eq. (26) reduces to

$$|a(t)|^2=|\varphi(t,0)|^2. \tag{33}$$

The straggling phenomenon previously discussed is thus identified with a characteristic behavior of wave packets.

It has been frequently suggested that the results may be altered on considering the scattering problem. This point will be dealt with in a subsequent paper.

[13] The Laplace transform of $a(t)$ is

$$\bar{a}(z)=\bar{R}(\zeta)=\int_0^\infty R(\tau)\exp\left[-\tau\left\{\frac{1}{D}\left(z+\frac{1}{D}\right)\right\}^{\frac{1}{2}}\right]d\tau,$$

using Eqs. (20) and (27). If we then find the inverse Laplace transform of the integrand as a function of z (reference 8, pages 402 and 148) and take absolute values, Eq. (26) follows.