

Threshold Behavior of the X-Ray Spectra of Light Metals

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A simple model to describe the x-ray process in light metals is used to study the transition rate near the threshold. For the absorption case, the problem consists of calculating the response of a band of free electrons to the sudden creation of a core hole potential and to the injection of the core electron into the band. Recently, Nozières *et al.* showed that the transition rate becomes singular at the threshold. We offer an explanation for how this comes about, and we give a rederivation of Nozières' result by a different approach, related to Zubarev's method of Green's functions. We set up and solve, for large times, integral equations for quantities directly connected to the response function. The model is studied explicitly in the case of absorption for spinless particles and *s*-wave scattering. The results can be extended to include emission processes, electrons with spin, and higher angular momenta.

I. INTRODUCTION

RECENTLY, the interest in the problems of x-ray absorption and emission of metals has been newly aroused by a prediction of Mahan,¹ that singularities should occur near the Fermi-level threshold, which are not density-of-states effects. Mahan, and later several other authors,^{2,3} found a divergence in the perturbation expansion of the transition rate due to the sharpness of the Fermi distribution, similar to the divergence found by Kondo in connection with the problem of a localized magnetic impurity in a metal. In an oversimplified model, the metal is represented by a simple band of free electrons and one deep-lying core state, from which an electron is elevated into the band in the x-ray absorption process, while in the emission process a conduction electron drops into the deep core hole. The situation is described by the following Hamiltonian^{3,4}:

$$H = \sum_k \epsilon_k a_k^\dagger a_k + E_0 b^\dagger b + \sum_{kk'} V_{kk'} a_k^\dagger a_k' b b^\dagger. \quad (1)$$

The first term refers to the free-electron system described by a_k^\dagger , a_k , the second term to the deep-level state described by b^\dagger , b , and the interaction term tells that once the hole state is present the conduction electrons have to react and to rearrange in its Coulomb potential. Apparently the following approximations have been adopted: The Coulomb interaction between the conduction electrons has been ignored, since one can argue that the quasiparticle character of the Fermi-

liquid excitations is described well enough by the above Hamiltonian, and imagine that the renormalization due to the interaction has been done already. Further, the deep hole is strictly localized, i.e., the level is sharp. More stringent is the assumption that the deep hole cannot change its state and cannot have a finite lifetime by Auger-type transitions. This means that the lifetime of the hole is long compared to the time needed by the band electrons to adjust to the hole potential.

In view of these approximations, it is not surprising that a singular behavior near the threshold found on the basis of the above Hamiltonian shows up as a mere spike in the experimental data. For an investigation of the connection of theory and experiment, we refer to the work of Ausman and Glick⁵ on Li, Na, and Al.

Besides the perturbative approaches referred to above, Nozières *et al.* were the first to obtain the exact result for the transition rate. After they first tried a many-body approach using a parquet diagram expansion, which gave the answer in Born approximation, they showed, in the third part of their paper, that the calculation can be formulated in terms of a one-body problem. They developed a rather unusual approach still oriented by many-body diagram ideas, which, despite some delicate and not easily understandable arguments, led to the correct answer.

The purposes of this paper are the physical explanation of the effect, and the presentation of a different nonperturbative approach related in some ways to Zubarev's⁶ method of Green's functions for $T \neq 0$.

II. PROBLEM FORMULATION

As usual, we consider the interaction of the electrons in the metal with the photon field to be a weak perturbation and calculate the transition rate for absorption according to Fermi's "golden rule":

$$W_{\text{abs}} = 2\pi \sum_f \left| \sum_k w_k \langle f | a_k^\dagger b | i \rangle \right|^2 \delta(E_i - \omega - E_f), \quad (2)$$

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¹ G. D. Mahan, *Phys. Rev.* **163**, 612 (1967).

² P. Longe and A. J. Glick, *Phys. Rev. Letters* **15**, 589 (1965).

³ B. Bergerson and F. Brouers, *J. Phys. (Proc. Phys. Soc.)* **C2**, 651 (1969); see also Y. Mizuno and K. Ishikawa, *J. Phys. Soc. Japan* **25**, 627 (1968).

⁴ B. Roulet, J. Gavoret, and P. N. Nozières, *Phys. Rev.* **178**, 1072 (1969); P. Nozières, J. Gavoret, and B. Roulet, *ibid.* **178**, 1084 (1969); P. Nozière and C. T. de Dominicis, *ibid.* **178**, 1097 (1969).

⁵ G. A. Ausman and A. Glick (to be published).

⁶ D. N. Zubarev, *Usp. Fiz. Nauk* **71**, 71 (1960) [English transl.: *Soviet Phys.—Usp.* **3**, 320 (1961)].

where we took the dipole operator to be

$$H_{\text{int}} = \sum_k w_k a_k^\dagger b e^{-i\omega t} + \text{c.c.}$$

As we focus our attention to the behavior near the threshold, we will take w_k constant for simplicity. Though seemingly a many-body problem, the calculation of the transition rate can be formulated as a one-body problem, albeit a peculiar one. The interaction term is present either if the hole is present, and acts as an external potential on the band electrons, or if the deep level is filled and the interaction term is not there. The change of state can only be brought about by the emission or absorption of a photon. The difference to a static impurity problem is that the potential is not switched on adiabatically but, rather, suddenly.

Let us define an "initial Hamiltonian" for the case when the core hole is occupied, i.e., $b^\dagger b = 1$:

$$H_i = \sum_k \epsilon_k a_k^\dagger a_k, \quad (3)$$

(we have omitted the constant E_0). The initial state for the conduction electrons is

$$|i_0\rangle = \prod_{k=0}^{k_f} a_k^\dagger |0\rangle, \quad (4)$$

where $|0\rangle$ is the vacuum state. After the x-ray process has taken place, one has to consider a "final Hamiltonian," i.e., $bb^\dagger = 1$:

$$H_f = \sum_k \epsilon_k a_k^\dagger a_k + \frac{V}{N} \sum_{kk'} a_k^\dagger a_{k'}. \quad (5)$$

For simplicity, we have replaced $V_{kk'}$ by a constant V . A separable potential can still be managed, but it is no more realistic and makes the calculations clumsy.

The transition rate is conveniently calculated via the response function

$$\tilde{S}(t) = \frac{1}{N} \sum_{kk'} \langle i | b^\dagger(t) a_k(t) a_{k'}^\dagger b | i \rangle, \quad (6)$$

thereby circumventing the problem of fixing the final states. If we use $|i\rangle = b^\dagger |i_0\rangle$ and introduce H_i and H_f , we can get rid of the b, b^\dagger and have

$$\tilde{S}(t) = e^{+iE_0 t} \frac{1}{N} \sum_{kk'} \langle i_0 | e^{iH_i t} a_k e^{-iH_f t} a_{k'}^\dagger | i_0 \rangle. \quad (6')$$

The transition rate is connected with this quantity by

$$W_{\text{abs}}(\omega) = 2\pi\omega^2 \text{Im} \left(\frac{i}{\pi} \int_0^\infty e^{i(\omega + E_0)t} S(t) dt \right). \quad (7)$$

S is defined similarly to \tilde{S} without the phase factor $e^{+iE_0 t}$.

The calculation of $S(t)$ is a highly technical procedure which will be performed in Sec. III, and is not very

illuminating as to the physical idea behind the effect. The following discussion should help us to gain a little more insight into the problem. It was, so to speak, buried when the final states were thrown out, by introducing the correlation function. There is, however, an essential difficulty connected with the final states. Anderson⁷ has pointed out that the overlap of the N -particle ground states of the two systems, the one described by H_i and the other by H_f , tends to zero as the volume (or the number of particles N) goes to infinity:

$$\lim_{N \rightarrow \infty} \langle 0 | \prod_{k_1}^{k_f} a_{k_1} \sum_{k_2}^{k_f} c_{k_2}^\dagger | 0 \rangle \sim N^{-1/2(\delta/\pi)^2}. \quad (8)$$

The c_k^\dagger refers to the eigenstates of H_f , and δ is the phase shift at the Fermi energy. The orthogonality of the ground states of H_i and H_f implies that the final states appearing in the transition-rate formula cannot be constructed by applying a finite number of electron-hole pair operators c_k^\dagger and $c_{k'}$ on the ground state of H_f . So the final states are practically inaccessible to calculation.

Taking time into consideration, we find that by using the relationship

$$\lim_{t \rightarrow \infty} e^{iH_i t} e^{-iH_f t} a_k^\dagger | 0 \rangle = c_k^\dagger | 0 \rangle, \quad (9)$$

the expression

$$\langle 0 | \prod_{k_1}^{k_f} a_{k_1} e^{iH_i t} e^{-iH_f t} \prod_{k_2}^{k_f} a_{k_2}^\dagger | 0 \rangle \quad (10a)$$

is Anderson's overlap function for $t = \infty$; therefore, it is equal to zero for infinite volume. Of course, for $t = 0$ it is equal to one. What we would like to know is the intermediate time behavior of (10) or at least its asymptotic expression for large t .

A simple calculation helps us to guess how the relevant response functions should behave as $t \rightarrow \infty$. Consider the hierarchy of correlation functions

$$S_0(t) = \langle i_0 | e^{+iH_i t} e^{-iH_f t} | i_0 \rangle, \quad (10b)$$

$$S_1(t) = \langle i_0 | e^{+iH_i t} \Psi(1) e^{-iH_f t} \Psi^\dagger(1) | i_0 \rangle, \quad (10c)$$

$$S_2(t) = \langle i_0 | e^{+iH_i t} \Psi(1) \Psi(2) e^{-iH_f t} \Psi^\dagger(2) \Psi^\dagger(1) | i_0 \rangle, \quad (10d)$$

etc. The $\Psi^\dagger(j)$ represent s -wave packets of spinless electrons. If we put $V = 0$, we can easily calculate these correlation functions.

For this purpose we change over to an energy representation

$$\prod_{\epsilon=1}^n \Psi^\dagger(j) = \frac{1}{\sqrt{(n!)}} \sum_{\epsilon_1} \cdots \sum_{\epsilon_n} f(\epsilon_1 \cdots \epsilon_n) a_{\epsilon_1}^\dagger \cdots a_{\epsilon_n}^\dagger. \quad (11)$$

⁷ P. W. Anderson, Phys. Rev. Letters **18**, 1049 (1967); Phys. Rev. **164**, 352 (1967).

For s -wave scattering it is possible to take the energy as the only variable in the (antisymmetric) wave function f . In the general case, a decomposition with respect to spin and angular momentum is necessary, but then again each component can be considered a function of energy alone. The momentum can be expressed in terms of the energy, since there will be a dependence on its magnitude only. Therefore, in the case of s waves, we have to calculate

$$S_n(t) = \int_0^\infty d\epsilon_1 \cdots \int_0^\infty d\epsilon_n |f(\epsilon_1 \cdots \epsilon_n)|^2 e^{-i(\epsilon_1 + \cdots + \epsilon_n)t}. \quad (12)$$

To find the asymptotic time behavior of $S_n(t)$ we need to know $f(\epsilon_1 \cdots \epsilon_n)$ for small arguments. The first non-vanishing term of the Taylor expansion near $\epsilon_1 = \epsilon_2 = \cdots = \epsilon_n = 0$ is proportional to the Vandermonde determinant, or, equivalently,

$$f(\epsilon_1 \cdots \epsilon_n) \sim \prod_{i>j}^n (\epsilon_i - \epsilon_j). \quad (13)$$

This product consists of $\frac{1}{2}n(n-1)$ factors which, when inserted into (12), shows that

$$S_n(t) \sim t^{-n^2}. \quad (14)$$

The S_n describes the overlap between a wave function with n localized electrons being inserted into the conduction band and the development of this same wave function with time. Physically, they describe the spread of the n electron wave packets with time, or in a hydrodynamic picture the spread of a portion of fermion fluid equivalent to n electrons. Indeed, such a picture, in which the electron system behaves approximately as a fluid with density waves of boson character as its low-lying excitations, is very convenient and helpful to find out what happens if $V \neq 0$. In a previous paper,⁸ we used the Tomonaga model, which is characterized by these features and showed that for small V (i.e., in Born approximation) one correctly derives the essential features of the asymptotic time behavior of $S_1(t)$. This experience guides us in including V into the discussion of $S_n(t)$ and makes it natural to reinterpret the electron number n . The spread of the electrons injected into the band has to be taken into account as before, but now there is an additional amount of fermion liquid to be moved about to shield the potential, namely, δ/π for s -wave scattering, so that this amount has to be subtracted from n . A special case is $S_0(t)$, where only the potential acts to gather δ/π electrons in the vicinity of the potential source, so that simply $n \rightarrow n_0 = \delta/\pi$. This provides the asymptotic time behavior of the overlap considered by Anderson; it behaves as $t^{-(\delta/\pi)^2}$.

For our x-ray problem $S_1(t)$ is the response function we need to calculate the transition rate. When an x ray is absorbed, one electron is elevated into the band, and

at the same time V is switched on. Therefore, we expect that

$$S_1(t) \sim t^{-(1-\delta/\pi)^2} \quad (15)$$

or, using (7),

$$W_{\text{abs}} \sim (\omega + E_0)^{2\delta/\pi - (\delta/\pi)^2}.$$

It is easy to extend the arguments to the emission case. If we start out with a quiescent Fermi sea and a screened hole, and by emitting an x-ray photon an electron drops into the core hole, a band hole spreads, and the band has also to take up with the δ/π electrons "freed" in this process. The number of particles appearing in the exponent of t is then $\delta/\pi - 1$, which implies, of course, the same asymptotic time behavior of $S_1(t)$ for emission and absorption.

The plausible derivation of (15) will be backed up by an exact calculation for the absorption case in Sec. III. For a generalization to include spin and higher-order phase shifts, we refer the reader to Sec. VI.

III. CALCULATION OF RESPONSE FUNCTION

A. General Formulation

We wish to give an exact derivation of the threshold behavior. Let us go back to the response function (7). It is convenient to replace $|i_0\rangle\langle i_0|$ by its finite-temperature expression

$$|i_0\rangle\langle i_0| \rightarrow \frac{e^{-\beta H i}}{\text{Tr}(e^{-\beta H i})}.$$

Then

$$S(t) = \frac{1}{N} \sum_{kk'} \frac{\text{Tr}(e^{-\beta H i} e^{+iH_i t} a_k e^{-iH_j t} a_{k'}^\dagger)}{\text{Tr}(e^{-\beta H i})}. \quad (16)$$

We introduce the notation

$$\frac{\text{Tr}(e^{-\beta H i} e^{+iH_i t} e^{-iH_j t} A)}{\text{Tr}(e^{-\beta H i} e^{+iH_i t} e^{-iH_j t})} = \langle A \rangle \quad (17)$$

and

$$a_k(\tau) = e^{+iH_j \tau} a_k e^{-iH_j \tau} = \sum_{k'} G_{kk'}(\tau) a_{k'}, \quad (18)$$

where $G_{kk'}(\tau)$ is a unitary transformation

$$G_{kk'}(-\tau) = G_{k'k}^*(\tau). \quad (19)$$

For mathematical reasons, which will soon be apparent, we make use of the quantities

$$C(t) = \ln \left(\frac{\text{Tr}(e^{-\beta H i} e^{+iH_i t} e^{-iH_j t})}{\text{Tr}(e^{-\beta H i})} \right) \quad (20)$$

and

$$\langle a_k(\tau) a_{k'}^\dagger + a_{k'}^\dagger a_k(\tau) \rangle = G_{kk'}(\tau). \quad (21)$$

This Green's function no longer depends upon β and t . Of course this is not true for the quantities of interest $\langle a_{k'}^\dagger a_k(\tau) \rangle$ or $\langle a_k(\tau) a_{k'}^\dagger \rangle$. To calculate them, we shift

⁸ K. D. Schotte and U. Schotte, Phys. Rev. **182**, 479 (1969).

operators under the trace, and, using (18), we have

$$\langle a_k(\tau)a_{k'}^\dagger \rangle = \sum_{k''} e^{-i\epsilon_{k''}(t+i\beta)} G_{k''k'}^*(t) \langle a_{k''}^\dagger a_k(\tau) \rangle, \quad (22)$$

$$\langle a_{k'}^\dagger a_k(\tau) \rangle = \sum_{k''} \langle a_k(\tau)a_{k''}^\dagger \rangle e^{+i\epsilon_{k''}(t+i\beta)} G_{k''k'}(t). \quad (23)$$

Combining this with the above Green's function, we finally get the following integral equations:

$$\langle a_{k'}^\dagger a_k(\tau) \rangle + \sum_{k''} e^{-i\epsilon_{k''}(t+i\beta)} \times G_{k''k'}^*(t) \langle a_{k''}^\dagger a_k(\tau) \rangle = G_{kk'}(\tau), \quad (24)$$

$$\langle a_k(\tau)a_{k'}^\dagger \rangle + \sum_{k''} \langle a_k(\tau)a_{k''}^\dagger \rangle e^{+i\epsilon_{k''}(t+i\beta)} \times G_{k''k'}(t) = G_{kk'}(\tau). \quad (25)$$

What we have given so far is an adaptation of Zubarev's method for temperature-dependent Green's functions applicable to the x-ray problem. Here t and β are the inverse "temperatures."

In principle, we can now calculate $S(t)$. To shorten the notation, we introduce

$$\frac{1}{N} \sum_{kk'} \langle a_k(\tau=t)a_{k'}^\dagger \rangle = L(t), \quad (26)$$

$$\frac{1}{N} \sum_{kk'} \langle a_k^\dagger a_{k'}(\tau=0) \rangle = N(t). \quad (27)$$

So we can write

$$S(t) = L(t)e^{C(t)}, \quad (28)$$

or, taking into account that

$$dC(t)/dt = -iVN(t), \quad C(0) = 0, \quad (29)$$

$$S(t) = L(t) \exp\left(-iV \int_0^t N(t) dt\right). \quad (30)$$

B. Derivation of Asymptotically Valid Integral Equations

In order to achieve an asymptotic expansion of $S(t)$, we have to study the integral equations (24) and (25). Introducing the auxiliary quantities

$$\sum_{k'} \langle a_k^\dagger a_{k'}(\tau=0) \rangle = n(k), \quad (31)$$

$$\sum_{k'} \langle a_{k'}(\tau=t)a_k^\dagger \rangle = l(k), \quad (32)$$

we find

$$n(k) + e^{-i\epsilon_k(t+i\beta)} \sum_{k'} G_{kk'}^*(t) n(k') = 1, \quad (33)$$

$$e^{-\beta\epsilon_k} e^{+i\epsilon_k t} l(k) + \sum_{k'} G_{kk'}^*(t) l(k') = 1. \quad (34)$$

The Laplace transform of the Green's function $G_{kk'}(t)$, namely,

$$G_{kk'}(\omega) = \int_0^\infty G_{kk'}(t) e^{i\omega t} dt, \quad (35)$$

is well known. It has the form

$$\frac{1}{i} G_{kk'}(\omega) = \frac{\delta_{kk'}}{\omega - \epsilon_k} + \frac{1}{\omega - \epsilon_k} \frac{1}{\omega - \epsilon_k - \epsilon_{k'}} t_{kk'}(\omega). \quad (36)$$

Inverting the transformation,

$$G_{kk'}(t) = \frac{1}{2\pi} \int_{-\infty}^\infty G_{kk'}(\omega + i\eta) e^{-i\omega t} d\omega, \quad (37)$$

where the $+i\eta$ indicates that we take that part of $G_{kk'}(\omega)$ which is analytic in the upper half-plane, we have for large t

$$\lim_{t \rightarrow \infty} G_{kk'}(t) = \delta_{kk'} e^{-i\epsilon_k t} + \frac{t_{kk'}(\epsilon_k + i\eta) e^{-i\epsilon_k t} - t_{kk'}(\epsilon_{k'} + i\eta) e^{-i\epsilon_{k'} t}}{\epsilon_k - \epsilon_{k'}}. \quad (38)$$

For $V = \text{const}$, $t_{kk'}$ is independent of k and k' . Extended throughout the complex plane, it is given by

$$t_{kk'}(z) \equiv t(z) = V/[1 - VF(z)], \quad (39)$$

where

$$F(z) = \int_{-\infty}^\infty \frac{\rho(x)}{x - z} dx \quad (40)$$

is the Hilbert transform of the density of states $\rho(x)$.

The asymptotic expression for $G_{kk'}(t)$ with (39) for $t(z)$ will be used as kernel of the integral equations (33) and (34). The terms neglected behave as e^{-Dt} for large times, where D is of the order of the conduction bandwidth. Going over from sums to integrals, the integral equations we have to deal with are

$$\rho(x)[1 - f(x)] e^{-ixt} = \rho(x)l(x) + \rho(x)[1 - f(x)] \times \int_{-\infty}^\infty \frac{t^-(x) - t^-(x') e^{-i(x-x')t}}{x - x'} \rho(x') l(x') dx', \quad (41)$$

$$\rho(x)f(x) = \rho(x)n(x) + \rho(x)[1 - f(x)] \times \int_{-\infty}^\infty \frac{t^-(x) - t^-(x') e^{-i(x-x')t}}{x - x'} \rho(x') n(x') dx', \quad (42)$$

where $f(x) = (1 + e^{\beta x})^{-1}$ and $t^-(x) \equiv t(x - i\eta)$.

C. Asymptotic Solutions for $L(t)$ and $N(t)$

The two integral equations just derived differ only by the inhomogeneous term; therefore, we shall demonstrate how to handle one of them (42) and give the result for the other (41).

Let us first sketch the procedure. We are only interested in

$$\int_{-\infty}^{\infty} \rho(x)n(x)dx' = N(t), \tag{43}$$

so what we do is transform (42) into an integral equation for $N(t)$, which for the asymptotic value of $N(t)$ turns out to be exactly soluble. Equation (42) has a nonsingular kernel, but we break up the kernel into two singular ones and start an iteration procedure with the following ansatz:

$$n(x) = n_0(x) + \tilde{n}_1(x)e^{-ixt} + n_1(x) + \tilde{n}_2(x)e^{-ixt} + n_2(x) + \dots \tag{44}$$

The idea is to separately collect oscillatory and non-oscillatory terms. In order to achieve this, infinitesimal quantities η have to be introduced in the denominator of the kernels. The contribution due to this change cancel out when everything is put together to obtain the original equation (42).

The iteration procedure starts with

$$f\rho = \rho n_0 + (1-f)\rho t^- \int_{-\infty}^{\infty} \frac{\rho n_0 dx'}{x-x'-i\eta} \tag{45}$$

For $\nu = 1, 2, \dots$, one has

$$e^{-ixt}(1-f)\rho \int_{-\infty}^{\infty} \frac{t^- \rho n_{\nu-1} e^{+ix't} dx'}{x-x'-i\eta} = e^{-ixt} \rho \tilde{n}_{\nu} - e^{-ixt}(1-f)\rho \int_{-\infty}^{\infty} \frac{\rho \tilde{n}_{\nu} t^- dx'}{x-x'+i\eta}, \tag{46}$$

$$-(1-f)\rho t^- \int_{-\infty}^{\infty} \frac{\rho \tilde{n}_{\nu} e^{-ix't} dx'}{x-x'+i\eta} = \rho n_{\nu} + (1-f)\rho t^- \int_{-\infty}^{\infty} \frac{\rho n_{\nu} dx'}{x-x'-i\eta} \tag{47}$$

It has been tacitly assumed that the argument of the functions appearing under the integral sign is x' . All the other functions depend on x .

Equation (45) is a special type of singular integral equation which can be solved by a standard procedure.⁹ One puts

$$\rho n_0 = \psi_0^+(x) - \psi_0^-(x), \tag{48}$$

where $\psi_0^+(z)$ and $\psi_0^-(z)$ are analytic, in the upper and lower complex plane, respectively.

Then (45) goes over into

$$f\rho = \psi_0^+ - \psi_0^- [1 + 2\pi i \rho (1-f)t^-]. \tag{49}$$

With

$$X^+/X^- = 1 + 2\pi i \rho (1-f)t^- \tag{50}$$

⁹ N. T. Muskhelishvili, *Singular Integral Equations* (P. Noordhoff Ltd., Groningen, The Netherlands, 1953).

or

$$t^+ X^+ / t^- X^- = 1 - 2\pi i \rho f t^+, \tag{51}$$

where use has been made of $1 + 2\pi i \rho t^- = t^- / t^+$ [see (39)], we have

$$X(z) = \exp\left(\frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\ln[1 + 2\pi i \rho (1-f)t^-]}{x-z} dx\right) \tag{52}$$

or

$$X(z) = \frac{V}{t(z)} \exp\left(\frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\ln(1 - 2\pi i \rho f t^+)}{x-z} dx\right). \tag{53}$$

From

$$\frac{1}{2\pi i} \left(\frac{1}{X^+ t^+} - \frac{1}{X^- t^-} \right) = \frac{\psi_0^+}{X^+} - \frac{\psi_0^-}{X^-}, \tag{49'}$$

we solve for

$$\psi_0(z) = [1 - t(z)X(z)/V] / 2\pi i t(z). \tag{54}$$

Corresponding to the ansatz (44), there will be a decomposition of

$$N(t) = N_0(t) + N_1(t) + N_2(t) + \dots, \tag{55}$$

the first term of which is to be calculated from (53) and (54):

$$N_0 = \int_{-\infty}^{\infty} [\psi_0^+(x) - \psi_0^-(x)] dx = -\frac{1}{V} \int_{-\infty}^0 \frac{\delta(x)}{\pi} dx \text{ for } T=0, \tag{56}$$

where $1 - 2\pi i \rho t^+ = e^{2i\delta}$ has been used. Clearly, N_0 is the only t -independent contribution in $N(t)$, so that N_0 gives rise to an energy shift of the deep hole state; that is, with (30), the threshold is shifted by

$$\Delta E = \int_{-\infty}^0 \frac{\delta(x)}{\pi} dx.$$

Equations (46) and (47) are solved in principle as (45). As before, we introduce sectional holomorphic functions

$$\rho \tilde{n}_{\nu} t^- = \varphi_{\nu}^+ - \varphi_{\nu}^-, \tag{57}$$

$$\rho n_{\nu} = \psi_{\nu}^+ - \psi_{\nu}^-. \tag{58}$$

To simplify the notation, we need, in addition, two other functions:

$$\chi_{\nu}(z) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\rho \tilde{n}_{\nu} e^{-ixt} dx}{x-z}, \tag{59}$$

$$\xi_{\nu}(z) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\rho n_{\nu} t^- e^{+ixt} dx}{x-z}. \tag{60}$$

We find that

$$\varphi_\nu(z) = -\frac{1}{2\pi i} \frac{1}{X(z)} \int_{-\infty}^{\infty} (X^+ - X^-) \frac{\xi_{\nu-1}^- dx}{x-z}, \quad (61)$$

$$\psi_\nu(z) = -\frac{X(z)}{2\pi i} \int_{-\infty}^{\infty} \left(\frac{1}{X^+} - \frac{1}{X^-} \right) \frac{\chi_\nu^+ dx}{x-z}. \quad (62)$$

We have to calculate

$$\begin{aligned} N_\nu(t) &= \int_{-\infty}^{\infty} (\rho \tilde{n}_\nu e^{-ixt} + \rho n_\nu) dx \\ &= \int_{-\infty}^{\infty} [(\chi_\nu^+ - \chi_\nu^-) + (\psi_\nu^+ - \psi_\nu^-)] dx. \end{aligned} \quad (63)$$

Inserting (62), one obtains, after some simple manipulations,

$$N_\nu(t) = \int_{-\infty}^{\infty} \frac{1}{X^-} (\chi_\nu^+ - \chi_\nu^-) dx. \quad (64)$$

In view of (59) and (57), this reads

$$N_\nu(t) = \int_{-\infty}^{\infty} \frac{e^{-ixt}}{t^- X^-} \varphi_\nu^+ dx. \quad (65)$$

To proceed further, we introduce the functionals

$$\mathfrak{F}(\tau; \varphi_\nu^+) = \int_{-\infty}^{\infty} \frac{e^{-ix\tau}}{t^- X^-} \varphi_\nu^+ dx, \quad (66)$$

$$\mathfrak{G}(\tau; \psi_\nu^-) = \int_{-\infty}^{\infty} X^+ t^- e^{+ix\tau} \psi_\nu^- dx, \quad (67)$$

and study how they are related. To this end we express φ_ν^+ , in terms of $\psi_{\nu-1}^-$, using Eqs. (58), (60), and (61), and ψ_ν^- , in terms of φ_ν^+ , using Eqs. (57), (59), and (62). Inserting these expressions in the right-hand sides of (66) and (67), we find

$$\begin{aligned} \mathfrak{F}(\tau; \varphi_\nu^+(\psi_{\nu-1}^-)) \\ = -i \int_t^\infty L_1(\tau + \tau_1 - t) \mathfrak{G}(\tau_1; \psi_{\nu-1}^-) d\tau_1, \end{aligned} \quad (68)$$

$$\mathfrak{G}(\tau; \psi_\nu^-(\varphi_\nu^+)) = i \int_t^\infty M_1(\tau + \tau_1 - t) \mathfrak{F}(\tau_1; \varphi_\nu^+) d\tau_1, \quad (69)$$

where

$$L_1(\tau) = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{e^{-ix\tau}}{t^- X^+ X^-} dx, \quad (70)$$

$$M_1(\tau) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} t^- X^+ X^- e^{+ix\tau} dx. \quad (71)$$

Defining

$$\mathfrak{N}(\tau) = \mathfrak{F}\left(\tau, \sum_{\nu=1}^{\infty} \varphi_\nu^+\right), \quad (72)$$

and using (55), we see that

$$N(t) = N_0 + \mathfrak{N}(\tau=t). \quad (73)$$

Thus, inserting (69) into (68) and summing over ν , one obtains an integral equation for $\mathfrak{N}(\tau)$, the solution of which we need at the point $\tau=t$:

$$\mathfrak{N}(\tau) = N_1(\tau) + \int_t^\infty K(\tau, \tau') \mathfrak{N}(\tau') d\tau', \quad (74)$$

where

$$K(\tau, \tau') = + \int_t^\infty L_1(\tau + \tau_1 - t) M_1(\tau_1 + \tau' - t) d\tau_1. \quad (75)$$

The inhomogeneous term on the right-hand side of (74) is equal to $\mathfrak{F}(\tau, \varphi_1^+)$, which can be calculated with the use of (68) and (54), and we find

$$N_1(\tau) = iK(\tau, t)/V. \quad (76)$$

Now without much additional work one can transform the integral equation (41) for $l(x)$ into a corresponding one for

$$\mathfrak{L}(\tau) = \mathfrak{F}\left(\tau, \sum_{\nu=1}^{\infty} \varphi_\nu^+\right), \quad (77)$$

where

$$\mathfrak{L}(\tau=t) = \int_{-\infty}^{\infty} \rho(x) \sum_{\nu=0}^{\infty} [\tilde{l}_\nu(x) e^{-ixt} + l_\nu(x)] dx \equiv L(t) \quad (78)$$

is needed to calculate the response function (28). The integral equations for $l(x)$ and $n(x)$ differ only by their inhomogeneous terms, which appear explicitly only in the first step of the iteration procedure. The solution of these first integral equations fixes $\mathfrak{F}(\tau; \varphi_1)$. In the case of

$$l(x) = \tilde{l}_1(x) e^{-ixt} + l_1(x) + \tilde{l}_2(x) e^{-ixt} + \dots, \quad (79)$$

one finds

$$\varphi_1(z) = 1/2\pi i [1 - 1/X(z)], \quad (80)$$

where

$$\varphi_1^+ - \varphi_1^- = \rho t^- \tilde{l}_1. \quad (81)$$

Inserting (80) into (66) and using (70), one finds

$$\mathfrak{F}(\tau, \varphi_1^+) = L_1(\tau) \quad (82)$$

for the inhomogeneous terms of the integral equation for $\mathfrak{L}(\tau)$, so that

$$\mathfrak{L}(\tau) = L_1(\tau) + \int_t^\infty K(\tau, \tau') \mathfrak{L}(\tau') d\tau. \quad (83)$$

To obtain the behavior of $L_1(t)$ and $M_1(t)$ for large t , one expands $X(z)$ defined by (51) for small arguments. For $T=0$, the asymptotic expressions for L_1 and M_1 become very simple:

$$L_1(t) \approx g/t^{1-2\delta/\pi}, \quad (84)$$

$$M_1(t) \approx h/t^{1+2\delta/\pi}, \quad (85)$$

where

$$g = -(A/\pi iV)e^{i\delta} \sin\delta \Gamma(1-2\delta/\pi), \quad (86)$$

$$h = -(V/\pi iA)e^{-i\delta} \sin\delta \Gamma(1+2\delta/\pi), \quad (87)$$

with

$$A = \exp\left(-\frac{1}{\pi} \int_{-\infty}^{\infty} \operatorname{sgn}(x) (\ln|x|) \frac{d\delta(x)}{dx} dx\right) \\ \equiv d^{-2\delta/\pi}, \quad (88)$$

where d is of the order of the bandwidth. $\delta = \delta(0)$ is the phase shift at the Fermi edge. In deducing these equations, it has been assumed that the density-of-states function is smooth and well behaved near the Fermi energy. With (84), (85), and (75), one calculates

$$K(\tau, \tau') = \frac{\pi g h}{2\delta} \frac{1}{\tau - \tau'} \left[\left(\frac{\tau}{\tau'}\right)^{2\delta/\pi} - 1 \right]. \quad (89)$$

With the substitutions

$$\tau = te^x \quad (90)$$

and

$$\nu(x) = +iV\mathfrak{N}(te^x)te^{(1/2-\delta/\pi)x}, \quad (91)$$

(74) goes over into

$$\nu(x) = \frac{\tan\delta \sinh(\delta/\pi)x}{2\pi \sinh\frac{1}{2}x} \\ - \frac{\tan\delta}{2\pi} \int_0^{\infty} \frac{\sinh(\delta/\pi)(x-x')}{\sinh\frac{1}{2}(x-x')} \nu(x') dx', \quad (92)$$

which is of the Wiener-Hopf type and can be solved exactly.¹⁰ One finds that

$$\nu(0) = (\delta/\pi)^2, \quad (93)$$

the demonstration of which will be given in the Appendix so that

$$N(t) = \mathfrak{N}(\tau=t) = -\frac{i\nu(0)}{Vt} = -\frac{i}{V} \left(\frac{\delta}{\pi}\right)^2 \frac{1}{t}. \quad (94)$$

In the same way, one transforms (83) into a Wiener-Hopf integral equation

$$\lambda(x) = ge^{-(1/2-\delta/\pi)x} \\ - \frac{\tan\delta}{2\pi} \int_0^{\infty} \frac{\sinh(\delta/\pi)(x-x')}{\sinh\frac{1}{2}(x-x')} \lambda(x') dx', \quad (95)$$

with

$$\lambda(x) = t^{1-2\delta/\pi} e^{(1/2-\delta/\pi)x} \mathfrak{L}(te^x). \quad (96)$$

We require that

$$\lambda(0) = g \frac{\Gamma^2(1-\delta/\pi)}{\Gamma(1-2\delta/\pi)}. \quad (97)$$

¹⁰ P. M. Morse, H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Co., New York, 1953).

Then, using (86) and (88), we finally have

$$L(t) = \mathfrak{L}(\tau=t) = \frac{\lambda(0)}{t^{1-2\delta/\pi}}. \quad (98)$$

We can now proceed to calculate the response function $S(t)$; making use of Eqs. (29), (56), (73), and (94), we have

$$\frac{i}{V} \frac{dC}{dt} = N(t) = -\frac{\Delta E}{V} - \frac{i}{V} \left(\frac{\delta}{\pi}\right)^2 \frac{1}{t}. \quad (99)$$

Since one knows $N(t)$ only asymptotically, $C(t)$ can be calculated up to an unknown real constant d' ,

$$C(t) = i\Delta Et - (\delta/\pi)^2 \ln(itd'). \quad (100)$$

The i in the argument of the logarithm has been introduced because $C(t) = C^*(-t)$ must hold.

IV. THRESHOLD BEHAVIOR OF TRANSITION RATE

The behavior of the response function for large times is finally given by

$$S(t) \sim e^{i\Delta Et} (it)^{-(1-\delta/\pi)^2}. \quad (101)$$

With (7) and

$$\operatorname{Im} \left[-\int_0^{\infty} e^{i(\omega+E_0+\Delta E)t} (it)^{-1+\alpha} dt \right] \\ = \Gamma(\alpha) \sin\pi\alpha (\omega+E_0+\Delta E)^{-\alpha} \\ \text{for } \omega+E_0+\Delta E > 0 \\ = 0 \quad \text{for } \omega+E_0+\Delta E < 0, \quad (102)$$

we find the important result

$$W_{\text{abs}} \sim \left(\frac{D}{\omega+E_0+\Delta E} \right)^{2\delta/\pi - (\delta/\pi)^2}, \quad (103)$$

where D is a "bandwidth energy."¹¹

We note that the mathematical procedure might seem too technical and heavy, as, in view of the possibility of the "plausible" explanation in Sec. II, it seems unnatural to break up the response function into two parts calculated separately:

$$S(t) = L(t) \cdot e^{C(t)}$$

OR

$$t^{-(1-\delta/\pi)^2} = t^{-1+2\delta/\pi} \cdot t^{-(\delta/\pi)^2}$$

¹¹ The proportionality factor as we found it (up to the dipole matrix element) is $d^{2\delta/\pi} d'^{-(\delta/\pi)^2} \Gamma^2(1-\delta/\pi) \Gamma[2\delta/\pi - (\delta/\pi)^2] \times \sin\pi[2\delta/\pi - (\delta/\pi)^2] (\sin\delta/\pi V)$ is of no great use for a quantitative calculation, as d' is unknown. It makes sense insofar as the first two terms provide the correct dimensionality for W_{abs} , and the others make sure that $W_{\text{abs}} > 0$, and that the whole expression tends toward the density of states ρ as $\delta \rightarrow 0$ (and $\delta \rightarrow -\pi V\rho$).

as we have done. This procedure also has the disagreeable consequence that our method works only for $0 \leq |\delta| < \frac{1}{2}\pi$ and has to be modified to include $\frac{1}{2}\pi \leq |\delta| < \pi$. While this is feasible and also desirable from a mathematical point of view, fortunately it is not necessary for physical reasons. As one can see easily from Friedel's sum rule, which for our problem reads

$$1 = \sum_l 2(2l+1) \frac{\delta_l}{\pi}, \quad (104)$$

δ can never be larger than $\frac{1}{2}\pi$. However, this breaking up of the response function and the separate treatment of the "hole propagator" $e^{C(t)}$ might be of advantage if lifetime effects for the hole have to be taken into account.

Without further calculations, we can complete the result to include spin and higher-order phase shifts by going back to the arguments of Sec. II. It was explained there that the general proportionality

$$S_n(t) \sim t^{-n^2}$$

should hold, where n is the amount of particles (not necessarily an integer number) shifted within the band. Now the real process is not only s wave scattering, but the other partial waves also take part in shielding the hole potential according to Friedel's sum rule. Let us assume that an electron of angular momentum l , m , and spin s has been created in the absorption process. As there is no interference between different channels, but only within the $\{lms\}$ channel, where the effects of shielding and electron injection interfere, the exponent n^2 has to be substituted by the sum over all channels ν :

$$n^2 \rightarrow \sum_{\nu} n_{\nu}^2, \quad (105)$$

which for an electron characterized by $\{l, m, s\}$ is given by

$$\begin{aligned} \sum_{\nu} n_{\nu}^2 &= \left(1 - \frac{\delta_l}{\pi}\right)^2 + \sum_{\{l'm's'\} \neq \{lms\}} \left(\frac{\delta_{l'}}{\pi}\right)^2 \\ &= 1 - 2\frac{\delta_l}{\pi} + \sum_{\text{all } l'} 2(2l'+1) \left(\frac{\delta_{l'}}{\pi}\right)^2. \end{aligned} \quad (106)$$

This has the important consequence that the exponent in the transition rate can either be positive or negative even if all δ_l are positive. This could explain that, for example, the K spectrum of Li goes smoothly to zero while there is a spike in the $L_{2,3}$ spectrum of Na, probably due to the divergence.^{4,5}

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APPENDIX: SOLUTION OF WIENER-HOPF EQUATIONS (92) AND (95)

To solve (92) we make the ansatz¹⁰

$$\begin{aligned} \nu(x) &= \nu_1(x) \quad x > 0 \\ &= \nu_2(x) \quad x < 0, \end{aligned} \quad (A1)$$

and introduce the Fourier transforms

$$\begin{aligned} \nu^+(y) &= \int_0^{\infty} e^{ixy} \nu_1(x) dx, \\ \nu^-(y) &= \int_{-\infty}^0 e^{ixy} \nu_2(x) dx, \end{aligned} \quad (A2)$$

which are analytic functions in the upper or lower half-plane of the complex variable y . Then Eq. (92) reads

$$\begin{aligned} \nu_1(x) + \nu_2(x) &= \frac{\tan \delta \sinh(\delta/\pi)x}{2\pi \sinh \frac{1}{2}x} \\ &- \frac{\tan \delta}{2\pi} \int_{-\infty}^{\infty} \frac{\sinh(\delta/\pi)(x-x')}{\sinh \frac{1}{2}(x-x')} \nu_1(x') dx'. \end{aligned} \quad (A3)$$

Using

$$\int_{-\infty}^{\infty} \frac{e^{ixy} \sinh(\delta/\pi)x}{\sinh \frac{1}{2}x} dx = 2\pi \frac{\sin 2\delta}{\cosh 2\pi y + \cos 2\delta}, \quad (A4)$$

Eq. (A3) can be written in the Fourier transformed form as an inhomogeneous Hilbert problem

$$\nu^+(y)Y^+(y)/Y^-(y) + \nu^-(y) = Y^+(y)/Y^-(y) - 1, \quad (A5)$$

with the auxiliary functions

$$\begin{aligned} Y(y) &= \Gamma\left(\frac{1}{2} + \frac{\delta}{\pi} - iy\right) \Gamma\left(\frac{1}{2} - \frac{\delta}{\pi} - iy\right) \Gamma^{-2}\left(\frac{1}{2} - iy\right), \\ & \hspace{15em} \text{Im } y > 0 \\ &= \Gamma^{-1}\left(\frac{1}{2} + \frac{\delta}{\pi} + iy\right) \Gamma^{-1}\left(\frac{1}{2} - \frac{\delta}{\pi} + iy\right) \Gamma^2\left(\frac{1}{2} + iy\right), \\ & \hspace{15em} \text{Im } y < 0 \end{aligned} \quad (A6)$$

which solve the homogeneous Hilbert problem

$$\frac{Y^+(y)}{Y^-(y)} = 1 + \frac{\tan \delta \sin 2\delta}{\cos 2\pi y + \cos 2\delta}. \quad (A7)$$

We solve for $\nu^{\pm}(y)$ taking into account the asymptotic behavior of $Y(y)$:

$$\lim_{y \rightarrow \infty} Y^+(y) = 1 + i(\delta/\pi)^2 1/y, \quad (A8)$$

and get

$$\begin{aligned} \nu^+(y) &= 1 - 1/Y^+(y), \\ \nu^-(y) &= -1 + 1/Y^-(y). \end{aligned} \quad (A9)$$

Inverting the Fourier transform, we have finally

$$\nu(x=0^+) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \nu^+(y) dy = (\delta/\pi)^2. \quad (\text{A10})$$

Integral equation (95) can be solved in exactly the same way, by introducing λ_1 and λ_2 for $x > 0$ or $x < 0$, as before. We have then, instead of (94),

$$\lambda_1(x) + \lambda_2(x) = g e^{-(1/2 - \delta/\omega)x} \theta(x)$$

$$-\int_{-\infty}^{\infty} \frac{\tan \delta \sinh(\delta/\pi)(x-x')}{2\pi \sinh \frac{1}{2}(x-x')} \lambda_1(x') dx', \quad (\text{A11})$$

where θ is the step function. Its Fourier-transformed version is

$$\lambda^+(y) Y^+(y) + \lambda^-(y) Y^-(y) = \frac{g Y^-(y)}{\frac{1}{2} - \delta/\pi - iy}, \quad (\text{A12})$$

giving for $\lambda^+(y)$,

$$\lambda^+(y) = \frac{\eta Y^-(-i(\frac{1}{2} - \delta/\pi))}{(\frac{1}{2} - \delta/\pi - iy) Y^+(y)}. \quad (\text{A13})$$

For $\lambda(0^+)$ one finds

$$\lambda(0^+) = \frac{1}{\pi} \int_{-\infty}^{\infty} \lambda^+(y) dy = g Y^- \left(-i \left(\frac{1}{2} - \frac{\delta}{\pi} \right) \right). \quad (\text{A14})$$

Propagation of Light Pulses in a Laser Amplifier*

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The problem of a light pulse propagating in a nonlinear laser medium is investigated. The electromagnetic field is treated classically and the active medium consists of thermally moving atoms which have two electronic states with independent decay constants γ_a and γ_b in addition to the decay constant γ_{ab} describing the phase memory. The self-consistency requirement that the field sustained by the polarized medium be equal to the field inducing the polarization leads to coupled equations of motion for the density matrix, and equations of propagation for the electromagnetic field. Although the theory is developed for a Doppler-broadened gaseous medium, it may also be applied to a solid medium with inhomogeneous broadening. A unified treatment is given encompassing a wide range of pulse durations from cw signals to psec pulses. Continuous pumping is allowed, as well as any amount of detuning of the carrier frequency of the pulse from the atomic resonance frequency. The three independent decay constants γ_a , γ_b , and γ_{ab} provide greater flexibility than that obtained by using $1/T_1$ and $1/T_2$. The equations are solved analytically in a few specialized cases and numerically in the general case. Flow charts for accomplishing the numerical integration are given. Among the special problems considered is the apparent paradox of pulses propagating faster than the velocity of light under circumstances described by Basov *et al.* It is shown that this contradiction with relativity arises from the use of an unphysical initial condition.

I. INTRODUCTION

WE present a theoretical investigation of the behavior of light pulses traveling in an amplifying laser medium. A semiclassical description of the interaction between matter and radiation will be used, treating the medium quantum mechanically and the radiation field according to Maxwell's theory. The basic ideas are derived from Lamb's theory of optical masers.¹ However, some of his original assumptions and restrictions are relaxed in order to properly apply the theory to the problem at hand. Since there are differences between the problems of a self-sustained oscillator and of

an amplifier, it is desirable to develop the theory from first principles.

The medium shall be considered to be a collection of two-level "atoms" (Fig. 1) coupled only through their interaction with the over-all radiation field. If a population inversion between the levels a and b is established, such a medium is capable of amplifying light in a frequency band around the separation of the levels.

In order to carry out necessary statistical summations, it is convenient to represent the state of a two-level atom by means of a 2×2 density matrix ρ . This is related to the wave function description in the follow-

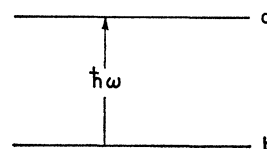


FIG. 1. Energy diagram of the two-level atom. The levels have a resonance transition frequency $\omega > 0$.

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