Singularities in the X-Ray Absorption and Emission of Metals. III. One-Body Theory Exact Solution

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The singularities of x-ray absorption or emission in metals are studied by a new "one-body" method, which describes the scattering of conduction electrons by the *transient* potential due to the deep hole. Using the linked-cluster theorem, the net transition rate in the time representation is expressed as the product of two factors: a one-electron transient Green's function L, and the deep-level Green's function G. These factors obey simple Dyson equations, which can be solved asymptotically by using Muskhelishvili's method. The x-ray transition rate is found to behave as $1/\epsilon^{\alpha}$, where ϵ is the frequency measured from the threshold, and α an exponent involving the various phase shifts δ_l which describe scattering by the deep hole. α may be >0 (infinite threshold) or <0 (zero threshold). The experimental implications of these results and their relation to the Friedel sum rule are briefly discussed.

I. INTRODUCTION

IN the first two papers of this series,[1,2] x-ray absorption and emission in metals was studied by the methods of perturbation theory. Special attention was paid to final-state interaction of the conduction electrons with the localized disturbance created by the x ray. To the extent that *lifetime* and *recoil* of the deep localized hole may be neglected,[3] we showed that the x-ray spectrum should display a characteristic singularity near the Fermi level threshold. The theory was carried out on a simplified model, which we briefly recall:

(i) We consider *free* conduction electrons, with energy ϵ_k and creation operator $a_k^\dagger$. In order to simplify notation, their spin is not explicitly mentioned—it will be restored at the end by inserting the appropriate factors of 2. There is no periodic lattice potential, and hence the Fermi surface is spherical. (Such an approximation is known to be quite good in view of the small pseudopotentials involved in band theory.) Coulomb interaction between conduction electrons is ignored: It would simply act to renormalize quasiparticles near the Fermi surface. We assume that such a renormalization has been carried out.

(ii) The process is supposed to involve a *single* x-ray deep state, with creation operator $b^\dagger$ and unrenormalized energy E_0. If the deep state is degenerate, a single component is involved.

(iii) We only retain *intraband* scattering processes, in which the deep level is unchanged, while the conduction electron remains in the same band. Internal Auger effect, which could lead to nonradiative decay of the deep hole, is neglected. Scattering between two different components of a degenerate deep level is ignored.

The above assumptions are summarized in the following model Hamiltonian:

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

(Note that the scattering term exists only when the deep level is empty.) The coupling to the x-ray field is described by a perturbation.

$$H_X=\sum_k W_k a_k^\dagger b e^{-i\omega t} + \text{c.c.}, \quad (2)$$

when ω is the x-ray frequency. In order to calculate the transition rate, it is convenient to introduce the response function

$$S(t-t')=\langle 0|\, T\{H_X(t)H_X(t')\}\,|0\rangle , \quad (3)$$

where T is the time-ordering operator, and $|0\rangle$ the *initial* "ground state" (with the deep level filled or empty, respectively, for absorption or emission). The transition rate is proportional to the imaginary part of the Fourier transform $S(\omega)$.

In I and II, the last term of (1) was treated as a *many-body* interaction. Formally, the problem is similar to the Kondo effect, in that conduction electrons scatter on a *two-state* system (the deep level being either empty or full). It may be attacked along the same lines, for instance, using Abrikosov's[4] perturbation approach. A direct transposition of Abrikososov's theory to the x-ray problem was carried out in I: by summing the so-called "parquet" graphs, we obtained an explicit expression for the response function $S(\omega)$. II was devoted to a highly self-consistent formulation, which is valid arbi-

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[1] B. Roulet, J. Gavoret, and P. Nozières, second preceding paper, Phys. Rev. **178**, 1072 (1969), hereafter referred to as I. The equations in this paper will be cited with a prefix I.

[2] P. Nozières, J. Gavoret, and B. Roulet, preceding paper, Phys. Rev. **178**, 1084 (1969), hereafter referred to as II.

[3] For a detailed discussion of the various broadening effects associated with lifetime of the hole, bandwidth of the deep level, etc., see I.

[4] A. A. Abrikosov, Physics **2**, 5 (1965).

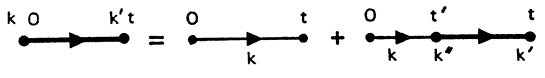

FIG. 1. The Dyson equation for the conduction-electron Green's function $G_{\mathbf{k}\mathbf{k}'}$ in the emission case. The thin line denotes the zeroth-order term $G_{\mathbf{k}0}$, the heavy line corresponds to the renormalized $G_{\mathbf{k}\mathbf{k}'}$. The cross denotes the interaction vertex, which carries a factor $-iV_{\mathbf{k}\mathbf{k}''}$.

trarily close to the singular transition threshold. In order to complete such a perturbation calculation, we had to make simplifying assumptions on the matrix elements $V_{\mathbf{k}\mathbf{k}'}$ and $W_{\mathbf{k}}$, namely,

$$\begin{aligned} V_{\mathbf{k}\mathbf{k}'} &= -Vu_{\mathbf{k}}u_{\mathbf{k}'}, \\ W_{\mathbf{k}} &= Wu_{\mathbf{k}}, \\ u_{\mathbf{k}} &= 1 \quad \text{if} \quad |\epsilon_{\mathbf{k}}-\mu| < \xi_0, \ =0 \text{ otherwise} \end{aligned} \tag{4}$$

(μ is the chemical potential, ξ_0 a cutoff $\sim\mu$). Physically, the choice (4) eliminates any selection rule associated with rotational symmetry, and retains only S-wave scattering by the localized hole. The problem can then be solved in the weak coupling limit:

$$g=\nu_0 V \ll 1$$

(where ν_0 is the one spin density of states at the Fermi surface). In the vicinity of the threshold frequency ω_0, the absorption rate is found to behave as

$$\mathrm{Im}S(\omega) \sim \left(\frac{\xi_0}{\omega-\omega_0}\right)^{2\vartheta}. \tag{5}$$

According to (5), we expect the transition rate to be *infinite* at threshold (for both emission and absorption), in agreement with the prediction of Mahan.[5]

Actually, such a many-body approach is not necessary in the present problem. Instead of treating the last term of (1) as a many-body interaction, we may consider it as a one-body scattering potential which is established *suddenly* at the time of the x-ray transition. In an absorption experiment, the scattering potential

$$\sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}'} \tag{6}$$

is applied suddenly when the x ray is absorbed; in an emission process, the potential (6) is suddenly cancelled. We are then interested in the *transient* response of conduction electrons to that abrupt change of potential —in contrast to the ordinary impurity problem, in which one studies the equilibrium configuration of conduction electrons in a potential which is established *adiabatically*. Viewed from that vantage point, we face a *one-body scattering problem*, although an unusual one since the scattering potential is time-dependent.

Physically, the simplification stems from the fact that the deep hole is structureless.[6] It may exist or not exist. But once it is created (or destroyed) by the x ray, it just remains there, and the potential felt by conduction electrons is constant. There is no dynamical degree of freedom of the hole, except to appear or disappear *once*. In contrast, a magnetic impurity keeps flipping its spin all the time; it is essential to keep track of its spin history, which correlates successive collisions of conduction electrons. For that reason, it is impossible to reduce the Kondo effect to a time-dependent one-body problem.[7] The major interest of the many-body approach developed in I and II is that it is not specific to the x-ray problem; the formalism is geared to describe dynamics of the scatterer, and may thus be transposed to a wide variety of problems. For instance, the self-consistent formulation of II should prove very useful in the more complicated case of the Kondo effect—yet, it is not required in the x-ray problem.

The present paper is devoted to the "one-body approach" to x-ray emission and absorption. As might be expected, the algebra is much simpler than in I and II—so simple, indeed, that the singularity near threshold may be calculated exactly, for *arbitrary coupling strength*. For simplicity, the method is exposed, using the model interaction,[4] which retains only s-wave scattering on the deep hole. The general equations are established in Sec. II; their asymptotic solution close to the threshold is obtained in Sec. III. We find that the exponent in (5) involves the phase shift at the Fermi surface, δ, rather than the coupling strength $g\sim\tan\delta$. The extension to a more general interaction $V_{\mathbf{k}\mathbf{k}'}$, involving all phase shifts δ_l, is carried out is Sec. IV. We show that such a generalization is not trivial, since it may replace the divergence near threshold by a *zero* discontinuity [the exponent in (5) becoming negative]. The physical implications of these results, as well as their relation to the Friedel sum rule, are briefly discussed in the conclusion.

II. "ONE-BODY" FORMULATION

We wish to calculate the quantity

$$F_{\mathbf{k}\mathbf{k}'}(t-t') = \langle 0 | T\{a_{\mathbf{k}}^{\dagger}(t) b(t) b^{\dagger}(t') a_{\mathbf{k}'}(t')\} | 0 \rangle \tag{7}$$

from which the x-ray response function is easily obtained. Another quantity of physical interest is the deep-electron Green's function[8]

$$\mathcal{G}(t-t') = \langle 0 | T\{b(t) b^{\dagger}(t')\} | 0 \rangle. \tag{8}$$

Since only one deep level is involved, $F_{\mathbf{k}\mathbf{k}'}$ and $\mathcal{G}$ always propagate in the same time direction; both vanish for $t>t'$ (absorption) or $t<t'$ (emission). For instance, the zeroth-order term of $\mathcal{G}$ is given by

$$\begin{aligned} \mathcal{G}_0(t) &= e^{-iE_0 t}\theta(t) \qquad \text{(emission)} \\ &= -e^{-iE_0 t}\theta(-t), \quad \text{(absorption)} \end{aligned} \tag{9}$$

[5] G. D. Mahan, Phys. Rev. **163**, 612 (1967).

[6] We explicitly eliminated internal transitions between different components of a degenerate deep state.

[7] The nearly systematic cancellation of singularities noticed in I and II was indeed an indication that the x-ray problem was basically simpler than the Kondo effect.

[8] Note that for convenience $\mathcal{G}$ is here defined without a fracto i, in contrast to I and II.

where θ is the usual step function.

The conduction-electron Green's function is defined as[8]

$$G_{\mathbf{k}\mathbf{k}'}(t-t')=\langle 0|T\{a_{\mathbf{k}}(t)a_{\mathbf{k}'}^{\dagger}(t')\}|0\rangle. \quad (10)$$

In the absorption case, it describes propagation in the absence of a deep hole, and thus reduces to its zeroth-order term

$$G_{\mathbf{k}\mathbf{k}'}(t)=G_{\mathbf{k}0}\delta_{\mathbf{k}\mathbf{k}'}=\delta_{\mathbf{k}\mathbf{k}'}e^{-i\epsilon_{\mathbf{k}}t}\theta(t) \quad \text{if } \epsilon_{\mathbf{k}}>\mu$$
$$=-\delta_{\mathbf{k}\mathbf{k}'}e^{-i\epsilon_{\mathbf{k}}t}\theta(-t) \quad \text{if } \epsilon_{\mathbf{k}}<\mu. \quad (11)$$

In the emission case, the initial state involves the *static* potential of the deep hole. $G_{\mathbf{k}\mathbf{k}'}$ then obeys the Dyson equation pictured on Fig. 1, which may be written as

$$G_{\mathbf{k}\mathbf{k}'}(t)=G_{\mathbf{k}0}(t)\delta_{\mathbf{k}\mathbf{k}'}$$
$$-i\sum_{\mathbf{k}''}\int_{-\infty}^{+\infty}dt'G_{\mathbf{k}0}(t')V_{\mathbf{k}\mathbf{k}''}G_{\mathbf{k}''\mathbf{k}'}(t-t'). \quad (12)$$

The Fourier transform $G_{kk'}(\epsilon)$ is easily expressed in terms of the scattering matrix $t_{\mathbf{k}\mathbf{k}'}(\epsilon)$ [see (I.10)]. To the extent that we use the full propagator $G_{\mathbf{k}\mathbf{k}'}$, the remaining interaction in (1) may be written as

$$H_1=\sum_{\mathbf{k}\mathbf{k}'}V_{\mathbf{k}\mathbf{k}'}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}'}b b^{\dagger} \quad \text{(absorption)}$$
$$=-\sum_{\mathbf{k}\mathbf{k}'}V_{\mathbf{k}\mathbf{k}'}a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}'}b^{\dagger}b \quad \text{(emission)}. \quad (13)$$

In both cases, H_1 is a *final-state* interaction, which acts only when the x-ray transition has taken place.

In the approach of I and II, propagation of the deep electron was described *explicitly*. If we represent $\mathcal{G}_0$ and $G_{\mathbf{k}\mathbf{k}'}$, respectively, by dashed and full lines, the functions $F_{\mathbf{k}\mathbf{k}'}$ and $\mathcal{G}$ are given by all graphs of Figs. 2(a) and 2(b). We note that the dashed line runs monotonically from t' to t; moreover, according to (13), all the interaction vertices H_1 must lie in the time interval (t',t), when the perturbation brought about by the x ray is present. In a conventional calculation based on the Fourier transforms $\mathcal{G}(\epsilon)$, these features are hidden.

As was pointed out in the Introduction, the only real time dependence of the scattering potential is its limitation to the interval (t,t'). Within that interval, "propagation" of the deep hole should have no physical significance. Such a conclusion is indeed immediate if one looks at (9). In the emission case, the over-all contribution of the dashed propagators is a mere phase

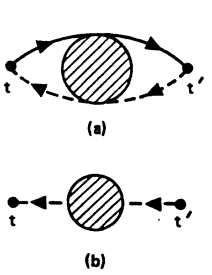

FIG. 2. The general graphs contributing to $F_{\mathbf{k}\mathbf{k}'}$ [Fig. 2(a)] or $\mathcal{G}$ [Fig. 2(b)] in the many body approach of I and II.

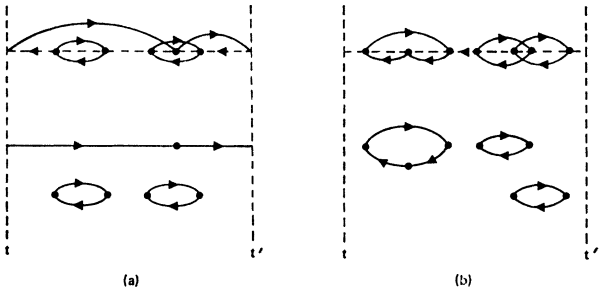

FIG. 3. The passage from many-body graphs (where conduction electrons interact with the deep-level, dotted line) to one-body graphs (where they interact with a transient scattering potential). Closed one-body loops may arise from both self-energy and vertex renormalization in the many-body approach. Fig. 3(a) corresponds to $\bar{F}_{\mathbf{k}\mathbf{k}'}$, Fig. 3(b) to $\bar{\mathcal{G}}$.

factor

$$e^{-iE_0(t-t')},$$

which is completely independent of the intermediate history of the deep hole. In the absorption case, the minus sign in (9) may be absorbed by changing the sign of the matrix element $V_{\mathbf{k}\mathbf{k}'}$ [cf. (13)]: Again, propagation of the deep hole is irrelevant. We may then simplify the calculation along the following lines:

(i) Introduce "reduced" quantities

$$\bar{F}_{\mathbf{k}\mathbf{k}'}(t)=\pm e^{iE_0t}F_{\mathbf{k}\mathbf{k}'}(t),$$
$$\bar{\mathcal{G}}(t)=\pm e^{iE_0t}\mathcal{G}(t), \quad (14)$$

$\pm$ correspond, respectively, to emission and absorption, so as to get rid of the minus sign in (9).

(ii) In order to calculate $\bar{F}$ and $\bar{\mathcal{G}}$, erase the deep-hole lines in the diagrams of Fig. 2, and replace the interaction vertices by static potential vertices, as shown on Fig. 3. Propagation of the deep hole is forgotten; the only requirement is that all vertices must be in the range (t,t'), when the interaction H_1 is effective.

(iii) To each vertex associate a scattering matrix element $V_{\mathbf{k}\mathbf{k}'}$ in the absorption case, $-V_{\mathbf{k}\mathbf{k}'}$ in the emission case [the difference reflecting the change of sign in (13)]. Every conduction-electron line corresponds to a renormalized propagator $G_{\mathbf{k}\mathbf{k}'}$.

The physical meaning of such a formulation is quite clear: We start from an initial "equilibrium state" characterized by the propagator $G_{\mathbf{k}\mathbf{k}'}$. The hole is created (or destroyed) for a *finite* interval of time, and we calculate the *transient* response of *each* conduction electron to that perturbation. We really have a time-dependent *one-body* problem, in which the hole history enters only through the boundaries (t,t').

We see on Fig. 3(a) that a one-body graph for $\bar{F}_{\mathbf{k}\mathbf{k}'}$ involves one open line running from t to t', plus any number of closed loops.[9] The open line corresponds to

[9] The closed loops arise from both self-energy and vertex corrections in the old many-body approach [the only difference being in the time ordering of vertices—see Fig. 3(a)]. The large cancellation between self-energy and vertex renormalization noticed in II is thus hardly surprising.

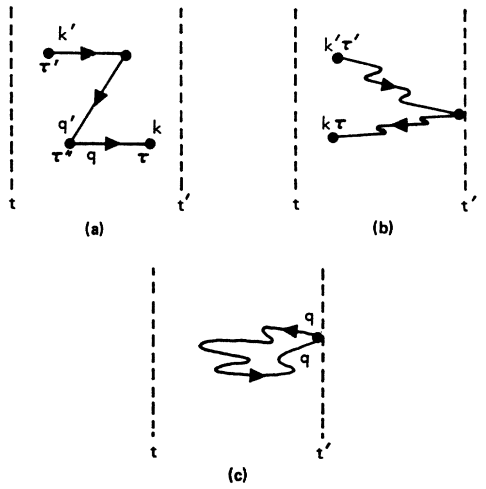

FIG. 4. (a) A graph contributing to the transient conduction-electron Green's function $\varphi_{kk'}(\tau,\tau';t,t')$. All vertices lie in the finite range (t,t'). The last branch is singled out to give Eq. (17). (b) Derivation with respect to t amounts to fixing *any* intermediate vertex at time t; on either side of that vertex, there is a complete propagator φ, denoted by a wavy line. (c) Similar analysis for the time derivative of the closed loop contribution $C(t)$.

the electron effectively created (or destroyed) by the x ray, while the closed loops describe the readjustment of the Fermi sea to a new transient situation. The Green's function $\mathcal{G}$ involves only closed loops, as shown on Fig. 3(b). We note that closed loops play the same role as vacuum fluctuations in ordinary perturbation theory: They can be summed by using the same linked cluster theorem, which remains valid even if the scattering potential is explicitly time-dependent. Let $C(t-t')$ be the contribution of all single closed loops, $L_{kk'}(t-t')$ being that of the open line in Fig. 3(a). The linked cluster theorem tells us that

$$\tilde{\mathcal{G}}(t)=e^{C(t)},$$
$$\bar{F}_{kk'}(t)=L_{kk'}(t)e^{C(t)}. \tag{15}$$

The net transition amplitude $\bar{F}_{kk'}$ appears as the product of a one-body factor $L_{kk'}$ multiplied by the deep-hole propagator $\tilde{\mathcal{G}}$.[10]

At this stage, it is convenient to introduce the one (conduction) electron Green's function

$$\varphi_{kk'}(\tau,\tau';t,t')=\langle T\{a_k(t)a_{k'}^{\dagger}(t')\}\rangle \tag{16}$$

calculated in the presence of the transient potential H_1 (in contrast to $G_{kk'}$ which is calculated in the *initial* state). $\varphi_{kk'}$ is given by all *open line* graphs of Fig. 4(a), with all vertices restrained to the interval (t,t'). By isolating the last branch of each diagram [Fig. 4(a)], we obtain a Dyson equation for φ. In the absorption case $(t<t')$, we find[11]

$$\varphi_{kk'}{}^{a}(\tau,\tau';t,t')=G_{kk'}{}^{a}(\tau-\tau')$$
$$-i\int_{t}^{t'}d\tau''\sum_{qq'}G_{kq}{}^{a}(\tau-\tau'')V_{qq'}\varphi_{q'k'}{}^{a}(\tau'',\tau';t,t') \tag{17a}$$

(t and t' enter only as the boundaries of the integration over τ''). In the emission case $(t'<t)$ we must replace G^a by G^e, $V_{qq'}$ by $-V_{qq'}$, and permute the boundaries t and t': We obtain

$$\varphi_{kk'}{}^{e}(\tau,\tau';t,t')=G_{kk'}{}^{e}(\tau-\tau')$$
$$+i\int_{t'}^{t}d\tau''\sum_{qq'}G_{kq}{}^{e}(\tau-\tau'')V_{qq'}\varphi_{q'k'}{}^{e}(\tau'',\tau';t,t'). \tag{17b}$$

Once φ is known, the function $L_{kk'}$ is obtained by letting $\tau\to t'$, $\tau'\to t$:

$$L_{kk'}(t-t')=-\varphi_{k'k}(t',t;t,t'). \tag{18}$$

When t and t' go to infinity, the restrictions on vertices are lifted: $\varphi_{kk'}$ reduces to the *equilibrium* propagator in the *final* state—which is of course the same as the initial-state propagator for the reverse case[11]:

$$t\to-\infty,\ t'\to+\infty:\quad \varphi_{kk'}{}^{a}(\tau,\tau')\to G_{kk'}{}^{e}(\tau-\tau'),$$
$$t\to+\infty,\ t'\to-\infty:\quad \varphi_{kk'}{}^{e}(\tau,\tau')\to G_{kk'}{}^{a}(\tau-\tau'). \tag{19}$$

The results (17) and (19), are clearly in agreement with our earlier definition (12). We note that t and t' enter only as integration boundaries: Hence, the derivative $\partial\varphi/\partial t$ is obtained by setting *any* vertex in the graph at the edge of the integration range. As shown in Fig. 4(b), we have

$$\frac{\partial\varphi_{kk'}(\tau,\tau')}{\partial t}=i\sum_{qq'}\varphi_{kq}(\tau,t)V_{qq'}\varphi_{q'k'}(t,\tau'). \tag{20}$$

The differential equation (20) is valid in both cases, and is completely equivalent to the integral equation (17).

The closed loop contribution $C(t)$ may be inferred from $\varphi_{kk'}$ in a similar way. Derivation with respect to t amounts to fixing *any* vertex of the loop at the boundary t [Fig. 4(c)], so that

$$\frac{\partial C(t-t')}{\partial t}=-i\sum_{qq'}V_{qq'}\varphi_{q'q}(t,t). \tag{21}$$

(Note the minus sign arising from the closed loop.) Equation (21), although exact, leads to somewhat ambiguous calculations. In what follows, we shall use an alternative approach to calculate C. Let us multiply every vertex by a constant factor λ, keeping the propagator $G_{kk'}$ constant; applying the operator $\lambda\partial/\partial\lambda$ to C, and letting λ go to 1, amounts to multiplying every graph by its number of vertices n. Such an n-fold

[10] The physical meaning of such a relation is best understood by returning to energy space: Then the product $L_{kk'}\tilde{\mathcal{G}}$ becomes a convolution of $L_{kk'}(\epsilon)$ and $\tilde{\mathcal{G}}(\epsilon)$. But the spectral density $\mathrm{Im}\mathcal{G}$ is known to characterize the broadening of the deep level. The above convolution may then be viewed as the blurring of a "bare" one-electron spectrum characterized by $L_{kk'}(\epsilon)$, due to the finite width of the deep level.

[11] The indices a and e refer, respectively, to absorption and emission; in what follows, we shall often shorten the notation by omitting the variables t and t' in φ.

repetition would also be achieved by "marking" successively each vertex of the graph (whose time τ varies from t' to t). Hence, C obeys the equation

$$\left(\frac{\lambda\partial C(t-t')}{\partial\lambda}\right)_{\lambda=1}=-i\sum_{qq'}\int_{t'}^{t}V_{qq'}\varphi_{q'q}(\tau,\tau)d\tau. \quad (22)$$

Equation (22) will be used in Sec. III.

When $|t-t'|\to\infty$, the derivative $\partial C/\partial t$ becomes constant, and the main term of C may be written as

$$\begin{aligned} C&\to -i\Delta^e(t-t') \quad \text{(emission)}\\ &\to -i\Delta^a(t'-t) \quad \text{(absorption)}. \end{aligned} \quad (23)$$

Here $-i\Delta$ represents the contribution of all closed loops, with *no* restriction on time except that one vertex has not been integrated over (the extreme right or the extreme left). According to the usual rules of perturbation theory, Δ is simply the change in ground-state energy due to the static perturbation H_1 present in the final state. An additional confirmation is provided by (22), which yields

$$\begin{aligned} \frac{\lambda\partial\Delta^e}{\partial\lambda}\bigg|_{\lambda=1}&=\sum_{qq'}V_{qq'}G_{q'q}^a(0),\\ \frac{\lambda\partial\Delta^a}{\partial\lambda}\bigg|_{\lambda=1}&=-\sum_{qq'}V_{qq'}G_{q'q}^e(0). \end{aligned} \quad (24)$$

We recover the well-known result that $\lambda\partial\Delta/\partial\lambda$ is equal to the expectation value of H_1.

In an absorption process, the *final* ground-state energy (with the hole) differs from the initial energy by an amount $(-E_0+\Delta^a)$; in the reverse emission process, the net energy change, from equilibrium to equilibrium, is $(E_0+\Delta^e)$. Since the two transitions are inverse of each other, it is physically obvious that

$$\Delta^e=-\Delta^a=\Delta. \quad (25)$$

The transition threshold is thus the same in absorption and emission: There is no "Stokes shift." The relation (15) may be checked by using (22). For arbitrary λ, we may write in the limit $|t-t'|\to\infty$:

$$\begin{aligned} \varphi_{qq'}(\tau,\tau)&\to G_{qq'}{}^{1-\lambda}(0) \quad \text{(emission)}\\ &\to G_{qq'}{}^{\lambda}(0), \quad \text{(absorption)} \end{aligned}$$

where G^λ is the propagator calculated with a net potential $\lambda V_{kk'}a_k^\dagger a_{k'}$. In analogy with (24), we have (with obvious shorthand notation):

$$\begin{aligned} \frac{\partial\Delta^e}{\partial\lambda}&=\mathrm{Tr}VG^{1-\lambda},\\ \frac{\partial\Delta^a}{\partial\lambda}&=-\mathrm{Tr}VG^{\lambda}. \end{aligned}$$

Equation (25) follows by integrating from $\lambda=0$ to $\lambda=1$.

In the limit $t\to\infty$, the dominant term of C gives rise to a phase factor $\exp[-i\Delta t]$ in the reduced Green's function $\tilde{\mathcal{G}}$. In the full $\mathcal{G}$, we may lump all exponential factors together: E_0 is simply replaced by the renormalized deep-level energy $(E_0+\Delta)$. Mathematically, the dominant term of C acts to *shift the branch point* of the propagator $\mathcal{G}(\epsilon)$. On the other hand, it does not give rise to any *broadening* of the deep level. Such a broadening leads to *decay* of the Green's function $\mathcal{G}(t)$ for large times; it will arise from the next terms of $C(t)$, which diverge more slowly than t. We shall see in Sec. III that C actually behaves as

$$C\to -i\Delta t+\alpha\ln t. \quad (26)$$

The second term of (26), although smaller, is the only important one in determining the shape of the spectrum near threshold. In what follows, we shall usually ignore the shift Δ, the actual threshold frequency $\omega_0=\mu-E_0-\Delta$ being considered as an experimental parameter.

III. ASYMPTOTIC SOLUTION FOR *S*-WAVE SCATTERING

Let us assume that the potential created by the deep hole is spherically symmetric; for a free conduction-electron gas, $V_{kk'}$ depends only on the angle between k and k', and may be expanded in a series of normalized spherical harmonics Y_{lm}

$$V_{kk'}=\sum_{lm}V_l(k,k')Y_{lm}(\hat{k})Y_{lm}(\hat{k}') \quad (27)$$

(where $\hat{k}$ denotes a unit vector in the direction of $\mathbf{k}$). In what follows, we shall assume that *each* component $V_l(k,k')$ is *separable*, of the form

$$V_l(k,k')=-V_l u_l(\epsilon_k)u_l(\epsilon_{k'}). \quad (28)$$

u_l is a cutoff function more or less centered on the Fermi surface, and such that $u(\mu)=1$; the minus sign ensures that $V_0>0$, as befits a Coulomb *attraction* with the deep hole. The approximation (28) simplifies the theory without affecting much the physical results. We shall see that the singularity near threshold depends on the interaction *on the Fermi surface:* the functions u_l only provide a cutoff in otherwise logarithmically divergent integrals. Since we shall not specify that cutoff, we may rely on the separable approximation (28) to obtain the correct result. Likewise, we may expand the x-ray matrix element in a series of spherical harmonics.

$$W_k=\sum_{lm}W_{lm}(\epsilon_k)Y_{lm}(\hat{k}). \quad (29)$$

For simplicity, we shall assume that W_{lm} is proportional to the same function u_l that enters (28)

$$W_{lm}(\epsilon_k)=W_{lm}u_l(\epsilon_k). \quad (30)$$

Such an approximation renders the calculation much more symmetrical, without affecting the nature of results; it is in no way essential and could easily be removed in a more quantitative calculation (W_{lm} only enters as an over-all multiplicative factor).

In this section, we shall only consider s-wave scattering on the impurity, and thus retain the $l=0$ term in (27) and (29). (For simplicity, we drop the subscript 0.) Because of the separable interaction (28), momentum variables in a given graph are decoupled, and we can perform at once all momentum sums. Instead of the functions $\varphi_{\mathbf{k}\mathbf{k}'}$, $G_{\mathbf{k}\mathbf{k}'}$, $\bar{F}_{\mathbf{k}\mathbf{k}'}$, there will enter only the combinations

$$\varphi=\sum_{\mathbf{k}\mathbf{k}'}\varphi_{\mathbf{k}\mathbf{k}'}u_{\mathbf{k}}u_{\mathbf{k}'} \tag{31}$$

with similar definitions for G, $\bar{F}$. Each vertex is then associated to a mere factor $\pm V$. There is only one dimension left: the time t.

A. Asymptotic Form of Propagators

Let $\nu(\epsilon)$ be the one-spin density of states (in the absence of a hole). In the absorption case, the initial propagator G^a reduces to its zeroth-order term, and is obtained from (11):

$$\begin{aligned} G^a(t)&=\int_{\mu}^{\infty}\nu(\epsilon)u^2(\epsilon)e^{-i\epsilon t}d\epsilon \quad (t>0)\\ &=-\int_{-\infty}^{\mu}\nu(\epsilon)u^2(\epsilon)e^{-i\epsilon t}d\epsilon \quad (t<0). \end{aligned} \tag{32}$$

For large times t, G^a is controlled by the discontinuity at $\epsilon=\mu$; its limiting behavior is, for both signs of t,

$$G^a(t)\to(\nu_0/it)e^{-i\mu t}. \tag{33}$$

The factor $\exp(-i\mu t)$ appears in *all* one-electron propagators; we shall eliminate it by choosing the energy origin at the Fermi level ($\mu=0$).[12] The validity of the asymptotic form (33) is best judged by looking at a specific example, for instance,

$$\nu(\epsilon)=\text{const},$$
$$u(\epsilon)=e^{-|\epsilon|/\xi_0},$$

where ξ_0 is a cutoff of the order of the conduction bandwidth. The integral (32) is then straightforward and yields

$$G^a(t)=\frac{\nu_0}{it+(1/\xi_0)\operatorname{sgn}t}. \tag{34}$$

The limit (33) is correct when $\xi_0|t|\gg1$, that is for t larger than a typical atomic time.

Knowing G^a, we may calculate the general propagator φ^a by using Eq. (17a), which after momentum summation becomes

$$\varphi^a(\tau,\tau';t,t')=G^a(\tau-\tau')+iV\int_t^{t'}G^a(\tau-\tau'')\varphi^a(\tau'',\tau';t\,t')d\tau''. \tag{35}$$

[12] This exponential might also be lumped with the phase factor present in F [see (14)]: We would then write

$$F(t)=e^{i\omega_0 t}\bar{F}(t),$$

where $\omega_0=\mu-E_0-\Delta$ is the renormalized x-ray threshold frequency.

Let us assume that *all* time intervals in φ^a are large:

$$|t-t'|,\ |\tau-\tau'|,\ |t-\tau|,\ \cdots\gg\xi_0^{-1}. \tag{36}$$

We can then replace G^a by its asymptotic form (33), *except* in the integral where the argument $(\tau-\tau'')$ may be arbitrarily small. However, we shall see that when the conditions (36) are met, φ^a is a slowly varying function of its arguments; in the region $\tau''\approx\tau$, where G^a departs from (33), we may assume that φ^a is practically constant. The "fine structure" of G^a near $\tau=\tau''$ enters only through its integral

$$A=\int_{\tau-\alpha}^{\tau+\alpha}G^a(\tau-\tau'')d\tau'', \tag{37}$$

where α is a cutoff $\gg\xi_0^{-1}$, yet smaller than the characteristic time scale of φ^a. Such a contribution to (35) could also be obtained by adding to the asymptotic form (33) a term $A\delta(t)$; the fine structure of G^a near $t=0$ is then ignored, but its *total weight* is treated correctly, which is enough as far as (35) is concerned.

In what follows, we shall rely entirely on the above *asymptotic* form of G^a, which with slightly different notation may be written as

$$G^a(t)=-i\nu_0[P(1/t)+\tan\theta\pi\delta(t)]. \tag{38}$$

Here P stands for "principal part" [so that the corresponding term does not contribute to (37)]. The angle θ is defined by

$$\nu_0\tan\theta=\frac{iA}{\pi}=\frac{1}{\pi}\int_{-\infty}^{+\infty}\nu(\epsilon)u^2(\epsilon)P(1/\epsilon)d\epsilon \tag{39}$$

[see (32)]. The approximation (38) is central to our theory. We expect it to give the correct *asymptotic* behavior for *large* time intervals. For short intervals, it is wrong; for instance, we shall see that the function φ diverges when τ, $\tau'=t,t'$: Such divergences are spurious, and must be healed by introducing a cutoff $\sim\xi_0^{-1}$.

A similar analysis may be carried out in the emission case. The function G^e then obeys Eq. (12), which simplifies if we make a Fourier transformation

$$G^e(\epsilon)=\frac{G^a(\epsilon)}{1-iVG^a(\epsilon)}. \tag{40}$$

The Fourier transform of (38) is itself given by

$$\begin{aligned} G^a(\epsilon)&=(\pi\nu_0/\cos\theta)\times(e^{-i\theta}) \quad \text{if} \quad \epsilon>0\\ &\quad\times(-e^{+i\theta}) \quad \text{if} \quad \epsilon<0. \end{aligned} \tag{41}$$

On combining (40) and (41), and inverting the Fourier transform, we find

$$\begin{aligned} &G^e(t)=(-i\nu_0/\beta)[P(1/t)+\tan\theta'\pi\delta(t)],\\ &\tan\theta'=\tan\theta-\pi g/\cos^2\theta,\\ &\beta=1-2\pi g\tan\theta+\pi^2g^2/\cos^2\theta \end{aligned} \tag{42}$$

(where $g=\nu_0V$ is the coupling constant). That (42) is indeed a solution of (12) is easily verified.

The preceding results may be expressed in terms of the *phase shift* of conduction electrons at the Fermi surface, due to scattering on the deep hole. The phase shift $\delta(\epsilon)$ may be defined by constructing an eigenstate with the following wave function in momentum space[13]

$$C_k = \delta(\epsilon_k-\epsilon)-\frac{\tan\delta}{\pi}P\left(\frac{1}{\epsilon_k-\epsilon}\right)+\text{regular term.}$$

With a separable scattering potential like (28), δ can be calculated explicitly, and is given by

$$\tan\delta(\epsilon)=\frac{\pi V u^2(\epsilon)\nu(\epsilon)}{1-Vy(\epsilon)},$$
$$y(\epsilon)=\int_{-\infty}^{+\infty}\nu(\epsilon')u^2(\epsilon')P\left(\frac{1}{\epsilon'-\epsilon}\right)d\epsilon'. \tag{43}$$

On comparing (43) with (39), we see that the phase shift at the Fermi surface, $\delta(\mu)=\delta$, is given by

$$\tan\delta=\frac{\pi g}{1-\pi g\tan\theta}. \tag{44}$$

It is then straightforward to verify that

$$\theta'=\theta-\delta,$$
$$\frac{1}{\beta}=\frac{1}{\pi}\frac{d\delta}{dg}. \tag{45}$$

The effect of the scattering potential is completely characterized by δ, as could be expected.

B. Solution of the Integral Equation

We consider first the absorption case. By inserting (38) into (35), we obtain the following equation for φ^a:

$$\varphi^a(\tau,\tau')[1-\pi g\tan\theta]=G^a(\tau-\tau')+g\int_t^{t'}\varphi^a(\tau'',\tau')P\left(\frac{1}{\tau-\tau''}\right)d\tau''. \tag{46}$$

(46) is an integral equation with respect to the variable τ. Retaining only the "active" variable, and making use of (44), we may write it as

$$\varphi^a(\tau)=f^a(\tau)+\frac{1}{\pi}\tan\delta\int_t^{t'}\varphi^a(\tau'')P\left(\frac{1}{\tau-\tau''}\right)d\tau'', \tag{47}$$

where we have set

$$f^a(\tau)=\frac{-i\nu_0}{1-\pi g\tan\theta}\left[P\left(\frac{1}{\tau-\tau'}\right)+\pi\tan\theta\,\delta(\tau-\tau')\right]. \tag{48}$$

(47) is a standard singular integral equation, as discussed in the famous book of Muskhelishvili.[14] Among its possible solutions, we retain the *perturbative* one, which reduces to G^a when $g\to 0$. According to Muskhelishvili, such a solution is given by

$$\varphi^a(\tau)=\cos^2\delta\left\{f^a(\tau)-\frac{1}{\pi}\tan\delta\left(\frac{\tau-t}{t'-\tau}\right)^{\delta/\pi}\times\int_t^{t'}\left(\frac{t'-\tau''}{\tau''-t}\right)^{\delta/\pi}f^a(\tau'')P\left(\frac{1}{\tau''-\tau}\right)d\tau''\right\}. \tag{49}$$

(We assume $t<\tau$, $\tau'<t'$.) When f^a is replaced by its expression (48), the calculation of φ^a is reduced to a quadrature. The δ-function contribution to f^a is trivially integrated; the principal part, on the other hand, leads to an integral of the form

$$\int_t^{t'}\left(\frac{t'-\tau''}{\tau''-t}\right)^{\delta/\pi}P\left(\frac{1}{\tau''-\tau'}\right)P\left(\frac{1}{\tau''-\tau}\right)d\tau''. \tag{50}$$

In evaluating (50), we make use of the identity

$$P\left(\frac{1}{\tau''-\tau'}\right)P\left(\frac{1}{\tau''-\tau}\right)=P\left(\frac{1}{\tau-\tau'}\right)\times\left\{P\left(\frac{1}{\tau''-\tau}\right)-P\left(\frac{1}{\tau''-\tau'}\right)\right\}+\pi^2\delta(\tau''-\tau')\delta(\tau''-\tau).$$

The integral (50) can then be calculated by using the integration contour of Fig. 5 (paying due attention to the various determinations of the integrand). The algebra is lengthy, but straightforward, so that we shall only quote the result.[15]

$$\varphi^a(\tau,\tau';t,t')=G^e(\tau-\tau')\left[\frac{(t'-\tau')(\tau-t)}{(t'-\tau)(\tau'-t)}\right]^{\delta/\pi}, \tag{51}$$

where G^e is the emission Green's function, given by (42). The result (51) is remarkably simple; we note that it verifies the condition (19) when $t'\to+\infty$, $t\to-\infty$: The *transient* character of φ^a is entirely contained in the last algebraic factor. Of course, (51) is only valid in the asymptotic limit where all time intervals are $\gg\xi_0^{-1}$.

A similar analysis may be carried out in the emission case. The equation for φ^e is then obtained by making the following replacements in (35):

$$G^a\to G^e,$$
$$V\to -V,$$
$$t\rightleftarrows t'.$$

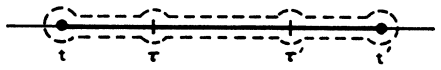

FIG. 5. Contour of integration for calculating the integral (50). The heavy line is the branch cut of the integrand; on going around one branch point, the function is multiplied by $\exp[\pm 2i\delta]$. The principal-part integration excludes the half circles surrounding the singular points τ and τ'.

[13] See, for instance, W. Kohn, Phys. Rev. 84, 695 (1951).
[14] N. I. Muskhelishvili, *Singular Integral Equations* (P. Noordhoff Ltd., Groningen, The Netherlands, 1953), Chap. XIV.
[15] That (51) is indeed a solution of (46) may be verified by using the same integration contour as for the calculation of (50).

On using (42), we thus find

$$\varphi^e(\tau,\tau')\left[1+\frac{\pi g}{\beta}\tan\theta'\right]=G^e(\tau-\tau')$$
$$-\frac{g}{\beta}\int_{t'}^{t}\varphi^e(\tau'',\tau')P\left(\frac{1}{\tau-\tau''}\right)d\tau''.$$

With the help of (44), this equation may be cast in the form

$$\varphi^e(\tau)=f^e(\tau)-\frac{1}{\pi}\tan\delta\int_{t'}^{t}\varphi^e(\tau'')P\left(\frac{1}{\tau-\tau''}\right)d\tau'', \quad (52)$$

where we have set

$$f^e(\tau)=\frac{G^e(\tau-\tau')}{1+(\pi g\tan\theta')/\beta}.$$

(52) is similar to (47) and can be solved by the same method. One thus finds (for $t'<\tau$, $\tau'<t$)

$$\varphi^e(\tau,\tau';t,t')=G^a(\tau-\tau')\left[\frac{(\tau'-t')(t-\tau)}{(\tau-t')(t-\tau')}\right]^{\delta/\pi}. \quad (53)$$

The analogy with (51) is complete; the "transient factor" is the same in both cases.

The x-ray response function involves the quantity $L_{\mathbf{k}\mathbf{k}'}$ defined in (18), obtained by letting $\tau=t'$, $\tau'=t$. According to (51) and (53), φ is then infinite. We know that such a divergence is spurious, being due to our asymptotic approximation on G^e and G^a; the divergence must be healed by introducing a cutoff of order ξ_0. We shall see later that this cutoff must be pure imaginary, in order to ensure a *real* spectral density for the response function [a fact which could be suspected from the particular example (36)]. If we take this into account, and also restore the missing phase factor $e^{i\mu t}$, we obtain (after performing momentum sums)

$$L^a(t)=(i\nu_0/t)(i\xi_0 t)^{2\delta/\pi}e^{i\mu t}\theta(-t),$$
$$L^e(t)=(i\nu_0/\beta t)(i\xi_0 t)^{2\delta/\pi}e^{i\mu t}\theta(t), \quad |\xi_0 t|\gg 1. \quad (54)$$

The result (54) is correct within *logarithmic accuracy*[16] (the cutoff ξ_0 being only known within a factor ~ 1). The only thing which is known exactly is the *exponent* of t.

C. Contribution of Closed Loops

The closed loop contribution $C(t)$ is best calculated using Eq. (22),[17] which involves the apparently divergent factor $\varphi(\tau,\tau)$. In order to clarify the nature of that divergence, let us expand the last factor of (51) and (53) in powers of $(\tau-\tau')$; in the limit $\tau-\tau'\to 0$, we find

$$\varphi^a(\tau,\tau')\to G^e(\tau-\tau')-\frac{i\nu_0}{\beta}\frac{\delta}{\pi}\left[\frac{1}{t'-\tau}+\frac{1}{\tau-t}\right],$$
$$\varphi^e(\tau,\tau')\to G^a(\tau-\tau')+i\nu_0\frac{\delta}{\pi}\left[\frac{1}{\tau-t'}+\frac{1}{t-\tau}\right]. \quad (55)$$

The divergence appears only in the first term G^e or G^a—it is clearly due to our asymptotic approximation, and would disappear in a more realistic calculation. The important point is that these seemingly singular terms are *completely independent of t and t'*; when carried over into (22), they will give a contribution to C proportional to $(t-t')$: They are thus responsible for the energy shift Δ of the deep hole. In contrast, the last terms of (55) depend on t and t', and will control the *decay* of the Green's function $\mathcal{G}$ when $|t-t'|\to\infty$. We are not interested in the shift Δ, which has been absorbed in the phenomenological threshold ω_0: We shall, therefore, discard the singular terms of (55), and retain only the last regular terms, which although smaller convey all the relevant physical information.[18]

We carry the momentum summation in (22), and replace $\varphi(\tau,\tau)$ by the last term of (55). The integral over τ has a logarithmic divergence at both ends, which we eliminate by introducing the usual cutoff ξ_0^{-1}. We thus find

$$\lambda\frac{\partial C^a(t)}{\partial\lambda}=-\frac{2g}{\beta}\frac{\delta}{\pi}\ln|\xi_0 t|,$$
$$\lambda\frac{\partial C^e(t)}{\partial\lambda}=-2g\frac{\delta}{\pi}\ln|\xi_0 t|. \quad (56)$$

We consider first the absorption case: The initial propagator G^a is then g-independent, and we may write

$$\lambda\frac{\partial C^a}{\partial\lambda}=g\frac{\partial C^a}{\partial g}. \quad (57)$$

Let us replace β by its expression (65): The integration over g is immediate and yields

$$C^a=-(\delta/\pi)^2\ln|\xi_0 t|. \quad (58)$$

The emission case is somewhat more complicated, as G^e then depends on g: The derivation in (57) must be taken *at constant G^e*, i.e., at constant β and θ' [see (42)]. We shall therefore write

$$\lambda\frac{\partial C^e}{\partial\lambda}=g\left.\frac{\partial C^e}{\partial g}\right|_{\beta\theta'}=g\left.\frac{\partial C^e}{\partial\delta}\frac{\partial\delta}{\partial g}\right|_{\beta\theta'}. \quad (59)$$

Now, a glance at (52) shows that, when expressed in

[16] Such a logarithmic error renders the factor β in $L^e(t)$ somewhat meaningless.

[17] Equation (21), although apparently simpler, leads to difficulties as the function $\varphi(t,t)$ is singular, both in the factor G and in the "transient" algebraic factor. One must use a cutoff ξ_0^{-1}, which precludes a *precise* calculation of C. Since C enters as an exponent, such an approximation is unacceptable.

[18] Note that in writing (55), we tacitly assumed that the t-dependent part of φ^a and φ^e is continuous when $(\tau-\tau')\to 0$, even when $|\tau-\tau'|<\xi_0^{-1}$. That such a continuity exists is not obvious—although plausible since the t dependence comes from intermediate times far away from τ and τ'.

terms of θ' and β, the phase shift is given by

$$\tan\delta=\frac{\pi g}{\beta+\pi g\tan\theta'} \tag{60}$$

from which it follows that

$$\left.\frac{\partial\delta}{\partial g}\right|_{\beta,\theta'}=1.$$

We can then perform the integration over δ in (56): We thus find that $C^e=C^a$.

The deep-level Green's function $\mathcal{G}$ is given by (15). Again, we shall see that the cutoff in (58) must be pure imaginary if $\mathcal{G}$ is to have a real spectral density: We thus replace ξ_0 by $i\xi_0$. We also restore the missing phase factors and sign [see (14)]. We thus obtain

$$\mathcal{G}(t)=e^{-i(E_0+\Delta)t}\frac{1}{(i\xi_0 t)^{(\delta/\pi)^2}}\times[-\theta(-t)]\quad\text{(absorption)}$$
$$\times[+\theta(t)]\quad\text{(emission)}. \tag{61}$$

From (15), (54), and (61), we may calculate the original x-ray response function F (summed over momenta):

$$F(t)=(iv_0/|t|)[i\xi_0 t]^{2\delta/\pi-\delta^2/\pi^2}e^{i\omega_0 t}\times\theta(-t)\quad\text{(absorption)}$$
$$\times\theta(t)/\beta,\quad\text{(emission)} \tag{62}$$

where ω_0 is the x-ray threshold. We see that F has a very unusual power dependence as a function of t. The factor L tends to increase the response function, while $\mathcal{G}$ acts to quench the divergence. Let us emphasize again that (61) and (62) are only valid within logarithmic accuracy (ξ_0 being roughly determined).

D. Spectral Representation of F and $\mathcal{G}$

According to (61) and (62), the functions $\mathcal{G}$ and F have the same general form

$$y(t)=(A/it)(i\xi_0 t)^\alpha e^{-i\omega_1 t}\theta(\pm t). \tag{63}$$

Let us consider for instance the emission case ($t>0$). We know from first principles that both functions have a *real* spectral density $z(\epsilon)$, such that,

$$y(t)=e^{-i\omega_1 t}\int_0^\infty d\epsilon\, z(\epsilon)e^{-i\epsilon t}.$$

It is easily verified that (63) implies

$$z(\epsilon)=\frac{A}{\Gamma(1-\alpha)}\left(\frac{\xi_0}{\epsilon}\right)^\alpha \tag{64}$$

(where Γ is the usual γ function). We note that the factor $(\xi_0/\epsilon)^\alpha$ is *real*, which justifies our choice of an imaginary cutoff in the time representation.

It is equally easy to calculate the ordinary Fourier transform

$$y(\epsilon)=\int_0^\infty y(t)e^{i\epsilon t}dt.$$

If we measure the energies from the branch point ω_1, we find that[19]

$$y(\epsilon)=-iAe^{i\pi\alpha}\Gamma(\alpha)(\xi_0/\epsilon)^\alpha. \tag{65}$$

It is then easy to verify that for $\epsilon>0$

$$\mathrm{Re}\,y=\pi z.$$

We recover the usual properties of response functions.

The quantities of physical interest are the spectral densities. Measured from their respective branch points, they behave as

$$\frac{1}{\epsilon}\left(\frac{\epsilon}{\xi_0}\right)^{(\delta/\pi)^2}\quad\text{for the Green's function }\mathcal{G},$$
$$\left(\frac{\xi_0}{\epsilon}\right)^{2\delta/\pi-(\delta/\pi)^2}\quad\text{for the response function }F. \tag{66}$$

[The exact coefficients may be figured out from (64)]. In the weak coupling limit ($\delta\sim\pi g\ll 1$), (66) agrees with the results of the many body approach of I and II.

The x-ray transition rate is proportional to the spectral density of F. Thus when

$$\alpha=\frac{2\delta}{\pi}-\left(\frac{\delta}{\pi}\right)^2$$

is positive, the absorption (emission) rate should be infinite at threshold, in agreement with the prediction of Mahan.[5] Conversely, $\alpha<0$ means that there is no sharp threshold (the amplitude of the discontinuity being exponentially small).[20] We shall see in the conclusion that this second possibility may explain certain features of the experimental data.

IV. INFLUENCE OF SPIN AND HIGHER-ORDER PHASE SHIFTS

The effect of the electron spin is easily included if we assume that the spin of conduction electrons is conserved in the interaction with the deep hole. Put another way, we ignore exchange processes in which the deep hole and one conduction electron would both reverse their spin. Such an approximation was in fact implicit in our statement that only *one* deep level is involved; if

[19] Actually, the integration over t should be cut off at $t\sim\xi_0^{-1}$: What enters (65) is $(\xi_0/\epsilon)^\alpha-1$, rather than $(\xi_0/\epsilon)^\alpha$. Such a correction is necessary if one wants to recover the zeroth-order result by expanding in powers of α.

[20] One verifies easily that, whatever the sign of α, the asymptotic form of $y(t)$ depends only on the spectral density *near threshold* (for large t, only small values of ϵ avoid destructive interference). Hence, our logarithmic approximations do not affect conclusions regarding the shape of z near $\epsilon=0$.

we were to release it, we would face a Kondo problem which is far more complicated. Under such restriction, spin is conserved along any open or closed line in the "one-body" graphs. The only change is that L and C are multiplied by a factor 2 (each line corresponding to either spin direction). The change in L simply doubles the transition rate (there are twice as many conduction electrons involved); on the other hand, the change in C is much more drastic, as it changes the exponent α in (63). The behavior near threshold (66) is replaced by

$$\begin{aligned} &\frac{1}{\epsilon}\left(\frac{\epsilon}{\xi_0}\right)^{2(\delta/\pi)^2} && \text{for the Green's function } \mathcal{G}, \\ &\left(\frac{\xi_0}{\epsilon}\right)^{(2\delta/\pi)(1-\delta/\pi)} && \text{for the response function } F. \end{aligned} \tag{67}$$

Spin thus increases the deep-level broadening, which in turn tends to quench the x-ray singularity near threshold.

The angular dependence of the matrix element $V_{\mathbf{k}\mathbf{k}'}$ may be treated in much the same way. Let us replace $V_{\mathbf{k}\mathbf{k}'}$ by its general form (27), and further assume that each coefficient is separable, as shown in (28). Each vertex involves a sum over (l,m); for every single term of this sum, we may carry out momentum sums, as in the preceding section (momentum variables are completely decoupled). A propagator joining two vertices (l,m) and (l',m') will then give rise to a factor

$$\sum_{\mathbf{k}\mathbf{k}'} G_{\mathbf{k}\mathbf{k}'} u_{lm}(\epsilon_k) Y_{lm}(\hat{k}) u_{l'm'}(\epsilon_{k'}) Y_{lm}(\hat{k}'). \tag{68}$$

Because of rotational invariance, $G_{\mathbf{k}\mathbf{k}'}$ depends only on the angle between $\mathbf{k}$ and $\mathbf{k}'$. (68) thus vanishes except when $(l,m)=(l',m')$. We conclude that the angular momentum (l,m) is *conserved* along any line of the graph, exactly as for spin. Each value (l,m) defines an independent "channel," yielding a contribution A_{lm} to any open or closed line; the total contribution is simply the sum of the *partial* A_{lm}.

For each value (l,m), we can reproduce the analysis carried out for s-wave scattering. Because Y_{lm} is normalized, we need only replace V and u by V_l and u_l. The corresponding contribution of the open line L_{lm} and of the closed loops C_{lm} is obtained by replacing δ by the appropriate lth phase shift δ_l in our former results (54) and (58). The deep-level Green's function is then obtained from (15)

$$\tilde{\mathcal{G}}(t)=\exp\sum_{lm} C_{lm}(t), \tag{69}$$

while the x-ray response function follows from (3), (15), (29), and (30)

$$S(t)=\sum_{lm} |W_{lm}|^2 L_{lm}(t). \tag{70}$$

We note that the Green's function $\tilde{\mathcal{G}}$ is a *product* of factors $\mathcal{G}_{lm}$ (the partial-wave sum appears in the *exponent*). In contrast, the open line contribution to S is a *sum* over (l,m), each term being weighted by the corresponding x-ray matrix element $|W_{lm}|^2$.

Let us replace C_{lm} and L_{lm} by their values in (69) and (70). Taking spin into account, we find that, for large times t, the functions $\mathcal{G}$ and S behave as

$$\begin{aligned} &\mathcal{G}(t)\sim\frac{1}{(i\xi_0 t)^{\alpha}}, \\ &\alpha=2\sum_l (2l+1)\left(\frac{\delta_l}{\pi}\right)^2; \end{aligned} \tag{71}$$

$$\begin{aligned} &S(t)\sim\sum_{lm} |W_{lm}|^2 \frac{(i\xi_0 t)^{\alpha_l}}{t}, \\ &\alpha_l=2\frac{\delta_l}{\pi}-2\sum_l (2l+1)\left(\frac{\delta_l}{\pi}\right)^2 \end{aligned} \tag{72}$$

(for simplicity, we retained only the significant factors in (61) and (62), dropping the exponentials, step functions, etc.). The corresponding spectral densities are given by

$$\begin{aligned} &\frac{1}{\epsilon}\left(\frac{\epsilon}{\xi_0}\right)^{\alpha} && \text{for the Green's function } \mathcal{G} \\ &\sum_{lm} |W_{lm}|^2\left(\frac{\xi_0}{\epsilon}\right)^{\alpha_l} && \text{for the response function } S. \end{aligned} \tag{73}$$

We expect (73) to provide the exact asymptotic behavior of $\mathcal{G}$ and S near $\epsilon=0$; we note that each term of S has its own exponent α_l.

V. CONCLUSION

The basic physical result of this paper is contained in (73). The spectral density of S is nothing but the x-ray absorption (emission) rate measured experimentally. The singularity in (73) thus determines the behavior of the spectrum near the threshold frequency ω_0. We see that for each (l,m) the transition rate at threshold is either *infinite* ($\alpha_l>0$) or *zero* ($\alpha_l<0$). Such a singularity arises as a compromise between the plain *resonance* in the scattering of conduction electrons (which always gives a divergence in L), and the *broadening* of the deep level (measured by $\mathcal{G}$) which tends to quench that resonance. The sign of α_l depends on which of these two effects dominates. We note that the linked cluster theorem allows a very simple treatment of the broadening effect: In the time representation, the total response function F is simply the product of a one-electron factor L times $\tilde{\mathcal{G}}$; the corresponding convolution in the energy representation obviously accounts for the influence of broadening on the observed spectrum.

The matrix element W_k may be written as

$$W_k \sim \int d\mathbf{r}\Psi_d^*(\mathbf{r}) i\boldsymbol{\eta}\cdot\nabla\Psi_k(\mathbf{r}), \tag{74}$$

where $\boldsymbol{\eta}$ is the x-ray polarization vector, Ψd the deep-level wave function, Ψ_k the conduction-electron wave function. Ψ_k is actually a Bloch state

$$\Psi_k = e^{i\mathbf{k}\cdot\mathbf{r}} u_k(\mathbf{r}),$$

where u_k incorporates the core structure and the effect of the periodic lattice. The angular components W_{lm} then depend critically on the rotational symmetry of the deep and conduction states. If both are s states, W_{lm} possesses only a component $l=1$. On the other hand, by varying the nature of the initial state (K,L,M transitions), one should be able to sample other values of (l,m), in varying amounts. One cannot make more precise statements without a detailed analysis of specific materials and transitions.

The nature of the singularity is controlled by the exponents α_l, i.e., by the various phase shifts δ_l describing scattering of conduction electrons on the deep hole. Because of the long range of Coulomb interactions, these phase shifts are not independent; they obey the well-known Friedel sum rule[21]

$$\sum_l (2l+1)\delta_l = \frac{\pi}{2} \tag{75}$$

(which by the way shows that a strictly weak coupling theory is never possible). If we assume that only one phase shift is nonzero, say δ_{l_0}, then α_l is completely determined from (75); according to (72), we have

$$\begin{aligned} \alpha_l &= -\frac{1}{2(2l_0+1)} \quad \text{if} \quad l \neq l_0. \\ &= +\frac{1}{2(2l_0+1)} \quad \text{if} \quad l = l_0. \end{aligned} \tag{76}$$

The discontinuity at threshold should be infinite for $l=l_0$, and zero for $l\neq l_0$ (the singularity being weaker for increasing l_0). However, such an assumption of a single phase shift is completely arbitrary; again, definite statements can only be made in specific cases.

Experimentally, a sharp Fermi level threshold is observed in the emission spectra of certain simple metals; in several cases, there is a definite enhancement of the spectrum near threshold (e.g., in Al, Mg, and to a lesser extent in Na); it is likely that in these cases the relevant α_l are >0. On the other hand, in many transition metals (e.g., Cu), there is no sharp Fermi level threshold at all—a feature which is very surprising, since the conduction electrons do have a discontinuous distribution. This longstanding anomaly may be understood if we assume that in those metals the relevant α_l are <0; the discontinuity is washed out by the deep-level broadening. A numerical discussion of specific cases is needed to support this interpretation.

In conclusion, we should emphasize again that we have neglected many possibly important physical effects. The finite lifetime of the hole, as well as its recoil, will tend to blur the threshold singularity. (It is possible to incorporate lifetime effects into the present formalism, although the calculation does not look very tractable.) Another approximation is that of a single deep state; if the deep hole may scatter from one state to another, we face a Kondo-like problem. The formalism of this paper, based on a structureless hole, is then useless. In addition to the above "physical" approximations, we assumed a centrally symmetric scattering potential, with separable components V_{lm}. The latter approximation may probably be avoided by using a t-matrix formulation; we did not push the question further, since it is clear that only the vicinity of the Fermi surface is involved; the separability assumption should then be unimportant.

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