Infrared catastrophy and excitons in the X-ray spectra of metals

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INFRARED CATASTROPHY AND EXCITONS IN THE X-RAY SPECTRA OF METALS

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Résumé. — Les singularités aux seuils des spectres X des métaux sont étudiées par une méthode nouvelle, utilisant une description des états initiaux et finaux à l'aide de déterminants de Slater. Le calcul des spectres de raies et de bande se ramène à celui d'un unique déterminant, pour lequel une approximation asymptotique est mise au point. On étudie particulièrement le cas où le potentiel final est assez fort pour lier un électron : les spectres d'absorption possèdent alors deux seuils, dont les caractéristiques sont précisées. La position de ces seuils, ainsi que la nature des singularités sont en accord avec les prédictions d'Hopfield [3]. Lorsque la densité des électrons diminue, le spectre évolue continûment vers celui d'un isolant, la divergence au seuil se transformant en une raie d'exciton élargie par effet Auger.

Abstract. — The singularities near the edges of X-ray spectra in metals are investigated by a new method, using a description of initial and final states in terms of Slater determinants. The calculation of line and band spectra is reduced to that of a single determinant, for which an asymptotic approximation is developed. Special attention is paid to the case in which the final potential is strong enough to bind an electron : the absorption spectrum then possesses two thresholds, whose characteristics are found. The position of the threshold, as well as the nature of the singularities agree completely with the predictions of Hopfield [3]. When the number of electrons decreases, the spectrum goes continuously into that of an insulator, the infrared catastrophy divergence turning into an Auger broadened exciton line.

I. **Introduction.** — As originally suggested by Mahan [1], the X-ray emission or absorption band spectrum of metals displays a characteristic threshold singularity, arising from the interaction between conduction electrons and the localized disturbance due to the X-ray transition. Depending on the parameters, the transition probability $I(\omega)$ may be either infinite near threshold (Fig. 1*a*), or instead zero, with no discontinuity (Fig. 1*b*) [2]. Near the threshold ω_0, $I(\omega)$ behaves as

$$I(\omega) \sim \frac{1}{|\omega - \omega_0|^{\alpha}} \qquad (1)$$

where α is a critical exponent, which is positive in case (*a*), negative in case (*b*). Such an unusual behaviour has its origin in the readjustement of the conduction electrons to the sudden change in the ionic core potential brought about by the X-ray transition. The latter tends to excite electron hole pairs out of the Fermi sea, by a process analogous to the Auger effect. Because of the large density of pair states, the number of such pairs is infinite, even though the total energy transferred to the electrons is finite. As pointed out by Hopfield [3], we may speak of an *infrared catastrophy* in which infinitely many excitations of an infinitely small energy are created, in much the same way as photons in the scattering of two charged particles.

The above discussion is concerned with band spectra, in which the transition occurs between a deep core state and the conduction band. As shown by Doniach [4], a similar effect is expected in line emission spectra, involving transitions between two discrete core states. Because the conduction electrons are scattered differently in the initial and final states, they must again readjust to their new surroundings : the transition involves Auger excitation processes, leading to an asymmetric broadening of the sharp line on the low energy side. The spectrum has again the shape (1) (with however a different exponent) [5].

A theoretical treatment of this « infrared catastrophy » was proposed by Roulet, Gavoret and Nozières [6], [7], and by Nozières and De Dominicis [8]. It is formulated in a simplified model based on the following assumptions :

(i) The disturbance in the inner shells is supposed to have no recoil : it remains localized at a given site in the lattice.

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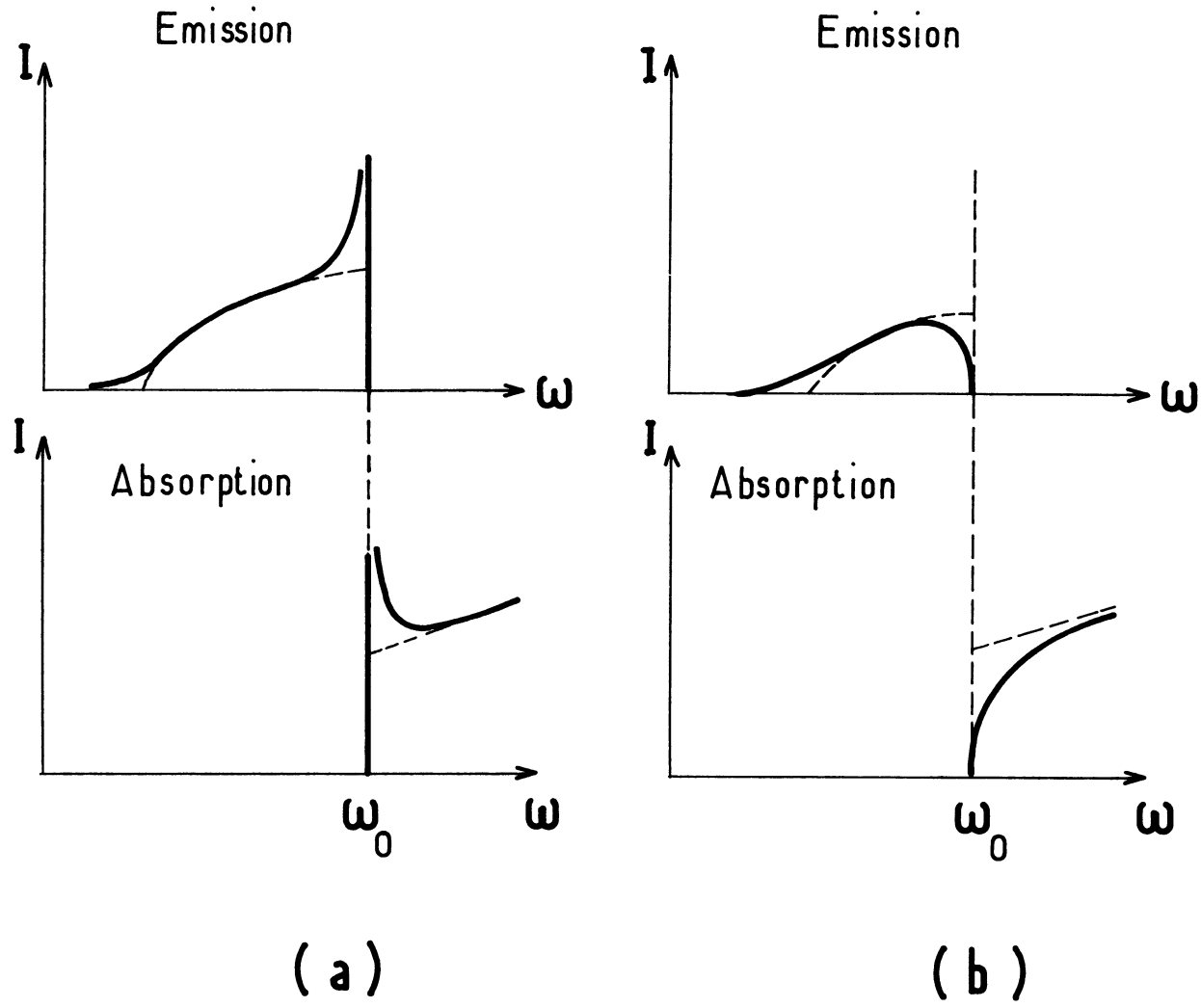

FIG. 1. — Typical behaviours for the band X-ray spectra of metals. The full line corresponds to the actual spectra, the dotted line to a one electron approximation. Besides the usual low energy Auger tail in the emission case, the spectra display either a singularity near threshold (case *a*) or instead no discontinuity at all (case *b*).

(ii) The deep hole is considered as structureless, acting only as a scattering potential for the conduction electrons. Exchange processes involving Coulomb transitions between different core states are completely neglected (they would lead to Kondo singularities).

(iii) The Coulomb interaction between conduction electrons is ignored. We assume that it is included in the form of renormalized quasiparticles ; this is certainly correct close enough to the threshold, for processes which involve electron hole pairs with energies much smaller than the Fermi energy μ.

(iv) Finally, the finite lifetime of the X-ray excited-state is not taken into account.

Let us consider first band spectra, and let b^* be the creation operator for the deep core state involved in the transition (with bare energy ε_0). The above assumptions are summarized in the following model hamiltonian

$$H = \varepsilon_0 \, b^* \, b + \sum_k \varepsilon_k \, c_k^* \, c_k + \sum_{kk'} V_{kk'} \, c_k^* \, c_{k'} \, bb^* \, . \quad (2)$$

c_k^* is the creation operator for conduction electrons (spin indices have been omitted). $V_{kk'}$ is the matrix element for scattering from the excited atom, which appears only when the deep level is empty. The coupling to the X-ray field is described semi-classically by a perturbation

$$H_X = \sum_k W_k \, c_k^* \, b \, e^{i\omega t} + C.C \, . \quad (3)$$

The transition rate is proportional to the imaginary part of the Fourier transform $S(\omega)$ of the response function

$$S(t - t') = < H_X(t) \, H_X(t') > . \quad (4)$$

In the case of emission line spectra, we introduce the operator b^* which produces the transition between the two core states, with bare energies

$$\varepsilon_1 \quad \text{and} \quad \varepsilon_2 = \varepsilon_1 + \varepsilon_0 \, .$$

The model hamiltonian is then

$$H = \varepsilon_0 \, b^* \, b + \sum_k \varepsilon_k \, c_k^* \, c_k + \sum_{kk'} (V^1_{kk'} - V_{kk'} \, b^* \, b) \, c_k^* \, c_{k'} \quad (5)$$

where V^1 and $V^2 = V^1 - V$ are the scattering potentials before and after the transition. The X-ray coupling has the form

$$H_X = Wb\, e^{i\omega t} + c.c \tag{6}$$

the transition rate being again given by (4). Within the model, the calculation of the spectrum is reduced exactly to that of the appropriate correlations functions,

$$\begin{cases} \mathcal{G}(t - t') = < T\{ b(t)\, b^*(t') \} > \\ \mathcal{F}(t - t') = \sum_{kk'} W_k\, W_{k'}^* \times \\ \qquad \times < T\{ b(t)\, c_k^*(t)\, c_{k'}(t')\, b^*(t') \} > \end{cases} \tag{7}$$

(where T is the usual chronological operator).

As shown in ref. [8], the inner core distrubance only acts as a *transient one body* potential acting on the conduction electrons. When calculating $\mathcal{G}(t - t')$ or $\mathcal{F}(t - t')$, one need only study the response of the Fermi sea to the scattering potential $\pm V_{kk'}$ applied between times t and t'. The problem is easily formulated in field theoretical language. $\pm e^{i\varepsilon_0 t}\, \mathcal{G}$ corresponds to the « vacuum amplitude », *i. e.*, to the diagonal element of the S-matrix in the initial ground state ; the linked cluster theorem allows to write

$$\mathrm{Log} \mid \pm e^{i\varepsilon_0 t \mathcal{G}} \mid = C \tag{8}$$

where C is the sum of all simply connected closed loops. Similarly, the function $\mathcal{F}$ takes the form

$$\mathcal{F} = \mathcal{G}L \tag{9}$$

where L is the contribution of an open conduction electron line going from t to t'. The problem is thus reduced to solving a Dyson equation for the electron Green's function in the transient potential $V_{kk'}$. Up to that point, the model is treated exactly.

In order to proceed further, approximations are needed. An asymptotic solution may be found, which is valid in the limit of long times (*i. e.* close to the threshold). The Dyson equation then reduces to a singular integral equation of the Mushkhelishvili type, whose solution is known. The asymptotic solution is controlled by the phase shifts δ_l of conduction electrons off the transient potential $V_{kk'}$ (or more exactly by the changes in δ_l brought about by $V_{kk'}$). It is found that

$$\mathcal{G}(t) \sim \frac{e^{-i(\varepsilon_0 - \Delta)t}}{t^\beta} . \tag{10}$$

Δ is the change in the ground state energy of conduction electrons arising from $V_{kk'}$, which according to Friedel [9] may be written as

$$\Delta = - \sum 2(2\,l + 1) \int_0^\mu \frac{\delta_l(\varepsilon)}{\pi}\, d\varepsilon \tag{11}$$

(the origin of energy has been chosen at the bottom of the conduction band). The exponent β involves the phase shifts at the Fermi surface, $\delta_l(\mu) = \delta_l$

$$\beta = 2 \sum_l (2\,l + 1) \frac{\delta_l^2}{\pi^2} . \tag{12}$$

(We note that each spin angular momentum channel l, m, s contributes independently to Δ and β.) In similar fashion, a partial wave analysis of $W_{k'}$ yields following form of the open line contribution

$$\begin{cases} L(t) \sim \sum_{lm} \mid W_{lm} \mid^2 \frac{e^{i\mu t}}{t^{\gamma_l}} \\ \text{with} \quad \gamma_l = 1 - \frac{2\,\delta_l}{\pi} . \end{cases} \tag{13}$$

The shape of the spectrum is obtained by Fourier transforming $\mathcal{F}$ and $\mathcal{G}$. The threshold is located at $\omega_0 = - \varepsilon_0 + \Delta$ for line spectra, at $\omega_0 = \mu - \varepsilon_0 + \Delta$ for band spectra. Near the threshold, we indeed find the behaviour (1), with

$$\begin{cases} \alpha = 1 - \beta & \text{for line spectra} \\ \alpha = 1 - \gamma_l - \beta & \text{for the } l, m \text{ component of band spectra.} \end{cases} \tag{14}$$

The results are particularly simple if we consider only a single channel — e. g. s-wave scattering for spinless particles ; then we have

$$\begin{cases} \beta = \frac{\delta^2}{\pi^2} \\ \gamma_l + \beta = \left[\frac{\delta}{\pi} - 1 \right]^2 . \end{cases} \tag{15}$$

Such an approach only provides the asymptotic behaviour of the spectrum. It should noted that it is non perturbative, in that it does not assume $V_{kk'}$ to be small. However, there remains an ambiguity in the definition of the phase shift : should it be the actual δ, or its determination in the range $(0, \pi)$? Mushkhelishvili's method cannot answer that question, as different determinations of δ correspond to different solutions of the same integral equations. The result (15) has a finite range of validity, but it is not clear where it breaks down.

The critical exponents β and γ_l are closely related to the number of conduction electrons n_l which must be brought in each channel near the excited core in order to achieve the new equilibrium ground state. This was shown very clearly by Hopfield [3]. According to the Friedel sum rule [9], an extra potential $V_{kk'}$ gives rise to an excess localized charge in the ground state, which in the channel (l, m, s) is equal to δ_l/π. In the simple case of line emission spectra, the net charge n_l to be brought from infinity in that channel is equal to $- \delta_l/\pi$. From (1) and (12), it follows that the critical exponent α may be written in the form

$$\alpha = 1 - \sum_{lms} n_l^2 . \tag{16}$$

It turns out that (16) is correct in all cases studied so far. Consider for instance the (l, m, s) component of the absorption band spectrum. The net charge $n_{l'}$ needed *in the conduction* band is given by

$$n_{l'} = \begin{cases} \delta_{l'}/\pi & \text{if } l'\,m'\,s' \neq lms \\ (\delta_l/\pi) - 1 & \text{if } l'\,m'\,s' = lms\,. \end{cases} \quad (17)$$

(Since one extra electron has been provided by the core in the l, m, s channel.) Inserting (17) and (16), one recovers the critical exponent of $\mathcal{F}_{lm}(\omega)$. It thus appears that the physical origin of the infrared catastrophy lies in the difficulty of bringing electrons from infinity to the neighbourhood of the excited site.

One may wonder what happens to these infrared singularities when the Fermi-energy goes to zero. The answer is straightforward if the potential $V_{kk'}$ has no bound state : all the phase shifts δ_l then go to zero, and the singularities disappear. The spectrum of $\mathcal{G}$ goes into a single discrete line at frequency $-\varepsilon_0$; the emission part of $\mathcal{F}$ goes to zero altogether, while the absorption part reflects the usual density of one particle states in the conduction band (see Fig. 2).

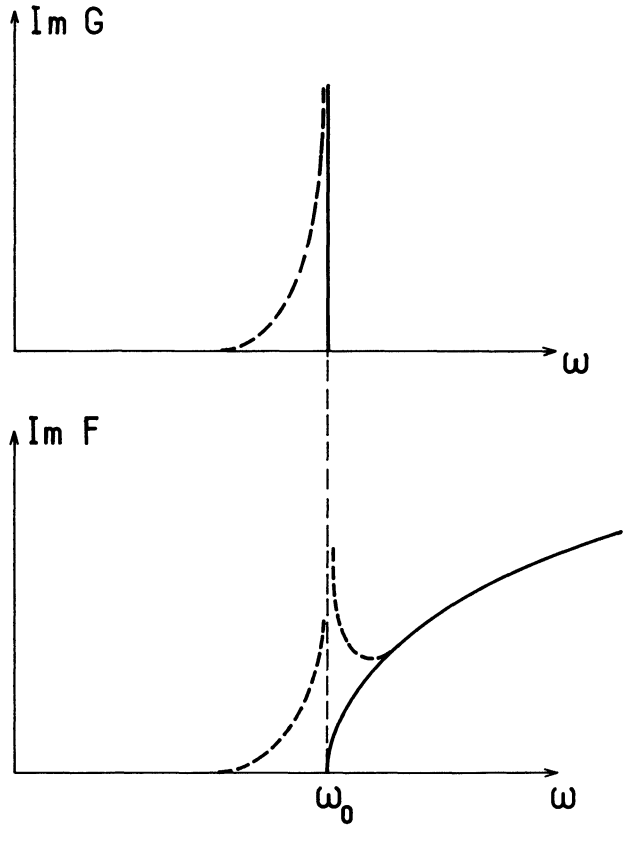

FIG. 2. — The spectrum of $\mathcal{G}$ and $\mathcal{F}$ when $\mu \to 0$, in the absence of bound states. The full line refers to the limit $\mu = 0$, the dotted line to μ small, but finite. The shift of the threshold ω_0 has been ignored in drawing the curves.

The situation is less clear if the potential $V_{kk'}$ of the core hole is strong enough to bind a conduction electron, thereby forming an exciton state. Let us consider only the case of band spectra, and let $|\,\Psi_0\,>$ and $|\,\overline{\Psi_0}\,>$ be the ground state of conduction electrons respectively in the absence and presence of the deep hole. For a strict insulator, the absorption spectrum has the usual form shown on figure 3, the exciton line lying at an energy $-\varepsilon_0 - \varepsilon_B$, where ε_B is the exciton binding energy ; there is no emission, for lack of an electron to fill the deep hole. If a few electrons are introduced in the conduction band, the absorption spectrum should not vary appreciably, as in state $|\,\Psi_0\,>$ these electrons are spread throughout the crystal, far from the excited site. On the other hand, in state $|\,\overline{\Psi_0}\,>$ one of these electrons is in the bound state, and a sharp line should appear at $-\varepsilon_0 - \varepsilon_B$ in the emission spectrum. If μ is small but finite, we expect these spectra to broaden as shown on figure 3,

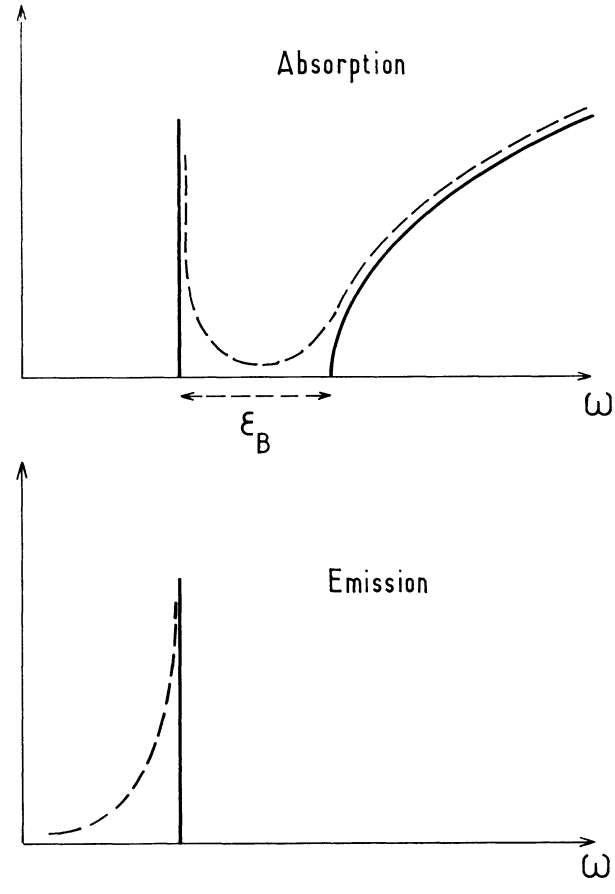

FIG. 3. — Absorption and emission band spectra in the presence of a bound state with binding energy ε_B. The full line refers to $\mu \to 0$ (although not $\equiv 0$ in order to have emission), the dotted line to μ small but finite. The shift of the threshold as μ increases is not taken into account in drawing the dotted curve.

because of the Auger excitation of conduction electrons. We recover « infrared » singularities, which here appear as a broadened exciton line (we note that when $\mu \to 0$, the threshold goes to $-\varepsilon_0 - \varepsilon_B$, not to $-\varepsilon_0$). When μ increases, the threshold shifts, while the gap between exciton and the continuum gradually fills in. It is likely that for $\mu \gg \varepsilon_B$, the influence of the

exciton is no longer noticeable : we recover the usual Fermi edge singularity.

The main purpose of this paper is to clarify the nature of absorption and emission spectra in the presence of a bound exciton : how does the exciton singularity appear in the calculation, where is the threshold, does there remain a discontinuity at the edge of the continuum absorption, what are the critical exponents ? Admittedly, the problem is somewhat academic, in view of the crudeness of the model. We nevertheless feel that these points must be elucidated in order to appreciate the nature of infrared singularities, and the way they evolve when one goes from a conductor to an insulator. Actually, this example belongs to the general problem of inelastic broadening of collective excitations, which is far from trivial. Moreover, in the course of solving this problem, we introduce a new approach, based on a remark of Friedel [10], which is more explicit than the field theoretical method. That, too, sheds some light on the nature of the phenomenon.

If in a given channel there exists a bound state, the corresponding phase shift goes to π at the bottom of the band, instead of zero. The question arises to whether (11) and (13) remain valid in that case. The approach of reference [8] is not appropriate, since it does not specify the determination of δ. Moreover, it relies on the assumption that the one electron propagator $G(r, r', t)$ varies smoothly for large t, because of the destructive interference between various continuum states. This assumption breaks down when there is a bound state, which gives rise to an undamped oscillatory term in G. As it stands, the argument of Hopfield does not help either — first it does not constitute a proof — and also one may wonder whether in (16) n_l should include or not the electron bound to the deep hole. We shall indeed show that (16) is correct if we do include the bound electron — but that must be proved. It turns out that the most convenient method is the one proposed by Friedel in 1952, and described in reference [10]. We shall see how it can be expanded as far as to describe exactly the various singularities.

Let us consider for instance the absorption case, and let H and $\overline{H}$ be the conduction electron hamiltonian in the initial and final states (*i. e.* without and with the scattering potential $V_{kk'}$). As shown by Friedel [10], the propagator $\mathcal{G}(t)$ may be written as

$$\begin{aligned}\mathcal{G}(t) &= - < \Psi_0 \mid b^*(0)\, b(t) \mid \Psi_0 > \\ &= - \mathrm{e}^{-i\varepsilon_0 t} < \Psi_0 \mid \mathrm{e}^{i(\overline{H}-E_0)t} \mid \Psi_0 > \end{aligned} \qquad (18)$$

where E_0 is the ground state energy of H (for an N-electron system). (18) may be expanded on to the eigenstates $\mid \overline{\Psi}_n >$ of $\overline{H}_0$, with energy $\overline{E}_n$, which yields

$$- \mathcal{G}(t)\, \mathrm{e}^{i\varepsilon_0 t} = \sum_n \left| < \Psi_0 \mid \overline{\Psi}_n > \right|^2 \mathrm{e}^{i(\overline{E}_n - E_0)t}. \qquad (19)$$

The calculation of $\mathcal{G}$ is thus reduced to that of the overlap of two Slater determinants, one built with plane wave states, the other with scattering states. It was shown by Anderson [11] that any such matrix elements is exponentially small for large systems : it is the summation over n which yields a finite result — and which in fact constitutes the difficult part of the calculation. In the same way, one may write $\mathcal{F}(t)$ in the form

$$\mathcal{F}(t) = \mathrm{e}^{-i\varepsilon_0 t} \sum_{kk'} W_k\, W_{k'}^* \sum_n < \Psi_0\, c_{k'} \mid \overline{\Psi}_n > \times \\ \times < \overline{\Psi}_n \mid c_k^*\, \Psi_0 > \mathrm{e}^{i(\overline{E}_n - E_0)t}. \qquad (20)$$

(20) resembles (19), but for the fact that there is one more electron in the Slater determinants. According to (19) and (20), the threshold energies correspond to the minimum $\overline{E}_n$. Let $\overline{E}_0 = E_0 + \Delta$ be the ground state energy of $\overline{H}$ for an N-electron system (Δ is the ground state shift given by (11)). It is clear that the threshold are located at

$$\begin{aligned} \omega_0 &= - \varepsilon_0 + \Delta \qquad \text{for} \quad \mathcal{G}(\omega) \\ \omega_0 &= - \varepsilon_0 + \Delta + \mu \qquad \text{for} \quad \mathcal{F}(\omega) \end{aligned} \qquad (21)$$

(in agreement with the field theoretical results).

If $\overline{H}$ possesses a bound state, the eigenstates $\mid \overline{\Psi}_n >$ fall into two classes, depending on whether the bound state is full or empty ; each class gives a continuous spectrum, but with a different threshold. The absolute threshold corresponds to the bound state filled, and is given by (21). The secondary threshold, which corresponds to the bound state empty, is shifted towards higher energies by an amount $(\mu + \varepsilon_B)$. In practice, the secondary threshold will be broadened if we take into account the Coulomb interaction between conduction electrons, which acts to damp the bound states. In our model, however, the two thresholds should be sharply defined, and we may study the nature of the singularity near each of them. In the reverse emission case, the bound state is filled in the initial ground state $\mid \overline{\Psi}_0 >$, and we expect only a single threshold given by (21). Note that when $\mu \to 0$, the absolute threshold corresponds to the exciton state, while the secondary one corresponds to the bottom of the conduction band, as pointed out by Friedel [10].

If the system is enclosed in a spherical box, the one particle eigenstates correspond to definite quantum numbers (l, m, s) both for H and $\overline{H}$. In calculating the overlaps $< \Psi_0 \mid \overline{\Psi}_n >$, it is clear that the different angular momentum and spin channels will be completely decoupled. For simplicity, we consider only a single channel, that where there exists a bound state — say the S-wave channel. From now on, the momentum k will be a scalar refering to the radial part of the wave function. Moreover, we assume that the particles are spinless (we ignore the existence of two spin channels). We are almost forced to this oversimplification by our neglect of the Coulomb interaction between conduction electrons. Such an approximation

was sensible near the Fermi level, where it amounted to a renormalization of a quasiparticles. On the other hand, it becomes very bad far from the Fermi level, especially for the bound state. As it stands, nothing prevents the excited core from accomodating two bound electrons with opposite spins — a situation which would alter drastically the shape of $\mathcal{G}(\omega)$ and $\mathcal{F}(\omega)$. In practice, the repulsion between the bound electrons will very likely prevent the formation of such a double bound state. This could only be included in the theory by using an extended Hartree-Fock scheme, in which the potential felt by spin up electrons depends on the occupancy of spin down states. Since we only wish to achieve a qualitative understanding, such complications do not appear worthwhile, and we choose to ignore spin altogether (an attitude which probably amounts to assuming an infinite repulsion of conduction electrons with opposite spins near the excited site). However crude an approximation, it is not worse than the neglect of the Coulomb interaction between conduction electrons (for instance, the use of a statically screened $V_{kk'}$ is very bad far from the Fermi level).

In order to simplify the algebra, we shall consider only band spectra, and we shall assume that $V_{kk'}$ is separable

$$V_{kk'} = V u_k u_{k'} \tag{22}$$

where u_k is a form factor which accounts for the range of the potential and ensures convergence. We shall also assume that $W_k = u_k$, within a constant factor which can be taken out of $\mathcal{F}$: this is by no means essential, but it makes the calculation easier. With the choice of (22), the scattering states are known explicitly, and the overlaps can be readily evaluated.

II. **Absorption spectrum in the absence of a bound state.** — Our method for calculating the correlation functions $\mathcal{F}$ and $\mathcal{G}$ is best introduced by considering the simplest possible case, that of an absorption experiment in the absence of a final bound state. The initial state $| \Psi_0 >$ in (19) is then a Slater determinant of N *plane waves*, with wave vectors $k < k_F$. Let χ_K be the corresponding one electron wave function : $| \Psi_0 >$ is an $N \times N$ determinant

$$| \Psi_0 > = \frac{1}{\sqrt{N\,!}} \operatorname{Det} \| \chi_K(r_i) \| . \tag{23}$$

Similarly, the final states $| \Psi_n >$ are Slater determinants of *scattering states* $\bar{\chi}_q$ (in the final potential $\bar{V}$). In the expression (19) of $\mathcal{G}$, $| \bar{\Psi}_n >$ involves any combination of N different such states.

Anderson [11] has shown that all the matrix elements $< \Psi_0 | \bar{\Psi}_n >$ are exponentially small — this is the so called « orthogonality catastrophe ». In particular, he evaluated explicitly the overlap of the two ground states, $< \Psi_0 | \bar{\Psi}_0 >$, by an elegant method based on the use of Cauchy determinants ; he thus showed that this overlap behaved as $N^{-\delta^2/2\pi^2}$ when $N \to \infty$. Such an approach, although very concise, is not very useful in evaluating (19) : Anderson's algebra must be carried out for each state $| \bar{\Psi}_n >$, and then the sum over N-body intermediate states is a rather formidable task.

Actually, the matrix elements of $e^{i\bar{H}t}$ can be evaluated directly, if we note that $\bar{H}$ is a sum of *one electron* hamiltonians :

$$\bar{H} = \sum_{i=1}^{N} \bar{h}_i .$$

If in $< \Psi_0 | e^{i\bar{H}t} | \Psi_0 >$ we expand the two Slater determinants (23), we therefore obtain an expression of the form

$$< \Psi_0 | e^{i\bar{H}t} | \Psi_0 > = \frac{1}{N\,!} \sum_{P,P'} (-1)^{p+p'} \times \prod_{i=1}^{N} \int d\tau_i \, \chi^*_{K_i(P)} \, e^{i\bar{h}_i t} \, \chi_{K_i(P')} \tag{24}$$

(where P and P' are any permutation of the N wave vectors $K < K_F$). Clearly, (24) depends only on the relation permutation $P - P'$: the remaining summation cancels the $N\,!$ in the denominator. (24) can thus be cast in the very simple form

$$< \Psi_0 | e^{i\bar{H}t} | \Psi_0 > = \operatorname{Det} \| \Lambda_{KK'} \| \tag{25}$$

where $\Lambda_{KK'}$ is a *one electron* matrix element

$$\Lambda_{KK'} = \int d\tau \chi^*_K \, e^{i\bar{h}t} \, \chi_{K'} . \tag{26}$$

The summation over the N-body states $| \bar{\Psi}_n >$ is completely avoided. (25) appears as a *single* determinant, constructed on the N plane wave states occuped in the ground state $| \Psi_0 >$.

In order to calculate the propagator $\mathcal{G}$ given by (19), we must shift the energies by an amount

$$E_0 = \sum_{K<K_F} \varepsilon_K .$$

We see at once that

$$\begin{cases} -\mathcal{G}(t) \, e^{i\varepsilon_0 t} = \operatorname{Det} \| \lambda_{KK'} \| = \rho \\ \lambda_{KK'} = e^{-i\varepsilon_K t} \Lambda_{KK'} = \int d\tau \chi^*_K \, e^{i(\bar{h}-\varepsilon_K)t} \, \chi_{K'} . \end{cases} \tag{27}$$

Note that $\bar{h}$ is the one electron hamiltonian *after* the transition, while χ_K is an eigenstates of the corresponding operator h *behore* the transition. If $\bar{h}$ were equal to h, λ would be a unit matrix ; because of the final state interaction, λ is not diagonal, and ρ is a complicated function of t.

The response function $\mathcal{F}$ given by (20), can be calculated along similar lines. It is easily verified that

$$\mathcal{F}(t) \, e^{i\varepsilon_0 t} = \sum_{pp'} u_p \, u_{p'} \, e^{i\varepsilon_p t} \, \rho_{pp'} \tag{28}$$

where $\rho_{pp'}$ is again a determinant of matrix elements $\lambda_{kk'}$, but this time of dimension $(N+1) \times (N+1)$. It rows are labelled by the N states $K < K_F$ *and* by p, its columns by the states $k < k_F$ *and* by p' (*). (Note that the summation over p and p' may be extended to all space, since the determinant $\rho_{pp'}$ automatically vanishes if p or $p' < K_F$.) We expand the determinant $\rho_{pp'}$ along the last row and column, in the usual way, which yields

$$\rho_{pp'} = \lambda_{pp'} - \sum_{K,K' < K_F} \lambda_{pK} A_{KK'} \lambda_{K'p'}$$

where $A_{KK'}$ is the minor obtained from the $N \times N$ matrix λ by suppressing the row K and column K'. If we note that $A_{KK'}/\rho$ is just the K, K' element of the inverse $N \times N$ matrix λ^{-1}, we see that $\mathcal{F}$ takes the simple form

$$\mathcal{F} = L\mathcal{G}$$

$$L = - \sum_{pp'} u_p u_{p'} e^{i\varepsilon_p t} [\lambda_{pp'} - \lambda_{pK} (\lambda^{-1})_{KK'} \lambda_{K'p'}] . \quad (29)$$

As expected, $\mathcal{F}$ has the form (9), the « open line » contribution being simply expressed in terms of λ^{-1}. In order to complete the comparison with the field theoretical approach, we note that

$$\mathrm{Log}\, \rho = \mathrm{Log} \parallel \mathrm{Det}\, \lambda \parallel = \mathrm{Tr} \{ \mathrm{Log}\, \lambda \} . \quad (30)$$

On comparing with (8), we see that the « closed loop » contribution c is simply the trace of the $N \times N$ matrix Log λ. It follows from (30) that

$$\frac{dC}{dt} = \mathrm{Tr} \left\{ \lambda^{-1} \frac{d\lambda}{dt} \right\} . \quad (31)$$

We are thus left with the mathematical problem of inverting the $N \times N$ matrix λ.

Our first task, of course, is to calculate $\lambda_{KK'}$. This can be done by inserting in the middle of (27) a complete set of scattering states $\bar{\chi}_p$ (including the bound state when it exists : see section III). Let x_p^k be the overlap of $\bar{\chi}_p$ and χ_K : (27) becomes

$$\lambda_{KK'} = \sum_p x_p^{K*} x_p^{K'} e^{(\bar{\varepsilon}_p - \varepsilon_K)t} . \quad (32)$$

The overlap x_p^K is calculated in appendix A, and is given by (A.11) ; in general, the summation in (32) cannot be performed explicitly. Let us however consider the asymptotic limit of *large t* (specifically, $\varepsilon_F t \gg 1$). Because of *destructive interference*, the summation in (32) is controlled by the region $p \approx k \approx k'$, in which the factors x are singular (put another way, $\lambda_{KK'}$ is negligible unless $k \approx k'$). We may then replace x_p^K and $x_p^{K'}$ by their approximate form (A.12) ; moreover, the slowly varying factors δ_p and v_p may be replaced by δ_K and v_K (or by $\delta_{K'}$ and $v_{K'}$ which are the same when $k \approx k'$). (32) thus becomes

$$\lambda_{KK'} = \frac{\sin^2 \delta_K}{\pi^2} \sum_p \frac{e^{i(p - K - \delta_K/\pi)\tau}}{(p - K - \delta_K/\pi)(p - K' - \delta_K/\pi)} \quad (33)$$

(with $\tau = t/v_K$). The summation over p converges rapidly, and can be extended from $-\infty$ to $+\infty$: it is then readily evaluated by Poisson's formula, which yields for the matrix

$$\left\{ \begin{array}{l} \lambda = \mathbf{1} - \mathbf{X} \\ X_{KK'} = \dfrac{\sin \delta_K \, e^{-i\delta_K}}{\pi v_K} \dfrac{1 - e^{i(\varepsilon_{K'} - \varepsilon_K)t}}{\varepsilon_K - \varepsilon_{K'}} . \end{array} \right. \quad (34)$$

(34) is the central result of this paper, on which all subsequent calculations will be based. Let us emphasize again that it is only valid for large t, when destructive interference acts fully. (The fact that (34) yields the exact result $\mathbf{X} = 0$ when $t = 0$ is accidental, and will not remain true when there is a bound state.) Such an approximation only provides the qualitative nature of the spectrum in a narrow frequency range around the singularities ; it gives no information on the general behaviour far from the thresholds. The extent to which this limitation can be released is briefly discussed in Appendix B.

In the weak coupling limit ($\delta \ll \pi$), $\mathbf{X}$ is small quantity, and we may calculate λ^{-1} (as well as log λ) as a power series in $\mathbf{X}$. In order to gain some insight into the structure of the result, let us consider the first terms of the expansion of $C = \mathrm{Log}\, \rho$ (see eq. (30)). The lowest contribution is

$$C^{(1)} = - \sum_K X_{KK} = - it \sum_K \frac{\sin \delta_K}{\pi v_K} e^{-i\delta_K}$$

$$= - \frac{it}{\pi} \int_0^\mu \sin \delta \, e^{-i\delta} \, d\varepsilon \quad (35)$$

(where μ is the Fermi energy). For small phase shifts, $\sin \delta \, e^{-i\delta} \approx \delta$: on comparing with (8), (10) and (11), we see that (35) is nothing but the leading part of the *threshold shift* Δ. More generally, this shift will arise from those terms of C which are linear in t. If we proceed to second order, we find

$$C^{(2)} = - \frac{1}{2} \sum_{KK'} X_{KK'} X_{K'K}$$

$$= \int_0^\mu d\varepsilon \, d\varepsilon' \frac{\sin^2 \delta \, e^{-2i\delta}}{\pi^2} \frac{1 - \cos(\varepsilon - \varepsilon')t}{(\varepsilon - \varepsilon')^2} . \quad (36)$$

Were it not for its finite range (from 0 to μ), the ε'-integration would yield a factor t, thereby providing a further contribution to the threshold Δ. In addition to that term, there appears corrections due to « edge » effects, in the range $\varepsilon, \varepsilon' \approx \mu$. (The other limit $\varepsilon, \varepsilon' \approx 0$ is unimportant, as sin δ is then negligibly small.)

(*) The notation K is systematically used for the N momenta $< K_F$, while p refers to an arbitrary momentum, $>$ or $< k_F$.

Detailed calculation shows that in the limit of large t, $C^{(2)}$ behaves as

$$C^{(2)} = \frac{t}{\pi} \int_0^{\mu} d\varepsilon \sin^2 \delta(\varepsilon)\, e^{-2i\delta(\varepsilon)} - \\ - \operatorname{Log} t \frac{\sin^2 \delta\, e^{-2i\delta}}{\pi^2} \quad (37)$$

(with here $\delta = \delta(\mu)$). The first term of (37) contributes to the threshold shift Δ. The second term gives rise to the characteristic power behaviour of $\mathfrak{G}$ near threshold : indeed, the coefficient of Log t is just the lowest order approximation to the exact exponent (12).

The structure (37) persists to all higher orders : the term $C^{(n)}$ contains a part linear in t, which contributes to Δ, and a term $\sim$ Log t, which contributes to the exponent β. If we were able to sum the full series, we would get exact results for these quantities. Actually, this summation can be performed easily for the linear term, in a way which sheds some light on the convergence of the expansion. For large t, $X_{KK'}$ is negligible unless $\varepsilon_K \approx \varepsilon_K$, which allows us to write

$$\begin{cases} C = \operatorname{Tr} \log (1 - X) \\ \quad = - \sum_{n=1}^{\infty} \int_0^{\mu} \frac{d\varepsilon_1}{n} \left(\frac{\sin \delta_1\, e^{-i\delta_1}}{\pi} \right)^n a_n \\ a_n = \int_0^{\mu} d\varepsilon_2 \dots d\varepsilon_n\, f(\varepsilon_1 - \varepsilon_2) \dots f(\varepsilon_n - \varepsilon_1) \\ f(\varepsilon) = \dfrac{1 - e^{-i\varepsilon t}}{\varepsilon} . \end{cases} \quad (38)$$

When calculating the leading linear term, we may neglect edge effects and extend the integration from $-\infty$ to $+\infty$ in the expression of a_n : a_n thus appears as the n^{th} convolution of f :

$$a_n = f(\varepsilon = 0) .$$

The Fourier transform of f is

$$f(\tau) = \begin{cases} 2i\pi & \text{if } 0 < \tau < t \\ 0 & \text{otherwise} \end{cases}$$

from which it follows that

$$a_n = (2i\pi)^{n-1}\, it . \quad (39)$$

Inserting (39) into (38), we find

$$C \sim - \frac{t}{2\pi} \int_0^{\mu} d\varepsilon_1 \sum_{n=1}^{\infty} \left(\frac{1 - e^{-2i\delta_1}}{n} \right)^n . \quad (40)$$

The series in (40) converges if $| 1 - e^{-2i\delta_1} | < 1$; its sum is then equal to

$$- \operatorname{Log} [1 - (1 - e^{-2i\delta_1})] = 2i\tilde{\delta}_1$$

$$\tilde{\delta}_1 = \begin{cases} \delta_1 & \text{if } 0 < \delta_1 < \dfrac{\pi}{6} \\ \delta_1 - \pi & \text{if } \dfrac{5\pi}{6} < \delta_1 < \pi . \end{cases} \quad (41)$$

(In the intermediate range $(\pi/6, 5\pi/6)$, the determination $\tilde{\delta}_1$ cannot be deduced from a series expression). To the extent that the series convergences in the whole range $0 < \varepsilon_1 < \mu$, we recover the *exact* result (11), which is obtained by replacing $\sin \delta\, e^{-i\delta}$ by the phase shift $\tilde{\delta}$ in the first order expression (35). We shall use this result later when discussing the appropriate determination of phase shift.

A similar calculation of the exponent β appears very difficult. Instead, we shall try to invert the matrix $\mathbf{1} - \mathbf{X}$ directly, by a method closely related to that of reference [8]. We note that the matrix element of $\mathbf{X}$ can be written as

$$X_{KK'} = \frac{i \sin \delta_K}{\pi \nu_K} e^{-i\delta_K} \int_0^t e^{-i(\varepsilon_K - \varepsilon_{K'})\tau}\, d\tau . \quad (42)$$

The fact that $X_{KK'}$ is separable before the τ integration suggests that we try a solution of the form

$$(\lambda^{-1})_{KK'} = \delta_{KK'} + \frac{i \sin \delta_K\, e^{-i\delta_K}}{\pi \nu_K} \times \\ \times \int_0^t d\tau\, d\tau'\, e^{i(\varepsilon_{K'}\tau' - \varepsilon_K \tau)}\, \varphi(\tau, \tau') \quad (43)$$

where φ is at the moment an unknown function. The condition $\lambda\lambda^{-1} = 1$ is satisfied if

$$\varphi(\tau, \tau') = \delta(\tau - \tau') + \int_0^t g(\tau - \tau'')\, \varphi(\tau'', \tau')\, d\tau'' \quad (44)$$

where we have set

$$g(\tau) = \sum_k \frac{i \sin \delta_K}{\pi \nu_K} e^{-i\delta_K} e^{i\varepsilon_K \tau} \\ = \int_0^{\mu} \frac{i \sin \delta}{\pi} e^{-i\delta} e^{i\varepsilon\tau}\, d\varepsilon . \quad (45)$$

The inversion of λ is thus *exactly* reduced to the solution of the integral equation (45) — a problem very similar to that encountered in reference [8].

If the integral in (44) extended from $-\infty$ to $+\infty$, the solution would have the form

$$\varphi_\infty(\tau, \tau') = \delta(\tau - \tau') + \tilde{g}(\tau - \tau') .$$

$\tilde{g}$ is easily obtained by a Fournier transform. Indeed, it follows from (45) that

$$g(\varepsilon) = (1 - e^{-2i\delta})\, \theta(\mu - \varepsilon)$$

and therefore

$$\tilde{g}(\varepsilon) = \frac{g}{1 - g} = (e^{2i\delta} - 1)\, \theta(\mu - \varepsilon) . \quad (46)$$

Because of the finite boundaries in (44), φ departs from φ_∞ : these « edge effects » can only be calculated approximately.

In the limit of large τ, $g(\tau)$ and $\tilde{g}(\tau)$ are controlled by the discontinuity of their spectrum at $\varepsilon = \mu$. If we

average out rapid oscillations near $\tau = 0$, they can be replaced by their asymptotic form [8]

$$\begin{cases} \gamma(\tau) = e^{i\mu\tau} \dfrac{\sin\delta}{\pi} e^{-i\delta} \dfrac{1}{\tau - i\varepsilon} \\ \tilde{\gamma}(\tau) = e^{i\mu\tau} \dfrac{\sin\delta}{\pi} e^{i\delta} \dfrac{1}{\tau - i\varepsilon} . \end{cases} \tag{47}$$

In (47), $\delta = \delta(\mu)$ is the phase shift at the Fermi level. When g is replaced by γ, (44) takes the form of a standard singular integral equation, equivalent to a Hilbert problem. The corresponding solution may be found in the book of Mushkelishvili [12] ; we shall not go through the algebra, which is standard : we only quote the result (see [8])

$$\varphi(\tau - \tau') = \delta(\tau - \tau') + \tilde{\gamma}(\tau - \tau') \left[\frac{\tau(t - \tau')}{\tau'(t - \tau)}\right]^{\tilde{\delta}/\pi} . \tag{48}$$

$\tilde{\delta} = \delta + k\pi$ is a determination of the Fermi surface phase shifts which is still unspecified. As expected, φ reduces to φ_∞ if $0 \ll \tau, \tau' \ll t$: the edge effects are entirely contained in the last factor of (48).

Actually, (48) is not yet the correct solution ; as it remains singular near $\tau = \tau'$: as a consequence, the replacement of g by γ in (44) is not a satisfactory approximation when $\tau \sim \tau'' \sim \tau'$; put another way, (48) does not account correctly for the « local » behaviour near $\tau = \tau'$. That difficulty can be by-passed if we consider the difference $\varphi - \varphi_\infty$: to the extent that edge effects are small for large t, the difference should be regular when $\tau \sim \tau'$, and the corresponding region should contribute a negligible amount to the integral

$$\int_0^t g(\tau - \tau'') \left[\varphi(\tau'', \tau') - \varphi_\infty(\tau'' - \tau')\right] d\tau'' .$$

In that integral, the replacement of g by γ is thus permissible : the asymptotic solution is correct for $(\varphi - \varphi_\infty)$, although not for φ. We are thus led to replace (48) by the more accurate result

$$\varphi(\tau, \tau') = \delta(\tau - \tau') + \tilde{g}(\tau - \tau') + \tilde{\gamma}(\tau - \tau') \left\{ \left[\frac{\tau(t - \tau')}{\tau'(t - \tau)}\right]^{\tilde{\delta}/\pi} - 1 \right\} \tag{49}$$

(49), which is only valid for large t ($\mu t \gg 1$), constitutes the basis of our approximation solution.

We now turn to the actual solution of our problem. We begin with the open line contribution L, which is somewhat simpler to calculate. As shown in Appendix A, the first term of (29) is negligible in the limit of large t (it behaves as $t^{-3/2}$). The sums over p and p' appearing in the second term of (29) are evaluated in (A.17) ; we thus obtain

$$L = \sum_{KK'} \frac{\sin\delta_K \, e^{-i\delta_K}}{\pi v_K u_K V} e^{+i\varepsilon_K t} (\lambda^{-1})_{kk'} \frac{\sin\delta_{K'} \, e^{-i\delta_{K'}}}{\pi v_{K'} u_{K'} V} . \tag{50}$$

We now replace λ^{-1} by its expression (43). In the summation over k and k', the main asymptotic contribution comes from the vicinity of the Fermi level, so that we can neglect the k dependence of δ, v and u. Using the definition (45) of g, we may cast (50) in the form

$$L = - \frac{i \sin\delta \, e^{-i\delta}}{\pi v u^2 V^2} \times \times \left[g(t) + \int_0^t d\tau \, d\tau' \, \varphi(\tau, \tau') \, g(\tau') \, g(t - \tau) \right] . \tag{51}$$

From the integral equation (44) obeyed by φ, it follows that

$$L = \frac{- i \sin\delta \, e^{-i\delta}}{\pi v u^2 V^2} \varphi(t, 0) . \tag{52}$$

When φ is replaced by the solution (48), or (49), we obtain

$$L \sim \frac{e^{i\mu t}}{t} (\xi_0 \, t)^{2\tilde{\delta}/\pi} \tag{53}$$

where ξ_0 is a cut off $\sim \mu$, arising from our asymptotic approximation. (53) is exactly the result of reference [8].

The « closed-loop » contribution C is given by (30). It turns out that the relation (31) cannot be used within our asymptotic approximation. Instead, we assume that the interaction is changed infinitesimally in such a way that the phase shifts vary by an amount

$$d\delta_K = \sin\delta_K \, e^{i\delta_K} \, d\alpha . \tag{54}$$

The corresponding variations of the matrix $\mathbf{X}$ and of C are

$$\begin{cases} d\mathbf{X} = \mathbf{X} \, d\alpha \\ dC = - \operatorname{Tr}(\lambda^{-1} \, d\mathbf{X}) = - \operatorname{Tr}(\lambda^{-1} - \mathbf{1}) \, d\alpha . \end{cases} \tag{55}$$

We replace λ^{-1} by its expression (43), and carry the momentum sum, making use of (45) : we thus obtain

$$dC = - \int_0^t d\tau \, d\tau' \, \varphi(\tau, \tau') \, g(\tau' - \tau) \, d\alpha . \tag{56}$$

From (44), it follows that

$$\begin{cases} dC = - \int_0^t d\tau \, \bar{\varphi}(\tau, \tau') \, d\alpha \\ \bar{\varphi}(\tau, \tau') = \varphi(\tau, \tau') - \delta(\tau - \tau') . \end{cases} \tag{57}$$

The quantity $\bar{\varphi}(\tau, \tau)$ is readily obtained from (49) ; replacing $\tilde{g}$ and $\tilde{\gamma}$ by their expressions (46) and (47), we find

$$\bar{\varphi}(\tau, \tau) = \int_0^\mu \frac{i \sin\delta_K \, e^{i\delta_K}}{\pi} d\varepsilon_K + + \sin\delta \, e^{i\delta} \frac{\tilde{\delta}}{\pi^2} \left[\frac{1}{\tau} + \frac{1}{t - \tau}\right] . \tag{58}$$

We can now carry the τ integration in (57) ; making use of (54), we see that

$$dC = -it \int_0^{\mu} \frac{d\delta_K}{\pi} d\varepsilon - \frac{2\,\tilde{\delta}\,d\delta}{\pi^2} \text{Log}\,(\xi_0\, t)\,. \quad (59)$$

If we assume that the determination $\tilde{\delta}$ remains the same throughout the range of integration over $d\delta_K$, (59) yields at once

$$C = -it \int_0^{\mu} \frac{\tilde{\delta}_K}{\pi} d\varepsilon - \frac{\tilde{\delta}^2}{\pi^2} \text{Log}\,(\xi_0\, t)\,. \quad (60)$$

(60) is the generalization to all orders of the approximation results (35) and (37). The first term corresponds to the shift of the threshold Δ, and agree with (11) (remember that here we ignore spin) ; the second term gives rise to the infrared catastrophy of $\mathcal{G}$, and agrees with (12). We recover exactly the results of reference [8], which need no further discussion.

The only point which needs to be clarified is the choice of the determination $\tilde{\delta}$. For weak coupling, the phase shift δ_K remains $< \pi/6$ in the whole range $(0, \mu)$; the same conclusion holds for strong coupling if μ is small enough *and if* there exists no bound state (in which case $\delta_K \to 0$ when $\varepsilon_K \to 0$). According to our previous discussion, the perturbation expansion in powers of $\sin\delta\, e^{-i\delta}$ should then converge, and the determination to be chosen is $\tilde{\delta} = \delta$. If the coupling is strong and μ large, δ_K may exceed $\pi/6$ at the Fermi level : $\tilde{\delta}$ remains undetermined. We can however invoke a continuity argument : it is hard to imagine how increasing μ could lead to a discontinuous change of $\tilde{\delta}$ (and of the exponent β in (10)). Somehow, the nature of the infrared singularity should vary continuously with the electron density. We are thus led to *assume* that *in the absence of a bound state* $\tilde{\delta}$ is equal to δ whatever μ, thereby extrapolating the low density result. (As shown in section III, this is not true when there is a bound state.) With such a choice, $\mathcal{G}(\omega)$ has a threshold at $(\varepsilon_0 - \Delta)$, where Δ is the change of ground state energy due to the final potential ; near the threshold it has the form (1) with an exponent α given by Hopfield's rule (16) (the displaced charge (17) involves the *real* phase shift δ). The threshold of $\mathcal{F}$ lies at $(\varepsilon_0 + \mu - \Delta)$, and the corresponding exponent is again given by (16) : we recover all the results quoted in the introduction.

III. **Influence of a bound electron in the final state.** — We now assume that the final state potential in an absorption experiment is strong enough to bind a conduction electron. This bound state is necessary in order to produce, together with the scattering states, a *complete* basis of one electron wave functions. Consequently, the matrix element $\lambda_{KK'}$, given by (32), acquires a new term, and we may write

$$\boldsymbol{\lambda} = \mathbf{1} - \mathbf{X} + \mathbf{Y} \quad (61)$$

$\mathbf{X}$ is the contribution of scattering states, given by the same expression (34) as in the preceding section, while

$$Y_{kk'} = \frac{\alpha_B^2\, u_K\, u_{K'}}{(\varepsilon_B - \varepsilon_K)\,(\varepsilon_B - \varepsilon_{K'})}\, e^{i(\varepsilon_B - \varepsilon_K)t} \quad (62)$$

is that of the bound state (with energy ε_B, normalization constant α_B given by (A.14)). We note that Y is a *separable* matrix, of the form

$$\begin{cases} Y = \bar{\mathbf{y}} \otimes \mathbf{y} \\ y_{k'} = \dfrac{\alpha_B\, u_{K'}}{\varepsilon_B - \varepsilon_{K'}} \\ \bar{y}_K = y_K\, e^{i(\varepsilon_B - \varepsilon_K)t}\,. \end{cases} \quad (63)$$

This feature will allow an *exact* treatment of the bound state part, which is fortunate since $Y_{KK'}$ oscillates rapidly with t and does not lend itself to the asymptotic method introduced previously.

Let us consider for instance the propagator $\mathcal{G}$ given by (27). With the same notations as before, we may write

$$C = \text{Log}\,\rho = \text{Tr Log}\,[\mathbf{1} - \mathbf{X} + \mathbf{Y}]\,. \quad (64)$$

Keeping in mind that

$$\text{Tr Log}\,\mathbf{AB} = \text{Tr Log}\,\mathbf{A} + \text{Tr Log}\,\mathbf{B}\,,$$

we obtain

$$C = \text{Tr Log}\,(\mathbf{1} - \mathbf{X}) + \text{Tr Log}\left[\mathbf{1} + \frac{1}{\mathbf{1} - \mathbf{X}}\,\bar{\mathbf{y}} \otimes \mathbf{y}\right]. \quad (65)$$

The first term of (65) is the contribution C_S of scattering states alone. The fact that Y is separable permits an explicit calculation of the second term : on expanding the logarithm, we verify that

$$\text{Tr Log}\left[\mathbf{1} + \frac{1}{\mathbf{1} - \mathbf{X}}\,\bar{\mathbf{y}} \otimes \mathbf{y}\right] = \text{Log}\left[1 + \langle y \,|\, \frac{1}{1 - X} \,|\, \bar{y} \rangle\right].$$

The net propagator $\mathcal{G}$ is thus given *exactly* by

$$\mathcal{G} = \mathcal{G}_S\left[1 + \sum_{KK'} \left(\frac{1}{1 - X}\right)_{KK'} y_K\, \bar{y}_{K'}\right] = \mathcal{G}_S[1 + A_B]\,. \quad (66)$$

The influence of the bound state is entirely contained in the second term of the bracket, A_B.

It is interesting to note that the result (66) can also be obtained by expanding the determinant ρ in powers of $e^{i\varepsilon_B t}$. The zeroth order term is of course $\mathcal{G}_S$. The first order term can be cast in the form (66) by using the relationship between the minors of ρ and the elements of the inverse matrix $(1 - X)^{-1}$. The higher order terms cancel out when all the various combinations of wave vectors are taken into account : this

was to be expected since the bound state can only be occupied once in the N-body intermediate states.

According to section II, the « continuum » part $\mathcal{G}_S$ behaves as

$$\mathcal{G}_S \sim \frac{e^{-i(\varepsilon_0 - \tilde{\Delta})t}}{(\xi_0 t)^{\delta^2/\pi^2}}$$
$$\tilde{\Delta} = -\int_0^\mu \frac{\tilde{\delta}(\varepsilon)}{\pi} d\varepsilon \qquad (67)$$

where $\tilde{\delta}(\varepsilon)$ is a determination of the phase shift which for the moment we do not specify. In order to calculate A_B, we use the expression (43) of $(1 - X)^{-1}$, which leads to

$$A_B = \sum_k \frac{\alpha_B^2 u_K^2}{(\varepsilon_B - \varepsilon_K)^2} e^{i(\varepsilon_B - \varepsilon_K)t} +$$
$$+ \sum_{KK'} \frac{\alpha_B^2 u_K u_{K'}}{(\varepsilon_B - \varepsilon_K)(\varepsilon_B - \varepsilon_{K'})} e^{i(\varepsilon_B - \varepsilon_{K'})t} \frac{i \sin \delta_K}{\pi \nu_K} e^{-i\delta_K} \times$$
$$\times \int_0^t d\tau\, d\tau'\, \varphi(\tau, \tau')\, e^{i(\varepsilon_{K'}\tau' - \varepsilon_K \tau)}. \qquad (68)$$

For large times t, the integrals are controlled by the region $\varepsilon_K, \varepsilon_{K'} \approx \mu$, in which $u_K = u$, $\varepsilon_K = \mu$, $\delta_K = \delta$. We can then perform the momentum sums in (68), and we find (using the expression (45) of g) :

$$A_B = \frac{\alpha_B^2 u^2}{(\varepsilon_B - \mu)^2} e^{i\varepsilon_B t} \left[\frac{i\nu}{t} e^{-i\mu t} + \right.$$
$$\left. + \frac{\pi \nu}{i \sin \delta} e^{i\delta} \int_0^t d\tau\, d\tau'\, g(-\tau)\, \varphi(\tau, \tau')\, g(\tau' - t) \right]. \qquad (69)$$

From the equation (44) obeyed by φ, it follows that the integral in (69) is just the difference

$$\varphi(0, t) - g(-t) ;$$

the part $-g(-t)$ cancels out the first term in the bracket. Using the solution (48) for φ, we obtain the explicit result, valid for large t :

$$A_B \sim \text{Cte} \frac{e^{i(\varepsilon_B - \mu)t}}{t(\xi_0 t)^{2\delta/\pi}}. \qquad (70)$$

In order to obtain explicit results, we must now specify the determination $\tilde{\delta}$ of the phase shift to be used. We shall rely on an argument similar to that of section II. When $\varepsilon_K \to 0$, the *real* phase shift δ_K goes to π when there is a bound state. If μ is small enough, δ_K will certainly remain in the range $5/6 - \pi$ when ε_K varies between 0 and μ. We then know from our perturbation expression (41) that $\tilde{\delta} = \delta - \pi$ at least for the threshold shift Δ : we *assume* that the same determination holds for the exponent β. If μ increases, $\delta(\mu)$ will eventually lie below $5\pi/6$, and the series expansion will not converge. We may nevertheless invoke the *continuity* of the determination $\tilde{\delta}$ as a function of μ : one hardly sees how $\tilde{\delta}$ could jump suddenly for a critical μ. We thus claim that in the presence of a bound state $\tilde{\delta} = \delta - \pi$, whatever the Fermi level μ.

We are now in a position to collect our results. The spectrum of $\mathcal{G}$ possesses two thresholds.

(i) An *absolute threshold*, arising from $\mathcal{G}_S$ A_B, and corresponding to the case where the final bound state is filled. That threshold is displaced by an amount

$$\Delta_1 = \tilde{\Delta} + \varepsilon_B - \mu = \varepsilon_B - \int_0^\mu \frac{\delta}{\pi} d\varepsilon$$
$$= -\int_{-\infty}^\mu \frac{\delta}{\pi} d\varepsilon \qquad (71)$$

(remember that $\delta(\varepsilon)$ jumps from π to 0 at the bound state energy ε_B). (71) is just the usual result giving the difference between the initial and final ground state energies — which of course was to be expected. The exponent β defined in (10) is given by

$$\beta_1 = \frac{\tilde{\delta}^2}{\pi^2} + 1 + \frac{2\tilde{\delta}}{\pi} = \frac{\delta^2}{\pi^2}. \qquad (72)$$

According to Friedel, δ/π is the net number n_1 of particles brought near the impurity by the final potential V in the ground state : we see that $\beta_1 = n_1^2$, in accordance with Hopfield's rule of thumb. What is important is therefore the *total* number of displaced electrons, including the bound one, and not only those displaced in the continuum.

(ii) A *secondary threshold*, arising from $\mathcal{G}_S$, corresponds to final states in which the bound state is empty. It is displaced by an amount

$$\Delta_2 = \tilde{\Delta} = \Delta_1 + \mu - \varepsilon_B \qquad (73)$$

(the difference $\Delta_2 - \Delta_1$ being the energy required to excite the bound electron to the lowest empty state of the conduction band). The corresponding exponent is

$$\beta_2 = \frac{\tilde{\delta}^2}{\pi^2} = \left(\frac{\delta}{\pi} - 1\right)^2. \qquad (74)$$

Since the bound electron is absent, the excess localized charge is then $n_2 = \delta/\pi - 1$: again, we have $\beta_2 = n_2^2$.

Near the two thresholds, the Fourier transform $\mathcal{G}(\omega)$ has the form (1), with exponents $\alpha_{1,2} = 1 - \beta_{1,2}$. The shape of the (line) absorption spectrum is sketched on figure 4. Actually, the secondary threshold is broadened by the Coulomb interaction between conduction electrons. In our model, $0 < \delta < \pi$, and thus α_1 and α_2 are both positive.

It is interesting to consider the limit $\mu \to 0$ (*i. e.* the transition toward the insulator). The phase shift δ at the Fermi surface is then close to π : α_1 is very small, while α_2 is close to 1. The singularity at the absolute threshold Δ_1 is very mild — indeed, this whole part of the spectrum is vanishingly small when $\mu \to 0$; this could be expected, as in that case there one very few conduction electrons near the excited site : the

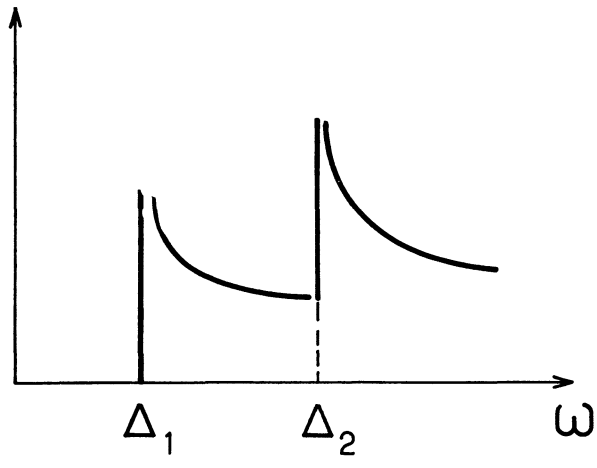

FIG. 4. — The spectrum of $\mathcal{G}(\omega)$ in the absorption case, when there exists a bound state in the final potential. Note that the secondary threshold at Δ_2 would be broadened by the Coulomb interaction between conduction electrons.

chance to find one of them available to fill the localized bound state is negligible (put another way, the overlap of the bound state with the initial conduction electron density is very small). The secondary threshold Δ_2, on the other hand, is very close to a δ-function, which gathers most of the spectrum of $\mathcal{G}$. Physically, that means that the readjustment of the conduction electrons plays a minor role — essentially because dilute electrons are too far from the excited site to feel its final state potential. Our conclusions thus agree fully with physical intuition.

A similar analysis may be carried out for the function $\mathcal{F}$ characterizing band absorption spectra, given by (29). For that purpose, we need to invert

$$\lambda = \mathbf{1} - \mathbf{X} + \mathbf{Y} .$$

On expanding in powers of $\mathbf{Y} = \bar{\mathbf{y}} \otimes \mathbf{y}$, we obtain the *exact* result

$$\lambda^{-1} = \lambda_S^{-1} - \frac{\lambda_S^{-1} \mid \bar{y} > < y \mid \lambda_S^{-1}}{1 + A_B} \qquad (75)$$

where $\lambda_S = \mathbf{1} - \mathbf{X}$ is the part of λ due to the continuum of scattering states. It is then straightforward to collect the various parts of the factor L in (29), making use of the relation (A.17). We shall not go through the algebra, which is easy, but tedious. We find that*

$$L = L_S - \frac{\alpha_B^2}{V^2} \frac{e^{i\varepsilon_B t}}{1 + A_B} \times$$

$$\times \left[1 + \sum_{KK'} \frac{u_K}{\varepsilon_B - \varepsilon_K} \frac{\sin \delta_{K'} \, e^{-i\delta_{K'}}}{\pi \nu_{K'} \, u_{K'}} (\lambda_S^{-1})_{KK'}\right]^2 . \qquad (76)$$

(*) In deriving (76), we need the fact that $e^{i\varepsilon_K t}(\lambda_S^{-1})_{KK'}$ is symmetric under the interchange $K \to K'$.

L_S is the contribution found in section II in the absence of bound states,

$$L_S \sim \frac{1}{t} (\xi_0 \, t)^{2\tilde{\delta}/\pi} e^{i\mu t} . \qquad (77)$$

Using the expression (43) of λ_S^{-1}, as well as the equation (44) obeyed by $\varphi(\tau, \tau')$, one finds that the second term in the bracket of (76) is independent of t and of order 1. Disregarding an unlikely cancellation with the first term 1, the whole bracket of (47) is a number of order unity, denoted as a.

The physical response function governing band spectra is thus

$$\mathcal{F} = L\mathcal{G} = \mathcal{G}_S \left[L_S + L_S A_B - a \frac{\alpha_B^2}{V^2} e^{i\varepsilon_B t}\right] \qquad (78)$$

(see (66) and (76)). Using (70) and (77), we see that the term

$$L_S A_B \sim \frac{e^{i\varepsilon_B t}}{t^2}$$

is negligible as compared to the last term in the bracket of (78). The absorption band spectrum thus contains two parts.

(i) An *absolute* threshold arising from the last term of (78) located at

$$\omega_1 = \varepsilon_B + \tilde{\Delta} = \Delta_1 + \mu . \qquad (79)$$

In that case, the absorption process leaves the bound state occupied.

The corresponding part of $\mathcal{F}(t)$ behaves as $t^{-\gamma_1}$, with

$$\gamma_1 = \frac{\tilde{\delta}^2}{\pi^2} = \left(\frac{\delta}{\pi} - 1\right)^2 . \qquad (80)$$

Once more, $\gamma_1 = n_1^2$, where n_1 is the excess localized charge which, together with the conduction electron created by the X-ray, is required to achieve the new equilibrium.

(ii) A *secondary* threshold, due to the first term of (78), and located at

$$\omega_2 = \mu + \tilde{\Delta} = \omega_1 + \mu - \varepsilon_B . \qquad (81)$$

That part corresponds to excited states in which the bound state is empty, the corresponding electron being in some empty state of the continuum ($\varepsilon_p \geqslant \mu$). The corresponding part of $\mathcal{F}(t)$ has an exponent

$$\gamma_2 = \frac{\tilde{\delta}^2}{\pi^2} + 1 - 2\frac{\tilde{\delta}}{\pi} = \left(\frac{\tilde{\delta}}{\pi} - 1\right)^2 = \left(\frac{\delta}{\pi} - 2\right)^2 . \qquad (82)$$

Here again $\gamma_2 = n_2^2$, since out of the δ/π localized extra conduction electrons, one is removed because the bound state is empty, and another one is supplied by the X-ray process.

Near the two thresholds, the spectrum has the form (1), with exponents $\alpha_{1,2} = 1 - \gamma_{1,2}$. Since

$0 < \delta < \pi$, the exponent α_1 is positive, while α_2 is negative. The main threshold thus displays a singularity of the « infrared catastrophy » type, while the second threshold appears only as a shoulder, with infinite slope. The shape of such a band absorption spectrum is sketched on figure 5 (note that the singularity at ω_2 will be blurred by the interaction between conduction electrons). In the limit of a near insulator (μ small), the Fermi surface phase shift is close to π : α_1 is close to 1, while α_2 is very small. The main threshold is very singular, and becomes a δ-function in the insulating limit : it then corresponds to the usual *exciton* absorption line, as foreseen in the introduction

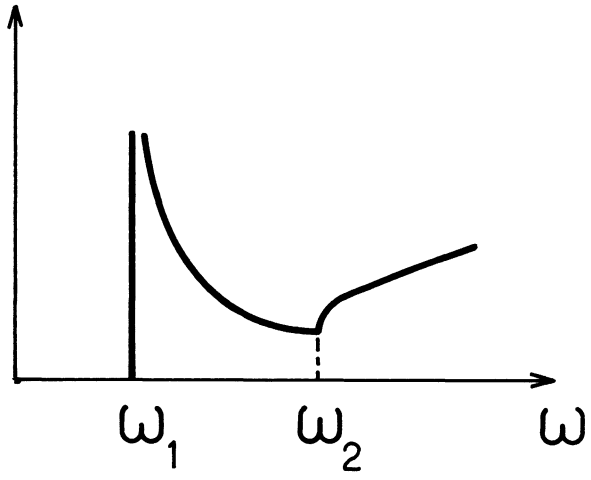

FIG. 5. — The spectrum of $\mathcal{F}(\omega)$ in the absorption case, when there exists a bound state.

(indeed, its position ω_1 then reduces to ε_B). The secondary threshold tends toward a step function when $\alpha_2 \to 0$. In the insulating limit, it lies at $\omega_2 = 0$ and marks the onset of *continuum* absorption. When μ increases, the gap between the exciton and the continuum fills up progressively as shown on figure 3. We note that for small μ the rearrangement of conduction electrons after the transition is relatively unimportant (it broadens slightly the characteristic absorption spectrum of an insulator). For larger μ, $\gtrsim \varepsilon_B$, the Auger processes are far more effective : the distinction between exciton and continuum becomes somewhat meaningless (although the spectrum retains two well defined thresholds). The singular spike at the absolute threshold may be viewed as a *remnant* of the exciton line, considerably broadened by Auger excitation of the other conduction electrons.

To concluse this section, we note that the relation (16) is verified in all cases, thereby confirming the prediction of Hopfield. n_l is the net number of particles which must be brought near the impurity at equilibrium, *including* the bound electron. It is interesting to note that the shape of the spectrum is the same whether the bound state is due to the final interaction or whether it was preexistent. In the former case, treated here, one may interpret the absolute threshold of $\mathcal{F}$ as a process in which the core electron fills the newly created bound state, the rest of the Fermi sea readjusting to the new environment ; the corresponding exponent γ_1 is given by (80). In a typical line spectrum, one would instead consider the transition of an electron between two preexistent core states : the spectrum is then described by $\mathcal{G}$, with an exponent δ^2/π^2 (assuming that there is no further bound state created in the process). In the latter case, the bound state is not considered as belonging to the conduction electrons, and the phase shift is thus shifted by π : the exponents are the same in the two descriptions, given by Hopfield's rule.

IV. **Emission spectrum.** — The correlation function $\bar{\mathcal{F}}$ and $\bar{\mathcal{G}}$ can be evaluated by the same method for emission spectra. We first consider the simple case in which the potential V is not strong enough to create a bound state. Using (7), the propagator $\bar{\mathcal{G}}(t)$ and the response function $\bar{\mathcal{F}}(t)$ may be written as

$$\begin{aligned}
\bar{\mathcal{G}}(t) &= \theta(t) < \bar{\Psi}_0 \mid b(t)\, b^*(0) \mid \bar{\Psi}_0 > \\
&= \theta(t)\, e^{-i\varepsilon_0 t} < \bar{\Psi}_0 \mid e^{-i(H-\bar{E}_0)t} \mid \bar{\Psi}_0 > \\
\bar{\mathcal{F}}(t) &= \theta(t) \sum_{pp'} u_p\, u_{p'} \times \\
&\qquad \times < \bar{\Psi}_0 \mid b(t)\, c_p^*(t)\, c_{p'}(0)\, b^*(0) \mid \bar{\Psi}_0 > \\
&= \theta(t)\, e^{-i\varepsilon_0 t} \sum_{pp'} u_p\, u_{p'} \times \\
&\qquad \times < \bar{\Psi}_0 \mid c_p^*\, e^{-i(H-\bar{E}_0)t}\, c_{p'} \mid \bar{\Psi}_0 > \qquad (83)
\end{aligned}$$

where the initial state $\mid \bar{\Psi}_0 >$ is the Slater determinant of the N *scattering* states $\bar{\chi}_K$ with energy $\bar{\varepsilon}_K < \mu$ and the fundamental energy $\bar{E}_0$ is given by

$$\bar{E}_0 = \sum_{K \leqslant K_F} \bar{\varepsilon}_K .$$

We note that (83) differs from the absorption result (18) by changing plane waves into scattering waves, $\bar{H}$ into H and i into $-i$ in the expectation values. Such a correspondence makes the transposition from absorption to emission very easy. We introduce a matrix $\bar{\lambda}$ defined as

$$\begin{cases} \bar{\lambda}_{KK'} = \int d\tau \bar{\chi}_K^*\, e^{i(h-\bar{\varepsilon}_K)t}\, \bar{\chi}_{K'} \\ e^{i\varepsilon_0 t}\, \bar{\mathcal{G}}(t) = \det \bar{\lambda} = \bar{\rho} . \end{cases} \qquad (84)$$

The matrix elements $\bar{\lambda}_{KK'}$ can be calculated by inserting a complete set of plane waves χ_p and using the overlap x_K^p of $\bar{\chi}_K$ and χ_p, given by (A.11)

$$\bar{\lambda}_{KK'} = \sum_p x_K^p\, x_{K'}^p\, e^{i(\varepsilon_p - \bar{\varepsilon}_K)t} . \qquad (85)$$

For large times t, x_K^p may be replaced by its asymptotic form (A.12). Since x_K^p is negligible unless $k \approx p$, we may ignore the momentum dependence of δ_K : it follows that

$$x_K^p(\delta) = - x_p^K(-\delta) .$$

On comparing (85) with (32), we see that the above symmetry relation permits a direct evaluation of $\bar{\lambda}_{KK'}$, which is obtained from $\Lambda_{KK'}$ by changing i into $-i$, and δ into $-\delta$. The latter change was to be expected : the potential discontinuities are opposite in the absorption and emission case, as well as the change of localized charge, which becomes $-\delta/\pi$ in the emission case instead of $+\delta/\pi$ in the absorption one.

The calculation of $\bar{\lambda}$ proceeds as in section II. From (34), it follows that $\bar{\lambda}$ has the form

$$\bar{\lambda} = 1 - \bar{X} .$$

Using (8) and (60), we obtain $\bar{\mathcal{G}}(t)$ by a mere transposition of our former results

$$\bar{\mathcal{G}}(t) = \frac{e^{-i\varepsilon_0 t} e^{-it\int_0^\mu (\delta_k/\pi)d\varepsilon}}{(\xi_0 t)^{\delta^2/\pi^2}} = -\mathcal{G}(t) . \qquad (86)$$

The discussion of the phase shift determination can be reproduced exactly. δ is the usual determination that goes to 0 when $K \to 0$.

The calculation of the response function is a little more complicated because $c_{p'}$ destroys a plane wave state and $|\bar{\Psi}_0>$ is composed of scattering states. We must first transform c_p^* into the operator $\bar{c}_p^*$ which creates a scattering state $\bar{\chi}_p$:

$$c_p^* = \sum_{p'} x_{p'}^K \bar{C}_{p'}^* .$$

If we note that only the one electron states included in $|\bar{\Psi}_0>$ can be destroyed, the expression (83) of $\bar{\mathcal{F}}(t)$ may be transformed as

$$\bar{\mathcal{F}}(t)\, e^{i\varepsilon_0 t} = \sum_{\substack{KK' \\ pp'}} u_p u_{p'} x_K^p x_K^{p'} \bar{\rho}_{KK'} e^{+i\bar{\varepsilon}_K t} \qquad (87)$$

where $\bar{\rho}_{KK'}$ is the minor of $\bar{\lambda}$ obtained by suppressing the K row and the K' column. $\rho_{KK'}$ is equal to the KK' element of the inverse matrix $\bar{\lambda}^{-1}$, multiplied by its determinant $\bar{\rho}$. Hence, $\bar{\mathcal{F}}$ takes the usual simple form (see (A.4) and (A.5))

$$\bar{\mathcal{F}} = \bar{L}\bar{\mathcal{G}}$$

$$\bar{L} = \sum_{KK'} a_K a_{K'} \bar{\lambda}_{KK'}^{-1} e^{i\bar{\varepsilon}_K t} \qquad (88)$$

$$a_K = \sum_p u_p x_K^p = \frac{\alpha_K}{V} .$$

The main contribution in $\bar{L}$ comes from the vicinity of the Fermi level. If we neglect the K dependence of α_K, $\bar{L}$ looks like the expression (50) of L, and can be calculated in the same way. We only quote the result

$$\bar{L} \sim \frac{e^{i\mu t}}{t} (\xi_0 t)^{2\delta/\pi} . \qquad (89)$$

When there is no bound state, we find exactly the same results for emission and for absorption, in agreement with reference (8).

When the potential increases, a conduction electron can be bound : the initial state $|\bar{\Psi}_0>$ in (83) is now the Slater determinent of the bound state and of $N-1$ scattering states. The corresponding matrix elements of $\bar{\lambda}$ are

$$\bar{\lambda}_{BB} = <\bar{\chi}_B | e^{i(h-\varepsilon_B)t} | \bar{\chi}_B> = \sum_p e^{i(\varepsilon_p - \varepsilon_B)t} | <\bar{\chi}_B | \chi_p> |^2$$

$$\bar{\lambda}_{KB} = \bar{\lambda}_{BK} e^{i(\varepsilon_B - \bar{\varepsilon}_K)t} = <\bar{\chi}_K | e^{i(h-\bar{\varepsilon}_K)t} | \bar{\chi}_B> \qquad (90)$$

(the elements $\bar{\lambda}_{KK'}$ are unchanged). We expand $\bar{\lambda}$ along that extra row and column. If we denote by $(\mathbf{1} - \mathbf{X})$ the $(N-1) \times (N-1)$ matrix due to scattering states alone, we find

$$e^{i\varepsilon_0 t} \bar{\mathcal{G}}(t) = \mathrm{Det} \parallel \mathbf{1} - \bar{\mathbf{X}} \parallel \times \times \left\{ \bar{\lambda}_{BB} + \sum_{KK'} \bar{\lambda}_{BK} \left(\frac{1}{1-\bar{X}} \right)_{KK'} \bar{\lambda}_{K'B} \right\} . \qquad (91)$$

The bracket of (91) is similar to the expression (29) of the open line contribution L in the absorption case. The first term is small, since the summation over p in (90) extends over all space : it behaves as $1/t^{3/2}$, and is negligible when $t \to \infty$, exactly as the first term of (29). In order to calculate the second term, we replace $\bar{\lambda}_{KB}$ by its asymptotic form

$$\bar{\lambda}_{KB} = \frac{\alpha_B u_K e^{-i\delta_K}}{\bar{\varepsilon}_K - \varepsilon_B} . \qquad (92)$$

(91) and (29) are formally identical if we neglect the momentum dependence of $\bar{\lambda}_{KB}$, an approximation which is valid in the asymptotic limit. We shall not go through the calculation, which is similar to that of section II ; we find

$$\sum_{KK'} \bar{\lambda}_{BK} \left(\frac{1}{1-\bar{X}} \right)_{KK'} \lambda_{K'B} \simeq \simeq \frac{\alpha_B^2 \nu_0}{(\varepsilon_B - \mu)^2} \frac{e^{i(\varepsilon_B - \mu)t}}{t} \frac{1}{(\xi_0 t)^{2\tilde{\delta}/\pi}} . \qquad (93)$$

Except for the additional factor $e^{i\varepsilon_B t}$, (93) is obtained from (53) through the usual replacement $i \to -i$, $\tilde{\delta} \to -\tilde{\delta}$. As discussed in section III, the determination $\tilde{\delta}$ is that which vanishes when $\mu \to 0$: in the present case, $\tilde{\delta} = \delta - \pi$ (note that with our separable potential, $0 < \delta < \pi$, so that $\tilde{\delta}$ is negative). From (86), we know that

$$\mathrm{Det} \parallel \mathbf{1} - \bar{\mathbf{X}} \parallel = \frac{e^{-i\tilde{\Delta}t}}{(\xi_0 t)^{\delta^2/\pi^2}}$$

$$\tilde{\Delta} = \int_0^\mu \frac{\tilde{\delta}_K}{\pi} d\varepsilon . \qquad (94)$$

Combining (91), (93) and (94), we finally obtain

$$\begin{cases} e^{i\varepsilon_0 t} \bar{\mathcal{G}}(t) \simeq \dfrac{e^{-i\Delta t}}{(\xi_0 t)^{\delta^2/\pi^2}} \\ \Delta = \mu - \varepsilon_B + \tilde{\Delta} = \displaystyle\int_{-\infty}^{\mu} \frac{\delta_K}{\pi} d\varepsilon . \end{cases} \qquad (95)$$

As expected, the emission spectrum possesses a single threshold, at the same place and with the same exponent as the absolute absorption threshold. There is no secondary threshold, since in that case we are sure that the bound state is filled before the X-ray transition takes place. Once more, Hopfield's rule for the exponent is verified.

The function $\bar{\mathcal{F}}(t)$ may be obtained in a similar way. In (83), c_p is expressed in terms of the operator $\bar{c}_p$ and $\bar{c}_B$ which destroy a scattering state $\bar{\chi}_K$ or the bound state $\bar{\chi}_B$. $\mathcal{F}$ thus appears as a sum of $(N-1)$ dimensional determinants, some with the bound state full, others with the bound state empty. Whenever there is a row or column involving the bound state, we expand as for $\bar{\mathcal{G}}$. The calculation is straightforward, but tedious. We shall not give it, since it yields the expected result that the emission threshold ; its position is controlled by the difference between the ground state energies of $(N+1)$ electrons with the potential as compared to N electrons without the potential ; the exponents, given by Hopfield's rule [3], are the same in the two cases (since n is opposite in emission and absorption).

In conclusion, we see that the presence of a bound state does not affect the results of reference [8]. For both band and line spectra, the absorption possesses two threshold, while the emission has only one, which is identical to the absolute one for absorption. In *all* cases, the critical exponents are correctly given by Hopfield's prediction.

Appendix A. — Let a_p, a_p^* be the destruction and creation operators for a plane wave with momentum p (with no scattering potential). The one-electron hamiltonian in the presence of the potential is

$$\bar{h} = \sum_p \varepsilon_p \, a_p^* \, a_p + \sum_{pp'} V u_p \, u_{p'} \, a_p^* \, a_{p'} \, . \qquad (A.1)$$

The scattering states (eigenstates of $\bar{h}$) are characterized by creation operators

$$\bar{a}_p^* = \sum_{p'} x_p^{p'} \, a_{p'}^* \qquad (A.2)$$

which obey the equation of motion

$$[\bar{h}, \bar{a}_p^*] = \bar{\varepsilon}_p \, \bar{a}_p^* \, . \qquad (A.3)$$

With our separable potential, (A.3) is easily solved, and yields

$$x_p^{p'} = \frac{\alpha_p \, u_{p'}}{\bar{\varepsilon}_p - \varepsilon_{p'}} \qquad (A.4)$$

$$1 = \sum_{p'} \frac{V u_{p'}^2}{\bar{\varepsilon}_p - \varepsilon_{p'}} \, . \qquad (A.5)$$

α_p is a normalization constant ; (A.5) is the dispersion equation for the scattering state energy $\bar{\varepsilon}_p$.

As shown by Friedel [10], the scattering states are sandwiched between consecutive free states, the p^{th} state being such that

$$\bar{\varepsilon}_p = \varepsilon_p - \frac{\delta_p}{\pi \nu_p} \, . \qquad (A.6)$$

ν_p is the density of states at energy ε_p (in the channel studied) ; δ_p is the *phase shift* at that energy, which for a separable potential is given by

$$\begin{cases} \operatorname{tg} \delta_p = - \dfrac{\pi V u_p^2 \, \nu_p}{1 + V y_p} \\ y_p = \sum_{p'} u_{p'}^2 \, P \left[\dfrac{1}{\varepsilon_{p'} - \varepsilon_p} \right] . \end{cases} \qquad (A.7)$$

The normalization constant α_p is fixed by the condition

$$\sum_{p'} | \, x_p^{p'} \, |^2 = 1 \, . \qquad (A.8)$$

Let us replace $x_p^{p'}$ by its expression (A.4) : we see that the summation (A.8) is controlled by the region $p' \approx p$ (which would yield a double pole if the p' variable were continuous). In that region we may write

$$\bar{\varepsilon}_p - \varepsilon_{p'} = \frac{(p - p')}{\nu_p} - \frac{\delta_p}{\pi \nu_p} \, . \qquad (A.9)$$

Since δ, ν, u are practically constant over the relevant range of p', the summation can be carried out by means of Poisson's formula. After some simple algebra, we find

$$\alpha_p = \frac{\sin \delta_p}{\pi u_p \, \nu_p} \, . \qquad (A.10)$$

The overlap between a free state p' and a scattering state p is thus

$$x_p^{p'} = \int d\tau \bar{\chi}_p^* \, \chi_{p'} = \frac{\sin \delta_p}{\pi \nu_p} \, \frac{u_{p'}}{u_p} \, \frac{1}{\bar{\varepsilon}_p - \varepsilon_{p'}} \, . \qquad (A.11)$$

If p' is close to p, we can use (A.9), and set $u_{p'} = u_p$: (A.11) then reduces to

$$x_p^{p'} = \frac{\sin \delta_p}{\pi} \, \frac{1}{p - p' - \delta_p / \pi} \qquad (A.12)$$

a result which has been widely used by Anderson [11].

If the potential V is strong enough, there appears a bound state, whose energy $\varepsilon_B < 0$ is a root of the dispersion equation (5). The overlap of that state with a plane wave p is equal to

$$x_B^p = \frac{\alpha_B \, u_p}{\varepsilon_B - \varepsilon_p} \qquad (A.13)$$

where the normalization constant is given by

$$\frac{1}{\alpha_B^2} = \sum_p \frac{u_p^2}{(\varepsilon_B - \varepsilon_p)^2} \, . \qquad (A.14)$$

With the help of (5), one verifies that

$$\alpha_B^2 = V^2 \frac{d\varepsilon_B}{dV}. \qquad (A.15)$$

In this paper, we use widely the matrix

$$\lambda_{pp'} = \sum_n x_n^p \, x_n^{p'} \, e^{i(\bar{\varepsilon}_n - \varepsilon_p)t}$$

where n is any scattering (or bound) eigenstate of $\bar{h}$. On using (A.4) and (A.5), it is easily verified that

$$\begin{cases} \sum_p u_p \, e^{i\varepsilon_p t} \, \lambda_{pp'} = \sum_n \frac{\alpha_n}{V} x_n^{p'} \, e^{i\bar{\varepsilon}_n t} \\ \sum_{p'} u_{p'} \, \lambda_{pp'} = \sum_n \frac{\alpha_n}{V} x_n^{p*} \, e^{i(\bar{\varepsilon}_n - \varepsilon_p)t} \\ \sum_{pp'} u_p \, u_{p'} \, \lambda_{pp'} \, e^{i\varepsilon_p t} = \sum_n \frac{\alpha_n^2}{V^2} e^{i\bar{\varepsilon}_n t}. \end{cases} \qquad (A.16)$$

In the limit of large t, the summation over *scattering* states n is limited by destructive interference, and is controlled by the singularity of x_n^p. The corresponding contribution can be obtained along the same lines as (33). To that we must add (when it is exists) the contribution of the bound state, which stands out as a single oscillatory term. We thus find

$$\begin{cases} \sum_p u_p \, e^{i\varepsilon_p t} \, \lambda_{pp'} = \\ \qquad = -\frac{\sin \delta_{p'} \, e^{-i\delta_{p'}}}{\pi v_p \, V u_p} e^{i\varepsilon_p t} \left(+ \frac{\alpha_B^2 \, u_{p'}}{V(\varepsilon_B - \varepsilon_{p'})} e^{i\varepsilon_B t} \right) \\ \sum_{p'} u_{p'} \, \lambda_{pp'} = -\frac{\sin \delta_p \, e^{-i\delta_p}}{\pi v_0 \, V u_p} \left(+ \frac{\alpha_B^2 \, u_p}{V(\varepsilon_B - \varepsilon_p)} e^{i(\varepsilon_B - \varepsilon_p)t} \right) \\ \sum_{pp'} u_p \, u_{p'} \, \lambda_{pp'} \, e^{i\varepsilon_p t} = \sum_q \frac{\sin^2 \delta_q}{\pi^2 \, v_q^2 \, V^2 \, u_q^2} e^{i\bar{\varepsilon}_q t} \left(+ \frac{\alpha_B^2}{V^2} e^{i\varepsilon_B t} \right). \end{cases} \qquad (A.17)$$

In the last of these relations, the first term is negligible for large t, since there is no cut off on the summation over ε_q (the lower limit $\varepsilon_q = 0$ gives a contibution $\sim t^{-3/2}$, which is negligible as compared to the other terms). These results are used in sections II and III.

Appendix B. — The results obtained in this paper are based on an asymptotic evaluation of $\mathcal{G}$ and $\mathcal{F}$ for large times t. Thus, they provide only the nature of the singularities near the thresholds — namely the exponents α in (1). The cut of ξ_0 (which appears as a multiplicative factor in the spectrum) lies outside the range of our theory. Of course, so does the spectrum far from the thresholds. Here, we briefly discuss to what extent one can overcome these limitations.

Approximations were made at two stages : in the evaluation of λ (where we used the approximate expression (34)), and in the inversion of λ (*i. e.*, in the solution of eq. (44)). While the former approximation could be reconsidered, the second one appears critical. For dense systems (large μ), there is little we can do we are faced with an intermediate coupling problem, and there exists no obvious approximation scheme. On the other hand, for dilute systems, sin δ is small at the Fermi level : somehow, the final state interaction should be a small perturbation, and we should be able to calculate the spectrum far from the threshold, at distances $\gg \mu$. (Close to the threshold, infrared divergences require a more accurate solution.)

Let us consider for instance line spectra in the absence of a bound state, characterized by the function $\mathcal{G}$. According to (30), we have

$$\mathcal{G} = \exp \left[\mathrm{Tr} \, \mathrm{Log} \, \lambda \right]. \qquad (B.1)$$

Far from the threshold, we cannot use the asymptotic expression of λ (34). On the other hand, we can use the orthogonality of the scattering states to write the *exact* expression

$$\lambda_{KK'} = \delta_{KK'} + \sum_p \frac{\sin^2 \delta_p}{\pi^2 \, u_p^2 \, v_p^2} \times \\ \times \frac{u_K \, u_{K'}}{(\bar{\varepsilon}_p - \varepsilon_K)(\bar{\varepsilon}_p - \varepsilon_{K'})} \left[e^{i(\bar{\varepsilon}_p - \varepsilon_K)t} - 1 \right] \qquad (B.2)$$

(cf. (32), (A.4) and (A.10)). (B.2) provides an *exact* expression of the matrix $\mathbf{X} = \mathbf{1} - \lambda$. For *dilute* systems, we expect $\mathbf{X}$ to be a small perturbation ; that was obvious for large t (in the asymptotic expressions (34), sin δ_K is small) — on the other hand, for $t \to 0$ the bracket of (B.2) vanishes. As an interpolation procedure, we can therefore assume X to be small, and expand (B.1) to lowest order

$$\mathcal{G} \approx 1 - \mathrm{Tr} \, \mathbf{X} = 1 + \sum_{pK} \frac{\sin^2 \delta_p}{\pi^2 \, u_p^2 \, v_p^2} \times \\ \times \frac{u_K^2}{(\bar{\varepsilon}_p - \varepsilon_K)^2} \left[e^{i(\bar{\varepsilon}_p - \varepsilon_K)t} - 1 \right] \qquad (B.3)$$

(remember that $K < K_F$, while p is arbitrary). (B.3) provides at once the Fourier transform $\mathcal{G}(\omega)$ for $\omega > \mu$:

$$\mathcal{G}(\omega) \sim \sum_{pK} \frac{\sin^2 \delta_p}{\pi^2 \, u_p^2 \, v_p^2} \frac{u_K^2}{\omega^2} \delta(\omega - \bar{\varepsilon}_p + \varepsilon_K). \qquad (B.4)$$

Physically, the result (B.4) describes first order processes in which the final state potential ships an electron from the initial unperturbed state k to some scattering state p. If μ is really small, ε_K is negligible and $u_K = u_0$. (B.4) then reduces to

$$\mathcal{G}(\omega) \sim N \sum_p \frac{u_0^2}{u_p^2} \frac{\sin^2 \delta_p}{\pi^2 \, v_p^2} \frac{\delta(\omega - \bar{\varepsilon}_p)}{\omega^2} \qquad (B.5)$$

(in agreement with the result of Friedel). In fact (B.4) can be obtained directly from the Anderson expansion (19) if we assume that only *one* electron is affected by the final potential : in $| \Psi_n >$, all particles are in plane wave states, except that of wave vector K which is replaced by a scattering state p.

The result (B.4) is somewhat academic. On the

other hand, there is some interest infinding the shape of the band spectrum for an extrinsic insulator between the exciton line and the continuum, in the intermediate region of figure 3 *i. e.*, in calculating the Auger tail of excitons. In principle, that can be done by the above method : treat exactly the bound state part of λ, and expand to lowest order the continuum contribution (making use of (75) and (78)). In fact, the algebra is very difficult, as one finds a large number of complicated terms. Physically, there are two processes which interfere : the X-ray can shift the core electron into the bound state, while a conduction electron is excited in a scattering state ; conversely, the core electron can go into the continuum while a conduction electron falls into the bound state. Clearly, our approach is unnecessarily complicated : in that approximation we are faced with a two particle process, and it is much simpler to use the Anderson expansion (19), assuming that all but two of the electrons are unaffected by the final potential. In calculating the overlap $< \Psi_0 \mid \overline{\Psi}_n >$, we assume that *only two* particles, with initial momenta K and K', are shipped in new states, one in the bound state and the other in some scattering state p. We shall not pursue this calculation, which has a spirit quite different from that of this paper.

References

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[2] In practice, these singularities are somewhat rounded off, for a number of reasons : lifetime effects, recoil of the core electrons, etc... : see reference [6] for a detailed discussion.

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[5] Once again, lifetime effects tend to bluw the line : as shown by Doniach, the Auger broadening results in a skew-shaped line, which indeed is often observed experimentally.

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