Electron Interaction Effects on the Soft-X-Ray Emission Spectrum of Metals. Reformulation of the First-Order Theory

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The Longe and Glick many-body theory of metal x-ray emission spectra is reformulated in order to eliminate spurious divergences in the main band. The formalism is then extended to allow a calculation of the absorption spectrum.

INTRODUCTION

Longe and Glick, [1,2] in papers hereafter referred to as I, have used the dielectric-constant formalism of the many-body theory to calculate to first order in the random-phase-approximation (RPA) effective potential, the effect of electron-electron correlations on the emission spectra of simple metals. In the tailing and plasmon band region, good agreement with experiment was obtained. One of the most interesting features of this theory was to show that certain interference terms play an important role in determining the emission intensity. This confirmed earlier calculations[3,4] performed by one of us in the Bohm and Pines formalism.

The first-order theory of I however is only valid in the low-energy part of the spectrum. It breaks down in the region of the main band spectrum because of an improper normalization of the many-body Golden Rule. The purpose of this paper is to obtain a correct first-order theory for the main band by extending a technique used by Nozières and de Dominicis[5] (ND) to deal with the Fermi-edge singularity. ND investigated the asymptotic behavior of the exact response function at the Fermi edge taking account only of a static electron-hole interaction. Here we will consider also the electron-electron interaction, investigate the response function for the whole spectrum of energy, but we will restrict the theory to the first order in the effective RPA frequency-dependent electron-electron and electron-hole interactions. This program will be performed by treating the deep core hole as an external and transient potential suddenly switched off/on at the moment of the x-ray emission/absorption as in the ND model. A two-Hamiltonian model will be used and diverging secular terms will be avoided by grouping energy shifts consistently.

MODEL

We will calculate the emission and absorption intensity in the semiclassical theory of radiation using the Golden Rule (with $\hbar = 1$):

$$I(\nu) = I^{-1} \sum_{i,f} \delta(E_f - E_i \pm \nu) \left| \langle \Psi_f \left| \Theta \right| \Psi_i \rangle \right|^2 , \qquad (1)$$

where, as in I, $\Theta = \sum \vec{n} \cdot \vec{p}_k$ is the dipolar operator applied to all the electrons of the system and $\vec{n}$ is a unit polarization vector in the direction of the vector potential. One sums over all possible final states and averages over the $\vec{p}$ near-degenerate initial states.[6] The functions Ψ_i and Ψ_f are solution of the Schrödinger equation for the interacting electron gas with energies E_i and E_f. In our model we introduce two different Hamiltonians for this electron gas; one is used before and the other after the x-ray transition, and we pass *suddenly* from one Hamiltonian to the other at the moment of this transition.

a. Emission. In emission the initial Hamiltonian is

$$H^e = \sum_n H_n + \tfrac{1}{2} \sum_{m,n} V_{mn} - \sum_n V_n - E_b \qquad (2)$$

acting on $N+1$ conduction-electron states. The first term is the one-electron Hamiltonian whose solution is a Slater determinant of Bloch waves. The second term is the electron-electron Coulomb interaction. The third term is the Coulomb interaction of the electron with the localized core hole considered as an attractive impurity and E_b is the energy of this vacant state in the one-electron picture. We will assume that all the many-elec-

tron states are obtained from the one-electron states by switching on adiabatically the last terms.

The initial state in emission is taken to be the ground state of (2) with energy

$$E_i^e = E^{N+1} - \mu_b = E^N + \mu_0 - \mu_b$$
$$= E^N + E_0 + \Sigma_0 - E_b - \Sigma_b \ .$$

Here E^N is the ground-state energy of N interacting electrons without a core hole present, μ_0 is the electron chemical potential and Σ_0 is the (real) self-energy at the Fermi momentum and energy, and Σ_b is the shift in the core hole "chemical potential" μ_b due to the polarization of the conduction electrons. In our model we assume Σ_b to be real, neglecting nonradiative Auger processes.

The final Hamiltonian in emission simply describes an N interacting electron system without core hole and is

$$H^a = \sum_n H_n + \tfrac{1}{2} \sum_{m,n} V_{mn} \ . \tag{3}$$

The possible final energies can be written

$$E_f^e = E^N + \Delta E^e \ ,$$

where E^N is the ground state of H^a, and ΔE^e is the excitation energy of the final state.

b. Absorption. The situation is reversed in absorption. In the initial state we have N conduction electrons and no core hole. The initial Hamiltonian is H^a given by (3) and the initial energy is the ground-state energy $E_i^a = E^N$. The final state is an $N+1$ conduction-electron system polarized by a core hole. The final Hamiltonian is H^e given by (2) with the final energy

$$E_f^a = E^N + \mu_0 - \mu_b + \Delta E^a \ .$$

The frequency of the emitted/absorbed x-ray photon is then

$$\nu = \mu_0 - \mu_b \mp \Delta E^{a,e} \ .$$

Here and below, the upper signs and indices are related to emission, the lower ones to absorption. One has, of course, $E^{a,e} \geq 0$, and $E^{a,e} = 0$ corresponds to the frequency at the Fermi edge, which is the same for both absorption and emission spectra. For practical reasons, we will introduce

$$\omega \equiv \nu + E_0 - \mu_0 + \mu_b \ , \tag{4}$$

which is, as in I, the frequency measured from the bottom of the emission band obtained by the Bloch-Sommerfeld model. The low-energy features of the emission spectra will thus correspond to negative ω, and the argument of the δ function in (1) will be $\omega - E_0 \pm E^{e,a}$.

If we compare the present formulation with that used in I, one point has to be emphasized. In I, the core electron was a member of the many-electron system and the initial state in emission was not an eigenstate of the unique Hamiltonian used in I. This brought serious difficulties concerning the adiabatic switching and the normalization of expression (1) and finally gave the divergences unsolved in I. In the two-Hamiltonian formalism the initial state in emission is a correct eigenstate of H^e and the main divergence of I will not occur if we handle the energy shifts correctly. The effect of the core hole charge as in ND is solely that of a transient external potential which acts before/after the x-ray process, neglecting flipping of the core hole between the l degenerate levels.[7]

FIRST-ORDER THEORY

As it is desirable to avoid explicit reference to the final states, particularly because of Anderson's orthogonality theorem,[8] we rewrite [as in I Eq. (1)] in the form

$$I(\nu) = (1/\pi l)\,\mathrm{Re} \int_0^\infty ds\, e^{\mp i\nu s} \sum_i \langle \Psi_i \mid \Theta^\dagger(s)\Theta(0) \mid \Psi_i \rangle \ . \tag{5}$$

Using ω defined by (4) and introducing some auxiliary notations, we write (5) in the form

$$I^{e,a}(\omega) = \mathrm{Re} F^{e,a}(\omega) \ , \tag{6}$$

$$F^{e,a}(\omega) = \int_0^\infty ds\, e^{\mp i\omega s} F^{e,a}(s) \ , \tag{7}$$

$$F^{e,a}(s) = e^{\mp i(\Sigma_0 - \Sigma_b)s} M^{e,a}(s) \ , \tag{8}$$

$$M^{e,a}(s) = e^{\pm i E_b s} \sum_i \langle \Psi_i \mid \Theta^\dagger(s)\Theta(0) \mid \Psi_i \rangle \ . \tag{9}$$

A constant factor $1/\pi l$ has been dropped in (6) (see Ref. 6). The Heisenberg operators have an asymmetrical form

$$\Theta(t) = \exp(iH^{e,a}t)\,\Theta\,\exp(-iH^{a,e}t) \ ,$$

with[7]

$$\Theta = \sum_k \langle B_i \mid \vec{n} \cdot \vec{p}_{\vec{k}} \mid \vec{k} \rangle a_{\vec{k}}$$
$$= \sum_k \delta_{3i} H a_{\vec{k}}$$

in emission and

$$\Theta = \sum_k \delta_{3i} H a_{\vec{k}}^\dagger$$

in absorption. From this point on we only consider $L_{2,3}$ spectra. The three p-bound states ($l=3$) have the three spacial directions as axis. Since we place the polarization vector $\vec{n}$ along $0x_3$, only the state $i=3$ will play a role in the x-ray transition. Introducing the two evolution operators

$$U^{e,a}(t,t') = e^{-iH^{e,a}(t-t')} \ ,$$

(9) takes the form

$$M^{e,a}(s) = \sum_{k'k} M_{k'k}^{e,a}(s) \tag{10}$$

with

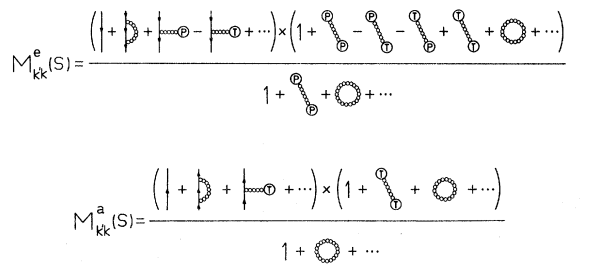

FIG. 1. Diagrammatic representation of $M_{k',k}(s)$.

$$M^{e}_{\vec{k}',\vec{k}}(s) = e^{iE_b s}\langle \Psi^{e}_3 | U^{e}(0,s) a^{\dagger}_{\vec{k}'} U^{a}(s,0) a_{\vec{k}} | \Psi^{e}_3\rangle \quad (11a)$$

for the emission and

$$M^{a}_{\vec{k}',\vec{k}}(s) = e^{-iE_b s}\langle \Psi^{a}_3 | U^{a}(0,s) a_{\vec{k}} U^{e}(s,0) a^{\dagger}_{\vec{k}'} | \Psi^{a}_3\rangle \quad (11b)$$

for the absorption. We have dropped the constant factor H^2.

We write (10) and (11) in the interaction representation where

$$\tilde{\mathcal{O}}(t) \equiv e^{iH_0 t}\, \mathcal{O}\, e^{-iH_0 t} .$$

H_0 is the common first term of H^a and H^e. We have, assuming the adiabatic hypothesis,

$$M^{e}_{\vec{k}',\vec{k}}(s) = e^{iE_b s}\,\frac{\langle \Phi_0 | \tilde{U}^{e}(\infty,s)\tilde{a}^{\dagger}_{\vec{k}}(s)\tilde{U}^{a}(s,0)\tilde{a}_{\vec{k}'}(0)\tilde{U}^{e}(0,-\infty)|\Phi_0\rangle}{\langle \Phi_0 | \tilde{U}^{e}(\infty,-\infty)|\Phi_0\rangle} \quad (12a)$$

for emission and

$$M^{a}_{\vec{k}',\vec{k}}(s) = e^{-iE_b s}\,\frac{\langle \Phi_0 | \tilde{U}^{a}(\infty,s)\tilde{a}_{\vec{k}}(s)\tilde{U}^{e}(s,0)\tilde{a}^{\dagger}_{\vec{k}'}(0)\tilde{U}^{a}(0,-\infty)|\Phi_0\rangle}{\langle \Phi_0 | \tilde{U}^{a}(\infty,-\infty)|\Phi_0\rangle} \quad (12b)$$

for absorption. Let us assume that for emission H_0 and $|\Phi_0\rangle$ are related to a system of $N+1$ independent conduction electrons and for absorption, to N electrons.

Since we will calculate (6) up to first order in the RPA effective interaction, we can expand (12a) and (12b). Diagrammatically (12a) and (12b) take the form given in Fig. 1. Our conventions are similar to those used in I. The bubble lines represent the RPA interaction. The particle lines (with arrows) represent holes if they go down or electrons above the Fermi level if they go up, the time going upward. Because of the creation and annihilation operators in (12a) and (12b), we have the particle lines and open lines starting down at time 0 and ending up at time s. In this paper the core hole is not described by a propagator, represented by a double line in I, but by an external attractive Coulomb potential suddenly switched on or off at times 0 and s. In the space-time representation this potential can be written

$$v(r,t) = v_P(r) - v_T(r,t) , \quad (13)$$

where

$$v_P(r) = -e^2/r$$

is a permanent component and

$$v_T(r,t) = -[\eta(t) - \eta(t-s)]e^2/r$$

is a transient component. In the diagrams, these two components are represented by circled P's and T's. In Fig. 1, all the diagrams contributing to the zeroth and first-order term s are drawn. The denominators and the second factor of the numerators represent "vacuum" contributions. It is important to note that these vacuum contributions do not cancel each other. In other terms, the linked cluster theorem cannot be applied here, as already discussed by two of us in Ref. 9. We can now expand (8). For this, let us write

$$F^{e,a}(s) = \sum_{\vec{k},\vec{k}'} F^{e,a}_{\vec{k}',\vec{k}}(s) ,$$

with

$$F^{e,a}_{\vec{k}',\vec{k}}(s) = e^{\mp i(\Sigma_0 - \Sigma_b)s} M^{e,a}_{\vec{k}',\vec{k}}(s) . \quad (14)$$

Up to first order, (14) is represented diagrammatically in Fig. 2. The terms a_1 and b_1 of this figure come from the exponential factor. We can group the first-order terms of Fig. 2 into three series labeled a, b, and c. The zero-order term is labeled O. The O term and a, b, and c series can be related, respectively, to the O_1, A_1, and C_1 terms of I (see I, Fig. 8). They will give the same contribution for the low-energy features ($\omega < 0$) except for small changes due to the simplification of the vertex.[7] For the rest of the spectra ($\omega > 0$) there will be important changes. The b series is no longer divergent, as was the B_1 term of I. This is due to the above treatment of the vacuum contribution and to the introduction of the b_1 term describing the core energy shift. The A_1 term of I, not diverging, is, however, also modified here by the introduction of the a_1 term also

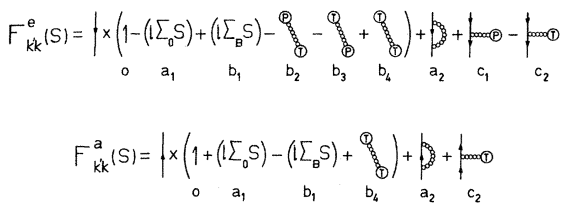

FIG. 2. Zero- and first-order diagrams in the expansion of $F_{k'k}(s)$ in the effective RPA potential.

describing an energy shift. Only the C_1 term of I and the c series give the same contribution in both papers.

To calculate the contribution to (14) from Fig. 2, the propagator for the effective interaction (bubble line) requires some attention. In the c series of Fig. 2 it is just

$$V(k,\omega)=v(k)\,\epsilon^{-1}(k,\omega)=4\pi e^2k^{-2}\,\epsilon^{-1}(k,\omega)\,,$$

while in the b series we must use

$$v(k)\,[\epsilon^{-1}(k,\omega)-1\,] \tag{15}$$

to take into account that the core hole interacts with itself indirectly via the polarization of the medium. In the a series we have instead

$$v(k)\,[\epsilon^{-1}(k,\omega)-e^{i\omega\lambda}\,]\,,$$

where λ is a positive infinitesimal. This takes into account that the Fock term in the self-energy only can involve an electron hole line. We use the RPA dielectric constant for $\epsilon(k,\omega)$. The unit of momentum is twice the Fermi momentum and energies are expressed in units of four times the Fermi energy.

The contributions to $F^{e,a}_{kk'}$ are then calculated using diagrammatic rules recalled in I. They are substituted into (7) and the integration over s is carried out. The real part is extracted to obtain (6). Grouping the terms of the series a, b, and c we obtain finally the intensities

$$I^{e,a}_0(\omega)=\pi\int dk\,\eta_k\delta(\omega-k^2)$$
$$=2\pi^2\,\omega^{1/2}\,\eta[\mp(\omega-\tfrac{1}{4})]\,, \tag{16a}$$

$$I^{e,a}_a(\omega)=\int d\vec{k}\left[-(2\pi)^{-3}\int d\vec{p}\,\eta_p\int d\vec{q}\,\delta(\vec{k}-\vec{p}+\vec{q})\,\mathrm{Im}\,V_{\mp}(q,\omega-p^2)\right.$$
$$\left.\times\frac{\partial}{\partial(k^2)}\left(\frac{P}{\omega-k^2}\right)+\pi\frac{\partial\delta(\omega-k^2)}{\partial(k^2)}\,[\mathrm{Re}\,\Sigma(k,\omega)-\Sigma_0]\right], \tag{16b}$$

$$I^{e,a}_b(\omega)=-(2\pi)^{-3}\int d\vec{p}\,\eta_p\int d\vec{q}\int\frac{du}{u^2}\,\mathrm{Im}\,V_{\mp}(q,u)[\delta(u-\omega+p^2)-\delta(\omega-p^2)]\,, \tag{16c}$$

$$I^{e,a}_c(\omega)=\int d\vec{k}\int d\vec{p}\,2(2\pi)^{-3}\int d\vec{q}\,\delta(\vec{k}-\vec{p}+\vec{q})P\left(\frac{\eta_p\,\mathrm{Im}\,V_{\mp}(q,\omega-p^2)}{(\omega-k^2)(\omega-p^2)}\right.$$
$$\left.-\frac{\pi\delta(\omega-k^2)\eta_k}{\omega-p^2}\,[\eta_{p>}\,\mathrm{Re}\,V_+(q,\omega-p^2)-\eta_{p<}\,\mathrm{Re}\,V_-(q,\omega-p^2)-\tfrac{1}{2}(\eta_{p>}-\eta_{p<})\mathrm{Re}\,V(q,0)]\right)+I^{e,a}_{\mathrm{core}}(\omega)\,, \tag{16d}$$

where

$$I^{e,a}_{\mathrm{core}}(\omega)=-(2\pi)^2\,P\int d\vec{k}\,\eta_k\,\delta(\omega-k^2)\int d\vec{p}\,\frac{\eta_{k'>}}{\omega-p^2}\int dq\,\delta(k-p+q)\,\mathrm{Re}\,V(q,0)\,. \tag{17}$$

When the symbol < or > is missing in the step function η_k, one has to take $\eta_{k<}$ for emission (e) or $\eta_{k>}$ for absorption (a). The function $V_+(k,\omega)$ and $V_-(k,\omega)$ designate the two parts of $V(k,\omega)$ analytic, respectively, in the upper and lower half of the complex frequency plane.[9] The function $\Sigma(k,\omega)$ is the electron self-energy calculated using (15) and $\Sigma_0=\Sigma(\frac{1}{2},\frac{1}{4})$. The secular terms containing the core hole self-energy Σ_b cancel each other.

For $\omega<0$, except for small changes due to the simplification of the vertex, Eqs. 16 are identical to the results of I. For $\omega>0$ in addition to modifications already mentioned, the main difference from I is the occurence of a second δ function in (16c) which eliminates the divergence throughout the band. We have isolated the term $I_{\mathrm{core}}(\omega)$ which represents the static part of the transient electron-core-hole interaction. It is the only term which depends strongly on the large k values of $V(k,\omega)$. For that reason $I_{\mathrm{core}}(\omega)$ is very sensitive to the form of the electron wave function in the vicinity of the core hole and must be treated with special care. This point has been discussed elsewhere.[10]

This term together with (16b) is singular at $\omega=E_F$. The physical origin of this singularity has been discussed by Mahan,[11] Nozières and de Domi-

nicis,[5] and in Ref. 12. As in the formalism of ND, the edge singularity is a compromise between the plain resonance in the scattering (I_{core}) and the broadening of the deep levels (included in terms *b*). A discussion of this singularity in the first-order theory including electron-electron correlation is given in Ref. 10. The failure of perturbation theory for $\omega = 0$ is reflected in the fact that $I(\omega)$ tends to $-\infty$ at 0^+. This is due to a slight dispersion of the energy shift of the levels from E_F to 0.[13] In the first-order theory this difficulty can be avoided by introducing a frequency-dependent energy shift in (8). By using the standard technique of Bogoliubov *et al.* it is possible to take account of the slightly nonlinear energy scale introduced by the energy shift dispersion as has been done in connection with a discussion of the Auger broadening.[14,15]

Though the first-order theory describes correctly plasmon and electron-hole excitations in the tailing of the band, one can question the validity of a first order theory in the main band on the ground that higher-order corrections may not be neglected. Before going further towards a complete renormalized theory, however, it was necessary to clarify the formal difficulties met in the theory of Longe and Glick. This was the purpose of this paper.

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[6]We have dropped a factor proportional to ν^n. The exponent has been shown by Y. Cauchois [in *Soft X-Ray Band Spectra*, edited by D. J. Fabian (Academic, New York, 1969), p. 71] to be $n=2$ for emission and $n=1$ for absorption, and the factor varies slowly over the considered frequencies.

[7]This means that diagrams such as Fig. 5(c′) and 5(d′) of I are neglected. The vertex contribution $g_{ij}(k)$ [Eq. (16) of I] is approximated by a Kronecker δ_{ij} and $h_{3j}(k)$ [Eq. (17) of I] becomes $\delta_{3j}H$, where H is a constant for the L band. As in I the third vertex contribution [Eq. (18) of I] is ignored. Since we neglect the relaxation of the core hole state due to interactions with the conduction electrons, we will forget the second bubble in the definition of the effective interaction (Fig. 6 of I). The introduction of a structureless scattering center, which is required here by the two-Hamiltonian treatment, modifies only slightly the results of I in the tailing region and gives to the Bloch-Sommerfeld term [Eq. (23) of I] a simplified shape proportional to $\omega^{1/2}$. This causes a change by at most 11% at the Fermi edge. All the terms neglected in the present two-Hamiltonian treatment by this simplified core hole are probably not higher than a few percent.

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