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MANY BODY EFFECTS AND THE INFLUENCE OF THE CORE HOLE ON METAL X-RAY SPECTRA

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Résumé. — Nous discutons quelques difficultés se présentant dans le calcul des effets à N corps et dans l'étude de l'influence du niveau lié vacant sur les spectres X des métaux. Nous montrons comment éliminer ces difficultés. Plus particulièrement nous mettons l'accent (1) sur la nécessité d'un développement systématique des calculs par rapport à l'interaction effective, ce qui permet de tenir compte des forts effets d'annulation, (2) sur la nécessité, quelque peu contradictoire, d'une théorie renormalisée afin d'éliminer des divergences fictives apparaissant au bas de la bande principale du spectre d'émission, (3) sur la nécessité d'extraiter systématiquement les déplacements d'énergie pour éliminer les divergences dues aux termes séculaires, (4) enfin sur l'importance de l'utilisation d'un pseudopotentiel pour décrire l'interaction avec la lacune de l'état lié.

Abstract. — We discuss some difficulties that arise in the computation of many body effects and of the effect of the core hole on the shape of metal X-ray spectra, and how they can be overcome. In particular we emphasize the need for (1) a systematic expansion in an effective interaction to take into account strong cancellation effects, (2) the somewhat contradictory need for a renormalized theory to eliminate a spurious divergence at the bottom of the parent band in emission spectra, (3) the necessity of systematically extracting energy shifts to overcome divergencies due to secular terms and (4) the importance of using a pseudopotential for the interaction with the core hole.

1. Introduction. — The shape of metal soft X-ray emission and absorption spectra are affected by electron-electron correlations in the conduction band and by the polarization of the medium caused by the deep localized core hole. The effect shows up mainly near the Fermi edge and towards the low energy side of emission spectra, while the main part of the spectra appear to be relatively little affected.

In section 2, we consider the satellite and tailing regions of the spectra. In section 3, the behavior near the emission and absorption edges and, in section 4, the main parts of the spectra are discussed. We will be mostly concerned with $L_{2,3}$ spectra and concentrate on the "simple" metals such as Na, Al and Mg, where the $L_{2,3}$ levels appear to be long lived compared to typical relaxation times for disturbances in the conduction band. We only consider many body effects and effects due to the polarization of the conduction electrons caused by the deep localized core hole, neglecting band structure effects and the variation in the transition probabilities between levels. We concentrate on qualitative aspects of the problem and refer elsewhere for details of calculations.

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probe the electronic density of states. We refer to the 2 angular correlation of the annihilation radiation from positrons in metals [11]. In this case one measures a geometrical average over the probability for the annihilating particles to have a given c.m. momentum. This probability is proportional to the electron momentum distribution in the case of non-interaction thermalized positrons. The positron lifetime, which also can be measured, is very strongly affected by the polarization of the conduction electrons, which the positron causes before it annihilates [12]. The observed angular correlation is, however, quite similar to what one expects from the independent particle model, although there are detectable deviations from this model [13]. Carbotte and Kahana [14] have explained this from a strong destructive interference between the polarization clouds of the annihilating particles, in a crude sense one becomes the polarization cloud of the other. Both the positron and the electrons have, however, momentum distributions which differ markedly from what can be obtained from the independent particle model. When the electron momentum distribution can be measured directly, as in the Compton scattering technique, one sees pronounced tails [15], in qualitative agreement with the theory of Daniel and Vosko [16].

We conclude that, when describing strongly interacting particles of opposite charge in a metal, it is important to describe the polarization of the medium by each particle and interference effects in equivalent approximations. Otherwise one might miss important cancellation effects. When such effects are present, this suggests a low order systematic perturbation expansion in terms of a suitable effective interaction. When cancellation effects are absent, as in the case of the positron lifetime, a non perturbative approach may be required [17]. In the particular case of the correlations between the core hole and the conduction electrons participating in the soft X-ray process, first order theory gives satisfactory results in the satellite and tailing regions [4]. The cancellation effects discussed above are operative also in absorption spectra [18] and to our knowledge no plasmon satellite has been observed in such spectra.

3. Edge phenomena. — We will first discuss the expected behavior of the spectra when the width of the core level due to Auger and radiative lifetimes, temperature, recoil and self absorption are neglected. In this case we can use the semi-classical theory of radiation and the golden rule

$$I(v) = l^{-1} \sum_{i=1}^{l} \sum_f \delta(E_f - E_i \pm v) \left| \langle f | \theta | i \rangle \right|^2 .$$

(1)

We put $h = 1$; $\theta = \sum n_i p_i$ is the dipolar operator applied to all the electrons of the system and $n$ is a unit polarization vector in the direction of the vector potential. One sums over all possible final states and averages over the $l$ initial states. The exponent $n$ in (1) should be $n = 2$ for emission and $n = 1$ for absorption if $I(v)$ is to be interpreted as a intensity [19]. In Eq. (1) and below the upper sign refers to emission, while the lower sign refers to absorption.

The simplifying assumptions above leads us to a two Hamiltonian model for the X-ray transition. In *emission* the initial state is taken to be the $N+1$ conduction electron ground state of

$$H^a = \sum_n H_n + \frac{1}{2} \sum_{n,m} V_{n,m} - \sum_n \epsilon_n - E_B .$$

(2)

The first term on the right hand side of (2) is a one electron Hamiltonian, which is diagonalized by Slater determinants of Bloch waves. The second term is the Coulomb electron-electron interaction. The third term is the Coulomb interaction of the conduction electrons 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. The final state in emission contains $N$ conduction electrons, no core hole and is describable by a Hamiltonian

$$H^a = \sum_n H_n + \frac{1}{2} \sum_{n,m} V_{n,m} .$$

(3)

The energy of the final state differs from the ground state energy of (3) by an excitation energy $\Delta E^a$.

In the initial state in *absorption* the $N$ conduction electrons are in the ground state of (3), and there is no core hole. The final state in absorption is an excited state of (2) with excitation energy $\Delta E^a$. The frequency of the emitted/absorbed X-ray photon is thus

$$\nu = \mu_0 - \mu_B \mp \Delta E^{\pm a} .$$

(4)

Here $\mu_0$ is the conduction electron chemical potential, and $\mu_B$ is the energy of the vacant state in the core. The latter quantity is shifted from the value $E_B$ in (2) because of the interactions. Clearly $\Delta E^{\pm a} \geq 0$, and $\Delta E^{\pm a} = 0$ corresponds to the frequency at the Fermi edge, which coincides for absorption and emission spectra.

It was first noted by Pirenne and Longe [20], that the simplified model discussed above gives rise to singular behavior of the spectra near the Fermi edge. By neglecting the electron-electron interaction term $V_{n,m}$ and representing the core hole potential $V_n$ by a separable potential, Nozières and de Dominicis [21] succeeded in finding an exact solution to the asymptotic behavior of the spectra near the edge

$$I(v) \sim |v - \mu_0 + \mu_B|^{-\alpha} .$$

(5)

Similar results have been obtained by several authors, among them Bergersen and Brouers [22], using more intuitive methods.

There are two different physical effects which contribute to the exponent $\alpha$ in (5). The first effect is related to the Anderson orthogonality theorem [23]. It implies that, as the system develops in time after a core hole is
suddenly destroyed or created, there is a relaxation, and the memory of the way this process had occurred gets lost, even when lifetime effects are neglected. A further consequence is that the core hole cannot be considered as a «quasihole» in the usual many body sense [24]. The absence of a sharp core level gives a negative contribution to the exponent $\alpha$ in (5). A compensating effect arises from singularities in the vertex corrections due to correlations of the conduction electron participating in the soft X-ray process with the core hole. Because the interaction is attractive the effect tends to enhance the spectral intensity near the edge. At metallic densities the correlations of the conduction electrons with the screened core hole tend to be largely s-like. Radiative transitions involving s-electrons are forbidden in K-spectra, and from case of core states that are of interest for the particular spectral regions, transitions involving s-electrons are allowed, and one might expect a spike near the edge. The above qualitative argument is confirmed by more detailed calculations [25] and also by experiment [26, 27].

Because of lifetime effects, the observed $L_{2,3}$ spectra are not actually singular near the edge [26]. The most important lifetime effects come from Auger transitions. We will not discuss these here, but direct the reader to Ref. [18] and [24] and the articles quoted therein. Instead we assume here and in the next section that it is adequate to calculate the spectrum in the infinite lifetime case, and to incorporate lifetime effects post bellum by folding the result with an appropriate Lorentzian in the spirit of Wigner and Weisskopf [28]. In effect, this assumes that the «orthogonalization time », i.e. the time it takes for correlations such as (6) to die out, must be short compared to the Auger lifetime [24]. This seems to be the case for the $L_{2,3}$ spectra of simple metals such as Mg, Al and Na, is doubtful in the case of the Li K-spectra and is probably not true for the $L$ and $M$ spectra of the transition metals.

Because of lifetime effects the exponent $\alpha$ in (5) is not directly observable. Instead the relative spectral weight of the spike or dip near the edge appears more suitable for comparison with experiment. To obtain such quantities it is necessary, however, to calculate the spectra in the main parts of the bands. Actually if edge effects turn out to carry little spectral weight, it may not be necessary to know the precise form of the edge singularity to obtain a good semiquantitative agreement with experiment.

4. The main parts of the bands. — We will here discuss how to overcome certain difficulties that arise in calculations of the spectra in the main parts of the bands. Calculations making use of the arguments below are reported elsewhere [18, 29]. As previously mentioned we will neglect lifetime effects. This allows us to use the two Hamiltonian model described in the previous section.

It is desirable to avoid explicit reference to the final states. For this reason we rewrite (1) in the form

$$I^f(\nu) = \frac{\nu^2}{\pi} \sum_{l=1}^{\infty} \text{Re} \int_0^\infty ds \exp(iE_\nu - \nu s) \left\langle N | U^f(\nu, s) \theta_i^f(s) U^f(s, 0) \theta_i(0) U^f(0, -\infty) | N + 1 > - N + 1 | U^f(\nu, -\infty) | N + 1 > \right\rangle. (7)$$

$$I^p(\nu) = \frac{\nu^2}{\pi} \sum_{l=1}^{\infty} \text{Re} \int_0^\infty ds \exp(i(\nu - E_\nu) s) \left\langle N | U^p(\nu, s) \theta_i(s) U^p(s, 0) \theta_i^p(0) U^p(0, -\infty) | N > - N | U^p(\nu, -\infty) | N > \right\rangle. (8)$$

Here we have used the interaction representation and the adiabatic hypothesis, switching on/off the interactions in the distant past/future. In absorption we do not expect any difficulties from this, in emission we can only use the adiabatic hypothesis because we have neglected lifetime effects. The operator $U^\text{inv}(t, t')$ is the Dyson time evolution operator that goes with the Hamiltonian $H^{\text{inv}}$. We have

$$\theta_i(s) = \sum_k < i | n_k p_k | k > a_{k,n} e^{-i\pi k} \nu \left\langle k \right| (9)$$

where $| i >$ is one of the $l$ possibly near degenerate core states that are of interest for the particular spectral regions, $a_{k,n}$ is the annihilation operator for a conduction electron with wave vector $k$, energy $\epsilon_k$ in the one electron picture and spin $\sigma$. We have avoided explicit reference to core electron operators, $| N >$ is thus just a Slater determinant of the $N$ lowest conduction electron states.

The explicit introduction of a two Hamiltonian model helps us to notice, that between times 0 and $s$ the numerators and denominators in (7), (8) have different time evolution operators. For this reason unlinked vacuum contributions will not completely cancel out, i.e., the linked cluster theorem will not apply here [22]. The unlinked terms which should be included are divergent throughout the main band, but this divergence cancels with contributions from other terms. The failure to include the unlinked terms thus leads to spurious divergencies throughout the parent band.

If now we expand (7) and (8) in a formally correct fashion a new difficulty arises, namely terms which diverge badly at the Fermi edge, worse than could be expected from the Nozières and de Dominicis theory. These are secular terms arising from the shift of the Fermi edge due to interactions. As pointed out in
A shifted edge gives rise in perturbation theory to δ-function and δ-function derivative singularities at the position of the old edge. The way out of this difficulty is to make separate perturbation expansions for the position and the shape of the spectra. This means that one should not expand the quantity $I(v)$ in perturbation theory but instead $I(v + D)$ where

$$D = \Sigma_0 - \Sigma_B,$$  \hspace{1cm} (10)

is the shift of the Fermi edge, due to a shift $\Sigma_0$ of the Fermi energy and a shift $\Sigma_B$ of the core level caused by the interaction. These quantities again have perturbation expansions of their own.

Unfortunately, the theory gives rise to one further spurious divergency, at the bottom of the emission parent band. In the one electron picture the spectrum exhibits here a slope discontinuity. The true spectrum, on the other hand, tapers smoothly off, because of the width of deep lying conduction electron states. The spectrum is also slightly stretched, because of a dispersion in the level shifts. These kind of changes are very awkward to handle in perturbation theory. To see this consider the conduction electron density of states

$$N(E + \Sigma_0) \sim \frac{\Gamma_r(E)}{(E - p^2/2m - A_r(E) + \Sigma_0)^2 + I_r^2(E)}$$  \hspace{1cm} (11)

where $A_r(E)$ and $\Gamma_r(E)$ are the real and imaginary parts of the conduction electron self-energy. Both $A_r(E)$ and $\Gamma_r(E)$ can be computed in perturbation theory if proper attention is given to shifts such as (10). When the results are substituted in (12) it is easy to see that the resulting expansion of $N(E + \Sigma_0)$ will contain terms which are badly divergent at $E = 0$. Exactly this difficulty also occurs when emission spectra are calculated in perturbation theory. As can be seen from (11) a way out is to use only renormalized electron propagators. A calculation of the electronic density of states along these lines has been carried out by Lundqvist [8]. In the bottom of the parent band region this calculation probably also is adequate to describe emission spectra of the simple metals. A

renormalized calculation is also necessary if one wishes to obtain corrections to the total depth of the parent band. Note, however, that because of the cancellation effects discussed in section 2, the latter spectra are more free electron like than the actual density of states. Furthermore a calculation of soft X-ray spectra where all propagators and vertices are renormalized does not appear numerically feasible at the moment.

Apart from the difficulty at the bottom of the main band, a first order theory can be constructed [18] which gives qualitatively most of the observed features of $L_{2,3}$ spectra of the simple metals and which are not due to band structure effects. Notably the theory gives:

1. A reasonable tailing region in emission spectra;
2. A weak plasmon satellite in emission and practically no plasmon effect in absorption;
3. The spike at the emission and absorption Fermi edges and the depression after the spike in absorption;
4. The absence of a gap between the emission and absorption bands.

As perhaps could be expected, the enhancement of the spectral intensity in the main band due to core hole interactions is very sensitive to the short range properties of the core hole potential used. The potential in this region is in turn strongly affected by the orthogonalization of the conduction electrons to other core states. The order of magnitude of this effect has been obtained [29] using an Ashcroft [31] type pseudopotential. When a suitably chosen such potential was used [18, 29] we obtained a good semi quantitative agreement with the observed emission [27] and absorption [26] spectra of sodium. Perhaps one can say in view of the many obstacles an improved calculation must overcome, that a better agreement is likely to be fortuitous. On the other hand, this would be desirable if the many body aspects of the theory could be reformulated so as to facilitate the elimination of spurious divergencies without losing important cancellation effects.

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DISCUSSION

LONGE. — La question de Friedel était plus ou moins : « Retrouvez-vous la forme exponentielle de la singularité au bord de Fermi ? »

Réponse : Non, une théorie du premier ordre en l'interaction effective électron-électron (ou électron-trou) donnera une forme logarithmique du type

\[ W_f \left( 1 - 2 \frac{\delta_0}{\pi} \ln \frac{\xi}{|\omega - \omega_0|} \right) \]

au lieu de la forme exponentielle \( W_f \left( \frac{\epsilon}{|\omega - \omega_0|} \right)^{\alpha_1} \) de Nozières et de Dominicis. Cette forme logarithmique approchée doit cependant rester acceptable dans pratiquement toute la bande sauf au voisinage immédiat du bord de Fermi, ceci surtout pour les bandes \( L (l = 0) \) où \( \omega_0 \sim \frac{2}{\pi} \delta_0 \) est positif.