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Many-electron singularity in x-ray photoemission and x-ray line spectra from metals

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Abstract. It is pointed out that the spectra of x-ray induced fast photoelectrons from metal should have a characteristic skew line shape resulting from Kondo-like many-electron interactions of the metallic conduction electrons with the accompanying deep hole in the final state. The same line shape should also occur for the discrete line spectra of x-rays emitted from metals. This mechanism could account for the well known asymmetries observed for Kα lines.

1. Discussion

A couple of years ago, Mahan (1967) suggested that an electron excited up to the Fermi surface of a metal from a core state by the absorption of an x-ray (or the converse emission process) would scatter in a singular way, analogous to that occurring in the Kondo effect, from the transient, screened Coulomb, potential of the accompanying deep (and immobile) hole, and thus lead to a singular peak in the soft x-ray absorption (emission) cross section at threshold. More recently, Nozières and de Dominicis (1969) (to be referred to as ND) have shown that what actually happens is a combination of the above singular electron–hole scattering together with a transient and singular re-adjustment of the ground state of the entire Fermi gas to the presence of the effective potential of the hole. Depending on the sign and strength of this potential, these two effects may reinforce or cancel, leading to the possibility of either threshold peaks or zeros in the x-ray absorption cross section.

In this paper we discuss two related measurements which, in principle, provide a direct way of studying the transient re-adjustment of the ground state of the Fermi gas to the sudden appearance of the hole potential. These are: (i) the measurement of the detailed line shape of fast photoelectrons emitted as a result of the absorption of monochromatic x-rays by the metal; (ii) the measurement of the line shape of discrete x-ray lines emitted as a result of electron transitions between inner shell states of an excited atom in a metal. In the first case the energy $\epsilon_k$ is a direct measurement of the energy of the hole state $E_h$ (measured relative to the Fermi level) left behind in the metal:

$$\epsilon_k = \omega + E_g - E_h - W$$

where $\omega$ is the x-ray energy ($\hbar = 1$), $E_g$ the initial ground state energy of the metal, and $W$ is the work function. Thus the maximum photoelectron energy $\epsilon_{\text{max}}$ corresponds to the ground state of the hole + metal, while photoelectrons emitted below the maximum correspond to events in which the hole + Fermi sea is left in an excited state. Excited states with energies very close (a fraction of an electron-volt) to the ground state are those in which the Fermi sea is excited by the creation of low energy conduction electron–hole pairs (i.e. charge density fluctuations). It turns out that since the energy of creating pairs goes continuously to zero as the momentum transfer to the pair, an infra-red catastrophe occurs in which it is very favourable to produce a large number of very low energy pairs. Thus the photoemission cross section $d\sigma/d\epsilon$ is changed from a $\delta$-function (for $\delta$-function
ingoing x-ray spectrum) in the absence of pair formation to a singular (though integrable) curve tailing off on the low energy side of $\epsilon_{\text{max}}$ (figure 1, curve A). In the second type of measurement, a deep hole which has previously been formed by the absorption of an x-ray (or by knocking out an inner shell electron with a fast primary electron) captures an electron from an adjacent inner shell of the atom with emission of an x-ray, i.e. the hole moves 'up' to a higher atomic level. When this happens the effective screened potential acting on the conduction electrons changes somewhat, so that again the Fermi sea has to undergo a drastic re-adjustment to the new potential. The emitted x-ray can thus leave the Fermi sea in a many-pair excited state, with accompanying distortion of the x-ray line shape.

![Figure 1. Singular line shape for singularity index $\alpha = 0.3$: curve A, in the absence of lifetime broadening—broken curve, arbitrary units (equation (9)); curve B, with finite hole lifetime—full curve (equation (18)); energy measured in units of $\gamma$.](image)

In practice both types of event will be rounded out by lifetime effects (figure 1, curve B). However, in the photoemission case, the resulting tailing of the line shape has to be distinguished from events in which the escaping electron loses energy to the Fermi sea. We can, conceptually, distinguish two types of such energy loss: energy loss to the bulk metal (e.g. plasmon emission), and energy loss to surface states of the metal (e.g. surface plasmons). In the analysis which follows we assume that the probability of bulk energy loss by the escaping photoelectron is a function of thickness of the metallic target, and goes to zero as the film thickness goes to zero. This will not apply to surface energy loss, but presumably the probability of this process will decrease with increasing escape energy of the photoelectron, so it can be distinguished by varying the incident photon energy. In contrast, the excitations of the Fermi sea accompanying the final hole state are an intrinsic property of the metal, so they should not depend either on film thickness (above a few atomic layers) or on incident photon energy.

2. Photoemission

In the photoemission case the final state of the system may be written

$$|\Psi_f\rangle = c_k^+ |\Psi_{\text{hole}}\rangle$$  \hspace{1cm} (1)

where $c_k^+$ is a creation operator for the fast photoelectron and $|\Psi_{\text{hole}}\rangle$ is a wave function...
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of the hole + Fermi sea. The photoemission scattering cross section may then be written, to lowest order in the x-ray field, as

$$\frac{d\sigma}{d\epsilon} \propto \sum_{\text{hole states}} |\langle \Psi_g | j c_k^+ | \Psi_{\text{hole}} \rangle|^2 \delta(\omega - \epsilon_k - \epsilon_h)$$

(2)

where $|\Psi_g\rangle$ is the initial ground state of the metal, $j$ is the electron–hole current coupling to the x-ray field:

$$j = \sum_k j_k (b^+ c_k^+ + bc_k)$$

(3)

($b^+$ is the hole creation operator) and $\epsilon_h = E_h - E_g + W$. We shall treat the current matrix elements $j_k$ as constant.

Introducing the Hamiltonian of the hole + Fermi sea (ND)

$$H = H_{\text{cond}} + H_1$$

$$= \sum_p \epsilon_p c_p^+ c_p + \epsilon_0 b^+ b + \frac{v}{N} \sum_{pp'} b^+ c_p^+ c_p$$

(4)

we now make the important approximation, discussed in §1, of neglecting all interactions of the escaping electron with the other electrons in the metal. We may thus write

$$\frac{d\sigma}{d\epsilon} \propto \text{Re} \left[ \frac{1}{\pi} \int_0^\infty \text{d}t <b(t)b^+(0)> \exp \{i(\omega - \epsilon_h)t\} \right]$$

(5)

where $b^+(t) = \exp (iHt) b^+ \exp (-iHt)$. The hole–hole correlation function in (5) is directly related to the hole propagator introduced by ND.

By noticing (ND, Langreth 1969) that, owing to the large energy of formation of a hole, only one hole can be present at a time, this correlation function may also be written directly in terms of the Hamiltonian $H_{\text{cond}}$ of the conduction electrons in the absence of the hole, and the Hamiltonian $H_{\text{cond}} + H_v$ of the electrons in the presence of a static hole potential:

$$H_v = \frac{v}{N} \sum_{pp'} c_p^+ c_{p'}$$

(6)

We have

$$<b(t)b^+(0)> = \langle \Psi_g | \exp(iH_{\text{cond}}t) \exp(i(H_{\text{cond}} + H_v)t) | \Psi_g \rangle$$

$$= \sum_{E_v} \langle \Psi_g | \Psi_{E_v} \rangle \langle \Psi_{E_v} | \Psi_g \rangle \exp \{i(E_g - E_v)t\}$$

(7)

where $|\Psi_{E_v}\rangle$ are the complete set of states, and $E_v$ their energies, for the electrons moving in a static hole potential (6). Thus (5) depends essentially on the overlaps between the ground state of the unperturbed Fermi gas and the complete set of states of the Fermi gas in the presence of the potential, shown by Anderson (1967) to be very singular.

A rough estimate of the photoemission cross section (5) may be obtained by using the asymptotic formula of ND for this correlation function, valid for long times, i.e. energy transfers

$$\epsilon = \epsilon_{\text{max}} - \epsilon_k \ll D$$

where $D$ is the conduction band width.

For the case of equation (6), which leads only to s-wave scattering (short-range potential) and inserting

$$<b(t)b^+(0)> = \frac{\exp(-i\epsilon_0t)}{(iDt)^2}$$

(8)
where \( \alpha = (\delta/\pi)^2 \) and \( \delta \) is the phase shift for scattering of conduction electrons from the hole potential (we assume \( \alpha < 1 \)) we have

\[
\frac{d\sigma}{d\epsilon} \propto \frac{\sin (\alpha/2)}{\Gamma(\alpha)\epsilon^{1-\alpha}}
\]

(9)

where \( \Gamma \) is the gamma function. This is plotted in figure 1, curve A. For a general potential, ND show that \( \alpha \) is given by

\[
\alpha = \sum_{l=0}^{\infty} (2l + 1)(\delta_l/\pi)^2
\]

where \( \delta_l \) is the phase shift of the \( l \)th partial wave.

3. X-ray line spectrum

In this case we have two hole potentials corresponding to the two hole states, creation operators \( b_{1}^{+}, \ b_{2}^{+} \), leading to the Hamiltonian

\[
H = H_{\text{cond}} + \epsilon_1 b_{1}^{+} b_{1} + \epsilon_2 b_{2}^{+} b_{2} + b_{1}^{+} b_{1} H_{v1} + b_{2}^{+} b_{2} H_{v2}
\]

(10)

where

\[
H_{v1,2} = \frac{\hbar}{N} \sum_{p'p} c_{p'}^{+} \epsilon_p c_{p}
\]

(11)

The transition probability per unit time for emission of an x-ray, frequency \( \omega \), is then given by

\[
\frac{dW(\omega)}{dt} \propto \sum_{E_2} \langle \Psi_1 \arrowvert j \arrowvert \Psi_2 \rangle^2 \delta(\omega + E_2 - E_1)
\]

(12)

where \( \Psi_1 \) is assumed to be the ground state of the Fermi sea in the presence of hole-1 states and \( \Psi_2 \) are the set of excited hole-2 states. We may now write \( j \) as

\[
j = j_{1,2}(b_{1}^{+} b_2 + b_{2}^{+} b_1)
\]

(13)

where \( j_{1,2} \) is a matrix element. Thus we may write

\[
\frac{dW(\omega)}{dt} \propto \frac{\text{Re}}{\pi} \int_{0}^{\infty} dt \langle b_{2}(t) b_{1}^{+}(t) b_{1}(0) b_{2}^{+}(0) \rangle \exp(i\omega t).
\]

(14)

To evaluate this we eliminate the hole operators, as in equation (7), to give

\[
\frac{dW(\omega)}{dt} \propto \frac{\text{Re}}{\pi} \int_{0}^{\infty} dt \exp[i(\omega - \epsilon_1 + \epsilon_2)t] \langle \Psi_1 \exp(iH_{1}t) \exp(-iH_{2}t) \arrowvert \Psi_1 \rangle
\]

(15)

where \( H_{1} = H_{\text{cond}} + H_{v1} \), and similarly for \( H_{2} \). The difference from (7) is that a different potential acts in \( H_{1} \) and \( H_{2} \). The right-hand side of (15) could be evaluated by the method of ND. However, a much simpler way of evaluating it in the weak coupling limit \( vN(0) \ll 1 \) (\( N(0) = \text{density of conduction electron states at the Fermi level} \) has recently been given by Schotte and Schotte (1969). They observe that the effect of the hole potential is to displace the electron density oscillators of the Fermi sea. By using their method, it is straightforward to show that (15) has the same form as (9), except that, in the weak coupling limit, the phase shift that comes in is the difference of the scattering phase shifts in the two hole states:

\[
\frac{dW(\omega)}{dt} \propto \frac{1}{\epsilon^{1-\beta}}
\]

(16)
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where

\[ \beta = \left( \frac{\delta_1}{\pi} - \frac{\delta_2}{\pi} \right) \text{ and } \epsilon = (\omega - \epsilon_1 + \epsilon_2). \]

We have used here the weak-coupling (Born approximation) result:

\[ \tan \delta \simeq \delta \simeq \pi \nu N(0). \]

We shall assume (without proof) that this still holds for \( \nu N(0) \lesssim 1. \)

4. Line shapes

The above singular line shapes will in practice be modified by the finite lifetime of destruction of the hole states by electron capture. The detailed theory of the resulting time dependence would require a higher order treatment of the interaction with the x-ray field. We guess at the effect of this by assuming a form

\[ \langle b(t)b^*(0) \rangle = \frac{\exp(-\gamma t)\exp(-i\epsilon_0 t)}{(i\Delta t)^2}. \]

On performing the Fourier transformation, we find a photoelectron yield function–spectral line shape

\[ Y(\epsilon) = \frac{\Gamma(1 - \alpha)}{(\epsilon^2 + \gamma^2)^{(1-\alpha)/2}} \cos \left\{ \frac{\pi \alpha}{2} + \theta(\epsilon) \right\}, \]

with

\[ \theta(\epsilon) = (1 - \alpha) \tan^{-1}(\epsilon/\gamma) \]

where \( \epsilon \) is measured relative to the maximum energy in the absence of lifetime broadening. For the line-shape case, \( \beta \) (equation (16)) is to be substituted for \( \alpha \). This function is plotted in figure 1, curve B, and leads for \( \alpha > 0 \) to a skew spectral line. A simple measure of this skewness is the asymmetry index used by x-ray spectroscopists (see §5 below): the ratio of \( |\text{peak energy} - \frac{1}{2}\text{-height energy}| \) on the low frequency to that on the high frequency side of the line. For equation (18) the position \( \epsilon_{\text{max}} \) of the peak is given by

\[ \epsilon_{\text{max}} = \gamma \cot \left( \frac{\pi}{2 - \alpha} \right) \]

and the asymmetry index (calculated numerically) is tabulated in table 1 as a function of \( \alpha \).

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>Asymmetry index</th>
<th>( \alpha )</th>
<th>Asymmetry index</th>
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<tr>
<td>0.00</td>
<td>1.000</td>
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<tr>
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<td>1.411</td>
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</tr>
<tr>
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<td>1.191</td>
<td>0.26</td>
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</tr>
<tr>
<td>0.14</td>
<td>1.291</td>
<td>0.30</td>
<td>1.935</td>
</tr>
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</table>
A much more sensitive way of showing up this asymmetry is to plot
\[ X(\varepsilon) = 1/Y(\varepsilon) \]  
(21)
as a function of \((\varepsilon - \varepsilon_{\text{max}})^2\). For a Lorentzian this leads to the same straight line above and below the peak. For the function (18), \(X(\varepsilon)\) plotted as a function of \((\varepsilon - \varepsilon_{\text{max}})^2\), with \(\varepsilon_{\text{max}}\) given by (20), is still remarkably straight for \(|\varepsilon| \geq \gamma\), but has very different slopes on each side of the peak (figure 2). This plot shows that even for fairly low asymmetry, where the line shape still looks very Lorentzian, the inverse plot shows up a very clear difference in slope between the low frequency and high frequency sides of the peak.

5. Observed line shapes of x-ray line spectra
Detailed line shapes of \(K\alpha_{1,2}\) lines in transition and other metals have been known since 1935 (Sandström 1957). Skewness of the lines similar to that in figure 1, curve B, is observed and varies considerably from element to element. The asymmetry index varies fairly smoothly across the 3d transition series for the \(K\alpha\) line with a maximum value at Fe (Bearden and Shaw 1935, see also Parratt 1936). For Fe the \(K\alpha_1\) line has a width at \(\frac{1}{2}\) height of about 5 ev and an asymmetry index of 1.6. If the mechanism described in \(\S\) 3 is responsible for this asymmetry,† this would correspond to \(|\delta_L - \delta_K| \approx \frac{1}{2}\pi\) using table 1. This is based on the assumption that the line corresponds to a transition in a singly ionized atom. Multiple ionization could possibly lead to extra satellite contributions.

A crucial test of this interpretation is the observation of the line shape of \(K\alpha_1\) from an insulating iron compound. The change of the x-ray line spectrum on going from metals to their oxides was looked for by Sanner (1941). Unfortunately the resolution of his data does not appear to allow for a detailed study of the line shape. Sanner reported no detectable shift of the \(K\alpha_1\) line for Fe to FeO (such as would be expected from equation (20)). However, a similar observation for \(\text{Cu} \rightarrow \text{CuO}\) was later contradicted by Nordling et al. (1958, p. 499) who found a small shift on oxidation, in disagreement with Sanner. Thus, detailed measurement of \(K\alpha\) line shapes in metal oxides appears not to have been carried out, and this is an experiment which should be done to provide a conclusive test of the mechanism of the present paper.

6. Photoelectron line shapes
Experimentally, skew line shapes for emitted photoelectrons have been observed by Siegbahn and collaborators (Nording et al. 1958) for very fast photoelectrons (several

† This was suggested, in a qualitative way, by Parratt (1936).
hundred electron-volts). Part of the observed asymmetry can be accounted for by the tail of the plasmon-energy loss peak (Sokolowski 1958). There may also be a contribution due to the mechanism described in § 2. But in comparing the form (18, 19) with experiment it must be emphasized that equation (8) is an asymptotic formula only valid for times \( t \) long compared with \( \hbar/D \) (\( D \) the band width). It is not clear how breakdown of (8) at shorter times will affect the form of (18), since the latter is the convolution of (8) with a Lorentzian form, so that the low energy singularity of (8) could still affect the line shape of (18) in the wings of the line.

It is hard to make a detailed comparison of the line shapes observed by Nordling et al. with the above theory, since the resolution of their \( \beta \)-ray spectrometer was of the order of 8 ev (Nordling et al. 1958, page 495). In spite of this a detectable change of asymmetry in their data on going from Cu to CuO was seen by plotting the inverse line shape as in equation (21) (after subtracting off an estimate of the background). In studying this asymmetry we should remember that the source radiation (e.g. the Cu K\( \alpha \), line) already has some asymmetry, as discussed in § 5. Conveniently enough, the convolution of the source spectrum with the photoelectron yield function just leads to an addition of the singularity indices \( \alpha_s, \alpha_p \) for the source radiation and the photoelectric yield. Thus, the convoluted line shape should still be of the same form (18) as that of the source and the yield functions separately. This may partly explain the fact that the data of Nordling et al. (1958) still show some asymmetry for the CuO case, i.e. this may just be the source asymmetry. (There could also, presumably, be phonon contributions to the asymmetry in the insulator.)

We conclude that experiments with higher resolution and more monochromatic source radiation would, if feasible, provide a much more convincing test of the mechanism proposed in this paper. What is required is (i) that the hole state is far enough below the conduction band to be immobile, and (ii) that the emitted photoelectron be far enough above the work-function threshold (say 10–20 ev) for surface effects not to be strongly energy dependent.

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We should like to thank Mr K. Long and Dr S. Engelsberg for helpful conversations. We are very grateful to the Materials Physics Division, A.E.R.E., Harwell, for the generous partial support of this research. One of us (M.S.) wishes to acknowledge the support of the Leverhulme Foundation. We are grateful to Dr T. Claeson for sending us a copy of Sanner's thesis (the British Museum copy was apparently the victim of a bombing raid).

Note added in proof. Recently Fadley, Shirley, Freeman, Bagus and Mallow have demonstrated the existence of multiplet splittings in x-ray photoemission from core states of Fe atoms. Unresolved splitting would also contribute to the asymmetry of x-ray lines. The results of this paper should still apply to line shape of individual components of these multiplets.

References

Sanner, V. H., 1941, Dissertation, published by the University of Uppsala.