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Effects of Initially Excited Hole States on the Soft-X-Ray Emission Spectra of Metals

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A general theory of the effects of Coulomb excitation of a deep hole state in a solid on the subsequent soft-x-ray emission line shape is given. For excitation energies well above threshold it is shown that the emission corresponds to the decay of a nonrelaxed initial hole state which is suddenly introduced into the solid. Using a weak-coupling approximation, a generalization of the Weisskopf-Wigner formula for radiative line shapes is derived which includes the enhancement of the high-energy tail of an emission line or edge due to initial excitations. Comparison of the approximate results with measurements of the K edge of Li metal provides a reasonable explanation of the observed discrepancy between absorption and emission line shapes.

I. INTRODUCTION

The development of a semiquantitative theory of many-electron excitations associated with high-energy transitions in solids (far uv, soft-x-ray, etc.) by Mahan,[1] Nozières and collaborators,[2] Hedin and Lundquist,[3] Langreth,[4] Doniach[5] and others, leads to a need for a closer examination of the experimentally observed line and edge shapes in a variety of experiments. A class of experiments of considerable practical importance is that of soft-x-ray emission. However, in contrast to a straightforward absorption-edge measurement, such experiments embody an essential physical complication: they involve the preparation of a highly excited state of the solid, usually by Coulomb excitation through electron bombardment of a target.

Empirically it has long been recognized that such initial excitation processes will involve many-electron excited states[6] (often referred to as "double excitation") with energies near threshold of

$$E_i = E_{\text{hole}} + \mathcal{E}_{\vec{k}} + \Delta E_{\text{many-electron}} , \tag{1}$$

where E_{hole} is the single electron energy of a deep-hole state, $\mathcal{E}_{\vec{k}}$ is a conduction-electron energy above the Fermi level and $\Delta E_{\text{many-electron}}$ represents additional electronic excitations of the solid (electron-hole pairs, plasmons, etc.).

The importance of these initially excited states is that, if the lifetime of the high-energy excitation is fairly short (experimentally typical core-state hole lifetimes are of order 0.1–1 eV^{-1}), the initial excitation can provide additional energy for the soft-x-ray emission process, over and above the minimum, $E_{\text{hole}} + \mathcal{E}_F$, which marks the high-energy threshold for single-electron–deep-hole recombination, thus leading to an increased strength in the high-energy tail of the emission edge.

This is to be contrasted with the corresponding absorption-edge data. In an absorption experiment the transition is from the initial ground state of the solid to a definite excited state; therefore it will have a sharp threshold energy of $E_{\text{hole}} + \mathcal{E}_F$ and will not be expected to show any enhancement on the tail of the edge.

The relevant time scale for the outward propagation of an excitation from the initially excited hole, and hence of dissipation of the additional initial energy, is determined by the conduction bandwidth E for a simple metal. This is to be compared with the half-width (or inverse lifetime) λ for the hole state. For simple metals such as the alkalis, λ/E is of order 10^{-2} and the initial hole excitation leads to appreciable modification of the emission spectrum only out in the tail of the edge.

For narrow-band systems such as transition metals, λ/E becomes much larger. This provides a qualitative understanding of the fact that the effects of double excitation or emission-edge spectra is known to be of importance in transition metals and their compounds.[7]

In this paper we give, for the first time, a quantitative theory of the effects of initial hole excitation on soft-x-ray emission spectra. The original approach to the calculation of emission spectra was due to Wigner and Weisskopf,[8] who assumed that, at an initial time $t=0$, an atom could be placed in an excited state E_i from which it decays to the ground state by following the Schrödinger equation of the coupled atom–radiation-field system. In the present paper we follow the work of McMullen and Bergersen[9] in calculating instead the full scattering cross section for the fast exciting electron impinging on a solid causing the subsequent emission of a soft x-ray. This approach, which is based on a generalization of the usual Feynman-Dyson S-matrix theory due to Keldysh[10] avoids the need to make assumptions about unstable initial states.

Our principal physical result is that, provided the initial excitation process (by the fast electron) is far from threshold, the initially excited state can be thought of as the result of the instantaneous stripping of a core electron from the inner shell to create an effective initial state

$$|\psi_i\rangle = d^\dagger_{\text{core}}\,|\psi_G\rangle \quad , \tag{2}$$

where $|\psi_G\rangle$ is the full ground state of the solid, $d^\dagger_{\text{core}}$ is the core-hole creation operator and $|\psi_i\rangle$ is the *effective* initial wave function. Since the hole introduces a sudden change in the system, $|\psi_i\rangle$ will, in fact, be a complex linear combination of excited hole states whose spectral density will show up as a strengthening of the high-energy tail of the subsequent soft-x-ray emission edge.

Within a particular approximation scheme we show that the resulting soft-x-ray spectrum will be given by a generalization of the Weisskopf-Wigner formula:

$$I(\omega) = \int_{\mu}^{0} d\omega'\,|\phi(\omega')|^2 R_G(\omega-\omega') \quad , \tag{3}$$

where $R_G(\omega-\omega')$ is the emission spectrum corresponding to a hole in its initial ground state and $|\phi(\omega')|^2$ is a broadening function which takes the form of a skew Lorentzian incorporating the natural lifetime of the hole state, but skewed by an increase in the high-energy tail due to the persistence of initial excitations. In the long-lifetime limit, the excitations die out before the x ray is emitted and $|\phi|^2$ reduces to the usual Weisskopf-Wigner Lorentzian.[11]

In order to test out these ideas against experiment we apply our general results to an idealized one-band model of a simple metal. The results are compared to soft-x-ray absorption and emission experiments on Li metal. We argue that a real experimental discrepancy between the line shapes of the absorption and emission edges in Li metal can be resolved as being due to initial hole excitation effects.

II. FORMULATION FOR SCATTERING CROSS SECTION

The general formula for the soft-x-ray emission intensity is

$$I(\omega) = \omega \sum_f |\langle f|\,S\,|i\rangle|^2\,\delta(E_i - E_f - \omega) \quad , \tag{4}$$

where S is the usual S matrix, $|i\rangle$ and $|f\rangle$ are the exact eigenstates of the system before and after the interaction ($\hbar = 1$) with eigenvalues E_i and E_f, respectively, and ω is the energy of the emitted soft x ray. In the case of a Coulomb excitation process,

$$|i\rangle = c^\dagger_{\vec{k}}\,|\psi_N\rangle \quad , \tag{5}$$

where $c^\dagger_{\vec{k}}$ is the creation operator for the fast bombarding electron and $|\psi_N\rangle$ is the exact ground state of the N-electron solid, while $|f\rangle$ includes the outgoing x ray and is summed over all possible excited states of the solid.

Equation (4) can be rewritten in the following form:

$$I(\epsilon_{\vec{k}}, \omega) = \omega \lim_{\tau\to\infty} [P_{\epsilon_{\vec{k}},\omega}(\tau)/\tau] \quad , \tag{6}$$

where τ is the duration of the scattering process, and $P(\tau)$ is the probability for observing a soft x ray with energy ω at time τ after an incident electron with energy $\epsilon_{\vec{k}}$ has penetrated the metal at time $-\infty$. We now follow the approach of McMullen and Bergersen[9] and recast (6) in correlation function form using the generalized path-ordering formalism of Keldysh.[10,12]

A principal assumption is that the fast-electron excitation process may be treated in lowest Born approximation. We therefore expand (6) to lowest order in the Coulomb excitation energy

$$H_c = \sum_{\vec{k}_1,\vec{k}_2} [M_{\vec{k}_1,\vec{k}_2}(\vec{k})\, d\, c^\dagger_{\vec{k}_1} c_{\vec{k}_2} c_{\vec{k}} + \text{h. c.}) \tag{7}$$

and radiation field energy

$$H_x = \sum_{q\lambda} (2\pi/\omega_q\Omega)^{1/2} \sum_{\vec{k}_0} (j_{\vec{k}_0}\, a^\dagger_{q\lambda}\, c_{\vec{k}_0}\, d + \text{h. c.}) \tag{8}$$

and pick out the term corresponding to a process in which the initial excitation leads to a final soft-x-ray emission event. The operators $c^\dagger_{\vec{k}}$, $a^\dagger_{q\lambda}$, and $d^\dagger$ are creation operators for conduction electrons, a photon of energy ω, and the deep level, respectively. The resulting transition probability, assuming constant matrix elements, is given by

$$\begin{aligned} P_{\epsilon_{\vec{k}},\omega}(\tau) \propto \sum_{\vec{k}_{0,1,2}} & \int_{-\infty}^{\tau} dt_1^- \int_{-\infty}^{\tau} dt_2^- \int_{\tau}^{-\infty} dt_1^+ \int_{\tau}^{-\infty} dt_2^+ \\ & \times e^{i\omega(t_2^- - t_2^+) - i\epsilon_{\vec{k}}(t_1^- - t_1^+)} \\ & \times \langle \Psi_N |\, P\{ c_{\vec{k}'_2}(t_1^+)\, c_{\vec{k}'_1}(t_1^+)\, d^\dagger(t_1^+)\, d(t_2^+)\, c^\dagger_{\vec{k}'_0}(t_2^-) \\ & \times c_{\vec{k}_0}(t_2^-)\, d(t_1^-)\, c^\dagger_{\vec{k}_1}(t_1^-)\, c^\dagger_{\vec{k}_2}(t_1^-)\} |\, \Psi_N \rangle \quad . \end{aligned} \tag{9}$$

Here, P represents the Keldysh path-ordering operator, the time dependence of the Heisenberg representation is generated by the full Hamiltonian of the solid, the minus sign denotes the forward leg of the scattering process and the plus sign the return leg. This formula thus represents a generalization of the Van Hove–Placzek[13] formula for neutron scattering to classes of scattering process in which additional particles (in this case the photon) are measured in the final state.

Our main physical result now comes from the assumption that provided the initial energy $\epsilon_{\vec{k}}$ is far above the deep-hole creation threshold, then in the intermediate state the fast electron and the knocked-out core electron will both be going at a relatively high energy (several hundred eV). We therefore neglect the effects of their interaction with the solid on the process we are interested in. Equation (9) therefore may be rewritten as

$$P_{\epsilon_{\vec{k}},\omega}(\tau) \propto \sum_{\vec{k}_{0,1,2}} \int_{-\infty}^{\tau} dt_1^- \int_{-\infty}^{\tau} dt_2^- \int_{\tau}^{-\infty} dt_2^+ \int_{\tau}^{-\infty} dt_1^+ e^{i\omega(t_2^- - t_2^+)} \times e^{i(\epsilon_{\vec{k}_1}+\epsilon_{\vec{k}_2}-\epsilon_{\vec{k}})(t_1^- - t_1^+)} R_{\vec{k}_0\vec{k}_0'}(t_1^-, t_2^-, t_2^+, t_1^+) , \quad (10)$$

where

$$R_{\vec{k}_0,\vec{k}_0'}(t_1^-, t_2^-, t_2^+, t_1^+) = \langle \Psi_N | P\{d^\dagger(t_1^+) d(t_2^+) \times c_{\vec{k}_0'}^\dagger(t_2^+) c_{\vec{k}_0}(t_2^-) d^\dagger(t_2^-) d(t_1^-)\} | \Psi_N \rangle . \quad (11)$$

Finally, the neglect of matrix elements and assumption that $\epsilon_{\vec{k}_1}, \epsilon_{\vec{k}_2} \gg 0$ allows us to integrate over $\epsilon_{\vec{k}_2}$ and $\epsilon_{\vec{k}_1}$ to give

$$P_{\epsilon_{\vec{k}},\omega}(\tau) \propto \sum_{\vec{k}_0} \int_{-\infty}^{\tau} dt_1^- \int_{-\infty}^{\tau} dt_2^- \int_{\tau}^{-\infty} dt_2^+ \int_{\tau}^{-\infty} dt_1^+ e^{i\omega(t_2^- - t_2^+)} \times \delta(t_1^- - t_1^+) R_{\vec{k}_0,\vec{k}_0'}(t_1^-, t_2^-, t_2^+, t_1^+) . \quad (12)$$

Thus it may be seen that for $\epsilon_{\vec{k}}$ far above threshold, the x-ray emission at (t_2^+, t_2^-) is the response to sudden creation of a "bare" (i.e., unrelaxed) hole at $t_1 = t_1^- = t_1^+$.

III. APPROXIMATE EVALUATION

In order to evaluate the cross section we will consider the model of a single parabolic conduction band with a deep core level. To emphasize the many-electron nature of the x-ray threshold process, we will use the usual simplified core-hole conduction-electron model

$$H = H_0 + H ,$$
$$H_0 = \sum_{\vec{k}} \epsilon_{\vec{k}} c_{\vec{k}}^\dagger c_{\vec{k}} , \quad (13)$$
$$H_1 = -V \sum_{\vec{k}\vec{k}'} c_{\vec{k}}^\dagger c_{\vec{k}'} d d^\dagger u_{\vec{k}} u_{\vec{k}'} ,$$

where

$$u_{\vec{k}} = 1, \quad \text{if } |\epsilon_{\vec{k}} - \mu| < E .$$

Then the deep-hole x-ray emission correlation function R [Eq. (11)] may be written in the interaction representation as

$$R_{\vec{k}_0\vec{k}_0'}(t_1^-, t_2^-, t_2^+, t_1^+) = \langle \Phi_N | P\{\mathfrak{U}(-\infty^-, -\infty^+) d^\dagger(t_1^+) d(t_2^+) \times c_{\vec{k}_0}^\dagger(t_2^+) c_{\vec{k}_0}(t_2^-) d^\dagger(t_2^-) d(t_1^-)\} | \Phi_N \rangle , \quad (14)$$

where $|\Phi_N\rangle$ is the Schrödinger ground state of the metal with a filled deep level and a filled Fermi sea, and

$$\mathfrak{U}(t, t') = T\{\exp[-i \int_{t'}^{t} d\tau H_1(\tau)\} . \quad (15)$$

For the present case of a static hole with no internal degrees of freedom it is convenient to factor out the initial and final parts of the hole propagator:

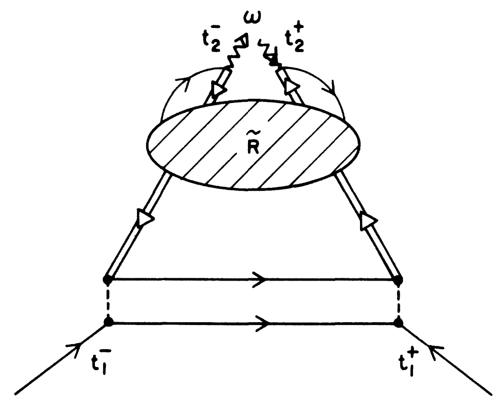

FIG. 1. General diagram for initial hole-excitation process.

$$R_{\vec{k}_0\vec{k}_0'}(t_1^-, t_2^-, t_2^+, t_1^+) = g(t_2^- - t_1^-) g^*(t_2^+ - t_1^+) \times \tilde{R}_{\vec{k}_0\vec{k}_0'}(t_1^- t_2^- t_2^+ t_1^+) , \quad (16)$$

where $\tilde{R}$ represents all many-electron diagrams without hole self-energy insertions as in Fig. 1.

In Eq. (16), g represents the dressed hole propagator. The Hamiltonian of the model does not contain broadening effects such as Auger decay processes. So we include the effects of these and other broadening processes in an *ad hoc* way by writing

$$g(t) = e^{-\lambda t} \tilde{g}(t) , \quad (17)$$

where $\tilde{g}(t)$ contains all many-body dressing effects and λ is the mean-width parameter for the deep-hole state. In simple metals Bergersen and Carbotte[14] have shown that phonon-induced broadening of the hole state may also produce important, possibly even dominant, contributions to λ.

A typical diagram in $\tilde{R}(t_1^-, t_2^-, t_2^+, t_1^+)$ is shown in Fig. 2.

We now proceed to evaluate R in a weak-coupling, asymptotic large-time limit. This limits the validity of our results to energy shifts $\Delta\mathcal{E}$ relative to the threshold energy which are small compared to the conduction band width E. In our analysis we will closely follow the approach of Nozières and de Dominicis.[2] The hole propagators can be erased since they give an over-all damping factor $e^{-\lambda t}$ in Eq. (14) which already has been included via Eq. (17). We first considered the contribution from the electron lines such as A in Fig. 2 then those from the cross bubble such as B.

The diagrams of the conduction-electron propagators involved with the x-ray emission vertex can be summed up with the help of the Muskhelishvili solution of a singular integral equation[15,16] for two nonintersecting time intervals. If we take the asymptotic limit of the Keldysh Green's functions[10]

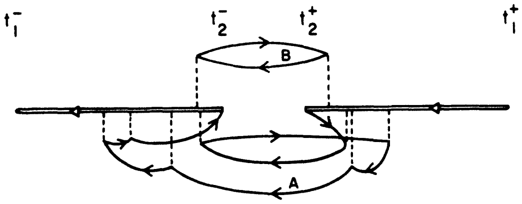

FIG. 2. A typical diagram used to calculate $R(t_1^-, t_2^-, t_2^+, t_1^+)$.

$(G^{--}, G^{+-}, G^{-+}, G^{++})$ involved in Fig. 2, then they will all reduce to the same form after momentum sums, i.e., $-i\nu_0 P(1/t)$. Denoting this form by $G(t)$ the relevant integral equation becomes,

$$\varphi(\tau, \tau') = G(\tau-\tau') - iV\int_{t_1^-}^{t_2^-} G(\tau-\tau'')\varphi(\tau'', \tau')d\tau'' - iV\int_{t_2^+}^{t_1^+} G(\tau-\tau'')\varphi(\tau'', \tau')d\tau'' , \quad (18)$$

where φ is a sum of all lines such as line A in Fig. 2. For $t_1^- = t_1^+$, the two integrals simply add so,

$$\varphi(\tau, \tau') = G(\tau-\tau') - iV\int_{t_2^+}^{t_2^-} G(\tau-\tau'')\varphi(\tau'', \tau')d\tau'' . \quad (19)$$

This is exactly the same as Eq. (17a) of Nozières and de Dominicis,[2] which in the asymptotic limit has the solution

$$\varphi(\tau, \tau') \xrightarrow[\tau \to t_2^+]{\tau' \to t_2^-} \varphi(t_2^+, t_2^-) \propto P(1/(t_2^- - t_2^+)) \left| (t_2^+ - t_2^-)iE \right|^{2\delta/\pi} . \quad (20)$$

δ is the phase shift involved in the conduction-electron core-hole scattering process.

The bubble in Fig. 2 can be written in the following form:

$$C^{+-}(t_1^-, t_2^-, t_2^+, t_1^+) = \tfrac{1}{2}V^2 \int_{t_1^-}^{t_2^-} d\tau^- \int_{t_2^+}^{t_1^+} d\tau^+ \times \sum_{\vec{k}\vec{k}'} G_{\vec{k}}^{+-,0}(\tau^+, \tau^-) G_{\vec{k}'}^{-+,0}(\tau^-, \tau^+) . \quad (21)$$

With

$$iG_{\vec{k}}^{+-,0}(\tau^+, \tau^-) = -n_{\vec{k}} e^{-i\epsilon_{\vec{k}}(\tau^+ - \tau^-)} ,$$

$$iG_{\vec{k}'}^{-+,0}(\tau^-, \tau^+) = (1 - n_{\vec{k}'}) e^{-i\epsilon_{\vec{k}'}(\tau^- - \tau^+)} ,$$

Eq. (20) becomes

$$C^{+-}(t_1^-, t_2^-, t_2^+, t_2^+, t_1^+) = +g^2 \int_{t_1^-}^{t_2^-} d\tau \int_{t_2^+}^{t_1^+} d\tau' \left(\frac{1 - e^{-iE(\tau'-\tau)}}{\tau' - \tau}\right)^2$$

$$= -g^2 \int_0^{t_2^- - t_1^+} d\tau \int_0^{\tau} d\tau' \left(\frac{1 - e^{iE\tau'}}{\tau'}\right)^2 - g^2 \int_0^{t_2^+ - t_1^-} d\tau \int_0^{\tau} d\tau' \left(\frac{1 - e^{-iE\tau'}}{\tau'}\right)^2 + g^2 \int_0^{t_2^+ - t_2^-} d\tau \int_0^{\tau} d\tau' \left(\frac{1 - e^{iE\tau'}}{\tau'}\right)^2 , \quad (22)$$

where $g = \nu_0 V$. Using the bubble as the proper self-energy in a linked-cluster summation, we get

$$e^{C^{+-}(t_1^-, t_2^-, t_2^+, t_1^+)} \quad (23)$$

as the sum of all cross bubbles through second order.

The important observation to make is that Eqs. (20), (22), and (23) show that R can be written as a product of functions of time differences in $(t_2^- - t_1^+)$, $(t_2^+ - t_1^-)$, and $(t_2^+ - t_2^-)$. Hence

$$\tilde{R}(t_1^-, t_2^-, t_2^+, t_1^+) \equiv \Delta(t_2^- - t_1^+)\Delta^*(t_2^+ - t_1^-) R_G(t_2^+ - t_2^-) , \quad (24)$$

where

$$\Delta(t_2^- - t_1^+) = \exp\left[-g^2 \int_0^{t_2^- - t_1^+} d\tau \int_0^{\tau} d\tau' \left(\frac{1 - e^{iE\tau'}}{\tau'}\right)^2\right] , \quad (25)$$

$$\Delta^*(t_2^+ - t_1^-) = \exp\left[-g^2 \int_0^{t_2^+ - t_1^-} d\tau \int_0^{\tau} d\tau' \left(\frac{1 - e^{-iE\tau'}}{\tau'}\right)^2\right] ,$$

and R_G is the Nozières–de Dominicis emission probability correlation function in which the hole is considered to be born in its fully relaxed ground state, i.e., does not depend on t_1^-, t_1^+.

Thus the final form for the cross section may be written as

$$I(\epsilon_{\vec{k}}, \omega) = \int_{-\mu}^{0} d\omega' \left| \phi(\omega - \omega') \right|^2 R_G(\omega') D(\omega') , \quad (26)$$

where

$$\phi(\omega) = \int_{-\infty}^{+\infty} d\tau\, e^{i\omega\tau} g(\tau)\Delta^*(\tau) \quad (27)$$

and $D(\omega)$ is an appropriate transition density. (Details of this step are given in the Appendix.)

IV. CALCULATION OF THE EMISSION EDGE SHAPE

To determine the skewed Lorentzian function $\phi(\omega)$, we calculate

$$\phi(\omega - \Omega) = \int_0^{\infty} dt\, e^{i(\omega-\Omega)t} e^{-\lambda t} g^{--}(t)\Delta(t) . \quad (28)$$

Using a linked cluster expansion in the second-order bubble, g^{--} is given by

$$g^{--}(t_2^- - t_1) = e^{C^{--}(t_2^- - t_1)/2} , \quad (29)$$

where

$$C^{--}(t_2^- - t_1) = \frac{V^2}{2} \int_{t_1}^{t_2^-} d\tau \int_{t_1}^{t_2^-} d\tau' \sum_{\vec{k}\vec{k}'} G_{\vec{k}}^{--,0}(\tau, \tau') \times G_{\vec{k}'}^{--,0}(\tau', \tau)$$

and

$$iG_{\bar{k}}^{--,0}(\tau,\tau')=\{(1-n_{\bar{k}})\,\Theta(\tau'-\tau)-n_{\bar{k}}\,\Theta(\tau-\tau')\}\,e^{-i\epsilon_{\bar{k}}(\tau-\tau')}\;.$$

Working out the k summations and the possible time orderings, we get

$$C^{--}(t_2^- - t_1)=+2g^2\int_0^{t_2^- - t_1}d\tau\int_0^{\tau}d\tau'\left(\frac{1-e^{-iE\tau'}}{\tau'}\right)^2\;, \tag{30}$$

while for C^{++} one finds the complex-conjugate expression. Using Eq. (25) one has, to second order in g^2,

$$\begin{aligned} g^{--}(t_2^- - t_1)\,\Delta(t_2^- - t_1)\,\Delta(t_2^+ - t_1)\,g^{++}(t_2^+ - t_1) &= \exp\left[\tfrac{1}{2}C^{--}(t_2^- - t_1)+C^{+-}(t_1,t_2^-,t_2^+,t_1)\right.\\ &\quad\left.+\tfrac{1}{2}C^{++}(t_2^+ - t_1)\right]\;. \end{aligned} \tag{31}$$

It turns out after careful calculation that

$$\begin{aligned} \mathrm{Re}[\tfrac{1}{2}C^{--}(t_2^- - t_1)+C^{+-}(t_1^-,t_2^-,t_2^+,t_1^+)&\\ +\tfrac{1}{2}C^{++}(t_2^+ - t_1)]&=0 \end{aligned} \tag{32}$$

so that only the imaginary parts of the bubbles contribute. After much tedious work we get

$$g(t_2^- - t_1)\,\Delta(t_2^- - t_1)=e^{ig^2F(t_2^- - t_1)}\;, \tag{33}$$

where

$$\begin{aligned} F(t)&=(2\ln 2)\,Et-2\,\mathrm{Si}(Et)+\mathrm{Si}(2Et)\\ &\quad+2\int_0^{Et}d(Et)\,\mathrm{Ci}(E\tau)-\int_0^{2Et}d(2Et)\,\mathrm{Ci}(2E\tau)\;, \end{aligned} \tag{34}$$

Si and Ci are the sine and cosine integrals. Thus we finally have

$$\phi(\omega-\Omega)=\int_0^{\infty}dt\,e^{i(\omega-\Omega)-\lambda t}\,e^{ig^2F(t)}\;. \tag{35}$$

V. APPLICATION TO Li SOFT-X-RAY EMISSION SPECTRUM

Using our basic expression, Eq. (3), the soft-x-ray emission spectrum is given by convolving the Nozières–de Dominicis emission edge, given asymptotically by

$$R_G(t_2^+ - t_2^-)\to P\left(\frac{1}{t_2^+ - t_2^-}\right)|t_2^+ - t_2^-|^{\alpha_1} \tag{36}$$

with the skewed excitation function $|\phi|^2$.

To make semiquantitative contact with the above strong-coupling limit, we make the arbitrary substitution

$$2g^2\to\alpha=\sum_l 2(2l+1)(\delta_l/\pi)^2\;, \tag{37}$$

where δ_l are the phase shifts for conduction-electron–deep-hole scattering, in the second-order calculations of Sec. IV. We find that $|\phi|^2$ depends critically on the parameter λ/E, where λ is the lifetime of the x-ray hole and E is the width of the filled conduction band. The dependence of $|\phi|^2$ on the hole-electron coupling strength g is weak. The spectrum of $|\phi|^2$ gives a measure of the degree of

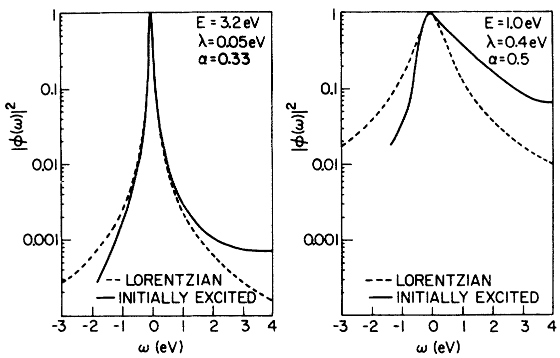

FIG. 3. (a) $|\phi|^2$ used to find the Li K-emission intensity spectrum; coupling strength is $\alpha=0.33$ and $\lambda/E=0.05/3.2$. (b) $|\phi|^2$ for a larger $\lambda/E=\frac{4}{10}$ and a larger coupling strength $\alpha=0.5$.

modification that the initial excitations can introduce in the Lorentzian only broadened $|\phi|^2$, shown in dashed lines in Fig. 3. For $\lambda/E\ll 1$ (a case satisfied by simple metals), the difference from a Lorentzian is small, but as λ/E approaches unity (e.g., in transition metals), the difference becomes large.

For illustrative purposes, we have plotted $|\phi|^2$ for $\lambda/E=0.5/32$ with $\alpha=0.33$ and $\lambda/E=\frac{4}{10}$ with $\alpha=0.5$ in Fig. 3. Notice that the high-energy side of the spectrum is always enhanced over the Lorentzian tail, denoted by the dashed lines. This behavior will always result in the enhancement of the emission tail over the Lorentzian broadened tail. To calculate the spectral intensity we must know the appropriate $R_G(\omega)$ in Eq. (36). Here α_1 is given by

$$\alpha_1=2\delta_1/\pi-\alpha\;, \tag{38}$$

where δ_1 is the p-wave phase shift appropriate to the s-state core hole of the Li K shell.

For the purposes of illustration we use a density-of-states–matrix-element factor

$$D(\Omega)\propto\Omega^{3/2}\;. \tag{39}$$

This will be only very roughly correct for Li where it is known that the wave functions are distorted very considerably away from plane-wave-like behavior. We use

$$R_G(\Omega)\propto|1/\Omega|^{\alpha_1} \tag{40}$$

and assume $\lambda/E=0.5/32$ with $\alpha=0.33$. The comparison with Li metal K-emission spectrum of Sagawa[17] is given in Fig. 4. The inhibition behavior, which is characteristic of $l=1$ transitions, is fitted by taking $\alpha_1=-0.3$ in Eq. (36). We find that for $\lambda=0.05$ eV and $E=3.2$ eV, which is approximately the width of the Fermi band for Li, the Li K-emission threshold tail is well fitted by

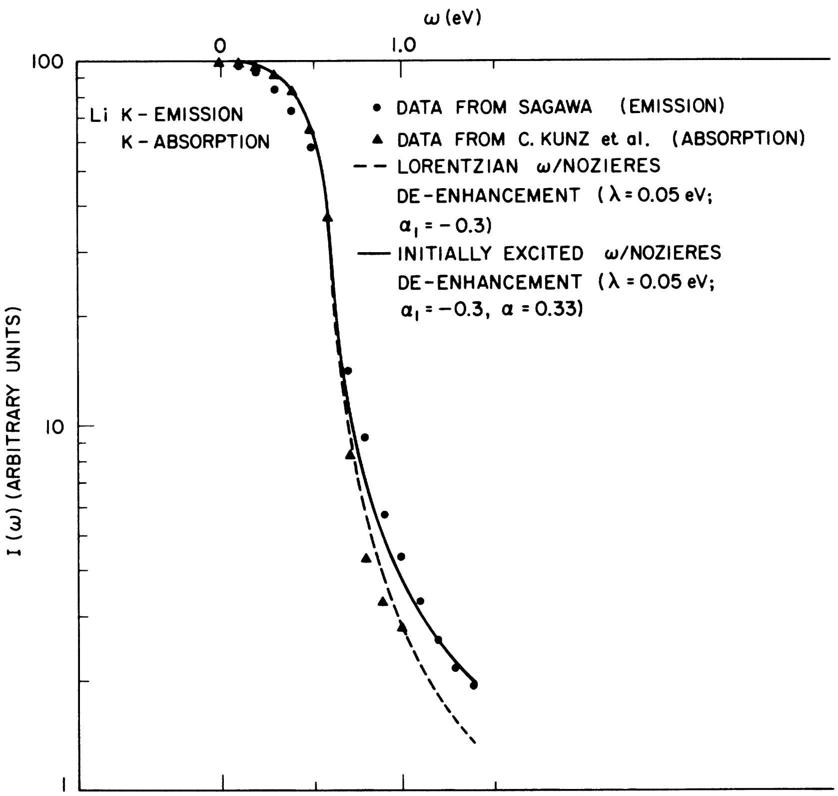

FIG. 4. Computed Li emission and absorption threshold tails compared with Li K spectra due to Sagawa (Ref. 17) and Kunz *et al.* (Ref. 19).

this choice of parameters. The values of α and α_1 are to be compared with the set given by Ausman and Glick[18] for Li ($\alpha = 0.2$, $\alpha_1 = -0.104$). The value 0.05 eV is consistent with the value found recently by Bergersen *et al.*,[14] for the lattice-relaxation-induced core-hole width. Since the Auger width and self-radiative width are small for Li,[20] this is the dominant contribution to λ for this metal. To see if our predicted enhancement over the absorption process is reasonable, we have plotted on the same graph the absorption data taken recently by C. Kunz *et al.*[19] The agreement is satisfactory up to uncertainties in the background for both emission and absorption data.

Because experimental data for both emission and absorption in transition metals are inherently more complex, we have not attempted to make a detailed fit for $\lambda/E \approx 1$, although Fig. 3(b) gives an indication of the considerable amount of enhancement expected in the emission tail for narrow-band materials.

VI. CONCLUDING REMARKS

The above results show that the initial hole excitation effects are rather weak for simple metals such as Li for which $\lambda/E \ll 1$. They are expected to become increasingly important for transition metals or other narrow-band systems. However in these materials the internal degrees of freedom of the deep hole become exchange-coupled to the d bands, and the above treatment, although qualitatively useful, would require appropriate generalization to include such effects.

It should be pointed out that the general approach of this paper based on the Keldysh formalism applies not only to the soft-x-ray emission process, but to many other classes of experiment involving measurement of one or more particles in the final state, such as photoemission and Auger spectroscopy.

APPENDIX

After substituting Eqs. (16) and (24) into Eq. (12), letting $\tau \to \infty$, and doing one time integral to get rid of the Dirac δ function $\delta(t_1^- - t_1^+)$, we get

$$P(\epsilon_{\vec{k}}, \omega) \propto \int_{-\infty}^{+\infty} dt_1 \left(\int_{-\infty}^{+\infty} dt_2^- \, e^{i\omega t_2^-} g(t_2^- - t_1) \Delta(t_2^- - t_1) \right) \times \left(\int_{-\infty}^{+\infty} dt_2^+ \, e^{-i\omega t_2^+} g^*(t_2^+ - t_1) \Delta^*(t_2^+ - t_1) \right) \times R_G(t_2^+ - t_2^-) \ . \tag{A1}$$

Now $\int_{-\infty}^{+\infty} dt_1$ is undefined but in a finite-time scattering theory we actually have $\int_{-\tau/2}^{+\tau/2} dt_1$, and this is divided out by $1/\tau$ in Eq. (6). With

$$R_G(t_2^+ - t_2^-) = \int_{-\infty}^{+\infty} d\Omega \, e^{i\Omega(t_2^+ - t_2^-)} R_G(\Omega) \ ,$$

we multiply both sides of Eq. (A1) by

$$e^{-i(\omega-\Omega)t_1+i(\omega-\Omega)t_1}=1$$

to get

$$I(\epsilon_{\vec{k}},\omega)\propto\int_{-\infty}^{+\infty}d\Omega\,R_G(\Omega)\left(\int_{-\infty}^{+\infty}d(t_2^- - t_1)\times e^{i(\omega-\Omega)(t_2^- - t_1)}g(t_2^- - t_1)\Delta(t_2^- - t_1)\right)\times\left(\int_{-\infty}^{+\infty}d(t_2^+ - t_1)\,e^{-i(\omega-\Omega)(t_2^- - t_1)}g^*(t_2^+ - t_1)\Delta^*(t_2^+ - t_1)\right). \quad \text{(A2)}$$

Since the Nozières x-ray function $R_G(\Omega)$ has a cutoff $\theta(-\Omega)\theta(\Omega+\mu)$, we finally get

$$I(\epsilon_{\vec{k}},\omega)\propto\int_{-\mu}^{0}d\mu\,R_G(\Omega)\,[\phi(\omega-\Omega)]\,[\phi(\omega-\Omega)]^*\ , \quad \text{(A3)}$$

where

$$\phi(\omega-\Omega)=\int_0^{+\infty}dt\,e^{i(\omega-\Omega)t}g(t)\,\Delta(t)\ .$$

The density-of-states and matrix-element-squared term $D(\Omega)$ has been inserted in Eq. (A3) to make contact with the one-electron theory.

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[20]*Note added in proof.* It has recently been pointed out by P. H. Citrin [Phys. Rev. Lett. 31, 1164 (1973)] and by B. Bergersen (private communication) that the Auger linewidth in Li metal will be appreciable, as opposed to the free atom, where it is rigorously zero. Inclusion of this effect will tend to reduce our estimate of $\alpha_1 = -0.3$.