Renormalized theory of soft-x-ray spectra of metals

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The renormalized theory of soft-x-ray emission spectra of light metals is reexamined to check the importance of a subtraction term proposed by Longe. We also comment on the general requirements of a renormalized theory and the importance of lifetime effects near the high-energy threshold.

I. INTRODUCTION

While deriving a first-order theory of soft-x-ray emission spectra of metals, Longe and Glick[1] (hereafter referred to as I) showed that one of the graphs (B_1) representing the excitation of the conduction electrons by the initial hole in the core states, diverged logarithmically in the entire main-band region. In order to alleviate this problem, as well as the problem of discontinuity[2] in slope at the lower edge of the main band, Bose and Glick[3] (hereafter referred to as II) developed a renormalized theory incorporating the real and imaginary parts of the self-energy of electrons both in the conduction band and the core states. In this theory both of the above problems disappeared and reasonably good agreement with experiment was obtained except near the high-energy edge, where the theory was not expected to be accurate.

A few years ago Bergersen, Brouers, and Longe[4] (BBL) proposed a modified first-order theory starting with a two-Hamiltonian model[5] and argued that there would be an additional "subtraction term" arising from the mixed normalization of the many-body states and this term would cancel the divergence of B_1 of I in the main band. In a recent comment on our renormalized theory Longe[6] worked with a one-Hamiltonian model and obtained the same subtraction term from a first-order expansion of both the numerator and denominator of the intensity function. Longe argued that since the BBL theory with this subtraction term is the "complete first-order theory" it provides the proper starting point for constructing a renormalized theory. Therefore, he claimed, the results found in II are not reliable. In this paper we study the reliability of the results found in II by computing a renormalized subtraction term of the BBL type. We show that the results are not strongly modified by this term and that the theory of II can be used as a basis for studying many-body effects in more complicated materials. We also comment on the type of improvements needed to get better agreement with experiment particularly at the high-energy edge where lifetime effects strongly modify structure due to the threshold singularity.

II. RENORMALIZED THEORY WITH A SUBTRACTION TERM

Using the notation of Longe,[6] the emission intensity can be calculated from the Fourier transform in t of the function [Ref. 6, Eq. (6)]

$$\mathfrak{F}(t; T_1, T_2) = \frac{\langle \Phi_i | T[U(T_2, T_1)\theta^\dagger(t)\theta(0)] | \Phi_i \rangle}{\langle \Phi_i | U(T_2, T_1) | \Phi_i \rangle} \tag{1}$$

in the limits $T_1 \to -\infty$, and $T_2 \to +\infty$. If the lifetime effects are neglected and the core hole treated as an external potential switched off between times 0 and t, then the limiting function $\mathfrak{F}(t)$ can be written in the form [Ref. 6, Eq. (8)]

$$\mathfrak{F}(t) = F_0(t) e^{G(t)} / e^{G(0)} \,. \tag{2}$$

However, in first order both the numerator and denominator diverge. Longe and, earlier, BBL claimed that the way to circumvent this difficulty is to carefully play off the numerator against the denominator. By expanding the combined exponentials they obtained a first-order theory of the form

$$\mathfrak{F}(t) \approx F_0(t) + f_0(t)[G(t) - G(0)] \,, \tag{3}$$

where $f_0(t)$ is the zero-order approximation to $F_0(t)$; and $F_0(t)$ and $G(t) - G(0)$ are taken to next-lowest nonvanishing order in the electron-core coupling constant. Carrying out this calculation they found the spectrum[4] shown in Fig. 3 and 4 of BBL. An examination of their results, however, shows that their spectrum goes negative over the low-frequency part of the main-band region, and hence is physically meaningless in this region. Thus the need for a renormalized theory remains in spite of the subtraction term $f_0(t)G(0)$ which removes the divergent part of $f_0(t)G(t)$.

In the renormalized theory of II the denominator in Eq. (2) was disregarded. Neglect of this term can be justified by noting that $e^{G(0)}$ is time independent. It is in fact a normalization constant for the initial state with core hole. When the Fourier transform of $\mathfrak{F}(t)$ is taken to obtain the x-ray spectrum this factor affects the scale of absolute intensity, but not the spectral shape which is to be compared with experiment. In the first-order theory $e^{G(0)}$ is divergent, as is the time-dependent numerator. It is only by carefully playing off numerator against denominator that one can obtain finite results. This has been done in BBL and by Longe.[6] We have no disagreement with the uniqueness or consistency of their calculation. However, as pointed out above, the first-order calculation is not adequate over the main-band region. Any finite-order perturbation theory involves divergences which might be made finite by carefully playing off terms, but the spectrum would not be analytically reliable—it would involve singularities, negative regions, and discontinuities in slope which are unphysical.

Thus a renormalized theory is needed in order to obtain a meaningful spectrum. Longe has recognized that the denominator would not affect the results of a fully (exact) renormalized theory, but the question remains as to its importance in a partially renormalized theory such as that of II.

In II the finite Auger lifetime of the core state was included as a renormalization effect. Even though the lifetime is small it provides a natural cutoff which removes the divergences of numerator and denominator which plagued the first-order theory. We proceeded under the assumption that once the divergences are gone the constant denominator can be disregarded for finding the relative intensity. Longe, however, argues that the lifetime broadening is so small that the denominator must still be considered in order to make an expansion such as in Eq. (3), even for a renormalized theory. With lifetime effects $\mathfrak{F}(t)$ no longer can be put into the simple form of Eq. (2), but we have explored Longe's conjecture by introducing a renormalized subtraction term which reduces to the form used in BBL and Ref. 6 when the Auger lifetime and the conduction-electron–electron interactions are turned off. With renormalization the subtraction term becomes [compare with the second term in Ref. 6, Eq. (12)]

$$I_x = \frac{1}{8\pi^4}\int_0^\infty \frac{d\omega'\,[\omega' + \Sigma_1(E_B') - \Sigma_1(\omega' + E_B')]^2}{\{[\omega' + \Sigma_1(E_B') - \Sigma_1(\omega' + E_B')]^2 + \Sigma_2(\omega' + E_B')^2\}^2} \times \int d^3k_v\, |g(k_v)|^2\, \mathrm{Im} V_+(k_v, \omega') I_0^R(\omega)\,, \quad (4)$$

$$I_x = C I_0^R(\omega)\,. \quad (5)$$

Equation (4) contains the real and imaginary parts of the core-state self-energy (Σ_1 and Σ_2, respectively), as calculated in II and evaluated using the renormalized bound-state energy E_B'. The $\vec{k}_v$ integral contains bound-to-bound matrix elements $g(k_v)$ and the imaginary part of the dynamically screened Coulomb interaction $V_+(\vec{k}_v, \omega)$. Carrying out the ω' and $\vec{k}_v$ integrals gives a constant C which multiplies the spectrum $I_0^R(\omega)$. We find $C = -0.746$.

There remains some question as to the proper choice of $I_0^R(\omega)$ needed to be consistent with the renormalizations used in II. In the first-order theory of BBL this term was taken as the zero-order spectrum $I_0(\omega)$. If $I_0(\omega)$ is used in the renormalized theory then a nonphysical discontinuity of slope reappears at the low-energy end of the main band. This discontinuity was healed in the renormalized theory of II by many-electron processes. If one views the theory of II as giving the leading terms in an expression in the coupling between conduction and core states with conduction-conduction coupling to all orders then $I_0(\omega)$ should be replaced by $I_A(\omega)$ of II. In graphical terms this entails replacing graph 0_1 of Fig. 1 in II by graph 0 of Fig. 5 in II. We will call this procedure *approximation A*. The subtraction term $CI_A(\omega)$ is then of the same order as $I_B(\omega)$ and $I_C(\omega)$ of II. A third alternative *(approximation AC)* is the inclusion of both $I_A(\omega)$ and $I_C(\omega)$ in $I_0^R(\omega)$. This latter choice is analogous to using $F_0(t)G(0)$ in Eq. (3) to construct the subtraction term.

Figure 1 compares the spectrum obtained in II

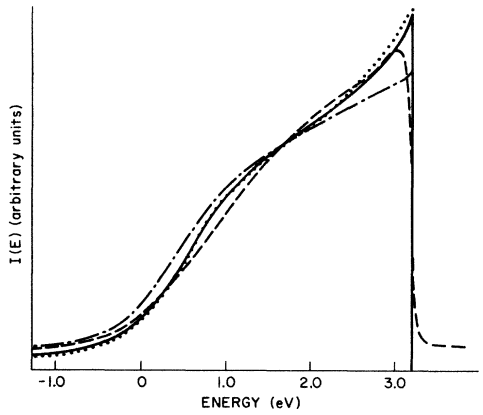

FIG. 1. Soft-x-ray emission spectrum of sodium vs energy from the bottom of the conduction band. The solid line is the spectrum obtained in II; the dotted line shows approximation *A* and the dash-dot line shows approximation *AC*. The dashed line is taken (Ref. 8) from the experimental spectrum of Crisp and Williams (Ref. 7). The curves are normalized so that they give the same intensity 1.5 eV below the Fermi level.

(solid line) with approximations A (dotted line) and AC (dash-dot line). The dashed line is an experimental spectrum taken from Crisp and Williams.[7] In plotting these results the curves were normalized to have the same value 1.5 eV below the top of the conduction band.[8] It can be seen that using only $I_{\mathcal{A}}(\omega)$ in the subtraction term results in a scale change due to C, but almost no change in the spectrum from that found in II. The inclusion of $I_C(\omega)$ in $I_0^R(\omega)$ does alter the shape significantly, but note that vertex corrections to $I_B(\omega)$ have not been included in the theory of II. Their inclusion in the subtraction term alone raises doubt about the consistency of approximation AC. Therefore A is thought to give the more reliable results. We have included the experimental curve as a qualitative indication of what is observed. However, it should not be used to judge the relative merits of the calculated spectra. The differences between approximation A and AC are no larger than the differences between the spectrum found by Crisp and Williams[7] and that found by Skinner.[9] The two experimental spectra are thought to be of comparable accuracy. (A comparison of our results with Skinner's spectrum can be found in II.)

III. BEHAVIOR NEAR THE HIGH-ENERGY EDGE

Near the high-energy threshold the calculated spectrum shows the greatest departure from the experimental shape. The peak near threshold has been attributed to the transient response of the electron gas to the change in the core potential during x-ray emission.[10] Nozières and de Dominicis[5] (ND) found that the behavior at the edge is nonanalytic, and thus cannot be calculated by perturbation theory. Perturbation theory always gives a divergence at the edge while the ND theory can give a suppressed edge when the core state has s symmetry.[10] Even when ND predicts an exhanced edge, as in the present case, perturbation theory is a poor approximation since the logarithmic divergence of perturbation theory is much weaker than the power law predicted by ND. To improve the solution, Mahan[11] inferred an exponential sum of perturbation theory. Similarly, Longe,[12] using the first-order solution of BBL, inferred coefficients of the ND power law. However, in a renormalized theory such as used in II, with or without BBL's subtraction term, there is no simple way to carry out a similar sum of terms. The difficulty occurs because of the dynamical nature of the core potential which is associated with the absence of a core electron. It was only by treating the potential as a simple external force that ND were able to obtain their exact model solution at the threshold. When the dynamical nature of the potential is taken into account, even to the limited extent of including the core-hole lifetime as is done in II, then Eq. (2) loses strict validity.

The importance of lifetime effects becomes increasingly clear when one tries to compare with experiment. As noted above, the ND solution gives a more strongly divergent threshold than does perturbation theory. The edge shown in Fig. 1 is similar to the perturbation theory edge except that it is damped by Γ_B. It appears that much stronger damping would be needed to account for the observed shape. Elsewhere[13] it has been found that the core lifetime is enhanced by a many-body effect, so that its value is more like $\Gamma_B = 0.017$ eV rather than 0.002 eV used in II. Phonon effects[14-16] have been found to play an even more important role, providing a Gaussian broadening (halfwidth) of about 0.05 eV. Thus the need for a more accurate treatment of the edge, in the sense of ND, appears to be less important for an L spectrum (or for any case where the edge is enhanced) than the need for a better treatment of lifetime and phonon effects.

Longe[6] has criticized the theory in II claiming that it does not reduce to his first-order expansion of the ND result because of neglect of the subtraction term. The calculations of Sec. II show that with renormalization the subtraction term does not have a major effect on the shape of the edge. Indeed, to improve the renormalized theory, one must be more concerned with a proper treatment of broadening effects than with reproducing the exact features of the ND model solution. Similar conclusions appear to hold for core states with s symmetry. Broadening mechanisms play a crucial role in determining the observed spectral shapes.[17]

IV. CONCLUSION

In conclusion, we have shown that the BBL subtraction term does not play a crucial role in modifying the calculated soft-x-ray spectrum of sodium. With or without this term the renormalized theory of II provides a good fit, within experimental uncertainty, to the observed spectrum except near the high-energy edge.

By inclusion of many-body processes as self-energy effects we have eliminated the spurious discontinuity of slope and negative region found by BBL at the bottom of the main-band region. The spectrum falls off smoothly at lower frequencies until the onset of the plasmon satellite. The satellite calculated in II indicated the existence of residual plasmaron structure. This feature of the spectrum has been called into question by calculations of Bergersen and co-workers[18] and by Minn-

hagen.[19] They showed that for solvable models perturbation theory can indicate plasmaron structure even when it is absent from the exact solution. To date, no experiments have definitely confirmed or disproved the presence of a plasmaron. In any case, the effect is weak and normally would be obscured by noise.[20]

Longe[6] has proposed a criterion for an acceptable renormalized theory of soft-x-ray emission. He requires that at the high-energy threshold the theory must reproduce the power-law behavior of the idealized ND model. We feel that to improve the theory of II higher priority must be given to the proper treatment of departures from the ND model, such as the broadening effect arising from lifetime and electron-lattice interactions. It is only by systematically taking these effects into account that one can hope to get a better description of the spectrum near the high-energy edge.

Even though the description of the high-energy edge is not complete, the theory of II appears to provide a sufficiently good spectrum everywhere else that it would be of interest to apply it to more complicated metals. Such a study could elucidate the extent to which many-electron processes modify spectral features arising from structure in the density of states.

There remains a pressing need for a more precise experimental determination of the spectrum of sodium. With such a spectrum one could hope to distinguish between approximations A and AC used in this paper. It is also desirable to experimentally probe the role of different lifetime mechanisms on the high-energy threshold. By varying lattice order, impurity concentration, and temperature one can examine the importance of the ND effect, explore the energy region over which it is operative, and determine to what extent it is masked by the different scattering mechanisms.

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