Effects of plasmon dispersion and damping on strengths and shapes of plasmon satellites in x-ray photoemission spectra of metals

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We calculate the effect of bulk- and surface-plasmon dispersion and damping on satellite strengths in photoelectron spectra in x-ray photoemission from core levels of metals. The calculation reveals an appreciable reduction in satellite intensities when compared with predictions of previous dispersionless infinite-lifetime models. Comparison with experimental data shows good agreement for the value of the mean free path for short-range processes and the shapes of satellite lines in the spectra.

I. INTRODUCTION

In the last few years considerable attention has been paid to the problem of bulk- and surface-plasmon excitation in x-ray photoemission from core levels of metals.

The theoretical interpretation of these satellites requires a many-body theory of photoemission which would include both inelastic and elastic scattering processes. In the absence of such a theory, the first theoretical approaches were based on the so-called three-step model.[1] In spite of the fact that the quantum-mechanical interference between different scattering mechanisms was neglected, this model was often used to describe many-body effects in x-ray photoemission spectroscopy (XPS).[1–4]

Later, two equivalent approaches were developed in which all scattering mechanisms were properly accounted for. The first is the so-called quadratic-response formalism, or a 3-j correlation-function approach.[5–7] The second is based on the Green-function perturbation method used to describe the plasmon-excitation probability.[8–11] At the same time several authors[12–16] developed a model based on a semiclassical calculation of the correlation function, describing the response of the plasmon field to the created electron-hole pair. In the XPS regime, when the recoil of the localized hole and the fast electron can be neglected, this model becomes physically equivalent to the Green-function approach,[8] and provides useful quantitative predictions for strengths of plasmon-loss lines in photoelectron spectra.

In all these models plasmons were assumed to be infinite-lifetime-independent boson excitations of the system. In spite of a large number of experimental studies in this field,[17–32] comparison of experimental data with theoretical predictions was made only in a few papers.[24,25,29–32] However, even in these papers it was clearly indicated that the existing theoretical models appreciably overestimated plasmon-excitation probabilities. It was natural to expect that a better description of plasmon modes might lead to better agreement between theory and experiment.

Dispersion and damping of plasmons were included phenomenologically in several related problems, e.g., in x-ray photoemission from core levels of adsorbates treated in a semiclassical model by Šokčević *et al.*[33] Later, a similar approach including only dispersion was used to study the problems of energy loss of fast charged particles passing through a thin metallic film[34] and of image potential at a solid surface.[35]

However, we feel that the inclusion of plasmon damping is essential because it leads to appreciable reduction of the plasmon-excitation probability and, on the other hand, it properly describes the cutoff of plasmon modes.

The plan of the paper is as follows. In Sec. II the derivation of the photoelectron spectrum and its application to XPS are briefly reviewed. Expressions for satellite intensities and for the shape of the spectrum in the region of the first bulk- and surface-plasmon losses are derived. Matrix elements for photoemission from core levels of metals are calculated by using the explicit summation over bulk modes. Plasmon dispersion and damping are included semiphenomenologically.

In Sec. III the results obtained are applied to photoemission from the $2p$ core level of Al. Values of the parameters describing plasmon dispersion and damping are used from experiments. Matching the theoretical intensity of the first bulk-plasmon loss with the experimental one, the mean free path for short-range scattering is calculated, which is close to the usually accepted value. For this value of the mean free path we obtain rather good agreement in the shape of the spectrum.

In Sec. IV we make a brief comparison with other papers which considered the effect of plasmon dispersion and damping and analyzed experimental results. A summary of the results is given in Sec. V.

II. FORMULATION OF THE PROBLEM

The main aim of this paper is to study the influence of plasmon excitations on photoelectron spectra. We adopt a model[36] which assumes that, at least in the XPS limit, one

can separate plasmon-excitation probabilities from other (low-energy and short-range) processes, calculate their probabilities exactly, taking properly into account the nonlocal character of that scattering, and, finally, convolute all processes to obtain the true spectra in order to compare them with experiment. Since the various aspects of such a problem were extensively studied in our previous papers,[14,36] we shall not repeat the discussion here; we repeat only the main steps leading to expressions for the photoelectronic spectrum and then we apply this result to our case.

A. Derivation of the photoelectron spectrum

If a metal is perturbed by an external electromagnetic field, then the photoabsorption cross section is given by the expression

$$\sigma(\omega_0)=\sum_{i,f} |\langle f|h|i\rangle|^2\delta(E_i+\omega_0-E_f) . \tag{2.1}$$

Here, the Hamiltonian

$$h=\frac{1}{c}\int d\vec{r}\,\vec{j}(\vec{r})\cdot\vec{A}(\vec{r}) \tag{2.2}$$

describes the external perturbation (ω_0 being its frequency).

The initial state $|i\rangle$ is the metal with N electrons. The final state $|f\rangle$ is an $(N-1)$-electron system (generally excited) plus the photoelectron. These states can be expressed in terms of the adiabatically decoupled states $|\phi_i\rangle$ and $|\phi_f\rangle$, respectively.[36] There exists an energy shift ΔE_i between the free and the interacting initial states:

$$e^{iHt}U|\phi_i\rangle=\tilde{U}e^{-i(H_0+\Delta E_i)t}|\phi_i\rangle . \tag{2.3}$$

The decoupled final state $|\phi_f\rangle$ has the form

$$|\phi_f\rangle=|p\rangle\,|N-1\rangle , \tag{2.4}$$

i.e., in the $t\to\infty$ limit the excited photoelectron is decoupled from the metal. This implies $\Delta E_f=0$.

Then, from (2.1) one obtains the spectrum of electrons emitted with energy E_p:[36]

$$\frac{d\sigma}{dE_p}=g(E_p)\sum_{\lambda}|M_{\lambda p}|^2\frac{1}{2\pi}\times\int dt\,e^{i(E+\Delta E_\lambda)}\times\langle\phi_i|B^\dagger_{p\lambda}(t)c^\dagger_p c_p B_{p\lambda}(0)|\phi_i\rangle . \tag{2.5}$$

The operators in the correlation function are

$$B_{p\lambda}(t)=e^{iH_0t}\tilde{U}(\infty,0)c^\dagger_p c_\lambda\tilde{U}(0,-\infty)e^{-iH_0t} , \tag{2.6}$$

$$B_{p\lambda}(0)=U(\infty,0)c^\dagger_p c_\lambda U(0,-\infty) . \tag{2.7}$$

All other notation is given elsewhere.[36]

B. Application to the XPS from core levels

In the following we consider only those scattering processes of the excited electron-hole pair in which energy losses are much smaller than the electron kinetic energy. Such a system is described by the Hamiltonian

$$H=H_0+H_I , \tag{2.8}$$

$$H_0=H_e+E_\lambda c^\dagger_\lambda c_\lambda+\sum_i\omega_i a^\dagger_i a_i . \tag{2.9}$$

In Eq. (2.9) the first term, describing the free electron, has the form

$$H_e=n_p\left[E_p-\frac{\vec{p}}{m}\cdot\vec{\nabla}\right] , \tag{2.10}$$

i.e., we can describe the outgoing electron in the wave-packet approximation.[36] The second term describes the free deep level and the third term the free-plasmon field. Owing to the high kinetic energy of the outgoing electron, its interaction with the boson field takes the form[36]

$$H^p_I=\sum_i n_p V^i_p a_i+\text{H.c.} \tag{2.11}$$

Similarly, the interaction of the deep recoilless hole has the form[36]

$$H_I=\sum_i n_\lambda V^i_\lambda a_i+\text{H.c.} \tag{2.12}$$

For such a form of the interaction Hamiltonian, the problem can be solved exactly. The spectral function $P(E)$ is given by[36]

$$P(E)=\frac{1}{2\pi}\int dt\,e^{i(E_\lambda+\Delta E_\lambda+\omega_0-E)t}P(t) , \tag{2.13}$$

where (we consider only one mode, as the contributions from various modes are added up)

$$P(t)=\exp[|Q_h+Q_e|^2(e^{-i\omega t}-1)] , \tag{2.14}$$

with $Q_h\equiv Q_h(0)$ and $Q_e\equiv Q_e(0)$, and

$$Q_e(t)=-i\int_0^\infty V_p(\tau)e^{-i\omega(t+\tau)}d\tau , \tag{2.15}$$

$$Q_h(t)=i\int_{-\infty}^0 V_\lambda(\tau)e^{-i\omega(t+\tau)}d\tau . \tag{2.16}$$

C. Satellite intensities

It is obvious that approximations (2.11) and (2.12) are not valid for scattering mechanisms with large energy transfers. However, these mechanisms transfer a considerable amount of spectral weight from the low-energy and characteristic (plasmon) loss region. Nevertheless, if we only consider the characteristic loss region in the spectra, then the damping of the photoelectron current caused by these short-range (but large-energy-transfer) processes can be well approximated by the mean-free-path approximation, i.e.,

$$I_{\text{obs}}=I_0e^{-z/\lambda} , \tag{2.17}$$

where λ is a mean free path for short-range scattering processes. Generally, λ depends on energy. However, owing to the fact that it does not change much in the region of interest ($\approx$20 eV around the no-loss line),[28,37] we will take it to be a constant.

Although the theory outlined in this paper can be easily adapted for the low-energy ("line-shape") region, we will

not adopt it here because this subject has already been extensively discussed in the literature.[38–40]

However, since the three types of scattering processes described above differ markedly in energy and range, it is rather a good approximation to treat them independently and obtain the final result by convolution.

From Eq. (2.13) for $P(E)$ one can derive the intensity of plasmon satellites with m bulk and n surface plasmons excited for electrons originating from depth z inside the metal:

$$P_{mn}(z)=\exp(-A_B-A_S)\frac{A_B^m A_S^m}{m!n!} . \tag{2.18}$$

It is seen from (2.14) that each A contains the contributions from the hole, the electron, and their interference. We denote them by h, e, and i, respectively.

The observed spectrum is then obtained by integration over the crystal, i.e.,

$$P_{mn}=\int dz\, e^{-z/\lambda}P_{mn}(z) . \tag{2.19}$$

Here the low-energy processes contribute only to the broadening and asymmetry of plasmon lines.[38–40]

However, we can obtain another form for terms describing the losses in the spectra. Consider the term describing the excitation of one bulk plasmon. One can interchange the order of integration over z and k to obtain

$$P_{1B}(E)=\int \frac{4\pi\omega^2 d\omega}{|d\omega/dk|} I_B(k)\delta(E-\omega(k)) , \tag{2.20}$$

where

$$I_B(k)=\int dz\, e^{-z/\lambda}e^{-[A_B(z)+A_S(z)]}A_B(z,k) . \tag{2.21}$$

Equation (2.20) would give the shape of the first bulk-plasmon loss in the spectra if the no-loss line had the form of the δ function.

In order to obtain the real spectrum, one has to take into account two additional points:

(a) the shape $P_0(E)$ of the no-loss line;
(b) the background $D(E)$ in the characteristic loss region, mostly due to secondary electrons.

Then the expression for the shape of the first bulk satellite has the form

$$S(E)=\int dE' P_{1B}(E')P_0(E-E')+D(E) . \tag{2.22}$$

An analogous expression holds for the first surface-plasmon satellite in the spectra.

D. Matrix elements

In our previous papers[14,15,41] we used the so-called closure relation to perform the summation over bulk modes in order to obtain the matrix elements entering into (2.13). A similar approach was used by some other authors.[13] However, the summation over bulk modes can be performed explicitly,[42] and one obtains [$\vec{k}=(\vec{K},k_z)$]

$$A_B=2\int d^3k\, A_B(k) , \tag{2.23}$$

$$A_B(k)=A_B^e(k)+A_B^h(k)+A_B^i(k) , \tag{2.24}$$

$$A_B^e(k)=c^2\frac{1}{\beta^4}[4k_z^2v_\perp^2+4k_z^2v_\perp^2\cos^2(k_zz)+4b^2\sin^2(k_zz)-8k_z^2v_\perp^2\cos(k_zz)\cos(bz/v_\perp)-8bk_zv_\perp\sin(k_zz)\sin(bz/v_\perp)] ,$$

$$A_B^h(k)=c^2\frac{1}{\alpha^2}\sin^2(k_zz) , \tag{2.25}$$

$$A_B^i(k)=-\frac{c^2}{\alpha^2\beta^2}\sin(k_zz)\{\omega[2k_zv_\perp\sin(bz/v_\perp)-2b\sin(k_zz)]-2\gamma k_zv_\perp[\cos(k_zz)-\cos(bz/v_\perp)]\} .$$

Here,

$$\alpha^2=\gamma^2+\omega^2,\quad \beta^2=(k_zv_\perp)^2-b^2 ,$$
$$b=\omega+\vec{K}\cdot\vec{v}_{||},\quad c^2=8\pi e^2h^2(k)\frac{1}{K^2+k_z^2} , \tag{2.26}$$

and other notation is given elsewhere.[41]

Expressions for the surface-plasmon contribution remain the same[14] and we do not repeat them here.

In Eq. (2.23) the integration is performed over a sphere of radius k_c, where k_c is a three-dimensional cutoff wave vector. At this point it is interesting to note that if we integrate the bulk term (2.25) over the region

$$k_x^2+k_y^2\le k_c^2,\quad -\infty<k_z<\infty \tag{2.27}$$

we obtain the same results as those obtained previously by use of the closure relation. This means that the latter approach overestimates plasmon-excitation probabilities *a priori* by including the unphysical regions of k space in the integration.

Baird *et al.*[29] compared the prediction of our dispersionless- and independent-plasmon model with experiment. They showed that this model appreciably overestimated plasmon-excitation probabilities.

Although the reduction of the probabilities in the model with the explicit summation over the bulk modes is surprisingly large, as compared with the model in which the closure relation is used, these quantities are still too large even if some other small improvements are made, as discussed by Baird *et al.*[29] This indicates that further improvement should include a better description of plasmon modes.

In our considerations we will further solve the problem

approximately in the same way we did for photoemission from adsorbed core levels,[33] i.e., by including plasmon dispersion and damping phenomenologically.

At this point we want to comment. The only problem that can be solved exactly when there is plasmon dispersion is the case where the dispersion is only due to the geometry of the specimen.[43] (However, in this case there is no damping.)

We therefore proceed by replacing the plasmon frequency in the plasmon propagator by the exact self-energy (e.g., for bulk plasmons):

$$\omega_B^0 \rightarrow \omega_B(k) - i\Gamma_B(k) , \tag{2.28}$$

where the dispersion ω_B and the damping Γ_B are functions of k. By introducing this into expressions for $P(E)$, one obtains

$$A_B(k,z) = | Q_e^B + Q_h^B |^2 , \tag{2.29}$$

where

$$Q_h^B = -c \sin(k_z z)/\{i\omega_B(k) + [\Gamma_B(k) + \gamma]\} , \tag{2.30}$$

$$Q_e^B = \tfrac{1}{2} c \{ [k_z v_\perp - b + i\Gamma_B(k)]^{-1} (e^{-ik_z z} - e^{-\Gamma_B(k)z/v_\perp - ibz/v_\perp}) + [k_z v_\perp + b + i\Gamma_B(k)]^{-1} (e^{ik_z z} - e^{-\Gamma_B(k)z/v_\perp - ibz/v_\perp}) \} . \tag{2.31}$$

Inserting (2.31) in (2.29), we obtain the extrinsic and intrinsic contributions, as well as the interference between them. Then, integrating over k, one obtains the excitation probability for bulk plasmons if the photoelectron is excited at the depth z inside the metal.

Similarly, for the surface-plasmon contribution we have ($\vec{K}$ is now a two-dimensional wave vector)

$$Q_h^S = g \frac{1}{\sqrt{K}} [\gamma + \Gamma_S(k) + i\omega_S(k)]^{-1} e^{-Kz} , \tag{2.32}$$

$$Q_e^S = -g \frac{1}{\sqrt{K}} \{ [Kv_\perp + \Gamma_S(K) + ib(K)]^{-1} e^{-Kz} + [Kv_\perp + \Gamma_S(K) + ib(K)]^{-1} [K - ib(K)/v_\perp]^{-1} (e^{-ib(K)z/v_\perp} - e^{-Kz}) \} . \tag{2.33}$$

(cf. Ref. 33).

III. APPLICATION TO XPS FROM THE 2p LEVEL OF ALUMINUM

To compare the predictions of our model with experiment, we apply it to the photoemission from the $2p$ level of Al. For parameters describing the plasmon dispersion and damping we take the values quoted by Duke and Landman:[45]

$$\begin{aligned} &\hbar\omega_S(K) = 10.75 + 1.1K + 2K^2 , \\ &\Gamma_S(K) = 1.85 + 3K , \\ &\hbar\omega_B(k) = 15.2 + 3.05k^2 , \\ &\Gamma_B(k) = 0.53 + 0.1k^2 + 1.05k^4 . \end{aligned} \tag{3.1}$$

Here the energy is measured in eV and k (K) in Å^{-1}. The analytical expressions (3.1) for Γ_B and Γ_S were taken to be valid from $k=0$ to values of k close to k_c. For values of the wave vector approaching k_c, the damping was assumed to grow exponentially,[45] so that in the following calculations it provides a natural cutoff for the plasmon contribution.

We consider the electrons emerging normally to the surface with the kinetic energy $E_0 = 1410$ eV, corresponding to the experiment of Baird *et al.*[29]

In Fig. 1 the bulk contributions A_B for the three models are given for comparison. The result denoted by (1) shows the results for the independent-plasmon model, i.e., without dispersion and damping, in which the closure relation has been used. The curve denoted by (2) is also calculated in the independent-plasmon model, but with the explicit summation over the bulk modes. Finally, the curve denoted by (3) shows the results with the inclusion of dispersion and damping. As can be seen from the figure, almost two-thirds of a total reduction, in comparison with earlier models, is due to the explicit summation over the bulk modes. However, this is still not sufficient to remove the discrepancy between theoretical predictions and experiment.

Figure 2 shows the various contributions (electron, hole, and interference) to the bulk term $A_B(z)$. Again, the results for the independent-plasmon model are also given for comparison. As expected, the hole contribution is

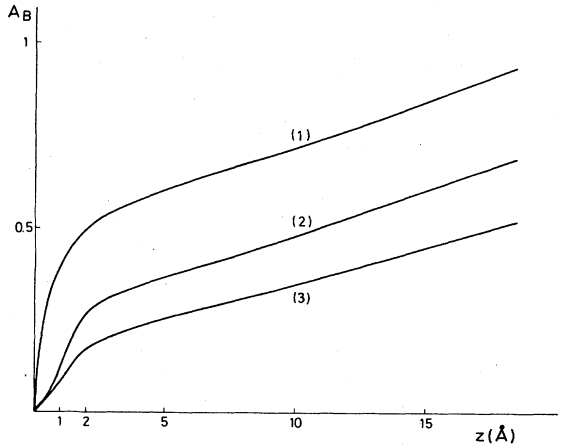

FIG. 1. Bulk term [see Eq. (2.18)] as a function of excitation depth z for three models: (1) independent-plasmon model using the closure relation, (2) independent-plasmon model with the explicit summation over bulk modes, and (3) plasmon dispersion and damping included.

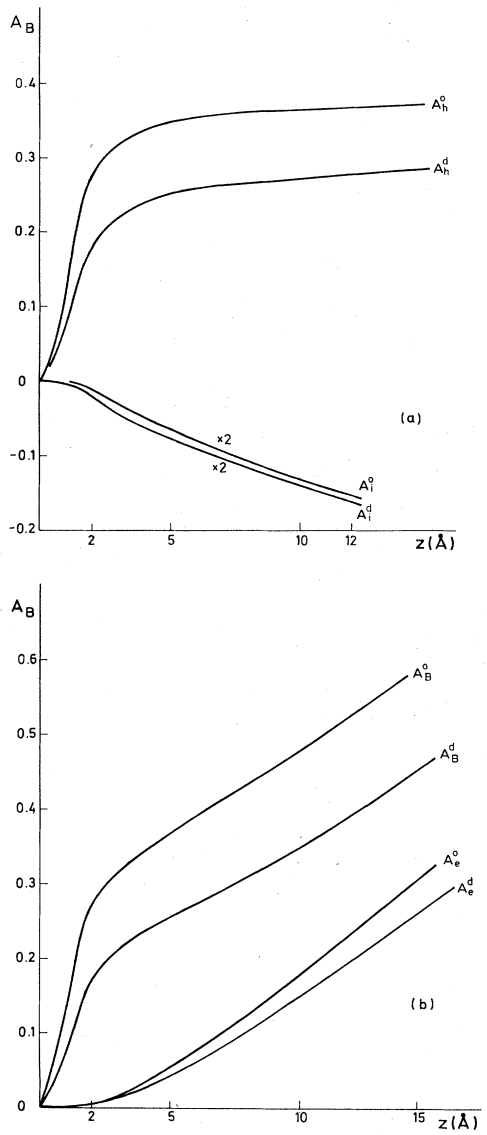

FIG. 2. (a) Intrinsic (A_h) and interference (A_i) contributions to the bulk term (2.25) as a function of excitation depth z. Superscripts are as follows: o, the results of the independent-plasmon model; d, plasmons with dispersion and damping. (b) Extrinsic contribution (A_e) and total (A_B) bulk term.

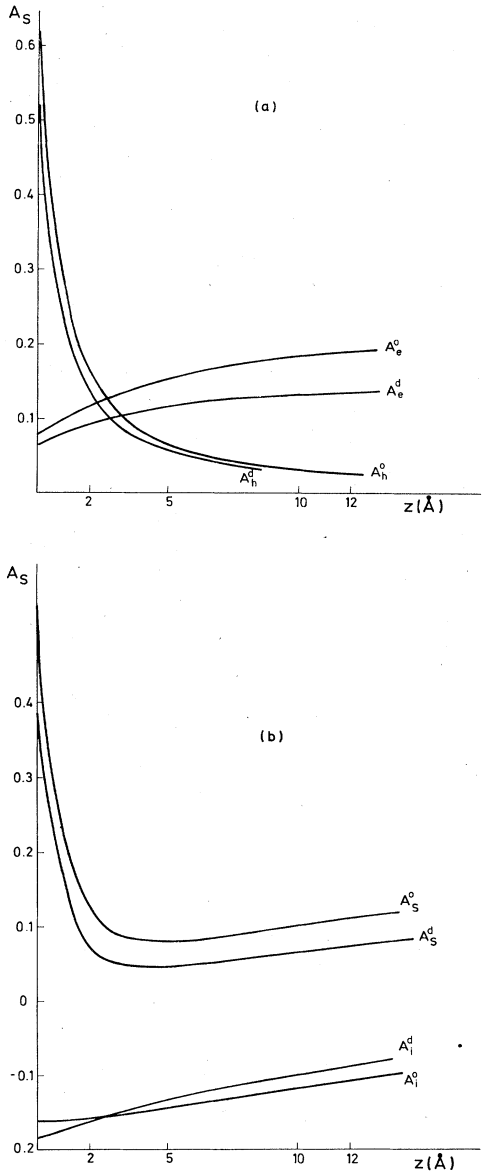

FIG. 3. (a) Intrinsic (A_h) and extrinsic (A_e) contributions to the surface term. (b) Interference (A_i) contribution and total surface term.

mostly affected, while the changes in the electron contribution and the interference are smaller. It is worth noting that the interference term (which is negative) has a larger absolute value than that in the independent-plasmon model. This means that the sum $A_h + A_i$ is even more reduced, and therefore the electron ("extrinsic") contribution becomes more pronounced.

For the surface term $A_S(z)$ the trends are the same, as can be seen from Fig. 3, where its various contributions are given.

As we have already said, using Eq. (2.22) for $S(E)$, we can, in principle, obtain the shape of the spectra in the region of the first two characteristic losses. However, in Eq. (2.22) the values of the no-loss line $P_0(E)$ and of the background $D(E)$ should be known. As we are mostly interested in the plasmon contribution to the satellites in the spectra, we should use the best possible shapes for $P_0(E)$ and $D(E)$. Obviously, the best choice is to use experimentally observed shapes for them.

We will take $D(E)$ in the region of the first surface and bulk loss to be linearly proportional to the energy loss (also see the spectrum in Ref. 29):[31]

$$D(E)=C(E_0'-E)\ . \tag{3.2}$$

Here, E_0' is the energy of the edge of the no-loss line (i.e., it is the threshold energy in the excitation spectrum of the $2p$ electron). The quantity C was estimated from the experimental results of Baird *et al.*[29] (see Fig. 5).

The shape of $P_0(E)$ (which is due not only to low-energy processes, but also to some other sources, such as

instrumental resolution, natural width of the x ray, and the finite lifetime of the core level) was approximated by two half-Gaussians with different widths.

The resulting spectrum $S(E,\lambda)$ still depends on the mean free path for short-range attenuation processes. Its value has been varied until the relative intensity

$$\bar{P}_{1B}/\bar{P}_0 , \tag{3.3}$$

where

$$\bar{P}_{1B}=\int P_{1B}(E)dE, \quad \bar{P}_0=\int P_0(E)dE \tag{3.4}$$

become equal to the experimental value $\bar{P}_{1B}/\bar{P}_0=0.52$.[29] This yields $\lambda=29$ Å, close to the usually accepted values.[37,46] We have fitted the bulk-plasmon relative intensity because it has better statistics, as can be seen from the experimental points in Fig. 5 (cf. also Ref. 29).

Figure 4(a) shows the first bulk loss line before convolution (i.e., P_{1B}). Similarly, Fig. 4(b) represents P_{1S}.

The total spectrum after convolution in the energy region of the first bulk and surface loss, $S=S_{1B}+S_{1S}$, is shown in Fig. 5.

We see from Fig. 5 that the agreement in shape is rather good. Since λ was found by matching the bulk loss values, the agreement for the bulk-plasmon peak is better. For this value of λ, $\bar{P}_{1S}/\bar{P}_0=0.082$, which still lies within the error range of the results obtained by Baird *et al.*[29]

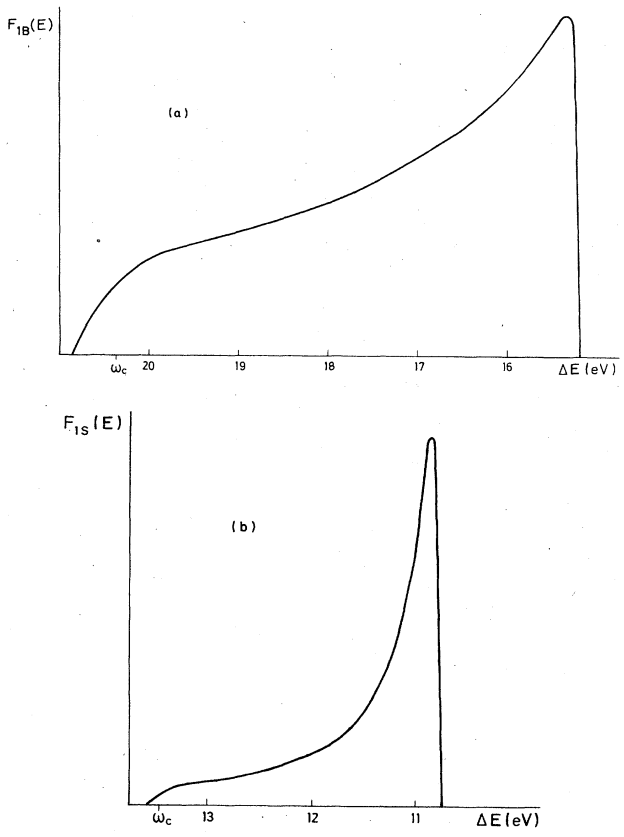

FIG. 4. (a) Shape of the first bulk-plasmon satellite before the convolution with the no-loss line. [$\omega_c=\omega(k_c)$.] (b) Shape of the first surface-plasmon satellite before the convolution with the no-loss line.

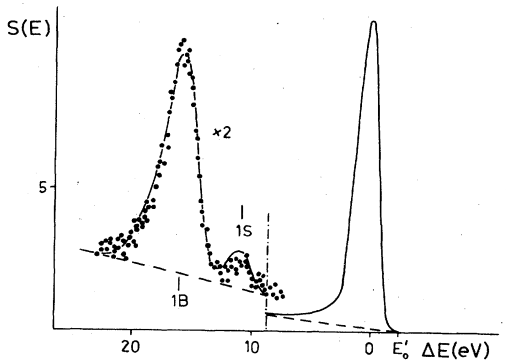

FIG. 5. Comparison of our theoretical results (solid line, in arbitrary units) for $\lambda=29$ Å with the experimental results (dots) of Baird *et al.* (Ref. 29) for the XPS spectra from the $2p$ level of Al. Other parameters are the Gaussian half-widths $\sigma_L=1.17$ eV and $\sigma_R=0.68$ eV, and the background constant $C=0.05$ 1 eV.

(they obtained $0.02\leq\bar{P}_{1S}/\bar{P}_0\leq 0.095$).

As can be seen from Fig. 4, the shape and broadening of the (convoluted) loss line is mainly due to plasmon dispersion effects. However, since the asymmetry of the no-loss line is in the opposite direction (towards lower kinetic energies), as compared with P_{1B} and P_{1S}, the final spectral lines are more symmetrical, as can be seen from Fig. 5. Generally speaking, the influence of dispersion on the final shape (and therefore on the strength) of the satellite is stronger than that of damping. However, damping is essential for $k\rightarrow k_c$ because it provides a cutoff for plasmon modes.

IV. DISCUSSION AND COMPARISON WITH OTHER MODELS

Laramore and Camp[47] used an approach similar to ours to include the effect of dispersion and damping on the screening of the core hole in the metal. Practically, they computed Q_B and Q_S in a similar way, but assumed that the damping retained the behavior (3.1) even for $k>k_c$ and extended the integration region to infinity. Their approach overestimated the plasmon contribution.

At the same time, Ashley and Ritchie[48] considered the influence of the plasmon damping on the mean free path in an infinite metal. They used the available experimental data for the damping, correctly integrated only to k_c. For the plasmon dispersion they used the results for the jellium model.

Later, Pardee *et al.*[24] used a model in which they described the extrinsic scattering in the mean-free-path approximation and neglected interference effects. However, there is an inconsistency in the derivation of their Eq. (12). Even if a plasmon emission is treated as a purely intrinsic process, the information about it is carried by the outgoing electron. The outgoing electron can be removed from the plasmon-satellite region by some other scattering process, and therefore the total excitation probability should be weighted by the factor $\exp(-z/\lambda)$ describing the escape probability. Nevertheless, the fit obtained by Pardee *et al.* was rather good. The main reason for that

is obvious from our Fig. 2: Owing to the large cancellation between the intrinsic and interference terms, the total contribution is mostly influenced by the extrinsic-term behavior. A similar approach, based on the work of Pardee *et al.*, was later used by Steiner *et al.*,[27] Johansson and Lindau,[31] van Attekum and Trooster,[30] and Norman and Woodruff.[32]

The results of Bradshaw *et al.*[25] were previously discussed in our paper on photoemission from core levels of adsorbates.[33]

The discussion presented above also applies to the work of Penn.[4] Penn also neglected interference; to compensate for its influence, he used a reduced coupling between plasmons and the core hole. In the intrinsic part he considered only the bulk-plasmon contribution. In other aspects, there is much correspondence between his work and ours. The shape of the no-loss line was an input parameter. The nonplasmon contribution to the scattering probability in his transport equation relates to our mean free path for short-range scattering and to our background in Eq. (2.22). By including the dispersion and damping, he obtained good agreement with experimental data.

Later, two papers appeared in which only dispersion was included. Echenique *et al.*[35] treated the semiclassical image potential at a solid surface, while Sung and Ritchie[49] considered energy losses of fast charged particles passing through a thin metallic film. Apart from neglecting the damping, their approach is equivalent to that used in our earlier work on the problem of photoemission from adsorbed levels.[33]

More recently, Bose *et al.*[50] used the transition-matrix formalism to study plasmon modes. They obtained results for bulk- and surface-plasmon satellites (including shape) as functions of excitation depth (distance), i.e., without integrating over the metal in the case of photoemission from the bulk. They used different parameters to describe the plasmon dispersion, and neglected the damping completely (but used a sharp cutoff wave vector instead). This means that the comparison of their results with ours is not straightforward. However, there exist some similarities between their results and our Fig. 4. (Note the different behavior for $k \to k_c$.)

An important point should be stressed here. If the damping of plasmon modes is included, the Hamiltonian cannot be written in a form similar to Eqs. (2.9) and (2.11). Because of that, we have to introduce the dispersion and damping at the end of the calculation. This immediately raises the question of the validity of our approximation (2.28) for the plasmon propagator. As can be seen from our procedure, the dominant contribution to the matrix elements in (2.14) comes from intermediate wave vectors k. For small k, the available phase space is small. For values of k approaching k_c, both the dispersion and the damping strongly suppress the integrand.

On the other hand, a quasiparticle is a good description of a plasmon mode if the pole of Green function (i.e., its complex energy) is close to the real axis.[51] This is certainly true in our case for small k [compare $\omega_B(0)$ and $\Gamma_B(0)$], but fails for large k ($k \to k_c$). However, for large k's the contributions from the integrals (2.25) are small, so we expect that the error involved in our calculation is not large.

The parameters describing the dispersion and damping in (2.1) are those which are usually accepted to describe the behavior for k's of interest. However, it is out of the scope of this paper to discuss various aspects of the problem of plasmon dispersion and damping, and the interested reader should consult the book by Raether.[52]

V. CONCLUSIONS

In this paper we have studied the influence of plasmon dispersion and damping on the strengths and shapes of plasmon satellites in the XPS spectra of metals. We have shown that dispersion and damping lead to an appreciable reduction of the plasmon-excitation probability. In our calculations we have used experimental values for the parameters describing dispersion and damping. Most other authors used values from the jellium model which completely neglected the damping, and the terms describing dispersion differed from the experimental values. With respect to this point, the approach of Penn[4] is similar to ours. On the other hand, he used a three-step model in which the interference between the electron and hole scatterings was neglected. Moreover, Penn neglected the surface-plasmon contribution to the intrinsic scattering.

Inclusion of damping also provides a natural cutoff for plasmon modes.

Using the mean-free-path approximation to describe short-range scattering processes, we were able to calculate the shape of the first surface- and bulk-plasmon lines in the spectra. Comparing these results with experimental spectra, we have obtained good agreement for the mean free path for short-range processes at $E_0 = 1410$ eV. Our result, $\lambda = 29$ Å, is close to the generally accepted value.

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