PHYSICAL REVIEW B VOLUME 27, NUMBER 10 15 MAY 1983

Plasmon satellites in the x-ray photoemission spectra of metals and adsorbates

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(Received 10 June 1982; revised manuscript received 17 February 1983)

Surface and bulk-plasmon satellites for the x-ray photoemission spectra of simple metals have been calculated using the transition-matrix approach. Intensities for photoemission at various depths, z_0, from the surface of the sample are presented. It is found that the singularity at the upper edge of the bulk-plasmon satellite is exactly canceled by the "*begrenzung*" effect, making the spectrum finite everywhere, especially at the satellite edge. The surface-plasmon satellite intensity agrees with previous phenomenological calculations. The present approach also allows calculation of the surface spectra for photoemission from adsorbates ($z_0<0$). The calculated adsorbate spectra are in qualitative agreement with recent experimental data.

I. INTRODUCTION

In recent years, there has been considerable interest in the experimental and theoretical studies of both bulk- and surface-plasmon satellites of the x-ray photoemission spectra (XPS) of metals.[1–21] Most theoretical calculations have been carried out on the basis of various phenomenological models for the plasmon; however, it has been generally recognized that there are three basic processes which can contribute to the plasmon satellite. These are as follows: An extrinsic process which corresponds to the production of a plasmon by the excited photoelectron, an intrinsic process which corresponds to the excitation of a plasmon by the hole which is created, and an interference term which occurs due to quantum interference between the intrinsic and the extrinsic processes. In many theoretical investigations the dispersion and attenuation[22] of the plasmon have been ignored. In several others, the strength and line shapes of the satellites have been calculated by retaining the plasmon dispersion. However, we are not aware of any quantum-mechanical calculation of the line shape of the surface-plasmon satellites for photoemission from adsorbed atoms, which includes all of the above three processes.

In this paper we undertake a systematic, quantum-mechanical study of the surface- *and* bulk-plasmon satellite in the core-level x-ray photoemission spectra of semi-infinite metals. Along with the surface and pure bulk contributions we also consider a third contribution, the so-called "*begrenzung*" effect. Like the surface plasmon, this effect is essentially related to the presence of the surface. The *begrenzung* term modifies only the structure of the *bulk*-plasmon satellite and does not contribute to the intensity of the surface-plasmon satellite. Referring to the recently developed S- and T-matrix approach,[11] we have calculated the surface- and bulk-plasmon satellites, including the *begrenzung* effect for photoemission from metallic ions or impurity atoms inside the metal, and also from atoms or molecules adsorbed on the surface of the metal.

II. FORMALISM

In our model, we consider a semi-infinite metallic sample extending from $z=0$ to $z=\infty$. The surface of the sample, at $z=0$, may also be viewed as a substrate on which atoms and molecules can be adsorbed. We will consider photoelectrons of energy $E_k=k^2/2m$, which are emitted normal to the surface due to the absorption of incident x rays of frequency ω by core electrons of energy E_B located a distance z_0 from the surface. In this paper, we calculate the satellite band intensities from depth z_0 for both positive z_0 (i.e., for photoelectrons emitted from the metallic ions or impurities *inside* the metal) and negative z_0 (i.e., for photoelectrons originating from adsorbed atoms or molecules *outside* the metal).

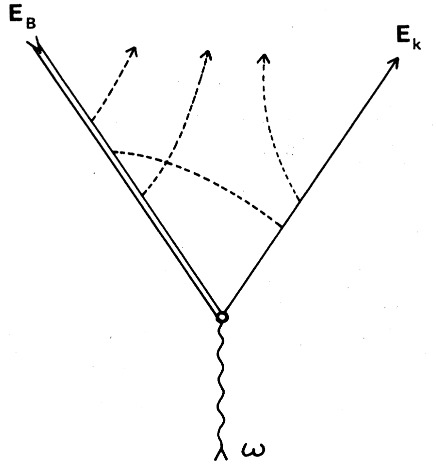

FIG. 1. Diagram representing the process of photoemission from near or within a metal showing intrinsic, extrinsic, and interference processes. Dashed lines represent surface- or bulk-plasmon production. Bulk modes are absent for core hole (double line) outside the metal.

The process of core-level photoemission in a metal is shown schematically in Fig. 1. The wavy line represents the x-ray photon which produces a core-hole-excited electron pair at $z=z_0$. The downward directed double line represents the core hole while the single line pointing upward represents the ejected photoelectron. The process of surface- or bulk-plasmon production is represented by the dashed lines. The extrinsic plasmon lines are the outgoing lines attached to the photoelectron propagator while the intrinsic plasmon lines are those attached to the core-hole propagator. The interference term occurs due to the cross product between the intrinsic and extrinsic processes. Note that the bulk plasmons can be created only for $z_0>0$.

Using the imaginary part of an appropriate effective interaction, in the random-phase approximation, the S- and/or the T-matrix elements were developed for the first plasmon satellites in the photoelectron intensity $J_1(E_k,\omega+E_B,z_0)$. The imaginary part of the effective interaction (via surface- and bulk-plasmon excitation) acting between two electrons located at z and z' can be expressed as the following sum of three terms[23]:

$$\operatorname{Im}V_+(z,z',q_{\|},\omega')=\frac{-\pi^2e^2}{q_{\|}}[A_{bk}(z,z')+A_{bg}(z,z')+A_s(z,z')] \quad (1)$$

with

$$A_{bk}(z,z')=\omega_p\delta(\omega'-\omega_p)e^{-q_{\|}|z-z'|}\Theta(z)\Theta(z')$$

related to the bulk plasmon,

$$A_{bg}(z,z')=-\omega_p\delta(\omega'-\omega_p)e^{-q_{\|}(z+z')}\Theta(z)\Theta(z')$$

related to the *begrenzung* correction to the bulk-plasmon excitation, and

$$A_s(z,z')=\omega_s\delta(\omega'-\omega_s)e^{-q_{\|}(|z|+|z'|)}$$

related to the surface term. Here $q_{\|}$ is the component of the wave vector parallel to the surface, ω_p and ω_s are the bulk- and surface-plasmon energies, respectively, with dispersions described later, and Θ is the usual unit step function, the surface being located at $z=0$.

As in Refs. 11 and 12, the plasmon satellite intensities due to photoelectrons produced at depth z_0 can be written, for zero- and one-plasmon processes, as

$$J_0(E_k,\omega_0,z_0)=\delta(E_k-\omega_0)\,, \quad (2a)$$

$$J_1(E_k,\omega_0,z_0)=T(E_k,\omega_0,z_0)\,, \quad (2b)$$

where[24] $\omega_0=\omega+E_B=\omega-|E_B|$ is the energy transferred to the photoelectron in the absence of plasmon excitation as shown in Eq. (2a), and T is the transition matrix element

$$T(E_k,\omega_0,z_0)=\frac{-1}{\pi(2\pi)^2}\int d^2q_{\|}\int_{-\infty}^{\infty}dz'\int_{-\infty}^{\infty}dz\,\operatorname{Im}[V_+(z,z',q_{\|},\omega_0-E_k)]\mathscr{I}^*(z')\mathscr{I}(z) \quad (3)$$

with

$$\mathscr{I}(z)=\frac{1}{2\pi}\int d^3p\,\delta(\vec{p}_{\|}-\vec{q}_{\|})e^{-ip_zz_0+i(k+p_z)z}\left[\frac{1}{\omega_0-E_k}-\frac{1}{\omega_0-E_p+i\lambda}\right]$$

$$=\frac{\delta(z-z_0)}{\omega_0-E_k}e^{ikz_0}+i\frac{m}{R}e^{ikz+iR|z-z_0|}\,. \quad (4)$$

Here $\vec{p}$ is the electron momentum before the excitation of a plasmon of momentum $\vec{q}$; $\vec{k}=(0,0,-k)$ is the electron momentum after plasmon excitation (outgoing photoelectron) and $R=(2m\omega_0-q_{\|}^2)^{1/2}$. The first term in $\mathscr{I}(z)$ corresponds to the intrinsic process and the second to the extrinsic process. With the use of the interaction potential given in Eq. (1), the T-matrix elements for the plasmon bands have been calculated. We will now consider the surface- and the bulk-plasmon satellites separately.

A. Surface-plasmon satellite

In the case of surface-plasmon excitation, the plasmon wave vector is parallel to the surface. Here only the surface term A_s in Eq. (1) has to be used. Since it is separable in z and z', the T-matrix element giving the intensity can be written as

$$J_{1,s}(E_k,\omega_0,z_0)=\frac{e^2}{4\pi}\int d^2q_{||}\frac{\omega_s(q_{||})}{q_{||}}\times\delta(\omega_0-E_k-\omega_s(q_{||}))\,|M_s|^2 \tag{5}$$

with

$$M_s=\int_{-\infty}^{\infty}dz\,e^{-q_{||}|z|}\mathscr{J}(z)=\frac{1}{\omega_s(q_{||})}e^{-q_{||}|z_0|}e^{ikz_0}+i\frac{m}{R}\mathscr{E}_s \tag{6}$$

and

$$\mathscr{E}_s=\int_{-\infty}^{\infty}dz\exp(-q_{||}|z|+ikz+iR|z-z_0|)\ .$$

For the surface-plasmon frequency $\omega_s(q_{||})$ we use the linear dispersion relation[25]

$$\omega_s(q_{||})=\omega_s^0+\beta q_{||} \tag{7}$$

with $\omega_s^0=\omega_p^0/\sqrt{2}$, ω_p^0 being the classical bulk-plasmon frequency, and $\beta=(k_F/2m)\sqrt{3/5}$, k_F being the Fermi momentum. All integrations for the surface-plasmon satellite can be easily carried out, resulting in the following expressions for the intrinsic, interference (or cross: $\times$) and extrinsic contributions to the intensity:

$$J_{1,s}^{i}=\frac{e^2}{2\beta\omega_s(q_{||})}e^{-2q_{||}|z_0|}\ , \tag{8}$$

$$J_{1,s}^{\times}=-\frac{me^2}{\beta R}e^{-q_{||}|z_0|}\mathrm{Im}(e^{-ikz_0}\mathscr{E}_s)\ , \tag{9}$$

$$J_{1,s}^{e}=\frac{m^2e^2\omega_s(q_{||})}{2\beta R^2}\,|\mathscr{E}_s|^2\ , \tag{10}$$

where $q_{||}=(\omega_0-E_k-\omega_s^0)/\beta$. The closed-form expression for $\mathscr{E}_s$ is

$$\mathscr{E}_s=\Theta(-z_0)e^{-iRz_0}\left[\frac{1}{q_{||}-ik_+}+\frac{1-e^{(q_{||}+ik_+)z_0}}{q_{||}+ik_+}+\frac{e^{(q_{||}+ik_+)z_0}}{q_{||}+ik_-}\right]+\Theta(z_0)e^{iRz_0}\left[\frac{1}{q_{||}+ik_-}+\frac{1-e^{-(q_{||}-ik_-)z_0}}{q_{||}-ik_-}+\frac{e^{-(q_{||}-ik_-)z_0}}{q_{||}-ik_+}\right] \tag{11}$$

with $k_\pm=k\pm R$. It should be noted that in the extrinsic term there is a small contribution which survives in the limit $z_0\to-\infty$. Such terms are due to our model where the metal sample is semi-infinite. There is actually a far removed second surface which must give rise to an equal and opposite contribution. For this reason such terms do not contribute and, therefore, we ignore them.

B. Bulk-plasmon satellite

In the case of bulk-plasmon production, the plasmon wave vector is not parallel to the surface. For the first two terms of $\mathrm{Im}V_+(z,z',q_{||},\omega')$ in Eq. (1), which correspond to the bulk-plasmon excitation and its *begrenzung* correction, we introduce their Fourier transform in Eq. (3). In this way we can appropriately include the bulk-plasmon dispersion when integrating over the intermediate states. This Fourier transform is

$$\frac{1}{2q_{||}}e^{-q_{||}|z|}=\frac{1}{2\pi}\int\frac{dq_z}{q^2}e^{iq_zz}$$

with $q^2=q_{||}^2+q_z^2$. A three-dimensional $\vec{q}$ can then be reintroduced as required by the dispersion rule of $\omega_p(q)$. The analysis at this point breaks into two parts: (1) bulk terms and (2) *begrenzung* terms.

1. Bulk terms

In this case Eq. (3) is separable in z and z', and the resulting expression for the intensity becomes

$$J_{1,bk}(E_k,\omega_0,z_0)=\frac{e^2}{4\pi^2}\int d^3q\frac{\omega_p(q)}{q^2}\delta(\omega_0-E_k-\omega_p(q))\,|M_b(q_z)|^2\ , \tag{12}$$

with

$$M_b(q_z)=\int_0^\infty dz\, e^{-iq_z z}\mathscr{I}(z)$$
$$=\frac{\Theta(z_0)}{\omega_p(q)}e^{i(k-q_z)z_0}+i\frac{m}{R}\mathscr{E}_b(q_z) \tag{13}$$

and

$$\mathscr{E}_b(q_z)=\int_0^\infty dz\exp[i(k-q_z)z+R\,|z-z_0|\,]\ .$$

Here we use the quadratic dispersion relation for the bulk plasmon

$$\omega_p(q)=\Theta(q_c-q)(\omega_p^0+\alpha q^2)$$

with (14)

$$\alpha=3k_F^2/(10m^2\omega_p^0)\ .$$

The expressions for the intrinsic, cross, and extrinsic contributions can be shown to match those found in previous work.[12] In the present study, no further approximations are made, since these results are to be combined with different expressions for the *begrenzung* contributions. The three bulk contributions to the plasmon satellite are

$$J^i_{1,bk}=\Theta(z_0)\frac{e^2}{2\pi\alpha q\omega_p(q)}\ , \tag{15}$$

$$J^\times_{1,bk}=-\Theta(z_0)\frac{me^2}{\pi\alpha q^2}\times\int_{-q}^{q}dq_z\left[\frac{1}{2m\omega_p(q)-q^2+2kq_z}-\frac{\cos[(R-k+q_z)z_0]}{2R(R-k+q_z)}\right]\ , \tag{16}$$

and

$$J^e_{1,bk}=\Theta(z_0)\frac{2m^2e^2\omega_p(q)}{\pi\alpha q^2}\times\int_{-q}^{q}dq_z\frac{\sin^2[(R-k+q_z)z_0/2]}{R[R^2+(k-q_z)^2]}\ . \tag{17}$$

In each of these expressions q is fixed by the delta function in the effective interaction to the value: $q=[(\omega_0-E_k-\omega_p^0)/\alpha]^{1/2}<q_c$.

2. *Begrenzung* terms

In our formalism, the *begrenzung* term cannot be written in terms of a matrix element times its complex conjugate due to the inseparability of the effective interaction in z and z'. Here Eq. (2b) for $J_{1,bg}$ takes a form similar to Eq. (5) for $J_{1,s}$; the only change is due to the replacement of A_s by A_{bg}. As shown in the form of these interaction terms, this requires a minus sign in front of the expression for $J_{1,bg}$, the replacement of ω_s by ω_p and the introduction of step functions $\Theta(z)$. Using the mentioned Fourier transform of $e^{-q_{\|}|z+z'|}/q_{\|}$, one obtains

$$J_{1,bg}(E_k,\omega_0,z_0)=\frac{-e^2}{4\pi^2}\int d^3q\frac{\omega_p(q)}{q^2}\delta(\omega_0-E_k-\omega_p(q))M_b^*(q_z)M_b(-q_z)\ , \tag{18}$$

where M_b is given by Eq. (13). The expressions for the intensities are

$$J^i_{1,bg}=-\Theta(z_0)\frac{e^2}{2\pi\alpha q\omega_p(q)}\frac{\sin(2qz_0)}{2qz_0}\ , \tag{19}$$

$$J^\times_{1,bg}=\Theta(z_0)\frac{me^2}{\pi\alpha q^2}\int_{-q}^{q}dq_z\left[\frac{\cos(2q_zz_0)}{2m\omega_p(q)-q^2+2kq_z}-\frac{\cos[(R-k-q_z)z_0]}{2R(R-k+q_z)}\right]\ , \tag{20}$$

and

$$J^e_{1,bg}=-\Theta(z_0)\frac{m^2e^2\omega_p(q)}{\pi\alpha q^2}\int_{-q}^{q}dq_z\left[\frac{kR^{-1}+\cos(2q_zz_0)}{[(k-q_z)^2-R^2][(k+q_z)^2-R^2]}-\frac{\cos[(R-k-q_z)z_0]}{R(R-k+q_z)[R^2-(k+q_z)^2]}\right]\ . \tag{21}$$

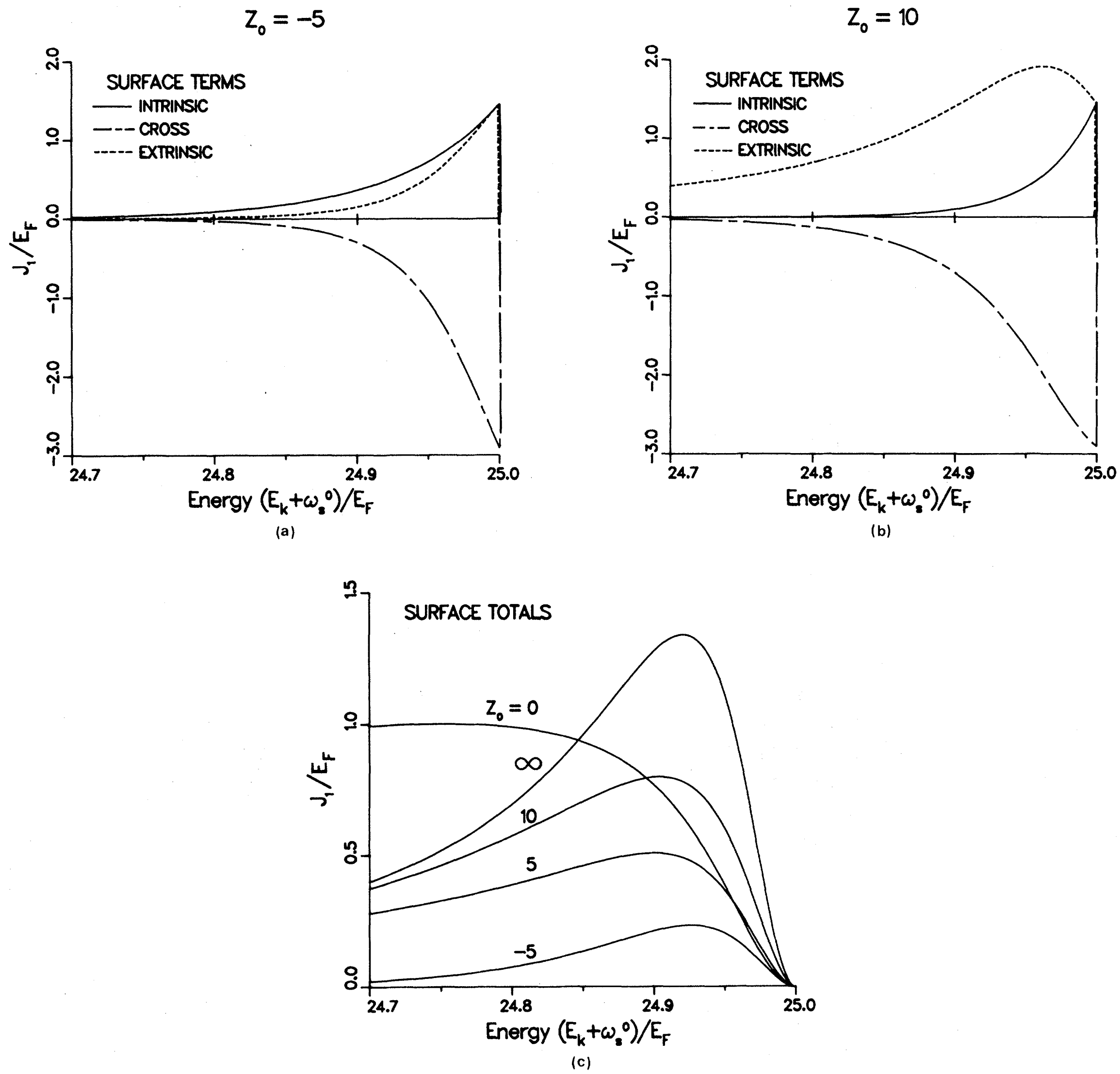

FIG. 2. Intrinsic, cross, and extrinsic contributions to the surface-plasmon satellite for photoemission (a) from outside the metal ($z_0=-5k_F^{-1}$) and (b) from within the metal ($z_0=10k_F^{-1}$). (c) Total intensity from intrinsic, cross, and extrinsic contributions to the surface-plasmon satellite for various distances from the surface (z_0 in units of k_F^{-1}).

Here again $q=[(\omega_0-E_k-\omega_p^0)/\alpha]^{1/2}<q_c$ has to be used.

III. RESULTS

Three sets of results corresponding to the surface plasmon, bulk terms, and the *begrenzung* effect have been obtained by using Eqs. (5)–(21). We will discuss each of them separately.

A. Surface-plasmon satellite

Using Eqs. (8)–(11), it is easy to show that as $z_0\to\infty$, there exists an asymptotic spectrum which is equal to the extrinsic spectrum. This is similar to the behavior of the peak intensities previously reported.[2,3] It is interesting to note that at the upper end point, where $q_{\parallel}\to 0$, each term is finite, independent of z_0 and the sum of the three cancels exactly:

$$J_{1,s}^{i}(\omega_0-\omega_s^0,\omega_0,z_0)=J_{1,s}^{e}(\omega_0-\omega_s^0,\omega_0,z_0)$$
$$=-\tfrac{1}{2}J_{1,s}^{\times}(\omega_0-\omega_s^0,\omega_0,z_0)$$
$$=\frac{e^2}{2\beta\omega_s^0}\,,$$

with

$$\omega_s^0=\omega_p^0/\sqrt{2}\,.$$

Notice that the expression for the intrinsic intensity [Eq. (8)] is a manifestly even function of z_0 and note that due to the sinusoidal terms in Eq. (9), the interference term can have oscillations with respect to E_k and become positive for the proper choice of parameters, in contrast to previous calculations.[3,9] Both effects have appeared in our numerical calculations.

In Figs. 2(a) and 2(b) we have plotted the intrinsic, extrinsic, and interference terms of the surface-plasmon spectra for two values of z_0, one positive and one negative, for aluminum using $k_F = 1.75$ Å^{-1}, $\omega_p^0 = 15.8$ eV, and an x-ray energy $\omega = 25E_F = 291$ eV. The total contributions are shown in Fig. 2(c). These results agree with the results obtained using other approaches,[3,9] and the results for $z_0 \geq 0$ are also in agreement with those of Inglesfield[13] who used a perturbative approach. It is important to note that the present approach also allows us to calculate the line shape of the surface-plasmon satellites for $z_0 < 0$, i.e., for photoemission from adsorbed atoms or molecules.

In Fig. 3 we plot the maximum value of the total surface-plasmon satellite intensity as a function of z_0. The sharp peak, found at $z_0 = 0$, reaches a value of 1.003. Notice that this curve shows a minimum at $z_0 = 3.59k_F^{-1} = 2.05$ Å and a broad maximum around $z_0 = 28k_F^{-1}$. The minimum occurs due to the competition among the contributions from the intrinsic, extrinsic, and interference terms. The origin of the broad maximum is essentially in the extrinsic term for which the asymptotic curve is found to not be an enveloping one. The origin of the structures is explained in Sec. IV.

B. Bulk-plasmon satellite (including *begrenzung* contribution)

Figure 4 shows the intrinsic, the cross, and the extrinsic contributions, both bulk and *begrenzung*, to the bulk-plasmon satellite for $z_0 = 10k_F^{-1}$. Note that the *begrenzung* term is basically a negative correction, even though it may have oscillations. As shown in Eqs. (15)—(17), the pure bulk intrinsic contribution is independent of z_0; however, the extrinsic (and cross) contributions increase in magnitude as z_0 increases. Being a surface correction, the intrinsic *begrenzung* intensity decreases as z_0 increases. However, since the extrinsic and cross intensities involve the photoelectron trajectory crossing the surface, these terms in the *begrenzung* contribution increases in magnitude as z_0 increases. The periodic factors in the equations for the begrenzung terms give rise to the oscillations in Fig. 4 and are discussed in Sec. IV.

All six intensities given by Eqs. (15)—(17) and (19)—(21) diverge at the upper edge of the spectrum; however, as is obvious from Eqs. (12) and (18), the intrinsic, interference, and extrinsic terms, taken in pairs (bulk and *begrenzung*) cancel exactly at this edge. The total spectrum is therefore finite as was indicated in a recent work.[13] Figure 5 shows the net contributions to the bulk-plasmon satellite from the intrinsic, interference, and extrinsic processes, again

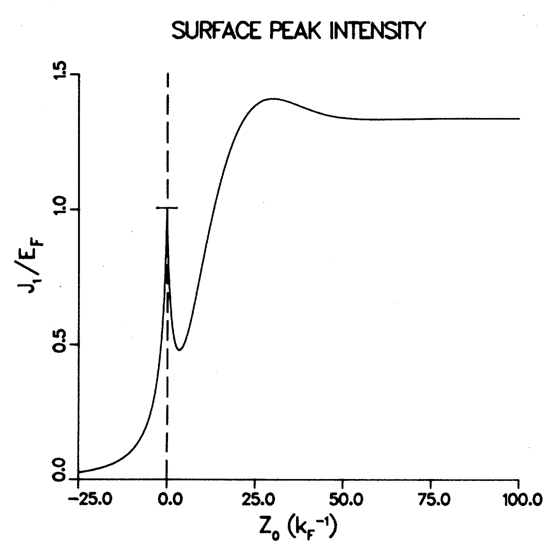

FIG. 3. Peak (maximum with respect to E_k) of the total surface-plasmon satellite intensity vs distance of ionization center from the surface.

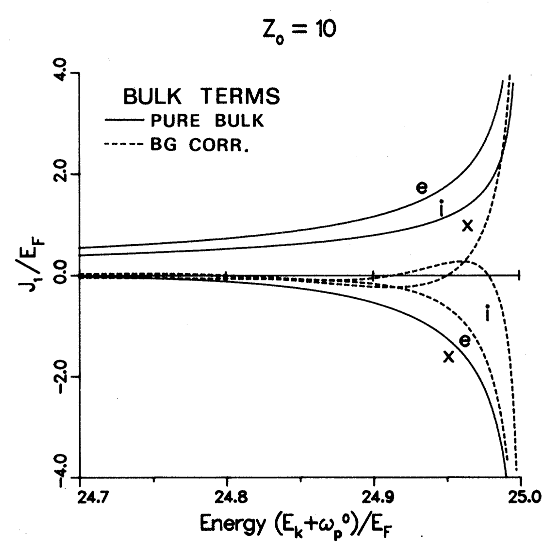

FIG. 4. Bulk [and *begrenzung* (BG) correction]: intrinsic (i), cross ($\times$), and extrinsic (e) contributions to the bulk-plasmon satellite. All six contributions diverge at the upper edge ($z_0 = 10k_F^{-1}$).

for $z_0=10k_F^{-1}$. Each contribution smoothly goes to zero at the upper edge. The total of these three contributions is shown in Fig. 6 for several values of z_0. Note the various structures which arise, due to the competition of the three processes and also due to the oscillating behavior, with respect to E_k, of the *begrenzung* terms. The origin and nature of these oscillations are discussed in the following section.

IV. CONCLUSIONS

In this work we have undertaken a systematic study of the surface- and bulk-plasmon satellites in the x-ray photoemission spectra of simple metals. Using a transition-matrix approach,[11,12] we have derived quantum-mechanical expressions for the line shapes of these spectra. The satellite intensities for photoemission at various depths, z_0, from the surface of the sample have been calculated.

Our theory for the bulk-plasmon satellite includes a detailed study of the *begrenzung* effect, i.e., the correction to the bulk-plasmon satellite due to the presence of the surface. Using the present approach we have been able to show analytically that the singularity at the upper edge of the bulk-plasmon satellite is exactly cancelled by the *begrenzung* effect. Results have been compiled for the individual terms (i.e., intrinsic, cross, and extrinsic), each of which has this cancellation. This result is interesting as it indicates that at the upper edge of the spectrum, the bulk-plasmon intensity approaches zero and not infinity. This should become evident in a carefully conducted experiment of the bulk-plasmon satellite.

For the surface-plasmon satellite, agreement is found between the present work and results obtained by using alternative phenomenological approaches. Excellent agreement is found between the present results and the spectra reported by Inglesfield[13] for photoemission from inside the metal, i.e., for $z_0 \geq 0$. However, our theory for the surface-plasmon satellite extends into the $z_0<0$ region and is applicable to the problem of photoemission from adsorbed atoms or molecules. To our knowledge, this is the first quantum-mechanical calculation of the surface-plasmon satellite line shape during photoemission from adsorbates. Recently, several measurements of the surface plasmon satellites due to photoemission from adsorbed atoms and molecules have been reported[15,16,18,19]; our results are in qualitative agreement with these measurements. Our calculation of the peak intensity of the surface-plasmon satellite versus z_0 (Fig. 3), shows features (maxima and minima), not all of which have been found in the literature.

The various oscillations calculated in this paper are an interesting feature of the study of the bulk- and surface-plasmon satellites of the x-ray photoemission spectra of semi-infinite metal samples. They are probably not easy to detect experimentally, being at the limit of instrumentation resolution. However, they play some role in the spectral shift and variation of the intensity maxima as a function of z_0, the depth at which the photoelectron is produced, as emphasized in Fig. 3.

Physically, these oscillations are a quantum effect which can be directly related to the uncertainty principle. The photoelectron interacts with the plasmon field for a very short interval of time, τ. This time

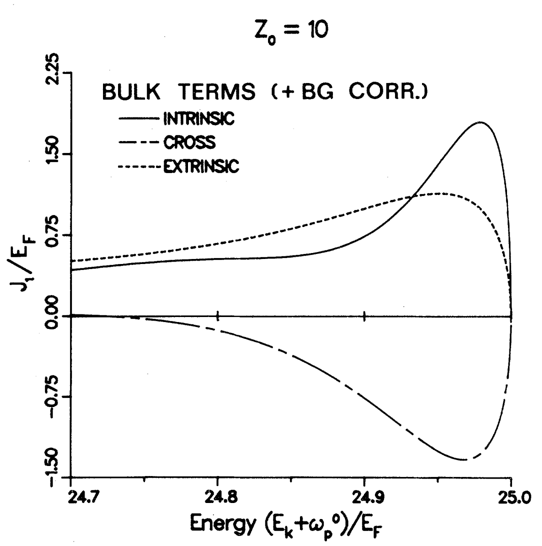

FIG. 5. Bulk-plasmon satellite (including *begrenzung* correction). Each contribution is zero at the upper edge ($z_0=10k_F^{-1}$).

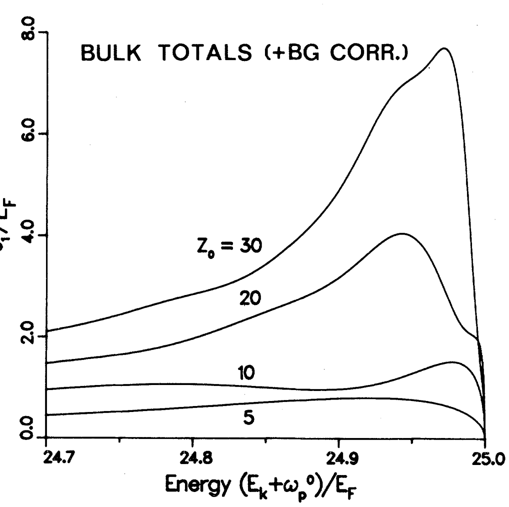

FIG. 6. Total of all bulk and *begrenzung* contributions to bulk-plasmon satellite for various depths of ionization (z_0 in units of k_F^{-1}).

interval is limited by two effects. The depth z_0 at which the photoelectron is produced will have an effect on both surface- and bulk-plasmon excitation. The other limitation is brought about by the finite extension ($\sim q_{||}^{-1}$) of the surface region. This only affects the surface and *begrenzung* contributions. Owing to this time limitation, between the photoproduction process and the surface crossing, the interaction with the plasmon field appears to be suddenly switched on and off. Such a situation is known to give rise to quantum oscillations in transition rates.

Let us conclude the paper with an estimation of the phase of these oscillations. This phase is of the order of $\tau\Delta E$ where ΔE is the uncertainty in the core-hole energy or photoelectron energy as "seen" by the plasmon field during the finite interval τ. For the intrinsic terms, the interaction with the core hole is recoilless; the uncertainty $\Delta E = \Delta E_B$ is thus negligible and no oscillation should be expected. The situation, however, is different for the extrinsic (and cross) terms where one has $\Delta E = \Delta E_p = (p_{||}\Delta p_{||} + p_z \Delta p_z)/m$ and $\tau = m z_0/p_z$. Since $p_{||} = q_{||}$ is well determined for the surface-plasmon case, one has $\Delta p_{||} = 0$ and $\tau \Delta E_p = \Delta p_z z_0 = (p_z - k) z_0 = (R - k) z_0$ which is the phase of the oscillations of the extrinsic and cross terms. As mentioned before, the intrinsic terms should not have any oscillations in principle. However, there is an exception for the intrinsic *begrenzung* contribution. In spite of the lack of recoil of the core hole, an uncertainty occurs due to the lack of knowledge of the q_z component of the bulk-plasmon momentum which is undefined by an amount $\Delta q_z \approx q_{||}$ due to the reflection of the plasmon on the surface. This explains the oscillations in Eq. (19) which is the intrinsic term for the *begrenzung* contribution. The various oscillations and structures occurring in Figs. 2–6 are the combined effects of the oscillations of these individual terms and the competition among them.

ACKNOWLEDGMENTS

This work was supported in part by the North Atlantic Treaty Organization Research Grant No. 1433 and in part by the Fonds National de la Recherche Scientifique, Belgium and the Coopération Scientifique Internationale, Belgium. Preliminary results were reported at the International Conference on Solid Films and Surfaces, College Park, Maryland, June 1981.

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