Surface effects on the x-ray photoemission spectra of metals

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The effects of the presence of the surface on the main line shape and strength of the photoemission spectra of metals and adsorbates have been investigated. By using a modified Nozières-deDominicis theory, recently developed by Bose, Kiehm, and Longe for the bulk photoemission spectra of metals, the power-law exponent α and the intensity parameter ξ have been calculated as functions of z_0, the distance from the surface. With the use of these values, the asymmetry indices at half- and quarter-maxima, as well as the maximum intensities, have been calculated. These quantities are seen to be highly influenced by the presence of the surface for photoemission from adsorbate atoms outside the sample. The surface has moderate effects on the photoemission from atoms embedded inside the sample. The results obtained in this article can be utilized to estimate the distance of a photoemitting adsorbate atom, from the experimentally observed asymmetry indices and intensity maxima.

I. INTRODUCTION

In a one-electron model, the intensity of the x-ray photoemisson spectrum (XPS) from an inner core state of a metal may be described by a δ function as long as the lifetime of the core state is infinite. Many-body interactions in the metal introduce an asymmetrical width to the line shape of the XPS. These many-body effects have been studied some years ago by Doniach and Šunjić (DS) (Ref. 1), who extended the Nozières-deDominicis (ND) theory[2] of the edge effect in the x-ray spectra to the photoemission case.

The many-body effects which modify the δ-function shape are of two kinds: The ones which give a width λ to the line shape but maintain it in a symmetrical Lorentzian shape

$$I^L(\epsilon)=\frac{\lambda/\pi}{\epsilon^2+\lambda^2}\ , \tag{1}$$

and those which introduce an asymmetry and are directly related to the so-called edge effect. The width λ is related to the core-hole damping (generally due to internal Auger transition[3–5]) as well as to the photoelectron damping[6,7] (electron-hole pair and plasmon excitations). The edge effect, on the other hand, is associated with the creation of a large number of weak-energy electron-hole pairs during the photoemission process. As shown in DS it modifies Eq. (1) into the asymmetrical band shape

$$\begin{aligned} I^A(\epsilon)&=\frac{1}{\pi}\mathrm{Re}\int_0^\infty ds\frac{\exp[i(-\epsilon+i\lambda)s]}{(i\xi s)^\alpha} \\ &=\frac{\Gamma(1-\alpha)}{\pi\xi^\alpha}(\epsilon^2+\lambda^2)^{(\alpha-1)/2} \\ &\quad\times\cos\left[\alpha\frac{\pi}{2}+(1-\alpha)\tan^{-1}\left[\frac{\epsilon}{\lambda}\right]\right], \end{aligned} \tag{2}$$

where α is given by

$$\alpha=2\sum_{l=0}^{\infty}(2l+1)\left[\frac{\delta_l}{\pi}\right]^2. \tag{3}$$

The δ_l's in Eq. (3) are the phase shifts of the Fermi electrons scattered by the core hole. Note that when α goes to zero Eq. (2) reduces to the Lorentz function [Eq. (1)]. Thus the parameter α can be visualized as the asymmetry parameter introducing asymmetry in the XPS line shape.

In actual metals, for the density parameter r_s running from 2 to 5, α has been estimated to range from 0.12 to 0.25 according to an expression pro-

posed by Longe,[8] using the Born approximation, controlled by the Friedel sum rule, for the phase shifts, i.e.,

$$\alpha=(2\pi a_B k_F+2)^{-1}\,, \tag{3'}$$

where the core-hole potential $V(q)$ is the Thomas-Fermi potential.

In Eq. (2), ξ is a constant having the dimension of energy and is estimated roughly to be of the order of the Fermi energy $\epsilon_F=k_F^2/2m$. However, ξ as well as α would depend on energy ϵ if one wants to extend the DS model to lower energies.[9] Since the DS model is valid only for $\epsilon\ll\epsilon_F$, the calculation of ξ, as it appears in Eq. (2), is irrelevant, as it provides information only about the absolute photoemission intensity, which practically is impossible to measure experimentally.

The calculation of ξ, however, becomes interesting if one wants to study the evolution of the line shape [Eq. (2)] as a function of z_0, the normal distance of the photoemitting atom from the metal surface. This atom may be, for instance, an impurity atom embedded in the metal, or it may be an adsorbed atom or an atom belonging to an adsorbed molecule. In the latter case, the atom is outside the metal at a (negative) distance z_0 from the surface.

The aim of this paper is to study the evolution of the line shape of the photoemission from a metal [Eq. (2)] as a function of z_0. More precisely, we intend to calculate the z_0 dependence of ξ and α, which determines this evolution. The limit $z_0\to+\infty$ would correspond to the bulk situation described in DS and the limit $z_0\to-\infty$ would correspond to photoemission by a free atom (or molecule). Note that λ appearing in Eq. (2) should, in principle, depend on z_0 also. However, this dependence can be considered negligible if the core-hole lifetime, which depends mainly on the inner-core Auger transition,[3–5] is considered more important than the photoelectron damping.[6,7] We will assume such a situation as it is encountered in deep—core-level (K-level) photoemissions. Measurements are also more reliable in these situations.

The two quantities of experimental interest are (i) the intensity maximum and (ii) the asymmetry of the main line. It is particularly interesting to study the evolution of these quantities as a function of z_0.

II. INTENSITY MAXIMUM AND ASYMMETRY INDEX

Before proceeding to the calculation of $\alpha(z_0)$ and $\xi(z_0)$ in the next section, let us first show how they are related to the experimentally determined quantities, the intensity maximum and the asymmetry index. Introducing the dimensionless quantities $x\equiv\epsilon/\lambda$ and $J\equiv\pi\lambda I$, we find that the line shapes, Eqs. (1) and (2), can be represented by two functions independent of λ, except for an overall factor $(\lambda/\xi)^\alpha$ in J^A. One has

$$J^L(x)=\frac{1}{x^2+1} \tag{4}$$

and

$$J^A(x)=(\lambda/\xi)^\alpha A(x)\,, \tag{5}$$

with

$$A(x)=\Gamma(1-\alpha)(x^2+1)^{(\alpha-1)/2}\times\cos\left[\alpha\frac{\pi}{2}+(1-\alpha)\tan^{-1}x\right]. \tag{6}$$

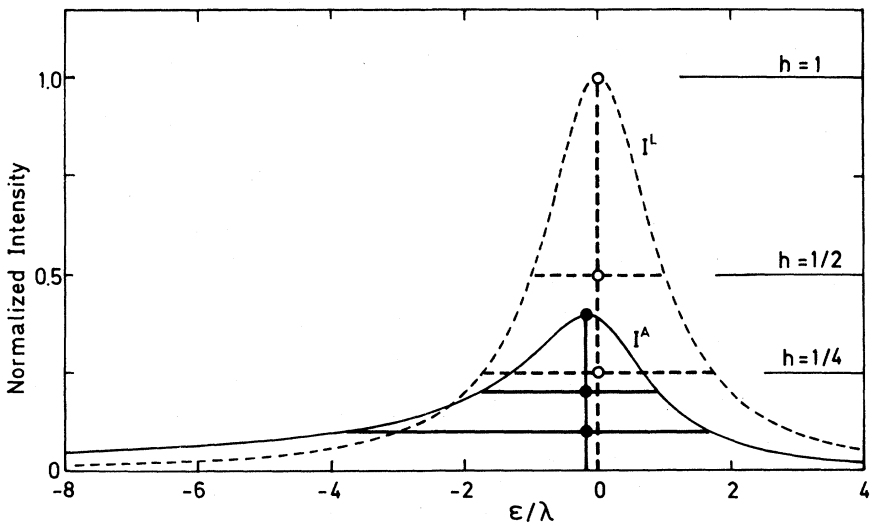

FIG. 1. Schematic representation of the photoelectron intensity for the symmetric (Lorentzian) and asymmetric cases.

Functions $J^L(x)$ and $A(x)$ are shown schematically in Fig. 1. The intensity maxima occur at $x=0$ in Eq. (4) and at

$$x = x_m \equiv \cot[\pi/(2-\alpha)]$$

in Eq. (5). The magnitudes of these maxima are

$$J^L_{\max} = 1$$

and

$$J^A_{\max} = \left[\frac{\lambda}{\xi}\right]^{\alpha} A_{\max} , \tag{7}$$

with

$$A_{\max} = \Gamma(1-\alpha)\left[\sin\frac{\pi}{2-\alpha}\right]^{2-\alpha} . \tag{8}$$

As in DS, we define the asymmetry index $a(\frac{1}{2})$ at half-maximum as the ratio of |peak energy minus energy at half-maximum| on the low-energy side to that on the high-energy side of the peak. Another asymmetry index $a(\frac{1}{4})$, which is easier to measure, can be introduced similarly by using the energies at quarter-maximum instead of half-maximum. One has $a(\frac{1}{4}) \geq a(\frac{1}{2}) \geq 1$, the equalities corresponding to the symmetric Lorentzian shape [Eq. (4)]. An important point to realize is that $a(1/n)$, which is calculated from Eq. (6), depends only on α. It neither depends on ξ nor on λ. However, the line asymmetry is probably not the easiest quantity to measure in the x-ray photoemission spectra.

The z_0 dependence of the intensity maximum should be easier to determine experimentally. This maximum given by Eqs. (7) and (8), however, depends on both ξ and α, and it tends to 1 (Lorentzian limit) for an atom or molecule at large distances from the metal and to the DS value (with ξ to be evaluated) when the atom is embedded at a few angstroms inside the metal (bulk photoemission).

To conclude this section we note that the significant quantities to calculate as functions of z_0 are $J^A_{\max}$, $a(\frac{1}{2})$, and $a(\frac{1}{4})$, which, in turn, implies that it is necessary to calculate both α and ξ as functions z_0.

III. CALCULATION OF THE POWER-LAW EXPONENT α AND THE INTENSITY PARAMETER ξ

The ND theory for the edge effect in the x-ray spectra and its extension to the XPS by DS use a separable core-hole potential. These theories show that the edge effect is described by a power law and then give expressions for the power-law exponent α as a function of the phase shift [see Eq. (3)]. They do not give an expression for ξ, the calculation of which would require the use of a more realistic potential.[8] Furthermore, the extension to the case where a surface is present requires reevaluation of the power-law exponent, as the phase shifts are not only determined by the scattering of the electrons by the core hole alone but also by the charges induced on the surface.

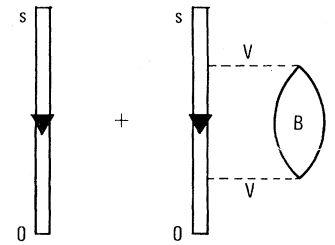

FIG. 2. Lowest-order diagrams contributing to the photoemission intensity.

The only way to evaluate α and ξ is then to introduce a realistic potential describing the interaction of the electrons with a core hole in the presence of the surface. This can be done by using a technique already used by the present authors (BKL) (Ref. 9) to extend the DS theory beyond the immediate neighborhood of $\epsilon=0$. The BKL theory is the lowest-order expansion of the ND theory where a ground-state propagator is calculated between times 0 and s, at which times the core-hole potential is suddenly introduced and removed, respectively (see Fig. 2). In the ND theory this propagator is calculated by means of a diagrammatic expansion where an unlimited number of vacuum loops, containing an unlimited number of core-hole vertices, represent the multiple scattering of the conduction electrons with the core hole. The BKL approximation consists of considering only one loop with two vertices (pair propagator). The power law given in Eq. (2) is then approximated by a logarithmic law,

$$I^A(\epsilon) = \delta(\epsilon)\left[1 - \alpha\ln\frac{\xi}{e^{\gamma}|\epsilon|} - \alpha\frac{P}{\epsilon}\Theta(\epsilon)\right] . \tag{9}$$

(Here we have assumed $\lambda=0$ and $\gamma=0.577\ldots$ is the Euler constant.) This line shape is not correct for $\epsilon\sim 0$, but it gives satisfactory expressions for α and ξ, where the core-hole potential appears quadratically. The important point is that in this approximation, these quantities can now be calculated using various types of realistic potentials. For instance, if the core potential $V(q)$ is spherical (i.e., no core-hole internal structure and no surface effect) one has

$$\alpha = \left[\frac{m}{2\pi^2}\right]^2 \int_0^{2k_F} dq\, q\,[V(q)]^2 . \tag{10}$$

Equation (10) yields Eq. (3') if $V(q)$ is taken to be the Thomas-Fermi potential with a constant screening length. Equation (10) is also directly related to Eq. (3) with the δ_l's calculated in the Born approximation.[8] This calculation has been shown to be quite satisfactory even for the x-ray edge of L bands where the power-law exponent depends strongly on δ_0, the most important phase shift.

Let us now give more details about this calculation and show how it can be adapted to the evaluation of $\alpha(z_0)$ and $\xi(z_0)$. The lowest-order propagators to calculate the photoemission intensity are shown in Fig. 2. As already mentioned, only one loop with two vertices is considered in our approximation. This loop B in Fig. 2 is related to the electron-hole pair propagator $B(q,\omega)$. The dotted lines represent the instantaneous interaction with the core hole which is represented by a double line propagating downward between times 0 and s. The two diagrams contribute to the intensity through the two terms

$$I_0=\frac{1}{\pi}\mathrm{Re}\int_0^\infty ds\, e^{-i\epsilon s}=\delta(\epsilon) \tag{11}$$

and

$$I_1=\frac{1}{\pi}\mathrm{Re}\int_0^\infty ds\, e^{-i\epsilon s}\int_0^\infty d\omega\frac{e^{-i\omega s}-1}{2i(\omega-i\lambda)}\alpha(\omega)\ , \tag{12}$$

with

$$\alpha(\omega)=(8\pi^4\omega)^{-1}\int d\vec{q}\,|V(q)|^2\mathrm{Im}\,B(q,\omega)\ . \tag{13}$$

The procedure consists in identifying I_0 and I_1 with Eq. (9), which yields an expression

$$\alpha(\epsilon)\ln\frac{\xi(\epsilon)}{e^\gamma|\epsilon|}=P\int_0^\infty d\omega\frac{\alpha(\omega)}{\omega+\epsilon}\ . \tag{14}$$

Equation (14) together with Eq. (13) allows the determination of functions $\alpha(\omega)$ and $\xi(\omega)$, and hence $\alpha(0)$ and $\xi(0)$ as required in the present problem. Note that Eq. (10) can be obtained from Eq. (13) by using the expression

$$\mathrm{Im}\,B(q,\omega)\approx\frac{m^2\omega}{2\pi q}\Theta(2k_F-q)\Theta(\omega)\ ,$$

which is valid for $\omega\sim 0$. Here Θ is the usual step function.

To calculate $\alpha(z_0)$ from Eq. (13), we need an explicit potential $V(z,z_0,\vec{q}_{||})$ to describe the interaction between the core hole, treated as a point charge localized at a distance z_0 (positive or negative) from the surface, and a conduction electron located at a distance z (positive) from the surface. Here $\vec{q}_{||}$ is a two-dimensional wave vector parallel to the surface. In this paper, for $V(z,z_0,\vec{q}_{||})$ we will use two approximate potentials which were discussed extensively by Heinrichs[10] a few years ago. These potentials were calculated by procedures where a part of the problem was treated phenomenologically and the remaining part in a self-consistent way. The first potential is based on the step-density approximation (SDA) where the unperturbed electron density is uniform right up to the surface where it then drops abruptly to zero from its bulk value. The other potential is calculated in the dielectric approximation (DA) in which the dielectric function everywhere in the metal, even close to the surface, is replaced by its known asymptotic form in the bulk. According to Heinrichs, the potentials calculated in SDA and DA should be treated on equal footing and it is not possible, *a priori*, to discriminate against one in favor of the other. However, the validity of both of these treatments is restricted to situations where the distance of the perturbing charges from the surface is larger than the range of electron density variation near the jellium edge. This point is important and makes the present calculations invalid for $|z_0|\leq k_F^{-1}$. With these approximations, the SDA or DA potentials can be introduced in Eq. (13) by simply replacing $V(q)$ with

$$V(z_0,\vec{q})=\int_0^\infty dz\, e^{iq_z z}V(z,z_0,\vec{q}_{||})\ . \tag{15}$$

In principle, $B(q,\omega)$ appearing in Eq. (13) should be calculated by introducing wave functions for electrons reflected by a surface. However, by using the usual pair propagator $B(q,\omega)$ with the electrons simply described by plane waves in this paper, we are performing the calculations consistent with the approximations used to obtain $V(z,z_0,\vec{q}_{||})$ in SDA or DA. Under these conditions, both α and ξ can be calculated as functions of z_0 by using Eqs. (13) and (14), respectively.

IV. RESULTS AND CONCLUSIONS

The power-law exponent $\alpha(z_0)$ and the intensity parameter $\xi(z_0)$ have been calculated numerically by using Eqs. (13) and (14) in conjunction with Eq. (15) in both SDA and DA for the electron density parameters $r_s=2$–5. The results are plotted in Figs. 3 and 4 as functions of the distance z_0 from the surface of the metal. In both approximations, α and ξ show similar z_0 dependence even though the values obtained in DA are somewhat larger. Figure 3 shows that the power-law exponent α falls off rather rapidly outside the sample and inside the sample it attains the bulk values within a distance of several k_F^{-1} from the surface. Similar z_0 dependence of α for negative z_0's has been calculated by Gadzuk and

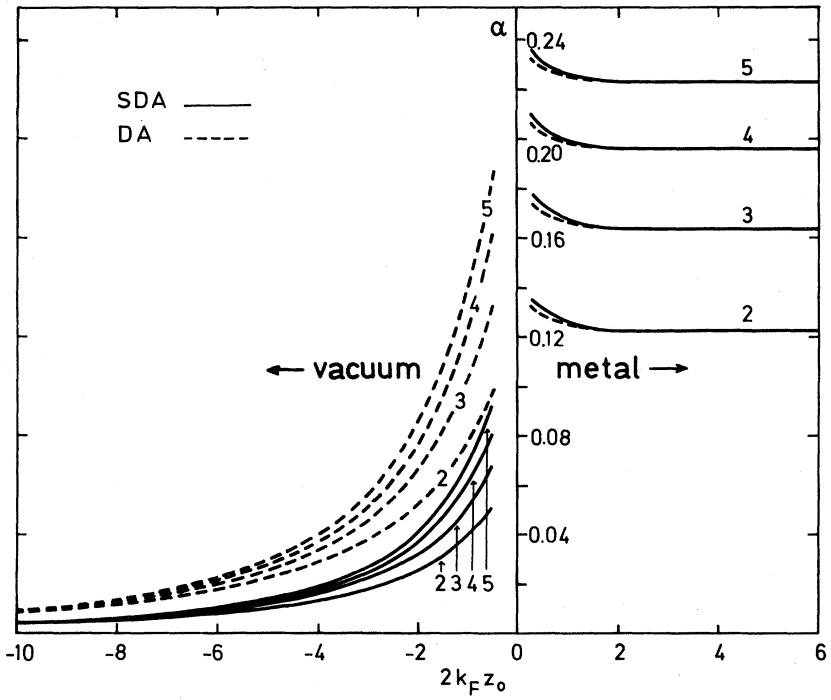

FIG. 3. Power-law exponent α for density parameters $r_s=2$—5 calculated in the sudden density approximation (SDA) and dielectric approximation (DA) is plotted as a function of z_0 (in units of $2k_F$), z_0 being the distance from the surface of the metal.

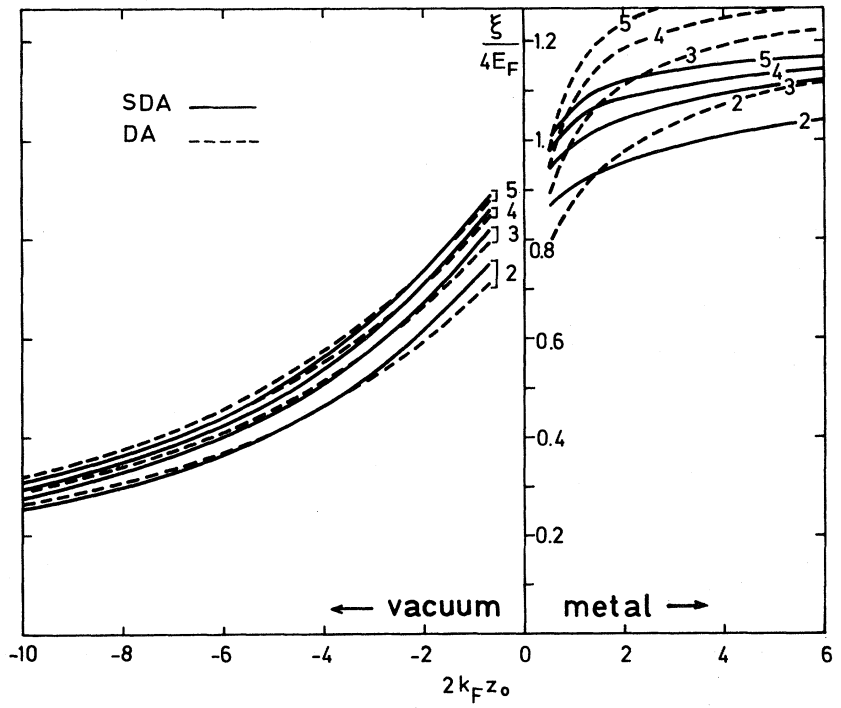

FIG. 4. Intensity parameter ξ for $r_s=2$—5 is plotted as a function of z_0 (in units of $2k_F$).

Metiu.[11] As shown in Fig. 4, the intensity parameter ξ also falls off to a constant value outside the sample and increases to its bulk value inside the sample. However, this approach to the bulk value is slower than that for the exponent α.

Knowing the parameters α and ξ we can calculate the photoemission intensities for the symmetric (Lorentzian) and the asymmetric cases by using Eqs. (4) and (5). These intensities are shown schematically in Fig. 1, as functions of the parameter $x \equiv \epsilon/\lambda$. The asymmetry indices $a(\frac{1}{2})$ and $a(\frac{1}{4})$ correspond to the asymmetry at half-maximum ($h=\frac{1}{2}$) and quarter-maximum ($h=\frac{1}{4}$), respectively.

These asymmetry indices for $r_s=4$ are plotted in Fig. 5. As expected, the index $a(\frac{1}{4})$ is larger than $a(\frac{1}{2})$. They fall off rapidly outside the sample and at large negative z_0's the asymmetry indices approach zero. This is expected, as it simply indicates that far away from the metal the photoemission line is symmetric, i.e., photoemission from an atom far away from the sample is not affected by the presence of the surface. However, near the surface the photoemission from adsorbed atoms or molecules is strongly affected by the presence of the metal surface and the line shape is highly asymmetric. Inside the sample asymmetry indices are large and attain the bulk values within a distance of a few k_F^{-1} from the surface.

In Fig. 6 we have plotted the ratio of the intensity maxima for the asymmetric and the symmetric Lorentzian cases. As expected, the ratio approaches 1 for large negative values of z_0 where the emission intensity becomes symmetric as it corresponds to emission from an isolated atom. For small negative z_0's and for all positive z_0's, this ratio is different from 1 indicating that for these values of z_0 the photoemission is highly influenced by the metal. Note that variation of this ratio is negligible inside the sample. However, it should be pointed out that a typical escape depth of the photoelectrons in the XPS experiments is of the order of 10—20 Å and one may, therefore, expect the intensity maximum to be also affected by the inelastic scatterings of the photoelectrons when they are created inside the sample. Since we have not included such extrinsic scattering process in the present calculation, the intensity maximum does not show any appreciable change as a function of z_0 when the core hole is inside the sample. In real XPS measurements the photocurrent will show significant z_0 dependence as it will be modified by the above scatterings.

In conclusion, we would like to mention that in a previous article[12] we had calculated the z_0 dependence of the surface- and bulk-plasmon satellite intensities during photoemission from a metal and showed that they were strongly modified by the

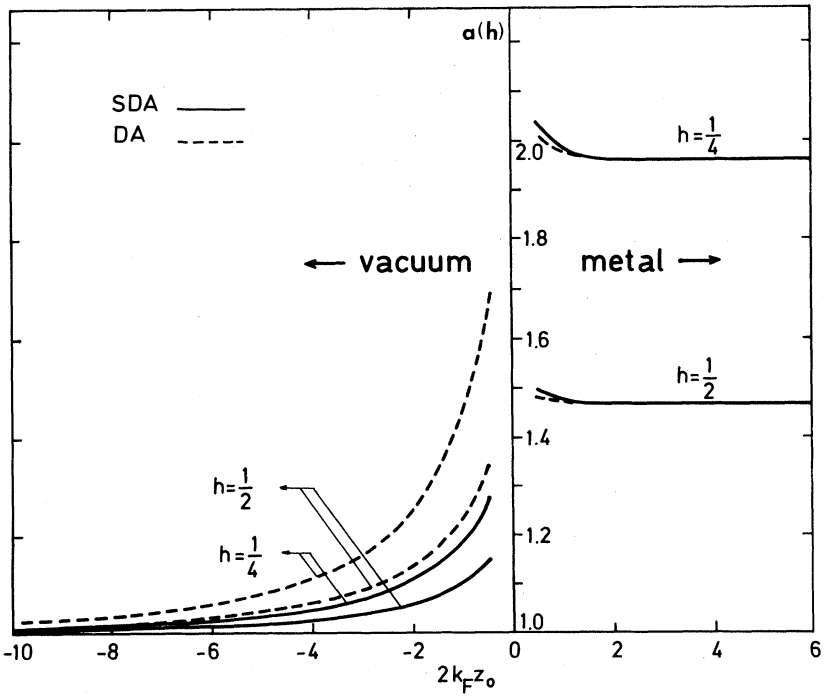

FIG. 5. Asymmetry indices at half-maxima ($h=\frac{1}{2}$) and quarter-maxima ($h=\frac{1}{4}$) for density parameter $r_s=4$ are plotted as functions of z_0.

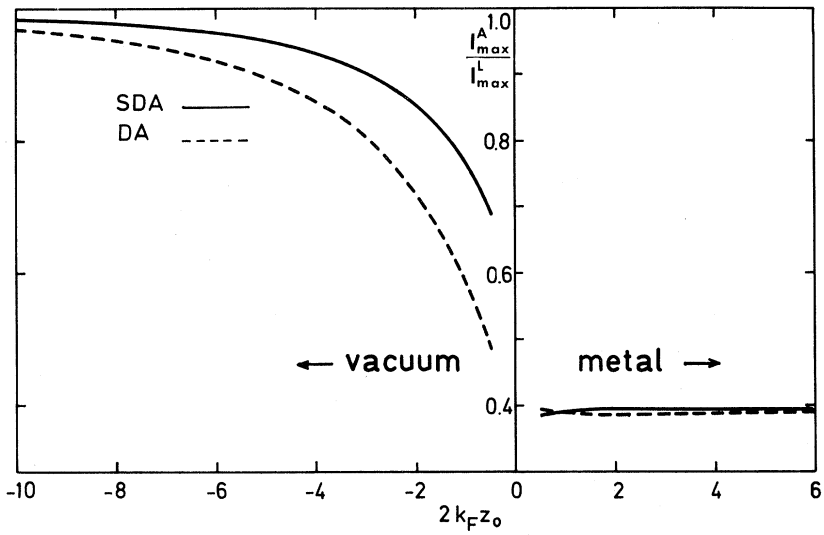

FIG. 6. Ratio of the intensity maxima given by Eq. (7) for the asymmetric and symmetric (Lorentzian) cases for $r_s=4$ is plotted as a function of z_0.

presence of the surface. We were able to calculate these satellites not only for emissions from atoms inside the sample but also from the adsorbates. In the present article we have extended this study of the surface effects to the main lines of the photoemission spectra of metals. The results obtained in these papers are interesting as they can be utilized to estimate the distance of a photoemitting adsorbate atom from the surface of the metal. As indicated in Figs. 5 and 6, the experimentally observed asymmetry index and/or the intensity maximum would give us such an estimate.

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