PHYSICAL REVIEW B VOLUME 27, NUMBER 10 15 MAY 1983

Sum rules for surface response functions with application to the van der Waals interaction between an atom and a metal

B. N. J. Persson
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

P. Apell
Physics Department, University of Pennsylvania, Philadelphia, Pennsylvania 19104-3859
(Received 17 December 1982)

We derive powerful sum rules for several important surface response functions which describe the response of a metal surface to an external time-dependent electric field. As an illustration, the van der Waals interaction between a particle and a metal is discussed.

I. INTRODUCTION

In recent years a major theoretical effort has been launched in describing the interaction between electromagnetic radiation and a "realistic" metal surface.[1-4] This constitutes what has been termed nonlocal optics since in contrast to the classical (local) treatment the dielectric response of the medium is dealt with particular attention to its spatial features.

It is a well-known fact from elementary classical electromagnetic treatments that when exposed to radiation an induced charge will be set up which resides right on the interface. This singular surface charge is the hallmark of the local optical treatment. However it is obvious that this has to spread out spatially in a more realistic interface model. A convenient measure of this spreading out of the induced surface charge is its center of gravity, henceforth denoted $d_\perp$ (a length). This has both real and imaginary parts, connected by a Kramers-Kronig relation, describing the reactive as well as lossy response of the perturbed metal. $d_\perp$ is the length of nonlocal optics, and plays the same central role for the surface response of a metal as the polarizability does in characterizing the response of an atom. Causality and free-particle behavior at high frequencies ($\omega \to \infty$) lead to simple and useful restrictions on the analytical structure of the atoms polarizability as well as on $d_\perp(\omega)$, leading to sum rules which are the main objectives of this paper. They put specific limitations on $d_\perp$'s evaluation within different models for the metal response, and thus helps to guide in judging the significance of various model results. $d_\perp(\omega)$ enters in most situations when we want to know the response to an electromagnetic perturbation such as the surface plasmon damping and dispersion,[5-8] the surface photoelectric effect,[9,10] friction forces on a charged particle,[11] the position of the effective image plane,[12] damping of excited molecules outside a metal,[13,14] etc., and has recently been applied to the nonlocal properties of small metal particles.[15] In fact most of the so-called nonlocal calculations in recent years have been more or less indirect ways of calculating $d_\perp$. We will therefore focus on this very useful quantity and in the next section we will first derive a set of very powerful sum rules for $d_\perp$. These sum rules show very clearly that an accurate description of the surface region of the metal is crucial in order to obtain reliable results. Simple models, such as the so-called semiclassical infinite-barrier model, fail completely and should not be used for quantitative purposes. We further propose a simple analytical form for $d_\perp$ which can be used as a guide in situations where the significance of nonlocal effects has to be estimated without having to resort to heavy numerical calculations. In the final section we also compare our $d_\perp$ with an interpolation formula frequently used in atom-surface scattering for finding the effective—image-plane position.[16,17]

II. SUM RULES

In this section we will derive some very useful sum rules for the centroid of the induced charge density $d_\perp(\omega)$, at an irradiated metal-vaccum interface.

$d_\perp$ is defined as

$$d_\perp = \frac{\int dz\, z\rho_{\rm ind}}{\int dz\, \rho_{\rm ind}}\ , \tag{1}$$

where $\rho_{\rm ind}$ is the induced charge density. To make this definition well defined for $\omega > \omega_p$, where bulk plasmons can be excited, one must imagine that the bulk plasmons are damped (damping γ) and take the limit $z \to \infty$ before letting $\gamma \to 0$. Being a linear

response function, causality requires $d_\perp(\omega)$ to be an analytical function of ω for $\mathrm{Im}\omega > 0$. Since, furthermore, $d_\perp(\omega) \sim \omega^{-2}$ as $\omega \to \infty$ (see Appendix A) it follows that $d_\perp(\omega)$ must satisfy the Kramers-Kronig relations

$$\mathrm{Re}d_\perp(\omega) = \frac{2}{\pi}\int_0^\infty d\omega' \frac{\omega' \mathrm{Im}d_\perp(\omega')}{\omega'^2 - \omega^2} , \tag{2a}$$

$$\mathrm{Im}d_\perp(\omega) = -\frac{2}{\pi}\int_0^\infty d\omega' \frac{\omega\, \mathrm{Re}d_\perp(\omega')}{\omega'^2 - \omega^2} . \tag{3a}$$

Multiplying Eq. (2a) with ω^2 and Eq. (3a) with ω and taking the limit $\omega \to \infty$ gives

$$\int_0^\infty d\omega\, \omega\, \mathrm{Im}[-d_\perp(\omega)] = \frac{\pi}{2}\lim_{\omega\to\infty} \omega^2 \mathrm{Re}d_\perp(\omega) , \tag{2b}$$

$$\int_0^\infty d\omega\, \mathrm{Re}d_\perp(\omega) = \frac{\pi}{2}\lim_{\omega\to\infty} \omega\, \mathrm{Im}d_\perp(\omega) . \tag{3b}$$

In Appendix A it is shown that

$$\omega^2 d_\perp(\omega) \to \int_{-\infty}^{\infty} dz\, n_0(1-n_0) - \frac{1}{4\pi}\int_0^\infty dz(1-n_0) \equiv \frac{2}{\pi}\eta$$

as $\omega \to \infty$. Here $n_0(z)$ is the ground-state density profile normalized so that $n_0 \to 1$ well inside the metal (i.e., as $z \to \infty$). Combining this result with Eqs. (2b) and (3b) gives the following two sum rules which are the main result of this paper:

$$\int_0^\infty d\omega\, \omega\, \mathrm{Im}[-d_\perp(\omega)] = \eta(r_s) , \tag{2c}$$

$$\int_0^\infty d\omega\, \mathrm{Re}d_\perp(\omega) = 0 . \tag{3c}$$

In the above expressions all frequencies are measured in units of the bulk-plasma frequency and all lengths in units of the inverse Fermi wave number $1/k_F = \alpha r_s a_0$ where $\alpha = (\frac{4}{9}\pi)^{1/3}$, $a_0 = \hbar^2/me^2$ (Bohr radius), and r_s is the electron-gas density parameter. Notice that η is a function only of r_s.

From Eq. (2a) we can also relate the static—image-plane position[18] $d_\perp(0)$ to the *loss function* $\mathrm{Im}d_\perp(\omega)$ via

$$d_\perp(0) = \frac{2}{\pi}\int_0^\infty d\omega \frac{\mathrm{Im}d_\perp(\omega)}{\omega} \equiv -\zeta(r_s) . \tag{4}$$

Similarly, for small ω Eq. (3a) reduces to

$$\mathrm{Im}(-d_\perp) = \omega\xi(r_s), \quad \omega \ll 1 \tag{5}$$

where

$$\xi = \frac{2}{\pi}\int_0^\infty d\omega' \frac{\mathrm{Re}d_\perp(\omega')}{\omega'^2} .$$

Thus the *loss function* $\mathrm{Im}d_\perp(\omega)$ increases linearly with ω for frequencies much smaller than the plasma frequency, as has been shown earlier in Ref. 14.

In Fig. 1 $\xi(r_s)$, $\eta(r_s)$, and $\zeta(r_s)$ are shown as a function of r_s as obtained within the so-called jellium model. In this model the metal-ion cores are smeared out into a positive uniform background occupying one-half space ($z \geq 0$). The interaction between the electrons is accounted for by use of the density-functional approach within the local-density approximation.

Another surface response function of great interest is the so-called complex—image-plane position $d_{\mathrm{IP}}(\omega)$, which is related to $d_\perp(\omega)$ via

$$d_{\mathrm{IP}}(\omega) = \frac{\epsilon_0}{\epsilon_0 + 1} d_\perp(\omega) , \tag{6}$$

where

$$\epsilon_0 = 1 - \omega^{-2} .$$

Since $d_{\mathrm{IP}} \to d_\perp/2$ as $\omega \to \infty$ it follows that d_{IP} will satisfy the following sum rules:

$$\int_0^\infty d\omega\, \omega\, \mathrm{Im}(-d_{\mathrm{IP}}) = \tfrac{1}{2}\eta , \tag{7}$$

$$\int_0^\infty d\omega\, \mathrm{Re}d_{\mathrm{IP}} = 0 , \tag{8}$$

where η was given earlier in Eq. (2c). We have thus derived two sets of surface response sum rules. In principle it is possible to derive a whole set of them using standard methods, but the two presented are the most interesting ones.

Finally, in connection with spherical metal parti-

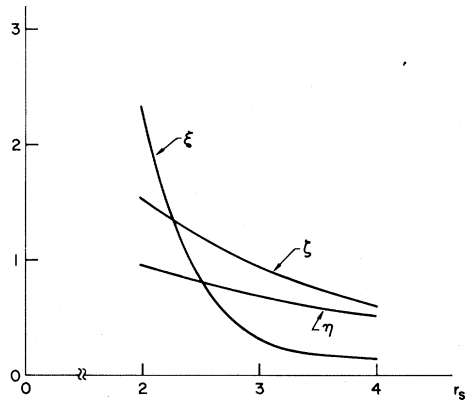

FIG. 1. Parameters ξ, η, and ζ are ground-state quantities which (in the jellium model) only depend on the electron-density parameter r_s. They are evaluated within the local-density approximation to the density-functional approach (Ref. 19). The functions ξ and η are defined in Eqs. (5) and (2c), respectively, and the values for ζ $[= -d_\perp(0)]$ are taken from Ref. 18.

cles one can introduce another surface response function[15] $d_R(\omega)\to d_\perp(\omega)$ as the particle radius $R\to\infty$. Again, for $d_R(\omega)$ one can derive sum rules very similar to those presented above.

It is interesting to compare the values of η obtained with a Lang-Kohn profile with the results of simpler models. For example, in the infinite-barrier model the electrons are forced to occupy one-half space due to an infinite barrier. The ground-state electron density in this model is

$$n_0(z)=1-3j_1(2k_Fz)/2k_Fz\ ,$$

where $j_1(x)$ is a spherical Bessel function. For this density profile η can be calculated analytically,

$$\eta=\frac{3\pi^2}{80}-\frac{3}{16}\approx 0.18\ ,$$

and is independent of r_s. This value of η is about $\frac{1}{3}$ of the prediction for a Lang-Kohn profile with $r_s=3$. There exist several other models, such as the semiclassical infinite-barrier model or the plasmon pole approximation, which have been used frequently for the nonlocal description of metal surfaces. However, it has been shown by Feibelman that these models are very crude and we will not discuss them further here.

III. van der WAALS INTERACTION BETWEEN AN ATOM AND A SOLID

$d_\perp(\omega)$ determines the influence of a metal surface on all dynamical processes involving electric fields which vary slowly over the surface. We illustrate this here with the van der Waals interaction between a particle and a metal. For other applications see the review work by Feibelman.[1] See also Ref. 14 for a detailed discussion of electron-hole pair quenching of excited states above metal surfaces and Ref. 15 for applications to small metallic particles.

Recently, puzzling experimental results have been reported involving the van der Waals interaction between a particle and a metal. For example, there are results which suggest that the interaction between a cesium atom and a gold surface might be 30% smaller than expected from the Lifshitz formula.[20] Quite aside from these rather speculative results, there is a growing interest in the role of the van der Waals interaction in connection with helium beam diffraction experiments from metal surfaces.[17]

The classical formula for the van der Waals interaction between an atom [with the polarizability $\alpha(\omega)$] and a semi-infinite metal is[21]

$$U(z)=-\frac{\hbar}{4\pi}\int_0^\infty du\,\alpha(iu)\frac{\epsilon(iu)-1}{\epsilon(iu)+1}\frac{1}{z^3}\ , \tag{9}$$

where z is the distance to the metal surface and where $\epsilon(\omega)$ is the bulk dielectric function of the metal. In this model the metal surface (or, more correctly, the *image plane*) is located at $z=0$. But, as is now known, the image plane depends on the frequency and Eq. (9) must therefore be replaced by[16]

$$\begin{aligned}U(z)&=-\frac{\hbar}{4\pi}\int_0^\infty du\,\alpha(iu)\frac{\epsilon(iu)-1}{\epsilon(iu)+1}\frac{1}{[z+d_{\rm IP}(iu)]^3}\\&\approx-\frac{\hbar}{4\pi}\int_0^\infty du\,\alpha(iu)\frac{\epsilon(iu)-1}{\epsilon(iu)+1}\\&\quad\times\left[1-3\frac{d_{\rm IP}(iu)}{z}\right]\frac{1}{z^3}\ ,\end{aligned} \tag{10}$$

where $d_{\rm IP}(\omega)$ is defined in Eq. (6).

An often-used form for $d_{\rm IP}$ was introduced by Zaremba and Kohn,[16]

$$d_{\rm IP}(iu)\approx\frac{d_\perp(0)}{2u^2+1} \tag{11a}$$

which has the correct limits $d_{\rm IP}(0)=d_\perp(0)$ and $d_{\rm IP}(i\infty)=0$. However the leading term in the high-frequency expansion is $\sim d_\perp(0)/2u^2$, which is $-\zeta/2u^2$ in our notation, while we know that it has to be $\sim-\eta/\pi u^2$. Thus as a simple approximation to $d_{\rm IP}(iu)$ we propose

$$d_{\rm IP}(iu)\approx\frac{d_\perp(0)}{1+\zeta\pi u^2/\eta} \tag{11b}$$

instead of Eq. (11a). This approximation has the correct $u\to0$ and $u\to\infty$ limits, but it is not clear yet how accurate this form is. Therefore, to check this, we will now present a simple analytical approximation to $d_{\rm IP}(iu)$ which satisfies the sum rule (2c) as well as conditions (4) and (5). It can be shown that $\mathrm{Im}d_\perp(\omega)$ has its main weight below the plasma frequency.[22] We will therefore make the following ansatz:

$$\mathrm{Im}[-d_\perp(\omega)]=A(1+a\omega^2+b\omega^4)\omega\Theta(1-\omega)\ , \tag{12}$$

where $\Theta(x)$ is the usual unit step function, i.e., $\Theta=0$ for $x<0$ and $\Theta=1$ for $x>0$. The coefficients A, a, and b are obtained from Eqs. (2c), (4), and (5). $d_\perp(\omega)$ is obtained directly from $\mathrm{Im}d_\perp(\omega)$ by analytical continuation:

$$\begin{aligned}-d_\perp=\frac{A}{\pi}\Bigg[&(1+a\omega^2+b\omega^4)\omega\ln\left[\frac{\omega-1}{\omega+1}\right]\\&+B+a'\omega^2+b'\omega^4\Bigg]\ ,\end{aligned} \tag{13}$$

where a', b', and B must be chosen so that

$d_\perp \to 2\eta/\pi\omega^2$ as $\omega \to \infty$. This gives

$$B = 2(1 + a/3 + b/5) ,$$

$$a' = 2(a + b/3) ,$$

$$b' = 2b .$$

In Fig. 2 we show $\mathrm{Im}[-d_\perp(\omega)]$ as a function of ω. Also shown are the numerical results of Feibelman.[1] The agreement is not perfect, but the approximation (13) is certainly much more accurate than that used by Zaremba and Kohn.[16] Also, it is straightforward to improve upon the given approximation by including further terms $c\omega^6 + d\omega^8 + \cdots$ in the polynomial approximation of $\mathrm{Im}d_\perp$, and to adjust the coefficients $c, d, \ldots$ to get an optimal fit.

Figure 3 shows how $\mathrm{Re}d_\perp(\omega)$ varies with ω. Figure 4 shows how $d_{\mathrm{IP}}(iu)$ varies with u. The Zaremba-Kohn curve is calculated from Eq. (11a) while the curve "present work" is obtained from Eqs. (6) and (13). The dashed line in Fig. 4 is calculated from Eq. (11b) and is obviously a very good approximation to the more exact expression based on Eq. (13). We note that $d_{\mathrm{IP}}(iu)$ is a smoothly varying function of u. This is in sharp contrast to the behavior along the real ω axis where d_{IP} has resonance structures. All singularities (poles and branch lines) of $d_{\mathrm{IP}}(\omega)$ are located below the real ω axis in the complex ω plane. When following the $\omega = iu$ axis we are never close to any of these singularities and $d_{\mathrm{IP}}(iu)$ is consequently a smooth function of u. Actually, one can prove that $d_{\mathrm{IP}}(iu)$ is a real-valued, monotonically decreasing function of u (see Appendix B):

$$d_{\mathrm{IP}}(iu) = \frac{2}{\pi}\int_0^\infty d\omega \frac{\omega}{\omega^2+u^2}\mathrm{Im}[d_{\mathrm{IP}}(\omega)]$$

$$= \frac{2}{\pi}\frac{u^2+1}{2u^2+1}\int_0^\infty d\omega \frac{\omega}{\omega^2+u^2}\mathrm{Im}[d_\perp(\omega)] .$$

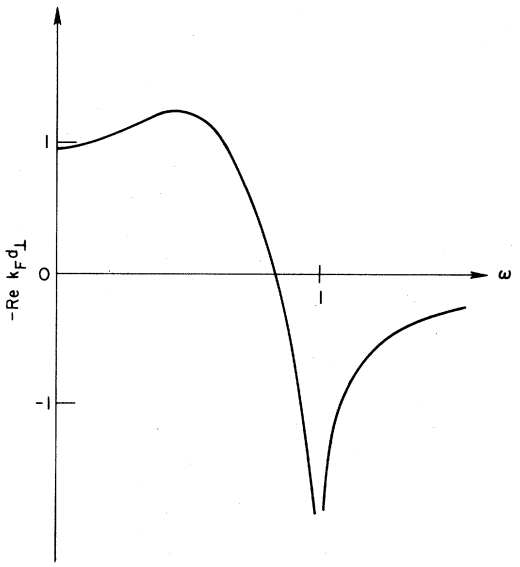

FIG. 3. Real part of $-d_\perp(\omega)$ as a function of ω calculated from Eq. (13) ($r_s = 3$).

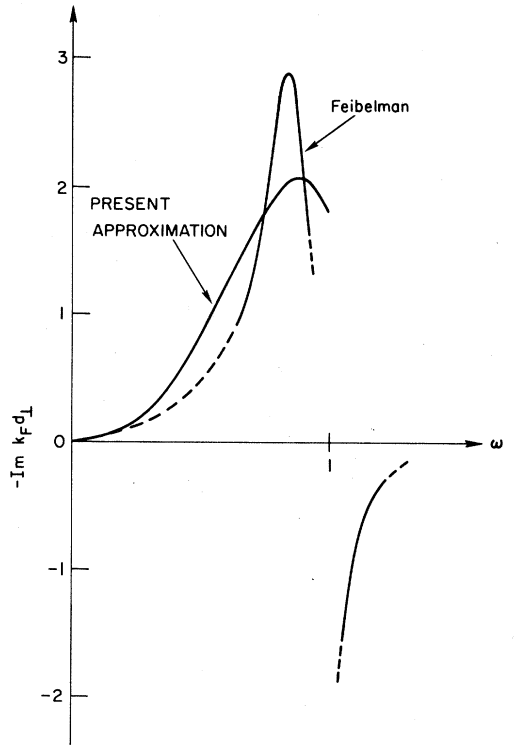

FIG. 2. Imaginary part of $-d_\perp(\omega)$ as a function of ω. The curve "present approximation" is calculated from Eq. (13) while the other curve has been obtained earlier by Feibelman ($r_s = 3$).

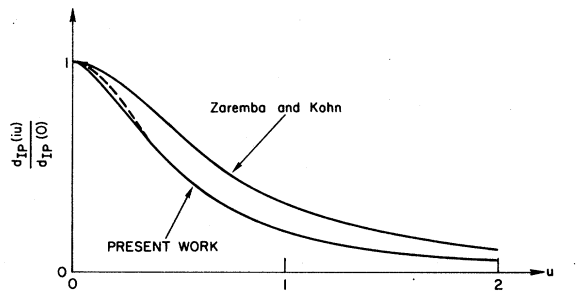

FIG. 4. Function $-d_\perp(\omega)$ along the imaginary positive axis $\omega = iu$. The Zaremba-Kohn curve is obtained from Eq. (11a) and the other full curve from Eq. (13). The dashed curve is calculated from Eq. (11b) ($r_s = 3$).

The difference between the Zaremba-Kohn estimate of $d_{IP}(iu)$ and the present more accurate results are never larger than $0.2d_{\perp}(0) \sim 0.2$ Å. For z values ~ 6 Å in Eq. (10) this gives at most a 10% correction to the value calculated with the Zaremba-Kohn ansatz and it is obvious that a deviation in the van der Waals interaction of about 30% as seen experimentally for particles passing hundreds of Å from the surface is not due to a nonlocal effect.

IV. CONCLUSIONS

From causality and the free-particle behavior at high frequencies, we have derived powerful sum rules for two important surface response functions. These sum rules show that several frequently used models for the electromagnetic response of a metal surface are very crude. To obtain reliable results one must use a realistic surface potential, such as the one obtained by Lang and Kohn.[23] This result is consistent with numerical results obtained earlier by Feibelman[1] which, for example, show that the semiclassical infinite-barrier model underestimates the probability for electron-hole pair excitations by a factor of 10 and completely fails in the description of the bulk plasmons for $\omega > \omega_p$.

The sum rules we have derived are valid even if the atomic structure of the solid is taken into account. Of course, in this case n_0, ρ_{ind}, etc., depends not only on z but also on the coordinate parallel to these surfaces $\vec{x}_{||}$. Thus n_0, for example, will exhibit periodic oscillations parallel to the metal surface, with the periodicity determined by the lattice constant. Now if we replace n_0 $(\vec{x}_{||},z)$ with its average over $\vec{x}_{||}$,

$$n_0(z) \equiv \frac{1}{A} \int_A d^2x_{||} n_0(\vec{x}_{||},z) ,$$

where A is a surface unit cell, then all the formulas presented in Sec. II are still valid.

Another important question is whether $n_0(z)$ should contain all the electrons in the system or only those in the conduction band. The situation here is similar to that of the f-sum rule for the bulk dielectric function. The answer is that strictly speaking all the electrons should be included. Nevertheless, for practical purposes one can usually get good results even if only the conduction-band electrons are considered in the sum rule, as in the discussion above, provided one is not interested in such frequencies ω that deeper levels are probed.

In Sec. III we discussed the van der Waals interaction between a particle and a metal. It was shown that the effective (dynamical) image-plane position d_{IP}, defined in Eq. (6) deviates by less than 0.2 Å from earlier estimates by Zaremba and Kohn.[16] Thus the numerical results presented by these authors and often used in atom-surface scattering calculations, should be accurate enough for most practical purposes.

This is the second work in a series of three papers devoted to the description of dynamical processes at surfaces. The basic assumption of this work, as well as of the first work,[14] is that the external field varies slowly over the metal surface. In the third paper we will abandon this assumption, and fields which vary arbitrarily rapidly in space will be studied. This is especially important when the probes are in the immediate vicinity of the metal surface, as is often the situation in the studies of surface-phenomena.

ACKNOWLEDGMENTS

We would like to thank N. D. Lang for providing numerical data for $n_0(z)$ ($r_s = 2$, 3, and 4). We thank Ph. Avouris, J. E. Demuth, N. D. Lang, and A. R. Williams for useful discussions. One of us (P.A.) gratefully acknowledges an IBM fellowship.

APPENDIX A

Here we will study $d_{\perp}(\omega)$ as $\omega \to \infty$. Assume that the metal occupies the half-space $z > 0$ ($z = 0$ is chosen at the edge of the positive background in the jellium model) and let

$$\rho_{ext} = \delta(z + L) e^{-i\omega t}$$

be a time-dependent external charge density located on the sheet $z = -L$ outside the metal. Consider the Maxwell equation

$$\vec{\nabla} \cdot \hat{\epsilon} E = 4\pi \rho_{ext} ,$$

where $\hat{\epsilon}$ is the dielectric integral operator of the metal. Integrating this equation from a point just outside the metal (where the electric field is $E_0 \hat{z}$) to an arbitrary point z inside the metal [where the electric field is $E_z(z)\hat{z}$] gives

$$\hat{\epsilon} E_z(z) = E_0 .$$

That is,

$$E_z(z) = \hat{\epsilon}^{-1} E_0 ,$$

and we can calculate the induced density $\rho_{ind}(z,\omega)$ from

$$\rho_{ind} = \frac{1}{4\pi} \vec{\nabla} \cdot \vec{E} = \frac{1}{4\pi} \frac{d}{dz} \hat{\epsilon}^{-1} E_0 .$$

Thus

$$\int dz \, \rho_{ind} = \frac{1}{4\pi} \left[\frac{1}{\epsilon_0} - 1 \right] E_0 , \tag{A1}$$

where (ω is measured in units of ω_p)

$$\epsilon_0 = 1-\omega^{-2}$$

is the bulk dielectric function. In deriving (A1) we have utilized that $\hat{\epsilon}\to 1$ outside the metal and $\hat{\epsilon}\to\epsilon_0$ inside the metal. Next we must calculate

$$\int dz\, z\rho_{\rm ind} = \frac{1}{4\pi}\int dz\, z\frac{d}{dz}\hat{\epsilon}^{-1}E_0 \ . \tag{A2}$$

Equations (A1) and (A2) give

$$\epsilon_{ij}(\vec{x},\vec{x}';\omega) = [1-\omega^{-2}n_0(z)]\delta(\vec{x}-\vec{x}')\delta_{ij} - \frac{e^2}{\hbar\omega^2}C_{ij}(\vec{x},\vec{x}';\omega)$$

where $C_{ij}(\vec{x},\vec{x}';\omega)$ is the so-called *current-current* response function:

$$C_{ij}(\vec{x},\vec{x}';\omega) = \sum_n \left[\frac{\langle 0|J_i(\vec{x})|n\rangle\langle n|J_j(\vec{x}')|0\rangle}{\omega+i\delta-\omega_n} - \frac{\langle 0|J_j(\vec{x}')|n\rangle\langle n|J_i(\vec{x})|0\rangle}{\omega+i\delta+\omega_n}\right]$$

$$\to \frac{1}{\omega}\langle 0|[J_i(\vec{x}),J_j(\vec{x}')]|0\rangle$$

$$+\frac{1}{\hbar\omega^2}\langle 0|[[J_i(\vec{x}),H],J_j(\vec{x}')]|0\rangle + \cdots$$

as $\omega\to\infty$. Now, $[J_i(\vec{x}),J_j(\vec{x}')]=0$ and the leading contribution to $C_{ij}(\vec{x},\vec{x}'\omega)$ for large ω is thus

$$C_{ij}(\vec{x},\vec{x}';\omega)\sim\frac{\omega^{-2}}{\hbar}\langle 0|[[J_i(\vec{x}),H],J_j(\vec{x}')]|0\rangle \ .$$

To order ω^{-4} we then set

$$\epsilon_{ij}^{-1}(\vec{x},\vec{x}';\omega)\sim[1+\omega^{-2}n_0(z)+\omega^{-4}n_0^2(z)]\delta(\vec{x}-\vec{x}')\delta_{ij}+\frac{e^2}{\hbar^2\omega^4}\langle 0|[[J_i(\vec{x}),H],J_j(\vec{x}')]|0\rangle \ ,$$

and, consequently,

$$\int d^3x'\epsilon_{ij}^{-1}(\vec{x},\vec{x}';\omega) = [1+\omega^{-2}n_0(z)+\omega^{-4}n_0^2(z)]\delta_{ij}+\frac{e^2}{\hbar^2\omega^4}\langle 0|[[J_i(\vec{x}),H],P_j/m]|0\rangle \ , \tag{A3}$$

where P_i is the total momentum operator for the electrons. Now, let us write $H=H_0+H'$ where

$$H' = -e^2\int d^3x' U(\vec{x}')\psi^\dagger(\vec{x}')\psi(\vec{x}') \ ,$$

where $U(\vec{x})$ is the potential from the positive background, i.e.,

$$\nabla^2 U = -4\pi\Theta(z) \ .$$

We have

$$[J_i,H'] = -\frac{\hbar e^2}{mi}U_{,i}\psi^\dagger\psi \ ,$$

where

$$U_{,i} = \frac{\partial U(\vec{x})}{\partial x_i} \ .$$

If we denote

$$d_\perp(\omega) = \frac{\epsilon_0}{1-\epsilon_0}\int dz\, z\frac{d}{dz}\hat{\epsilon}^{-1}\cdot\vec{1}$$

$$\to\omega^2\int dz\, z\frac{d}{dz}\hat{\epsilon}^{-1}\cdot\vec{1} \quad \text{as } \omega\to\infty \ .$$

To evaluate

$$\hat{\epsilon}^{-1}\cdot\vec{1} = \int d^3x'\epsilon^{-1}(\vec{x},\vec{x}';\omega)$$

as $\omega\to\infty$, we use the Kubo formula

$$[J_i,H_0] = \hat{F}_i \ ,$$

then

$$[J_i,H] = \hat{F}_i - \frac{\hbar e^2}{mi}U_{,i}\psi^\dagger\psi \ . \tag{A4}$$

Since

$$[\hat{F}_i,P_j] = -\frac{\hbar}{i}\hat{F}_{i,j}$$

we get

$$\langle 0|[[J_i,H],P_j]|0\rangle = -\frac{\hbar}{i}\left[F_{i,j}-\hbar\frac{e^2}{mi}U_{,i}n_{0,j}\right] \ , \tag{A5}$$

where $F_i=\langle 0|\hat{F}_i|0\rangle$. The term $F_{i,j}$ in this expression can be eliminated as follows. Since

$$\langle 0 | [J_i,H] | 0 \rangle = 0$$

we get, from Eq. (A4),

$$F_i - \frac{\hbar e^2}{mi} U_{,i} n_0 = 0$$

from which it follows that

$$F_{i,j} = \frac{\hbar e^2}{mi} (U_{,i} n_0)_{,j} \ .$$

Substituting this into Eq. (A5) gives

$$\langle 0 | [[J_i,H],P_j] | 0 \rangle = \frac{\hbar^2 e^2}{m} U_{,ij} n_0 = -4\pi \frac{\hbar^2 e^2}{m} \Theta(z) n_0 \ , \quad \text{(A6)}$$

where the last equality is valid for $i=j=3$. Substituting (A6) into (A3) gives

$$\int d^3\vec{x}\,' \epsilon_{33}^{-1}(\vec{x},\vec{x}\,';\omega) = 1 + \omega^{-2} n_0 + \omega^{-4} n_0^2 - \frac{1}{4\pi} \omega^{-4} \Theta(z) n_0 \ .$$

We can now calculate

$$\begin{aligned} d_\perp(\omega) &\sim \omega^2 \int dz\, z \frac{d}{dz} \hat{\epsilon}^{-1} \cdot \vec{1} \\ &= \omega^2 \int dz\, z \frac{d}{dz} \left[1 + \omega^{-2} n_0(z) + \omega^{-4} n_0^2(z) - \frac{1}{4\pi} \omega^{-4} \Theta(z) n_0(z) \right] \\ &= \int dz\, z \frac{d}{dz} \left[n_0 + n_0^2 \omega^{-2} - \frac{1}{4\pi} \Theta(z) n_0 \omega^{-2} \right] \\ &= \int dz\, z \frac{d}{dz} \left[n_0 - \Theta(z) + [n_0^2 - \Theta(z)] \omega^{-2} - \frac{1}{4\pi} \Theta(z) [n_0 - \Theta(z)] \omega^{-2} \right] \\ &= - \int dz \left[n_0 - \Theta(z) + \omega^{-2} [n_0^2 - \Theta(z)] - \omega^{-2} \frac{1}{4\pi} \Theta(z) [n_0 - \Theta(z)] \right] . \end{aligned}$$

Now, charge neutrality implies that

$$\int dz [n_0 - \Theta(z)] = 0$$

since $\Theta(z)$ is the positive background. Therefore,

$$d_\perp(\omega) \sim \omega^{-2} \int dz \left[n_0(z)[1-n_0(z)] - \Theta(z) \frac{1}{4\pi} [1-n_0(z)] \right] \quad \text{(A7)}$$

as $\omega \to \infty$.

APPENDIX B

Since $d_\perp(\omega)$ is analytical in the upper ω half-plane we get, from Cauchy's theorem,

$$d_\perp(z) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega \frac{d_\perp(\omega)}{\omega - z} \ ,$$

where z is an arbitrary point in the upper half-plane. In particular, if $z = iu$, we get

$$d_\perp(iu) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega \frac{d_\perp(\omega)}{\omega - iu} = \frac{1}{2\pi i} \int_0^{\infty} d\omega \left[\frac{d_\perp(\omega)}{\omega - iu} - \frac{d_\perp(-\omega)}{\omega + iu} \right] .$$

But $d_\perp(z) = d_\perp^*(-z^*)$ (this relation is valid for any retarded response function) gives $d_\perp(\omega) = d_\perp^*(-\omega)$ and thus

$$d_\perp(iu) = \frac{1}{2\pi i} \int_0^{\infty} d\omega \frac{d_\perp(\omega)(\omega + iu) - d_\perp^*(\omega)(\omega - iu)}{\omega^2 + u^2} = \frac{1}{\pi} \int_0^{\infty} d\omega \frac{\omega\, \mathrm{Im} d_\perp(\omega) + u\, \mathrm{Re} d_\perp(\omega)}{\omega^2 + u^2} \ . \quad \text{(B1)}$$

Substituting $\mathrm{Re}d_\perp$ for $\mathrm{Im}d_\perp$ using

$$\mathrm{Re}d_\perp(\omega)=\frac{1}{\pi}\,\mathrm{Re}\int_{-\infty}^{\infty}d\omega'\frac{\mathrm{Im}d_\perp(\omega')}{\omega'-\omega-i\epsilon}$$

into (B1) and interchanging the ω and ω' integrations gives finally

$$d_\perp(iu)=\frac{2}{\pi}\int_0^\infty d\omega\frac{\omega\,\mathrm{Im}d_\perp(\omega)}{\omega^2+u^2}\ .$$

Since $-\mathrm{Im}d_\perp(\omega)$ is a positive definite quantity in our approximation it follows that $-d_\perp(iu)$ is a monotonically decreasing function of u (this property can actually be proved to be of more general validity) and so, therefore, will be $-d_{\mathrm{IP}}(iu)$, since

$$d_{\mathrm{IP}}(iu)=\frac{u^2+1}{2u^2+1}d_\perp(iu)\ .$$

[1]P. J. Feibelman, Prog. Surf. Sci. 12, No. 4 (1982); Phys. Rev. B 22, 3654 (1980); 12, 1319 (1975); 14, 762 (1976).

[2]K. L. Kliewer, Surf. Sci. 101, 57 (1980).

[3]G. Mukhopadhyay and S. Lundqvist, Phys. Scr. 17, 69 (1978).

[4]F. Forstmann and R. R. Gerhards, Festkörperprobleme 22, 291 (1982).

[5]P. J. Feibelman, Phys. Rev. B 9, 5077 (1974).

[6]P. Apell, Phys. Scr. 24, 795 (1981).

[7]J. Harris and A. Griffin, Phys. Lett. 34A, 51 (1971).

[8]J. Harris and A. Griffin, Phys. Lett. 37A, 387 (1971).

[9]H. J. Levinson, E. W. Plummer, and P. J. Feibelman, Phys. Rev. Lett. 43, 952 (1979).

[10]P. Apell, Phys. Scr. 25, 57 (1982).

[11]W. L. Schaich, Phys. Rev. B 14, 1488 (1974); Solid State Commun. 15, 357 (1974).

[12]P. J. Feibelman, Phys. Rev. B 22, 3654 (1980).

[13]B. N. J. Persson, J. Phys. C 11, 4251 (1978); B. N. J. Persson and M. Persson, Surf. Sci. 3, 609 (1980).

[14]B. N. J. Persson and N. Lang, Phys. Rev. B 26, 5409 (1982).

[15]P. Apell and A. Ljungbert, Phys. Scr. 26, 113 (1982); Solid State Commun. (in press).

[16]E. Zaremba and W. Kohn, Phys. Rev. B 13, 2270 (1976); 15, 1769 (1977).

[17]J. Harris and A. Liebsch, Phys. Rev. Lett. 49, 341 (1982).

[18]N. D. Lang and W. Kohn, Phys. Rev. B 7, 3541 (1973).

[19]For the numerical evaluation of ξ, see Ref. 14. Note that the definition of ξ in this paper differs from that given in Ref. 14 [ξ(new)$=\xi$(old) $\omega p/6\omega_F$].

[20]M. J. Mehl and W. L. Schaich, Surf. Sci. 99, 553 (1980).

[21]E. M. Lifshitz, Zh. Eksp. Teor. Fiz. 29, 94 (1955) [Sov. Phys.—JETP 2, 72 (1956)].

[22]From the expression for the surface power adsorption, (Ref. 1), $P(\omega)\sim-(1-\omega^2)\mathrm{Im}d_\perp(\omega)$ and the condition that $P(\omega)$ must be positive definite, it follows that $-\mathrm{Im}d_\perp(\omega)$ must change sign at the plasma frequency ($\omega=1$). It then follows from the sum rule (2c) that $-\mathrm{Im}d_\perp(\omega)$ must have its main weight below $\omega=1$.

[23]N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).