Microscopic calculation of electromagnetic fields in refraction at a jellium-vacuum interface*

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For a long-wavelength electromagnetic wave of frequency ω, incident on a jellium-vacuum interface, the spatial dependence of the vector potential, $\vec{A}(\vec{r};\omega)$, is evaluated in the surface region. A simple integral equation is derived which relates $\vec{A}(\vec{r};\omega)$ to the jellium nonlocal conductivity tensor $\overleftrightarrow{\sigma}(\vec{r};\vec{r},\omega)$; numerical calculations based on this equation are reported, in which the random-phase approximation to $\overleftrightarrow{\sigma}(\vec{r};\vec{r},\omega)$ was used—the required single-electron wave functions were evaluated via the self-consistent surface-barrier potentials of Lang and Kohn. Families of graphs of $\vec{A}(\vec{r};\omega)$ are presented, for fixed bulk electron concentration as a function of frequency and for fixed ω_p/ω (where ω_p is the plasma frequency) as a function of bulk electron concentration. The sensitivity of $\vec{A}(\vec{r};\omega)$ to the shape of the surface potential barrier, at fixed ω and bulk electron concentration, is also explored. The use of the results obtained for $\vec{A}(\vec{r};\omega)$ is proposed for the calculation of refraction effects in surface photoemission and in reflection spectroscopy.

I. INTRODUCTION

Recently there has been a great deal of interest in using photoemission as a probe of the bonding of the atoms which lie in the outermost layer(s) of a solid.[1–5] However, the detailed interpretation of photoemission data requires the use of a theory of photoemission, which even in its simplest form (the independent-particle approximation[6–8]) presumes one's ability to calculate initial and final electron wave functions, as well as the spatial form of the electromagnetic field which is responsible for photoexcitation in the first place.

In the recent past, considerable progress has been reported in the calculation of self-consistent wave functions corresponding to electron states below the vacuum level for semi-infinite solids.[9,10] At the same time, relatively reliable techniques have been developed[11–14] (in connection with low-energy–electron-diffraction theory) for the calculation of electron wave functions at energies 30–300 eV above the vacuum level. It is not known to what extent the approximations used at energies $\gtrsim 30$ eV will have to be refined in order to extend continuum wave-function calculations down to the energy range 0–30 eV which is commonly explored in photoemission experiments[15]; but in any event a good start has been made in the work for energies $\gtrsim 30$ eV.

The same cannot be said for calculations of the electromagnetic field which excites photoelectrons. Of course in the high-frequency regime, defined as the frequency range in which the index of refraction of the solid under study is closely equal to 1, there is no difficulty; the electromagnetic field may be represented by a transverse plane wave, appropriately polarized, which is undisturbed by its crossing of the solid surface. However, for a wide variety of solids, in the vacuum ultraviolet frequency range $\lesssim 30$ eV common to many photoemission experiments, the index of refraction is far from 1,[16] and the amplitude and phase of an electromagnetic wave will change sharply in the surface region.[17] Additionally, in the range of frequencies corresponding to a solid's plasmon band, sharp variations in the electromagnetic field will be induced not only near the surface due to dielectric mismatch, but also in the solid's interior, due to bulk-plasmon excitation.[18] Finally, because of the nonuniformity of the charge density within the solid (corresponding to the discrete nature of the ionic charge), an electromagnetic wave will suffer further scatterings, giving rise to what are generally called "local-field corrections" to the spatial behavior.

To date, some calculations have been reported of local-field corrections for infinite solids[19,20] but none for semi-infinite ones. There has also been some work concerning the behavior of the electromagnetic field in the neighborhood of a surface where refraction is occurring,[18,21–23] notably that of Endriz[21] which was specifically concerned with refraction effects in surface photoemission; but this work has been based on approximations whose reliability is open to some question. [In Ref. 21 Endriz presents neither results for the form of the vector potential in the surface region, nor the equations used to obtain the results. In any event, one may be inclined to doubt the validity of the hydrodynamic approximation used in Ref. 21 to describe the dielectric response of a semi-infinite free-electron solid, because it does not take account of Landau damping. The calculations of Refs. 18, 22, and 23 are based on the assumption that the dielectric behavior of a semi-infinite free-electron solid can be described in terms of the (wave-vector-dependent) dielectric constant of the infinite electron gas.]

In the present article, the results are presented of a microscopic calculation of the spatial behavior of an electromagnetic field in the neighborhood of a jellium-vacuum interface. The calculation takes account of the possibility of plasmon excitation for the appropriate range of frequencies. However, local-field effects are totally ignored, by virtue of the use of a smeared-out positive background charge (the jellium approximation); for nearly-free-electron metals, one hopes that the neglect of such effects may not be too serious an approximation.

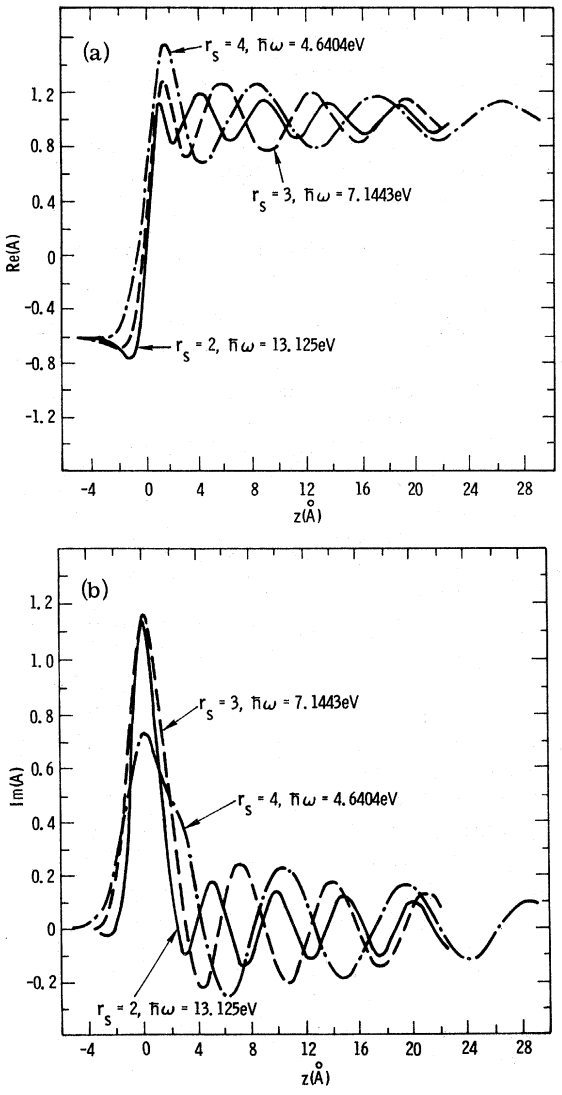

FIG. 1. Real and imaginary parts of $A^z_{\vec{k}_\parallel\to 0,\omega}(z)$ vs z calculated for electron-gas radii r_s and photon energies $\hbar\omega$ given by $(r_s, \hbar\omega) = (2, 13.125\text{ eV})$, $(3, 7.1443\text{ eV})$, and $(4, 4.6404\text{ eV})$. In each case, $\omega/\omega_p(r_s) = 0.7875$, where $\omega_p(r_s)$ is the classical plasma frequency, given by $\hbar\omega_p(r_s) = 47.139\text{ eV}/r_s^{3/2}$. The normalization of $A_{\vec{k}_\parallel\to 0,\omega}(z)$ has been arbitrarily chosen to guarantee that in each case $A^z_{\vec{k}_\parallel\to 0,\omega}(z\to\infty) = 1$. See Sec. IV below for further discussion of this graphs.

Examples of the main numerical results of the present work are illustrated in Figs. 1(a) and 1(b), and are thoroughly discussed in Sec. IV below. However, one can immediately grasp from these two figures their important implication with regard to photoemission of electrons from a surface: the electric field which is responsible for photoejection from the surface region is anything but spatially constant there.

Of course a rapid variation in field near a surface will have a large effect on the matrix elements which govern the probability that a surface electron will be photoemitted. Experimentally, therefore, refraction effects should play an important role in determining the intensities[24] of surface-related peaks in photoelectron energy distributions (PED's), and, via changes in the solid's index of refraction with photon frequency ω, in determining the way in which these intensities change with ω.

One should also expect that a sharp variation in field strength near a surface will affect one's interpretation of observed photoelectron angular distribution (PAD's). After all, the implication of Figs. 2 and 3 is that not only the electromagnetic field's magnitude, but also its direction varies rapidly near a surface where refraction is important. Thus, for example, in the photoemission of an electron which is tightly bound near a solid's surface, the field direction sensed by the electron (which helps to determine, e.g., the direction of maximum photocurrent) will depend strongly on refractive effects, and will change with ω as the solid's index of refraction does. Thus refraction should cause PAD's to change with ω.

Finally, it should be noted that refraction-induced electromagnetic-field variation at surface will affect not only photoemission data, but data in any experiment in which surface electrons are optically excited. Thus in the analysis of reflection spectroscopy, for example, one should also expect the intensities of surface features to be strongly affected by refraction.

With this motivation in mind, the present article focuses on the calculation of the vector potential $\vec{A}(\vec{r};\omega)$ in the neighborhood of a flat jellium-vacuum interface, for the case of a long-wavelength transverse electromagnetic wave of frequency ω, incident from the vacuum. The use of the calculated values of $\vec{A}(\vec{r};\omega)$ to estimate the importance of refractive effects in photoemission is the subject of an accompanying article.[25]

In Sec. II, Maxwell's equations together with appropriate boundary conditions are shown to lead to a simple integral equation for $A^z_{\vec{k}_\parallel\to 0,\omega}(z)$, the z component (normal to the surface) of the vector potential corresponding to the reflection and re-

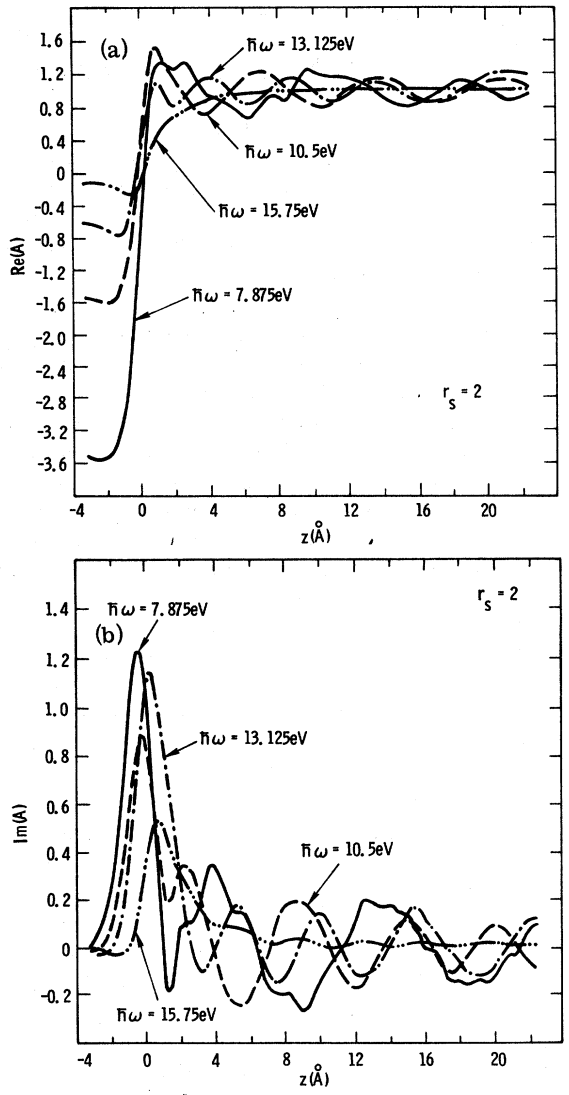

FIG. 2. Real and imaginary parts of $A^{z}_{\vec{k}_{\parallel}\to 0,\omega}(z)$ vs z calculated using the $r_s = 2$ Lang-Kohn potential barrier (Ref. 51), for various photon frequencies below $\omega_p(r_s = 2)$ [$\hbar\omega_p(r_s = 2) = 16.666$ eV]. In each case $A^{z}_{\vec{k}_{\parallel}\to 0,\omega}(z \to \infty)$ has been normalized to 1; therefore [cf., Eq. (2.46b)], $A^{z}_{\vec{k}_{\parallel}\to 0,\omega}(z \to -\infty)$ must equal $\epsilon^T(0,\omega) = 1 - \omega_p^2/\omega^2$.

fraction of an electromagnetic wave of frequency ω, and of small wave vectors $\vec{k}_{\parallel}$ along the jellium surface. This integral equation permits one to determine $A^{z}_{\vec{k}_{\parallel}\to 0,\omega}(z)$ in terms of $\sigma^{zz}_{\vec{k}_{\parallel}\to 0,\omega}(z, z')$, the z-z component of the jellium nonlocal conductivity tensor. The method used to solve the equation is described in Sec. III, and in Sec. IV, numerical solutions for $A^{(z)}_{\vec{k}_{\parallel}\to 0,\omega}(z)$ are presented and discussed.

II. DERIVATION OF A SIMPLE EQUATION FOR VECTOR POTENTIAL WHICH DESCRIBES THE REFRACTION OF A LONG-WAVELENGTH ELECTROMAGNETIC WAVE

In this section a simple integral equation [Eq. (2.45)] is derived, which yields the spatial behavior of the vector potential $\vec{A}(\vec{r};\omega)$ corresponding to the refraction and reflection of a long-wavelength electromagnetic wave incident on a flat jellium solid. The starting point for the derivation is the Maxwell wave equation, which, in the gauge corresponding to scalar potential φ identically zero, may be written in the form[26]

$$\nabla^2\vec{A}(\vec{r};\omega) + (\omega^2/c^2)\vec{A}(\vec{r};\omega) - \vec{\nabla}[\vec{\nabla}\cdot\vec{A}(\vec{r};\omega)] = -(4\pi/c)\vec{J}(\vec{r};\omega). \quad (2.1)$$

For a sufficiently weak field, the induced current $\vec{J}(\vec{r};\omega)$ is linear in $\vec{A}(\vec{r};\omega)$, and is given by the consitutive relation

$$\vec{J}(\vec{r};\omega) = \int d^3r'\, \vec{\sigma}(\vec{r},\vec{r}';\omega)(i\omega/c)\vec{A}(\vec{r}';\omega), \quad (2.2)$$

in which $\vec{\sigma}(\vec{r},\vec{r}';\omega)$ is the solid's (in general nonlocal) conductivity tensor, and where $\vec{A}(\vec{r}';\omega)$ is the total vector potential at $\vec{r}'$, i.e., where

$$\vec{A}(\vec{r}';\omega) \equiv \vec{A}_{\rm tot}(\vec{r}';\omega) \equiv \vec{A}_{\rm ext}(\vec{r}';\omega) + \vec{A}_{\rm ind}(\vec{r}';\omega), \quad (2.3)$$

$\vec{A}_{\rm ext}(\vec{r}';\omega)$ and $\vec{A}_{\rm ind}(\vec{r}';\omega)$ being, respectively, the externally imposed and the induced vector potentials.[27]

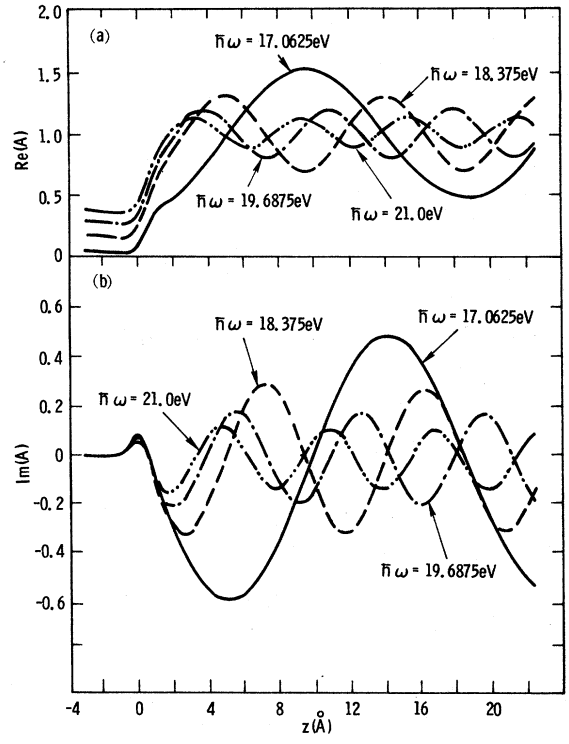

FIG. 3. Real and imaginary parts of $A^{z}_{\vec{k}_{\parallel}\to 0,\omega}(z)$ vs z, calculated using the $r_s = 2$ Lang-Kohn potential barrier (Ref. 51), for various photon frequencies above $\omega_p(r_s = 2)$. In each case $A^{(T)z}_{\vec{k}_{\parallel}\to 0,\omega}(z \to \infty)$ has been normalized to 1. Thus [cf., Eq. (2.46b)], $A^{z}_{\vec{k}_{\parallel}\to 0,\omega}(z \to -\infty)$ necessarily equals $1 - \omega_p^2/\omega^2$.

In order that $\vec{A}(\vec{r};\omega)$ correspond to the scattering of an electromagnetic wave, it must of course satisfy not only Eq. (2.1), but also the scattering boundary condition, i.e., that

$$\vec{A}_{\rm ind}(\vec{r};\omega)\equiv\vec{A}(\vec{r};\omega)-\vec{A}_{\rm ext}(\vec{r};\omega)$$

behave as a sum of outgoing waves as $|\vec{r}|\to\infty$. The simultaneous satisfaction of the two conditions on $\vec{A}(\vec{r};\omega)$ is achieved by requiring that it satisfy the particular integral form of Eq. (2.1),

$$\vec{A}(\vec{r};\omega)=\vec{A}_{\rm ext}(\vec{r};\omega)+\int d^3r''\,\frac{e^{i(\omega/c)|\vec{r}-\vec{r}''|}}{|\vec{r}-\vec{r}''|}\times\left(\frac{i\omega}{c^2}\int d^3r''\,\vec{\sigma}(\vec{r}',\vec{r}'';\omega)\cdot\vec{A}(\vec{r}'';\omega)-\frac{1}{4\pi}\vec{\nabla}'[\vec{\nabla}'\cdot\vec{A}(\vec{r}',\omega)]\right).\tag{2.4}$$

It can easily be verified that the function $\vec{A}(\vec{r};\omega)$ defined by Eq. (2.4) satisfies Eq. (2.1) provided that

$$(\nabla^2+\omega^2/c^2)\vec{A}_{\rm ext}(\vec{r};\omega)-\vec{\nabla}[\vec{\nabla}\cdot\vec{A}_{\rm ext}(\vec{r};\omega)]=0;\tag{2.5}$$

and it is obvious by inspection of Eq. (2.4) that the form of its kernel forces $\vec{A}(\vec{r};\omega)$ to satisfy the outgoing-wave boundary condition [except in the range of frequencies where the homogeneous part of Eq. (2.4) has solutions (which correspond to plasmons; cf., below)].

For a plane wave incident on the solid, one takes

$$\vec{A}_{\rm ext}(\vec{r};\omega)=\vec{A}^{(0)}_{\vec{k},\omega}\,e^{i\vec{k}\cdot\vec{r}},\tag{2.6a}$$

which satisfies Eq. (2.5) provided that

$$\vec{k}\cdot\vec{A}^{(0)}_{\vec{k},\omega}=0,\tag{2.6b}$$

and that

$$|\vec{k}|=\omega/c\,.\tag{2.6c}$$

For the case of refraction by a flat jellium solid, i.e., one which is translationally invariant in (by convention) $x-y$ planes, the conductivity tensor $\vec{\sigma}(\vec{r},\vec{r}';\omega)$ assumes the simpler form

$$\vec{\sigma}(\vec{r},\vec{r}';\omega)\equiv\vec{\sigma}(\vec{x}-\vec{x}',z,z';\omega),\tag{2.7}$$

where $\vec{x}$ and $\vec{x}'$ are vectors in the x-y planes, i.e., where

$$\vec{r}\equiv(\vec{x},z).\tag{2.8}$$

Thus, Eq. (2.4) can be simplified by Fourier transforming in $\vec{x}$, yielding the equation

$$\vec{A}_{\vec{k}_\parallel,\omega}(z)=\vec{A}^{(0)}_{\vec{k},\omega}\,e^{ik_\perp z}+(2\pi i/k_\perp)\int dz'\,e^{ik_\perp|z-z'|}\left\{\frac{i\omega}{c^2}\int dz''\,\vec{\sigma}_{\vec{k}_\parallel,\omega}(z',z'')\cdot\vec{A}_{\vec{k}_\parallel,\omega}(z'')-\frac{1}{4\pi}\left(i\vec{k}_\parallel+\hat{u}_z\frac{\partial}{\partial z'}\right)\left[\left(i\vec{k}_\parallel+\hat{u}_z\frac{\partial}{\partial z'}\right)\cdot\vec{A}_{\vec{k}_\parallel,\omega}(z')\right]\right\},\tag{2.9}$$

wherein $k_\parallel$ and $k_\perp$ are defined by

$$\vec{k}\equiv(\vec{k}_\parallel,k_\perp),\tag{2.10}$$

where $\vec{A}_{\vec{k}_\parallel,\omega}(z)$ and $\vec{\sigma}_{\vec{k}_\parallel,\omega}(z,z')$ are defined by

$$\vec{A}(\vec{r};\omega)\equiv\vec{A}_{\vec{k}_\parallel,\omega}(z)\,e^{i\vec{k}_\parallel\cdot\vec{x}}\tag{2.11a}$$

and

$$\vec{\sigma}(\vec{x}-\vec{x}',z,z';\omega)\equiv\int[d^2k_\parallel/(2\pi)^2]\,e^{i\vec{k}_\parallel\cdot(\vec{x}-\vec{x}')}\,\vec{\sigma}_{\vec{k}_\parallel,\omega}(z,z'),\tag{2.11b}$$

and where $\hat{u}_z$ is a unit vector which points in the $+z$ direction.

The remainder of this section is devoted to the reduction of Eq. (2.9) to a more manageable form, for the case of a long-wavelength incident wave. The reduction begins with the introduction of the information that $\vec{\sigma}_{\vec{k}_\parallel,\omega}(z,z')$ is negligibly small if either z or z' is only slightly (~ 1 Å) outside the jellium surface, while it is given to a good approximation by its bulk jellium form (fixed by rotational as well as translational invariance[27]),

$$\vec{\sigma}_{\vec{k}_\parallel,\omega}(z-z')=\int\frac{dk_\perp}{2\pi}\,e^{ik_\perp(z-z')}\times\left(\vec{1}\,\sigma^{(1)}(k;\omega)+\frac{\vec{k}\vec{k}}{k^2}\,\sigma^{(2)}(k;\omega)\right)\tag{2.12}$$

if z or z' or z' is any greater than a few Å within the jellium. [In Eq. (2.12), $\vec{1}$ is the unit matrix and $k\equiv|\vec{k}|=(|\vec{k}_\parallel|^2+k_\perp^2)^{1/2}$.] This information implies that $\vec{A}_{\vec{k}_\parallel,\omega}(z)$ behaves "asymptotically" already at *microscopic* distances on either side of the jellium surface, and thereby permits the simplification of Eq. (2.9) in the long-wavelength limit.

In order to take advantage of the knowledge that $\vec{\sigma}_{\vec{k}_\parallel,\omega}(z,z')$ heals rapidly within the jellium (which henceforth will be assumed to be in the right half-space), one makes use of the identity

$$e^{ik_\perp|z-z'|}\equiv e^{ik_\perp(z-z')}-2i\Theta(z'-z)\sin k_\perp(z-z'),\tag{2.13}$$

in which $\Theta(x)$ is the ordinary step function. Substituting Eq. (2.13) into Eq. (2.9), one finds that if $\vec{A}_{\vec{k}_\parallel,\omega}(z)$ satisfies the homogeneous equation

$$\vec{A}_{\vec{k}_{\parallel},\omega}(z)=\frac{4\pi}{k_\perp}\int_z^\infty dz'\sin k_\perp(z-z')\left\{\frac{i\omega}{c^2}\int_{-\infty}^{\infty}dz''\,\vec{\vec{\sigma}}_{\vec{k}_{\parallel},\omega}(z',z'')\cdot\vec{A}_{\vec{k},\omega}(z'')\right.$$
$$\left.-\frac{1}{4\pi}\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z'}\right)\left[\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z'}\right)\cdot\vec{A}_{\vec{k}_{\parallel},\omega}(z')\right]\right\}, \tag{2.14a}$$

and is normalized according to the equation

$$\vec{A}^{(0)}_{\vec{k}_{\parallel},\omega}=-\frac{2\pi i}{k_\perp}\int_{-\infty}^{\infty}dz'\,e^{-ik_\perp z'}\left\{\frac{i\omega}{c^2}\int_{-\infty}^{\infty}dz''\,\vec{\vec{\sigma}}_{\vec{k}_{\parallel},\omega}(z',z'')\cdot\vec{A}_{\vec{k}_{\parallel},\omega}(z'')\right.$$
$$\left.-\frac{1}{4\pi}\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z'}\right)\left[\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z'}\right)\cdot\vec{A}_{\vec{k}_{\parallel},\omega}(z')\right]\right\}, \tag{2.14b}$$

then $\vec{A}_{\vec{k}_{\parallel},\omega}(z)$ will necessarily be the (unique) solution to Eq. (2.9).

The point of converting Eq. (2.9) to the pair of Eqs. (2.14a), is that by virtue of the healing of $\vec{\vec{\sigma}}_{\vec{k}_{\parallel},\omega}(z',z'')$, Eq. (2.14a) can be solved explicitly for values of z greater than $\vec{\vec{\sigma}}_{\vec{k}_{\parallel},\omega}(z,z')$ healing depth. Thus assuming the jellium surface region to be delimited by the relation,

$$|z|\ll Z, \tag{2.15}$$

where Z is of the order of a few Å, one can rewrite Eq. (2.14a) in the form

$$\vec{A}_{\vec{k}_{\parallel},\omega}(z)=\vec{A}^{(\mathrm{I})}_{\vec{k}_{\parallel},\omega}(z;Z)+\vec{A}^{(\mathrm{II})}_{\vec{k}_{\parallel},\omega}(z;Z), \tag{2.16}$$

where $\vec{A}^{(\mathrm{I})}_{\vec{k}_{\parallel},\omega}(z;Z)$, given by

$$\vec{A}^{(\mathrm{I})}_{\vec{k}_{\parallel},\omega}(z;Z)\equiv\frac{4\pi}{k_\perp}\int_Z^\infty dz'\sin k_\perp(z-z')\left\{\frac{i\omega}{c^2}\int dz''\,\vec{\vec{\sigma}}_{\vec{k}_{\parallel},\omega}(z',z'')\cdot\vec{A}_{\vec{k}_{\parallel},\omega}(z'')\right.$$
$$\left.-\frac{1}{4\pi}\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z'}\right)\left[\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z'}\right)\cdot\vec{A}_{\vec{k}_{\parallel},\omega}(z')\right]\right\}, \tag{2.17}$$

can be explicitly evaluated by means of one's ability to solve Eq. (2.14a) for $z\gtrsim Z$. Since, as will be shown shortly, $\vec{A}^{(\mathrm{II})}_{\vec{k}_{\parallel},\omega}(z;Z)$ [defined by Eq. (2.14a), (2.16), and (2.17)] can also be expressed in a simple form, Eq. (2.14a) therefore provides the means for reducing the determination of $\vec{A}_{\vec{k}_{\parallel},\omega}(z)$ in the long-wavelength limit to a manageable problem.

The solution of Eq. (2.14a) for $z\gtrsim Z$ proceeds as follows: Since z has been specifically assumed to be greater than the conductivity healing depth, Eq. (2.14a) may be written in the form

$$\vec{A}_{\vec{k}_{\parallel},\omega}(z\gtrsim Z)\approx\frac{4\pi}{k_\perp}\int_z^\infty dz'\sin k_\perp(z-z')\left\{\frac{i\omega}{c^2}\int dz''\,\vec{\vec{\sigma}}^{\infty}_{\vec{k}_{\parallel},\omega}(z'-z'')\cdot\vec{A}_{\vec{k}_{\parallel},\omega}(z'')\right.$$
$$\left.-\frac{1}{4\pi}\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z'}\right)\left[\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z'}\right)\cdot\vec{A}_{\vec{k}_{\parallel},\omega}(z')\right]\right\}, \tag{2.18}$$

which is trivially solved with the ansatz

$$\vec{A}_{\vec{k}_{\parallel},\omega}(z\gtrsim Z)\approx\vec{T}_{\vec{k}_{\parallel},\omega}e^{ik'_\perp z}. \tag{2.19}$$

Substituting Eq. (2.19) into Eq. (2.18), making use of Eq. (2.12), and assuming $k'_\perp$ to have at least a small positive imaginary part due to absorption, one finds that Eq. (2.19) solves Eq. (2.18) provided that $\vec{T}_{\vec{k}_{\parallel},\omega}$ and $k'_\perp$ satisfy the equation

$$\vec{T}_{\vec{k}_{\parallel},\omega}=\frac{1}{k'^2_\perp-k^2_\perp}\left[\frac{4\pi i\omega}{c^2}\sigma^{(1)}(k';\omega)\vec{T}_{\vec{k}_{\parallel},\omega}+\left(\frac{4\pi i\omega}{c^2}\frac{1}{k'^2}\sigma^{(2)}(k';\omega)+1\right)\vec{k}'(\vec{k}'\cdot\vec{T}_{\vec{k}_{\parallel},\omega})\right], \tag{2.20}$$

where

$$\vec{k}' \equiv (\vec{k}_{\parallel}, k_{\perp}'). \tag{2.21}$$

Taking the dot product of both sides of Eq. (2.20) with $\vec{k}'$, one obtains the requirement that

$$(\vec{k}' \cdot \vec{T}_{\vec{k}_{\parallel},\omega}) \epsilon^{(L)}(k'; \omega) = 0, \tag{2.22}$$

where the longitudinal dielectric constant $\epsilon^{(L)}(\vec{k}'; \omega)$ is defined by

$$\epsilon^{(L)}(k'; \omega) \equiv 1 + (4\pi i/\omega)\, \sigma^{(L)}(k'; \omega) \equiv 1 + (4\pi i/\omega)[\sigma^{(1)}(k'; \omega) + \sigma^{(2)}(k'; \omega)]. \tag{2.23}$$

Equation (2.22) implies that Eq. (2.18) can have both transverse and longitudinal solutions:

(i) The transverse solutions [denoted henceforth by the superscript (T)] correspond to the satisfaction of Eq. (2.22) by means of the relation

$$\vec{k}^{(T)'} \cdot \vec{T}^{(T)}_{\vec{k}_{\parallel},\omega} = 0. \tag{2.24}$$

In order to determine $k_{\perp}^{(T)'}$, one substitutes Eq. (2.24) back into Eq. (2.20), thereby finding that

$$k_{\perp}^{(T)'2} = k_{\perp}^2 + k^2[4\pi i \sigma^{(1)}(k^{(T)'}; \omega)/\omega]. \tag{2.25}$$

Noting that $\sigma^{(1)}(k^{(T)'}; \omega)$ is related to the transverse dielectric constant $\epsilon^{(T)}(k^{(T)'}; \omega)$ by the equation[27]

$$\epsilon^{(T)}(k^{(T)'}; \omega) = 1 + (4\pi i/\omega)\, \sigma^{(1)}(k^{(T)'}; \omega), \tag{2.26}$$

Eq. (2.25) can be rewritten in the familiar form

$$k^2 = k^{(T)'2}/\epsilon^{(T)}(k^{(T)'}; \omega). \tag{2.27}$$

(ii) The longitudinal solutions of Eq. (2.28) [denoted henceforth with the superscript (L)] correspond to the satisfaction of Eq. (2.22) by means of the relation

$$\epsilon^{(L)}(k^{(L)'}; \omega) = 0. \tag{2.28}$$

Equation (2.28) is, of course, precisely the criterion for the existence of a plasmon of wave-vector $k^{(L)'}$ and frequency ω,[28] and only has real solutions for $k^{(L)'}$ if ω lies in a band of frequencies for which the jellium solid has undamped plasmons.[29] [If the relation

$$\mathrm{Im} k^{(L)'}(\omega) \ll 1/Z \tag{2.29}$$

is not satisfied, then clearly the longitudinal solution to Eq. (2.18) will not play a role in the asymptotic behavior of $\vec{A}_{\vec{k}_{\parallel},\omega}(z \gg Z)$.] In order to verify that the satisfaction of Eq. (2.28) implies that $\vec{A}_{\vec{k}_{\parallel},\omega}(z \gtrsim Z)$ is longitudinal, one takes the cross product of both sides of Eq. (2.20) with $\vec{k}^{(L)'}$, thereby deriving the condition

$$[k^{(L)'2} - k^2 \epsilon^{(T)}(k^{(L)'}; \omega)](\vec{k}^{(L)'} \times \vec{T}^{(L)}_{\vec{k}_{\parallel},\omega}) = 0. \tag{2.30}$$

Since, in general, the equation

$$k^2 = k^{(L)'2}/\epsilon^{(T)}(k^{(L)'}; \omega) \tag{2.31}$$

cannot be solved simultaneously with Eq. (2.28), Eq. (2.30) implies that

$$\vec{k}^{(L)'} \times \vec{T}^{(L)}_{\vec{k}_{\parallel},\omega} = 0, \tag{2.32}$$

or that the wave corresponding to $\vec{k}^{(L)'}$ is longitudinal.

The most general solution of Eq. (2.18) can now be written in the form[30]

$$\vec{A}_{\vec{k}_{\parallel},\omega}(z \gtrsim Z) \approx \vec{T}^{(T)}_{\vec{k}_{\parallel},\omega} e^{ik_{\perp}^{(T)'} z} + \vec{T}^{(L)}_{\vec{k}_{\parallel},\omega} e^{ik_{\perp}^{(L)'} z} \tag{2.33}$$

(in which the longitudinal component vanishes for ω outside the plasmon band), which can be substituted back into Eq. (2.17) to obtain an explicit expression for $\vec{A}^{(I)}_{\vec{k}_{\parallel},\omega}(z; Z)$.[31] Carrying out the z' and z'' integrations, one thus obtains the formula[32]

$$\vec{A}^{(I)}_{\vec{k}_{\parallel},\omega}(z; Z) = \vec{T}^{(T)}_{\vec{k}_{\parallel},\omega} e^{ik_{\perp}^{(T)'} z}\left(\cos k_{\perp}(z - Z) + i\frac{k_{\perp}^{(T)'}}{k_{\perp}}\sin k_{\perp}(z - Z)\right) + \vec{T}^{(L)}_{\vec{k}_{\parallel},\omega} e^{ik_{\perp}^{(L)'} z}\left(\cos k_{\perp}(z - Z) + i\frac{k_{\perp}^{(L)'}}{k_{\perp}}\sin k_{\perp}(z - Z)\right). \tag{2.34}$$

For long-wavelength incident light and for $|z| \lesssim Z$, one has that

$$k_{\perp} Z \ll 1, \tag{2.35}$$

and moreover, using Eq. (2.27), that

$$k_{\perp}^{(T)'} Z \ll 1. \tag{2.36}$$

(However, in general one may not assume that $k_{\perp}^{(L)'}$, given by Eq. (2.28), is small compared to Z^{-1}.) Thus, in the long-wavelength limit, Eq. (2.34) assumes the simpler form

$$\vec{A}^{(I)}_{\vec{k}_{\parallel},\omega}(z; Z) \approx \vec{T}^{(T)}_{\vec{k}_{\parallel},\omega} + \vec{T}^{(L)}_{\vec{k}_{\parallel},\omega} e^{ik_{\perp}^{(L)'} z}[1 + ik_{\perp}^{(L)'}(z - Z)]. \tag{2.37}$$

To complete the reduction of Eq. (2.14a), consider finally the quantity $\vec{A}^{(II)}_{\vec{k}_{\parallel},\omega}(z; Z)$, given by [cf., Eq. (2.16)],

$$\vec{A}^{(II)}_{\vec{k}_{\parallel},\omega}(z; Z) \equiv \frac{4\pi}{k_{\perp}} \int_Z^z dz' \sin k_{\perp}(z - z') \left\{\frac{i\omega}{c^2} \int dz'' \, \vec{\sigma}_{\vec{k}_{\parallel},\omega}(z', z'') \cdot \vec{A}_{\vec{k}_{\parallel},\omega}(z'')\right.$$

$$-\frac{1}{4\pi}\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z'}\right)\left[\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z'}\right)\cdot\vec{A}_{\vec{k}_{\parallel},\omega}(z')\right]\ . \tag{2.38}$$

Equation (2.38) may be rewritten in a more useful form, using the identity (charge conservation)

$$\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z}\right)\cdot\vec{A}_{k_{\parallel},\omega}(z)=-\frac{4\pi i}{\omega}\int dz'\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z}\right)\cdot\vec{\sigma}_{\vec{k}_{\parallel},\omega}(z,z')\cdot\vec{A}_{\vec{k}_{\parallel},\omega}(z')\,, \tag{2.39}$$

which is a direct consequence of Eqs. (2.1) and (2.2). Substituting Eq. (2.39) into Eq. (2.38), one obtains the equation for $\vec{A}^{(II)}_{\vec{k}_{\parallel},\omega}(z;\,Z)$,

$$\vec{A}^{(II)}_{\vec{k}_{\parallel},\omega}(z;\,Z)=\int_z^Z dz'\,\frac{\sin k_\perp(z-z')}{k_\perp}\left[k^2\vec{1}+\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z'}\right)\left(i\vec{k}_{\parallel}+\hat{u}_z\frac{\partial}{\partial z'}\right)\right]\frac{4\pi i}{\omega}\int dz''\,\vec{\sigma}_{\vec{k}_{\parallel},\omega}(z',z'')\cdot\vec{A}_{\vec{k}_{\parallel},\omega}(z'')\,. \tag{2.40}$$

In the long-wavelength limit it is evident that the only term on the right-hand side of Eq. (2.40), which is of zeroth order in the small wave numbers $(k, k_\perp, |\vec{k}_{\parallel}|)$, is the one which involves $\partial^2/\partial z'^2$. Thus for long wavelengths and for $k_\perp|z|\ll 1$, Eq. (2.40) assumes the approximate form

$$\vec{A}^{(II)}_{\vec{k}_{\parallel},\omega}(z;\,Z)\approx\int_z^Z dz'\,(z-z')\,\frac{\partial^2}{\partial z'^2}\left[\frac{4\pi i}{\omega}\,\hat{u}_z\int dz''\,\sigma^{\gamma z}_{\vec{k}_{\parallel},\omega}(z',z'')\cdot\vec{A}^{\gamma}_{\vec{k}_{\parallel},\omega}(z'')\right]\,, \tag{2.41}$$

wherein summation over the repeated Cartesian index, $\gamma=x,y,z$, is implied. The z' integration in Eq. (2.41) may be carried out trivially, yielding

$$\vec{A}^{(II)}_{\vec{k}_{\parallel},\omega}(z;\,Z)=\frac{4\pi i}{\omega}\,\hat{u}_z\left((z-Z)\frac{\partial}{\partial z'}\int dz''\,\sigma^{\gamma z}_{\vec{k}_{\parallel},\omega}(z',z'')\cdot A^{\gamma}_{\vec{k}_{\parallel},\omega}(z'')\Big|_{z'=z}\right.$$
$$\left.+\int dz''\,[\sigma^{\gamma z}_{\vec{k}_{\parallel},\omega}(Z,z'')-\sigma^{\gamma z}_{\vec{k}_{\parallel},\omega}(z,z'')]\,A^{\gamma}_{\vec{k}_{\parallel},\omega}(z'')\right)\,, \tag{2.42}$$

and the terms in Eq. (2.42) evaluated at $z'=Z$ may then be calculated explicitly, using Eq. (2.33) for $\vec{A}_{\vec{k}_{\parallel},\omega}(z\gtrsim Z)$, and the "healed" form of $\vec{\sigma}_{\vec{k}_{\parallel},\omega}(z',z'')$ given in Eq. (2.12). That is, one obtains from Eqs. (2.12) and (2.33) the expression

$$\int dz''\,\sigma^{\gamma z}_{\vec{k}_{\parallel},\omega}(z',z'')A^{\gamma}_{\vec{k}_{\parallel},\omega}(z'')\xrightarrow[z'\gtrsim Z]{}\sigma^{(1)}(k_\perp^{(T)\prime};\,\omega)\,T^{(T)z}_{\vec{k}_{\parallel},\omega}e^{ik_\perp^{(T)\prime}z'}$$
$$+[\sigma^{(1)}(k_\perp^{(L)\prime};\,\omega)\,T^{(L)z}_{\vec{k}_{\parallel},\omega}+\sigma^{(2)}(k_\perp^{(L)\prime};\,\omega)\,k_\perp^{(L)\prime}(\vec{k}_\perp^{(L)\prime}\cdot\vec{T}^{(L)}_{\vec{k}_{\parallel},\omega})/k^{(L)\prime 2}\,e^{ik_\perp^{(L)\prime}z'}]\,. \tag{2.43}$$

Substituting Eq. (2.43) into (2.42), and neglecting all but zeroth order in $k_\perp^{(T)\prime}$ and in $k_{\parallel}$, one then arrives at the greatly simplified expression for $\vec{A}^{(II)}_{\vec{k}_{\parallel}\to 0,\omega}(z;\,Z)$,[33]

$$\vec{A}^{(II)}_{\vec{k}_{\parallel}\to 0,\omega}(z;\,Z)\approx\frac{4\pi i}{\omega}\,\hat{u}_z\left(e^{ik_\perp^{(L)\prime}z}\,[1+ik_\perp^{(L)\prime}(z-Z)][\sigma^{(1)}(k_\perp^{(L)\prime},\,\omega)+\sigma^{(2)}(k_\perp^{(L)\prime},\,\omega)]\right.$$
$$\left.\times T^{(L)z}_{\vec{k}_{\parallel}\to 0,\omega}+\sigma^{(1)}(0;\,\omega)\,T^{(T)z}_{\vec{k}_{\parallel}\to 0,\omega}-\int dz''\,\sigma^{zz}_{\vec{k}_{\parallel}\to 0,\omega}(z,z'')A^{z}_{\vec{k}_{\parallel}\to 0,\omega}(z'')\right)\,. \tag{2.44}$$

Substituting Eqs. (2.44) and (2.37) into Eq. (2.16), one now obtains the promised simple integral equation for $\vec{A}_{\vec{k}_{\parallel}\to 0,\omega}(z)$,[34]

$$\vec{A}_{\vec{k}_{\parallel}\to 0,\omega}(z)=\vec{T}^{(T)}_{\vec{k}_{\parallel}\to 0,\omega}+\frac{4\pi i}{\omega}\,\hat{u}_z\,\sigma^{(1)}(0;\,\omega)\,T^{(T)z}_{\vec{k}_{\parallel}\to 0,\omega}-\frac{4\pi i}{\omega}\int dz''\,\sigma^{zz}_{\vec{k}_{\parallel}\to 0,\omega}(z,z'')A^{z}_{\vec{k}_{\parallel}\to 0,\omega}(z'')\,. \tag{2.45}$$

This equation is the basis for all the calculations in Sec. III and IV below.

Note that in addition to providing a means for calculating the behavior of $\vec{A}_{\vec{k}_{\parallel}\to 0,\omega}(z)$ in the surface region, Eq. (2.45) also guarantees that $\vec{A}_{\vec{k}_{\parallel}\to 0,\omega}(z)$ will satisfy the classical matching conditions across the surface, i.e.,

$$\begin{cases}A^{x,y}_{\vec{k}_{\parallel}\to 0,\omega}(-Z)=A^{x,y}_{\vec{k}_{\parallel}\to 0,\omega}(+Z) & \text{(2.46a)}\\ A^{z}_{\vec{k}_{\parallel}\to 0,\omega}(-Z)=\epsilon^{(T)}(0;\,\omega)\,A^{(T)z}_{\vec{k}_{\parallel}\to 0,\omega}(Z)\,, & \text{(2.46b)}\end{cases}$$

where, in Eq. (2.46b), $A^{(T)z}_{\vec{k}_{\parallel}\to 0,\omega}(Z)$ is the z-component of the transverse part of $\vec{A}_{\vec{k}_{\parallel}\to 0,\omega}(z)$ evaluated at $z=Z$. The satisfaction of Eq. (2.46a) by Eq.

(2.45) is obvious, since the latter implies that $A^x_{\vec{k}_{\parallel}\to 0,\omega}(z)$ and $A^y_{\vec{k}_{\parallel}\to 0,\omega}(z)$ are constant in z. As for Eq. (2.45b), note first that Eq. (2.44) does imply that

$$A^z_{\vec{k}_{\parallel}\to 0,\omega}(z\to\text{“}\infty\text{”}) = T^{(T)z}_{\vec{k}_{\parallel}\to 0,\omega} + T^{(L)z}_{\vec{k}_{\parallel}\to 0,\omega} e^{ik_\perp^{(L)\prime} z}, \tag{2.47}$$

as it should to be consistent with Eq. (2.33). To see this result, note that for $z \approx Z$,

$$\sigma^{zz}_{\vec{k}_{\parallel}\to 0,\omega}(z, z'') \approx \sigma^{zz\infty}_{\vec{k}_{\parallel}\to 0,\omega}(z - z''), \tag{2.48}$$

and therefore, that [cf., Eq. (2.43) and Ref. 33]

$$\int dz''\, \sigma^{zz}_{\vec{k}_{\parallel}\to 0,\omega}(Z, z')\left[T^{(T)z}_{\vec{k}_{\parallel}\to 0,\omega} + T^{(L)z}_{\vec{k}_{\parallel}\to 0,\omega} e^{ik_\perp^{(L)\prime} z''}\right] \approx \sigma^{(1)}(0;\omega)\, T^{(T)z}_{\vec{k}_{\parallel},\omega} + \left[\sigma^{(1)}(k_\perp^{(L)};\omega) + \sigma^{(2)}(k_\perp^{(L)};\omega)\right] T^{(L)z}_{\vec{k}_{\parallel}\to 0,\omega} e^{ik_\perp^{(L)\prime} z}. \tag{2.49}$$

Substituting Eq. (2.49) into (2.45), and using Eqs. (2.23) and (2.28), one finds that Eq. (2.45) does indeed imply the validity of Eq. (2.47). On the other hand, at $z = -Z$, one has that

$$\sigma^{zz}_{\vec{k}_{\parallel}\to 0,\omega}(-Z, z'') \approx 0. \tag{2.50}$$

Thus, Eq. (2.45) also implies that[35]

$$A^z_{\vec{k}_{\parallel}\to 0,\omega}(-Z) = \left(1 + \frac{4\pi i}{\omega}\sigma^{(1)}(0;\omega)\right) T^{(T)z}_{\vec{k}_{\parallel}\to 0,\omega} \equiv \epsilon^{(T)}(0;\omega)\, T^{(T)z}_{\vec{k}_{\parallel}\to 0,\omega}. \tag{2.51}$$

Comparing Eqs. (2.51) and (2.47), both implied by Eq. (2.45), one sees finally that the latter implies the satisfaction of Eq. (2.46b), as was to be demonstrated.

The next section of this article is addressed to the problem of solving Eq. (2.45) numerically.

III. DESCRIPTION OF METHOD USED TO SOLVE Eq. (2.45)

In this section the method is described, by which Eq. (2.45) was solved for $A^z_{\vec{k}_{\parallel}\to 0,\omega}(z)$. Since the techniques involved here are closely similar to those which have been used previously, in studies of surface plasmons at a jellium-vacuum interface,[36–38] and which have been described at length in Ref. 38 (henceforth referred to as I), the discussion below is somewhat abbreviated. In particular a number of proofs are omitted, which have already appeared in I.

Before one can solve Eq. (2.45), one obviously needs to specify an explicit (if in general approximate) form for the response function,

$$\sigma(z, z';\omega) \equiv \sigma^{zz}_{\vec{k}_{\parallel}\to 0,\omega}(z, z'), \tag{3.1}$$

corresponding to the solid of interest. In the present work, the form used for $\sigma(z, z';\omega)$ is that given by the random-phase approximation[28](RPA), which has the virtues that it can be expected to yield a reasonable qualitative description of the collective behavior of the electron gas, and that it is relatively simple.

Within the RPA, $\sigma(z, z';\omega)$ has the explicit representation,

$$\sigma(z, z';\omega) = -\frac{e^2}{i\omega}\left(\frac{n_0(z)}{m}\delta(z - z') + \frac{2}{\hbar}\int\frac{d^2k}{(2\pi)^2}\int_{\kappa,\kappa'}\frac{\Theta_{k,\kappa} - \Theta_{k,\kappa'}}{\omega + i\delta - \omega_{\kappa'} + \omega_\kappa} j_{\kappa\kappa'}(z) j_{\kappa'\kappa}(z')\right). \tag{3.2}$$

In Eq. (3.2), the current density $j_{\kappa\kappa'}(z)$ is defined by

$$j_{\kappa\kappa'}(z) = \frac{\hbar}{2mi}\left(\Psi^*_\kappa(z)\frac{d\Psi_{\kappa'}(z)}{dz} - \frac{d\Psi^*_\kappa(z)}{dz}\Psi_{\kappa'}(z)\right), \tag{3.3}$$

where the $\Psi_\kappa(z)$ are the single-electron wave functions which correspond to the jellium solid in its ground state; thus the $\Psi_\kappa(z)$ satisfy the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + V(z) - \hbar\omega_\kappa\right)\Psi_\kappa(z) = 0, \tag{3.4}$$

where $V(z)$ is the ground-state self-consistent single-electron potential. The frequencies ω_κ in Eq. (3.2) are those given by Eq. (3.4).

The integrals on κ and κ' in Eq. (3.2) cover all solutions to Eq. (3.4), above as well as below the vacuum level, and the quantities $\theta_{k,\kappa}$ are zero-temperature Fermi functions, i.e.,

$$\Theta_{k,\kappa} \equiv \Theta(E_F - \hbar^2k^2/2m - \hbar\omega_\kappa), \tag{3.5}$$

where

$$E_F \equiv \hbar^2 k_F^2/2m \tag{3.6}$$

is the Fermi energy and $\Theta(x)$ is the ordinary step function. Finally, $n_0(z)$ is the electron-density profile corresponding to the jellium solid in its ground state; thus

$$n_0(z) = 2\int \frac{d^2k}{(2\pi)^2} \int_0^\infty \frac{2d\kappa}{\pi}\, \Theta_{k,\kappa} \left|\Psi_\kappa(z)\right|^2 . \qquad (3.7)$$

The factor 2 in Eq. (3.7) and in the second term of Eq. (3.2) arises from spin summation, while the weight $2/\pi$ in the κ integral of Eq. (3.7) corresponds to the normalization of the wave functions $\Psi_\kappa(z)$ below the vacuum level to unit sinusoidal amplitude as $z \to \infty$.

The choice of a specific approximate form for $\sigma(z, z'; \omega)$, of course, automatically implies the choice of a form for $\sigma^{(1)}(0; \omega)$ [which is also required in Eq. (2.45)], according to the relation (cf., Eq. (2.43))

$$\sigma^{(1)}(0; \omega) = \lim_{z\to\infty} \int dz'\, \sigma(z, z'; \omega) . \qquad (3.8)$$

Substituting Eq. (3.2) into Eq. (3.8) then, it can be shown fairly straightforwardly (see Appendix A) that Eq. (3.2) implies that

$$\sigma^{(1)}(0; \omega) = -e^2 n_\infty / im\omega , \qquad (3.9)$$

where

$$n_\infty \equiv n_0(z \to \infty) . \qquad (3.10)$$

At this point, one is prepared to take the first step toward the numerical solution of Eq. (2.45), namely, the numerical evaluation of $\sigma(z, z'; \omega)$ via Eq. (3.2). In order to carry out this step, one attempts to reduce the number of numerical integrations to the minimum. As is shown in Appendix B, this task can be accomplished directly, leading to a form of Eq. (3.2) which requires only a single numerical integration, viz.,

$$\frac{4\pi i}{\omega}\sigma(z, z'; \omega) = -\frac{\omega_p^2}{\omega^2}\frac{\hbar^2}{4\pi^2 m n_\infty}\int_0^{k_F} d\kappa\,(k_F^2 - \kappa^2)\Big[\Theta(z - z')\Big(\frac{1}{W_+(\kappa)} j^+_{\kappa,\omega}(z) j^-_{\kappa,\omega}(z') + \frac{1}{W^*_-(\kappa)} j^{+*}_{\kappa,-\omega}(z) j^{-*}_{\kappa,-\omega}(z')\Big)$$

$$+\Theta(z' - z)\Big(\frac{1}{W_+(\kappa)} j^+_{\kappa,\omega}(z') j^-_{\kappa,\omega}(z) + \frac{1}{W^*_-(\kappa)} j^{+*}_{\kappa,\omega}(z') j^{-*}_{\kappa,-\omega}(z)\Big)\Big] . \qquad (3.11)$$

In Eq. (3.11), the quantities $j^\pm_{\kappa,\omega}(z)$ are defined by

$$j^\pm_{\kappa,\omega} \equiv \Psi_\kappa(z)\frac{d\Psi^\pm_{\omega_\kappa+\omega}(z)}{dz} - \frac{d\Psi_\kappa(z)}{dz}\Psi^\pm_{\omega_\kappa+\omega}(z), \qquad (3.12)$$

where the wave functions $\Psi^\pm_{\omega_\kappa+\omega}$ are solutions of the Schrödinger equation

$$\Big(-\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + V(z) - \hbar(\omega_\kappa + \omega)\Big)\Psi^\pm_{\omega_\kappa+\omega}(z) = 0, \qquad (3.13)$$

satisfying outgoing-wave boundary conditions, respectively, as $z \to \pm\infty$. The constants $W_\pm(\kappa)$ in Eq. (3.6) are Wronskians, and serve to normalize the $\Psi^\pm_{\omega_\kappa+\omega}(z)$; they are defined by

$$W_\pm(\kappa) \equiv \frac{\hbar^2}{2m}\Big(\frac{d\Psi^+_{\omega_\kappa\pm\omega}(z)}{dz}\Psi^-_{\omega_\kappa\pm\omega}(z) - \Psi^+_{\omega_\kappa\pm\omega}(z)\frac{d\Psi^-_{\omega_\kappa\pm\omega}(z)}{dz}\Big) . \qquad (3.14)$$

Having developed a sufficiently simple means for evaluating $\sigma(z, z'; \omega)$, the next problem one must face in attempting to solve numerically for $A^z_{k_\parallel\to 0,\omega}(z)$ is that the z' integration on the right-hand side of Eq. (2.45) covers all values of z' from $-\infty$ to ∞. As a result, solution by conversion of Eq. (2.45) to a matrix equation would seem to require storing and inverting an infinite matrix in the computer, no matter how coarse a mesh one used.

In order to circumvent this difficulty one takes recourse to a method similar to one which was previously developed in connection with the theory of surface plasmons.[39] In particular, one determines the explicit asymptotic form of $A^z_{k_\parallel\to 0,\omega}(z)$ as $z \to \infty$, and one makes use of this knowledge to convert Eq. (2.45) to an approximate integral equation on a compact domain. [The asymptotic region $z \to -\infty$, i.e., the vacuum region presents no real difficulty because $\sigma(z, z'; \omega)$ vanishes rapidly as z or $z' \to -\infty$.[40]]

Briefly, that is, one shows[41] that Eq. (2.45) implies that as $z \to \infty$,

$$A^z_{k_\parallel\to 0,\omega}(z) \to T^{(T)z}_{k_\parallel\to 0,\omega}\Big(1 + \sum_{p=1}^{P}\frac{c_p e^{ik_p z}}{z^2} + \cdots\Big) + T^{(L)z}_{k_\parallel\to 0,\omega} e^{ik_\perp^{(L)\prime} z}, \qquad (3.15)$$

where $\{k_p\}$ is a set of P constants which are known explicitly,[42] and where $\{T^{(L)z}_{k_\parallel\to 0,\omega}/T^{(T)z}_{k_\parallel\to 0,\omega}, c_p\}$ is a set of $p+1$ constants which must be determined numerically. The integer P equals 6 if $\hbar\omega < E_F$ and 10 if $\hbar\omega > E_F$.[42] Thus choosing Z_M to be sufficiently large that Eq. (3.15) is true to the desired accuracy, one may rewrite Eq. (2.45) as an equation for the quantity $\bar{A}(z)$, defined by

$$\bar{A}(z) \equiv (A^z_{k_\parallel\to 0,\omega}(z)/T^{(T)z}_{k_\parallel\to 0,\omega}) - 1 , \qquad (3.16)$$

in the form

$$\bar{A}(z) \approx -\frac{\omega_p^2}{\omega^2} - \frac{4\pi i}{\omega}\int dz'\,\sigma(z, z'; \omega) - \frac{4\pi i}{\omega}\sum_{p=1}^{P} c_p \int_{Z_M} dz'\,\frac{\sigma(z, z'; \omega)\, e^{ik_p z'}}{z'^2}$$

$$-\frac{4\pi i}{\omega}\int_{Z_M}^{\infty} dz'\,\sigma(z,z';\omega)\,e^{ik_\perp^{(L)\prime}z'}\left(\frac{T^{(L)z}_{\vec{k}_\parallel\to 0,\omega}}{T^{(T)z}_{\vec{k}_\parallel\to 0,\omega}}\right)-\frac{4\pi i}{\omega}\int_{-Z_m}^{Z_M} dz'\,\sigma(z,z';\omega)\,\bar{A}(z'). \tag{3.17}$$

In Eq. (3.17), Z_m is positive and large enough that to the desired accuracy,

$$\sigma(z,\ z'\le Z_m;\ \omega)\approx 0. \tag{3.18}$$

Equation (3.17) can be solved numerically on a sufficiently fine mesh of points, since in this equation the domain of z' integration is compact.[43] However, the solutions of Eq. (3.17) for $\bar{A}(z)$ will depend on the as yet undetermined constants,

$$\{c_0\equiv T^{(L)z}_{\vec{k}_\parallel\to 0,\omega}/T^{(T)z}_{\vec{k}_\parallel\to 0,\omega},\ c_p\}.$$

In order to specify these constants, one requires that the function

$$F(\{c_0,c_p\})=\sum_{p'}\left|\ \bar{A}(z_{p'};\{c_0,c_p\})-c_0\,e^{ik_\perp^{(L)\prime}z_{p'}}-\sum_{p=1}^{P}\frac{c_p\,e^{ik_p z_{p'}}}{z_{p'}^2}\ \right|^2 \tag{3.19}$$

be a minimum, where $\{z_{p'}\}$ is a set of values of z in the neighborhood of (but smaller than or equal to) Z_M. [Typically $\{z_{p'}\}$ was taken to be the set of the last $2(P+1)$ points of the z-integration mesh.] This minimization criterion, which may straightforwardly be translated into $P+1$ simultaneous linear equations in the $P+1$ unknowns, $\{c_0, c_p\}$,[44] amounts to the requirement that the behavior of $\bar{A}(z)$ derived from Eq. (3.17) for $z\lesssim Z_M$ be consistent, to within a least-squares best fit, with the asymptotic form of $\bar{A}(z)$ given in Eq. (3.15).[45]

The results reported in the following section of this paper are all based on solving Eq. (3.17) for $\bar{A}(z_{p'};\{c_0,c_p\})$ and determining the $\{c_0,c_p\}$ by minimizing the function $F(\{c_0,c_p\})$ of Eq. (3.19). This method of determining $\bar{A}(z)$ was found to be insensitive to the values chosen for Z_M and Z_m, provided that they were taken to be sufficiently large, and to the precise values chosen for the $\{z_{p'}\}$. [For example, the $\bar{A}(z)$ obtained using the last $2(P+1)$ values of z for the set $\{z_{p'}\}$ was essentially identical to that obtained using the last $3(P+1)$ values.]

Finally, for frequencies overlapping the plasmon band,[29] it was verified that the computed values of

$$|\bar{A}(z)-c_0\,e^{ik_\perp^{(L)\prime}z}|$$

were actually decreasing with z, for z in the neighborhood of Z_M. The reason for carrying out this latter test is that for frequencies overlapping the plasmon band,[29] the homogeneous part of Eq. (2.45) [and, for that matter, of Eq. (2.9)] has solutions $\vec{A}^{(H)}_{\vec{k}_\parallel,\omega}(z)$, corresponding to bulk plasmons of frequency ω and of wave-vector $k_\perp^{(L)\prime}$ in the region $z\gtrsim Z_M$,[46] which impinge on the jellium-vacuum interface from the jellium side and reflected from it back into the jellium.[47] Thus, to any particular solution of Eq. (2.45), it would seem that one could add an arbitrary constant times $\vec{A}^{(H)}_{\vec{k}_\parallel,\omega}(z)$ and thereby obtain another solution. However, the $\vec{A}^{(H)}_{\vec{k}_\parallel,\omega}(z)$ are distinguished from the solutions of interest in the present case by the fact that as $z\to\infty$, they contain "ingoing" components, of the form $\exp -ik_\perp^{(L)\prime}z$. Thus, the uniqueness of the numerical solution to Eq. (2.45), for the case of light incident on the jellium from the vacuum, can be guaranteed, but only by ensuring that the boundary condition of Eq. (3.15) is properly taken into account. In the discussion to this point it has been tacitly assumed that the conversion of Eq. (2.45) to the set of equations, (3.17) plus those obtained in minimizing $F(\{c_0,c_p\})$, is equivalent to the imposition of the $z\to\infty$ boundary condition. However, by verifying that the computed values of

$$|\bar{A}(z)-c_0\,e^{ik_\perp^{(L)\prime}z}|$$

actually were decreasing with z, for $z\lesssim Z_M$ this tacit assumption was explicitly tested. [Clearly if $\bar{A}(z)$ contained a component of the form $\exp -ik_\perp^{(L)\prime}z$, the verification would have failed.]

Having recast Eq. (2.45) into a form which is amenable to computation, one final step is necessary before one can solve for $\bar{A}(z)$, namely, a method must be specified for the evaluation of the functions $g_p(z;\omega)$, $F(z;\omega)$, and $\bar{\sigma}(z;\omega)$, defined by

$$g_p(z;\omega)\equiv\int_{Z_M}^{\infty} dz'\,\sigma(z,z';\omega)\,e^{ik_p z'}/z'^2, \tag{3.20}$$

$$F(z;\omega)\equiv\int_{Z_M}^{\infty} dz'\,\sigma(z,z';\omega)\,e^{ik_\perp^{(L)\prime}z'}, \tag{3.21}$$

and

$$\bar{\sigma}(z;\omega)\equiv\int_{-\infty}^{\infty} dz'\,\sigma(z,z';\omega), \tag{3.22}$$

which appear in Eq. (3.17). However, the calculation of the $g_p(z;\omega)$ may be carried out by methods previously described in I,[48] while the evaluation of $F(z;\omega)$ is straightforward, using the explicitly known forms of $j^{\pm}_{\kappa,\omega}(z)$ in the asymptotic region of $z'\ge Z_M$ (for details see Appendix A). Finally the calculation of $\bar{\sigma}(z;\omega)$ is carried out by rewriting Eq. (3.22) in the form[49]

$$\bar{\sigma}(z;\omega)\approx\int_{-Z_m}^{Z_M} dz'\,\sigma(z,z';\omega)+\int_{Z_M}^{\infty} dz'\,\sigma(z,z';\omega), \tag{3.23}$$

wherein the first term may be computed by direct

numerical integration, and the second can be evaluated by again using the explicitly known asymptotic forms of the $j^{\pm}_{\kappa,\omega}(z)$. Thus at this point all of the elements have been presented which were incorporated into the computer program used to solve for $\bar{A}(z)$. The results of the computations are discussed in Sec. IV.

IV. RESULTS AND DISCUSSION

In this section, I present and discuss the results of solving Eq. (3.17) for a variety of potential barriers $V(z)$ [cf., Eq. (3.4)], and as a function of photon energy $\hbar\omega$. In general the results show that, to the extent that the behavior of the electromagnetic field within a few Å of a free-electron metal surface is important, $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ is not at all well approximated by its classical (step-function) form.

Among the specific questions explored below are the following:

(i) How does $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ scale with electron concentration (see Fig. 1)?

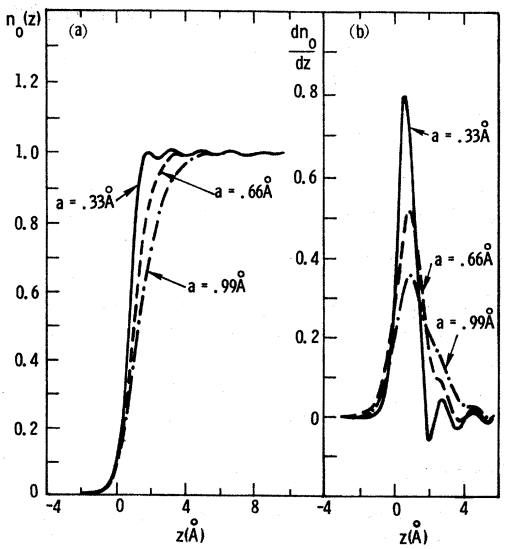

FIG. 5. Comparison of the static electron densities $n(z)$ and of their derivatives dn/dz corresponding to the potential barriers of Fig. 4. The densities have been normalized to 1 in the limit $z\to\infty$.

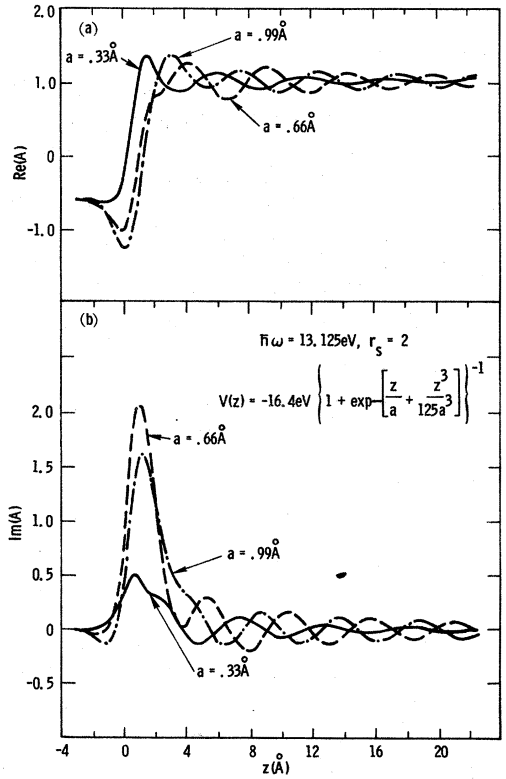

FIG. 4. Illustration of the sensitivity of $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ to surface-potential barrier shape. The curves shown have been calculated for $r_s=2$, $\hbar\omega=13.125$ eV, and for the potential barriers $V(z)=-16.4$ eV/$\{1+\exp -[z/a+(z/5a)^3]\}$, with $a=0.33$, 0.66, and 0.99 Å. At $a=0.66$ Å, $V(z)$ intersects the Lang-Kohn $r_s=2$ potential barrier at the values of z for which $V(z)=V_{LK}(z)=-1.64$ eV and $V(z)=V_{LK}(z)=-14.76$ eV.

(ii) How does $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ vary with ω for fixed electron concentration (see Figs. 2 and 3)?

(iii) How sensitive is $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ to the shape of the surface potential barrier $V(z)$ for fixed bulk electron concentration and photon energy (see Figs. 4 and 5)?

(iv) Finally, what physics can be seen to underly the specific form of $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ (see Figs. 6 and 7)?

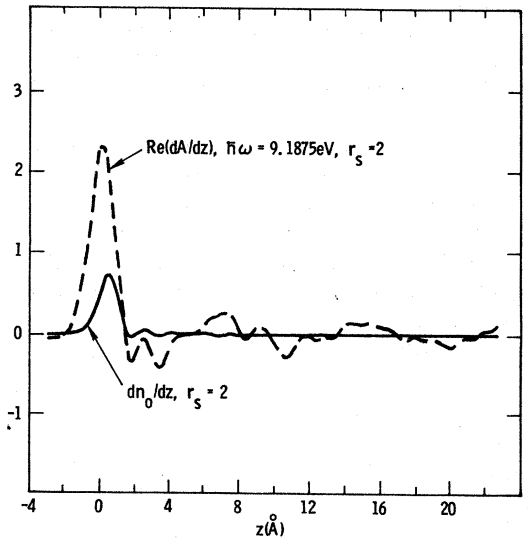

FIG. 6. Comparison of Re $[dA^{z}_{k_{\parallel}\to 0,\omega}(z)/dz]$ for $\hbar\omega=9.1875$ eV with the normalized static density derivative $(dn_0/dz)n_\infty^{-1}$. Both functions were calculated for $r_s=2$ using the corresponding Lang-Kohn potential barrier (Ref. 51).

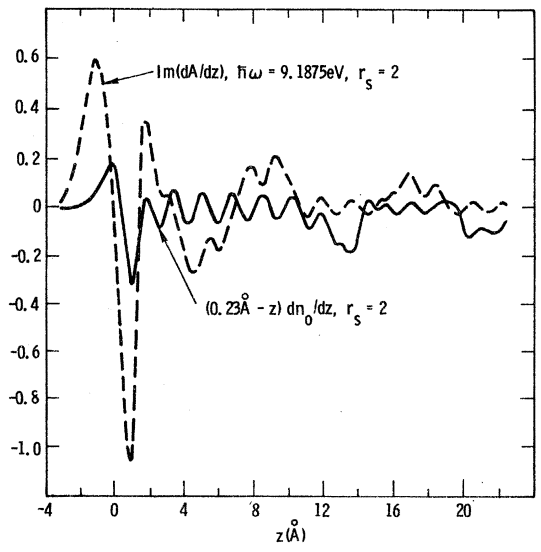

FIG. 7. Comparison of $\mathrm{Im}[dA^{z}_{k_{\parallel}\to 0,\omega}(z)/dz]$ for $\hbar\omega = 9.1875$ eV with the function $(0.23\ \text{Å} - z)n_{\infty}^{-1}(dn_0/dz)$, where $n_{\infty}^{-1}(dn_0/dz)$ is the normalized static electron-density derivative. Both functions were calculated for $r_s = 2$ using the appropriate Lang-Kohn potential barrier (Ref. 51).

The implications of the results for $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ regarding measurable optical properties of surfaces [such as surface photoelectric currents, and off-normal incidence reflectivities] are not discussed in the present article; they are the subject of forthcoming papers.[25,50]

Figure 1 (shown in Sec. I, above) indicates how the calculated form of $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ scales with bulk-electron concentration. The curves shown were calculated using the self-consistent surface-potential barriers $V_{\mathrm{LK}}(z; r_s)$ obtained by Lang and Kohn[51] for electron gas radii $r_s = 2$, 3, and 4, and for frequencies ω chosen such that in each case $\omega/\omega_p(r_s)$ was equal to 0.7875 and thus such that $\epsilon^{T}(0, \omega)$ was the same for each pair of values $(r_s, \hbar\omega)$, and the ratio $A^{z}_{k_{\parallel}\to 0,\omega}(z\to\infty)/A^{z}_{k_{\parallel}\to 0,k}(z\to\infty)$ was guaranteed at the outset [by the classical matching condition, Eq. (2.46b)] to be the same for all of the pairs. Thus by normalizing $A^{z}_{k_{\parallel}\to 0,\omega}(z\to\infty)$ to 1, in each case, the $z\to-\infty$ values of $\mathrm{Re}A^{z}_{k_{\parallel}\to 0,\omega}(z)$ were forced to equal -0.6125, and the $z\to\pm\infty$ values of $\mathrm{Im}A^{z}_{k_{\parallel}\to 0,\omega}(z)$ were necessarily equal to zero.

With these points in mind note that the scaling of $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ with r_s, in Fig. 1, is roughly what one would expect.[51] The initial peaks in the curves for different r_s line up reasonably well, and the Friedel-like oscillations in the region $z\to\infty$ behave as they should, i.e., they are of greater amplitude and longer wavelength for lower electron concentration[52] (or higher r_s). Note that, in general, oscillations of $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ persist to quite large depths (>20 Å) inside the metal.[53] This behavior presumably stems from the use of a model conductivity tensor which has no absorptive part in the bulk region [an idea which is at present being checked by introducing a relaxation time τ into Eq. (3.2) for $\sigma(z, z'; \omega)$].

Before leaving Fig. 1, it is worth remarking on the physical significance of $\mathrm{Im}\,A^{z}_{k_{\parallel}\to 0,\omega}(z)$, a quantity which can apparently be quite large within a few Å of the surface. Classically, for light incident on a solid whose dielectric constant is a real number, e.g., $1-\omega_p^2/\omega^2$, $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ is everywhere either in phase or 180° out of phase with $A^{z}_{k_{\parallel}\to 0,\omega}(z\to\infty)$. Thus if $A^{z}_{k_{\parallel}\to 0,\omega}(z\to\infty)$ equals 1, then $A^{z}_{k_{\parallel}\to 0,\omega}(z\to\infty)$ is everywhere real. Microscopically, by virtue of the satisfaction of Eq. (2.46b), it is still true that $A^{z}_{k_{\parallel}\to 0,\omega}(z\to\pm\infty)$ are either in phase or 180° out of phase. However, there is no longer any guarantee as to the phase of $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ for z near the surface. Thus in the microscopic case, the quantity

$$\varphi^{z}_{k_{\parallel}\to 0,\omega}(z) \equiv \tan^{-1}\left[\mathrm{Im}\,A^{z}_{k_{\parallel}\to 0,\omega}(z)/\mathrm{Re}\,A^{z}_{k_{\parallel}\to 0,\omega}(z)\right] \quad (4.1)$$

should be interpreted as the phase of $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ relative to that at $z\to\infty$; as can be seen in Fig. 1, for example, this phase can be far from 0° or 180° in the surface region, and it varies rapidly there. Similarly, the magnitude of $A^{z}_{k_{\parallel}\to 0,\omega}(z)$,

$$\left|A^{z}_{k_{\parallel}\to 0,\omega}(z)\right| \equiv \left\{\left[\mathrm{Re}A^{z}_{k_{\parallel}\to 0,\omega}(z)\right]^2 + \left[\mathrm{Im}A^{z}_{k_{\parallel}\to 0,\omega}(z)\right]^2\right\}^{1/2}, \quad (4.2)$$

also varies sharply near the surface and can overshoot its asymptotic value, 1, by 50% or more in its initial peak at the surface.

The spatial behavior of $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ is not only markedly nonclassical in the surface region, but also this behavior changes rapidly as a function of photon frequency. The frequency-dependence of $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ is exhibited in Figs. 2 and 3, which were calculated, respectively, for frequencies below and above ω_p, for $r_s = 2$, using the Lang-Kohn potential barrier.[51]

In Fig. 2 it is seen that below the plasma frequency [where $\epsilon^{T}(0, \omega) < 0$], $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ has a sharp peak near surface and then relaxes to its $z\to\infty$ value via Friedel-like oscillations.[54] The strength of the initial peak appears to be quite strongly frequency dependent, and indeed it seems to disappear entirely for frequencies near to (but smaller than) ω_p. This behavior should certainly be observable, for example, in a measurement of surface photoelectric yield versus frequency.[25] Above the plasma frequency, the large initial peak in $A^{z}_{k_{\parallel}\to 0,\omega}(z)$ does not reappear; at the same time the decaying Friedel oscillations in the bulk region ($z\to$ "∞") are completely overshadowed by non-decaying ones. These oscillations above ω_p clearly represent bulk

plasmons.[55] From their amplitude one easily obtains a prediction of the strength vs. frequency of the direct photoexcitation of bulk plasmons, a measurable surface property,[50,56] which may be expected to yield useful surface electronic structure information.) In both frequency ranges, $\omega \gtrless \omega_p$, as noted above, it is to be expected that the introduction of a finite relaxation time into the model $\sigma(z, z'; \omega)$ will cause a damping of the oscillations of $A^z_{k_\parallel \to 0, \omega}(z)$ as $z \to \infty$. The degree to which this effect is important is being studied at present.

A final phenomenological question concerning the behavior of $A^z_{k_\parallel \to 0, \omega}$ is its sensitivity to potential barrier shape. In particular, it is important to know, for a given electron concentration (i.e., for a given metal), the extent to which a measurement bearing on the spatial behavior of $A^z_{k_\parallel \to 0, \omega}(z)$ will contain surface electronic structure information. A partial answer to this question is contained in the curves of Figs. 4 and 5. In Fig. 4 is shown the forms of $A^z_{k_\parallel \to 0, \omega}$ which correspond to $r_s = 2$ and $\hbar\omega = 13.125$ eV, and to the surface-potential barriers $V(z)$ given by

$$V(z) = -16.4 \text{ eV}/(1 + e^{-[(z/a)+(z/5a)^3]}), \qquad (4.3)$$

with $a = 0.33$, 0.66, and 0.99 Å. [For all three values of a, $V(z)$ agrees with the $r_s = 2$ Lang-Kohn potential[51] at $z = \pm\infty$. For $a = 0.66$ Å, $V(z) = V_{LK}(z; r_s = 2)$ at the two values of z, where $V(z) = -0.1 \times 16.4$ eV and -0.9×16.4 eV.] In Fig. 5 is shown the static electron densities $n_0(z)$ and dn_0/dz corresponding to the potentials used in Fig. 4.

The curves of Fig. 5(a) indicate that, as one might expect, $n_0(z)$ rises more gradually for a more diffuse surface-potential barrier. However, in Fig. 5(b) one sees that even so the value of z at which $n_0(z)$ is rising most rapidly (a value which may reasonably be considered as the mean surface position) is independent of a. Thus the three potentials used correspond to electron surfaces in the same mean position, but of differing diffuseness. Returning to Figs. 4, then, one sees that for surfaces of different diffuseness the spatial behavior of $A^z_{k_\parallel \to 0, \omega}(z)$ is markedly different, and thus that $A^z_{k_\parallel \to 0, \omega}(z)$ is strongly surface-structure sensitive.

To this point, the discussion of the calculated behavior of $A^z_{k_\parallel \to 0, \omega}(z)$ has been entirely phenomenological. In contrast, Figs. 6 and 7 are intended to provide some insight into the physics which underlies this behavior. Figure 6 is a comparison of $\mathrm{Re}(dA^z_{k_\parallel \to 0, \omega}/dz)$ at a photon energy (9.1875 eV) below $\hbar\omega_p$ ($r_s = 2$), with the static electron-density derivative dn_0/dz. (Both curves are calculated for $r_s = 2$ using the appropriate Lang-Kohn potential barrier.[51]) According to Poisson's equation, in the limit $|k_\parallel| \to 0$, one has that

$$\frac{dA^z_{k_\parallel \to 0, \omega}(z)}{dz} = -\frac{4\pi c}{i\omega}\, \delta n_{k_\parallel \to 0, \omega}(z), \qquad (4.4)$$

in which $\delta n_{k_\parallel \to 0, \omega}(z)$ is the charge-density fluctuation at z of frequency ω. Thus the fact that the large initial peaks in $\mathrm{Re}[dA^z_{k_\parallel \to 0, \omega}(z)/dz]$ and dn_0/dz line up with each other in Fig. 6 implies that $\delta n_{k_\parallel \to 0, \omega}(z)$ has an imaginary part roughly of the form

$$-\alpha \frac{\omega}{4\pi c n_\infty} \frac{dn_0}{dz},$$

where α is a proportionality constant.

In Fig. 7, for the same r_s and $\hbar\omega$, $\mathrm{Im}[dA^z_{k_\parallel \to 0, \omega}(z)/dz]$ is compared to the function $(0.23 \text{ Å} - z)\, dn_0/dz$, and by virtue of the choice of the distance parameter 0.23 Å in the comparison function, the two curves again look reasonably similar in the surface region. (The value 0.23 Å was chosen by requiring the ratio of initial peak height to initial trough depth to be the same for the two curves.) Thus, again making use of Eq. (4.3), one sees that the real part of $\delta n_{k_\parallel \to 0, \omega}(z)$ behaves roughly as

$$\beta\left(\frac{\omega}{4\pi c n_\infty}\right)(0.23 \text{ Å} - z)\, \frac{dn_0}{dz}.$$

Combining the results of Figs. 6 and 7 (and making use of the smallness of ω/c), one finally obtains the expression

$$\delta n_{k_\parallel \to 0, \omega}(z) \approx n_0\{z(1 - \beta\omega/4\pi c n_\infty) + [i\alpha + (0.23 \text{ Å})\beta]\omega/4\pi c n_\infty\} - n_0(z), \qquad (4.5)$$

which provides a straightforward interpretation of the metal's response to the external electromagnetic field. In particular the response consists of a rigid motion of the mean electron surface with an amplitude $i\alpha + (0.23 \text{ Å})\beta$, plus an electron-surface-thickness oscillation with an amplitude $\beta\omega/4\pi c n_\infty$.

Similar comparisons between $dA^z_{k_\parallel \to 0, \omega}(z)/dz$ and dn_0/dz can be made at any frequency sufficiently fa below ω_p because (cf. Fig. 2) in this frequency range the initial peaks at the surface are always the most striking feature of $A^z_{k_\parallel \to 0, \omega}(z)$. It remains then to interpret the disappearance of the surface peaks above $\hbar\omega$. A proposed interpretation is as follows: Below ω_p the bulk electron gas is effectively incompressible. Therefore for imposed fields with $\omega < \omega_p$ either the bulk electrons can all move together, giving rise to an oscillation in surface position, or the surface electrons can compress and dilate, giving rise to surface thickness oscillations. Thus for $\omega < \omega_p$ the solid's response must be localized at the surface and should be roughly of the form given in Eq. (4.5). Above ω_p, however, the induced charge fluctuation cannot be localized at the surface because plasmons exist to transport charge oscillating at frequency ω to the interior. Thus $\delta n_{k_\parallel \to 0, \omega}$ no longer peaks strongly at the surface for $\omega > \omega_p$

V. PROSPECTS

Within the limitations imposed by the assumption of a flat surface and a free-electron metal, the

calculations reported here provide a foundation for evaluating a number of experimentally observable quantities. Among these are surface photoelectric currents (versus electron exit angle and energy and versus photon frequency), and off-normal-incidence reflectivity. Calculations of these effects are in progress, and will be reported shortly.[25,50]

APPENDIX A

This appendix comprises a derivation of Eq. (3.9) as a consequence of Eq. (3.8). That is, using Eq. (3.11) for $\sigma(z, z'; \omega)$, and defining the quantity $\bar{\sigma}(z; \omega)$ by[57]

$$\bar{\sigma}(z;\omega)\equiv\int dz'\,\sigma(z,z';\omega), \tag{A1}$$

it is shown that

$$\lim_{z\to\infty}\bar{\sigma}(z;\omega)=-e^2n_\infty/i\omega m. \tag{A2}$$

In order to carry out the proof, it is necessary to evaluate, in the limit as $z\to\infty$, the quantity $F_{\kappa,\omega}(z)$ defined by

$$F_{\kappa,\omega}(z)\equiv j^+_{\kappa,\omega}(z)\int_{-\infty}^{z}dz'\,j^-_{\kappa,\omega}(z') +j^-_{\kappa,\omega}(z)\int_{z}^{\infty}dz'\,j^+_{\kappa,\omega}(z'), \tag{A3}$$

in terms of which [cf., Eq. (3.11)] $\bar{\sigma}(z;\omega)$ may be expressed in the form

$$\bar{\sigma}(z;\omega)=-\frac{e^2}{i\omega m}\frac{\hbar^2}{4\pi^2m}\int_0^{k_F}d\kappa\,(k_F^2-\kappa^2)\times\left(\frac{F_{\kappa,\omega}(z)}{W_+(\kappa)}+\frac{F^*_{\kappa,-\omega}(z)}{W^*_-(\kappa)}\right). \tag{A4}$$

Thus one considers the behavior as $z\to\infty$ of the integrals $J^\pm_{\kappa,\omega}(z)$ defined by

$$J^\pm_{\kappa,\omega}(z)\equiv\int_z^\infty dz'\,j^+_{\kappa,\omega}(z') \tag{A5a}$$

and

$$J^-_{\kappa,\omega}(z)\equiv\int_\infty^z dz'\,j^-_{\kappa,\omega}(z'). \tag{A5b}$$

The asymptotic behavior of $J^+_{\kappa,\omega}(z)$ is easy to obtain because in Eq. (A5a) z' is always greater than z. Thus assume that z is sufficiently large that the single-electron potential $V(z)$ [cf., Eqs. (3.4) and (3.13)] has achieved its constant value $-V_0$ for the jellium interior. The wave functions $\Psi_\kappa(z)$ and $\Psi^+_{\omega_{\kappa^+\omega}}$ may then be written in their asymptotic forms[58]:

$$\Psi_\kappa(z\to\infty)\approx\sin(\kappa z+\delta_\kappa) \tag{A6a}$$

and

$$\Psi^+_{\omega_{\kappa^+\omega}}(z\to\infty)\approx t^+_{\omega_{\kappa^+\omega}}\exp[i(\kappa^2+2m\omega/\hbar)^{1/2}z], \tag{A6b}$$

where δ_κ and $t^+_{\omega_{\kappa^+\omega}}$ are, respectively, a phase shift and a transmission amplitude which depend on the form of $V(z)$.

Substituting Eqs. (A6) into Eq. (3.12), and substituting the result into Eq. (A5a), one finds that

$$J^+_{\kappa,\omega}(z\to\infty)=t^+_{\omega_{\kappa^+\omega}}\int_z^\infty dz'\exp[i(\kappa^2+2m\omega/\hbar)^{1/2}z][i(\kappa^2+2m\omega/\hbar)^{1/2}\sin(\kappa z+\delta_n)+\kappa\cos(\kappa z+\delta_\kappa)]. \tag{A7}$$

Although the z' integral in Eq. (A7) appears to be ill defined, one recalls [cf., Eq. (3.2)] that the wave vector $(\kappa^2+2m\omega/\hbar)^{1/2}$ is, in fact, an abbreviation for

$$[\kappa^2+(2m/\hbar)(\omega+i\delta)]^{1/2}=(\kappa^2+2m\omega/\hbar)^{1/2}+i\delta m/\hbar(\kappa^2+2m\omega/\hbar)^{1/2}+\cdots, \tag{A8}$$

whose infinitesimal positive imaginary part permits one to obtain the well-defined expression for $J^+_{\kappa,\omega}(z)$,

$$J^+_{\kappa,\omega}(z\to\infty)=-(\hbar/m\omega)\,t^+_{\omega_{\kappa^+\omega}}\exp[i(\kappa^2+2m\omega/\hbar)^{1/2}z][(\kappa^2+m\omega/\hbar)\sin(\kappa z+\delta_\kappa)+i\kappa(\kappa^2+2m\omega/\hbar)^{1/2}\cos(\kappa z+\delta_\kappa)], \tag{A9}$$

or, making use of Eqs. (A6),

$$J^+_{\kappa,\omega}(z\to\infty)=-\frac{\hbar}{m\omega}\left(\frac{d\Psi^+_{\omega_{\kappa^+\omega}}}{dz}\frac{d\Psi_\kappa}{dz}-\Psi^+_{\omega_{\kappa^+\omega}}(z)\frac{d^2\Psi_\kappa}{dz^2}\right)-\Psi^+_{\omega_{\kappa^+\omega}}(z)\,\Psi_\kappa(z). \tag{A10}$$

In order to evaluate $\bar{\sigma}(z\to\infty;\omega)$ [cf., Eq. (A4)], one also needs the quantity $J^{+*}_{\kappa,-\omega}(z\to\infty)$. For values of $\kappa^2>2m\omega/\hbar$, the wave function $\Psi^{+*}_{\omega_{\kappa-\omega}}(z)$ behaves asymptotically according to

$$\Psi^{+*}_{\omega_{\kappa-\omega}}(z\to\infty)=t^{+*}_{\omega_{\kappa-\omega}}\exp[-i(\kappa^2-2m\omega/\hbar)^{1/2}z], \tag{A11}$$

in which as above, the wave vector $(\kappa^2-2m\omega/\hbar)^{1/2}$ is to be interpreted as

$$[\kappa^2-(2m/\hbar)(\omega+i\delta)]=(\kappa^2-2m\omega/\hbar)^{1/2}-i\delta m/\hbar(\kappa^2-2m\omega/\hbar)^{1/2}+\cdots. \tag{A12}$$

Making use of Eq. (A12), one finds for $J^{+*}_{\kappa,-\omega}(z)$ that

$$J^{+*}_{\kappa,\omega}(z\to\infty)=\frac{\hbar}{m\omega}\left(\frac{d\Psi^{+*}_{\omega_{\kappa-\omega}}}{dz}\frac{d\Psi_\kappa}{dz}-\Psi^{+*}_{\omega_{\kappa-\omega}}(z)\frac{d^2\Psi_\kappa}{dz^2}\right)-\Psi^{+*}_{\omega_{\kappa-\omega}}(z)\,\Psi_\kappa(z), \tag{A13}$$

or, just what one would obtain by replacing ω by $-\omega$ and complex conjugation in Eq. (A10). In

the event that $\kappa^2 > 2m\omega/\hbar$ (which can obviously happen if $\hbar\omega < \hbar^2 k_F^2/2m$), Eq. (A13) remains valid, though the asymptotic form of $\Psi^{**}_{\omega_\kappa - \omega}(z)$ then becomes

$$\Psi^{**}_{\omega_\kappa - \omega}(z \to \infty) = t^{**}_{\omega_\kappa - \omega} \exp[-(2m\omega/\hbar - \kappa^2)^{1/2} z]. \quad \text{(A14)}$$

The evaluation of $\bar{\sigma}(z \to \infty;\ \omega)$ is completed by calculating the asymptotic behavior of the integrals $J^{-}_{k_F,\omega}(z)$ and $J^{-*}_{k_F,-\omega}(z)$. A new difficulty in this case is that although z may be large, the range of z' in the relevant integral, cf., Eq. (A5b) is not confined to the asymptotic region. Thus, in order to obtain a useful expression for $J^{-}_{k_F,\omega}(z \to \infty)$, one breaks the z' integration of Eq. (A5b) into two parts, writing

$$J^{-}_{k_F,\omega}(z) = \int_{-\infty}^{Z} dz'\, j^{-}_{k_F,\omega}(z') + \int_{Z}^{z} dz'\, j^{-}_{k_F,\omega}(z'), \quad \text{(A15)}$$

where

$$V(z) \approx -V_0, \quad z \geq Z. \quad \text{(A16)}$$

The first term on the right-hand side of Eq. (A16) is a perfectly well-defined constant, by virtue of the exponential decay of $\Psi_\kappa(z)$ as $z \to -\infty$. The second term, because of Eq. (A16), may be evaluated explicitly using the asymptotic forms of $\Psi_\kappa(z)$ [given in Eq. (A6a)] and of $\Psi^{-}_{\omega_\kappa - \omega}(z)$,

$$\Psi^{-}_{\omega_\kappa - \omega}(z \to \infty) = \exp[-i(\kappa^2 + 2m\omega/\hbar)^{1/2} z] + r^{-}_{\omega_\kappa + \omega} \exp[i(\kappa^2 + 2m\omega/\hbar)^{1/2} z]. \quad \text{(A17)}$$

Using Eqs. (3.12), (A6a), and (A17), then one finds that

$$\int_{Z}^{z} dz'\, j^{-}_{k_F,\omega}(z') = \left[\frac{\hbar}{m\omega}\left(\frac{d\Psi^{-}_{\omega_\kappa + \omega}}{dz'}\frac{d\Psi_\kappa}{dz'} - \Psi^{-}_{\omega_\kappa + \omega}(z')\frac{d^2\Psi_\kappa}{dz'^2}\right) + \Psi^{-}_{\omega_\kappa + \omega}(z')\Psi_\kappa(z)\right]^{z'=z}_{z'=Z}, \quad \text{(A18a)}$$

and similarly, that

$$\int_{Z}^{z} dz'\, j^{-*}_{k_F,-\omega}(z') = \left[\frac{-\hbar}{m\omega}\left(\frac{d\Psi^{-*}_{\omega_\kappa - \omega}}{dz'}\frac{d\Psi_\kappa}{dz'} - \Psi^{-*}_{\omega_\kappa - \omega}(z')\frac{d^2\Psi_\kappa}{dz'^2}\right) + \Psi^{-*}_{\omega_\kappa - \omega}(z')\Psi_\kappa(z')\right]^{z'=z}_{z'=Z}. \quad \text{(A18b)}$$

At this point one has all the information necessary to compute the quantities $F_{\kappa,\omega}(z \to \infty)$ and $F^{*}_{k_F,-\omega}(z \to \infty)$ which are needed in Eq. (A4). Using Eqs. (3.12), (3.14), (A10), and (A18a), for example, one easily finds that

$$F_{\kappa,\omega}(z \to \infty) = \frac{2m}{\hbar^2} W_+(\kappa)\left\{\frac{\hbar}{m\omega}\left[\left(\frac{d\Psi_\kappa}{dz}\right)^2 - \Psi_\kappa(z)\frac{d^2\Psi_\kappa}{dz^2}\right] + \Psi^2_\kappa(z)\right\} + j^{+}_{k_F,\omega}(z)\, R_{k_F,\omega}(Z), \quad \text{(A19)}$$

where $R_{k_F,\omega}(Z)$ is defined by

$$R_{k_F,\omega}(Z) \equiv \int_{-\infty}^{Z} dz'\, j^{-}_{k_F,\omega}(z') - \frac{\hbar}{m\omega}\left(\frac{d\Psi^{-}_{\omega_\kappa + \omega}}{dZ}\frac{d\Psi_\kappa}{dZ} - \Psi^{-}_{\omega_\kappa + \omega}(Z)\frac{d^2\Psi_\kappa}{dZ^2}\right) + \Psi^{-}_{\omega_\kappa + \omega}(Z)\Psi_\kappa(Z). \quad \text{(A20)}$$

Similarly, one finds that

$$F^{*}_{k_F,-\omega}(z \to \infty) = \frac{2m}{\hbar^2} W_-(\kappa)\left\{\frac{-\hbar}{m\omega}\left[\left(\frac{d\Psi_\kappa}{dz}\right)^2 - \Psi_\kappa(z)\frac{d^2\Psi_\kappa}{dz^2}\right] + \Psi^2_\kappa(z)\right\} + j^{+*}_{k_F,-\omega}(z)\, R^{*}_{k_F,-\omega}(Z). \quad \text{(A21)}$$

Thus, substituting Eqs. (A20) and (A21) into Eq. (A4), and using Eq. (3.7), one finds that

$$\bar{\sigma}(z \to \infty;\ \omega) = -e^2 n_\infty / i\omega m + R(z \to \infty;\ \omega), \quad \text{(A22)}$$

where

$$R(z;\ \omega) \equiv -\frac{e^2}{i\omega m}\frac{\hbar^2}{8\pi^2 m}\int_0^{k_F} d\kappa\,(k_F^2 - \kappa^2)\left(\frac{1}{W_+(\kappa)} j^{+}_{k_F,\omega}(z)\, R_{k_F,\omega}(Z) + \frac{1}{W^{*}_{-}(\kappa)} j^{+*}_{k_F,-\omega}(z)\, R^{*}_{k_F,-\omega}(Z)\right). \quad \text{(A23)}$$

Clearly, if one can show that

$$R(z \to \infty;\ \omega) = 0, \quad \text{(A24)}$$

then (A22) is identical to Eq. (A2) and the proof is complete. What follows, therefore, is a demonstration that Eq. (A24) is true.

The asymptotic properties of $R(z;\omega)$ are governed by both the behavior of $j^{+}_{\kappa,\omega}(z)$ and $j^{+*}_{k_F,-\omega}(z)$, and the analytic properties of the functions of κ, $R_{\kappa,\omega}(Z)$, and $R^{*}_{k_F,-\omega}(Z)$. Recalling the definition of $R_{\kappa,\omega}(Z)$, Eq. (A20), one notes that because $\Psi_\kappa(z)$ falls exponentially to zero as $z \to \infty$, for $0 \leq \kappa \leq k_F$, $R_{\kappa,\omega}(Z)$ is an analytic function of κ in the neighborhood of the segment $(0, k_F)$ of the real κ axis. At the same time, as $z \to \infty$,

$$j^{+}_{\kappa,\omega}(z\to-\infty)=t^{+}_{\omega_{\kappa'}+\omega}\exp[i(\kappa^2+2m\omega/\hbar)^{1/2}z][i(\kappa^2+2m\omega/\hbar)^{1/2}\sin(\kappa_z+\delta_\kappa)+\kappa\cos(\kappa_z+\delta_\kappa)]\,. \tag{A25}$$

Thus one can easily show,[59] using the Riemann-Lebesgue lemma,[60] that as $z\to-\infty$, the term in Eq. (A23) involving $j^{+}_{\kappa,\omega}(z)$ behaves as

$$z^{-2}(C_1\exp\{iz[(k_F^2+2m\omega/\hbar)^{1/2}+k_F]\}+C_2\exp\{iz[(k_F^2+2m\omega/\hbar)^{1/2}-k_F]\})\,, \tag{A26}$$

where C_1 and C_2 are constants.

Similarly, if $k_F^2>2m\omega/\hbar$, one finds that the term involving $j^{+}_{\kappa,-\omega}(z)$ in Eq. (A23) behaves asymptotically as

$$z^{-2}(C_3\exp\{iz[(k_F^2-2m\omega/\hbar)^{1/2}+k_F]\}+C_4\exp\{iz[(k_F^2-2m\omega/\hbar)^{1/2}-k_F]\}), \tag{A27}$$

and, in particular, that no difficulty arises in the κ integral at the point $\kappa=(2m\omega/\hbar)^{1/2}$. Finally, if $k_F^2<2m\omega/\hbar$, instead of Eq. (A27) one finds that the $j^{+}_{\kappa,-\omega}(z)$ term in Eq. (A23) gives rise to an asymptotic behavior of $R(z;\omega)$ of the form

$$z^{-2}(\bar{C}_3\exp\{z[-(2m\omega/\hbar-k_F^2)^{1/2}+ik_F]\}+\bar{C}_4\exp\{z[-(2m\omega/\hbar-k_F^2)^{1/2}-ik_F]\}). \tag{A28}$$

The important feature of Eqs. (A26)–(A28) is that all of these terms vanish as $z\to-\infty$, implying that $R(z;\omega)$ vanishes as $z\to-\infty$, which was to be proven. Thus Eq. (A2) is established as being correct.

APPENDIX B

In this appendix, Eq. (3.11) is shown to be a consequence of Eq. (3.2).

The first step in the proof is an interchange of dummy indices in Eq. (3.2), leading to the equivalent equation

$$\sigma(z,z';\omega)=-\frac{e^2}{i\omega}\left[\frac{n_0(z)}{m}\,\delta(z-z')+\frac{2}{\hbar}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2\,d\kappa'}{\pi}\,\Theta_{k,\kappa'}\int_\kappa\left(\frac{j_{\kappa'\kappa}(z)j_{\kappa\kappa'}(z')}{\omega+i\delta-\omega_\kappa+\omega_{\kappa'}}-\frac{j_{\kappa\kappa'}(z)j_{\kappa'\kappa}(z')}{\omega+i\delta-\omega_{\kappa'}+\omega_\kappa}\right)\right]. \tag{B1}$$

One proceeds by making use of the spectral representations of the outgoing and incoming Green's functions $G^{\pm}(z,z';\Omega)$, viz.,

$$G^{\pm}(z,z';\Omega)=\frac{1}{\hbar}\int_\kappa\frac{\Psi_\kappa(z)\Psi_\kappa^*(z')}{\Omega\pm i\delta-\omega_\kappa}\,, \tag{B2}$$

in terms of which Eq. (B1) can be written more compactly. Specifically, substituting Eq. (B2) into Eq. (B1), one obtains the formula

$$\frac{4\pi i\,\sigma(z,z';\omega)}{\omega}=-\frac{\omega_p^2}{\omega^2}\left(\frac{n_0(z)}{n_\infty}\,\delta(z-z')-\frac{\hbar^2}{2mn_\infty}\int\frac{d^2k}{(2\pi)^2}\int_0^\infty\frac{2\,d\kappa'}{\pi}\,\Theta_{k\kappa'}\lim_{z_1,z_2\to z}\lim_{z_3,z_4\to z'}\left(\frac{\partial}{\partial z_1}-\frac{\partial}{\partial z_2}\right)\left(\frac{\partial}{\partial z_3}-\frac{\partial}{\partial z_4}\right)\right.$$
$$\left.\times\{\Psi_{\kappa'}(z_1)\Psi_{\kappa'}(z_4)[G^{+}(z_2,z_3;\omega+\omega_{\kappa'})+G^{-}(z_2,z_3;-\omega+\omega_{\kappa'})]\}\right)\,. \tag{B3}$$

[In writing Eq. (B3), the wave functions $\Psi_{\kappa'}(z)$ have been assumed to be real. This assumption is possible since the Fermi factor $\Theta_{k\kappa'}$ forces $\hbar\omega_{\kappa'}$ to be below the vacuum level.]

The next steps in the derivation of Eq. (3.11) involve the use of the explicit representations of $G^{\pm}(z,z';\Omega)$,

$$G^{+}(z,z';\Omega)=\frac{1}{W(\Omega)}[\Psi_\Omega^{+}(z)\Psi_\Omega^{-}(z')\Theta(z-z')+\Psi_\Omega^{+}(z')\Psi_\Omega^{-}(z)\Theta(z'-z)]\,, \tag{B4}$$

and a similar expression for $G^{-}(z,z';E)$ which is obtained from Eq. (B4) using the relation [cf., Eq. (B2)],

$$G^{-}(z,z';\Omega)=[G^{+}(z,z';\omega)]^*\,, \tag{B5}$$

where the $\Psi_\Omega^{\pm}(z)$ have been defined in Eq. (3.13), and the Wronskian $W(\Omega)$ is defined by

$$W(\Omega)\equiv\frac{\hbar^2}{2m}\left(\frac{d\Psi_\Omega^{+}(z)}{dz}\,\Psi_\Omega^{-}(z)-\Psi_\Omega^{+}(z)\,\frac{d\Psi_\Omega^{-}}{dz}\right). \tag{B6}$$

Equation (B4) and the corresponding equation for $G^{-}(z,z';\Omega)$ are, of course, direct consequences of the differential equation satisfied by $G^{\pm}(z,z';\Omega)$, namely,

$$\left(\hbar\Omega+\frac{\hbar^2}{2m}\,\frac{d^2}{dz^2}-V(z)\right)G^{\pm}(z,z';\Omega)=\delta(z-z')\,. \tag{B7}$$

According to Eq. (B4), one has that

$$\frac{d}{dz}G^{+}(z,z';\Omega)=\frac{1}{W(\Omega)}\left(\frac{d\Psi_{\Omega}^{+}(z)}{dz}\Psi_{\Omega}^{-}(z')\Theta(z-z')+\Psi_{\Omega}^{+}(z')\frac{d\Psi_{\Omega}^{-}}{dz}\Theta(z'-z)\right), \tag{B8}$$

and consequently, that

$$\frac{d^2}{dz\,dz'}G^{+}(z,z';\Omega)=\frac{1}{W(\Omega)}\left(\frac{d\Psi_{\Omega}^{+}(z)}{dz}\frac{d\Psi_{\Omega}^{-}(z')}{dz'}\Theta(z-z')+\frac{d\Psi_{\Omega}^{+}(z')}{dz'}\frac{d\Psi_{\Omega}^{-}(z)}{dz}\Theta(z'-z)\right)-\frac{2m}{\hbar^2}\delta(z-z'). \tag{B9}$$

Using Eq. (B8), the analogous equation for $dG^{+}(z,z';\Omega)/dz'$, and finally, Eq. (B9), one sees that

$$\lim_{z_1,z_2\to z}\lim_{z_3,z_4\to z'}\left(\frac{\partial}{\partial z_1}-\frac{\partial}{\partial z_2}\right)\left(\frac{\partial}{\partial z_3}-\frac{\partial}{\partial z_4}\right)\Psi_{\kappa'}(z_1)\Psi_{\kappa'}(z_4)G^{+}(z_2,z_3;\omega+\omega_{\kappa'})$$

$$=-\frac{1}{W_{+}(\kappa')}\left[\Theta(z-z')\,j_{\kappa',\omega}^{+}(z)\,j_{\kappa',\omega}^{-}(z')+\Theta(z'-z)\,j_{\kappa',\omega}^{+}(z')\,j_{\kappa',\omega}^{-}(z)\right]+\frac{2m}{\hbar^2}\delta(z-z'), \tag{B10}$$

where $W_{+}(\kappa')$ and the $j_{\kappa',\omega}^{\pm}(z)$ have been defined, respectively, in Eqs. (3.14) and (3.12). Taking the complex conjugate of Eq. (B10) and replacing ω by $-\omega$, one obtains an equation equivalent to Eq. (B10) for the incoming Green's function. Substituting these two equations into Eq. (B3) one finds that the δ-function terms all cancel,[61] and finally, therefore, that Eq. (B3) is identical to Eq. (3.11), which was to be proven.

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[1]J. E. Demuth and D. E. Eastman, Phys. Rev. Lett. 32, 1123 (1974).

[2]E. W. Plummer, Proceedings of the Meeting of the Electrochemical Society, San Francisco, May 1974 (unpublished); Chem. Phys. Lett. (to be published).

[3]M. M. Traum, N. V. Smith, and F. J. DiSalvo, Phys. Rev. Lett. 32, 1241 (1974).

[4]J. W. Gadzuk, Solid State Commun. (to be published); Phys. Rev. B (to be published).

[5]A. Liebsch, Phys. Rev. Lett. 32, 1203 (1974).

[6]P. J. Feibelman and D. E. Eastman, Phys. Rev. B 10, 4932 (1974).

[7]G. D. Mahan, Phys. Rev. B 2, 4334 (1970).

[8]W. L. Schaich and N. W. Ashcroft, Phys. Rev. B 3, 2452 (1971).

[9]J. A. Appelbaum and D. R. Hamann, Phys. Rev. B 6, 2166 (1972); Phys. Rev. Lett. 31, 106 (1973).

[10]G. P. Alldredge and L. Kleinman, Phys. Rev. B 10, 559 (1974); Phys. Rev. Lett. 28, 1264 (1972); E. Caruthers, L. Kleinman, and G. P. Alldredge, Phys. Rev. B 8, 4570 (1973); B 9, 3325 (1974); B 9, 3330 (1974).

[11]G. E. Laramore, C. B. Duke, A. Bagchi, and A. B. Kunz, Phys. Rev. B 4, 2058 (1971).

[12]D. W. Jepsen, P. M. Marcus, and F. Jona, Phys. Rev. B 6, 3684 (1972); B 5, 3933 (1972); Phys. Rev. Lett. 26, 1365 (1971).

[13]S. Y. Tong and T. N. Rhodin, Phys. Rev. Lett. 26, 711 (1971).

[14]J. B. Pendry, J. Phys. C 4, 2515 (1971).

[15]The main question is the extent to which the surface-potential barrier must be described self-consistently in this lower-energy range.

[16]For a review of optical constants of a wide variety of materials, see P. O. Nilsson, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1974), Vol. 29.

[17]The importance of this effect in uv photoemission spectroscopy has been stressed by E. W. Plummer, Proceedings of the Physical Electronics Conference, Murray Hill, N. J., Feb. 1974 (unpublished); and by P. J. Feibelman, Surf. Sci. 46, 558 (1974).

[18]A. R. Melnyk and M. J. Harrison, Phys. Rev. B 2, 835 (1970); B 2, 851 (1970).

[19]N. Wiser, Phys. Rev. 129, 62 (1963); S. L. Adler, Phys. Rev. 126, 413 (1962).

[20]J. A. Van Vechten and Richard M. Martin, Phys. Rev. Lett. 28, 446 (1972); W. Hanke and L. J. Sham, Phys. Rev. Lett. 33, 582 (1974).

[21]J. G. Endriz, Phys. Rev. B 7, 3464 (1973).

[22]K. L. Kliewer, Proceedings of the Conference on uv Photoemission, Hamburg, 1974 (unpublished); Phys. Rev. Lett. 33, 900 (1974).

[23]F. Forstmann, Z. Phys. 203, 495 (1967).

[24]Not the peak positions, however, which are determined by energy conservation.

[25]P. J. Feibelman, Phys. Rev. Lett. 34, 1092 (1975).

[26]J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1962).

[27]P. J. Platzman and P. A. Wolff, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1973), Suppl. 13.

[28]D. Pines and P. Nozières, *Theory of Quantum Liquids* (Benjamin, New York, 1966).

[29]Within the random-phase approximation (used in the present calculations; cf. Sec. III), for a jellium solid, plasmons of energies between $\hbar\omega_p$ and a critical energy $\hbar\omega_c$ (cf., Ref. 28), are undamped. For Al density, as an example, $\hbar\omega_p = 15.83$ eV and $\hbar\omega_c = 20.48$ eV.

[30]More precisely, Eq. (2.33) represents the most general solution to Eq. (2.18) with waves traveling in the $+z$ direction. Clearly Eq. (2.18) also has solutions corresponding to waves traveling in the $-z$ direction. These must be eliminated in the physical situation being considered.

[31]This substitution is valid since $z' \geq Z$ in Eq. (2.17) and since $\bar{\sigma}_{\vec{k}_{\parallel},\omega}(z',z'')$ is a short-ranged function of

$|z'-z''|$.

[32]The derivation of Eq. (2.34) involves the use of Eqs. (2.24), (2.25), and (2.20).

[33]One makes use of the fact that, by virtue of rotational invariance in the plane of the surface, the quantities $\sigma^{xx}_{\vec{k}_{\parallel},\omega}(z,z'')$ and $\sigma^{yy}_{\vec{k}_{\parallel},\omega}(z,z'')$ are of $O(k_x^2)$ and $O(k_y^2)$, respectively, as $\vec{k}_{\parallel}\to 0$.

[34]The derivation involves the use of Eqs. (2.23) and (2.28).

[35]The reader may wonder at this point where Eq. (2.14b) is to play a role in the calculation of $\vec{A}_{\vec{k}_{\parallel},\omega}(z)$. The answer is that Eq. (2.14b) can be used to normalize $\vec{A}_{\vec{k}_{\parallel},\omega}(z)$ to the strength of the incident photon beam.

[36]P. J. Feibelman, Phys. Rev. Lett. 30, 975 (1973).

[37]P. J. Feibelman, Surf. Sci. 40, 102 (1973).

[38]P. J. Feibelman, Phys. Rev. B 10, 5077 (1974), referred to as I in the text.

[39]See Ref. 38, Sec. 3.

[40]In Eq. (3.11), for example, this result can be seen to follow from the fact that $\hbar\omega_\kappa$ is below the vacuum level, which implies that $\psi_\kappa(z)$ vanishes exponentially as $z\to-\infty$.

[41]The method is described at length in Appendix B of Ref. 38.

[42]$\{k_\rho\}=\{\pm 2k_F,\ (k_F^2+2m\omega/\hbar)^{1/2}\pm k_F,\ \pm m\omega/\hbar k_F\}$, if $k_F^2<2m\omega/\hbar$, while $\{k_\rho\}=\{\pm 2k_F,\ (k_F^2+2m\omega/\hbar)^{1/2}\pm k_F,\ \pm m\omega/\hbar k_F,\ (k_F^2-2m\omega/\hbar)^{1/2}\pm k_F,\ -(k_F^2-2m\omega/\hbar)^{1/2}\pm k_F\}$ if $k_F^2>2m\omega/\hbar$. See Appendix B of Ref. 38 for the method by which these statements are proven. Also note that the presence of the term $T^{(L)}_{\vec{k}_{\parallel}0,\omega}e^{ik_\perp^{(L)}z}$ in Eq. (3.15) does not give rise to any new elements in the $\{k_\rho\}$. That this is true can be seen by consulting Table I of Ref. 38, which implies that for $k^{(I)}=k_\perp^{(L)}>0$, there will only be a new element in the $\{k_\rho\}$ if the equation $(\kappa^2-2m\omega/\hbar)^{1/2}+\kappa=k_\perp^{(L)}$, has a solution such that $0<\kappa<k_F$. But within the RPA (cf., Ref. 28), one has that $k_\perp^{(L)2}<2m\omega/\hbar$, while $(\kappa^2-2m\omega/\hbar)^{1/2}+\kappa=k_\perp^{(L)}$ only has solutions for $k_\perp^{(L)2}>2m\omega/\hbar$. Thus the possibility of plasmon excitation adds no new elements to $\{k_\rho\}$.

[43]Assuming that the homogeneous part of the equation has no solution; cf., the discussion below.

[44]The equations are linear because $\bar{A}(z)$ depends linearly on the $\{c_0,c_\rho\}$, according to Eq. (3.17).

[45]In Ref. 32. the set $\{z_{\rho'}\}$ was taken to include exactly P elements. (In Ref. 32, ω was well below the bulk-plasmon band; thus c_0 was identically zero and only the P constants $\{c_\rho\}$ were to be determined.) Because the sets $\{z_{\rho'}\}$ and $\{c_\rho\}$ contained the same number of elements, the values obtained for the $\{c_\rho\}$ in that reference were numerically quite noisy. This noise did not affect the results of Ref. 32 for surface-plasmon dispersion and and damping, and was therefore ignored. In the present context, however, since the bulk-plasmon amplitude c_0 is a measurable quantity {cf., Refs. 18, 22, as well as M. Anderegg, B. Feuerbacher, and B. Fitton, [Phys. Rev. Lett. 27, 1565 (1971)], and P. J. Feibelman (unpublished)}, it is interesting to determine the $\{c_0,c_\rho\}$ accurately. The least-square-fitting procedure, described in the text, in which $\{z_{\rho'}\}$ contained more elements than $\{c_0,c_\rho\}$, was used because it was found to provide a noise-free determination of the $\{c_0,c_\rho\}$.

[46]$k_\perp^{(L)'}$ satisfies Eq. (2.28).

[47]Since momentum conservation does not hold in the surface region, the reflection of a bulk plasmon may be accompanied by the creation of electron-hole pairs. Thus the reflection amplitude need not equal 1 and will, in general, depend on barrier shape [P. J. Feibelman, (unpublished)].

[48]See Ref. 38, Eq. (3.13), and the text which follows.

[49]The lower cutoff of the z'-integration is permitted by Eq. (3.18).

[50]P. J. Feibelman (unpublished).

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

[52]Similar results obtain for the static electron density, for example. See e.g., Ref. 51.

[53]The position $z=0$ in all the figures corresponding to Lang-Kohn potential barriers (Ref. 51) is taken to be at the edge of the positive-background charge density (which Lang and Kohn take to be geometrically sharp).

[54]See, for example, Eq. (3.15).

[55]See, for example, Eq. (2.33).

[56]The photoexcitation of bulk plasmons has been observed in their potassium films by M. Anderegg, B. Feuerbacher, and B. Fitton [Phys. Rev. Lett. 27, 1565 (1971)].

[57]Note that Eq. (A1) is identical to Eq. (3.21).

[58]Derived from Eqs. (3.4) and (3.13).

[59]Reference 38, Appendix A.

[60]M. J. Lighthill, *Introduction to Fourier Analysis and Generalized Functions* (Cambridge U. P., Cambridge, England, 1962).

[61]One makes use of Eq. (3.7).