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Optical reflectance of nonlocal systems

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A microscopic perturbative theory developed earlier for the electric field near the surface of a metal having a nonlocal dielectric tensor is extended beyond the Born approximation. Expressions are derived for the reflection amplitudes of s- and p-polarized light, and they are compared with the results of previous workers by taking appropriate limits. A new, general dispersion relation of surface plasmons is given which takes into account possible band-structure effects near the surface. The influence of this more accurate theory on formulas for differential reflectance from an absorbate-covered metal surface is indicated.

I. INTRODUCTION AND FORMALISM

In a previous paper[1] (hereafter referred to as I), we outlined a procedure for obtaining the electric field near the surface of a metal having a nonlocal dielectric response function when light of either s polarization (i.e., electric field perpendicular to the plane of incidence) or p polarization (i.e., electric field parallel to the plane of incidence) is incident upon it. Our approach was perturbative in nature, and we derived formulas within the first Born approximation for changes in the reflection amplitudes of a metal from the classical Fresnel formulas,[2] which are caused by the nonlocality of the dielectric response near its surface. We also obtained, within the same approximation, expressions for the differential reflectance of an absorbate-covered metal, which are of interest in experiments on surface reflectance spectroscopy (SRS). It has been pointed out by Sipe[3] that the first Born approximation neglects the coupling between the surface region and the bulk material because it ignores the effects of the induced field on the response. Starting from a different standpoint and formalism, he has derived formulas for the modification of the reflection amplitude when the coupling between the surface region and the bulk is taken into account. In this paper we show how the perturbation theory of I can be extended beyond the first Born approximation in order to treat the bulk-surface region coupling to all orders. We obtain formulas for the modified reflection amplitudes which, for s-polarized light, are identical to Sipe's,[3] but for p-polarized light are more general than his results. Finally, we discuss what consequences this more accurate theory has for expressions of differential reflectance from an adsorbate-covered metal.

Our aim, quite simply, is to solve Eqs. (4.16), (4.5), and (4.6) of I for the electric field components exactly, without making the Born approximation; the notation of I is used throughout. Beginning with the simpler case of s polarization, we rewrite Eq. (4.16) of I with the help of the definition of Eq. (4.17b) as

$$E_y(z)=U_y(z)-\frac{\omega^2}{c^2}E_y(z_0)\,G_{yy}(z,z_0)\,\Lambda_y(\omega)\,. \tag{1}$$

Physically this equation describes the electric field (pointing along y) of s-polarized light incident in the xz plane on a metal surface located at $z=z_0$. Evaluating Eq. (1) at $z=z_0$, we obtain the surface electric field as

$$E_y(z_0)=U_y(z_0)I_s\,, \tag{2a}$$

where, on using Eqs. (3.10)–(3.14) of I,

$$I_s=1\Big/\left(1-i\,\frac{\omega^2}{c^2}\,\frac{\Lambda_y}{q_z+k_z}\right)\,. \tag{2b}$$

Taking the limit of Eq. (1) far into the vacuum region ($z\to-\infty$), we obtain

$$E_y(z)\underset{z\to-\infty}{\sim}e^{iq_z\tilde{z}}+\left(r_s^0+i\,\frac{\omega^2}{c^2}\,\frac{2q_z\Lambda_y}{(q_z+k_z)^2}\,I_s\right)e^{-iq_z\tilde{z}}\,, \tag{3}$$

where $\tilde{z}=z-z_0$ and $r_s^0=(q_z-k_z)/(q_z+h_z)$ is the Fresnel reflection amplitude of s-polarized light. The modified reflection amplitude can now be written in essentially the same form as Eq. (4.24) of I but with a renormalized $\Lambda_y(\omega)$, viz.,

$$r_s=r_s^0\{1+[2iq_z/(1-\epsilon_b)]\tilde{\Lambda}_y(\omega)\} \tag{4a}$$

and

$$\tilde{\Lambda}_y(\omega)=\Lambda_y(\omega)I_s=\Lambda_y(\omega)\Big/\left[1-i\left(\frac{\omega^2}{c^2}\Lambda_y(\omega)\Big/(q_z+k_z)\right)\right]\,. \tag{4b}$$

The case of p-polarized light, while straightforward, is a little more cumbersome. The starting point now is Eqs. (4.5) and (4.6) of I, which, with the help of the definitions of Eqs. (4.11), may be written as

$$E_x(z)=U_x(z)-\frac{\omega^2}{c^2}\{E_x(z_0)\,G_{xx}(z,z_0)\,\Lambda_x+D_z(z_0)\,[G_{xz}(z,z'')\,\epsilon_\omega(z'')]_{z''\to z_0}(-\Lambda_z)\}\,, \tag{5a}$$

$$D_z(z)=\epsilon_\omega(z)U_z(z)-\frac{\omega^2}{c^2}\{E_x(z_0)\,\epsilon_\omega(z)\,G_{zx}(z,z_0)\,\Lambda_x+D_z(z_0)\epsilon_\omega(z)[G_{zz}(z,z'')\epsilon_\omega(z'')]_{z''\to z_0}(-\Lambda_z)\}\,. \tag{5b}$$

We now evaluate the fields at $z=z_0$ and make use of the limits given in Eqs. (4.12) of I. We obtain the coupled linear equations

$$E_x(z_0)(1+L_x)-D_z(z_0)\,L_z=U_x(z_0)\,, \tag{6a}$$

$$E_x(z_0)\,\frac{Q}{q_z}\,L_x+D_z(z_0)\left(1-\frac{Q}{q_z}\,L_z\right)=\epsilon_\omega(z_0)U_z(z_0)\,, \tag{6b}$$

where

$$L_x=\frac{\omega^2}{c^2}\,\alpha(1+r_p^0)(1-r_p^0)\Lambda_x\,, \tag{6c}$$

$$L_z=\frac{\omega^2}{c^2}\,\alpha(1+r_p^0)^2\left(\frac{Q}{q_z}\right)\Lambda_z\,, \tag{6d}$$

and

$$\alpha=-i(\epsilon_b q_z+k_z)/(4\epsilon_b\,\omega^2/c^2)\,. \tag{6e}$$

The solution of the system of linear equations of Eqs. (6a) and (6b) may be written as

$$E_x(z_0)=U_x(z_0)\,I_x\,, \tag{7a}$$

$$D_z(z_0)=\epsilon_\omega(z_0)\,U_z(z_0)\,I_z\,, \tag{7b}$$

where

$$I_x=\left(1-\frac{Q}{q_z}\,L_z+\frac{\epsilon_\omega(z_0)\,U_z(z_0)}{U_x(z_0)}\,L_z\right)\Big/\Delta\,, \tag{7c}$$

$$I_z=\left(1+L_x-\frac{Q}{q_z}\,\frac{U_x(z_0)}{\epsilon_\omega(z_0)U_z(z_0)}\,L_x\right)\Big/\Delta\,, \tag{7d}$$

and the determinant Δ can be simplified to

$$\Delta=1+L_x-(Q/q_z)L_z\,. \tag{7e}$$

We substitute Eqs. (7a) and (7b) in Eq. (5a) and take the limit $z\to-\infty$ to obtain

$$E_x(z)\underset{z\to-\infty}{\sim}e^{iq_z\tilde z}-e^{-iq_z\tilde z}r_p^0\left(1-i\,\frac{(\epsilon_b q_z+k_z)}{4\epsilon_b}\,\frac{(1+r_p^0)(1-r_p^0)^2}{r_p^0}\,I_x\Lambda_x-i\,\frac{\epsilon_b q_z+k_z}{4\epsilon_b}\,\frac{Q^2}{q_z^2}\,\frac{(1+r_p^0)^3}{r_p^0}I_z\Lambda_z\right)\,, \tag{8}$$

where $r_p^0=(\epsilon_b q_z-k_z)/(\epsilon_b q_z+k_z)$ is the Fresnel reflection amplitude of p-polarized light. Equation (8) has the same form as Eq. (4.13) of I, but with Λ_x and Λ_z replaced by their renormalized counterparts

$$\tilde\Lambda_x(\omega)=I_x\Lambda_x(\omega),\quad \tilde\Lambda_z(\omega)=I_z\Lambda_z(\omega)\,. \tag{9}$$

After simple algebra, the modified reflection amplitude may be written as [Eq. (4.15) of I]

$$r_p=r_p^0\left(1-2iq_z\,\frac{k_z^2\tilde\Lambda_x(\omega)+\epsilon_b^2Q^2\tilde\Lambda_z(\omega)}{(1-\epsilon_b)(Q^2-\epsilon_b q_z^2)}\right)\,. \tag{10}$$

Equations (4) and (10) are our new formulas for the modified reflection amplitudes of s- and p-polarized light from a semi-infinite metal where the coupling of the surface region and the bulk material is fully taken into account.

II. RESULTS AND DISCUSSION

We wish to apply our results to various limiting cases and compare with previous results. It is convenient, for this purpose, to simplify the expressions for the renormalized coefficients $\tilde\Lambda\mu(\omega)$ ($\mu=x,y,z$). We note that from Eqs. (3.3)–(3.5) of I,

$$\epsilon_\omega(z_0)\,U_z(z_0)/U_x(z_0)=-\,\epsilon_b\,Q/k_z\,, \tag{11a}$$

while

$$L_x=-iq_z\,k_z\Lambda_x/(\epsilon_b q_z+k_z) \tag{11b}$$

and

$$L_z=-i\epsilon_b q_z\,Q\Lambda_z/(\epsilon_b q_z+k_z)\,. \tag{11c}$$

It therefore follows that, on using Eqs. (7c)–(7e),

$$I_x=(1+i\epsilon_b\,Q^2\Lambda_z/k_z)/\Delta\,, \tag{12a}$$

$$I_z=(1-ik_z\Lambda_x/\epsilon_b)/\Delta\,, \tag{12b}$$

where

$$\Delta=1-i(q_z k_z\Lambda_x-\epsilon_b\,Q^2\Lambda_z)/(\epsilon_b\,q_z+k_z)\,. \tag{12c}$$

Equations (4b) and (9) now give all the $\tilde\Lambda_\mu(\omega)$'s.

In order to make contact with the expressions derived by Sipe,[3] it is useful to rewrite his formulas [Eqs. (3.14) and (3.15) of Ref. 3] in our notation. For the modified reflection amplitude of s-polarized light, he obtains

$$r_s=r_s^0+(1+r_s^0)^2 n_{0y}/[1-n_{0y}(1+r_s^0)]\,. \tag{13}$$

Once we make the identification

$$n_{0y}=(i/2)(\omega^2/c^2)\,\Lambda_y/q_z\,, \tag{14}$$

and use the definition of r_s^0, it is easy to show that Eq. (13) reduces to Eq. (4a) of this paper. For p-polarized light, we make the identification

$$n_{0x}=(i/2)\,q_z\Lambda_x\ , \tag{15a}$$

$$n_{0z}=-(i/2)(Q^2/q_z)\Lambda_z\ . \tag{15b}$$

In deriving his formula for the modified reflection amplitude of p-polarized light, Sipe assumes $n_{0x}=0$, i.e., $\Lambda_x(\omega)=0$. While this is true for semi-infinite jellium within the random-phase approximation (RPA) this is *not* the most general situation. Sipe's formula for this special case in our notation is

$$r_p=r_p^0+(1+r_p^0)^2n_{0z}/[1-n_{0z}(1+r_p^0)]\ . \tag{16}$$

Straightforward, if lengthy, algebra can now be used to reduce Eq. (16) to Eq. (10) of this paper when $\Lambda_x(\omega)$ and hence $\tilde{\Lambda}_x(\omega)$ vanish. Our expression for the modified p-polarized reflection amplitude given in Eq. (10) is therefore more general than Sipe's, and reduces to his expression in the special case considered by him.

It is also possible to take appropriate limits of the expressions for reflection amplitudes derived in this paper and recover the results for the reflection of light from a conducting thin sheet. The latter problem has been studied by Mochán and Barrera[4] in their investigation of optical reflection from an inversion layer at a metal-oxide-semiconductor interface. For an infinitely thin sheet, there is no background medium, and hence, $\epsilon_b\to 1$ and $k_z\to q_z$ in such a way that $r_s^0\to 0$ and

$$\lim_{\epsilon_b\to 1}\frac{q_z-k_z}{1-\epsilon_b}=\tfrac{1}{2}(\omega^2/c^2)/q_z\ . \tag{17}$$

Equations (4) therefore yield

$$r_s\to r_s^{\text{sheet}}=\frac{i}{2}\,\frac{(\omega^2/c^2)\Lambda_y}{q_z-(i/2)(\omega^2/c^2)\Lambda_y}\ . \tag{18}$$

We note, however, that from Eqs. (4.17) of I in the sheet problem

$$\Lambda_y(\omega)\xrightarrow[\epsilon_b\to 1]{}\frac{4\pi i}{\omega}\int dz''\langle\sigma_{yy}(z'')\rangle\equiv\frac{4\pi i}{\omega}\langle\langle\sigma_{yy}\rangle\rangle\ . \tag{19a}$$

Substitution in Eq. (18) and the use of the fact that $q_z=(\omega/c)\cos\theta_i$, θ_i being the angle of incidence, now gives the result of Mochán and Barrera,[4] viz.,

$$r_s^{\text{sheet}}=\frac{-(2\pi/c)\langle\langle\sigma_{yy}\rangle\rangle}{\cos\theta_i+(2\pi/c)\langle\langle\sigma_{yy}\rangle\rangle}\ . \tag{19b}$$

For p-polarized light once again, $r_p^0\to 0$ as $\epsilon_b\to 1$ but

$$\lim_{\epsilon_b\to 1}\frac{\epsilon_b q_z-k_z}{1-\epsilon_b}=(\omega^2/c^2)/(2q_z)-q_z$$

$$=(Q^2-q_z^2)/(2q_z)\ . \tag{20}$$

Equation (10) thus leads to the result that in this limit,

$$r_p\to r_p^{\text{sheet}}=(-i/2q_z)[q_z^2\tilde{\Lambda}_x(\omega)+Q^2\tilde{\Lambda}_z(\omega)]\ , \tag{21a}$$

where, in the notation of Ref. 4,

$$\tilde{\Lambda}_x(\omega)\xrightarrow[\epsilon_b\to 1]{}\frac{4\pi i}{\omega}\langle\langle\sigma_{xx}\rangle\rangle\times\frac{1+\dfrac{4\pi}{\omega}\dfrac{Q^2}{q_z}\langle\langle S_{zz}\rangle\rangle}{1+\dfrac{2\pi}{\omega}\left(q_z\langle\langle\sigma_{xx}\rangle\rangle+\dfrac{Q^2}{q_z}\langle\langle S_{zz}\rangle\rangle\right)}\ , \tag{21b}$$

$$\tilde{\Lambda}_z(\omega)\xrightarrow[\epsilon_b\to 1]{}-\frac{4\pi i}{\omega}\langle\langle S_{zz}\rangle\rangle\times\frac{1+\dfrac{4\pi}{\omega}q_z\langle\langle\sigma_{xx}\rangle\rangle}{1+\dfrac{2\pi}{\omega}\left(q_z\langle\langle\sigma_{xx}\rangle\rangle+\dfrac{Q^2}{q_z}\langle\langle S_{zz}\rangle\rangle\right)}\ , \tag{21c}$$

with

$$\Lambda_x(\omega)\underset{\epsilon_b\to 1}{\equiv}\frac{4\pi i}{\omega}\langle\langle\sigma_{xx}\rangle\rangle\ ,\quad \Lambda_z(\omega)\underset{\epsilon_b\to 1}{\equiv}-\frac{4\pi i}{\omega}\langle\langle S_{zz}\rangle\rangle\ . \tag{21d}$$

Once we introduce the angle of incidence θ_i, and ignore terms of second order in the small quantities representing the response functions of the sheet, we recover the result of Ref. 4.

We turn next to the question of the dispersion relation of surface plasmons at the boundary of a nonlocal medium and vacuum. There is extensive discussion in the literature[3,5] about how the surface-plasmon dispersion relation may be obtained from the reflection amplitude of p-polarized light, either by setting $r_p(q_z)\to\infty$ or by analytically continuing $r_p(q_z)$ in the complex q_z plane and setting $r_p(-q_z)=0$. It is clear from Eq. (10) of this paper that $r_p\to\infty$ when either $\tilde{\Lambda}_x(\omega)$ or $\tilde{\Lambda}_z(\omega)$ blows up. Equations (9) and (12) further indicate that this situation cannot arise from the poles of either $\Lambda_x(\omega)$ or $\Lambda_z(\omega)$, but rather from the zero of Δ, the location of which can be obtained from Eq. (12c) as obeying the equation

$$\epsilon_b q_z+k_z=i(q_zk_z\Lambda_x-\epsilon_bQ^2\Lambda_z)\ . \tag{22a}$$

This equation may be rewritten equivalently as

$$\epsilon_b(\omega)(Q^2-\omega^2/c^2)^{1/2}+[Q^2-\epsilon_b(\omega)\omega^2/c^2]^{1/2}=-\{\epsilon_b(\omega)Q^2\Lambda_z(\omega)+(Q^2-\omega^2/c^2)^{1/2}[Q^2-\epsilon_b(\omega)\omega^2/c^2]^{1/2}\Lambda_x(\omega)\}\ , \tag{22b}$$

where the frequency dependence of various quantities has been displayed explicitly. We now consider several limiting cases.

(i) For a medium without any surface-induced nonlocality, $\Lambda_x(\omega)=\Lambda_z(\omega)=0$. Simple algebra with Eq. (22b) in that case leads to the well-known dispersion relation[6]

$$Q^2=\epsilon_b(\omega)(\omega^2/c^2)/[1+\epsilon_b(\omega)]\ . \tag{23}$$

(ii) For the semi-infinite jellium model considered by Sipe,[3] $\Lambda_x(\omega)=0$ and $\Lambda_z(\omega)=[1-\epsilon_b(\omega)]\,\Delta(\omega)/\epsilon_b(\omega)$, the latter equation being merely the definition of $\Delta(\omega)$.[5] Substitution in Eq. (22b) leads immediately to Eq. (4.19) of Ref. 3, viz.,

$$\epsilon_b(\omega)(Q^2-\omega^2/c^2)^{1/2}+[Q^2-\epsilon_b(\omega)\omega^2/c^2]^{1/2} = -Q^2[1-\epsilon_b(\omega)]\,\Delta(\omega)\,. \quad (24)$$

(iii) In order to derive the dispersion relation of Dasgupta and Bagchi,[5] one multiplies and divides the left-hand side of Eq. (24) by

$$\epsilon_b(Q^2-\omega^2/c^2)^{1/2}-(Q^2-\epsilon_b\,\omega^2/c^2)^{1/2}$$

and replaces the denominator by $2\epsilon_b(Q^2-\omega^2/c^2)^{1/2}$ by assuming the solution to lie close to that for the local case described by Eq. (23). One obtains

$$\frac{(\epsilon_b^2-1)\,Q^2-\epsilon_b(\epsilon_b-1)\,\omega^2/c^2}{2\epsilon_b(Q^2-\omega^2/c^2)^{1/2}}=-Q^2(1-\epsilon_b)\,\Delta\,. \quad (25)$$

This equation is identical to Eq. (11) of Ref 5—a feature noted earlier by Sipe.[3]

A physical point may be made about the new surface-plasmon dispersion relation of Eq. (22b) which is perhaps significant. The appearance of $\Lambda_x(\omega)$ in Eq. (22b) means that the dispersion relation will depend on the transverse response of the surface region to electric fields parallel to the surface. For the jellium model within the RPA, $\Lambda_x(\omega)$ vanishes, but it will be finite for a real system when band-structure effects due to the lattice are taken into consideration. A lattice structure, of course, will have an effect on $\Lambda_z(\omega)$ as well. In any event, both band-structure effects and the loss of translational symmetry normal to the surface are expected to affect the surface plasmon dispersion relation.

Finally we wish to consider expressions for the differential reflectance of light from an absorbate-covered metal within our present, more exact theory. Let us denote by $r_s^{(c)}$ $(r_s^{(a)})$ and $r_p^{(c)}$ $(r_p^{(a)})$ the reflection amplitudes of s- and p-polarized light respectively for the clean (adsorbate-covered) metal. These amplitudes are given, of course, by Eqs. (4a) and (10) with $\tilde\Lambda_\mu(\omega)$ replaced by $\tilde\Lambda_\mu^{(c)}(\omega)$ $[\tilde\Lambda_\mu^{(a)}(\omega)]$ where $\mu=x,y,z$. Then a simple calculation shows that, to linear order in the $\tilde\Lambda_\mu$'s,

$$\left(\frac{\Delta R_s}{R_s}\right)_a \equiv \frac{|r_s^{(a)}|^2-|r_s^{(c)}|^2}{|r_s^0|^2}=4q_z\,\mathrm{Im}\left(\frac{\delta\tilde\Lambda_y(\omega)}{\epsilon_b(\omega)-1}\right), \quad (26)$$

and

$$\left(\frac{\Delta R_p}{R_p}\right)_a \equiv \frac{|r_p^{(a)}|^2-|r_p^{(c)}|^2}{|r_p^0|^2} = 4q_z\,\mathrm{Im}\left(\frac{k_z^2\delta\tilde\Lambda_x(\omega)+\epsilon_b^2Q^2\delta\tilde\Lambda_z(\omega)}{(1-\epsilon_b)(Q^2-\epsilon_b q_z^2)}\right), \quad (27)$$

where

$$\delta\tilde\Lambda_\mu(\omega)=\tilde\Lambda_\mu^{(a)}(\omega)-\tilde\Lambda_\mu^{(c)}(\omega),\quad \mu=x,y,z\,. \quad (28)$$

Equations (26) and (27) are formally similar to Eqs. (5.7) and (5.5) of I, the only difference being that, unlike the case in I, $\delta\tilde\Lambda_\mu(\omega)$ can no longer be written simply as integrals over differences of dielectric response functions of the clean and the absorbate-covered metal surfaces. They may still be regarded, though, as parameters in terms of which the experimental SRS data ought to be interpreted.

In conclusion, we have derived in this paper expressions for the reflection amplitudes of s- and p-polarized light from a semi-infinite medium having a surface-induced nonlocality in the dielectric response tensor. We start from a microscopic theory[1] and only assume that the wavelength of light is large compared to the range of nonlocality of the response functions, but do not make any further approximations. The result for s- polarized light is the same as Sipe's,[3] while that for p-polarized light is more general. Using the latter we have derived a new, very general, dispersion relation for surface plasmons. We have also indicated how the effects of adsorption may be included in writing formulas for the differential reflectance of light.

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