

Perturbative approach to the calculation of the electric field near a metal surface

A. Bagchi

Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742

R. G. Barrera

Institute of Physics, University of Mexico, Mexico 20, D. F., Mexico

A. K. Rajagopal

Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803

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A systematic perturbational procedure is developed for the calculation of the electric field near a metal surface when electromagnetic radiation is incident upon it. The method is worked out in detail for a particularly simple choice of the "unperturbed model" for the metal. Asymptotic forms of the expression for the electric-field components are used to obtain corrections to the Fresnel formulas for the reflectivity for both *s*- and *p*-polarized light. Surface corrections to ellipsometric parameters are also derived. Connection is made between these results and those of previous theories. The procedure is applied to a metal surface with chemisorbed impurities, and is shown to lead to a new and useful expression for the differential reflectance in the case of *p*-polarized light. The result is discussed in terms of its utility in studying experimental data on surface-reflectance spectroscopy.

I. INTRODUCTION

Photoemission and optical reflectance have emerged in recent years as two of the most useful techniques for the investigation of metal surfaces with or without chemisorbed impurities. In both of these methods, a quantity of central interest is the variation of the electric field near the metal surface as radiation is incident upon the system and is reflected and refracted by it. The total electric field in the surface region enters the matrix element of photoemission from, e.g., a surface state, while the asymptotic form of the electric field far from the surface can be used to extract the expression for the reflection coefficient. The electric field near the surface of a metal has been studied by a number of authors¹⁻¹² using different models of the surface. In a series of papers,¹⁻⁴ Kliewer, Fuchs, and co-workers studied the surface impedance and reflection coefficient from a semi-infinite metal, bounded by a sharp surface, whose dielectric response function is nonlocal. They considered obliquely incident light of both *s* and *p* polarization, and the limiting boundary conditions of electrons being scattered either specularly^{1,2} or diffusely^{3,4} by the surface. For the case of *p* polarization, the problem of finding the electric field in the vicinity of the surface has been set up⁵ and solved numerically⁶ within the so-called semiclassical infinite-barrier model. Feibelman, on the other hand, has tried to determine the electromagnetic field at a jellium-vacuum interface^{7,8} by first obtaining the full quantum-mechanical conductivity tensor of the system

within the random-phase approximation (RPA), and then using it to solve numerically an integral equation for the relevant vector potential. The integral equation is derived from Maxwell's equations and is exact in the long-wavelength limit. The conductivity tensor in this method is also nonlocal, but it does not vanish at a sharp surface separating the metal from vacuum. Making use of the asymptotic form of the solutions for the electric field components away from the metal surface, Feibelman has also derived⁹ a useful expression for the reflection coefficient of *s*-polarized light, and a rather less transparent formula in the case of *p* polarization which involves the derivative of an electric field component which has to be determined numerically. An entirely different approach to the determination of the surface electric field is the hydrodynamic approach of Sauter¹⁰ and Forstmann.¹¹ This has proved very successful in the study of the photoexcitation of bulk plasmons by *p* polarized light.^{12,13}

In this paper, we present an alternate, perturbative approach to the calculation of the electric field near the surface of a metal when either *s*- or *p*-polarized radiation is incident upon it. The method is based on the postulate that there exist approximate, yet sensible, models of the metal dielectric response for which the surface electric field is exactly soluble. One obvious example of such a model is the usual Fresnel problem¹⁴ of a semi-infinite metal bounded by a sharp surface and described by a local dielectric function. We suppose that while we may not be able to find exact, i.e., closed-form, expressions for the elec-

tric field components in the neighborhood of the surface for the actual problem of a semi-infinite metal with its associated nonlocal dielectric function, we can nevertheless isolate a "nearby," soluble problem with a very similar dielectric function. The latter problem we consider as our unperturbed or background problem, and its solution for the field as the unperturbed solution. The difference between the actual and the assumed or soluble dielectric function we regard as a perturbation, in terms of which the true electric field components are to be expanded once the unperturbed solutions are subtracted out. Of course we would need the Green's function of the background problem in order to make such a perturbational expansion. The procedure outlined above has a number of advantages. First, it is physically appealing as being the correction to an unperturbed problem which, to begin with, should have a sensible, physical interpretation. Second, the method is systematic, and one knows from the order of the perturbation theory to what precise accuracy the correction terms are being treated. Third, it leads to a new and potentially useful expression for the change in the reflection coefficient of p -polarized light from the standard Fresnel result,¹⁴ caused by the nonlocal dielectric response of the surface. As we shall show below, this formula with a simple modification can be used to study differential reflectance of p -polarized light from a metal surface covered with chemisorbed impurities. We can also derive formulas that should be useful in ellipsometric studies. Finally, the procedure enables us to determine the exact way in which a metal surface responds to electric field components parallel and normal to the surface. This is very important in terms of providing an intuitive understanding of the response process. We should mention that a perturbative approach to determine the electric field components at the surface was developed earlier by Brodskii and Urbakh¹⁵ in their study of ellipsometric effects at the metal-electrolyte interface. The Green's-function technique we develop in this paper for p polarized radiation is, however, completely different from their scheme. Our method is also close in spirit to the theoretical studies of light reflection from surface states¹⁶ and metal-oxide-semiconductor field-effect transistor (MOSFET) systems,^{17,18} although the separability property of the conductivity tensor, which provides an essential ingredient in these studies, is not utilized explicitly in this paper. The separability property, of course, can be exploited here, but the problem becomes more complicated because of the presence of a continuum of states normal to the surface,¹⁹ rather than a handful of discrete states.

One interesting result to emerge from our work (and reported later in this paper) is that although the dielectric response of a metallic system is certainly nonlocal, the change in optical reflectivity brought about by the physical surface differing from the Fresnel model can be expressed, in the long-wavelength limit and the first Born approximation, entirely in terms of local functions which are appropriate averages of the corresponding nonlocal quantities. This is useful for purposes of modeling the surface dielectric response in optical studies, and brings up the question of how important the nonlocality of metallic response really is in understanding its optical properties. That question will be addressed in a later paper using simple models to describe a semi-infinite metal. The present paper is concerned exclusively with the theory behind our perturbative approach and its various consequences. Certain formulas of this paper on differential reflectance have already been reported,²⁰ as also numerical calculations based on these formulas for differential reflectance from ordered chemisorbed monolayers.⁴¹

The organization of the paper is as follows. The theoretical formalism involved in subtracting out a soluble, background problem from the actual problem, and expressing the result for the electric field as an integral over a Green's function, is presented in Sec. II. The formal solution serves as the starting point of an iterative scheme for obtaining the true solution as a perturbation series. We discuss separately the cases of s and p polarizations with obliquely incident light. In Sec. III, we choose the Fresnel problem as the background problem, and work out explicitly the Green's functions appropriate to it for both polarizations. The actual solutions for the various electric-field components are discussed in Sec. IV. We introduce the Born approximation and indicate ways of improving on it. The solutions in the Born approximation are studied to obtain optical reflectance and ellipsometric parameters in Sec. V. Our conclusions are contained in Sec. VI with suggestions for further research. Certain algebraic details concerning the Green's-function elements are presented as an Appendix.

II. THEORETICAL FORMALISM

Here we discuss the formal technique of solving for the electric field in reflection at a metal surface by first choosing and isolating a soluble, background problem, then subtracting it from the problem at hand and treating the difference as a perturbation. The metal exists in the half-space $z > 0$ with its surface parallel to the x - y plane. It will not be possible, in general, to identify a fixed

plane separating the metal from vacuum. Rather we imagine the interface to consist of a narrow surface region in the neighborhood of the $z=0$ plane. We further assume, for simplicity, that the metal is translationally invariant parallel to the x - y plane. Consider light to be incident on the surface in the x - z plane at an angle of θ_i to the surface normal. The electric and magnetic fields obey Maxwell's equations which can be recast in the form

$$\nabla \times (\nabla \times \vec{E}) = \nabla(\nabla \cdot \vec{E}) - \nabla^2 \vec{E} = -\frac{1}{c^2} \frac{\partial^2}{\partial t^2} \vec{D}, \quad (2.1a)$$

where, writing $\vec{\rho} = \hat{i}x + \hat{j}y$, we get

$$\vec{D}(\vec{r}, t) = \int d^3r' \int dt' \vec{\epsilon}(\vec{\rho} - \vec{\rho}', z, z'; t - t') \cdot \vec{E}(\vec{r}', t'). \quad (2.1b)$$

Making use of translational invariance, all field components can be written in the form

$$E_\mu(\vec{r}, t) = E_\mu(z) e^{i(\vec{Q} \cdot \vec{\rho} - \omega t)}, \quad \mu = x, y, \text{ or } z, \quad (2.2)$$

where $\vec{Q} = \hat{i}(\omega/c) \sin \theta_i$. The dielectric tensor has a similar Fourier transform and in it we make the long-wavelength approximation which is justified¹⁷ since $Q \ll k_F$, the Fermi momentum of the metal. The resultant dielectric tensor $\vec{\epsilon}(\vec{Q} \rightarrow 0, \omega; z, z')$ is known to be diagonal.¹⁹ Note that for p polarized light, we have $\vec{E} = (E_x, 0, E_z)$, and for s polarized light, we have $\vec{E} = (0, E_y, 0)$. We proceed to treat the two cases separately.

A. p polarization

Equations (2.1) lead here to the coupled integro-differential equations

$$\frac{d^2}{dz^2} E_x - iQ \frac{d}{dz} E_x + \frac{\omega^2}{c^2} \int dz' \epsilon_{xx}(0, \omega; z, z') E_x(z') = 0, \quad (2.3a)$$

$$-iQ \frac{d}{dz} E_x - Q^2 E_x + \frac{\omega^2}{c^2} \int dz' \epsilon_{zz}(0, \omega; z, z') E_z(z') = 0. \quad (2.3b)$$

We now subtract from the dielectric tensor under consideration a hypothetical dielectric tensor which corresponds to a problem having a sharp surface at $z=z_0$ separating vacuum from the metal. In other words, we subtract the dielectric tensor

$$\vec{\epsilon}^0(0, \omega; z, z') = \Theta(z_0 - z) \Theta(z_0 - z') \delta(z - z') \vec{I} + \Theta(z - z_0) \Theta(z' - z_0) \vec{\epsilon}^b(0, \omega; z - z'), \quad (2.4)$$

where \vec{I} is the unit tensor and $\vec{\epsilon}^b$ is the fully translationally invariant dielectric tensor for the bulk of the metal. We assume that the hypothetical problem with $\vec{\epsilon}^0$ as the dielectric tensor can be solved exactly for the fields. The choice of z_0 as the plane at which the background metal terminates is made for the sake of complete generality. We presume that this plane lies somewhere in the surface region of the metal, but do not specify it any further. Of course no physical result can depend on z_0 , as will be shown later on. The dielectric "perturbation" is defined by

$$\Delta \epsilon_{\mu\mu}(z, z') = \epsilon_{\mu\mu}(0, \omega; z, z') - \epsilon_{\mu\mu}^0(0, \omega; z, z'). \quad (2.5)$$

Let us also introduce the following notations:

$$M_{xx}(z, z'') = \delta(z - z'') \frac{d^2}{dz''^2} + \frac{\omega^2}{c^2} \epsilon_{xx}^0(0, \omega; z, z''), \quad (2.6a)$$

$$M_{xz}(z, z'') = -iQ \delta(z - z'') \frac{d}{dz''}, \quad (2.6b)$$

$$M_{zx}(z, z'') = -iQ \delta(z - z'') \frac{d}{dz''}, \quad (2.6c)$$

$$M_{zz}(z, z'') = -Q^2 \delta(z - z'') + (\omega^2/c^2) \epsilon_{zz}^0(0, \omega; z, z''). \quad (2.6d)$$

Equations (2.3) can then be written in a compact matrix notation as

$$\int_{-\infty}^{\infty} dz'' \begin{pmatrix} M_{xx}(z, z'') & M_{xz}(z, z'') \\ M_{zx}(z, z'') & M_{zz}(z, z'') \end{pmatrix} \begin{pmatrix} E_x(z'') \\ E_z(z'') \end{pmatrix} = -\frac{\omega^2}{c^2} \int_{-\infty}^{\infty} dz' \begin{pmatrix} \Delta \epsilon_{xx}(z, z') E_x(z') \\ \Delta \epsilon_{zz}(z, z') E_z(z') \end{pmatrix}. \quad (2.7)$$

The unperturbed or background problem is recovered by setting the right hand side of Eq. (2.7) to zero. This problem is assumed to be soluble, and we imagine the solutions for the field components to be written $E_x(z) = U_x(z)$ and $E_z(z) = U_z(z)$, when light is incident on the surface from the left, i.e., the vacuum side. We now try to solve Eq. (2.7) formally by introducing the matrix Green's function for the unperturbed problem, which obeys the equation

$$\int_{-\infty}^{\infty} dz'' \begin{pmatrix} M_{xx}(z, z'') & M_{xz}(z, z'') \\ M_{zx}(z, z'') & M_{zz}(z, z'') \end{pmatrix} \begin{pmatrix} G_{xx}(z'', z') & G_{xz}(z'', z') \\ G_{zx}(z'', z') & G_{zz}(z'', z') \end{pmatrix} = \delta(z - z') \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (2.8)$$

We shall assume that the Green's matrix for the background problem can be constructed by virtue of our knowledge of the solutions for the fields. In terms of this matrix Green's function, we "solve" Eq. (2.7)

formally by turning it from coupled integro-differential equations to a pair of coupled integral equations, viz.,

$$E_x(z) = U_x(z) - \frac{\omega^2}{c^2} \left(\int dz'' G_{xx}(z, z'') \int dz' \Delta \epsilon_{xx}(z'', z') E_x(z') + \int dz'' G_{xz}(z, z'') \int dz' \Delta \epsilon_{zx}(z'', z') E_z(z') \right), \quad (2.9a)$$

$$E_z(z) = U_z(z) - \frac{\omega^2}{c^2} \left(\int dz'' G_{zx}(z, z'') \int dz' \Delta \epsilon_{xx}(z'', z') E_x(z') + \int dz'' G_{zz}(z, z'') \int dz' \Delta \epsilon_{zz}(z'', z') E_z(z') \right). \quad (2.9b)$$

These integral equations describe the electric field components of p polarized light as it is incident from vacuum on the true metal surface. They serve as the starting point of our systematic, iterative procedure of solving for the fields. To be useful, of course, such a perturbation theory ought to be rapidly convergent. This is likely because the background dielectric tensor for subtraction, $\bar{\epsilon}^0(0, \omega; z, z')$, has been so chosen that $\Delta \epsilon_{\mu\nu}(z, z')$ of Eq. (2.5) is finite only over a narrow spatial range around $z, z'=0$, and it vanishes both as $z, z' \rightarrow \infty$ and as $z, z' \rightarrow -\infty$. The integral of $\Delta \epsilon_{\mu\nu}(z, z')$ is therefore bounded and finite. We shall discuss the question of convergence more fully when we explicitly introduce the perturbation series. In Sec. III, we take up a particularly simple, special form of $\bar{\epsilon}^0$ [cf. Eq. (2.4)] which corresponds to subtracting out the well-known Fresnel problem as the background problem.

B. s polarization

Equations (2.1) yield in this case the following equation for E_y :

$$\left(\frac{d^2}{dz^2} - Q^2 \right) E_y + \frac{\omega^2}{c^2} \int dz' \epsilon_{yy}(0, \omega; z, z') E_y(z') = 0. \quad (2.10)$$

Subtracting the same dielectric tensor as in Eq. (2.4) to describe the background metal, we arrive at the integro-differential equation

$$\left(\frac{d^2}{dz^2} - Q^2 \right) E_y + \frac{\omega^2}{c^2} \int dz' \epsilon_{yy}^0(0, \omega; z, z') E_y(z') = - \frac{\omega^2}{c^2} \int dz' \Delta \epsilon_{yy}(z, z') E_y(z'). \quad (2.11)$$

We imagine that the unperturbed or homogeneous problem, obtained by setting to zero the right-hand side of the above equation, has a known solution $E_y(z) = U_y(z)$ for light being incident from the vacuum side. We further imagine that the Green's function for the unperturbed problem is known, and it obeys the equation

$$\left(\frac{d^2}{dz^2} - Q^2 \right) G_{yy}(z, z') + \frac{\omega^2}{c^2} \int dz'' \epsilon_{yy}^0(0, \omega; z, z'') G_{yy}(z'', z') = \delta(z - z'). \quad (2.12)$$

With the help of this Green's function, we "solve" Eq. (2.11) formally by converting it into an integral equation

$$E_y(z) = U_y(z) - \frac{\omega^2}{c^2} \int dz'' G_{yy}(z, z'') \int dz' \Delta \epsilon_{yy}(z'', z') E_y(z'). \quad (2.13)$$

This equation describes the electric field distribution as s polarized light is incident on the metal from vacuum. We now proceed to set up an iterative solution for $E_y(z)$ after making a specific choice for the bulk dielectric function of Eq. (2.4).

III. FRESNEL PROBLEM AS UNPERTURBED PROBLEM

In order to make further progress at this stage, we make a specific choice of the function $\bar{\epsilon}^0(0, \omega; z - z')$ of Eq. (2.4), which describes the dielectric response of the metal in the bulk. We assume that it is a local function, thus converting the unperturbed problem into the standard Fresnel problem of reflection and refraction at a sharp surface separating vacuum from a local dielectric medium.¹⁴ Calling $\bar{z} = z - z_0$, we choose

$$\bar{\epsilon}^0(0, \omega; z, z') = \bar{\mathbb{I}} \epsilon_b(\omega) \delta(z - z'), \quad (3.1)$$

where $\epsilon_b(\omega)$ stands for the usual, frequency-dependent complex dielectric constant of the metal. The dielectric response tensor of the background problem is then

$$\bar{\epsilon}^0(0, \omega; z, z') = \bar{\mathbb{I}} \epsilon_\omega(z) \delta(z - z'), \quad (3.2a)$$

and $\epsilon_\omega(z)$ is the step function.

$$\epsilon_\omega(z) = \Theta(-\bar{z}) + \Theta(\bar{z}) \epsilon_b(\omega). \quad (3.2b)$$

The Fresnel or local model is admittedly not a good description for the bulk of a metal where non-locality of response is often important, as for example in plasmon dispersion. A superior starting point would be to use for $\tilde{\epsilon}^b$ the nonlocal dielectric response of the fully homogeneous medium—a choice similar in spirit to what has been made in some studies²¹⁻²³ on bounded semiconductors. Nevertheless, the use of the Fresnel model for subtraction purposes has a number of advantages. First, experiments on reflectance from metal surfaces are commonly analyzed on the basis of this model, where the Kramers-Kronig relationship is utilized to determine the real and imaginary parts of $\epsilon_b(\omega)$ introduced in (3.1). The use of this as the background problem enables us to find out to what degree reflectance from a metal is affected by the nonlocality of response associated with the surface.¹⁹ Second, the simplicity of the model allows us to obtain closed-form expressions for the Green's function, thus permitting us to obtain expressions for the reflectance change that are readily interpretable. Third, by using the same unperturbed problem first with a clean and then an adsorbate-covered metal surface, we are able to find new formulas for the change of reflectivity on chemisorption—especially for p polarized light—which should serve as the basis for data analysis. Previous attempts at analyzing the p polarized data have been hampered by the absence of a convenient formula. We turn now to the construction of the elements of the matrix Green's function, once more treating the two independent cases of linear polarization separately.

A. p polarization

The unperturbed problem is given by Eqs. (2.3), with ϵ_{xx} and ϵ_{zz} replaced by ϵ_{xx}^0 and ϵ_{zz}^0 , respective-

ly. The form of the functions in Eq. (3.2a) shows that we are now left with only coupled differential equations. Let us call their two linearly independent solutions $\vec{E}(z) = (U_x(z), 0, U_z(z))$ and $\vec{E}(z) = (V_x(z), 0, V_z(z))$, respectively, for light being incident on the surface from the vacuum side (left) and the metal side (right). The solutions can be written by simple inspection as ($\tilde{z} = z - z_0$)

$$U_x(z) = \begin{cases} e^{iq_x \tilde{z}} - r_p^0 e^{-iq_x \tilde{z}}, & \tilde{z} < 0, \\ (1 - r_p^0) e^{ik_x \tilde{z}}, & \tilde{z} > 0; \end{cases} \quad (3.3)$$

$$V_x(z) = \begin{cases} (1 + r_p^0) e^{-iq_x \tilde{z}}, & \tilde{z} < 0, \\ e^{-ik_x \tilde{z}} + r_p^0 e^{ik_x \tilde{z}}, & \tilde{z} > 0; \end{cases} \quad (3.4)$$

and

$$\left. \begin{matrix} U_x(z) \\ V_x(z) \end{matrix} \right\} = \frac{iQ}{(\omega^2/c^2)\epsilon_\omega(z) - Q^2} \frac{d}{dz} \begin{Bmatrix} U_x(z) \\ V_x(z) \end{Bmatrix}. \quad (3.5)$$

Here we have introduced the quantities q_x and k_x as the wave-vector components of light along the surface normal in vacuum and the metal, respectively. They are related to the angle of incidence θ_i and the angle of refraction θ_r by the formulas

$$q_x = (\omega/c) \cos \theta_i, \quad k_x = \epsilon_b^{1/2} (\omega/c) \cos \theta_r, \quad (3.6)$$

where the *complex* angle of refraction must be obtained from $\sin \theta_i / \sin \theta_r = [\epsilon_b(\omega)]^{1/2}$. Finally r_p^0 is the reflection amplitude of the unperturbed problem, i.e.,

$$r_p^0 = \frac{\epsilon_b q_x - k_x}{\epsilon_b q_x + k_x} = \frac{\sin 2\theta_i - \sin 2\theta_r}{\sin 2\theta_i + \sin 2\theta_r}. \quad (3.7)$$

Note that we have suppressed the frequency dependence of ϵ_b in the above two equations for ease of writing.

In a similar manner, the matrix equation obeyed by the Green's function is simplified on substituting Eqs. (3.2) in Eqs. (2.6) and (2.7). We obtain

$$\left(\begin{array}{cc} \frac{d^2}{dz^2} + \frac{\omega^2}{c^2} \epsilon_\omega(z) & -iQ \frac{d}{dz} \\ -iQ \frac{d}{dz} & \frac{\omega^2}{c^2} \epsilon_\omega(z) - Q^2 \end{array} \right) \begin{pmatrix} G_{xx}(z, z') & G_{xz}(z, z') \\ G_{zx}(z, z') & G_{zz}(z, z') \end{pmatrix} = \delta(z - z') \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \quad (3.8)$$

The solution for the Green's-function elements is sketched in the Appendix. We find

$$G_{xx}(z, z') = \alpha [\Theta(z - z') U_x(z) V_x(z') + \Theta(z' - z) V_x(z) U_x(z')], \quad (3.9a)$$

$$G_{zx}(z, z') = \alpha [\Theta(z - z') U_x(z) V_x(z') + \Theta(z' - z) V_x(z) U_x(z')], \quad (3.9b)$$

$$G_{xz}(z, z') = -\alpha [\Theta(z - z') U_x(z) V_x(z') + \Theta(z' - z) V_x(z) U_x(z')], \quad (3.9c)$$

$$G_{zz}(z, z') = -\alpha \{ [\Theta(z - z') U_x(z) V_x(z') + \Theta(z' - z) V_x(z) U_x(z')] - [1/\epsilon_\omega(z)] (c^2/\alpha \omega^2) \delta(z - z') \}, \quad (3.9d)$$

where

$$\alpha = -i (\epsilon_b q_x + k_x) / (4\epsilon_b \omega^2 / c^2). \quad (3.9e)$$

A similar Green's function was first derived by an independent technique by Eguluz and Maradudin.¹⁸ We comment in the Appendix on the connection between our Green's functions and those obtained by previous authors.^{17,18}

B. s polarization

This time we start with Eq. (2.10) and, for the unperturbed problem, substitute ϵ_{yy}^0 of Eq. (3.2a) for ϵ_{yy} . The two independent solutions for light being incident on the surface from the vacuum side and the metal side are $U_y(z)$ and $V_y(z)$, respectively, where

$$U_y(z) = \begin{cases} e^{iq_z \bar{z}} + r_s^0 e^{-iq_z \bar{z}}, & \bar{z} < 0, \\ (1 + r_s^0) e^{ik_z \bar{z}}, & \bar{z} > 0; \end{cases} \quad (3.10)$$

$$V_y(z) = \begin{cases} (1 - r_s^0) e^{-iq_z \bar{z}}, & \bar{z} < 0, \\ e^{-ik_z \bar{z}} - r_s^0 e^{ik_z \bar{z}}, & \bar{z} > 0; \end{cases} \quad (3.11)$$

and r_s^0 is the Fresnel reflection amplitude of s polarized light, i.e.,

$$r_s^0 = (q_z - k_z)/(q_z + k_z). \quad (3.12)$$

The corresponding unperturbed Green's function obeys [cf. Eq. (2.11)]

$$\left(\frac{d}{dz^2} - Q^2 + \frac{\omega^2}{c^2} \epsilon_\omega(z) \right) G_{yy}(z, z') = \delta(z - z'). \quad (3.13)$$

The solution is

$$G_{yy}(z, z') = [1/2ik_z(1 + r_s^0)] [\theta(z - z')U_y(z)V_y(z') + \theta(z' - z)V_y(z)U_y(z')]. \quad (3.14)$$

IV. SOLUTION FOR FIELDS: BORN APPROXIMATION

We now try to solve for the electric field components of light iteratively by making use of the Green's functions derived in Sec. III. The starting points are Eqs. (2.9) for the case of *p* polarization, and Eq. (2.13) for *s* polarization.

A. *p* polarization

We begin by recasting Eq. (2.9a) into a more convenient form by observing the fact that on substituting Eq. (3.2a) in Eq. (2.5), we have

$$\int dz' \Delta \epsilon_{xx}(z, z') E_x(z') = D_x(z) - \epsilon_\omega(z) E_x(z) = D_x(z) - \epsilon_\omega(z) \int dz' \epsilon_{xx}^{-1}(0, \omega; z, z') D_x(z'). \quad (4.1)$$

We have introduced here, in a formal manner, the inverse of the nonlocal dielectric tensor, which is also known to be a response function. From Eq. (2.9a), we obtain

$$E_x(z) = U_x(z) - \frac{\omega^2}{c^2} \left[\int dz'' G_{xx}(z, z'') \int dz' \Delta \epsilon_{xx}(z'', z') E_x(z') + \int dz'' G_{xx}(z, z'') \left(D_x(z'') - \epsilon_\omega(z'') \int dz' \epsilon_{xx}^{-1}(0, \omega; z'', z') D_x(z') \right) \right]. \quad (4.2)$$

Next we rewrite Eq. (3.9d) as

$$G_{xx}(z, z') = \bar{G}_{xx}(z, z') + [1/\epsilon_\omega(z)] (c^2/\omega^2) \delta(z - z'), \quad (4.3)$$

in preparation for writing an integral equation for $D_x(z)$. The advantage of this function is that, unlike $E_x(z)$, it is continuous across the surface in the Fresnel problem. Substitution of Eqs. (4.1) and (4.3) in Eq. (2.9b) yields, after a little algebra,

$$D_x(z) = \epsilon_\omega(z) U_x(z) - \frac{\omega^2}{c^2} \epsilon_\omega(z) \left[\int dz'' G_{xx}(z, z'') \int dz' \Delta \epsilon_{xx}(z'', z') E_x(z') + \int dz'' \bar{G}_{xx}(z, z'') \left(D_x(z'') - \epsilon_\omega(z'') \int dz' \epsilon_{xx}^{-1}(0, \omega; z'', z') D_x(z') \right) \right]. \quad (4.4)$$

Note here that $\bar{G}_{xx}(z, z')$ is the part of Eq. (3.9d) which does not have a delta function.

Equations (4.2) and (4.4) are still exact integral equations, which can be solved iteratively by writing down infinite series for E_x and D_x . It is more convenient to introduce at this point two approximations that greatly simplify the problem. First is the long-wavelength limit where we note that the

wavelength of light used in typical experiments on photoemission or optical reflectance is much larger than the range of nonlocality of either $\Delta \epsilon_{xx}(z, z')$ or $\epsilon_{xx}^{-1}(0, \omega; z, z')$. Accordingly, we remove the functions $E_x(z')$ and $D_x(z')$ occurring inside the z' integrals in these equations to outside by setting $z' = z''$. Furthermore, as a result of the long-wavelength approximation, the nonlocal fea-

tures of the response functions are integrated over, and the remaining dependence on z'' is concentrated in the neighborhood of the surface. The integrand for z'' integration falls off quickly to zero on either side of the nominal surface of the Fresnel problem, thus making it sufficient to eval-

uate $E_x(z'')$ and $D_x(z'')$ at $z''=0$ or $z''=z_0$. We can similarly evaluate the *continuous* functions $G_{xx}(z, z'')$, $\epsilon_\omega(z)G_{xx}(z, z'')$, $G_{xx}(z, z'')\epsilon_\omega(z'')$, and $\epsilon_\omega(z)G_{zz}(z, z'')\epsilon_\omega(z'')$, also at $z''=z_0$ and remove them from integrations. These approximations lead finally to the following equations:

$$E_x(z) = U_x(z) - \frac{\omega^2}{c^2} \left[E_x(z_0)G_{xx}(z, z_0) \int dz'' \int dz' \Delta \epsilon_{xx}(z'', z') + D_x(z_0) [G_{xx}(z, z'')\epsilon_\omega(z'')]_{z'' \rightarrow z_0} \int dz'' \right. \\ \left. \times \left(\epsilon_\omega^{-1}(z'') - \int dz' \epsilon_{zz}^{-1}(0, \omega; z'', z') \right) \right], \quad (4.5)$$

$$D_x(z) = \epsilon_\omega(z)U_x(z) - \frac{\omega^2}{c^2} \left[E_x(z_0)\epsilon_\omega(z)G_{xx}(z, z_0) \int dz'' \int dz' \Delta \epsilon_{xx}(z'', z') \right. \\ \left. + D_x(z_0)\epsilon_\omega(z) [G_{zz}(z, z'')\epsilon_\omega(z'')]_{z'' \rightarrow z_0} \int dz'' \left(\epsilon_\omega^{-1}(z'') - \int dz' \epsilon_{zz}^{-1}(0, \omega; z'', z') \right) \right]. \quad (4.6)$$

From the above equations, the field components may be obtained as perturbation or Born series by iteratively substituting for $E_x(z_0)$ and $D_x(z_0)$, starting with their values for the unperturbed problem. We now make the second approximation by terminating the Born series after the first term, which involves setting $E_x(z_0) = U_x(z_0)$ and $D_x(z_0) = [\epsilon_\omega(z)U_x(z)]_{z \rightarrow z_0}$. It is worth noting, in fact, that in this long-wavelength limit, writing down a perturbational series is not strictly necessary. It can be summed exactly because, evaluating Eqs. (4.5) and (4.6) at $z = z_0$, one obtains a pair of coupled algebraic equations which can be solved in principle for $E_x(z_0)$ and $D_x(z_0)$. Such a procedure, however, would be inconsistent with the order of perturbation implicit in the long-wavelength ap-

proximation. Hence, we confine ourselves to the first Born term. It should be adequate for fields computed to first order in R/λ , where R is a typical range of the surface region and λ is the wavelength of light. Let us define

$$\langle \epsilon_{xx}(z) \rangle = \int_{-\infty}^{\infty} dz' \epsilon_{xx}(0, \omega; z, z'), \quad (4.7a)$$

$$\langle \epsilon_{zz}^{-1}(z) \rangle = \int_{-\infty}^{\infty} dz' \epsilon_{zz}^{-1}(0, \omega; z, z'), \quad (4.7b)$$

so that, with Eq. (3.2a) used in Eq. (2.5),

$$\int dz' \Delta \epsilon_{xx}(z, z') = \langle \epsilon_{xx}(z) \rangle - \epsilon_\omega(z). \quad (4.7c)$$

The field components in the first Born approximation, therefore, are

$$E_x(z) = U_x(z) - \frac{\omega^2}{c^2} \left(U_x(z_0)G_{xx}(z, z_0) \int dz'' [\langle \epsilon_{xx}(z'') \rangle - \epsilon_\omega(z'')] + [\epsilon_\omega(z_0)U_x(z_0)]_{z_2 \rightarrow z_0} \right. \\ \left. \times [G_{xx}(z, z_1)\epsilon_\omega(z_1)]_{z_1 \rightarrow z_0} \int dz'' [\epsilon_\omega^{-1}(z'') - \langle \epsilon_{zz}^{-1}(z'') \rangle] \right), \quad (4.8)$$

$$D_x(z) = \epsilon_\omega(z)U_x(z) - \frac{\omega^2}{c^2} \epsilon_\omega(z) \left(G_{xx}(z, z_0)U_x(z_0) \int dz'' [\langle \epsilon_{xx}(z'') \rangle - \epsilon_\omega(z'')] \right. \\ \left. + [\tilde{G}_{zz}(z, z_1)\epsilon_\omega(z_1)]_{z_1 \rightarrow z_0} [\epsilon_\omega(z_0)U_x(z_0)]_{z_2 \rightarrow z_0} \int dz'' [\epsilon_\omega^{-1}(z'') - \langle \epsilon_{zz}^{-1}(z'') \rangle] \right). \quad (4.9)$$

Coupled with the Green's functions of Sec. III, these equations describe the fields associated with the reflection of p polarized light at the metal surface, within the specified approximations.

It is possible to make a number of physical points about the results of Eqs. (4.8) and (4.9). Even though the dielectric response of the metal is actually nonlocal, we find that in the long-wavelength limit, the electric fields of interest are expressed

in terms of two effectively local response functions, $\langle \epsilon_{xx}(z) \rangle$ and $\langle \epsilon_{zz}^{-1}(z) \rangle$. We also find that the response of the semi-infinite metal to an electric field parallel to the surface is transverse, occurring as ϵ_{xx} , while that to the field-component normal to the surface is essentially longitudinal, occurring as ϵ_{zz}^{-1} . Finally, we may evaluate the fields in the asymptotic region far from the metal and obtain a formula for the reflectance of p polarized

light entirely in terms of the properties of the system. The reflection amplitude r_p , which differs from the Fresnel result r_p^0 due to corrections arising from the detailed nature of the surface, can be obtained from either of the two limiting forms

$$E_x(z) \underset{z \rightarrow -\infty}{\sim} e^{iq_x z} - r_p e^{-iq_x z}, \quad (4.10a)$$

$$D_x(z) \underset{z \rightarrow -\infty}{\sim} e^{iq_x z} + r_p e^{-iq_x z}. \quad (4.10b)$$

Let us introduce two complex frequency-dependent quantities having the dimension of length

$$\Lambda_x(\omega) = \int_{-\infty}^{\infty} dz [\langle \epsilon_{xx}(z) \rangle - \epsilon_\omega(z)], \quad (4.11a)$$

$$\Lambda_x(\omega) = \int_{-\infty}^{\infty} dz [\langle \epsilon_{xx}^{-1}(z) \rangle - \epsilon_\omega^{-1}(z)]. \quad (4.11b)$$

These functions may be interpreted as the integrals of the difference of certain response functions of the original system and the background problem. They are therefore in the nature of being response

functions themselves. Also as $z \rightarrow -\infty$, we can use the formulas of Sec. III to derive the following results:

$$U_x(z_0) = 1 - r_p^0, \quad (4.12a)$$

$$[\epsilon_\omega(z)U_x(z)]_{z \rightarrow z_0} = -(Q/q_x)(1 + r_p^0), \quad (4.12b)$$

$$G_{xx}(z, z_0) = \alpha(1 + r_p^0)e^{-iq_x z}(1 - r_p^0), \quad (4.12c)$$

$$[G_{xx}(z, z_1)\epsilon_\omega(z_1)]_{z_1 \rightarrow z_0} = -\alpha(1 + r_p^0)e^{-iq_x z}(-Q/q_x)(1 + r_p^0), \quad (4.12d)$$

$$\epsilon_\omega(z)G_{xx}(z, z_0) = \alpha(Q/q_x)(1 + r_p^0)e^{-iq_x z}(1 - r_p^0), \quad (4.12e)$$

$$\epsilon_\omega(z)[\bar{G}_{xx}(z, z_1)\epsilon_\omega(z_1)]_{z_1 \rightarrow z_0} = -\alpha(Q/q_x)(1 + r_p^0)e^{-iq_x z}(-Q/q_x)(1 + r_p^0), \quad (4.12f)$$

where r_p^0 and α are given in Eqs. (3.7) and (3.9e), respectively. Substitution of the relevant forms in Eq. (4.8) yields, after a little algebra,

$$\begin{aligned} E_x(z) \underset{z \rightarrow -\infty}{\sim} e^{iq_x z} - e^{-iq_x z} r_p^0 \left(1 - \frac{i(\epsilon_b q_x + k_x)}{4\epsilon_b} \frac{(1 + r_p^0)(1 - r_p^0)^2}{r_p^0} \Lambda_x(\omega) \right. \\ \left. - \frac{i(\epsilon_b q_x + k_x)}{4\epsilon_b} \frac{Q^2}{q_x^2} \frac{(1 + r_p^0)^3}{r_p^0} \Lambda_x(\omega) \right) \\ = e^{iq_x z} - e^{-iq_x z} r_p^0 \left(1 - 2iq_x \frac{[k_x^2 \Lambda_x(\omega) + \epsilon_b^2 Q^2 \Lambda_x(\omega)]}{(1 - \epsilon_b)(Q^2 - \epsilon_b q_x^2)} \right). \end{aligned} \quad (4.13)$$

Use has been made here of the result that

$$\epsilon_b^2 q_x^2 - k_x^2 = (\epsilon_b - 1)(\epsilon_b q_x^2 - Q^2). \quad (4.14)$$

Equation (4.13) allows us to identify the reflection amplitude of p polarized light as [cf. Eq. (4.10a)]

$$r_p = r_p^0 \left(1 - 2iq_x \frac{[k_x^2 \Lambda_x(\omega) + \epsilon_b^2 Q^2 \Lambda_x(\omega)]}{(1 - \epsilon_b)(Q^2 - \epsilon_b q_x^2)} \right). \quad (4.15)$$

The same formula can also be obtained by combining Eqs. (4.9) and (4.12) after taking the limit $z \rightarrow -\infty$, and making use of the definition of Eq. (4.10b). It should be noted that the apparent singularity of the correction term at $Q = \epsilon_b^{1/2} q_x$ (for real ϵ_b) is not a cause for concern, since this is the Brewster condition when r_p^0 vanishes. The apparent singularity arises because we have expressed the correction to the reflection amplitude as a factor multiplying r_p^0 . A detailed discussion of the usefulness of this formula is given in the next section (Sec. V).

B. s polarization

The analysis in this case closely parallels that for p polarization. We start now with the integral equation (2.13), and make the long-wavelength ap-

proximation as in the previous case. We obtain

$$\begin{aligned} E_y(z) = U_y(z) - \frac{\omega^2}{c^2} E_y(z_0) G_{yy}(z, z_0) \\ \times \int dz'' \int dz' \Delta \epsilon_{yy}(z'', z'). \end{aligned} \quad (4.16)$$

Exactly as in Eqs. (4.7), we can write

$$\begin{aligned} \int \int_{-\infty}^{\infty} dz'' dz' \Delta \epsilon_{yy}(z'', z') = \int \int_{-\infty}^{\infty} dz'' dz' \\ \times [\epsilon_{yy}(0, \omega; z'', z') \\ - \epsilon_\omega(z'') \delta(z'' - z')] \\ = \int_{-\infty}^{\infty} dz'' [\langle \epsilon_{yy}(z'') \rangle - \epsilon_\omega(z'')] \end{aligned} \quad (4.17a)$$

$$\equiv \Lambda_y(\omega), \quad (4.17b)$$

the last relation being just a definition of $\Lambda_y(\omega)$.

Equation (4.16) now reads

$$E_y(z) = U_y(z) - (\omega^2/c^2) E_y(z_0) G_{yy}(z, z_0) \Lambda_y(\omega), \quad (4.18)$$

and one can easily solve for $E_y(z_0)$ as

$$E_y(z_0) = U_y(z_0) [1 + (\omega^2/c^2) G_{yy}(z_0, z_0) \Lambda_y(\omega)]^{-1} \quad (4.19)$$

to obtain a complete solution for the electric field. For a consistent perturbation theory, however, we must restrict ourselves to the first Born approximation where one sets $E_y(z_0) = U_y(z_0)$. The reflection amplitude is again obtained by taking the limit $z \rightarrow -\infty$ and using the definition

$$E_y(z) \underset{z \rightarrow -\infty}{\sim} e^{iq_z z} + r_s e^{-iq_z z}. \quad (4.20)$$

This limit is readily worked out when one notes that from Eqs. (3.10), (3.12), and (3.14),

$$U_y(z_0) = (1 + r_s^0) = 2q_z / (q_z + k_z), \quad (4.21a)$$

$$G_{yy}(z, z_0)_{z \rightarrow -\infty} = -[i / (q_z + k_z)] e^{-iq_z z}. \quad (4.21b)$$

Accordingly, in the first Born approximation,

$$E_y(z) \underset{z \rightarrow -\infty}{\sim} e^{iq_z z} + e^{-iq_z z} r_s^0 \{1 + [2iq_z / (1 - \epsilon_y)] \Lambda_y(\omega)\}, \quad (4.22)$$

since

$$q_z^2 - k_z^2 = (\omega^2/c^2) [1 - \epsilon_y(\omega)]. \quad (4.23)$$

This implies that the reflection amplitude for s polarized light is related to the corresponding Fresnel formula by

$$r_s = r_s^0 \{1 + [2iq_z / (1 - \epsilon_y)] \Lambda_y(\omega)\}. \quad (4.24)$$

V. OPTICAL REFLECTANCE AND ELLIPSOMETRY

A. Differential reflectance with chemisorbed overlayers

Optical reflectance or reflectivity is defined as the square of the modulus of the reflection amplitude. Calling R_p (R_s) the reflectivity of p (s) polarized light, we have

$$R_p = |r_p|^2, \quad R_s = |r_s|^2. \quad (5.1)$$

If R_p^0 and R_s^0 are the optical reflectances of the corresponding Fresnel problem of reflection at a sharp dielectric discontinuity at the surface, the differential reflectance of p polarized light is defined through

$$\Delta R_p / R_p^0 = (R_p - R_p^0) / R_p^0 = |r_p / r_p^0|^2 - 1. \quad (5.2)$$

A similar definition obtains for the differential reflectance of s polarized light. Using Eqs. (4.15) and (4.24), we find

$$\frac{\Delta R_p}{R_p^0} = 4q_z \text{Im} \left(\frac{k_x^2 \Lambda_x(\omega) + \epsilon_b^2 Q^2 \Lambda_x(\omega)}{(1 - \epsilon_b)(Q^2 - \epsilon_b q_z^2)} \right), \quad (5.3)$$

$$\Delta R_s / R_s^0 = 4q_z \text{Im} [\Lambda_y(\omega) / (\epsilon_b - 1)]. \quad (5.4)$$

Equations (5.3) and (5.4) are two of the major results of our formalism. They express the change

in reflectivity from the classical Fresnel result, to first order in q_z , entirely in terms of three complex system-dependent parameters, Λ_x , Λ_y , and Λ_z , which are functions of the frequency ω [cf. Eqs. (4.11) and (4.17)]. The reflectance change is brought about, in the first place, by the response of the metal surface not being describable within the simple Fresnel theory. That the parameters $\Lambda_\mu(\omega)$ [$\mu = x, y, \text{ or } z$] are characteristic of the surface of the system becomes clear when we note that their definitions involve integrals whose main contributions come from the surface region. Finally let us stress that, as mentioned in the previous section Eq. (5.3) does not have a real singularity at $Q = \epsilon_b^{1/2} q_z$ where R_p^0 itself vanishes, so that the first nonvanishing contribution to ΔR_p at this angle is of order q_z^2 .

Our results, furthermore, can be readily adapted to the situation of surface reflectance spectroscopy (SRS), where one studies the change in reflectance from a metal surface upon chemisorption. SRS has developed in recent years into a powerful tool, complementary to photoemission, for the investigation of metal surfaces covered with chemisorbed impurities.²⁴⁻²⁸ The method has been handicapped, however, by the absence of a convenient theoretical formula to analyze the experimental data on differential reflectance using p polarized light. What is needed is a theoretical formula which depends only on the dielectric response of the system, and incorporates in a simple, parametric way such well-known microscopic features of it as nonlocality and surface-induced anisotropy. Lacking that, experimental efforts have been concentrated largely on interpreting the data for s polarization,²⁴⁻²⁷ where the classical McIntyre-Aspnes formula²⁹ for a local dielectric model has been extended and justified by the nonlocal theory of Feibelman.⁹ The latter theory, unfortunately, gives a less useful expression for differential reflectance in the p polarized case. Experimental data for p polarization²⁸ have, therefore, been compared with either the corresponding data for s polarization or the results of a classical model,³⁰ representing the adsorbates by a *local* but *anisotropic* dielectric layer, whose microscopic validity has not been investigated. From Eq. (5.3), we can obtain a new microscopic expression for the differential reflectance of p polarized light on adsorption, which should greatly help the analysis of SRS data and thus enable the technique to realize its full potential. The result, correct to first order in q_z , is

$$\left(\frac{\Delta R_p}{R_p^0} \right)_a = 4q_z \text{Im} \left(\frac{k_x^2 \delta \Lambda_x(\omega) + \epsilon_b^2 Q^2 \delta \Lambda_x(\omega)}{(1 - \epsilon_b)(Q^2 - \epsilon_b q_z^2)} \right), \quad (5.5)$$

where

$$\delta\Lambda_x(\omega) = \int_{-\infty}^{\infty} dz [\langle \epsilon_{xx}^{(a)}(z) \rangle - \langle \epsilon_{xx}(z) \rangle] \quad (5.5a)$$

and

$$\delta\Lambda_x(\omega) = \int_{-\infty}^{\infty} dz [\langle \epsilon_{xx}^{-1(a)}(z) \rangle - \langle \epsilon_{xx}^{-1}(z) \rangle]. \quad (5.5b)$$

Here quantities labeled by the superscript (or subscript) a refer to the case when adsorbed impurities are present on the surface, while the corresponding objects without any superscript refer to the clean metal.

The chief merit of Eq. (5.5) lies in the fact that it expresses the differential reflectance in terms of two complex system-dependent parameters which represent, in a succinct way, the change in surface response in the presence of adsorbates. It is clear from their definition that $\delta\Lambda_x$ and $\delta\Lambda_x$

do not depend on any special feature of the background metal introduced for purposes of subtraction in Sec. II. In particular they are independent of the choice of z_0 [cf. Eq. (2.4)] as the plane at which the background metal terminates. This point will become clear in Sec. V B, where we show explicitly how Eq. (5.5) reduces to all previously reported results for changes in p -polarized reflection brought about by diffuse metal surfaces which are, however, describable by local dielectric functions. In addition, Feibelman's result⁹ for the differential reflectance of p -polarized light can be reduced to Eq. (5.3) after solving for the electric field formally in terms of $\tilde{\epsilon}^{-1}$ and carrying out a delicate integration by parts. The utility of Eq. (5.5) becomes even more apparent on rewriting it in terms of the angle of incidence θ_i . We find

$$\left(\frac{\Delta R_p}{R_p}\right)_a = 4\left(\frac{\omega}{c}\right) \cos\theta_i \operatorname{Im} \left(\frac{[\epsilon_b(\omega) - \sin^2\theta_i] \delta\Lambda_x(\omega) + \epsilon_b^2(\omega) \sin^2\theta_i \delta\Lambda_x(\omega)}{[1 - \epsilon_b(\omega)][\sin^2\theta_i - \epsilon_b(\omega) \cos^2\theta_i]} \right). \quad (5.6)$$

This equation enables us to determine the real and imaginary parts of $\delta\Lambda_x$ and $\delta\Lambda_x$ by performing measurements at four different values of θ_i , provided that we assume $\epsilon_b(\omega)$ to be known already from independent measurements of reflectance on the bulk metal. Useful control on the results is possible when we note that $\delta\Lambda_x(\omega)$ and $\delta\Lambda_x(\omega)$, being differences of response functions, must have their real and imaginary parts connected by appropriate Kramers-Kronig relations. The latter may be used either to test the results for consistency, or to extract information from fewer than four measurements by relying on some physically motivated extrapolation procedure. Such an extrapolation scheme has already been used successfully^{26,31} to study SRS data for s polarization.

For s -polarized light, our result of Eq. (5.4) for differential reflectance can be shown to be equivalent to those of previous theories^{9,32} once we express $\Lambda_y(\omega)$ as a function of conductivities instead of dielectric functions. When an adsorbed layer is present, the differential reflectance assumes the form

$$\left(\frac{\Delta R_s}{R_s}\right)_a = 4\left(\frac{\omega}{c}\right) \cos\theta_i \operatorname{Im} \left(\frac{\delta\Lambda_y(\omega)}{\epsilon_b(\omega) - 1} \right), \quad (5.7)$$

where

$$\delta\Lambda_y(\omega) = \int_{-\infty}^{\infty} dz [\langle \epsilon_{yy}^{(a)}(z) \rangle - \langle \epsilon_{yy}(z) \rangle]. \quad (5.7a)$$

This formula has already been studied experimentally to deduce values for the real and imaginary parts of $\delta\Lambda_y(\omega)$.^{26,31} Since the model we have been studying in this paper ignores effects of crystallin-

ity of the surface, clearly $\delta\Lambda_y = \delta\Lambda_x$, and the equality should be good in actual cubic systems for long-wavelength light waves, to the order of accuracy promised by our formulas. Thus the analysis of SRS data for p polarization, when carried out in conjunction with the analysis for s polarized data, may permit us to determine $\delta\Lambda_x(\omega)$ in Eq. (5.6) completely from measurements at only two angles of incidence. Further simplifications may result from a proper exploitation of the Kramers-Kronig relations. Numerical calculations for differential reflectance based on using Eq. (5.6) and a model adsorbate layer on isotropic substrates are currently in progress and will be reported elsewhere.⁴¹

B. Comparison with previous results

This subsection is devoted to the comparison of our result for the differential reflectance of p polarized light, in the appropriate limits, to the formulas derived by previous authors on models based on a local dielectric response. The first model we consider is the one studied by Drude,³³ who improved on the Fresnel model by imagining an extended surface region rather than a sharp surface. The dielectric response is local and isotropic, but depends on z in the surface region which is believed to have a length l . In other words, we assume

$$\epsilon_{zz}(0, \omega; z, z') = \epsilon_{xx}(0, \omega; z, z') = \langle \epsilon_{xx}(z) \rangle \delta(z - z'), \quad (5.8a)$$

so that [cf. Eqs. (4.7)]

$$\langle \epsilon_{xx}^{-1}(z) \rangle = 1 / \langle \epsilon_{xx}(z) \rangle, \quad (5.8b)$$

where $\langle \epsilon_{xx}(z) \rangle = 1$ for $z < 0$, $\langle \epsilon_{xx}(z) \rangle = \epsilon(z)$ —a function of z —for $0 < z < l$, and $\langle \epsilon_{xx}(z) \rangle = \epsilon_b$ for $z > l$. Substitute this function in Eqs. (4.11) and recall the definition of $\epsilon_\omega(z)$ given in Eq. (3.2b). We find

$$\Lambda_x(\omega) = p - \epsilon_b l - z_0(1 - \epsilon_b), \quad (5.9a)$$

$$\Lambda_x(\omega) = q - l/\epsilon_b + z_0(1 - \epsilon_b)/\epsilon_b, \quad (5.9b)$$

where we have defined (following Drude)

$$p = \int_0^l dz \langle \epsilon(z) \rangle; \quad q = \int_0^l dz / \langle \epsilon(z) \rangle. \quad (5.9c)$$

Use of these results in Eq. (5.3) yields

$$\frac{\Delta R_p}{R_p^0} = 4q_x \text{Im} \left(\frac{pk_x^2 - \epsilon_b l(k_x^2 + Q^2) + q\epsilon_b^2 Q^2 - z_0(1 - \epsilon_b)(k_x^2 - \epsilon_b Q^2)}{(1 - \epsilon_b)(Q^2 - \epsilon_b q_x^2)} \right). \quad (5.10)$$

But since

$$k_x^2 - \epsilon_b Q^2 = \epsilon_b q_x^2 - Q^2, \quad (5.11)$$

and z_0 is real, Eq. (5.10) is evidently independent of z_0 , supporting our earlier assertion of Sec. II that physical results like fractional reflectance change ought to be independent of z_0 . Finally, re-expressing all quantities in terms of the angles of incidence and refraction, θ_i and θ_r , we arrive at Drude's result³³

$$\frac{\Delta R_p}{R_p} = 4q_x \text{Im} \left(\frac{p \cos^2 \theta_r - l \epsilon_b + q \epsilon_b^2 \sin^2 \theta_r}{\epsilon_b \cos^2 \theta_i - \cos^2 \theta_r} \right), \quad (5.12)$$

apart from a trivial difference in sign attributable to the different way in which Drude defines his plane waves.

The McIntyre-Aspnes model²⁹ places an adsorb-

ate layer of a definite thickness d on the metal, but is otherwise similar to Drude's model in the sense that the dielectric response is still local and isotropic. Equations (5.8) are still valid, but this time we write

$$\langle \epsilon_{xx}^{(a)}(z) \rangle = \epsilon_a, \quad \langle \epsilon_{xx}(z) \rangle = 1, \quad -d < z < 0, \quad (5.13a)$$

$$\langle \epsilon_{xx}^{(a)}(z) \rangle = \langle \epsilon_{xx}(z) \rangle, \quad z < -d \text{ and } z > 0. \quad (5.13b)$$

Accordingly, from Eqs. (5.5a) and (5.5b), we obtain

$$\delta \Lambda_x(\omega) = d(\epsilon_a - 1), \quad (5.14a)$$

$$\delta \Lambda_x(\omega) = d(1 - \epsilon_a)/\epsilon_a. \quad (5.14b)$$

We substitute these in Eq. (5.5) and add and subtract suitable factors of ϵ_b . With a little manipulation, we derive the McIntyre-Aspnes formula²⁹

$$\begin{aligned} \left(\frac{\Delta R_p}{R_p} \right)_a &= 4q_x d \text{Im} \left(\frac{k_x^2(\epsilon_a - \epsilon_b) - \epsilon_b Q^2(\epsilon_a - \epsilon_b)/\epsilon_a + (\epsilon_b - 1)(k_x^2 - \epsilon_b Q^2)}{(1 - \epsilon_b)(Q^2 - \epsilon_b q_x^2)} \right) \\ &= 4q_x d \text{Im} \left(\frac{(\epsilon_a - \epsilon_b)}{(1 - \epsilon_b)} \frac{\epsilon_b \omega^2/c^2 - Q^2[1 + \epsilon_b/\epsilon_a]}{Q^2 - \epsilon_b q_x^2} \right). \end{aligned} \quad (5.15)$$

The most interesting aspect of the result of Eq. (5.3), however, is that because of the twin properties of nonlocality and surface-induced anisotropy of the dielectric response function of a semi-infinite medium, one finds, in general, that $\langle \epsilon_{xx}^{-1}(z) \rangle \neq 1/\langle \epsilon_{xx}(z) \rangle$. This implies that for reflectance purposes, the surface response may be approximated by an effective *local* but *anisotropic* response function. The anisotropy should be even more important when a chemisorbed layer is present, as has been noted in thin-film studies with ellipsometry.^{34,35} Thus, for purposes of analyzing the p polarized SRS data, the simplest model must assume a uniform, anisotropic dielectric layer to represent the adsorbate on top of an isotropic substrate, and this gives a zeroth-order microscopic justification to the model of Dignam, Moskovits, and Stobie.³⁰ Their result may be derived from Eqs. (5.5) if we assume

$$\langle \epsilon_{xx}^{(a)}(z) \rangle - \langle \epsilon_{xx}(z) \rangle = \begin{cases} \epsilon_1 - 1, & -d < z < 0, \\ 0, & \text{otherwise,} \end{cases} \quad (5.16)$$

and

$$\langle \epsilon_{xx}^{-1(a)}(z) \rangle - \langle \epsilon_{xx}^{-1}(z) \rangle = \begin{cases} 1/\epsilon_3 - 1, & -d < z < 0, \\ 0, & \text{otherwise,} \end{cases} \quad (5.17)$$

with $\epsilon_3 \neq \epsilon_1$. This implies that the adsorbate layer is being treated as a uniaxial medium with the axis of symmetry pointing along the surface normal, z . Substitution in Eqs. (5.5) and straightforward algebra lead to the result

$$\left(\frac{\Delta R_p}{R_p} \right)_a = 4q_x d \text{Im} \left(\frac{\epsilon_1 \cos^2 \theta_r - \epsilon_1 (n^2/\epsilon_1) \cos^2 \theta_a}{\epsilon_b \cos^2 \theta_i - \cos^2 \theta_r} \right). \quad (5.18)$$

Here θ_i is the angle of incidence, θ_a the angle of refraction in the ad-layer and θ_r the angle of refraction in the substrate. They are related to each other through

$$\sin\theta_i = n \sin\theta_a = \epsilon_b^{1/2} \sin\theta_r, \quad (5.19)$$

where the angle-dependent effective refractive index n of the ad-layer is given by³⁶

$$n^2/\epsilon_1 = 1 + (\epsilon_1^{-1} - \epsilon_3^{-1}) \sin^2\theta_i. \quad (5.20)$$

Note that in the limit when the adsorbate layer is isotropic, $\epsilon_1 = \epsilon_3 \Rightarrow n^2 = \epsilon_1$ and Eq. (5.18) goes over to the McIntyre-Aspnes formula.

C. Ellipsometry

So far in this section, we have been concerned only with the moduli of the reflection amplitudes r_p and r_s . Their phases, however, are important in ellipsometric studies where one determines the

change in the state of polarization of polarized light upon reflection at a surface. This change is commonly described by two angles ψ and Δ , defined through³⁵

$$r_p/r_s = \tan\psi e^{i\Delta}. \quad (5.21)$$

Let ψ and Δ refer to the angles for a clean metal, ψ_0 and Δ_0 the corresponding angles for the background Fresnel problem, and ψ_a and Δ_a the angles when chemisorbed impurities are present on the surface. The differences $(\Delta - \Delta_0)$ and $(\psi - \psi_0)$ are, of course, very small. They are caused, in the long-wavelength limit, by the surface response of the metal being different from the Fresnel model. From Eqs. (4.15) and (4.24) we have, to $O(q_x)$,

$$\tan\psi^{i\Delta} \cong \tan\psi_0 e^{i\Delta_0} \left[1 - \frac{2iq_x}{1 - \epsilon_b} \left(\frac{k_x^2 \Lambda_x(\omega) + \epsilon_b^2 Q^2 \Lambda_x(\omega)}{Q^2 - \epsilon_b q_x^2} + \Lambda_y(\omega) \right) \right]. \quad (5.22)$$

The change in ψ is related directly to reflectance changes discussed earlier in this section. The change in Δ is given, to lowest order in q_x , by

$$\Delta - \Delta_0 = -2q_x \operatorname{Re} \left(\frac{k_x^2 \Lambda_x(\omega) + \epsilon_b^2 Q^2 \Lambda_x(\omega) + (Q^2 - \epsilon_b q_x^2) \Lambda_y(\omega)}{(1 - \epsilon_b)(Q^2 - \epsilon_b q_x^2)} \right). \quad (5.23a)$$

In our model, $\Lambda_x(\omega) = \Lambda_y(\omega)$, and since $k_x^2 + Q^2 = \epsilon_b \omega^2/c^2$, the above equation may be rewritten compactly as

$$\Delta - \Delta_0 = -2q_x \operatorname{Re} \left(\frac{\epsilon_b Q^2 [\Lambda_x(\omega) + \epsilon_b \Lambda_y(\omega)]}{(1 - \epsilon_b)(Q^2 - \epsilon_b q_x^2)} \right). \quad (5.23b)$$

It is important to note that the change in Δ depends on two complex parameters, so that if the surface of a clean material is to be represented by a transition layer, as has been done³⁷ on Si (111), one should take into account the anisotropic nature of its dielectric response.

Ellipsometry measurements with physisorbed and chemisorbed objects down to submonolayer coverages have been reported by a number of investigators using semiconductor^{38,39} as well as metal⁴⁰ surfaces. Use of our formalism leads to the result

$$\Delta_a - \Delta = -2q_x \operatorname{Re} \left(\frac{\epsilon_b Q^2 [\delta\Lambda_x(\omega) + \epsilon_b \delta\Lambda_y(\omega)]}{(\epsilon_b - 1)(\epsilon_b q_x^2 - Q^2)} \right), \quad (5.24)$$

where $\delta\Lambda_x$ and $\delta\Lambda_y$ are given by Eqs. (5.5). An inspection of Eqs. (5.6) and (5.7) clearly shows that the ability to do ellipsometry simultaneously with differential reflectance measurements for both s and p polarizations would enable one to determine the real and imaginary parts of $\delta\Lambda_x$ and $\delta\Lambda_y$ from

experiments done at a single angle of incidence (but using many frequencies). Note that Eq. (5.22) goes over to Eq. (13) of Bootsma and Meyer³⁸ under the assumption that the chemisorbed layer is of thickness d , and isotropic in its dielectric properties, so that $\langle \epsilon_{xx}^{-1(a)}(z) \rangle = 1/\langle \epsilon_{xx}^{(a)}(z) \rangle$. It is more sensible, though, to treat the adsorbate as an anisotropic dielectric layer, as has already been recognized in the literature.³⁰

VI. CONCLUSION

In this paper we hope to convey two major results. First, we have developed a perturbative method of considerable generality to determine the electric field distribution in space in the problem of the reflection and refraction of light by an arbitrary metal surface. The method is based on isolating a background or unperturbed problem close to the actual problem, for which the electric field distribution can be solved exactly. The deviation of the actual solution for the electric field from the unperturbed solution is then expressed as an integration over the dielectric "perturbation," and can be written down as a perturbation series in inverse powers of the wavelength of light. We have chosen to apply the technique in this paper to the case where the background problem is the classical Fresnel problem of a local dielectric description of the metal with a sharp surface. Since the unperturbed solution in that case is exactly known,

considerable progress can be made in terms of setting up the perturbation theory. Our method can be applied, however, to a wide variety of situations and models. For example, it is possible to choose as our unperturbed problem a metal with a sharp surface having a nonlocal dielectric function, which can be either translationally invariant in the bulk,²¹⁻²³ or can be generalized to include specular reflection of electrons at the surface¹ as in the semi-classical infinite barrier model.⁵ What is necessary in either case is knowledge of the independent solutions and the Green's functions for the background problem. Our technique would then enable one to find out corrections to the electric field brought about by surface diffuseness or the presence of adsorbed objects. It will be of interest to study these more realistic background models to see what new light they may shed on the problem at hand.

The second result of the paper is that, by doing the first Born approximation and utilizing the long-wavelength nature of light waves, we have derived an expression for the change of reflectance of p polarized light brought about by chemisorbed impurities on a metal surface. Our formula depends only on the dielectric response functions of the clean- and the adsorbate-covered system, and it does not depend on the choice of a specific background problem used in the perturbation theory. As such, it should greatly facilitate the analysis and interpretation of experimental data in surface reflectance spectroscopy. In addition, we apply our formalism in this paper to study the change in reflectance of s polarized light caused by adsorption, and to problems of ellipsometry.

In the future we plan to carry forward the approach presented here in two directions. We are using the formulas developed here to estimate numerically the differential reflectance of both s - and p -polarized light from a metal substrate (assumed isotropic) covered with a monolayer of light gases. Electronic states in the chemisorbed layer form two-dimensional bands, and electronic transitions between them mainly contribute to the (anisotropic) dielectric response of the overlayer. Preliminary conclusions based on this study have already been reported.⁴¹ We are also interested in finding out how importantly the nonlocality of the dielectric response of a metal affects its optical reflectance. Numerical calculations based on simple, yet physical, models for a semi-infinite metal are now in progress to elucidate this point.

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APPENDIX

Here we sketch the derivation of the elements of the matrix Green's function, which were written in Eqs. (3.9), for the Fresnel problem with p polarized light. We begin with the matrix equation (3.8) written in pairs. The first pair of equations, coupling G_{xx} and G_{zx} , is

$$\left(\frac{d^2}{dz^2} + \frac{\omega^2}{c^2} \epsilon_\omega(z)\right) G_{xx}(z, z') - iQ \frac{d}{dz} G_{zx}(z, z') = \delta(z - z'), \quad (\text{A1a})$$

$$-iQ \frac{d}{dz} G_{xx}(z, z') + \left(\frac{\omega^2}{c^2} \epsilon_\omega(z) - Q^2\right) G_{zx}(z, z') = 0. \quad (\text{A1b})$$

Since the Green's functions obey homogeneous equations for $z \neq z'$, they can be expressed in terms of the solutions of the latter as given in Eqs. (3.3)–(3.5), i.e.,

$$G_{xx}(z, z') = \alpha[\theta(z - z')U_x(z)V_x(z') + \theta(z' - z)V_x(z)U_x(z')], \quad (\text{A2a})$$

$$G_{zx}(z, z') = \alpha[\theta(z - z')U_z(z)V_x(z') + \theta(z' - z)V_z(z)U_x(z')], \quad (\text{A2b})$$

where α is a constant coefficient which has to be determined, and Θ is the usual step function. Note that the outgoing-wave boundary condition has been imposed on the Green's function. Substituting these equations in Eq. (A1a), we obtain

$$\alpha\{-W(U_x, V_x) - iQ[U_z(z)V_x(z) - V_z(z)U_x(z)]\} = 1, \quad (\text{A3})$$

with $W(f, g) = fg' - gf'$ denoting the Wronskian of the two functions f and g . By direct substitution of Eqs. (3.3)–(3.5), we find

$$W(U_x, V_x) = \begin{cases} -\frac{4i\epsilon_b q_z^2}{\epsilon_b q_z + k_z}, & \tilde{z} < 0, \\ -\frac{4ik_z^2}{\epsilon_b q_z + k_z}, & \tilde{z} > 0. \end{cases} \quad (\text{A4})$$

Similarly,

$$U_z(z)V_x(z) - V_z(z)U_x(z) = \begin{cases} -4\epsilon_b Q/(\epsilon_b q_z + k_z), & \tilde{z} < 0, \\ -4Q/(\epsilon_b q_z + k_z), & \tilde{z} > 0. \end{cases} \quad (\text{A5})$$

The use of these results in Eq. (A3) shows that the combination within curly brackets is z independent,

thus yielding the value of α as

$$\alpha = \frac{\epsilon_b q_x + k_x}{4i\epsilon_b(\omega^2/c^2)}. \quad (\text{A6})$$

Equations (A2) are easily seen to satisfy Eq. (A1b) as well.

The second pair of equations following from Eq. (3.8) couples G_{xx} and G_{zz} , and has the form

$$\left(\frac{d^2}{dz^2} + \frac{\omega^2}{c^2} \epsilon_\omega(z)\right) G_{xx}(z, z') - iQ \frac{d}{dz} G_{zz}(z, z') = 0, \quad (\text{A7a})$$

$$-iQ \frac{d}{dz} G_{xx}(z, z') + \left(\frac{\omega^2}{c^2} \epsilon_\omega(z) - Q^2\right) \times G_{zz}(z, z') = \delta(z - z'). \quad (\text{A7b})$$

These functions obey homogeneous equations for $z \neq z'$. Furthermore, Eq. (A7b) does not impose any continuity requirement on $G_{xx}(z, z')$ at $z = z'$, i.e., it may have a δ -function part. Recognizing this, we try the very general *Ansatz*

$$G_{xx}(z, z') = \beta[\theta(z - z')U_x(z)V_x(z') + \theta(z' - z)V_x(z)U_x(z')], \quad (\text{A8a})$$

$$G_{zz}(z, z') = \beta[\theta(z - z')U_z(z)V_z(z') + \theta(z' - z)V_z(z)U_z(z') + \beta\gamma(z)\delta(z - z')], \quad (\text{A8b})$$

where β is a constant and $\gamma(z)$ is a function, both of which are unknown and to be determined. Substitute these formulas in Eq. (A7a). Consistency demands that

$$\delta(z - z') \left(\frac{dU_x}{dz} V_x - \frac{dV_x}{dz} U_x \right) + \frac{d}{dz} [\delta(z - z')(U_x V_x - V_x U_x)] - iQ \frac{d}{dz} [\gamma(z)\delta(z - z')] = 0. \quad (\text{A9})$$

Now the definition of Eq. (3.5) ensures that

$$\frac{dU_x}{dz} V_x - \frac{dV_x}{dz} U_x = 0. \quad (\text{A10})$$

Therefore, using Eqs. (A5) and (A6), we get

$$\gamma(z) = -\frac{1}{\epsilon_\omega(z)} \frac{4i\epsilon_b}{\epsilon_b q_x + k_x} = -\frac{1}{\epsilon_\omega(z)\alpha(\omega^2/c^2)}. \quad (\text{A11})$$

Next we substitute Eqs. (A8) in Eq. (A7b). After straightforward algebra, we find

$$-iQ\beta(U_x V_x - V_x U_x) + [(\omega^2/c^2)\epsilon_\omega(z) - Q^2]\beta\gamma(z) = 1. \quad (\text{A12})$$

Making use of Eqs. (A9) and (A10), we obtain

$$(\omega^2/c^2)\epsilon_\omega(z)(U_x V_x - V_x U_x)\beta = iQ. \quad (\text{A13})$$

Finally, a simple calculation with the help of Eq. (A5) leads to the result

$$\beta = \frac{i(\epsilon_b q_x + k_x)}{4\epsilon_b(\omega^2/c^2)} = -\alpha. \quad (\text{A14})$$

These results are concisely reproduced in Eqs. (3.9a)–(3.9e).

The Green's functions we derived in this paper are valid over all space. They reduce to Green's functions derived by previous authors^{17,18} in appropriate regions of space. For *s* polarized light, for example, Eqs. (3.10)–(3.14) show that when $\bar{z}, \bar{z}' > 0$, we get

$$G_{yy}(z, z') = \frac{1}{2ik_x} \left[e^{ik_x|z-z'|} + \left(\frac{k_x - q_x}{k_x + q_x} \right) e^{ik_x(\bar{z} + \bar{z}')} \right], \quad (\text{A15})$$

and this agrees with the result quoted in the Appendix of Ref. 17. In the *p*-polarized case, on the other hand, Eq. (3.9d) yields after appropriate substitutions ($\bar{z}, \bar{z}' > 0$)

$$G_{zz}(z, z') = \frac{c^2}{\epsilon_b \omega^2} \delta(z - z') + \frac{1}{2ik_x} \frac{Q^2}{\epsilon_b(\omega^2/c^2)} \times \left[e^{ik_x|z-z'|} + \left(\frac{\epsilon_b q_x - k_x}{\epsilon_b q_x + k_x} \right) e^{ik_x(\bar{z} + \bar{z}')} \right]. \quad (\text{A16})$$

Comparison with Eq. (B22) of Ref. 18 shows that the Green's function is the same as that of Eguluz and Maradudin except for the fact that the term $\exp[ik_x(\bar{z} + \bar{z}')]$ is multiplied by unity in their case instead of γ_p^0 as above. The difference arises from a different choice of the boundary condition at the nominal surface, where Eguluz and Maradudin insist on the vanishing of Green's functions of the type G_{xx} and G_{zz} . The factor of γ_p^0 multiplying the last exponential of Eq. (A16) appears, however, in the work of Dahl and Sham.¹⁷

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