Electrodynamics of optically thin transition layers of resonant inhomogeneously layered media

G. V. Rozhnov

State Research-Production-Commercial Engineering Enterprises "Oplot"
(Submitted 20 April 1992)
Zh. Eksp. Teor. Fiz. **103**, 740–757 (March 1993)

A general regular self-consistent procedure is developed to determine the reflection and transmission amplitude coefficients of polarized electromagnetic waves of arbitrarily layered inhomogeneous uniaxially anisotropic media perturbed by the presence of a surface layer of arbitrary physical origin and homogeneity. The result is applicable to the entire frequency range, including the vicinity of resonant natural modes of the medium. A connection is established between these coefficients and the integral effective-layer parameters of first and second order in thickness; these coefficients are uniquely expressed in terms of the microscopic susceptibility of the layer.

1. INTRODUCTION

Surface (including molecular) layers present on interfaces between media alter their optical properties (reflection and transmission coefficients, locations and widths of resonant natureal modes). A microscopic description of the surface region, which is obligatory in the case of adsorption by molecular layers, calls in general also for a like description of the volume,[1] thereby complicating the problem greatly. In a number of typical cases, however, when the surface effects are not small compared with the inhomogeneity of the volume, for example adsorption of a layer of resonant molecules, or when the layer is macroscopic but thin, $a \ll d \ll \lambda$ (a is the lattice constant, d the layer thickness, and λ the wavelength), a simpler formulation is possible, with the bulk of the material described by averaged equations of macroscopic electrodynamics, and the surface region by microscopic relations. Even in this simpler formulation, however, which is typical of most studies in this field[2–10] and is adopted also in the present paper, the results are particular and restricted. The reason is either the elementary character of the iteration method used to solve the equations by the Green's function (GF) method[2–4] (in which case only the nonresonant frequency region can be described), or the cumbersome system of equations involved when the problem is solved by "matching" the fields on the boundary[5–8] and by the FG method when a self-consistent method is used to solve the problem[9,10] (in which case analytic results can be obtained only for the simplest models of layered media and surface layers).

We develop here a regular self-consistent procedure for calculating the reflection and transmission amplitude coefficients of arbitrary inhomogeneously layered media which are perturbed by the presence of a surface layer of arbitrary physical nature and arbitrary degree of anisotropy. The procedure developed does not call for solving a cumbersome system of algebraic equations, and the obtained reflection and transmission coefficients have correct analytic properties in any finite order of expansion in powers of the perturbation. They are valid in the entire frequency range, including the vicinities of resonant natural modes of the medium.

The solution is obtained by the GF method, but in contrast to the traditional approach,[2–4,9,10] in which the radiative Green's function G is used, we employ retarded and advanced GF $G^{\pm}$ which, unlike G, have no pole singularities corresponding to natural modes of the unperturbed medium.

For an optically thin transition layer with arbitrary physical properties and degree of anisotropy, located on the interface of arbitrary inhomogeneously layered uniaxially anisotropic media, the formalism developed yield in elementary fashion the entire set of integral effective parameters of the layer of first, second, etc., order in thickness, in terms of which the optical characteristics of the medium are uniquely expressed. Similar equations were heretofore self-consistently solved only for various particular cases of spatial distribution of the contiguous media or of the form and degree of anisotropy of the transition layers, and as a rule only in an approximation linear in d/λ.

2. FORMULATION OF PROBLEM AND FUNDAMENTAL RELATIONS

According to the traditional formulation,[2–10] averaging of the icroscopic equations of linear electrodynamics in a layer plane $z = \text{const}$ over a dimension exceeding the characteristic scale of the inhomogeneities, leads for the field of a monochromatic electromagnetic (EM) wave

$$\mathbf{E}(\mathbf{r}, t) = \exp(-i\omega t + i\mathbf{b}\boldsymbol{\rho})\mathbf{E}(\mathbf{b}, z),$$

where $\boldsymbol{\rho} = (x,y)$ and $\mathbf{b}$ is the projection of the wave vector on the plane $z = \text{const}$, to the equation

$$(\text{rot rot} - k_0^2\hat{\varepsilon}_z)\mathbf{E}(\mathbf{b}, z) = k_0^2 \frac{4\pi i}{\omega}\,\delta\mathbf{j}(\mathbf{b}, z), \tag{1}$$

where

$$\text{rot} = \left(i\mathbf{b} + \hat{\mathbf{z}}\frac{d}{dz}\right)\times,$$

k_0 is the wave number in vacuum, and $\delta\mathbf{j}(\mathbf{b},z)$ is the current density or the polarization $\mathbf{P} = \delta\mathbf{j}/\omega$ of the transition layer, induced by the field $\mathbf{E}(\mathbf{b},z)$:

$$\delta j_l(\mathbf{b}, z) = \frac{\omega}{4\pi i}\int dz'\Delta\varepsilon_{lm}(\mathbf{b}, z, z')E_m(\mathbf{b}, z'), \tag{2}$$

$\Delta\hat{\varepsilon}(\mathbf{b},z,z')$ is the perturbation of the dielectric constant $\hat{\varepsilon}_z$ of the medium, due to the presence of the transition layer

$$\hat{\varepsilon}(\mathbf{b}, z, z') = \hat{\varepsilon}_z\delta(z - z') + \Delta\hat{\varepsilon}(\mathbf{b}, z, z'), \tag{3}$$

 1063-7761/93/030364-09$10.00

$\hat{\varepsilon}_z$ is the dielectric constant of the unperturbed medium

$$\hat{\varepsilon}_z = \varepsilon_\perp(z)\hat{P}_\perp + \varepsilon_\parallel(z)\hat{P}_\parallel,$$

$\hat{P}_\perp = \hat{\mathbf{z}}\hat{\mathbf{z}}$ and $\hat{P}_\parallel = 1 - \hat{P}_\perp$ are projection operators on the direction of the normal to the plane $z = \text{const}$ and on the plane $z = \text{const}$, respectively. The dependences of $\varepsilon_\perp(z)$ and $\varepsilon_\parallel(z)$ on z are arbitrary with a single restriction that they take on at infinity a constant value $\varepsilon_\perp(z) = \varepsilon_\parallel(z) = \varepsilon_j$, where $j = 1$ or 2, respectively, for $z \to +\infty$ and $-\infty$. This constraint is not fundamental and its only purpose is to simplify the expressions for the asymptotic expansion of the fields [see Eq. (9) below]. Any specific choice of the coordinate dependence of $\varepsilon_{\perp,\parallel}$ on z is determined by the distinctive features of the solved problem. It will be assumed henceforth that a complete set of linearly independent analytic solutions $\mathbf{E}^+_{j\beta}(\mathbf{b},z)$ of the unperturbed equation (1) with a zero right-hand side is known (the subscript $j = 1$, 2 labels the medium ε_j, in which is specified for $|z| \to \infty$ an incident $\beta = s^-$, or p-polarized EM wave[11,12]). The solutions $\mathbf{E}^+_{j\beta}$ are used to construct the GF equations (1),[11,12] after which the equation takes the integral form

$$\mathbf{E} = \mathbf{E}_0 + k_0^2\hat{G}\Delta\hat{\varepsilon}\,\mathbf{E}. \tag{4}$$

A feature of all the preceding studies in which the GF technique was used[2-4,9,10] was that $\mathbf{E}_0$ in (4) was the general solution of the unperturbed equation (1) at $\delta\mathbf{j} = 0$, which imposed on the GF G the condition of radiation at infinity. In contrast to the traditional approach, we choose below the unperturbed solution to be one of the independent solutions from the complete set $\mathbf{E}^+_{j\beta}$. This splits (4) into two pairs of independent equations

$$\begin{aligned} \mathbf{E}_{1\beta} &= \mathbf{E}^+_{1\beta} + k_0^2\hat{G}^+\Delta\hat{\varepsilon}\,\mathbf{E}_{1\beta}, \\ \mathbf{E}_{2\beta} &= \mathbf{E}^+_{2\beta} + k_0^2\hat{G}^-\Delta\hat{\varepsilon}\,\mathbf{E}_{2\beta} \end{aligned} \tag{5}$$

for the sought functions of the field $\mathbf{E} = \mathbf{E}_{j\beta}$ with subscripts $j = 1$, 2 and $\beta = s$, p in accord with the employed unperturbed solution $\mathbf{E}^+_{j\beta}$.

Since the perturbation $\Delta\hat{\varepsilon}$ is localized in the region of the transition layer $|z| \leqslant d$, the normalization of the solutions $\mathbf{E}_{j\beta}$ can always be reconciled with the normalization of the solutions $E^+_{j\beta}$ to unity amplitude of the transmitted wave.[11,12] It is necessary then to impose on the GF $G^\pm$ the conditions

$$\begin{aligned} G^+(z,z') &= 0 \quad \text{as} \quad z \to -\infty, \\ G^-(z,z') &= 0 \quad \text{as} \quad z \to +\infty. \end{aligned} \tag{6}$$

These functions are derived in Appendix A. They are analogs of the retarded G^+ and advanced G^- GF of the quantum theory of scattering, if the spatial variables z and z' are identified with the times t and t'. The presence of theta functions in $G^\pm$ in Eq. (A2) reduces Eqs. (5) to the Volterra type. In the traditional formulation, however, Eq. (4) is of the Fredholm type. A specific feature of Volterra equations is an empty set of eigensolutions for finite $\Delta\varepsilon$ (Ref. 13). Therefore the retarded and advanced GF $G^\pm$, in contrast to the radiative G, will have no pole singularities whatever connected with the eigenmodes of the unperturbed medium [see also, e.g., the expansion (A3)]. A simple iteration solution of (5) will contain no pole singularities in any order of the expansion of the fields $\mathbf{E}_{j\beta}$ in powers of the perturbation $\Delta\varepsilon$, and this expansion will converge uniformly in the entire frequency region, including the vicinity of the resonant eigenmodes of the unperturbed medium. The case when the perturbation $\Delta\varepsilon$ is not finite is considered at the end of the article.

We introduce in standard manner[14] the retarded and advanced scattering operators $T^\pm$, as the solution of the equations

$$T^\pm = k_0^2\Delta\varepsilon(1 + G^\pm T^\pm). \tag{7}$$

We obtain then from (5) for the sought functions $\mathbf{E}_{j\beta}$ the representation

$$\begin{aligned} \mathbf{E}_{1\beta} &= (1 + G^+T^+)\mathbf{E}^+_{1\beta}, \\ \mathbf{E}_{2\beta} &= (1 + G^-T^-)\mathbf{E}^+_{2\beta}. \end{aligned} \tag{8}$$

Calculation of the asymptote of (8) as $|z| \to \infty$ and taking (A3) into account we obtain for the solutions $\mathbf{E}_{1\beta}$ the expansion

$$\mathbf{E}_{1\beta}(z) = \begin{cases} \sum\limits_{\alpha=s,p} (\hat{\mathbf{e}}^+_{1\alpha}A^-_{\alpha\beta}e^{-i\eta_1 z} + \hat{\mathbf{e}}^-_{1\alpha}A^+_{\alpha\beta}e^{i\eta_1 z}) & \text{as} \quad z \to +\infty, \\ \hat{\mathbf{e}}^+_{2\beta}e^{-i\eta_2 z} & \text{as} \quad z \to -\infty, \end{cases} \tag{9}$$

where $\eta_j = (k_j^2 - \mathbf{b}^2)^{1/2}$ is the projection of the wave vector on the normal to the plane $z = \text{const}$ in the medium j, $\text{Re}(\text{Im})\eta_j \geqslant 0$ for $\text{Im}\varepsilon_j \geqslant 0$; $k_j = k_0\varepsilon_j^{1/2}$ is the wave number in the medium j; $\hat{\mathbf{e}}^\pm_{j\alpha}$ are the unit vectors of the $\alpha = s$- and p-polarized electromagnetic waves in the medium j;

$$\hat{\mathbf{e}}^\pm_{js} = \hat{\mathbf{s}} = [\hat{\mathbf{b}}\hat{\mathbf{z}}], \quad \hat{\mathbf{e}}^\pm_{jp} = \hat{\mathbf{p}}^\mp_j = (b\hat{\mathbf{z}} \pm \eta_j\hat{\mathbf{b}})/k_j.$$

The coefficients of the functions $A^\pm_{\alpha\beta}$ are determined by the matrix elements

$$A^\pm_{\alpha\beta} = a^\pm_{1\alpha}\delta_{\alpha\beta} \pm \frac{i}{2\eta_1}\int dz dz' \mathbf{E}^-_{2\alpha}(\mp\eta_1, z)\hat{T}^+(z,z')\mathbf{E}^+_{1\beta}(z'), \tag{10}$$

where

$$\mathbf{E}^\pm_{i\alpha}(\eta_j, z) = \mathbf{E}^\pm_{i\alpha}(z), \quad \mathbf{E}^-_{js} = \mathbf{E}^+_{js}, \quad \mathbf{E}^\pm_{jp} = \mathbf{E}_{jz} \pm \mathbf{E}_{jb},$$

$a^\pm_{j\alpha}$ are the coefficients of the asymptotic expansion of the fields $\mathbf{E}^+_{j\alpha}$, and the reflection r_α and transmission t_α coefficients are expressed in their terms:

$$r_\alpha = a^+_{1\alpha}/a^-_{1\alpha}, \quad t_\alpha = 1/a^-_{1\alpha}. \tag{11}$$

Just as the solution of Eqs. (5), the expansion of the coefficient functions (10) in power of $\Delta\varepsilon$, following substitution of the iteration solution of Eq. (7) in Eq. (10), will not contain pole singularities corresponding to eigenmodes of the unperturbed medium, in any order of the expansion in powers of the perturbation $\Delta\varepsilon$.

Renormalizing (9) to unity amplitude of the incident wave, i.e., multiplying (9) from the right by a matrix inverse to $\hat{A}_-$, where $\hat{A}_\pm$ and 2×2 matrices specified by the elements $[\hat{A}_\pm]_{\alpha\beta} = A^\pm_{\alpha\beta}$, we obtain for the amplitude reflection and transmission coefficients $r_{\alpha\beta}$ and $t_{\alpha\beta}$ of the perturbed medium following the incidence of a $\beta = s$- or p-polarized electromagnetic wave from the upper medium, the representation

$$r_{\alpha\beta} = [\hat{A}_+\hat{A}_-^{-1}]_{\alpha\beta}, \qquad t_{\alpha\beta} = [\hat{A}_-^{-1}]_{\alpha\beta}, \tag{12}$$

or, in expanded form

$$r_{ss} = (A_{ss}^+A_{pp}^- - A_{sp}^+A_{ps}^-)/D, \qquad r_{sp} = (A_{sp}^+A_{ss}^- - A_{ss}^+A_{sp}^-)/D,$$

$$r_{ps} = (A_{ps}^+A_{pp}^- - A_{pp}^+A_{ps}^-)/D, \qquad r_{pp} = (A_{pp}^+A_{ss}^- - A_{ps}^+A_{sp}^-)/D,$$

$$t_{ss} = A_{pp}^-/D, \qquad t_{pp} = A_{ss}^-/D, \tag{13}$$

$$t_{sp} = -A_{sp}^-/D, \qquad t_{ps} = -A_{ps}^-/D,$$

where $D = |\hat{A}_-|$ is the determinant of the matrix $\hat{A}_-$

$$D = A_{ss}^-A_{pp}^- - A_{sp}^-A_{ps}^-. \tag{14}$$

Equations (12) are meaningful only if the matrix $\hat{A}_-$ is not degenerate. Otherwise, for

$$D = 0, \tag{15}$$

which corresponds to the pole of the reflection/transmission coefficients, the solution (9) determines the field of the eigenmodes $\mathbf{E}_n(z)$ of the unperturbed medium. Condition (15) is then the dispersion law $\mathbf{b} = \mathbf{b}_n(\omega)$ of these modes. Taking (15) into account, we obtain from (9) from the eigensolutions the representation

$$\mathbf{E}_n(z) = \begin{cases} [(A_{ss}^-A_{pp}^+ - A_{sp}^-A_{ps}^+)\hat{\mathbf{p}}_{1-} + (A_{ss}^-A_{sp}^+ - A_{sp}^-A_{ss}^+)\hat{\mathbf{s}}]\exp(i\eta_1 z) & \text{as } z \to +\infty, \\ [A_{ss}^-\hat{\mathbf{p}}_{2+} - A_{sp}^-\hat{\mathbf{s}}]\exp(-i\eta_2 z) & \text{as } z \to -\infty. \end{cases} \tag{16}$$

The solutions (9), (10), (13), and (16) were obtained for the general case of an arbitrarily anisotropic susceptibility of the transition layer. All the elements of the matrices $\hat{A}_\pm$ are then different from zero, the reflection/transmission (12) coefficients contain off-diagonal components with $\alpha \neq \beta$, and the eigenmode field (16) is a mixture of s- and p-components. The entanglement of the s- and p-components is due to the elements $\Delta\varepsilon_{sb}$, $\Delta\varepsilon_{sz}$, $\Delta\varepsilon_{bs}$, and $\Delta\varepsilon_{zs}$ of the transition-layer tensor $\Delta\hat{\varepsilon}$. If the tensor $\Delta\hat{\varepsilon}$ has a block-diagonal structure such that $\Delta\varepsilon_{sb} = \Delta\varepsilon_{sz} = \Delta\varepsilon_{bs} = \Delta\varepsilon_{zs} = 0$, the cross coefficients $A_{\alpha,\beta}^{\pm}$ with $\alpha \neq \beta$ are zero. The matrices $r_{\alpha\beta}$ and $t_{\alpha\beta}$ are then diagonal and are determined by expressions that are simpler than (13)

$$r_{\alpha\alpha} = A_{\alpha\alpha}^+/A_{\alpha\alpha}^-, \qquad t_{\alpha\alpha} = 1/A_{\alpha\alpha}^-,$$

$\alpha = s$ or p, and the dispersion equation (15) breaks up into two independent ones

$$A_{ss}^- = 0, \qquad A_{pp}^- = 0,$$

for the two types $\alpha = s, p$ of the eigenmodes whose field is given by

$$\mathbf{E}_{n\alpha}(z) = \begin{cases} A_{\alpha\alpha}^+\hat{\mathbf{e}}_{1\alpha}^-\exp(i\eta_1 z), & z \to +\infty, \\ \hat{\mathbf{e}}_{2\alpha}^+\exp(-i\eta_2 z), & z \to -\infty. \end{cases}$$

In the general case the coefficient functions $A_{\alpha\beta}^{\pm}$ are not independent, and their relation is

$$A_{\alpha\beta}^+(\eta_1) = A_{\alpha\beta}^-(-\eta_1), \tag{17}$$

which follows from the analyticity of the solutions $\mathbf{E}_{j\beta}(z)$ in the variable z and from the form (9) of the solutions. It suffices therefore to calculate only the matrix of the coefficients $A_{\alpha\beta}^-$, and the other coefficients $A_{\alpha\beta}^+$ are obtained from (17).

The zeros of the determinant $|\hat{A}_-|$ of the matrix $A_{\alpha\beta}^-$ specifies dispersion equations (14), (15) for the eigenmodes of the perturbed medium. The zeros of the determinant of the matrix $\hat{A}_+$, on the other hand

$$|\hat{A}_+| = A_{ss}^+A_{pp}^+ - A_{sp}^+A_{ps}^+ = 0, \tag{18}$$

specify the position of the Brewster angle. In fact, from (12) we have for the determinant of the reflection-coefficient matrix $\hat{r} = |\hat{A}_+|/|\hat{A}_-|$. Therefore the zeros of (18) yield the zeros of $|\hat{r}|$. The condition $|\hat{r}| = 0$, however, determines in fact the position of the Brewster angle [15] at which an incident unpolarized beam becomes fully polarized upon reflection.

From the symmetry properties (17) of the coefficients $A_{\alpha\beta}^{\pm}$ follows the relation $|\hat{A}_+(\eta_1)| = |\hat{A}_-(-\eta_1)|$. Therefore each pole of the reflection-coefficient matrix in the complex η_1 plane corresponds at $\eta_1 = \eta_{1c}$ to a zero of the determinant of the matrix $\hat{r}$ at $\eta_1 = -\eta_{1c}$. This generalizes the known analytic properties of the quantum-theory scattering S matrix for a scalar field[16] to include the case of multicomponent fields. The solution (10) obtained for the coefficient functions $A_{\alpha\beta}^{\pm}$ has this property in any order of the expansion of the scattering operators $T^{\pm}$ in powers of the perturbation $\Delta\varepsilon$. The iteration solution of the traditional equation (4), however, does not have this property in any finite order of an expansion in powers of $\Delta\varepsilon$.

The general standard equation (7) for the scattering operators $T^{\pm}$, and expression (10) defined by it for the coefficient functions $A_{\alpha\beta}^{\pm}$, are not quite suitable for practical calculations in view of the singular behavior of the GF (A1) at $z = z'$ and of the discontinuous behavior, at abrupt interfaces, of the fields $\mathbf{E}_{j\alpha}^{\pm}$ making up the GF and used to calculate the matrix elements (10). These two circumstances are interrelated and can be excluded by a single transformation. A similar transformation, used in Ref. 11 for the particular case of a uniaxially anisotropic local $\Delta\varepsilon$, will be generalized in the next section to the general case of an arbitrarily anisotropic nonlocal $\Delta\hat{\varepsilon}$.

3. TRANSITION TO A BASIS OF CONTINUOUS FUNCTIONS

We introduce a new basic system of functions

$$\mathbf{X}_{j\alpha}^{\pm}(z) = \hat{U}(z)\mathbf{E}_{j\alpha}^{\pm}(z),$$

using for this purpose a symmetric 3×3 transition matrix

$$\hat{U}(z) = \hat{P}_\perp + \frac{\varepsilon_\parallel(z)}{a}\hat{P}_\parallel, \tag{19}$$

where the projection operators $\hat{P}_{\perp,\parallel}$ are those described above, and a is an arbitrary constant (chosen to simplify the equations that follow). The final result is independent of the choice of a. The basis $\mathbf{X}_{j\alpha}^{\pm}$ is obviously made up only of field components that are continuous on the boundary. We define the new scattering operators $\hat{t}^{\pm}$ by the relation

$$T^{\pm}(z, z') = U(z)t^{\pm}(z, z')U(z'). \tag{20}$$

We obtain then for the coefficient functions (10) the representation

$$A^{\pm}_{\alpha\beta} = a^{\pm}_{1\alpha}\delta_{\alpha\beta} \pm \frac{i}{2\eta_1}\int dzdz'\mathbf{X}^{-}_{2\alpha}(\mp \eta_1, z)\hat{t}^{+}(z, z')\mathbf{X}^{+}_{1\beta}(z'), \tag{21}$$

which contains only field components that are continuous on the boundary.

The new scattering operators $t^{\pm}$ satisfy, according to (7) and (20), the equation

$$t^{\pm} = k_0^2 U^{-1}\Delta\varepsilon U^{-1}(1 + UG^{\pm}Ut^{\pm}). \tag{22}$$

The Green's functions $G^{\pm}$ contain a singular increment (A1) which we shall move to the left-hand side of Eq. (22). Denoting by $G_0^{\pm} = UG'_{\pm}U$ the transformed nonsingular GF part $G^{\pm}$ (A1), (A2):

$$G_0^{\pm}(z, z') = \pm\, g_0(z, z')\theta[\pm (z - z')],$$

$$g_0(z, z') = \frac{i}{2\eta_1}\sum_{\alpha=s,p} t_\alpha[\mathbf{X}^{+}_{2\alpha}(z)\mathbf{X}^{-}_{1\alpha}(z') - \mathbf{X}^{+}_{1\alpha}(z)\mathbf{X}^{-}_{2\alpha}(z')],$$

where $\theta(z)$ is the Heaviside unit step function (we use dyad notation), and denoting the new perturbation of the problem by

$$\hat{\sigma} = \hat{U}^{-1}\left(1 + \Delta\hat{\varepsilon}\frac{\hat{P}_{\parallel}}{\varepsilon_{\parallel}}\right)^{-1}\Delta\hat{\varepsilon}\,\hat{U}^{-1}, \tag{23}$$

we obtain as a result from (22) for the modified scattering operators $t^{\pm}$ the equations

$$t^{\pm} = k_0^2\sigma(1 + G_0^{\pm}t^{\pm}), \tag{24}$$

which are fully equivalent to the initial (7). The inverse operator in (23) can be calculated explicitly:

$$\left(1 + \Delta\hat{\varepsilon}\frac{\hat{P}_{\parallel}}{\varepsilon_{\parallel}}\right)^{-1} = \left(\hat{P}_{\perp} + \hat{\varepsilon}\frac{\hat{P}_{\parallel}}{\varepsilon_{\parallel}}\right)^{-1}$$

$$= \hat{P}_{\perp} + \hat{P}_{\parallel}\varepsilon_{\parallel}\varepsilon_{zz}^{-1}\hat{P}_{\parallel} - \hat{P}_{\perp}\hat{\varepsilon}\,\hat{P}_{\parallel}\varepsilon_{zz}^{-1}\hat{P}_{\parallel}, \tag{25}$$

where $\hat{\varepsilon}$ is the dielectric-constant operator of the perturbed medium, given in expanded form by Eq. (3), and ε_{zz}^{-1} is an operator inverse to $\varepsilon_{zz} = \hat{P}_{\parallel}\hat{\varepsilon}\hat{P}_{\parallel}$ in the usual operator sense:

$$\int \varepsilon_{zz}^{-1}(z, z')\varepsilon_{zz}(z', z'')dz' = \delta(z - z'').$$

Substituting (25), (3) and (19) in (23) we obtain ultimately for σ the operator expression

$$\sigma = P_{\perp}(\varepsilon - \varepsilon P_{\parallel}\varepsilon_{zz}^{-1}P_{\parallel}\varepsilon - \varepsilon_{\perp})P_{\perp} + a^2P_{\parallel}(\varepsilon_{\parallel}^{-1} - \varepsilon_{zz}^{-1})P_{\parallel}$$
$$+ a(P_{\perp}\varepsilon P_{\parallel}\varepsilon_{zz}^{-1}P_{\parallel} + P_{\parallel}\varepsilon_{zz}^{-1}P_{\parallel}\varepsilon P_{\perp}). \tag{26}$$

Equations (21) and (24) complete the calculation of the coefficient functions of the pertubed medium. Equation (24) is the standard equation of the quantum theory of scattering,[14] in which the GF $G_0^{\pm}$ contains no pole singularities or singular terms whatever. The end result (10) and (21) is the same if the problem is correctly calculated in the discontinuous basis (7) and (10) or the continuous one (24) and (21). The initial transformation, in a number of studies,[2-4] of the initial system of equations (4) into continuous field components $\mathbf{E}_{\perp}$ and D_z, which violates the covariance of the equations and makes the subsequent computations very cumbersome, seems therefore superfluous. We assume hereafter that the free parameter a in (19) and (26) is equal to unity.

Up to now, the procedure developed was general, without any restrictions on the degree of polarization or on the thickness of the transition layer. The formalism developed above will be applied in the next section to the case of an optically thin transition layer.

4. OPTICALLY THIN TRANSITION LAYER

A simple iteration solution of Eq. (24) for the scattering operators $t^{\pm}$

$$t^{\pm}(z, z') = k_0^2\sigma(z, z')$$
$$+ k_0^4\int dz_1dz_2\sigma(z, z_1)G_0^{+}(z_1, z_2)\sigma(z_2, z') + \dots \tag{27}$$

yields a series in powers of the perturbation $\sigma(z,z')$. This perturbation is localized in the transition layer region $|z|$, $|z'|\leqslant d$. The characteristic range of variation of the fields $\mathbf{X}^{\pm}_{j\alpha}(z)$ contained in the GF $G_0^{\pm}$ and in the matrix elements (21) is of the order of η_m^{-1}, where η_m is the largest of the components of the field vectors along the normal in the contiguous media adjacent to the interface. The fields for optically thin transition layers are smooth functions of the variable z and can be expanded in powers of z under the integral signs in (21) and (27):

$$\mathbf{X}^{\pm}_{js}(z) = (E_{js} + E'_{js}z + \dots)\hat{\mathbf{s}},$$

$$\mathbf{X}^{\pm}_{jp}(z) = (D_j\hat{\mathbf{z}} \pm E_{jb}\hat{\mathbf{b}}) - iz[bE_{jb}\varepsilon_{\perp}(z)\hat{\mathbf{z}}$$
$$\pm \frac{D_j}{b}\left(k_0^2 - \frac{b^2}{\varepsilon_{\parallel}(z)}\right)\hat{\mathbf{b}}] + \dots \tag{28}$$

The dielectric constants $\varepsilon_{\perp}(z)$ and $\varepsilon_{\parallel}(z)$ in the linear terms of the expansion (28) reflect the discontinuous behavior of the derivatives, with respect to z, of the fields at $z = 0$; E_{js}, $E'_{js} = dE_{js}(z)/dz|_{z=0}$, while E_{jb} and $D_j = D_{jz}$ are the internal values of the s-, b-, and z-components of the electric field and of the displacement vector $\mathbf{D} = \hat{\varepsilon}_z\mathbf{E}$ in the transition-layer region, which are uniquely determined by the solutions $\mathbf{E}^{\pm}_{j\alpha}(z)$ of the unperturbed problem. If, however, one of the contiguous media is homogeneous all the way to the boundaries, these fields are expressed in terms of the external characteristics of the unperturbed problem, viz., the reflection/transmission coefficients (11). Thus, for example, if $\varepsilon_{\perp}(z) = \varepsilon_{\parallel}(z) = \varepsilon_1 = \text{const}$ at $z\geqslant 0$ (but $\varepsilon_{\perp,\parallel}(z)$ are arbitrary at $z\leqslant 0$), we have

$$E_{1s} = a^{+}_{1s} + a^{-}_{1s}, \qquad E_{2s} = 1,$$

$$E'_{1s} = i\eta_1(a^{+}_{1s} - a^{-}_{1s}), \qquad E'_{2s} = i\eta_1,$$

$$E_{1b} = (a^{-}_{1p} - a^{+}_{1p})\eta_1/k_1, \qquad E_{2b} = -\eta_1/k_1,$$

$$D_1 = (a_{1p}^+ + a_{1p}^-)b\varepsilon_1/k_1, \qquad D_2 = b\varepsilon_1/k_1.$$

If both contiguous media are homogeneous and isotropic all the way to the boundary, so that

$$\varepsilon_z = \varepsilon_1\theta(z) + \varepsilon_2\theta(-z), \tag{29}$$

then

$$a_{1s}^{\pm} = \frac{\eta_1 \mp \eta_2}{2\eta_1}, \qquad a_{1p}^{\pm} = \frac{\varepsilon_2\eta_1 \mp \varepsilon_1\eta_2}{2\eta_1(\varepsilon_1\varepsilon_2)^{1/2}}.$$

Each integration in (21) and (27), over the variables z an z', of the product of the perturbation $\sigma(z,z')$ by a power function of z and z'

$$\int dzdz' z^{n-1}\sigma(z, z')(z')^{m-1}$$

yields a factor of the order of d^{n+m}. Therefore, substituting the solution (27) in (21) and gathering together terms of like order of smallness in the parameters $\eta_m d$, we obtain an expansion of the coefficient functions $A_{\alpha\beta}^-$ in powers of d:

$$A_{\alpha\beta}^- = a_{1\alpha}^-\delta_{\alpha\beta} + \sum_{n=1}^{\infty} A_{\alpha\beta}^{-(n)}, \tag{30}$$

where $A_{\alpha\beta}^{-(n)} \sim (\eta_m d)^n$. The above expansion of the fields (28) up to the terms linear in d inclusive suffices to solve the problem in an approximation quadratic in $\eta_m d$.

We introduce now the effective integral parameters of the transition layer, of first order

$$\Lambda_{ij}(\mathbf{b}) = \int dzdz'\sigma_{ij}(\mathbf{b}, z, z') \tag{31}$$

and second order

$$\begin{aligned} \Gamma_{ij}(\mathbf{b}) &= \int dzdz' z\sigma_{ij}(\mathbf{b}, z, z'),\\ \Gamma_{ij}^{\perp}(\mathbf{b}) &= \int dzdz' z\varepsilon_{\perp}(z)\sigma_{ij}(\mathbf{b}, z, z'),\\ \Gamma_{ij}^{\parallel}(\mathbf{b}) &= \int dzdz' \frac{z}{\varepsilon_{\parallel}(z)}\sigma_{ij}(\mathbf{b}, z, z'), \end{aligned} \tag{32}$$

$$\Delta_{ijkl}(\mathbf{b}) = \int dz_1dz_2dz_3dz_4\theta(z_2 - z_3)\sigma_{ij}(\mathbf{b}, z_1, z_2)\sigma_{kl}(\mathbf{b}, z_3, z_4)$$

in thickness, respectively.

We obtain then from (21) and (27), for the coefficient functions (30), the linear terms

$$\begin{aligned} A_{ss}^{-(1)} &= -\frac{ik_0^2}{2\eta_1}E_{1s}E_{2s}\Lambda_{ss},\\ A_{pp}^{-(1)} &= -\frac{ik_0^2}{2\eta_1}(D_1D_2\Lambda_{zz} - E_{1b}E_{2b}\Lambda_{bb}\\ &\quad + D_2E_{1b}\Lambda_{zb} - D_1E_{2b}\Lambda_{bz}),\\ A_{sp}^{-(1)} &= -\frac{ik_0^2}{2\eta_1}E_{2s}(D_1\Lambda_{sz} + E_{1b}\Lambda_{sb}),\\ A_{ps}^{-(1)} &= -\frac{ik_0^2}{2\eta_1}E_{1s}(D_2\Lambda_{zs} - E_{2b}\Lambda_{bs}) \end{aligned} \tag{33}$$

and the quadratic terms

$$\begin{aligned} A_{ss}^{-(2)} &= -\frac{k_0^2}{2\eta_1}[bE_{1s}E_{2s}\Lambda_{sb}\Lambda_{sz} + i(E_{1s}E'_{1s} + E'_{1s}E_{2s})\Gamma_{ss}],\\ A_{pp}^{-(2)} &= -\frac{k_0^2}{2\eta_1}\{b^{-1}(D_2E_{1b} + D_1E_{2b})[b^2(\Gamma_{zz}^{\perp} + \Gamma_{bb}^{\parallel}) - k_0^2\Gamma_{bb}]\\ &\quad + b[(D_1D_2\Lambda_{zz} - E_{1b}E_{2b}\Lambda_{bb})\Lambda_{zb}\\ &\quad + D_2E_{1b}(\Delta_{zzbb} + \Delta_{zbzb}) - D_1E_{2b}(\Delta_{bbzz} + \Delta_{bzbz})]\},\\ A_{sp}^{-(2)} &= -\frac{k_0^2}{2\eta_1}\{iE'_{2s}(D_1\Gamma_{sz} + E_{1b}\Gamma_{sb}) + bE_{1b}E_{2s}(\Gamma_{zs}^{\perp} + \Delta_{sbzb}\\ &\quad + \Delta_{szbb}) + \frac{E_{2s}D_1}{b}[k_0^2\Gamma_{bs} - b^2(\Gamma_{bs}^{\parallel} - \Delta_{sbzz} - \Delta_{szbz})]\},\\ A_{ps}^{-(2)} &= -\frac{k_0^2}{2\eta_1}\{iE'_{1s}(D_2\Gamma_{sz} - E_{2b}\Gamma_{sb})\\ &\quad + bE_{1s}E_{2b}(\Gamma_{zs}^{\perp} - \Delta_{bbzs} - \Delta_{bzbs})\\ &\quad - \frac{E_{1s}D_2}{b}[k_0^2\Gamma_{bs} - b^2(\Gamma_{bs}^{\parallel} + \Delta_{zbzs} + \Delta_{zzbs})]\} \end{aligned} \tag{34}$$

The functions $A_{\alpha\beta}^+$, which we need to calculate the matrices of the amplitude reflection coefficients (13), are obtained from the symmetry relations (17), e.g.,

$$A_{sp}^{+(1)} = \frac{ik_0^2}{2\eta_1}E_{2s}(-\eta_1)[D_1(-\eta_1)\Lambda_{sz} + E_{1b}(-\eta_1)\Lambda_{sb}],$$

where $E_{2s}(\eta_1) = E_{2s}$, etc. To simplify the equations, the quadratic terms are written using the Onsager principle of the symmetry of the kinetic coefficients[17] and the assumption that the medium is nongyrotropic in the plane of the layers; the first of these, with averaging of the microscopic dielectric constant of the medium in the plane of the layers, leads to the relation[18]

$$\varepsilon_{ij}(\mathbf{b}, z, z') = \varepsilon_{ji}(-\mathbf{b}, z', z), \tag{35}$$

and the second to an even dependence of ε_{1j} on $\mathbf{b}$ (Ref. 21):

$$\varepsilon_{ij}(\mathbf{b}, z, z') = \varepsilon_{ij}(-\mathbf{b}, z, z'). \tag{36}$$

Similar relations hold also for the components of the modified perturbation tensor $\sigma_{ij}(\mathbf{b},z,z')$ [Eq. (26)]. The relations for the effective parameters under the conditions (34) and (35) are then

$$\begin{aligned} \Lambda_{ij}(\mathbf{b}) &= \Lambda_{ji}(-\mathbf{b}),\\ \Delta_{ijkl}(\mathbf{b}) &= \Lambda_{ij}(\mathbf{b})\Lambda_{kl}(\mathbf{b}) - \Delta_{lkji}(\mathbf{b}),\\ \tilde{\Gamma}_{ij}(\mathbf{b}) &\equiv \int dzdz'\sigma_{ij}(\mathbf{b}, z, z')z' = \Gamma_{ji}(-\mathbf{b}) \end{aligned} \tag{37}$$

with analogous relations for $\tilde{\Gamma}_{ij}^{\perp}(\mathbf{b})$ and $\tilde{\Gamma}_{ij}^{\parallel}(\mathbf{b})$. The supplementary assumption (36) that the medium is nongyrotropic leads to an even dependence of the parameters (31) and (32) relative to the replacement of $\mathbf{b}$ by $-\mathbf{b}$. As a result the argument $-\mathbf{b}$ in the right-hand sides of (37) can be replaced by $\mathbf{b}$. Under these assumptions, the contribution of the off-diagonal quadratic parameters of the type Γ_{bz} and $\tilde{\Gamma}_{ij}$, etc., vanishes from the coefficients of the second-order function.

No restrictions whatever were imposed in the derivation of (33) and (34) on the character of the anisotropy of the transition layer. The effective parameters enter in the coefficient functions in a basis ($\hat{\mathbf{s}},\hat{\mathbf{b}},\hat{\mathbf{z}}$) defined by the propagation direction of the electromagnetic wave and the normal to the surface. Their definition (31), (32) is specified, however, in an arbitrary basis. For the nongyrotropic transition layer model, the tensor $\hat{\Lambda}$ is symmetric, and can always be reduced in the corresponding coordinate frame to diagonal form. The parameter matrix $\hat{\Lambda}$ is therefore defined only by three functions $\lambda_j(\omega)$ that depend on the frequency and are independent of the orientation of the principal axes and of the electromagnetic-wave incidence angle. In particular, when the principal axes of the microscopic dielectric constant tensor of the transition layer are oriented in the plane of the layer $z = \text{const}$ and along the normal to it

$$\hat{\varepsilon} = E_1\hat{\mathbf{x}}\hat{\mathbf{x}} + E_2\hat{\mathbf{y}}\hat{\mathbf{y}} + E_3\hat{\mathbf{z}}\hat{\mathbf{z}}, \tag{38}$$

Where $E_j(z,z')$ are the principal values of the tensor $\varepsilon_{ij}(z,z')$, we have

$$\Lambda_{ss} = \lambda_1\cos^2\psi + \lambda_2\sin^2\psi, \qquad \Lambda_{bb} = \lambda_1\sin^2\psi + \lambda_2\cos^2\psi,$$

$$\Lambda_{zz} = \lambda_3,$$

$$\Lambda_{sb} = \Lambda_{bs} = (\lambda_1 - \lambda_2)\sin\psi\cos\psi, \tag{39}$$

$$\lambda_j = \int dzdz'[E_j(z,z') - \varepsilon_\perp(z)\delta(z-z')], \qquad j = 1, 2,$$

$$\lambda_3 = \int dzdz'[\varepsilon_\parallel^{-1}(z)\delta(z-z') - E_3^{-1}(z,z')],$$

ψ is the angle between the unit vectors $\hat{\mathbf{y}}$ and $\hat{\mathbf{b}}$. The remaining parameters Λ_{ij} are equal to zero.

Let us compare the above equations with the analogous results of other studies. If the transition layer is macroscopically thin, $a \ll d \ll \lambda$ (a is the lattice constant) and is uniaxially anisotropic with the principal optical axis normal to the plane of the layers, so that

$$E_1(z,z') = E_2(z,z') = E_\perp(z)\delta(z-z'),$$

$$E_3^{-1}(z,z') = E_\parallel^{-1}(z)\delta(z-z'),$$

while the contiguous media or homogeneous all the way to the separation boundary (29), then Eqs. (30), (33), and (34) yield, to second order in $\eta_m d$ inclusive, the diagonal reflection coefficients r_{ss} and r_{pp} (13) obtained in Ref. 5. For the same contiguous media and an arbitrarily anisotropic microscopic transition layer, Eqs. (13), (30), and (33) yield in an approximation linear in $\eta_m d$ the diagonal reflection and transmission coefficients $r_{\alpha\alpha}$ and $t_{\alpha\alpha}$ obtained in Ref. 8. The off-diagonal components $r_{\alpha\beta}$ and $t_{\alpha\beta}$ with $\alpha \neq \beta$, whose appearance is a characteristic distinguishing feature of the presence of an anisotropic transition layer on an isotropic substrate, are not cited in Ref. 8. For an inhomogeneous unperturbed medium of the "film on a substrate" type with an anisotropic transition layer of type (38) located on the interface between the film and the substrate, when an electromagnetic wave is incident along one of the principal axes (the angle ψ in (39) is then 0 or $\pi/2$), the coefficients (19), (30), and (33) yield, in an approximation linear in $\eta_m d$, the reflection coefficients $r_{\alpha\alpha}$ obtained in Ref. 9 ($\alpha = s,p$). Equations (13), (30), (33), and (34) contain thus all the known results of the preceding studies as a particular case.

The dispersion equations (14), (15) for the electromagnetic surface eigenwaves with coefficient functions specified in the linear approximation by Eqs. (30), (33), and (39) takes for homogeneous contiguous media (29) with anisotropic transition layer (38) the form

$$[\varepsilon_2\eta_1 + \varepsilon_1\eta_2 - ib^2\varepsilon_1\varepsilon_2\lambda_3 - i\eta_1\eta_2(\lambda_1\sin^2\psi + \lambda_2\cos^2\psi)]$$

$$\times[\eta_1 + \eta_2 - ik_0^2(\lambda_1\cos^2\psi + \lambda_2\sin^2\psi)]$$

$$= -k_0^2\eta_1\eta_2(\lambda_1 - \lambda_2)^2\sin^2\psi\cos^2\psi. \tag{40}$$

A similar equation was obtained in Ref. 7 using phenomenological boundary conditions. The main difference between (40) and the analogous error-corrected result of Ref. 7 [$\gamma_1\gamma_2$ in the Eq. (36) of Ref. 7 must be replaced by $(\omega/c)^2$ and the right-hand side of this equation reversed] is that our Eq. (40) contains in addition to the parameters λ_1 and λ_2 one more independent effective transition-layer parameter λ_3, which is missing from the results of Ref. 7. To explain the onset of this parameter, we express the phenomenological boundary conditions of Ref. 7 in terms of the effective integral parameters introduced above for the transition layer, confining ourselves to the linear approximation in the layer thickness.

Independently of the nature of the surface current $\delta\mathbf{j}$, we obtain from Eq. (1) for the discontinuities $\Delta\mathbf{H}$ and $\Delta\mathbf{E}$ of the magnetic and electric fields, in an approximation linear in d/λ, the expressions (see Appendix B)

$$[\hat{\mathbf{z}}, \Delta\mathbf{H}] = \frac{4\pi}{c}\int \delta\mathbf{j}_\perp(z)dz, \tag{41a}$$

$$\Delta\mathbf{E}_\perp = \frac{4\pi}{c}\frac{\mathbf{b}}{k_0}\int \varepsilon_\parallel^{-1}(z)\delta j_z(z)dz. \tag{41b}$$

Two other conditions for ΔD_z and ΔH_z are a consequence of Maxwell's equation (1) and of the conditions (41) [see (B1) and (B7)], and need not be written down. The first condition (41a) coincides with the one used in Ref. 7, but the second does not. The right-hand side of the second condition of [7] is zero. The reason is that

$$\int \delta j_z(z)dz = 0. \tag{42}$$

The right-hand side of (41b), however, is in general nonzero even under the physically justified condition (42), since the density of the normal component of the microcurrent enters in the right-hand side of (41b) with a weight $\varepsilon_\parallel^{-1}(z)$. The function $\varepsilon_\parallel^{-1}(z)$ cannot be taken outside the integral sign, as was done in Refs. 6 and 19, since it is discontinuous precisely in the region where the microcurrent $\delta j_z(z)$ is localized. The components $\delta\mathbf{j}_\perp$ and δj_z are independent and are generally speaking of the same order.

To establish the connection between the right-hand sides of (41) with the matrix $\hat{\Lambda}$ of the transition-layer effective parameters, we express in the microcurrent (2) the discontinuous z-component of the field in terms of the continuous $D_z = (\hat{\varepsilon}\mathbf{E})_z$ and $\mathbf{E}_\perp$, respectively, where $\hat{\varepsilon}$ is given by (3):

$$E_z = \hat{\varepsilon}_{zz}^{-1}D_z - \hat{\varepsilon}_{zz}^{-1}(\hat{\varepsilon}_{zx}E_x + \hat{\varepsilon}_{zy}E_y).$$

We obtain

$$\delta \mathrm{j} = \frac{\omega}{4\pi i}\hat{U}\hat{\sigma}\mathrm{X}, \tag{43}$$

where $\hat{U}$ and $\hat{\sigma}$ are given by Eqs. (19) and (26). The two integrals in (41) can be combined into $\int U^{-1}\delta \mathrm{j} dz$. We obtain then, taking (43) and (31) into account,

$$\frac{4\pi i}{\omega}\int U^{-1}\delta \mathrm{j} dz = \int \hat{\sigma}(z, z')\mathrm{X}(z')dzdz' = \hat{\Lambda}\mathrm{X}(z_0),$$

where $\mathrm{X}(z_0)$ is the sought value of the field at the boundary. For the boundary conditions (41) we obtain ultimately in the linear approximation

$$[\hat{\mathrm{z}}, \Delta \mathrm{H}] = -ik_0(\hat{\Lambda}\mathrm{X})_\perp, \tag{44a}$$

$$\Delta \mathrm{E}_\perp = -ib(\hat{\Lambda}\mathrm{X})_z. \tag{44b}$$

Comparison of (44a) with the analogous phenomenological equation (20) of Ref. 7 makes it possible to identify the matrix Λ_{ij} with the matrix ξ_{ij} introduced in Ref. 7 for the surface dielectric constant of the transition layer. In Ref. 7, however, only some of the components, $i = x$, y and $j = x,y,z$, were introduced in Ref. 7 for this matrix. The remaining components $i = z$ and $j = x,y,z$, which enter on a par in (44b), are not defined in Ref. 7.

Nontrivial solutions of the inhomogeneous set (44) exist if the determinant of its coefficients is

$$\begin{vmatrix} H_{2b} & -(H_{1b} + ik_0\Lambda_{ss}E_{1s}) & 0 & -ik_0(\Lambda_{sb}E_{1b} + \Lambda_{sz}D_1) \\ E_{2s} & -E_{1s} & 0 & 0 \\ 0 & ib\Lambda_{zs}E_{1s} & E_{2b} & -E_{1b} + ib(\Lambda_{zb}E_{1b} + \Lambda_{zz}D_1) \\ 0 & ib\Lambda_{bs}E_{1s} & D_2 & -D_1 + ib(\Lambda_{bb}E_{1b} + \Lambda_{bz}D_1) \end{vmatrix} = 0.$$

Its expansion, with allowance for the relations

$$E_{1s}(z)H_{2b}(z) - E_{2s}(z)H_{1b}(z) = \frac{2\eta_1}{k_1}a_{1s}^-,$$

$$D_2(z)E_{1b}(z) - D_1(z)E_{2b}(z) = \frac{2b\eta_1}{k_0^2}a_{1p}^-,$$

that follow from the independence of the Wronskian of the variable z, leads to the dispersion equation (14), (15) whose coefficients are given in the linear approximation by Eqs. (30) and (33). A particular case of this equation for homogeneous contiguous media (29) and the effective-parameter matrix $\hat{\Lambda}$ (39) corresponding to orientation of the microscopic dielectric tensor axes of the layer (38) is the dispersion equation (45).

Thus, the two approaches to the optics of thin transition layers—the method of effective boundary conditions and the proposed method of the retarded/advanced Green's functions—are equivalent. The latter, however, is preferable since it permits a simple iterational self-consistent solution of the problem in the most general formulation, and the result can be obtained without final solution of a cumbersome system of algebraic equation.

However, the iteration method used above to solve the basic equation (24) is inapplicable when the perturbation σ has singularities, as for example when the surface adsorbs molecules containing resonant eigenfrequencies in the investigated wavelength range. The very expansion (30) of the coefficient functions in powers of the parameter d/λ becomes in this case meaningless, as is correspondingly the introduction of the effective integral parameters (31), (32) of the surface layer, since the poles in the perturbation σ, due to the poles of the x and y components and to the zeros of the z components of the layer's microscopic-susceptibility tensor, lead to the onset of nth order poles in the coefficient functions $A_{\alpha\beta}^{-(n)}$ (30) and in the nth order poles in the coefficient functions $A_{\alpha\beta}^{-(n)}$ (30) and in the nth order integral parameters (31) and (32) ($n = 1,2,\cdots$). This situation requires an initially exact solution of the basic equation (24).

We consider now a model of a transition layer with factored dependences of the perturbation $\hat{\sigma}(z,z')$ on z and z':

$$k_0^2\hat{\sigma}(z, z') = R_0^{-1}\mathrm{f}(z)\mathrm{g}(z'), \qquad R_0 = \omega^2 - \omega_s^2 + i\omega\Gamma_s,$$

which permits an exact solution of Eq. (24). Here ω_s and Γ_s are the location and width of the molecule's proper transition, while $\mathbf{f}(z)$ and $\mathbf{g}(z)$ are functions localized on the boundary. We obtain then for the coefficient functions (21) the exact result

$$A_{\alpha\beta}^- = a_{1\alpha}^-\delta_{\alpha\beta} - \frac{i}{2\eta_1}R^{-1}(\mathrm{f}\mathrm{X}_{2\alpha}^-)(\mathrm{g}\mathrm{X}_{1\beta}^+),$$

$$R = \omega^2 - \omega_s^2 + i\omega\Gamma_s - (\mathrm{g}\hat{G}_0^+\mathrm{f}),$$

$$(\mathrm{g}\hat{G}_0^+\mathrm{f}) = \int \mathrm{g}(z)\hat{G}_0^+(z, z')\mathrm{f}(z')dzdz',$$

$$\begin{pmatrix}\mathrm{f}\\ \mathrm{g}\end{pmatrix}\mathrm{X}_{j\alpha}^{\pm} = \int \begin{matrix}\mathrm{f}(z)\\ \mathrm{g}(z)\end{matrix}\mathrm{X}_{j\alpha}^{\pm}(z)dz.$$

In contrast to the case of a finite perturbation [see the text following Eq. (11)], the functions $A_{\alpha\beta}^-$ have now pole singularities. These are due, however, not to the eigenmodes of the medium, but to resonance transitions of the adsorbed molecules.

An exact dispersion relation for the eigenmodes of the perturbed medium is, as before, Eq. (15). In particular, for the block-diagonal matrix $\mathbf{f}(z)\mathbf{g}(z')$ this equation reduces for arbitrary layered-inhomogeneous media to the form

$$a_{1\gamma}^-[\omega^2 - \omega_s^2 + i\omega\Gamma_s - (\mathrm{g}\hat{G}_0^+\mathrm{f})] = \frac{i}{2\eta_1}(\mathrm{f}\mathrm{X}_{2\gamma}^-)(\mathrm{g}\mathrm{X}_{1\gamma}^+), \tag{45}$$

where $\gamma = s$, p. A similar equation was obtained in Refs. 9 and 10 for the particular case of a three-layer medium (a film on a substrate), but there the square bracket of the left-hand side of Eq. (45) does not contain the last term, since the problem was solved in these references approximately, accurate to terms linear in d, which is incorrect in the vicinity of $\omega \simeq \omega_s$. The ignored term, as well as the right-hand side of Eq. (45), leads to a shift and broadening of the resonant transition of the molecules, and its contribution is of the same order as the right-hand side.

In conclusion, the author considers it his pleasant duty to thank M. I. Ryazanov for helpful and critical remarks made in a joint discussion of a number of questions touched upon in the article.

APPENDIX A

The Green's functions $G^{\pm}$

In a mixed $(\mathbf{b}, z)$ representation, in the dyad notation of Eq. (1), we obtain for the GF $G^{\pm}$ which satisfy Eq. (6)

$$\hat{G}^{\pm}(z, z') = -\frac{\hat{\mathbf{z}}\hat{\mathbf{z}}}{k_0^2\varepsilon_{\parallel}(z)}\delta(z-z') + \hat{G}'_{\pm}(z, z'), \tag{A1}$$

$$\hat{G}'_{\pm}(z, z') = \pm\hat{g}(z, z')\theta[\pm(z-z')], \tag{A2}$$

$$\hat{g}(z, z') = \frac{i}{2\eta_1}\sum_{\alpha=s,p} t_\alpha[\mathbf{E}^{+}_{2\alpha}(z)\mathbf{E}^{-}_{1\alpha}(z') - \mathbf{E}^{+}_{1\alpha}(z)\mathbf{E}^{-}_{2\alpha}(z')],$$

where the transmission coefficients t_α are defined by Eq. (11), the normal projection of the wave vector η_1 is defined in text following Eq. (9), and $\mathbf{E}^{-}_{j\alpha}$ in the text following Eq. (10). Calculating the asymptote of (A1) as $z\to\infty$, we obtain

$$\hat{G}^{+}_{z\to+\infty}(z, z') = \frac{i}{2\eta_1}\sum_{\alpha=s,p}[e^{i\eta_1 z}\hat{\mathbf{e}}^{-}_{1\alpha}\mathbf{E}^{-}_{2\alpha}(-\eta_1, z') - e^{-i\eta_1 z}\hat{\mathbf{e}}^{+}_{1\alpha}\mathbf{E}^{-}_{2\alpha}(\eta_1, z')], \tag{A3}$$

where the unit vectors of the polarization $\hat{\mathbf{e}}^{\pm}_{1\alpha}$ are given in the text following Eq. (9). Equation (A3) was derived using the relations

$$t_\alpha\mathbf{E}^{-}_{1\alpha}(z) - r_\alpha\mathbf{E}^{-}_{2\alpha}(z) = \mathbf{E}^{-}_{2\alpha}(-\eta_1, z), \tag{A4}$$

which follow from the analyticity of the solutions with respect to the variable z and from the normalization condition assumed for the functions $\mathbf{E}^{\pm}_{j\alpha}$ to unity amplitude of the transmitted wave. The latter cause also an absence of singularities in the right-hand side of (A4).

APPENDIX B

Conditions for discontinuity of the tangential components of the electric and magnetic fields on the boundary

We eliminate from the initial system of Maxwell's equations (1), written in terms of the $\mathbf{E}$ and $\mathbf{H}$ field components (at a magnetic permeability $\mu = 1$), the linearly dependent components

$$H_z = -\frac{i}{k_0}(\partial_x E_y - \partial_y E_x), \tag{B1}$$

$$\partial_x E_z = -ik_0 H_y + \partial_z E_x, \tag{B2}$$

$$\partial_y E_z = -ik_0 H_x + \partial_z E_y. \tag{B3}$$

As a result we obtain in place of (1) an equivalent system for the fields $\mathbf{E}_\perp$ and $\mathbf{H}_\perp$:

$$\partial_z\mathbf{F} - \frac{i}{k_0}\hat{L}\mathbf{F} = -\frac{4\pi}{c}\mathbf{K}, \tag{B4}$$

$$\mathbf{F} = \begin{pmatrix} E_x \\ H_y \\ E_y \\ -H_x \end{pmatrix}, \qquad \mathbf{K} = \begin{pmatrix} \dfrac{i\partial_x}{k_0\varepsilon_{\parallel}(z)}\delta j_z \\ \delta j_x \\ \dfrac{i\partial_y}{k_0\varepsilon_{\parallel}(z)}\delta j_z \\ \delta j_y \end{pmatrix}, \tag{B5}$$

$$\hat{L} = \begin{pmatrix} 0 & k_0^2 + \dfrac{\partial_x^2}{\varepsilon_{\parallel}} & 0 & \dfrac{\partial_x\partial_y}{\varepsilon_{\parallel}} \\ k_0^2\varepsilon_{\perp} + \partial_y^2 & 0 & -\partial_x\partial_y & 0 \\ 0 & \dfrac{\partial_x\partial_y}{\varepsilon_{\parallel}} & 0 & k_0^2 + \dfrac{\partial_y^2}{\varepsilon_{\parallel}} \\ -\partial_x\partial_y & 0 & k_0^2\varepsilon_{\perp} + \partial_x^2 & 0 \end{pmatrix}. \tag{B6}$$

In the mixed $(\mathbf{b},z)$ representation the operators ∂_x and ∂_y in (B1)–(B6) are replaced by the factors ib_x and ib_y. Equations (B2), (B3), and (1) lead directly also to equations for the components E_z and $D_z = (\hat{\varepsilon}\mathbf{E})_z$:

$$E_z = \frac{i}{k_0\varepsilon_{\parallel}}(\partial_x H_y - \partial_y H_x) - \frac{4\pi i}{\omega\varepsilon_{\parallel}}\delta j_z, \qquad D_z = \frac{i}{k_0}(\partial_x H_y - \partial_y H_x). \tag{B7}$$

We introduce the auxiliary function

$$\mathbf{F}^0(z) = \mathbf{F}^{>}(z)\theta(z-z_0) + \mathbf{F}^{<}(z)\theta(z_0-z),$$

where $\mathbf{F}^{\gtrless}(z)$ are exact solutions of the system (B4) outside the transition layer:

$$\mathbf{F}^{>}(z) = \mathbf{F}(z) \text{ for } z \geq d \text{ and } \mathbf{F}^{<}(z) = \mathbf{F}(z) \text{ for } z \leq 0;$$

$z = z_0$ is an arbitrary plane in the region of the transition layer, $0 \leqslant z_0 \leqslant d$. The function $\mathbf{F}^0(z)$ is a solution of the equation

$$\partial_z\mathbf{F}^0 - \frac{i}{k_0}\hat{L}\mathbf{F}^0 = \Delta\mathbf{F}(z_0)\delta(z-z_0), \tag{B8}$$

where $\Delta\mathbf{F}(z_0)$ is the discontinuity of the function $\mathbf{F}^{\gtrless}(z)$ on the plane $z = z_0$:

$$\Delta\mathbf{F}(z_0) = \mathbf{F}^{>}(z_0) - \mathbf{F}^{<}(z_0).$$

The field difference $\mathbf{F}(z) - \mathbf{F}^0(z)$ is localized in the region of the transition layer $0 \leqslant z \leqslant d$. It is equal to zero outside the layer. Subtracting (B8) from (B4) and integrating over z, we obtain for the discontinuity $\Delta\mathbf{F}(z_0)$ the expression

$$\Delta\mathbf{F}(z_0) = -\frac{4\pi}{c}\int\mathbf{K}dz + \frac{i}{k_0}\hat{L}\int(\mathbf{F} - \mathbf{F}^0)dz. \tag{B9}$$

Equation (B9) is exact and determines the discontinuity of the exact solutions $\mathbf{F}^{\gtrless}(z)$ on the boundary $z = z_0$ in terms of the exact solution $\mathbf{F}(z)$ and the solutions $\mathbf{F}^{\gtrless}(z)$ analytically continued into the region of the transition layer. The first term in the right-hand side of (B9) is of order d, and the second is of order d^2. To prove the last statement we express the difference $\mathbf{F}(z) - \mathbf{F}^0(z)$ in terms of the GF of Eq. (B4):

$$\mathbf{F}(z) - \mathbf{F}^0(z) = -\frac{4\pi}{c}\int_{-\infty}^{\infty}[\theta(z-z') - \theta(z-z_0)]\,\hat{f}(z)\hat{f}^{-1}(z')\mathbf{K}(z')dz',$$

where $\hat{f}(z)$ is the fundamental matrix of the solution of the inhomogeneous equation (B4) with a zero right-hand part. The function $\Theta(z,z'z_0) = \theta(z-z') - \theta(z-z_0)$ takes on the values $+1$ (-1) for $z' \leqslant z \leqslant z_0$ ($z_0 \leqslant z \leqslant z'$) and is equal to zero in the remaining region. Therefore

$$\left|\int_0^d\int_0^d dzdz'\Theta(z,z',z_0)\right| = d\left|z_0 - \frac{d}{2}\right| \le \frac{d^2}{2}.$$

Thus, in the approximation linear in the thickness of the transition layer we can neglect the second term in the right-hand side of (B9). Changing next to the expression of (B5) in components, we obtain the boundary condition (41).

[1]W. L. Mochan and R. G. Barrera, Phys. Rev. B **32**, 4984 and 4989 (1985).
[2]A. Bagehi, R. G. Barrera, and A. K. Rajakoral, *ibid.* B **20**, 4824 (1979).
[3]R. Del Sole, Sol. St. Commun. **37**, 537 (1981).
[4]V. A. Kosobukin and A. M. Samsonov, Zh. Tekh. Fiz. **54**, 19 (1984) [Sov. Phys. Tech. Phys. **29**, 10 (1984)].
[5]D. V. Sivukhin, Zh. Eksp. Teor. Fiz. **13**, 361 (1943).
[6]V. M. Agranovich and V. I. Yudson, Opt. Commun. **5**, 422 (1972).
[7]M. I. Ryazanov, Zh. Eksp. Teor. Fiz. **93**, 1281 (1987) [Sov. Phys. JETP **66**, 725 (1987)].
[8]W. L. Schaich and W. Chen, Phys. Rev. B **39**, 10714 (1989).
[9]V. A. Kosobukin, Opt. Spektrosk. **59**, 370 (1985).
[10]V. A. Kosobukin, Zh. Tekh. Fiz. **56**, 1481 (1986) [Sov. Phys. Tech. Phys. **31**, 879 (1986)].
[11]G. V. Rozhnov, Zh. Eksp. Teor. Fiz. **98**, 1737 (1990) [Sov. Phys. JETP **71**, 975 (1990)].
[12]G. V. Rozhnov, Ellipsometry in Science and Technology [in Russian], No. 2, Novosibirsk. Inst. Phys. Problems, USSR Acad. Sci. (1990), p. 3.
[13]V. S. Vladimirov, *Equations of Mathematical Physics* [in Russian], Nauka, Moscow (1988).
[14]R. G. Newton, *Scattering Theory of Waves and Particles*, McGraw, 1966.
[15]L. A. Apresyan and Yu. A. Kravtsov, *Theory of Radiation Transport* [in Russian], Nauka, Moscow (1983).
[16]A. I. Baz', Ya. B. Zel'dovich, and A. M. Perelomov, *Scattering, Reactions, and Decays in Nonrelativistic Quantum Mechanics* [in Russian], Nauka, Moscow (1966).
[17]L. D. Landau and E. M. Lifshitz, *Statistical Mechanics, Part 1*, Pergamon (1980).
[18]V. P. Silin and A. A. Rukhadze, *Electromagnetic Properties of Plasma and of Plasmalike Media* [in Russian], Moscow, Gosatomizdat (1961).
[19]V. M. Agranovich, V. I. Rupasov, and V. Ya. Chernyak, Fiz. Tverd. Tela **24**, 2992 (1982) [Sov. Phys. Solid State **24**, 1693 (1982)].

Translated by J. G. Adashko