JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN, Vol. 39, No. 2, AUGUST, 1975

Theory of Electromagnetic Response of Solid Surface

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(Received November 13, 1974)

Various phenomena related to the electromagnetic response of solid surface are expressed in terms of the surface admittance for S- and P-polarization in a way independent of model. Formulas are given for optical reflection, dispersion relation of surface wave, image force, energy loss of specularly reflected electrons, and dispersion force between solid bodies. A scheme to calculate the contribution of the surface admittance is presented by self-consistent field approach. Besides the fully self-consistent expression, perturbation formulas are given. The slowly varying field limit is investigated. Two dimensional model and layer model are discussed.

§ 1. Introduction

Electromagnetic response is one of the fundamental properties of solid surface. Apart from the traditional optical reflectance studies concerning bulk properties, various phenomena related to surface response have been investigated experimentally and theoretically. Absorption of radiation due to the transition between surface states has been observed for magnetic surface states,[1] electrons trapped by liquid helium,[2] and electric quantum level of MOS structure.[3] Reflection spectroscopy has been applied to study clean surface of silicon[4] and chemisorbed tungsten.[5] Clean and adsorbed surfaces of silicon have been studied by ellipsometry.[6,7] Energy loss of specularly reflected electrons has been used to detect surface plasmons[8] and surface phonons.[9] Image force of metals[10-12] and semiconductors,[13] collective mode of surface system,[14-16] and dispersion forces between two solid bodies[17] have called much attention of theoreticians.

Though in each case theories have been developed by many authors, a general scheme covering and correlating all the phenomena is not well established. In the case of bulk response the dielectric formulation is such a scheme. Various phenomena such as propagation of electromagnetic waves, energy loss of charged particles, screening of test charges, and dispersion of collective modes are expressed in terms of a basic quantity, i.e., frequency- and wave number-dependent dielectric tensor. One of the purpose of the present paper is to show that *surface admittance* plays the role of the basic quantity in the case of surface response.

Consider a material system filling the region $z>0$ and bounded by the surface at $z=0$. The surface plane is chosen in the region where wave function of electrons of the material is vanishingly small. The region $z<0$ will be called external, from which perturbations (radiation, charged particles, etc.) are applied. Assuming the translational symmetry along the surface, we shall consider Fourier component of all the field quantities in the form

$$F(z;\,k,\,\omega)\exp[i(kx-\omega t)]\,, \tag{1}$$

where the direction of the wave vector $\boldsymbol{k}$ along the surface is chosen to be the x-axis. In the following equations some arguments will be suppressed frequently. Assuming the rotational symmetry around the z-axis we decouple the Maxwell equations into two parts: (1) S-polarization (TE-mode) part for E_y, H_x, and H_z and (ii) P-polarization (TH-mode) part for E_x, E_z, and H_y. When external perturbation is applied, the external field is completely determined by external sources and boundary conditions at $z\to-\infty$ and $z=0$. The latter condition is given in terms of the surface admittance Y (inverse of surface impedance Z) defined by the following:

S-polarization;

$$Y_{\mathrm{S}}(k,\,\omega)=Z_{\mathrm{S}}^{-1}=-\frac{H_x(0)}{E_y(0)}\,. \tag{2}$$

P-polarization;

$$Y_{\mathrm{P}}(k,\,\omega)=Z_{\mathrm{P}}^{-1}=\frac{H_y(0)}{E_x(0)}\,. \tag{3}$$

It should be noted that Y_{S} and Y_{P} are functions of both k and ω. Historically, Reuter and Sondheimer[18] have calculated the surface impedance in the analysis of anomalous skin effect of metals. The calculation was concerned mainly with the case of normal incidence ($k = 0$). Kliewer and Fuchs[19] have calculated optical reflectivity of metals in terms of Z_S and Z_P for the case of non-normal incidence ($k \neq 0$). As they have pointed out, dependence of Z_S and Z_P on k is essentially needed for the description of the longitudinal component of the electric field contained in the P-polarization. These calculations have been restricted to the radiative region ($\varepsilon_0\omega^2/c^2 > k^2$, where ε_0 is the dielectric function of the external medium). In this paper we shall extend the domain of k and ω to the nonradiative region ($\varepsilon_0\omega^2/c^2 < k^2$) in order to treat quasi-electrostatic phenomena. With these points in mind, we are now able to express all the surface response in terms of Y_S and Y_P. We shall give formulas for some important examples in § 4.

The calculation of the surface admittance requires the knowledge of the self-consistent field inside the material. Throughout the paper we shall assume that the material consists of a homogeneous semi-infinite medium, hereafter called *substrate*, and the surface state. The latter may be either intrinsic (ideal surface state) or extrinsic (adsorbate, electric and magnetic quantum state, etc.). Most of previous calculations of the surface impedance have been concerned with the homogeneous semi-infinite medium (substrate problem). Response due to the surface state has been treated usually either by perturbation theory or on phenomenological models such as the dielectric layer model[20] and two dimensional (2D) model.[15,16] The only case where the contribution of the surface state has been treated self-consistently is the calculation of the surface impedance due to the magnetic surface state. Calculations have been, however, restricted mainly to the case of normal incidence.[21] Kaner and Makarov[22] have investigated surface waves due to the magnetic surface state, but considered only the S-polarization. The second purpose of the paper is to develop a general scheme for the self-consistent calculation of the contribution of the surface state to both Y_S and Y_P. Section 2 and 3 will be devoted to the problem. Present paper is restricted to the construction of a framework of the calculation. Various applications will be given elsewhere.

§ 2. Basic Equations for Self-Consistent Fields and Currents

Let us take quantum mechanical RPA approach and start with the equation

$$\nabla\times(\nabla\times\boldsymbol{E})-\frac{\omega^2}{c^2}\boldsymbol{E}=\frac{4\pi i\omega}{c^2}\boldsymbol{J}\,. \tag{4}$$

This approach has been employed by Newns[10] and Beck and Celli[23] in the calculation of quasi-electrostatic response of half-bounded electron gas. The calculation of Kaner and Makarov for the magnetic surface state case[22] has been done along the same line.

In the following we shall assume that the current can be decomposed into two terms: contributions of the substrate $\bar{\boldsymbol{J}}$ and that of the surface state $\boldsymbol{J}^{(s)}$. Then eq. (4) is rewritten as follows.

$$\left[\nabla\times(\nabla\times\boldsymbol{E})-\frac{\omega^2}{c^2}\boldsymbol{D}\right]_\alpha\equiv\int_0^\infty \mathrm{d}z'\hat{L}_{\alpha\beta}(z,z')E_\beta(z')$$
$$=\frac{4\pi i\omega}{c^2}J_\alpha^{(s)}(z)\ , \tag{5}$$

where $\boldsymbol{D}=\boldsymbol{E}+4\pi i\bar{\boldsymbol{J}}/\omega$. Indices $\alpha, \beta, \cdots$ run over x, y, z and summation should be taken over the dummy one. The decomposition of the current should be done in a way suitable to each case. In the case of magnetic surface states, contributions of cyclotron orbits scattered at the surface have been included in $\boldsymbol{J}^{(s)}$, while those of orbits which do not touch the surface in $\bar{\boldsymbol{J}}$.[21] Generally speaking, we should include contributions of electrons occupying states localized near the surface in $\boldsymbol{J}^{(s)}$. Contributions of free electrons and background lattice should be included in $\bar{\boldsymbol{J}}$ and represented in terms of the dielectric function $\bar{\varepsilon}\,(z, z')$ as

$$D_\alpha(z)=\int_0^\infty \mathrm{d}z'\bar{\varepsilon}_{\alpha\beta}(z,z')E_\beta(z')\,. \tag{6}$$

The function $\bar{\varepsilon}_{\alpha\beta}(z, z')$ is not generally a function of $z-z'$, because of scattering of electrons at the surface. For some scattering boundary conditions, for example, specular scattering[19,24] and dielectric approximation,[25] it can be expressed in terms of the dielectric function of *homogeneous infinite* medium. From a microscopic viewpoint, delocalized states are also modified by the surface scattering. For example, the quantum mechanical calculation of half-bounded electron gas shows that quantum interference of the incident and scattered waves yields the response much different from the classical one for the specular scattering at the surface.[23] If we are to concern with such a difference, we should include contributions of all the free electrons in $\boldsymbol{J}^{(s)}$. Thus we shall regard the decomposition as a step of the construction of a model for the surface system. In practice the following prescription will be helpful: choose $\bar{J}$ in such a way that we can solve the substrate problem (eq. (5) with $J^{(s)}=0$) in terms of the dielectric function of the homogeneous infinite system and retain all the rest in $J^{(s)}$.

The surface term $J^{(s)}$ is written down as follows:

$$J_{\alpha}^{(s)}(z)=\int_0^{\infty} dz' \sigma_{\alpha\beta}^{(s)}(z,z') E_{\beta}(z') . \tag{7}$$

The surface conductivity $\sigma^{(s)}$ is calculated by standard method in one electron approximation.[26]

$$\sigma_{\alpha\beta}^{(s)}(z,z';k,\omega)=\frac{ie^2}{\omega m}\Bigg[\sum_{\lambda} f_{\lambda}\langle\lambda|\delta(\hat{z}-z)|\lambda\rangle\delta(z-z')\delta_{\alpha\beta}$$
$$+\frac{1}{m}\sum_{\lambda,\mu}\frac{f_{\lambda}-f_{\mu}}{\mathcal{E}_{\lambda}-\mathcal{E}_{\mu}+\hbar\omega}\langle\lambda|\{e^{-ik\rho}\delta(\hat{z}-z),p_{\alpha}\}|\mu\rangle\langle\mu|\{e^{ik\rho}\delta(\hat{z}-z'),p_{\beta}\}|\lambda\rangle\Bigg]. \tag{8}$$

In the above λ denotes the quantum number of the surface state (2D wave vector $\boldsymbol{\kappa}$ and an integer n), $\mathcal{E}_{\lambda}$ the energy, f_{λ} the Fermi distribution function, $\hat{z}$ and $\boldsymbol{\rho}$ the position operators normal and parallel to the surface, and $\{A,B\}\equiv 1/2(AB+BA)$. Rewriting the first term on the right-hand side of eq. (8) for arbitrary $\boldsymbol{k}$ as

$$\sum_{\lambda,\mu} f_{\lambda}\langle\lambda|\delta(\hat{z}-z)e^{-ik\rho}|\mu\rangle\langle\mu|\delta(z-z')e^{ik\rho}|\lambda\rangle\delta_{\alpha\beta} ,$$

we see that $\sigma^{(s)}$ takes the following form.

$$\sigma_{\alpha\beta}^{(s)}(z,z')=\sum_i \Psi_i^{\alpha *}(z)\Xi^i_{\alpha\beta}\Psi_i^{\beta}(z') . \tag{10}$$

Here i represents the pair of states (λ,μ) and an index η, where η discriminates the first and second term of eq. (8). The relevant matrix element is denoted by $\Psi_i^{\alpha}(z)$ and the remaining factor by $\Xi^i_{\alpha\beta}$.

The solution of eq. (5) can be written down as follows.

$$E_{\alpha}(z)=\bar{E}_{\alpha}(z)+\frac{4\pi i\omega}{c^2}\int_0^{\infty} dz' \mathscr{D}_{\alpha\beta}(z,z')J_{\beta}^{(s)}(z') \tag{11a}$$

$$=\bar{E}_{\alpha}(z)+\frac{4\pi i\omega}{c^2}\int_0^{\infty} dz'\int_0^{\infty} dz'' \mathscr{D}_{\alpha\beta}(z,z')\sigma_{\beta\gamma}^{(s)}(z',z'')E_{\gamma}(z'') , \tag{11b}$$

where $\bar{E}(z)$ is the solution for $J^{(s)}=0$ (substrate problem) and $\mathscr{D}_{\alpha\beta}(z,z')$ is the Green function defined by the equation

$$\int dz' \hat{L}_{\alpha\beta}(z,z')\mathscr{D}_{\beta\gamma}(z',z'')=\delta_{\alpha\gamma}\delta(z-z'') . \tag{12}$$

Hereafter we shall concern ourselves with the solution of eq. (11b), assuming that $\bar{E}$ and $\mathscr{D}_{\alpha\beta}$ are already known. Substitution of eq. (10) into eq. (11b) leads to the following equation.

$$E_{\alpha}(z)=\bar{E}_{\alpha}(z)+\frac{4\pi i\omega}{c^2}\sum_i \phi_i^{\alpha\beta}(z)\Xi^i_{\beta\gamma}a_i^{\gamma} , \tag{13}$$

where

$$\phi_i^{\alpha\beta}(z)\equiv\int_0^{\infty} dz' \mathscr{D}_{\alpha\beta}(z,z')\Psi_i^{\beta *}(z') \tag{14}$$

and

$$a_i^{\gamma}\equiv\int_0^{\infty} dz' \Psi_i^{\gamma}(z')E_{\gamma}(z') . \tag{15}$$

Multiplying eq. (13) with Ψ_i^{α} and integrating over z, we obtain

$$a_i^{\alpha}=\bar{a}_i^{\alpha}+\frac{4\pi i\omega}{c^2}\sum_j \Gamma_{ij}^{\alpha\beta}\Xi^j_{\beta\gamma}a_j^{\gamma} , \tag{16}$$

$$\Gamma^{\alpha\beta}_{ij}\equiv\int_0^\infty \mathrm{d}z\int_0^\infty \mathrm{d}z'\mathscr{D}_{\alpha\beta}(z,z')\Psi_i^{\alpha}(z)\Psi_j^{\beta *}(z')\ , \tag{17}$$

where $\bar{a}_i^{\alpha}$ is defined by eq. (15) in which E_α is replaced by $\bar{E}_\alpha$. Thus the problem of finding the self-consistent solution is reduced to the solution of an algebraic equation. If the solution of eq. (16) is denoted by

$$a_i^{\alpha}=\sum_j B^{j\alpha}_{i\beta}\bar{a}_j^{\beta}\ , \tag{18}$$

the self-consistent field is given by

$$E_\alpha(z)=\bar{E}_\alpha(z)+\frac{4\pi i\omega}{c^2}\sum_{i,j}\phi_i^{\alpha\beta}(z)\Xi^i_{\beta\gamma}B^{j\gamma}_{i\delta}\bar{a}_j^{\delta}\ . \tag{19}$$

Equation (16) involves the integration over $\boldsymbol{\kappa}$ and is not easy to handle. In many cases, however, the matrix element Ψ_i^{α} can be approximated as

$$\Psi_i^{\alpha}(z)=g^{\alpha}_{mn,\eta}(\boldsymbol{\kappa})\Phi^{\alpha}_{mn,\eta}(z)\ . \tag{20}$$

Above formula holds exactly in the case where the motion along the z-axis is separable from the one along the surface (electric quantum level, electrons trapped by liquid helium). If we use eq. (20), we obtain equations similar to eqs. (13)$\sim$(17) with the following replacements: index i now represents a pair (m, n) and η, the function $\Psi_i^{\alpha}(z)$ is replaced by $\Phi_i^{\alpha}(z)$, and $\Xi^i_{\beta\gamma}$ by $\Pi^j_{\beta\gamma}\equiv\sum_{\kappa} g_j^{\beta *}(\boldsymbol{\kappa})g_j^{\gamma}(\boldsymbol{\kappa})\Xi^j_{\beta\gamma}$. It should be noted that Π^j has the van Hove singularity of 2D lattice due to the interband resonance. Near a resonance eq. (16) can be approximated by a truncated one with a few terms.

When $\boldsymbol{J}^{(s)}$ can be regarded as a small perturbation, eq. (11) may be treated by the iteration method. The lowest order solution is

$$\begin{aligned}\tilde{E}_\alpha(z)&=\bar{E}_\alpha(z)+\frac{4\pi i\omega}{c^2}\int_0^\infty \mathrm{d}z'\int_0^\infty \mathrm{d}z''\mathscr{D}_{\alpha\beta}(z,z')\sigma^{(s)}_{\beta\gamma}(z',z'')\bar{E}_\gamma(z'')\\&=\bar{E}_\alpha(z)+\frac{4\pi i\omega}{c^2}\sum_i\phi_i^{\alpha\beta}(z)\Xi^i_{\beta\gamma}\bar{a}_i^{\gamma}\ .\end{aligned} \tag{21}$$

The last line of the above equation can also be derived from the general formula (19) by putting $B^{j\gamma}_{i\delta}=\delta_{ji}\delta_{\gamma\delta}$.

§3. Contribution of Surface States to the Surface Admittance

Let us turn to the calculation of Y_{S} and Y_{P}. In the following, we shall assume the local form $\varepsilon(\omega)\delta(z-z')\delta_{\alpha\beta}$ for $\bar{\varepsilon}_{\alpha\beta}(z,z')$ to simplify the calculation. The following procedure is also applicable to the nonlocal case, if we use the Green function of the relevant medium. The surface states are here assumed to be embedded in the substrate. Extension to the case where the background dielectric function of the surface state is different from that of the substrate (electrons trapped by liquid helium, adsorbate on metals, etc.) can easily be done by using the Green function of the dielectric layer given in Appendix. Formulas for Y_{S} and Y_{P} derived in this section cover both the radiative and non-radiative regions.

2.1 S-Polarization

The relevant field quantity is E_y and all the equations are diagonal with respect to α. The Green function is

$$\mathscr{D}_{yy}(z,z')=\frac{i}{2p}\exp[ip|z-z'|]\ , \tag{22}$$

where

$$p=(\varepsilon\omega^2/c^2-k^2)^{1/2},\ \mathrm{Im}\,p>0\ . \tag{23}$$

The substrate solution $\bar{E}_y(z)$ is expressed as

$$\bar{E}_y(z)=-2pi\bar{E}_y(0)\mathscr{D}_{yy}(z,-0)\ . \tag{24}$$

The value at the surface is given by taking the limit $z\to 0$. Noting that $H_x=(ic/\omega)\mathrm{d}E_y/\mathrm{d}z$, we obtain the formula

$$Y_{\mathrm{S}}=\bar{Y}_{\mathrm{S}}\frac{1-\Lambda_{\mathrm{S}}}{1+\Lambda_{\mathrm{S}}}\ , \tag{25}$$

where $\bar{Y}_{\mathrm{S}}=cp/\omega$ is the surface admittance of the substrate and

$$\Lambda_{\mathrm{S}}=\frac{8\pi p\omega}{c^2}\sum_{i,j}\phi_i^{yy}(0)\Xi^i_{yy}B^{jy}_{iy}\phi_j^{yy\dagger}(0)\ , \tag{26}$$

$$\phi_i^{\alpha\beta\dagger}(z)\equiv\int_0^\infty \mathrm{d}z'\mathscr{D}_{\alpha\beta}(z',z)\Psi_i^{\alpha}(z')\ . \tag{27}$$

In the limit $|p|\to 0$ (*slowly varying field limit*), the formula (25) can be much simplified. Approximating $\mathscr{D}_{yy}(z,z')$ by $\mathscr{D}_{yy}(z,+0)$ and $E_y(z'')$ by $E_y(0)$ in eq. (11b), we determine $E_y(0)$ self-consistently and obtain

$$Y_{\mathrm{S}}=\bar{Y}_{\mathrm{S}}+\frac{4\pi}{c}\sigma^{(2\mathrm{D})}_{yy}\ , \tag{28}$$

where 2D conductivity $\sigma^{(2\mathrm{D})}_{yy}$ is defined by

$$\sigma^{(2\mathrm{D})}_{\alpha\beta}=\int_0^\infty \mathrm{d}z\int_0^\infty \mathrm{d}z'\sigma^{(s)}_{\alpha\beta}(z,z')\ . \tag{29}$$

The formula (28) corresponds to 2D model in which the surface current is assumed to be the sheet current, i.e.,

$$J^{(s)}_y(z)=J^{(2\mathrm{D})}_y\delta(z)=\sigma^{(2\mathrm{D})}_{yy}E_y(0)\delta(z)\ . \tag{30}$$

The model is valid when $|p|^{-1}$ is much larger than the spread of the product of the wave functions of the relevant pair states. It should be noted that the formula (28) holds also for the nonlocal model of the substrate.

The perturbation calculation yields

$$\delta Y_S = Y_S - \bar{Y}_S = -\frac{16\pi p^2}{c}\sum_i \phi_i^{yy}(0)\Xi^i_{yy}\phi_i^{yy\dagger}(0)\ . \tag{31}$$

In the limit $|p|\to 0$, the above formula agrees with that of the self-consistent calculation (eq. (28)). In this limit the field induced by $J_y^{(s)}$ is also slowly varying, because $\mathscr{D}_{yy}$ is a slowly varying function. The slowly varying self-consistent solution does not depend much on the detailed form of $\sigma_{yy}^{(s)}(z, z')$ and can be described by the perturbation theory apart from a constant factor. Later we shall see that the situation is quite different for P-polarization.

3.2 P-Polarization

In this case E_x and E_z are coupled by both $\hat{L}_{xz}$ and $\sigma_{xz}^{(s)}$. The Green functions are given by

$$\mathscr{D}_{xx}(z, z') = \frac{ic^2 p}{2\varepsilon\omega^2}\exp[ip|z-z'|]\ , \tag{32a}$$

$$\mathscr{D}_{xz}(z, z') = \mathscr{D}_{zx}(z, z') = -\frac{ic^2 k}{2\varepsilon\omega^2}\operatorname{sgn}(z-z')\exp[ip|z-z'|]\ , \tag{32b}$$

$$\mathscr{D}_{zz}(z, z') = -\frac{c^2}{\varepsilon\omega^2}\delta(z-z') + \frac{ic^2k^2}{2\varepsilon p\omega^2}\exp[ip|z-z'|]\ , \tag{32c}$$

and $E_\alpha(z)$ by

$$\bar{E}_\alpha(z) = -\frac{2i\varepsilon\omega^2}{c^2 p}\bar{E}_x(0)\mathscr{D}_{\alpha x}(z, 0)\ , \qquad \alpha = x, z\ . \tag{33}$$

Noting that $J_\alpha^{(s)}(0)=0$ and $H_y(0) = -(\omega/ck)D_z(0)$, we obtain the formula

$$Y_P = \bar{Y}_P\frac{1-\Lambda_P}{1+\Lambda_P}\ , \tag{34}$$

where $\bar{Y}_P = \varepsilon\omega/cp$ is the surface admittance of the substrate and

$$\Lambda_P = \frac{8\pi\varepsilon\omega^2}{c^4 p}\sum_{i,j}\phi_i^{x\alpha}(0)\Xi^i_{\alpha\beta}B^{j\beta}_{i\gamma}\phi_j^{\gamma x\dagger}(0)\ . \tag{35}$$

In contrast to the case of S-polarization, 2D model is generally inapplicable. If we assume the sheet current

$$J_\alpha^{(s)}(z) = J_\alpha^{(2D)}\delta(z)\ , \quad \alpha = x, z\ , \tag{36a}$$

we have

$$E_x(+0) - E_x(-0) = \frac{4\pi k}{\varepsilon\omega}J_z^{(2D)}\ , \tag{37a}$$

$$E_z(+0) - E_z(-0) = \frac{4\pi k}{\varepsilon\omega}J_x^{(2D)}\ . \tag{37b}$$

Both E_x and E_z are discontinuous across the current sheet and we cannot postulate $J_\alpha^{(2D)} = \sigma_\alpha^{(2D)}E_\beta(0)$. We need the precise variation of E_α *inside* the sheet to determine $J_\alpha^{(2D)}$, which is beyond 2D model. In the main context of the present calculation the situation can be seen by inserting eq. (32b) into eq. (13). Due to the singular nature of $\mathscr{D}_{xz}$ the function $\phi(z)$ is not a slowly varying function of z even in the limit $|p|\to 0$. Thus the full self-consistent expression (35) should be employed.

Under a special condition of either $J_x^{(s)}=0$ or $J_z^{(s)}=0$, we can safely use 2D model and obtain the following formulas:

$$\text{if } J_x^{(s)}=0,\ Z_P = \bar{Z}_P + \frac{4\pi ck^2}{\varepsilon^2\omega^2}\sigma_{zz}^{(2D)}\ , \tag{38}$$

$$\text{if } J_z^{(s)}=0,\ Y_P = \bar{Y}_P = \frac{4\pi}{c}\sigma_{xx}^{(2D)}\ . \tag{39}$$

These formulas hold also for the nonlocal model of the substrate. In practice the above formulas can be used when either $\sigma_{zz}^{(2D)}$ or $\sigma_{xx}^{(2D)}$ much predominates over the other (near resonance, low frequency limit for the surface free carrier, etc.).

Perturbation formula for Y_P is given by

$$\delta Y_P = Y_P - \bar{Y}_P = -\frac{16\pi\varepsilon^2\omega^4}{c^5 p^2}\sum_i \phi_i^{x\alpha}(0)\Xi^i_{\alpha\beta}\phi_i^{\beta x\dagger}(0)\ . \tag{40}$$

In the limit $|p|\to 0$, we obtain

$$\delta Y_P = \frac{4\pi}{c}\sigma_{xx}^{(2D)} - \frac{4\pi k^2}{cp^2}\sigma_{zz}^{(2D)}\ . \tag{41}$$

The above formula agreees with the exact one only when either $J_x^{(s)}=0$ (eq. (38)) or $J_z^{(s)}=0$ (eq. (39)). It should be noted that though the perturbation formula is applicable widely to the response to the external field, the self-consistent approach is essentially needed in the absence of external source, for example, in the case of surface waves and dispersion force.

§ 4. Formulas for Electromagnetic Responses

When external source current $\boldsymbol{J}^{\mathrm{ext}}$ is present, the electric field in the external region is written down as follows.

$$E_\alpha(z)=A_\alpha \exp(-ip_0 z)+\frac{4\pi i\omega}{c^2}\int_{-\infty}^{0}\mathrm{d}z'\mathscr{D}^{\mathrm{ext}}_{\alpha\beta}(z,z')J^{\mathrm{ext}}_\beta(z') . \tag{42}$$

Here $\mathscr{D}^{\mathrm{ext}}_{\alpha\beta}(z, z')$ is the Green function of the external semi-infinite medium and $p_0=(\varepsilon_0\omega^2/c^2-k^2)^{1/2}$. The first term on the right-hand side of eq. (42) represents the reaction of the surface. The coefficient A_α is determined by the matching condition of the surface admittances as follows.

$$A_y=r_{\mathrm{S}}(k,\omega)E_y{}^{\mathrm{ext}}(0) , \tag{43}$$

$$A_x=r_{\mathrm{P}}(k,\omega)E_x{}^{\mathrm{ext}}(0) , \tag{44a}$$

$$A_z=-r_{\mathrm{P}}(k,\omega)E_z{}^{\mathrm{ext}}(0)=\frac{k}{p_0}A_x . \tag{44b}$$

In the above equations, E^{ext}_α is defined as the second term on the right-hand side of eq. (42). Reflectivity coefficients r_{S} and r_{P} are given by

$$r_{\mathrm{S}}(k,\omega)=\frac{1-\dfrac{\omega}{cp_0}Y_{\mathrm{S}}(k,\omega)}{1+\dfrac{\omega}{cp_0}Y_{\mathrm{S}}(k,\omega)} , \tag{45}$$

$$r_{\mathrm{P}}(k,\omega)=\frac{1-\dfrac{cp_0}{\varepsilon_0\omega}Y_{\mathrm{P}}(k,\omega)}{1+\dfrac{cp_0}{\varepsilon_0\omega}Y_{\mathrm{P}}(k,\omega)} . \tag{46}$$

In the following these coefficients will be used both in the radiative and nonradiative regions.

4.1 Optical Reflection

Optical reflection phenomena (reflectance, ellipsometry, etc.) are analyzed in terms of r_{S} and r_{P} in the radiative region.[19] Perturbation formulas for the change in r_{S} and r_{P} due to the surface state are given by

$$\delta r_{\mathrm{S}}=\frac{2\sqrt{\varepsilon_0}\cos\theta}{\varepsilon-\varepsilon_0}\bar{r}_{\mathrm{S}}\delta Y_{\mathrm{S}} , \tag{47a}$$

$$\delta r_{\mathrm{P}}=\frac{-2\varepsilon\sqrt{\varepsilon_0}\cos\theta}{(\varepsilon-\varepsilon_0)\left(1-\dfrac{\varepsilon+\varepsilon_0}{\varepsilon}\sin^2\theta\right)}\bar{r}_{\mathrm{P}}\delta Z_{\mathrm{P}} , \tag{47b}$$

where θ is the angle of incidence. The differential reflectance is expressed as

$$\frac{\delta R_{\mathrm{S}}}{\bar{R}_{\mathrm{S}}}=4\sqrt{\varepsilon_0}\cos\theta\,\mathrm{Re}\cdot\left(\frac{\delta Y_{\mathrm{S}}}{\varepsilon-\varepsilon_0}\right) , \tag{48a}$$

$$\frac{\delta R_{\mathrm{P}}}{\bar{R}_{\mathrm{P}}}=-4\sqrt{\varepsilon_0}\cos\theta\,\mathrm{Re}\left[\frac{\varepsilon\delta Z_{\mathrm{P}}}{(\varepsilon-\varepsilon_0)\left(1-\dfrac{\varepsilon+\varepsilon_0}{\varepsilon}\sin^2\theta\right)}\right] . \tag{48b}$$

4.2 Surface wave

Surface wave is defined as the self-sustaining nonradiative field. Dispersion of the surface wave is given by the pole of r_{S} and r_{P}:

S-polarization,

$$1-\frac{c\alpha_0}{i\omega}Y_{\mathrm{S}}(k,\omega)=0 , \tag{49a}$$

P-polarization,

$$1+\frac{ic\alpha_0}{\varepsilon_0\omega}Y_{\mathrm{P}}(k,\omega)=0 , \tag{49b}$$

where $\alpha=-ip=(k^2-\varepsilon\omega^2/c^2)^{1/2}$. In the limit $|p|\to 0$, eq. (49a) tends to

$$\alpha+\alpha_0-\frac{4\pi i\omega}{c^2}\sigma^{(2\mathrm{D})}_{yy}=0 \tag{50}$$

derived by the present author on 2D model.[16] In the absence of the surface state, eq. (49b) becomes the familiar equation for the surface polariton:

$$\frac{\varepsilon}{\alpha}+\frac{\varepsilon_0}{\alpha_0}=0 . \tag{51}$$

Substituting eq. (39) into eq. (49b), we obtain the dispersion relation of the 2D surface carrier plasmon:[16]

$$\frac{\varepsilon}{\alpha}+\frac{\varepsilon_0}{\alpha_0}+\frac{4\pi i}{\omega}\sigma^{(2\mathrm{D})}_{xx}=0 . \tag{52}$$

Detailed investigation of the surface wave in the presence of the surface state will be given in a separate paper.

4.3 Image force

Consider a test charge q placed at $z=-b$ and oscillating with a frequency ω and an infinitesimal amplitude. The reaction field $E_z{}^r(-b)$ is given by

$$E^r_{z,\parallel}=-\frac{q}{\varepsilon_0}\int_0^\infty k\mathrm{d}k\,r_{\mathrm{P}}(k,\omega)\mathrm{e}^{-2\alpha_0 b} , \tag{53a}$$

$$E^r_{z,\perp}=-\frac{q}{\varepsilon_0}\int_0^\infty \mathrm{d}k\frac{k^3}{\alpha_0{}^2}r_{\mathrm{P}}(k,\omega)\mathrm{e}^{-2\alpha_0 b} . \tag{53b}$$

Formulas (53a) and (53b) correspond to the case where the direction of the oscillation is parallel and perpendicular to the surface, respectively. In the electrostatic limit, both the formulas tend to the classical one

$$E^r_z=\frac{\varepsilon-\varepsilon_0}{\varepsilon_0(\varepsilon+\varepsilon_0)}\frac{q}{4b^2} \tag{54}$$

in the absence of surface state.

4.4 Energy loss of electrons reflected from the surface

Let us take semiclassical approach after Lucas and Šunjić[27,28] by treating electron as a classical particle with charge q on a well-defined trajectory. Suppose an electron is specularly reflected at the origin at $t=0$. Assuming that the reflection is caused by strong interaction other than the electromagnetic one, we shall calculate the reaction field $\boldsymbol{E}^r$ in the Born approximation. Let us introduce a new co-ordinate system (X, Y, z) by choosing the X-axis in the plane of incidence. Velocities of the electron before and after the reflection are denoted by $(v_{\parallel}, 0, v_{\perp})$ and $(v_{\parallel}, 0, -v_{\perp})$, respectively. Source current is expressed in the new co-ordinate system as

$$J_X^{\text{ext}}(z, k_X, k_Y, \omega)=\frac{2qv_{\parallel}}{(2\pi)^3 v_{\perp}} \cos[(\omega-k_X v_{\parallel})z/v_{\perp}] , \tag{55a}$$

$$J_z^{\text{ext}}(z, k_X, k_Y, \omega)=\frac{2iq}{(2\pi)^3} \sin[(\omega-k_X v_{\parallel})z/v_{\perp}] . \tag{55b}$$

Denoting the angle between the x- and the X-axes by ϕ, we obtain the following expressions for the energy loss rate of the electron due to each polarization.

S-polarization,

$$\frac{\mathrm{d}W_{\mathrm{S}}}{\mathrm{d}t}=-\frac{2\pi}{c^2}\int_{-\infty}^{\infty}\omega\mathrm{d}\omega\int\mathrm{d}\boldsymbol{k}\frac{1}{\alpha_0}\,\mathrm{Im}r_{\mathrm{S}}\left|\int_{-\infty}^{0}\mathrm{d}z\mathrm{e}^{\alpha_0 z}J_X^{\text{ext}}\sin\phi\right|^2 . \tag{56a}$$

P-polarization,

$$\frac{\mathrm{d}W_{\mathrm{P}}}{\mathrm{d}t}=2\pi\int_{-\infty}^{\infty}\frac{\mathrm{d}\omega}{\varepsilon_0\omega}\int\mathrm{d}\boldsymbol{k}\frac{1}{\alpha_0}\,\mathrm{Im}\,r_{\mathrm{P}}\left|\int_{-\infty}^{0}\mathrm{d}z\mathrm{e}^{\alpha_0 z}[\alpha_0 J_X^{\text{ext}}\cos\phi+ikJ_z^{\text{ext}}]\right|^2 . \tag{56b}$$

In the quasi-electrostatic limit studied by Lucas and Šunjić,[25,26] formula (56b) tends to

$$\left(\frac{\mathrm{d}W}{\mathrm{d}t}\right)_{\mathrm{e.s.}}=\frac{4q^2v_{\perp}^2}{(2\pi)^5}\int_{-\infty}^{\infty}\frac{\omega\mathrm{d}\omega}{\varepsilon_0}\int\mathrm{d}\boldsymbol{k}\frac{k\,\mathrm{Im}\,r_{\mathrm{P}}}{[k^2v_{\perp}^2+(\omega-kv_{\parallel}\cos\phi)^2]^2} . \tag{57}$$

The last term in the integrand of formulas (56) and (57) has a peak at $\omega=kv_{\parallel}\cos\phi=\boldsymbol{k}\boldsymbol{v}$, which ensures energy-momentum conservation in the Born approximation. In formulas (53), (56), and (57) effect of the surface wave excitation is expressed by the contribution of the pole of r_{S} and r_{P}. Contribution of the surface state excitation is given by inserting the perturbational formulas for r_{S} and r_{P}. Extension to the Bragg reflection and photoemission case can easily be done by using relevant trajectory.[28]

4.5 Dispersion force between solid bodies

Theory of the dispersion force between solid bodies has been reviewed by Dyaloshinskii *et al.*[17] Consider two solid bodies 1 and 2 separated by the medium 0 having parallel surfaces. Though the original formula is derived on the local approximation to the dielectric function of the media 1 and 2, it can easily be extended to a model-independent form by expressing the thermal Green function of the electromagnetic field of the medium 0 in terms of the reflectivity coefficients at the surfaces. To achieve this end we should replace eq. (4.8) of ref. 17 by

$$\Delta=1-\mathrm{e}^{2\alpha_0 l}(r_{\mathrm{S},1}r_{\mathrm{S},2})^{-1} \tag{58a}$$

and eq. (4.11) by

$$\bar{\Delta}=1-\mathrm{e}^{2\alpha_0 l}(r_{\mathrm{P},1}r_{\mathrm{P},2})^{-1} . \tag{58b}$$

Here l is the distance between surfaces and indices 1 and 2 discriminate the reflectivity coefficients of each medium to the medium 0. Attractive force per unit area is given by

$$F(l)=-\frac{k_{\mathrm{B}}T}{2\pi}\sum_{n=0}^{\infty}{}'\int_0^{\infty}k\mathrm{d}k\alpha_0\left(\frac{1}{\Delta}+\frac{1}{\bar{\Delta}}\right) \tag{59}$$

derived in ref. 17. Integer n specifies the imaginary frequency in α_0, Δ, and $\bar{\Delta}$ by $\omega=2\pi ink_{\mathrm{B}}T/h$ and the prime on the summation means that the term with $n=0$ is given half weight. Recently it has been shown that the dispersion force between two atoms can also be expressed in terms of the elastic photon scattering amplitude of each atom.[29]

§ 5. Discussion

Some of the formulas derived in this paper have already been obtained by previous authors for special models and/or in approximate forms (local, quasi-electrostatic, perturbation, etc.). The present scheme is generalized in many respects:

effect of the retardation is fully taken into account; the basic quantities, Y_S and Y_P, cover both the radiative and nonradiative region; formulas for the various phenomena are given in a model-independent form; the response due to the surface state is treated self-consistently. Surface response functions have been introduced in a few papers on quasi-electrostatic responses. These functions can be expressed in terms of Y_P: the surface dielectric function of Newns[10] and Heinrichs[11] is $(cp_0/\varepsilon_0\omega)Y_P$; the function $S(K)$ of Beck and Celli[23] is $r_P(K, 0)$.

Introduction of the basic quantity enables us to correlate various phenomena from a unified point of view. Thus, each phenomenon illuminates different aspect of the surface admittance (or reflectivity coefficient, if the external medium is fixed). Compiling the results obtained by several methods, we can in principle determine experimentally the fundamental properties of the surface admittance. Kramers-Kronig relations for Y_S, Y_P, r_S, r_P, $\boldsymbol{\sigma}^{(s)}$, and $\boldsymbol{\sigma}^{(2D)}$ and the sum rule

$$\int_{-\infty}^{\infty} d\omega \mathrm{Re}\sigma_{\alpha\beta}^{(s)}(z, z'; \omega)=\frac{\pi e^2}{m} n(z)\delta(z-z')\delta_{\alpha\beta} \tag{60}$$

would be helpful.

The RPA approach is well founded in the bulk problem.[30] Many-body theory shows that the approximation is equivalent to the neglect of local field correction to the field acting on electrons.[31,32] It seems that the local field correction is not necessary to the surface state conductivity at least in the case of monolayer adsorbate. Validity of the approach, however, should be further investigated, because we are to deal with E_z which varies much in the region of the surface state.

Validity and limitation of 2D model has been discussed in § 2. Another phenomenological model frequently employed is the dielectric layer model in which one approximates the surface region by a homogeneous dielectric layer of thickness d placed on a substrate. Optical reflectivity of the model has been studied by McIntype and Aspnes.[20] Extending the model to the anisotropic case ($\varepsilon_{xx}=\varepsilon_{yy}=\varepsilon_{\parallel}$, $\varepsilon_{zz}=\varepsilon_{\perp}$), we shall show the Green function and the surface admittance in Appendix. Though the model would work well for the layer of thickness of several atomic layers, application of the model to mono- or submonolayer[5,6] requires a caution. In the following we shall investigate the monolayer limit carefully and compare the result with general one. Suppose a uniform static electric field $\boldsymbol{E}^{\mathrm{ext}}$ is applied to the layer. For tangential field the total polarization of the layer per unit area is

$$P_t=\frac{\varepsilon_{\parallel}-1}{4\pi} dE_t^{\mathrm{ext}} . \tag{61}$$

In the monolayer limit, P_t should tends to the sum of the atomic polarization, which is represented by the following limit

$$d\to 0,\ \varepsilon_{\parallel}\to\infty,\ \varepsilon_{\parallel}d\to 4\pi\chi_{\parallel}^{(2D)} , \tag{62}$$

where $\boldsymbol{\chi}^{(2D)}$ is 2D electric susceptibility. For the normal field we have

$$P_z=\frac{\varepsilon_{\perp}-1}{4\pi\varepsilon_{\perp}} dE_z^{\mathrm{ext}} . \tag{63}$$

We should take the limit

$$d\to 0,\ \varepsilon_{\perp}\to 0,\ d/\varepsilon_{\perp}\to -4\pi\chi_{\perp}^{(2D)} \tag{64}$$

to represent the monolayer limit properly. The above limit is equivalent to assume that the polarization density is proportional to D_z, not to E_z, and the susceptibility diverges. Taking the limit (62) and (64) in formulas (A·10) and (A·11), we obtain

$$Y_S=\bar{Y}_S+\frac{4\pi}{c}\sigma_{\parallel}^{(2D)} , \tag{65a}$$

$$Y_P=\frac{\bar{Y}_P+\dfrac{4\pi}{c}\sigma_{\parallel}^{(2D)}}{1+\dfrac{4\pi ck^2\sigma_{\perp}^{(2D)}}{\varepsilon^2\omega^2}\bar{Y}_P} . \tag{65b}$$

Lacking internal structure, the layer model in the monolayer limit is applicable only to the slowly varying field. Thus the above formulas agree with the general ones in the limit $|p|\to 0$: eq. (65a) agrees with eq. (28); eq. (65b) with eq. (38) or (39) in each case. When both $\sigma_{\parallel}^{(2D)}$ and $\sigma_{\perp}^{(2D)}$ are present, eq. (65b) holds only as a perturbation formula and agrees with eq. (41).

Though present paper is mainly concerned with the electronic surface state, the method will easily be applied to the surface phonon with appropriate modifications.

Acknowledgement

The present work has been developed during a group study of the surface wave at Kyusyu University. The author would like to thank members of the group, Professors M. Tsuji and S. Inoue, and Mr. Y. Ōmura for several helpful discussions.

Appendix. Green function and Surface Admittance of Dielectric Layer Model

Let us consider a dielectric layer occupying $0 \le z \le d$ and characterized by anisotropic local dielectric function

$$\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{\parallel}(\omega) , \qquad (\text{A}\cdot 1)$$

$$\varepsilon_{zz} = \varepsilon_{\perp}(\omega) . \qquad (\text{A}\cdot 2)$$

The layer is assumed to be placed on a substrate filling $z > d$. The Green functions are written down as follows:

$$\mathscr{D}_{yy}(z, z') = \frac{i}{2p} \{\exp ip_{\parallel}|z-z'| + \bar{r}_{\text{S}} \exp[-ip_{\parallel}(z+z'-2d)]\} , \qquad (\text{A}\cdot 3)$$

$$\mathscr{D}_{xx}(z, z) = \frac{ic^2 p'}{2\varepsilon_{\parallel}\omega^2} \{\exp ip'|z-z'| + \bar{r}_{\text{P}} \exp[-ip'(z+z'-2d)]\} , \qquad (\text{A}\cdot 4)$$

$$\mathscr{D}_{xz}(z, z') = -\frac{ic^2 k}{2\varepsilon_{\perp}\omega^2} \{\text{sgn}(z-z') \exp ip'|z-z'| + \bar{r}_{\text{P}} \exp[-ip'(z+z'-2d)]\} , \qquad (\text{A}\cdot 5)$$

$$\mathscr{D}_{zx}(z, z') = -\frac{ic^2 k}{2\varepsilon_{\perp}\omega^2} \{\text{sgn}(z-z') \exp ip'|z-z'| - \bar{r}_{\text{P}} \exp[-ip'(z+z'-2d)]\} , \qquad (\text{A}\cdot 6)$$

$$\mathscr{D}_{zz}(z, z') = -\frac{\varepsilon_{\parallel} c^2}{\varepsilon_{\perp}{}^2 \omega^2} \delta(z-z') + \frac{i\varepsilon_{\parallel} c^2 k^2}{2\varepsilon_{\perp}{}^2 \omega^2 p'} \{\exp ip'|z-z'| - \bar{r}_{\text{P}} \exp[-ip'(z+z'-2d)]\} , \qquad (\text{A}\cdot 7)$$

where

$$p_{\parallel} = (\varepsilon_{\parallel}\omega^2/c^2 - k^2)^{1/2} , \qquad (\text{A}\cdot 8)$$

$$p' = (\varepsilon_{\parallel}\omega^2/c^2 - \varepsilon_{\parallel}k^2/\varepsilon_{\perp})^{1/2} , \qquad (\text{A}\cdot 9)$$

and $\bar{r}_{\text{S}}$ and $\bar{r}_{\text{P}}$ are the reflectivity coefficients of the substrate to the dielectrics.

Surface admittances of the composite system (layer and substrate) at $z=0$ are given by

$$Y_{\text{S}} = \frac{cp_{\parallel}}{\omega} \frac{1-\bar{r}_{\text{S}} \exp i2p_{\parallel}d}{1+\bar{r}_{\text{S}} \exp i2p_{\parallel}d} , \qquad (\text{A}\cdot 10)$$

$$Y_{\text{P}} = \frac{\varepsilon_{\parallel}\omega}{cp'} \frac{1-\bar{r}_{\text{P}} \exp i2p'd}{1+\bar{r}_{\text{P}} \exp i2p'd} . \qquad (\text{A}\cdot 11)$$

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