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Interband Contributions to Optical Harmonic Generation at a Metal Surface

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The effect of interband transitions of electrons on the linear as well as the bilinear polarization induced in a metal by a light wave of (circular) frequency ω has been calculated. The calculation of the linear polarization or linear current density leads to the familiar expression for the dielectric constant $\epsilon(\omega)$. The part of the bilinear polarization varying as $e^{-2i\omega t}$ for free conduction electrons with a potential barrier at the surface is known to have the form

$$\mathbf{P}^{(2\omega)}(\mathrm{NL})=\alpha_{pl}\mathbf{E}^{(\omega)}\times\mathbf{H}^{(\omega)}+\beta_{pl}\mathbf{E}^{(\omega)}\nabla\cdot\mathbf{E}^{(\omega)},$$

where $\mathbf{E}^{(\omega)}$ and $\mathbf{H}^{(\omega)}$ are, respectively, the electric and magnetic fields varying as $e^{-i\omega t}$. It is shown that the introduction of a periodic potential leads to the same form for $\mathbf{P}^{(2\omega)}(\mathrm{NL})$ for isotropic metals, with α and β now containing both the intraband and interband contributions. Except near a resonance for interband transitions involving at least 3 bands, it is found that in the long-wavelength limit for the light wave the general expression for $\mathbf{P}^{(2\omega)}$ may be approximated by a form which may be completely specified in terms of $\epsilon(\omega)$ and $\epsilon(2\omega)$. By solving Maxwell's equations for the fundamental as well as the second-harmonic fields for arbitrary ϵ, α, and β, general expressions for both linear and bilinear reflection coefficients have been derived. These phenomenological solutions can be used to determine experimentally the residual 3-band contributions to $\mathbf{P}^{(2\omega)}(\mathrm{NL})$ which cannot be expressed in terms of the linear dielectric constant alone.

I. INTRODUCTION

WHEN a light beam of sufficiently high intensity is incident on the surface of a solid, one observes[1] in the reflected and transmitted beams not only the fundamental frequency of the incident wave but also its higher harmonics. For centrosymmetric solids like metals, no second-harmonic bilinear current is, however, induced in the medium in the lowest order electric dipole approximation[2] for the electromagnetic fields. This is, of course, not true if one considers higher order multipole expansions for the fields, and recently there has been a considerable interest, both theoretical and experimental, in calculating[3–5] and measuring the intensity[6,7] and the angle of polarization[8] of the second-harmonic wave generated in the beam reflected from a metal surface. From general physical arguments it can be shown that in an isotropic metal, to the lowest order in the incident field $\mathbf{E}_{\mathrm{inc}}$ of frequency ω, the component of the induced linear polarization varying as $e^{-i\omega t}$ has the form

$$\mathbf{P}^{(\omega)}(\mathrm{L})=(1/4\pi)[\epsilon(\omega)-1]\mathbf{E}^{(\omega)}, \qquad (1.1)$$

where $\epsilon(\omega)$ is the linear transverse dielectric constant and $\mathbf{E}^{(\omega)}$ is the component of the electric field in the medium varying as $e^{-i\omega t}$. The electric field $\mathbf{E}^{(\omega)}$ and the corresponding magnetic field $\mathbf{H}^{(\omega)}$ in the medium are of the same order as the incident field. Using similar arguments,[9] one can show that the component of the induced bilinear polarization varying as $e^{-2i\omega t}$ has the form

$$\mathbf{P}^{(2\omega)}(\mathrm{NL})=\alpha(\omega,\omega)(\mathbf{E}^{(\omega)}\times\mathbf{H}^{(\omega)})+\beta(\omega,\omega)(\mathbf{E}^{(\omega)}\nabla\cdot\mathbf{E}^{(\omega)}) \qquad (1.2)$$

and the component of the induced linear polarization varying as $e^{-2i\omega t}$ is given by

$$\mathbf{P}^{(2\omega)}(\mathrm{L})=(1/4\pi)[\epsilon(2\omega)-1]\mathbf{E}^{(2\omega)}, \qquad (1.3)$$

where $\mathbf{E}^{(2\omega)}$ is the induced second-harmonic field due to the nonlinear polarization of the medium. Since the current density $\mathbf{J}$ may be obtained from the polarization $\mathbf{P}$ by using the relation

$$\mathbf{J}=\partial\mathbf{P}/\partial t, \qquad (1.4)$$

the phenomenological relations given by Eqs. (1.1)–(1.3) are enough to give the fundamental and second-harmonic fields both inside and outside the medium which must be solutions of Maxwell's equations. For an incident transverse electromagnetic wave of frequency ω, $\nabla\cdot\mathbf{E}^{(\omega)}$ is zero everywhere except near the surface (within a distance of the order 10^{-8} cm for optical frequencies). The second term in Eq. (1.2) is, therefore, called the surface term, as compared to the first term, which is called the volume term.

In order to calculate the quantities ϵ, α, and β for a metal, one of us had earlier worked with the Sommerfeld model for metals where the conduction electrons are considered to be completely free except for a barrier

[1] N. Bloembergen, *Nonlinear Optics* (W. A. Benjamin, Inc., New York, 1965). See detailed references in this book.
[2] P. L. Kelley, J. Phys. Chem. Solids **24**, 1113 (1963). See the Appendix of this paper.
[3] S. S. Jha, Phys. Rev. **140**, A2020 (1965). Hereafter, this paper will be referred to as I. There is a misprint in Eq. (6.7) of this paper. A factor of ½ should be inserted on the right-hand side of this equation. However, this does not change any other results in this paper.
[4] S. S. Jha, Phys. Rev. Letters **15**, 412 (1965). A factor of ½ should occur on the right-hand side of Eq. (7) of this paper. Also, the first term in Eq. (13) should be multiplied by 32 and the second term by −32.
[5] N. Bloembergen and Y. R. Shen, Phys. Rev. **141**, 298 (1966); **145**, 390 (1966).
[6] F. Brown, R. E. Parks, and A. M. Sleeper, Phys. Rev. Letters **14**, 1029 (1965).
[7] N. Bloembergen, R. K. Chang, and C. H. Lee, Phys. Rev. Letters **16**, 986 (1966).
[8] F. Brown and R. E. Parks, Phys. Rev. Letters **16**, 507 (1966).
[9] See Ref. 3. See also, E. Adler, Phys. Rev. **134**, A728 (1964).

potential at the surface. It was shown in I that in order to calculate harmonic fields away from the surface, one may use the value of $\nabla\cdot\mathbf{E}^{(\omega)}$ as given by the classical Fresnel formula. This means that we may write

$$\nabla\cdot\mathbf{E}^{(\omega)}=[1-\epsilon(\omega)]E_x^{(\omega)}\delta(x-0^+)\,, \tag{1.5}$$

where we have assumed the metal slab to occupy the half-space $x\geqslant 0$. In the limit where the Fermi velocity v_f of the metal electron is small compared to the velocity of light c, one then finds in this model

$$\epsilon_{pl}=1-\omega_p^2/\omega^2\,, \tag{1.6}$$

$$\alpha_{pl}=\frac{ie^3n}{4m^2c\omega^3}\,, \tag{1.7}$$

$$\beta_{pl}=\frac{e^3n}{2m^2\omega_p^2\omega^2}=\frac{e}{8\pi m\omega^2}\,, \tag{1.8}$$

where $\omega_p=(4\pi ne^2/m)^{1/2}$, is the plasma frequency of the conduction electrons of density n. This simple free-electron model, however, can give quantitative results only for frequencies ω and 2ω which are small compared to the frequency where interband transitions of the core electrons become important. Bloembergen, Chang, and Lee[7] have recently done these nonlinear reflection experiments on silver and gold. By a careful analysis of their experimental data, they have shown that their results can be explained only when they include the contributions due to interband transitions, which become important for these metals in the visible region of the optical frequencies.

In order to go beyond the Sommerfeld model, one has to consider the periodic lattice potential in addition to the surface-barrier potential for the electrons. In this paper we will find a general expression for the bilinear polarization which allows for transitions between different energy bands introduced due to the periodic potential. Our calculation is based on the formulation[10] of this problem developed earlier. In Sec. II of this paper we will briefly review this formalism and write down the general expressions for the linear as well as the bilinear charge and current densities induced in the metal.

In Sec. III of this paper we will calculate the linear dielectric constant and the volume term of the bilinear polarization. While trying to find new expressions[11] for ϵ and α we will neglect the effect of the surface barrier in this section. We will then show that except for a term which involves at least 3 bands and which may become important only when ω or 2ω is near a resonance for interband transitions, we can obtain an expression for α in terms of the linear dielectric constant[12] $\epsilon(2\omega)$. The main effect of interband transitions in this approximation comes only through the linear dielectric constant which is known experimentally for many metals We will further show in Sec. IV that the surface term may likewise be written in terms of the linear dielectric constant alone. Finally, in Sec. V, we will solve Maxwell's equations for the fields varying with frequencies ω and 2ω for arbitrary and complex ϵ, α, and β, and find general expressions for both linear and bilinear reflection coefficients. We will discuss the limitations and usefulness of our approximations and generalizations in Sec. VI.

II. GENERAL FORMULATION OF THE PROBLEM

Following II, let the unperturbed states of the electrons be described by the solution of the Schrödinger equation

$$\mathcal{H}_0u_n^{(0)}=i\hbar(\partial u_n^{(0)}/\partial t)\,, \tag{2.1}$$

where

$$\mathcal{H}_0=p^2/2m+V(\mathbf{x}) \tag{2.2}$$

and where the potential $V(\mathbf{x})$ contains both the periodic potential and the surface-barrier potential in which the electrons of mass m and charge $-e$ are moving. Stationary solutions of Eqs. (2.1) and (2.2) may be represented by

$$u_n^{(0)}(\mathbf{x},t)=\Psi_n^{(0)}(\mathbf{x})e^{-(i/\hbar)E_nt}\,, \tag{2.3}$$

where

$$\mathcal{H}_0\Psi_n^{(0)}=E_n\Psi_n^{(0)}\,. \tag{2.4}$$

In the presence of the self-consistent electromagnetic fields represented by a vector potential $\mathbf{A}(\mathbf{x},t)$ induced due to an incident plane electromagnetic wave of frequency ω, the perturbed Schrödinger equation becomes

$$(\mathcal{H}_0+\mathcal{H}_1+\mathcal{H}_2)u_n=i\hbar(\partial u_n/\partial t)\,, \tag{2.5}$$

where

$$\mathcal{H}_1=(e/mc)(\mathbf{A}\cdot\mathbf{p}-\tfrac{1}{2}i\hbar\nabla\cdot\mathbf{A}) \tag{2.6}$$

and

$$\mathcal{H}_2=(e^2/2mc^2)\mathbf{A}\cdot\mathbf{A}\,. \tag{2.7}$$

In terms of the solutions u_n of the above equation, the total current and charge densities are, respectively, given by

$$\mathbf{J}=\sum_n[(-e\hbar/2mi)(u_n{}^*\nabla u_n-u_n\nabla u_n{}^*)-(e^2\mathbf{A}/mc)u_n{}^*u_n] \tag{2.8}$$

and

$$\rho=-e\sum_n(u_n{}^*u_n-u_n{}^{*(0)}u_n{}^{(0)})\,, \tag{2.9}$$

where the summations over n are for the occupied states only. Now let us expand the induced vector potential $\mathbf{A}$, the current density $\mathbf{J}$, and the charge density ρ as

$$\mathbf{A}(\mathbf{x},t)=\sum_{l=-\infty}^{+\infty}\mathbf{a}^{(l\omega)}(\mathbf{x})e^{-il\omega t}\,, \tag{2.10}$$

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[10] S. S. Jha, Phys. Rev. **145**, 500 (1966); hereafter, referred to as II.

[11] In order to calculate $\alpha(\omega,\omega)$ one may also use other formulations of the problem. For example, see, H. Cheng and P. B. Miller, Phys. Rev. **134**, A683 (1964); A. Pine, *ibid.* **139**, A901 (1965).

[12] In the long-wavelength limit (wave vector $\mathbf{q}\to 0$) the transverse and longitudinal dielectric constants are same.

$$\mathbf{J}(\mathbf{x},t)=\sum_{l=-\infty}^{+\infty}\mathbf{j}^{(l\omega)}(\mathbf{x})e^{-il\omega t},\tag{2.11}$$

$$\rho(\mathbf{x},t)=\sum_{l=-\infty}^{+\infty}\rho^{(l\omega)}(\mathbf{x})e^{-il\omega t},\tag{2.12}$$

where $\mathbf{a}^{(-l\omega)}=\mathbf{a}^{*(l\omega)}$, $\mathbf{j}^{(-l\omega)}=\mathbf{j}^{*(l\omega)}$, and $\rho^{(-l\omega)}=\rho^{*(l\omega)}$. If we treat the incident field represented by a vector potential $\mathbf{A}_{\text{inc}}$ as a small perturbation to the motion of the electrons, it is permissible to assume

$$|\mathbf{a}^{(l\omega)}|\sim|\mathbf{A}_{\text{inc}}|^{|l|},\quad\text{for}\quad l\neq 0\tag{2.13}$$

and

$$|\mathbf{a}^{(0)}|\sim|\mathbf{A}_{\text{inc}}|^{2},\quad\text{for}\quad l=0.\tag{2.14}$$

By using the standard time-dependent perturbation theory to solve Eq. (2.5) to lowest orders in $|\mathbf{A}_{\text{inc}}|$ one then obtains

$$\mathbf{j}^{(\omega)}(\mathbf{x})=\frac{-e\hbar}{2mi}\sum_n f_0(E_n)[\Psi_n^{*(0)}\nabla\Psi_n^{(1)\omega}-\Psi_n^{(1)\omega}\nabla\Psi_n^{*(0)}+\Psi_n^{*(1)-\omega}\nabla\Psi_n^{(0)}-\Psi_n^{(0)}\nabla\Psi_n^{*(1)-\omega}]-\frac{e^2\mathbf{a}^{(\omega)}}{mc}\sum_n f_0(E_n)\Psi_n^{*(0)}\Psi_n^{(0)},\tag{2.15}$$

$$\rho^{(\omega)}(\mathbf{x})=-e\sum_n f_0(E_n)[\Psi_n^{*(0)}\Psi_n^{(1)\omega}+\Psi_n^{*(1)-\omega}\Psi_n^{(0)}],\tag{2.16}$$

$$\mathbf{j}^{(2\omega)}(\mathrm{L})=\frac{-e\hbar}{2mi}\sum_n f_0(E_n)[\Psi_n^{*(0)}\nabla\Psi_n^{(1)2\omega}-\Psi_n^{(1)2\omega}\nabla\Psi_n^{*(0)}+\Psi_n^{*(1)-2\omega}\nabla\Psi_n^{(0)}-\Psi_n^{(0)}\nabla\Psi_n^{*(1)-2\omega}]-\frac{e^2\mathbf{a}^{(2\omega)}}{mc}\sum_n f_0(E_n)\Psi_n^{*(0)}\Psi_n^{(0)},\tag{2.17}$$

$$\begin{aligned}\mathbf{j}^{(2\omega)}(\mathrm{NL})=\frac{-e\hbar}{2mi}\sum_n f_0(E_n)[\Psi_n^{*(0)}\nabla\Psi_n^{(2)\omega,\omega}-\Psi_n^{(2)\omega,\omega}\nabla\Psi_n^{*(0)}+\Psi_n^{*(2)-\omega,-\omega}\nabla\Psi_n^{(0)}-\Psi_n^{(0)}\nabla\Psi_n^{*(2)-\omega,-\omega}]\\-\frac{e^2\mathbf{a}^{(\omega)}}{mc}\sum_n f_0(E_n)[\Psi_n^{*(0)}\Psi_n^{(1)\omega}+\Psi_n^{*(1)-\omega}\Psi_n^{(0)}]\\-\frac{e\hbar}{2mi}\sum_n f_0(E_n)[\Psi_n^{*(1)-\omega}\nabla\Psi_n^{(1)\omega}-\Psi_n^{(1)\omega}\nabla\Psi_n^{*(1)-\omega}],\end{aligned}\tag{2.18}$$

where we have introduced the Fermi distribution function $f_0(E_n)$ so that summations over n now extend to all the states, and where

$$\Psi_n^{(1)\omega}=-\sum_m\frac{\langle m|\mathcal{H}_1^{(\omega)}|n\rangle\Psi_m^{(0)}}{(E_m-E_n-\hbar\omega-i\epsilon)},\tag{2.19}$$

$$\Psi_n^{(2)\omega,\omega'}=\sum_m\left\{\sum_s\left[\frac{\langle m|\mathcal{H}_1^{(\omega)}|s\rangle\langle s|\mathcal{H}_1^{(\omega')}|n\rangle}{(E_s-E_n-\hbar\omega'-i\epsilon)}-\frac{e^2}{2mc^2}\langle m|\mathbf{a}^{(\omega)}\cdot\mathbf{a}^{(\omega')}|n\rangle\right]\frac{\Psi_m^{(0)}}{(E_m-E_n-\hbar\omega-\hbar\omega'-2i\epsilon)}\right\},\tag{2.20}$$

with

$$\mathcal{H}_1^{(\omega)}=(e/mc)(\mathbf{a}^{(\omega)}\cdot\mathbf{p}-\tfrac{1}{2}i\hbar\nabla\cdot\mathbf{a}^{(\omega)}).\tag{2.21}$$

Because of the continuity equation, the component of the charge density $\rho^{(l\omega)}$ is, of course, related to the component of the current density $j^{(l\omega)}$ by the equation

$$\rho^{(l\omega)}=\nabla\cdot\mathbf{j}^{(l\omega)}/il\omega.\tag{2.22}$$

Also from Eq. (1.4) the component of the induced polarization $\mathbf{P}^{(l\omega)}$ may be obtained from the current density by using the relation

$$\mathbf{P}^{(l\omega)}=(-\mathbf{j}^{(l\omega)}/il\omega).\tag{2.23}$$

In the next two sections we will calculate $\mathbf{j}^{(\omega)}$ and $\mathbf{j}^{(2\omega)}$ given by Eqs. (2.15), (2.17), and (2.18) for real metals.

III. VOLUME CURRENT DENSITY

In order to calculate the current densities $\mathbf{j}^{(\omega)}$ and $\mathbf{j}^{(2\omega)}$ inside the metal, it is permissible to neglect the effect of surface barrier. The surface potential affects these expressions only within a distance of the order v_f/ω or $\hbar/mv_f$ from the surface. Thus, in this section we will consider the potential $V(\mathbf{x})$ to contain only the periodic part. The unperturbed wave functions are then given by Bloch functions:

$$\Psi_n^{(0)}\rightarrow\Psi_{b\mathbf{k}}^{(0)}\rightarrow|b\mathbf{k}\rangle=(1/\sqrt{N})u_{b\mathbf{k}}(\mathbf{x})e^{i\mathbf{k}\cdot\mathbf{x}},\tag{3.1}$$

where N is the number of unit cells in the crystal, b denotes the band, $\mathbf{k}$ denotes the wave vector, and where the function $u_{b\mathbf{k}}(\mathbf{x})$ is cell-periodic. The δ-function normalization conditions for $\Psi_{b\mathbf{k}}^{(0)}$ requires

$$\int_{\text{cell}} u_{b'\mathbf{k}}^* u_{b\mathbf{k}} d\tau = \delta_{b'b}. \tag{3.2}$$

By assuming

$$\mathbf{a}^{(\omega)}(\mathbf{x}) = \mathbf{a}_1 e^{i\mathbf{q}\cdot\mathbf{x}} \tag{3.3}$$

we may now calculate the matrix elements of $\mathcal{H}_1^{(\pm\omega)}$ between different unperturbed states. They are given by[13]

$$\langle b'\mathbf{k}'|\mathcal{H}_1^{(\omega)}|b\mathbf{k}\rangle = (e/mc)\mathbf{a}_1 \times (b'\mathbf{k}+\mathbf{q}|\mathbf{p}+\hbar\mathbf{k}+\tfrac{1}{2}\hbar\mathbf{q}|b\mathbf{k})\delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}}, \tag{3.4}$$

$$\langle b'\mathbf{k}'|\mathcal{H}_1^{(-\omega)}|b\mathbf{k}\rangle = (e/mc)\mathbf{a}_1^* \times (b'\mathbf{k}-\mathbf{q}|\mathbf{p}+\hbar\mathbf{k}-\tfrac{1}{2}\hbar\mathbf{q}|b\mathbf{k})\delta_{\mathbf{k}',\mathbf{k}-\mathbf{q}}, \tag{3.5}$$

where, for any operator $\mathbf{O}$,

$$(b'\mathbf{k}'|\mathbf{O}|b\mathbf{k}) = \int_{\text{cell}} u_{b'\mathbf{k}'}^* \mathbf{O} u_{b\mathbf{k}} d\tau. \tag{3.6}$$

Similarly, one obtains

$$\langle b''\mathbf{k}''|\mathbf{a}^{(\omega)}\cdot\mathbf{a}^{(\omega)}|b\mathbf{k}\rangle = \mathbf{a}_1\cdot\mathbf{a}_1(b''\mathbf{k}+2\mathbf{q}|b\mathbf{k})\delta_{\mathbf{k}'',\mathbf{k}+2\mathbf{q}} \tag{3.7}$$

and

$$\langle b''\mathbf{k}''|\mathbf{a}^{(-\omega)}\cdot\mathbf{a}^{(-\omega)}|b\mathbf{k}\rangle = \mathbf{a}_1^*\cdot\mathbf{a}_1^*(b''\mathbf{k}-2\mathbf{q}|b\mathbf{k})\delta_{\mathbf{k}'',\mathbf{k}-2\mathbf{q}}. \tag{3.8}$$

Since $\mathbf{a}^{(\omega)}(\mathbf{x})$ has the form given by Eq. (3.3), the current density $\mathbf{j}^{(\omega)}(\mathbf{x})$ and $\mathbf{j}^{(2\omega)}(\text{NL})$ given by Eqs. (2.15) and (2.18) are expected to have the form

$$\mathbf{j}^{(\omega)}(\mathbf{x}) = \mathbf{j}_1(\mathbf{q})e^{i\mathbf{q}\cdot\mathbf{x}}, \quad \mathbf{j}^{(2\omega)}(\text{NL}) = \mathbf{j}_2^{(\text{NL})}(2\mathbf{q})e^{2i\mathbf{q}\cdot\mathbf{x}}. \tag{3.9}$$

Using Eqs. (2.15), (2.18)–(2.20), (3.4), (3.5), (3.7)–(3.9) and after properly shifting dummy symbols inside the summation signs, we then find

$$\mathbf{j}_1(\mathbf{q}) = \frac{-e^2 n}{mc}\mathbf{a}_1 + (e^2/m^2c)\sum_{\mathbf{k}bb'} (b\mathbf{k}|\mathbf{p}+\hbar\mathbf{k}+\tfrac{1}{2}\hbar\mathbf{q}|b'\mathbf{k}+\mathbf{q})(b'\mathbf{k}+\mathbf{q}|\mathbf{a}_1\cdot[\mathbf{p}+\hbar\mathbf{k}+\tfrac{1}{2}\hbar\mathbf{q}]|b\mathbf{k})M(b'\mathbf{k}+\mathbf{q}, b\mathbf{k}, \omega), \tag{3.10}$$

$$\begin{aligned}\mathbf{j}_2^{(\text{NL})}(2\mathbf{q}) = {} & (e^3/2m^2c^2)\mathbf{a}_1\cdot\mathbf{a}_1 \sum_{\mathbf{k}bb''} (b\mathbf{k}|\mathbf{p}+\hbar\mathbf{k}+\hbar\mathbf{q}|b''\mathbf{k}+2\mathbf{q})(b''\mathbf{k}+2\mathbf{q}|b\mathbf{k})M(b''\mathbf{k}+2\mathbf{q}, b\mathbf{k}, 2\omega) \\ & +(e^3/m^2c^2)\mathbf{a}_1 \sum_{\mathbf{k}bb'} (b\mathbf{k}|b'\mathbf{k}+\mathbf{q})(b'\mathbf{k}+\mathbf{q}|\mathbf{a}_1\cdot[\mathbf{p}+\hbar\mathbf{k}+\tfrac{1}{2}\hbar\mathbf{q}]|b\mathbf{k})M(b'\mathbf{k}+\mathbf{q}, b\mathbf{k}, \omega) \\ & -(e^3/m^3c^2) \sum_{\mathbf{k}bb'b''} (b\mathbf{k}|\mathbf{p}+\hbar\mathbf{k}+\hbar\mathbf{q}|b''\mathbf{k}+2\mathbf{q})(b''\mathbf{k}+2\mathbf{q}|\mathbf{a}_1\cdot[\mathbf{p}+\hbar\mathbf{k}+\tfrac{1}{2}3\hbar\mathbf{q}]|b'\mathbf{k}+\mathbf{q}) \\ & \times(b'\mathbf{k}+\mathbf{q}|\mathbf{a}_1\cdot[\mathbf{p}+\hbar\mathbf{k}+\tfrac{1}{2}\hbar\mathbf{q}]|b\mathbf{k})N(b''\mathbf{k}+2\mathbf{q}, b'\mathbf{k}+\mathbf{q}, b\mathbf{k}, \omega, \omega),\end{aligned} \tag{3.11}$$

where

$$M(b'\mathbf{k}',b\mathbf{k},\omega) = -\left[\frac{f_0(E_{b'\mathbf{k}'})-f_0(E_{b\mathbf{k}})}{(E_{b'\mathbf{k}'}-E_{b\mathbf{k}}-\hbar\omega-i\epsilon)}\right] \tag{3.12}$$

and

$$N(b''\mathbf{k}'',b'\mathbf{k}',b\mathbf{k},\omega,\omega) = \left[\frac{f_0(E_{b''\mathbf{k}''})-f_0(E_{b'\mathbf{k}'})}{(E_{b''\mathbf{k}''}-E_{b'\mathbf{k}'}-\hbar\omega-i\epsilon)} - \frac{f_0(E_{b'\mathbf{k}'})-f_0(E_{b\mathbf{k}})}{(E_{b'\mathbf{k}'}-E_{b\mathbf{k}}-\hbar\omega-i\epsilon)}\right]\frac{1}{(E_{b''\mathbf{k}''}-E_{b\mathbf{k}}-2\hbar\omega-2i\epsilon)}. \tag{3.13}$$

While deriving above expressions for the current densities we have used the fact that the Fourier transform of the functions of the form $[\Psi_{b\mathbf{k}}^{*(0)}\mathbf{p}\Psi_{b'\mathbf{k}'}^{(0)}]$ may be obtained from the relation

$$[\Psi_{b\mathbf{k}}^{*(0)}\mathbf{p}\Psi_{b'\mathbf{k}'}^{(0)}] = (b\mathbf{k}|\mathbf{p}+\hbar\mathbf{k}'|b'\mathbf{k}')e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{x}}.$$

At this point let us write down the assumed phase conventions for $u_{b\mathbf{k}}(\mathbf{x})$, with $E_{b\mathbf{k}}=E_{b-\mathbf{k}}$, and some other useful identities:

$$u_{b\mathbf{k}}(\mathbf{x}) = u_{b-\mathbf{k}}^*(\mathbf{x}), \tag{3.14}$$

$$u_{b\mathbf{k}}(\mathbf{x}) = u_{b-\mathbf{k}}(-\mathbf{x}), \tag{3.15}$$

$$(b'\mathbf{k}|\mathbf{p}|b\mathbf{k}) = -(b'-\mathbf{k}|\mathbf{p}|b-\mathbf{k}), \tag{3.16}$$

$$(b'\mathbf{k}|\mathbf{p}|b\mathbf{k}) = \frac{-m}{\hbar}(E_{b'\mathbf{k}}-E_{b\mathbf{k}}) \times\left(b'\mathbf{k}\left|\frac{\partial}{\partial\mathbf{k}}\right|b\mathbf{k}\right), \quad b\neq b' \tag{3.17}$$

$$(b\mathbf{k}|\mathbf{p}+\hbar\mathbf{k}|b\mathbf{k}) = \frac{m}{\hbar}\frac{\partial}{\partial\mathbf{k}}E_{b\mathbf{k}}, \tag{3.18}$$

$$\mathbf{q}\cdot\left(b\mathbf{k}\left|\mathbf{p}+\hbar\mathbf{k}+\frac{\hbar\mathbf{q}}{2}\right|b'\mathbf{k}+\mathbf{q}\right) = (m/\hbar)(E_{b'\mathbf{k}+\mathbf{q}}-E_{b\mathbf{k}})(b\mathbf{k}|b'\mathbf{k}+\mathbf{q}), \tag{3.19}$$

$$\frac{1}{\hbar\mathbf{q}^2}\sum_{\mathbf{k}bb'} \mathbf{q}\cdot(b\mathbf{k}|\mathbf{p}+\hbar\mathbf{k}+\tfrac{1}{2}\hbar\mathbf{q}|b'\mathbf{k}+\mathbf{q}) \times(b'\mathbf{k}+\mathbf{q}|b\mathbf{k})[f_0(E_{b\mathbf{k}})-f_0(E_{b'\mathbf{k}+\mathbf{q}})] = n, \tag{3.20}$$

[13] Couplings of the wave vector $\mathbf{q}$ to wave vectors $\mathbf{q}+\mathbf{G}$, where $\mathbf{G}$ is a reciprocal lattice vector, which give rise to local field corrections, have been neglected.

$$\sum_{\mathbf{k}bb'} (b\mathbf{k}|b'\mathbf{k}+\mathbf{q})(b'\mathbf{k}+\mathbf{q}|b\mathbf{k}) \times[f_0(E_{b\mathbf{k}})-f_0(E_{b'\mathbf{k}+\mathbf{q}})]=0, \quad (3.21)$$

and

$$\frac{1}{m}\sum_{\mathbf{k}bb'} \mathbf{q}\cdot(b\mathbf{k}|\mathbf{p}+\hbar\mathbf{k}+\tfrac{1}{2}\hbar\mathbf{q}|b'\mathbf{k}+\mathbf{q}) \times(b'\mathbf{k}+\mathbf{q}|\mathbf{p}+\hbar\mathbf{k}+\tfrac{1}{2}\hbar\mathbf{q}|b\mathbf{k})M(b'\mathbf{k}+\mathbf{q},b\mathbf{k},\omega) =n\mathbf{q}+\omega\sum_{\mathbf{k}bb'}(b\mathbf{k}|b'\mathbf{k}+\mathbf{q})(b'\mathbf{k}+\mathbf{q}|\mathbf{p}+\hbar\mathbf{k}+\tfrac{1}{2}\hbar\mathbf{q}|b\mathbf{k}) \times M(b'\mathbf{k}+\mathbf{q},b\mathbf{k},\omega). \quad (3.22)$$

Relations given by Eqs. (3.16)–(3.18) may be derived directly by using the $\mathbf{k}\cdot\mathbf{p}$ Schrödinger equation and the phase conventions for the periodic part $u_{b\mathbf{k}}$ of the Bloch functions. Explicit proofs for other relations may be found in an excellent article on the quantum theory of dielectric constant by Adler.[14]

A. Linear Dielectric Constant $\boldsymbol{\varepsilon}(\omega)$

By using the definition of the linear dielectric tensor $\boldsymbol{\varepsilon}(\mathbf{q},\omega)$,

$$[\boldsymbol{\varepsilon}(\mathbf{q},\omega)-1]\cdot\mathbf{E}(\mathbf{q},\omega)=4\pi\mathbf{P}(\mathbf{q},\omega), \quad (3.23)$$

and noting that

$$\mathbf{E}(\mathbf{q},\omega)=(i\omega/c)\mathbf{a}_1, \quad (3.24)$$

$$\mathbf{P}(\mathbf{q},\omega)=(-1/i\omega)\mathbf{j}_1(\mathbf{q}), \quad (3.25)$$

from Eq. (3.10) we obtain

$$\boldsymbol{\varepsilon}(\mathbf{q},\omega)=1-\frac{4\pi ne^2}{m\omega^2}+\frac{4\pi e^2}{m^2\omega^2}\sum_{\mathbf{k}bb'}(b\mathbf{k}|\mathbf{p}+\hbar\mathbf{k}+\tfrac{1}{2}\hbar\mathbf{q}|b'\mathbf{k}+\mathbf{q}) \times(b'\mathbf{k}+\mathbf{q}|\mathbf{p}+\hbar\mathbf{k}+\tfrac{1}{2}\hbar\mathbf{q}|b\mathbf{k})M(b'\mathbf{k}+\mathbf{q},b\mathbf{k},\omega). \quad (3.26)$$

In the long-wavelength limit ($\mathbf{q}\rightarrow 0$), this leads to

$$\boldsymbol{\varepsilon}(\omega)=1-\frac{4\pi ne^2}{m\omega^2}-\frac{4\pi e^2}{m^2\omega^2} \times\sum_{\mathbf{k}bb'}\frac{(b\mathbf{k}|\mathbf{p}|b'\mathbf{k})(b'\mathbf{k}|\mathbf{p}|b\mathbf{k})[f_0(E_{b'\mathbf{k}})-f_0(E_{b\mathbf{k}})]}{(E_{b'\mathbf{k}}-E_{b\mathbf{k}}-\hbar\omega-i\epsilon)}, \quad (3.27)$$

which is isotropic for a crystal of cubic symmetry.[14] By defining[15]

$$\left(\frac{1}{m^*}\right)_{b\mathbf{k},b'\mathbf{k}}=-\frac{2}{3}\frac{(b\mathbf{k}|\mathbf{p}|b'\mathbf{k})\cdot(b'\mathbf{k}|\mathbf{p}|b\mathbf{k})}{m^2(E_{b'\mathbf{k}}-E_{b\mathbf{k}})}, \quad (3.28)$$

$$\left(\frac{1}{m^*}\right)_{b\mathbf{k}}=\frac{1}{3\hbar^2}\nabla_{\mathbf{k}}^2E_{b\mathbf{k}}=\frac{1}{m}+\sum_{b'}\left(\frac{1}{m^*}\right)_{b\mathbf{k},b'\mathbf{k}}, \quad (3.29)$$

and

$$\frac{1}{m_b^*}=\frac{1}{n_b}\sum_{\mathbf{k}}\left(\frac{1}{m^*}\right)_{b\mathbf{k}}\rightarrow 0, \quad (3.30)$$

for a filled or an empty band, one may rewrite the real and imaginary parts of $\epsilon(\omega)$ in terms of the interband reciprocal mass tensor $(1/m^*)_{b\mathbf{k},b'\mathbf{k}}$ and the average effective mass m_c^* for the conduction electrons. This leads to familiar expressions given by many authors.[16]

B. Bilinear Volume Current Density

For $\mathbf{q}=0$, it can be shown by using Eqs. (3.14)–(3.16) and by changing dummy symbols inside the summation signs in Eq. (3.11) that $\mathbf{j}^{(\mathrm{NL})}(2\mathbf{q})$ identically vanishes. This, of course, is the reflection of the fact that in the electric dipole approximation there is no bilinear volume current.

In general, by using Eqs. (3.26) and (3.22), the first term of $\mathbf{j}_2^{(\mathrm{NL})}(2\mathbf{q})$ given by Eqs. (3.11) and (3.12) may be written as

$$\frac{e\omega}{2\pi mc^2}\mathbf{a}_1\cdot\mathbf{a}_1[\boldsymbol{\varepsilon}(2\mathbf{q},2\omega)-1]\cdot\mathbf{q}\underset{q\rightarrow 0}{\longrightarrow}\frac{e\omega}{2\pi mc^2}\mathbf{a}_1\cdot\mathbf{a}_1\mathbf{q}[\epsilon(2\omega)-1], \quad (3.31)$$

where $\epsilon(2\omega)$ is obtained from Eq. (3.27). The second term of Eq. (3.11) may likewise be written by using Eqs. (3.26) and (3.22) as

$$\frac{e\omega}{4\pi mc^2}\mathbf{a}_1\mathbf{q}\cdot[\boldsymbol{\varepsilon}(\mathbf{q},\omega)-1]\cdot\mathbf{a}_1\underset{q\rightarrow 0}{\longrightarrow}\frac{e\omega}{4\pi mc^2}\mathbf{a}_1\mathbf{q}\cdot\mathbf{a}_1[\epsilon(\omega)-1], \longrightarrow 0,\quad\text{for transverse } \mathbf{a}_1. \quad (3.32)$$

Thus we see that the first two terms of the nonlinear volume current density can be completely specified in terms of the linear dielectric constant alone. The third term in Eq. (3.11) involving $N(b''\mathbf{k}+2\mathbf{q}, b'\mathbf{k}+\mathbf{q}, b\mathbf{k}, \omega, \omega)$ in general cannot be simplified further. However, in the limit $\mathbf{q}\rightarrow 0$, for isotropic case, it is also of the form $\mathbf{a}_1\cdot\mathbf{a}_1\mathbf{q}$. In this limit, with $\mathbf{a}_1\cdot\mathbf{q}=0$, we then obtain

$$\mathbf{j}_2^{(\mathrm{NL})}(2\mathbf{q})=\frac{e\omega}{2\pi mc^2}\mathbf{a}_1\cdot\mathbf{a}_1\mathbf{q}[\epsilon(2\omega)-1]-\frac{e^3n}{m^2c^2\omega}\mathbf{a}_1\cdot\mathbf{a}_1\mathbf{q}\mathfrak{B}(\omega), \quad (3.33)$$

[14] S. L. Adler, Phys. Rev. **126**, 413 (1962).
[15] M. H. Cohen, Phil. Mag. **3**, 762 (1958); H. Ehrenreich and H. R. Phillip, Phys. Rev. **128**, 1622 (1962).
[16] See, for example, references in Ref. 15.

where

$$\mathfrak{B}(\omega)=\frac{\omega}{2nm}\left[\frac{\partial^2}{\partial \mathbf{q}^2}\mathfrak{B}(\mathbf{q},\omega)\right]_{\mathbf{q}=0} \tag{3.34}$$

and where after some simplifications one may write

$$\mathfrak{B}(\mathbf{q},\omega)=\frac{1}{3}\sum_{\mathbf{k}bb'b''}\mathbf{q}\cdot(b\mathbf{k}|\mathbf{p}+\hbar\mathbf{k}|b''\mathbf{k}+2\mathbf{q})(b''\mathbf{k}+2\mathbf{q}|\mathbf{p}+\hbar\mathbf{k}|b'\mathbf{k}+\mathbf{q})$$

$$\cdot\frac{(b'\mathbf{k}+\mathbf{q}|\mathbf{p}+\hbar\mathbf{k}|b\mathbf{k})}{(E_{b''\mathbf{k}+2\mathbf{q}}-E_{b\mathbf{k}}-2\hbar\omega-2i\epsilon)}\left[\frac{f_0(E_{b''\mathbf{k}+2\mathbf{q}})-f_0(E_{b'\mathbf{k}+\mathbf{q}})}{E_{b''\mathbf{k}+2\mathbf{q}}-E_{b'\mathbf{k}+\mathbf{q}}-\hbar\omega-i\epsilon}-\frac{f_0(E_{b'\mathbf{k}+\mathbf{q}})-f_0(E_{b\mathbf{k}})}{E_{b'\mathbf{k}+\mathbf{q}}-E_{b\mathbf{k}}-\hbar\omega-i\epsilon}\right]. \tag{3.35}$$

From Eqs. (1.2), (2.23), (3.24), and (3.33) and noting that $\nabla\cdot\mathbf{E}^{(\omega)}$ is zero inside the medium, we then find

$$\mathbf{j}^{(2\omega)V}(\mathrm{NL})=(\omega^2/c)\alpha\nabla(\mathbf{a}^{(\omega)}\cdot\mathbf{a}^{(\omega)})$$
$$=-2i\omega\alpha\mathbf{E}^{(\omega)}\times\mathbf{H}^{(\omega)} \tag{3.36}$$

with

$$\alpha=\frac{-ie}{4\pi mc\omega}[\epsilon(2\omega)-1]+\frac{ie^3n}{2m^2c\omega^3}\mathfrak{B}(\omega). \tag{3.37}$$

In order to evaluate $\mathfrak{B}(\omega)$, one has to expand the functions $u_{b,\mathbf{k}+\mathbf{q}}$, etc. in Eq. (3.35) in the form

$$u_{b\mathbf{k}+\mathbf{q}}=u_{b\mathbf{k}}+\mathbf{q}\cdot\frac{\partial}{\partial\mathbf{k}}u_{b\mathbf{k}}+\cdots \tag{3.38}$$

and use various identities given by Eqs. (3.14)–(3.22) to write it in a simpler form. However, we will not go into the details of this calculation here, except to point out that unless the band gaps Δ are equal to $\hbar\omega$, the term containing $\mathfrak{B}(\omega)$ in Eq. (3.37) may be neglected in comparison to the first term. In this case the interband contributions due to $\mathfrak{B}(\omega)$ are of higher orders in $(\hbar\omega/\Delta)$ for $\hbar\omega<\Delta$, and in $(\Delta/\hbar\omega)$ for $\Delta>\hbar\omega$, as compared to the interband contributions due to $\epsilon(2\omega)$. In this approximation one then obtains

$$\alpha\approx\frac{-ie}{4\pi mc\omega}[\epsilon(2\omega)-1], \tag{3.39}$$

which leads to Eq. (1.7) for the case when interband contributions in $\epsilon(2\omega)$ may be neglected, i.e., when $\epsilon(2\omega)=1-\omega_p^2/4\omega^2$. For bandgaps $\Delta_{bb'}$ and $\Delta_{b'b''}$ near to $\hbar\omega$, the expression for α given by Eq. (3.39) is not expected to be a good approximation.

IV. SURFACE CURRENT DENSITY

For calculating the surface current density, we will now have to include a potential $U(\mathbf{x})$ due to the surface barrier in the total potential $V(\mathbf{x})$. Unperturbed solutions $\Psi_n^{(0)}(\mathbf{x})$ of Eq. (2.4) in this case differ considerably from the solutions used in Sec. III of this paper for an infinite periodic lattice. Moreover, the exact variation of the surface potential $U(\mathbf{x})$ is quite complicated and it is very difficult to take care of this in any real calculation. Fortunately, for the case of linear reflection, except for the trivial variation of the density n of the electrons near the surface, only the component of the fundamental current normal to the surface[17] differs appreciably near the surface from the current in the bulk sample. This does not affect the solutions of Maxwell's equations for the fundamental fields away from the surface.

For the case of bilinear current density, let us examine the general expression given by Eq. (2.18). Let us first consider the second term of this equation. By comparing this with Eq. (2.16) for the linear charge density $\rho^{(\omega)}(\mathbf{x})$ and using Maxwell's equation

$$\nabla\cdot\mathbf{a}^{(\omega)}=(4\pi c/i\omega)\rho^{(\omega)}(\mathbf{x}), \tag{4.1}$$

the second term of Eq. (2.18) becomes

$$\frac{e\mathbf{a}^{(\omega)}}{mc}\rho^{(\omega)}(\mathbf{x})=\frac{ie\omega}{4\pi mc^2}\mathbf{a}^{(\omega)}\nabla\cdot\mathbf{a}^{(\omega)}$$
$$=\frac{-ie}{4\pi mc\omega}\mathbf{E}^{(\omega)}\nabla\cdot\mathbf{E}^{(\omega)}. \tag{4.2}$$

It should be pointed out here that the contribution of this term inside the volume goes to zero as obtained in Eq. (3.32). It was shown in I that for a Sommerfeld model for the metal this was the only term which contributed to the tangential components of the surface current. This trend may be correct even if one introduces the periodic part of the potential in our analysis. It will then mean that the tangential components of the first and third terms in $\mathbf{j}^{(2\omega)}(\mathrm{NL})$ do not differ near the surface from their values in the bulk sample. Therefore, if one does not care for the accuracy of the normal components of the surface current, one may write

$$\mathbf{j}^{(2\omega)s}(\mathrm{NL})\approx(-ie/4\pi m\omega)\mathbf{E}^{(\omega)}\nabla\cdot\mathbf{E}^{(\omega)}, \tag{4.3}$$

which leads to

$$\mathbf{P}^{(2\omega)s}(\mathrm{NL})=\beta\mathbf{E}^{(\omega)}\nabla\cdot\mathbf{E}^{(\omega)} \tag{4.4}$$

with

$$\beta=e/8\pi m\omega^2. \tag{4.5}$$

The equivalence of β obtained above and β_{pl} as given by Eq. (1.8), however, does not imply that there is no interband contribution to the surface current in this approximation. Since $\nabla\cdot\mathbf{E}^{(\omega)}$ is given by Eq. (1.5), $\mathbf{j}^{(2\omega)s}$

[17] L. I. Schiff and L. H. Thomas, Phys. Rev. 47, 860 (1935). See also I.

of Eq. (4.3) is given by

$$\mathbf{j}^{(2\omega)s}(\mathrm{NL})=-2i\omega\beta[1-\epsilon(\omega)]\mathbf{E}^{(\omega)}E_x^{(\omega)}\delta(x-0^+) \quad (4.6)$$

and the effect of interband contributions comes through the new value of $\epsilon(\omega)$. In the notations of Bloembergen, Chang, and Lee[18] the quantity β' defined as $\beta[1-\epsilon(\omega)]$, which really matters, is definitely different than β_{pl}'.

V. SOLUTIONS OF MAXWELL'S EQUATIONS

In this section we would find the fundamental and the second-harmonic fields for arbitrary values for the complex $\epsilon(\omega)$, $\alpha(\omega,\omega)$ and $\beta(\omega,\omega)$. This would allow us to obtain expressions for the linear as well as the bilinear reflectivity for the incident plane wave of frequency ω. Our problem is to solve Maxwell's equations

$$\nabla\times\nabla\times\mathbf{a}^{(\omega)}-(\omega^2/c^2)\mathbf{a}^{(\omega)}=(4\pi/c)\mathbf{j}^{(\omega)}, \quad (5.1)$$

$$\nabla\times\nabla\times\mathbf{a}^{(2\omega)}-(4\omega^2/c^2)\mathbf{a}^{(2\omega)}=(4\pi/c)[\mathbf{j}^{(2\omega)}(\mathrm{L})+\mathbf{j}^{(2\omega)}(\mathrm{NL})], \quad (5.2)$$

where

$$(4\pi/c)\mathbf{j}^{(\omega)}=(\omega^2/c^2)[\epsilon(\omega)-1]\mathbf{a}^{(\omega)}, \quad \text{for } x>0, \quad (5.3)$$

$$(4\pi/c)\mathbf{j}^{(2\omega)}(\mathrm{L})=(4\omega^2/c^2)[\epsilon(2\omega)-1]\mathbf{a}^{(2\omega)}, \quad \text{for } x>0, \quad (5.4)$$

$$(4\pi/c)\mathbf{j}^{(2\omega)}(\mathrm{NL})=(4\pi\omega^2/c^2)\alpha\nabla(\mathbf{a}^{(\omega)}\cdot\mathbf{a}^{(\omega)}), \quad \text{for } x>0, \quad (5.5)$$

$$\mathbf{j}^{(\omega)}=\mathbf{j}^{(2\omega)}(\mathrm{L})=\mathbf{j}^{(2\omega)}(\mathrm{NL})=0, \quad \text{for } x<0. \quad (5.6)$$

The boundary conditions to be imposed on the tangential components of $\mathbf{a}^{(\omega)}$ and $\mathbf{a}^{(2\omega)}$ at the interface of the metal ($x>0$) and the vacuum ($x<0$) are (i) $a_y^{(\omega)}$ and $a_z^{(\omega)}$ are continuous; (ii) $-\partial a_z^{(\omega)}/\partial x$ and $\partial a_y^{(\omega)}/\partial x-\partial a_x^{(\omega)}/\partial y$ are continuous; (iii) $a_y^{(2\omega)}$ and $a_z^{(2\omega)}$ are continuous;

$$\text{(iv)}\ -\left.\frac{\partial a_z^{(2\omega)}}{\partial x}\right|_{x=0^+}+\left.\frac{\partial a_z^{(2\omega)}}{\partial x}\right|_{x=0^-}=\frac{4\pi}{c}j_z^{(2\omega)s}(\mathrm{NL})=\frac{i8\pi\beta\omega^3}{c^3}[1-\epsilon(\omega)]a_z^{(\omega)}a_x^{(\omega)}|_{x=0^+}; \quad (5.7)$$

and (v)

$$\left[\frac{\partial a_y^{(2\omega)}}{\partial x}-\frac{\partial a_x^{(2\omega)}}{\partial y}\right]_{x=0^+}-\left[\frac{\partial a_y^{(2\omega)}}{\partial x}-\frac{\partial a_x^{(2\omega)}}{\partial y}\right]_{x=0^-}=\frac{-i8\pi\omega^3\beta[1-\epsilon(\omega)]}{c^3}a_y^{(\omega)}a_x^{(\omega)}|_{x=0^+}, \quad (5.8)$$

with the assumption that the incident wave is given by

$$\mathbf{A}_{\mathrm{inc}}=\mathbf{D}_1e^{i\mathbf{q}_0\cdot\mathbf{x}}e^{-i\omega t}+\text{complex conjugate}, \quad (5.9)$$

$$\mathbf{D}_1=(A_0\sin\theta\cos\phi, A_0\cos\theta\cos\phi, A_0\sin\phi), \quad (5.10)$$

$$\mathbf{q}_0=((\omega/c)\cos\theta, -(\omega/c)\sin\theta, 0). \quad (5.11)$$

As in I, we have assumed the metal to occupy the right half-space ($x>0$) and the light wave to be incident at an angle θ, with the angle of polarization ϕ with respect to the incident plane.

Solutions of these equations give

$$\mathbf{a}^{(\omega)}=\left[\mathbf{D}_1\exp\left(\frac{i\omega\cos\theta}{c}x\right)+\mathbf{G}_1\exp\left(\frac{-i\omega\cos\theta}{c}x\right)\right]\times\exp\left(\frac{-i\omega\sin\theta}{c}y\right), \quad \text{for } x<0, \quad (5.12)$$

$$\mathbf{a}^{(\omega)}=\mathbf{C}_1e^{-\gamma_1x}e^{i\delta_1x}\exp\left(-\frac{i\omega\sin\theta}{c}y\right), \quad \text{for } x>0, \quad (5.13)$$

$$\mathbf{a}^{(2\omega)}=\mathbf{G}_2\exp\left(\frac{-2i\omega\cos\theta}{c}x\right)\exp\left(\frac{-2i\omega\sin\theta}{c}y\right), \quad \text{for } x<0, \quad (5.14)$$

$$\mathbf{a}^{(2\omega)}=\mathbf{C}_2e^{-\gamma_2x}e^{i\delta_2x}\exp\left(-\frac{2i\omega\sin\theta}{c}y\right)-\frac{\pi\alpha\mathbf{C}_1\cdot\mathbf{C}_1}{\epsilon(2\omega)}\nabla\left[e^{-2\gamma_1x}e^{2i\delta_1x}\exp\left(-\frac{2i\omega\sin\theta}{c}y\right)\right], \quad \text{for } x>0, \quad (5.15)$$

with

$$\frac{c\gamma_1}{\omega}=+\frac{1}{\sqrt{2}}\{[(\sin^2\theta-\epsilon'(\omega))^2+\epsilon''^2(\omega)]^{1/2}\pm|(\sin^2\theta-\epsilon'(\omega))|\}^{1/2}, \quad (5.16)$$

$$\frac{c\delta_1}{\omega}=+\frac{1}{\sqrt{2}}\{[(\sin^2\theta-\epsilon'(\omega))^2+\epsilon''^2(\omega)]^{1/2}\mp|(\sin^2\theta-\epsilon'(\omega))|\}^{1/2}, \quad (5.17)$$

$$\frac{c\gamma_2}{\omega}=+\frac{1}{\sqrt{2}}\{[(\sin^2\theta-\epsilon'(2\omega))^2+\epsilon''^2(2\omega)]^{1/2}\pm|(\sin^2\theta-\epsilon'(2\omega))|\}^{1/2}, \quad (5.18)$$

$$\frac{c\delta_2}{\omega}=+\frac{1}{\sqrt{2}}\{[(\sin^2\theta-\epsilon'(2\omega))^2+\epsilon''^2(2\omega)]^{1/2}\mp|(\sin^2\theta-\epsilon'(2\omega))|\}^{1/2}, \quad (5.19)$$

where upper signs are for $\sin^2\theta-\epsilon'(\omega)>0$, or $\sin^2\theta-\epsilon''(2\omega)>0$, and lower signs are for $\sin^2\theta-\epsilon'(\omega)<0$ and $\sin^2\theta-\epsilon''(2\omega)<0$, and where

$$\epsilon(\omega)=\epsilon'(\omega)+i\epsilon''(\omega), \quad (5.20)$$

$$C_{1x}=\frac{\omega\sin\theta}{c(i\gamma_1+\delta_1)}C_{1y}, \quad (5.21)$$

[18] See Eqs. (29) and (26) of Ref. 7.

$$C_{1y}=\frac{2A_0c(i\gamma_1+\delta_1)\cos\theta\cos\phi}{\omega\epsilon(\omega)\cos\theta+c(i\gamma_1+\delta_1)}, \quad (5.22)$$

$$C_{1z}=\frac{2A_0\omega\cos\theta\sin\phi}{\omega\cos\theta+c(i\gamma_1+\delta_1)}, \quad (5.23)$$

$$G_{1x}=-G_{1y}\tan\theta, \quad (5.24)$$

$$G_{1y}=C_{1y}-A_0\cos\theta\cos\phi, \quad (5.25)$$

$$G_{1z}=C_{1z}-A_0\sin\phi, \quad (5.26)$$

$$C_{2x}=\frac{2\omega\sin\theta}{c(i\gamma_2+\delta_2)}C_{2y}, \quad (5.27)$$

$$C_{2y}=G_{2y}-\frac{2\pi i\omega\sin\theta\alpha\mathbf{C}_1\cdot\mathbf{C}_1}{c\epsilon(2\omega)}, \quad (5.28)$$

$$C_{2z}=G_{2z}, \quad (5.29)$$

$$G_{2x}=-G_{2y}\tan\theta, \quad (5.30)$$

$$G_{2y}=\frac{-4\pi\omega^2}{c}\cos\theta \times\left\{\frac{[1-\epsilon(\omega)]\beta(i\gamma_2+\delta_2)C_{1y}C_{1x}-i\sin\theta\alpha\mathbf{C}_1\cdot\mathbf{C}_1}{[2\omega\epsilon(2\omega)\cos\theta+c(i\gamma_2+\delta_2)]}\right\}, \quad (5.31)$$

$$G_{2z}=-\frac{8\pi\omega^3}{c^2}\left\{\frac{[1-\epsilon(\omega)]\beta C_{1z}C_{1x}}{[2\omega\cos\theta+c(i\gamma_2+\delta_2)]}\right\}. \quad (5.32)$$

By defining the reflection coefficient as the average energy flux reflected from the surface to the incident flux, for the linear reflection we obtain

$$R^{(\omega)}=\mathbf{G}_1{}^*\cdot\mathbf{G}_1/\mathbf{D}_1{}^*\cdot\mathbf{D}_1 =\cos^2\phi b(\theta,\omega)+\sin^2\phi d(\theta,\omega), \quad (5.33)$$

where

$$b(\theta,\omega)=\left|\frac{[\omega\epsilon(\omega)\cos\theta-c(i\gamma_1+\delta_1)]}{[\omega\epsilon(\omega)\cos\theta+c(i\gamma_1+\delta_1)]}\right|^2 \quad (5.34)$$

and

$$d(\theta,\omega)=\left|\frac{[\omega\cos\theta-c(i\gamma_1+\delta_1)]}{[\omega\cos\theta+c(i\gamma_1+\delta_1)]}\right|^2. \quad (5.35)$$

Similarly, the bilinear reflection coefficient is given by

$$R^{(2\omega)}=4\mathbf{G}_2{}^*\cdot\mathbf{G}_2/\mathbf{D}_1{}^*\cdot\mathbf{D}_1 =\left(\frac{e|E_{\mathrm{inc}}|}{mc\omega_p}\right)^2[\cos^4\phi\mathfrak{F}(\theta,\omega)+\cos^2\phi\sin^2\phi g(\theta,\omega)+\sin^4\phi h(\theta,\omega)], \quad (5.36)$$

where

$$\mathfrak{F}(\theta,\omega)=\cos^4\theta\sin^2\theta\frac{\omega_p{}^6}{\omega^6}\left|\frac{[4(\beta'/\beta_{pl}')(i\gamma_2'+\delta_2')(i\gamma_1'+\delta_1')+(\alpha/\alpha_{pl})\epsilon(\omega)]}{[\epsilon(2\omega)\cos\theta+i\gamma_2'+\delta_2'][\epsilon(\omega)\cos\theta+i\gamma_1'+\delta_1']^2}\right|^2, \quad (5.37)$$

$$g(\theta,\omega)=\cos^4\theta\sin^2\theta\frac{\omega_p{}^6}{\omega^6}\left\{\frac{|4\beta'/\beta_{pl}'|^2}{|\cos\theta+i\gamma_2'+\delta_2'|^2|\epsilon(\omega)\cos\theta+i\gamma_1'+\delta_1'|^2|\cos\theta+i\gamma_1'+\delta_1'|^2} +\frac{2}{|\epsilon(2\omega)\cos\theta+i\gamma_2'+\delta_2'|^2}\mathrm{Re}\left[\frac{(\alpha/\alpha_{pl})^*(4(\beta'/\beta_{pl}')(i\gamma_2'+\delta_2')(i\gamma_1'+\delta_1')+(\alpha/\alpha_{pl})\epsilon(\omega))}{(\epsilon(\omega)\cos\theta+i\gamma_1'+\delta_1')^2(\cos\theta-i\gamma_1'+\delta_1')^2}\right]\right\}, \quad (5.38)$$

and

$$h(\theta,\omega)=\cos^4\theta\sin^2\theta\frac{\omega_p{}^6}{\omega^6}\left|\frac{(\alpha/\alpha_{pl})}{[\epsilon(2\omega)\cos\theta+i\gamma_2'+\delta_2'][\cos\theta+i\gamma_1'+\delta_1']^2}\right|^2, \quad (5.39)$$

with

$$\beta'=[1-\epsilon(\omega)]\beta, \quad (5.40)$$

$$(i\gamma_1'+\delta_1')=(c/\omega)(i\gamma_1+\delta_1), \quad (5.41)$$

$$(i\gamma_2'+\delta_2')=(c/2\omega)(i\gamma_2+\delta_2). \quad (5.42)$$

In the limit where $\epsilon(\omega)=1-\omega_p{}^2/\omega^2$, $\alpha/\alpha_{pl}=1$ and $\beta/\beta_{pl}=1$, these expressions lead to the results derived[4] for the Sommerfeld model for metals.

VI. DISCUSSIONS

From the preceding calculations it is clear that the effect of interband transitions of the core electrons on bilinear polarization in the absorption regions for frequencies ω and 2ω is of the same order as that due to intraband transitions of the conduction electrons. This confirms the earlier predictions of Bloembergen and Shen.[5,7] We found further that, in the long-wavelength limit, the general expression for either α or β in the bilinear polarization contains a background part which is known completely in terms of the linear dielectric constant alone and a residual part which involves at least 3 bands. For frequencies ω and 2ω not very near the absorption edges for the interband transitions, the residual parts may always be neglected. However, for frequencies near the absorption edges it is better, at this stage, to determine the residual parts experimentally by comparing the experimental values with the phenomenological expressions obtained for the reflected intensities in Sec. V. Since there is no bilinear surface current for the incident light wave polarized perpendicular to the plane of incidence ($\phi=90°$), the experimental value for α may be obtained directly by doing experiments with $\phi=90°$. One could then find β by measuring the intensity and polarization of the second-harmonic reflected wave for $\phi=0°$.

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Single-Phonon Energy Transfer between Molecular Beams and Solid Surfaces*

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The quantum-mechanical lattice theory in thermal-accommodation-coefficient theory is approached from the same point of view as the lattice theory of neutron scattering and Mössbauer effects. Treating the surface atoms from a displacement-field-theoretic point of view, rather than from the customary single-particle point of view, is more consistent with other solid-state theories. Virtual-phonon processes occurring in the field formulation give rise to a nontrivial modification in existing single-phonon accommodation-coefficient theories. This modification takes the form of a pseudo-Debye-Waller factor. When the existing theoretical accommodation coefficients are modified by the pseudo-Debye-Waller factor, it is found that the resulting accommodation coefficient, obtained herein, displays trends similar to experimental data for helium accommodation on tungsten.

I. INTRODUCTION

SEVERAL quantum-mechanical theories for describing the energy-transfer process in a collision of an inert-gas atom with a solid surface have been presented.[1–5] In most of these treatments, explicit results are obtained for a collision process in which a single phonon is created or destroyed in the solid. The objective in these theories is an expression for the thermal accommodation coefficient (denoted here as AC). The philosophy of the accommodation coefficient has been discussed in quantum-mechanical papers[1–5] and in the series of papers by Goodman.[6]

The author has been impressed by the possible formal similarity in mathematical structure between single-phonon AC theory and the lattice-dynamic aspects of neutron-scattering theory[7] and Mössbauer effect theory.[8] In these three cases an external probe, the inert-gas atom, the neutron, or the recoiling nucleus, interacts with the phonon field of the lattice, usually through assumed single-phonon transitions. Calculations are usually done through time-dependent perturbation theory or Born approximations. The relevant quantities calculated, AC's, transition probabilities, or cross sections, are expressed in terms of the square of a matrix element of a lattice displacement field operator taken between initial and final states of the lattice differing by some stated number of phonons multiplied by a matrix element describing the change of state of the external probe. From the point of view of the lattice, the neutron and Mössbauer theories are identical. In both cases, lattice effects are represented principally through a Debye-Waller factor. It seems reasonable to

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