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# Second-Harmonic Radiation from Metal Surfaces*†

Joseph Rudnick and E. A. Stern‡
*Physics Department, University of Washington, Seattle, Washington* 98105
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A calculation is performed of the second-harmonic radiation generated by the reflection of incident radiation from a metal surface in a model that considers only plasma effects and neglects periodic lattice structure in the metallic bulk and any form of surface roughness. The radiation is due to three kinds of currents: one localized to within a few angstroms of the surface and parallel to it, another also localized at the surface but normal to it, and a bulk current in the skin-depth region of the incident light, a region several hundred angstroms thick. Previous expressions for the normal surface current are found to be incorrect, and a new expression is derived. The second-harmonic radiation due to the surface currents is sensitive to surface conditions, while the contribution of the bulk current is only weakly sensitive to them. Theoretical estimates suggest that changes in the radiation intensity with variation in surface condition are caused primarily by changes in the parallel surface currents due to variations in surface scattering. In the course of this investigation general relationships and explicit forms for the second-order response of an isotropic electron gas are given.

## I. INTRODUCTION

A noteworthy feature of metallic response to optical stimulation is its extreme linearity. Only with the intense fields available from laser sources is there detectable generation in a metal of second and higher harmonics of the incident beam.[1–4] The theory of such generation in the metallic *bulk* is by now well understood.[5–11] Second-harmonic (SH) generation by reflection of the incident beam from a metal surface, however, has important contributions from currents stimulated in the immediate vicinity of the surface, the region to which those currents are confined being the order of angstroms thick. The theory of bulk SH generation, being essentially a long-wavelength theory, is necessarily approximate when applied to the generation of such strongly localized currents. This paper is intended as a further step towards a theory of SH generation in a metal that is correct at the metal surface as well as in the bulk.

Before going in more detail into a calculation of SH generation at a metal surface, it is perhaps useful to review in a general way the currents contributing to SH generation in a metal subject to externally incident electromagnetic radiation. The metal is assumed to possess inversion symmetry in the bulk. The SH response of the metal consists of two currents—one extending into the bulk and one confined to the immediate region of the surface. The bulk current is proportional to $\vec{E}\times\vec{B}$, where $\vec{E}$ and $\vec{B}$ are the first-harmonic electric and magnetic fields in the metal. It is due to the action of the magnetic field, through the Lorentz force, on the current produced to first order by the electric field. The bulk current is longitudinal inside the metal and therefore does not radiate except if a boundary is present. As previous investigators[7] have shown, the SH radiation has contributions from the longitudinal bulk current within a skin depth at the SH frequency—typically several hundred angstroms thick. If, as is generally believed, the transition region in a flat metal surface between its interior and exterior is only a few angstroms thick, this bulk contribution to the SH radiation should be insensitive to the condition of the metal surface, neglecting the effects of extreme surface roughness or thick impurity layers.

As will be discussed in more detail in Sec. IV, at typical frequencies the SH surface currents are confined to the surface region of a few angstroms. There are in cubic metals two independent surface currents, one parallel to the surface and the other normal to it. The magnitude of the normal surface current and the radiation it generates are both sensitive to details of the shielding in the surface region. The magnitude of the parallel surface current is expected to be quite sensitive to surface scattering as discussed in Sec. V. The mechanisms that occur at the surface to produce the surface currents are twofold. One is the rapid variation of the normal component of the electric field at the surface, and the other is the breaking of inversion symmetry at the surface of a cubic metal.

Previous calculations of the magnitude of the SH surface currents[9,10] employed expressions which neglected the breaking of inversion symmetry and were valid in the long-wavelength local limit where the electromagnetic fields do not vary appreciably over the distance traveled by an electron during one cycle. Although the right magnitude of the radiation is obtained, in the surface region these approximations are not valid, and one requires a better calculation. Some previous calculations of the plasma contribution did not correctly apply self-consistency between the electromagnetic fields and the charges in the metals as discussed in some detail in Sec. IV. Including these effects alters the amount of radiation produced by the normal surface currents.

An outline of the paper is as follows. In Sec. II we qualitatively discuss the mechanisms producing the SH source terms. In Sec. III the linear electromagnetic fields are discussed in the context of the applicability of the local, or dipole, or long-wavelength approximation. A calculation of the SH source currents including nonlocal effects is given in Sec. IV for a model of a bounded electron gas with inversion symmetry. The gas is replaced by an infinite medium with an appropriate current sheet where the surface was. The effect of the inversion symmetry breaking and scattering by a boundary is added in Sec. V. In Sec. VI the calculation of the radiation generated by the SH sources is presented, while Sec. VII has a comparison of the theory with experiment. Section VIII consists of a summary. Appendix A gives the details of the calculation of the linear fields and the radiation by the SH sources including nonlocal effects. Appendix B presents the calculation of the second-order nonlinear response of the interior of an electron gas for all wavelengths of the exciting fields. Appendix C presents some general results concerning the second-order response of an electron gas.

## II. MECHANISM OF SH SURFACE SOURCE TERMS

Before becoming involved in the mathematics, we describe in a qualitative fashion the mechanisms that produce the SH surface currents. Production of SH currents in general requires that the medium respond nonlinearly to the driving fields. The discussion is restricted to currents produced to second order in the driving fields, which is an excellent approximation for SH production in metals.

We start with the standard model of this effect which neglects the presence of a boundary, and consider the interior of a medium with inversion symmetry. If the medium is perturbed by a uniform electric field $E$, the requirement of an $E^2$ contribution to the current implies that

$$\vec{j}=\sigma\vec{E}+\overleftrightarrow{\chi}:\vec{E}\vec{E}\ . \tag{1}$$

In a metal a current flows even at $\omega=0$, while an insulator current flows only for $\omega\neq 0$. If the direction of $\vec{E}$ is reversed, inversion symmetry requires that the current be equal in magnitude and flow in the opposite direction. $\overleftrightarrow{\chi}$ must therefore equal zero.

Now if we introduce a gradient to the electric field, the situation is changed. Nonlocal effects can be felt. The current at a given point depends in general on an integral of the contributions in a region surrounding the point. The current at a given point then depends on both the value of the electric field and its variation. Consider the field variation about $Z=0$ shown in Fig. 1, curve A, and assume that the region over which the integration should occur is that where the gradient is nonzero. Also assume that, because of nonlinearity, the contribution from the left-hand side of the origin is greater than the average by an amount more than the contribution from the right-hand side is less. Thus the current to the right is greater than that given by a uniform field equal to the value at the origin. Performing an inversion operation is equivalent to inverting curve A about the origin to obtain curve B. By symmetry, the same nonlinearity combined with the nonlocal effect produces now a current to the left which is equal in magnitude to that produced by curve A, again larger than the value given by a uniform field equal to the value at the origin. Thus we can satisfy the requirement of inversion symmetry of the medium, since the current at $Z=0$ reverses sign under inversion, and still have a nonlinear effect. It is the large gradient of the normal component of the $E$ field at a surface which generates by this mechanism the strongly localized SH surface currents.

If we now introduce a surface between the medium and vacuum, we destroy the inversion symmetry in the vicinity of the boundary. This introduces a new mechanism for nonlinear response. Consider a uniform electric field, applied to the medium at the boundary as in Fig. 2. We permit external charges and currents to be present in order to maintain a uniform electric field at the boundary. Right at the surface electrons are not as free to flow into the boundary as they are away from it. Thus we expect that the current in the surface

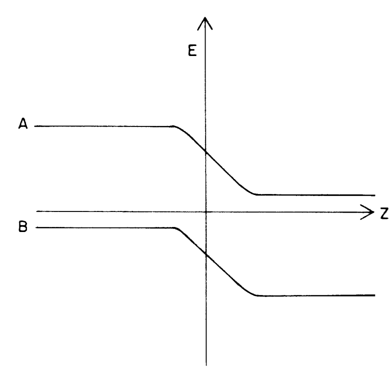


FIG. 1. Illustrating the effect of a spatial inversion operator on an electric field with a gradient. Curve A is the original field and B is the inverted one.

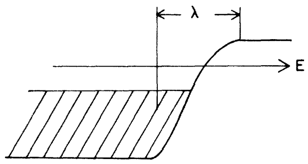


FIG. 2. Schematic of a metallic surface illustrating the parameters that produce the nonlinearity leading to a SH surface current.

region will be greater in magnitude when the electrons flow into the medium than when they reverse their flow. The inversion symmetry breaking of the boundary introduces this mechanism for SH production, which has been neglected in previous calculations. We show in Sec. V that this neglected mechanism is an important contributor to the normal surface current.

## III. LINEAR FIELDS

The SH radiation is only a very small fraction of the linear radiation in practical cases,[1-4] so that it is possible to treat the SH sources by perturbation theory. As is usually done,[5-11] we first solve for the linear fields neglecting the SH currents and then use those linear fields as the driving fields that create by nonlinearity the SH currents. In the standard solutions for the linear fields produced when an electromagnetic (EM) wave impinges on a surface it is assumed that the boundary is infinitely sharp and that a local approximation can be made to describe the response of the medium to the fields. The local, or dipole, approximation—that the polarization of the medium or current at a given point is dependent only on the value of the EM fields at that point—is valid as long as the distance an electron travels during the time $1/\omega$ is small compared to the distance over which the EM fields vary appreciably. For nonmagnetic media, $\vec{B}$, $\vec{H}$, and the tangential component of $\vec{E}$ are all continuous across the boundary, and the spatial variation of these fields is slow enough at optical frequencies to permit the use of the local approximation. Thus their values are accurately given by the standard results. However, the normal component of $\vec{E}$ is discontinuous across the boundary in the standard solution. It is clear that near the boundary the local approximation for the normal component of $\vec{E}$ is not valid and a better calculation, including nonlocal effects, must be employed to determine the actual variation of the normal component of $\vec{E}$ near the boundary. This is done in Appendix A. As one expects, the calculation verifies that $E$ normal makes its transition over a region of the order of the shielding length in the metal.

In order to calculate $E$ normal in the spirit of previous calculations, which neglect the breaking of inversion symmetry at the surface, the bounded medium is replaced in Appendix A by an infinite medium with a current sheet at the location of the boundary. The fields in the medium have reflection symmetry about the current sheet to simulate specular reflection at the surface. Such a model, which has been used rather extensively,[12] neglects correlations in the wave functions between the incoming and reflected electron states and thereby does not destroy inversion symmetry of the unperturbed electron states at the boundary. Nonlocal effects are included by using a wave-number-dependent dielectric function to describe the linear response of the medium to the electromagnetic fields. The calculation verifies explicitly that only the variation in $E$ normal within a few angstroms of the surface is inadequately described by the standard local theory.

## IV. SH SURFACE CURRENTS

Previous calculations yielding explicit expressions for the second-order response of metallic electrons used either the Boltzmann equation, classical hydrodynamics, or the long-wavelength limit of perturbation theory. All of those approximations possess the common requirement that the variation in the EM fields take place over a distance large compared to the Fermi wavelength of the metal. In the case of $E$ normal in the immediate vicinity of the metal surface that requirement is clearly not satisifed and classical or semiclassical calculations of the currents in the immediate surface region must be looked at with suspicion. *A priori* one expects a quantum-mechanical calculation to be necessary. For the parallel surface currents it turns out that all of the above approximations are adequate, but the proof is a quantum-mechanical one. For the normal surface current a full quantum-mechanical calculation is required.

In Appendix B a quantum-mechanical calculation of the second-order response of an isotropic electron gas is given. The basic equations have previously been presented[6] but in Appendix B the integrals are explicitly performed and expressed in terms of well-known functions.

The local approximation becomes valid when $qv_F \ll \omega$, where $v_F$ is the Fermi velocity of the metallic electrons and $q$ is the inverse of the characteristic length of variation of the EM field. As in Eq. (B4), and in agreement with Ref. 6, the second-order current becomes in this limit

$$\vec{j}_2(\vec{r}) = -\frac{n e_0^3}{i m^2 \omega^3}\left[\tfrac{1}{4}\vec{\nabla}(\vec{E}\cdot\vec{E}) + \vec{E}(\vec{\nabla}\cdot\vec{E})\right], \qquad (2)$$

where $n_0$ is the number of electron per unit volume and $e$ and $m$ are the electronic mass and charge, respectively. We note that only the first term in the brackets contributes in the bulk of the medium, while both terms contribute to the surface currents. A comparison with Eq. (14) of Ref. 10 indicates an interesting difference with Eq. (2) above. The coefficients of the last term in (2) is $(\omega_p/\omega)^2$ times the corresponding term in Ref. 10, where $\omega_p^2 = 4\pi n_0 e^2/m$. In order to understand the source of this discrepancy it is well to obtain a qualitative insight into the meaning of the last term in (2).

In particular, we will consider only that part of (2) which produces a current parallel to the surface:

$$\vec{j}_{2\parallel} = \frac{i\omega_p^2 e}{4\pi\omega^3}\,\vec{E}_\parallel \frac{dE_z}{dz}\ , \tag{3}$$

where $\vec{E}_\parallel$ and $\vec{j}_{2\parallel}$ are the incident electric field component and SH current component, respectively, parallel to the surface. The normal to the surface is chosen to be the positive $z$ direction so that the medium fills the half-space $z<0$. Now the SH current is given in the classical hydrodynamical model by

$$\vec{j}_2 = n_0\vec{v}_2 + n_1\vec{v}_1\ , \tag{4}$$

where $n_0$ is the electron density with no EM fields present, $n_1$ is the change in the electron density linear in the fields, $\vec{v}_1$ is the velocity change of the electrons linear in the fields, and $\vec{v}_2$ is the velocity change of the electrons second order in the fields. A result of the hydrodynamical calculations is that the first term on the right-hand side of (4) does not contribute to $\vec{j}_{2\parallel}$ of Eq. (3). $\vec{j}_{2\parallel}$ is therefore dependent entirely on linear effects.

We note that $n_1$ can be calculated from the long-wavelength relationship

$$n_1 = -\vec{\nabla}\cdot\vec{P}_1\ , \tag{5}$$

where $\vec{P}_1$ is the linear polarization of the medium given by

$$\vec{D}_1 = \vec{E}_1 + 4\pi\vec{P}_1 = \epsilon_1\vec{E}_1 \tag{6}$$

and $\vec{E}_1$ and $\vec{D}_1$ are the corresponding linear fields. Also, $\vec{v}_1$ can be calculated from the linear current by the relationship

$$\vec{j}_1 = n_0 e\vec{v}_1\ . \tag{7}$$

For an electron gas

$$\vec{v}_1 = ie\vec{E}_\parallel/m\omega\ . \tag{8}$$

Then from (4) we have

$$\vec{j}_{2\parallel} = -ie\vec{E}_\parallel(\vec{\nabla}\cdot\vec{P})/m\omega\ , \tag{9}$$

dropping the one subscript and using the previous convention that fields without subscripts are the linear ones.

Now, there are two ways of obtaining a rapidly varying longitudinal polarization in an electron gas. One is to introduce a violent inhomogeneity into the gas, such as a boundary. The other is to place an external charge distribution into the gas. Suppose there is no such charge distribution in the gas. Then

$$\vec{\nabla}\cdot\vec{D} = 0$$

and (10)

$$\vec{\nabla}\cdot\vec{P} = -\vec{\nabla}\cdot\vec{E}/4\pi\ .$$

Inserting (10) into (9), we obtain

$$\vec{j}_{2\parallel} = ie\vec{E}_\parallel(\vec{\nabla}\cdot\vec{E})/4\pi m\omega\ . \tag{11}$$

Expression (11) is appropriate for the case of a metal with a boundary. For an isotropic electron gas, taking

$$\epsilon = 1-(\omega_p/\omega)^2\ , \tag{12}$$

we have

$$\vec{P} = (\epsilon-1)\vec{E}/4\pi = -(\omega_p^2/4\pi\omega^2)\vec{E}\ . \tag{13}$$

Inserting (13) into (9), we obtain

$$j_{2\parallel} = (ie\omega_p^2/4\pi m\omega^3)E_\parallel(\nabla\cdot\vec{E})\ . \tag{14}$$

We note that (14) and (3) are the same expressions, as they should be since (3) was derived for an infinite medium. We also note that (11) and Eq. (14) of Ref. 10 are also the same. Expressions (11) and (14) give the parallel SH surface-type current resulting from two different configurations. Equation (11) is valid for a medium with a boundary where no external charges are present. Equation (14) is valid for an isotropic medium where external charges are necessary to produce rapidly varying longitudinal electric fields. Note that both expressions (11) and (14) are equal to (9), which in the local approximation can be written as

$$\vec{j}_{2\parallel} = \frac{ie\vec{E}_\parallel}{4\pi m\omega}\ \vec{\nabla}\cdot\left(\frac{4\pi n(\vec{r})e^2}{m\omega^2}\ \vec{E}(\vec{r})\right)\ . \tag{9$'$}$$

To further illustrate the point just developed, consider the local model of the electron gas. The relationship between the electric fields just inside the gas, $\vec{E}^i$, and outside, $\vec{E}^0$, is given by

$$E_z^i = E_z^0/\epsilon(\omega)\ , \tag{15}$$

$$\vec{E}_\parallel^i = \vec{E}_\parallel^0\ . \tag{16}$$

If we replace the real situation of a bounded metal by the model of Appendix A, namely, an isotropic medium with a current sheet, fields have reflection symmetry about the current sheet. In this model there is no boundary, so that all fields are interior ones, but the fields for $z<0$ are the same as the interior fields for the real situation. The fields on each side of the current sheet have the relation

$$E_z^i = E_{z-} = -E_{z+} , \tag{17}$$

$$\vec{E}_\parallel^i = \vec{E}_{\parallel -} = \vec{E}_{\parallel +} . \tag{18}$$

Here the fields just on the positive or negative $z$ side of the current sheet (located at $z=0$) are denoted by the subscripts + or −, respectively. As discussed, Eq. (11) is to be used with the fields of (15) and (16), while Eq. (14) is to be used with the fields of (17) and (18).

We now calculate the total surface current $\int_{-n}^{0} \vec{j}_{2\parallel}\, dz = \vec{j}_{2\parallel}^{\,t}$ using the two models, where $n$ is an infinitesimal and positive number. From the case of a surface, Eqs. (11), (15), and (16) give

$$\vec{j}_{2\parallel}^{\,t} = [ie(1-\epsilon)/4\pi m\omega]\, E_z^i \vec{E}_\parallel^i . \tag{19}$$

For the infinite medium with a current sheet, Eqs. (14), (17), and (18) give, in the region $z<0$,

$$\vec{j}_{2\parallel}^{\,t} = (ie\omega_p^2/4\pi m\omega^3)\, \vec{E}_\parallel^i E_z^i , \tag{20}$$

where, because of the mirror symmetry about the current sheet, we must remember that an equal amount of current is in the region $z>0$. We note that (19) and (20) are the same because $1-\epsilon = (\omega_p/\omega)^2$. Thus, as required, the same answer is obtained from the different expressions (11) and (14) *as long as they are applied to their respective models*. Needless to say, if they are applied to an incorrect model, the result will also be in error.

Let us now apply Eq. (2) to estimate the total surface current flowing in the $z$ direction, $j_{2z}^t = \int_{-n}^{0} j_{2z}\, dz$, where $j_{2z}$ is the $z$ component of the surface current given by (2):

$$j_{2z} = \frac{in_0 e^3}{m^2\omega^3}\left(\frac{1}{4}\,\frac{d(E_z^2)}{dz} + E_z \frac{dE_z}{dz}\right) , \tag{21}$$

$$j_{2z}^t = \frac{in_0 e^3}{m^2\omega^3}\;\frac{3}{4}\;(E_z^i)^2 . \tag{22}$$

The integral of (21) which leads to (22) is not well defined because the value of $E_z$ in the last term is not determined. We made the unjustified replacement

$$E_z \frac{dE_z}{dz} = \frac{1}{2}\,\frac{d}{dz}\,E_z^2$$

and set $E_z = 0$ at $z=0$. The uncertainty is an indication that the local approximation is not valid as discussed in Sec. III. Since Eq. (2) is applicable to the case of no boundary, we must use the fields of Eqs. (17) and (18), as we did.

If we incorrectly use the fields of Eqs. (15) and (16) in integrating (21), we obtain

$$j_{2z}^t = \frac{in_0 e^3}{m^2\omega^3}\;\tfrac{3}{4}[(E_z^0)^2 - (E_z^i)^2]$$

$$= \frac{in_0 e^3}{m^2\omega^3}\;[\epsilon^2(\omega) - 1]\;\tfrac{3}{4}\,(E_z^i)^2 . \tag{23}$$

This expression for $j_{2z}^t$ is $\epsilon^2(\omega)-1$ times larger than the previous value. It is much too large an estimate. It appears in previous work and the estimated value of $j_{2z}^t$ given in, say, Ref. 10, is $\epsilon^2 - 1$ times too large. When one remembers that in typical experimental conditions $\epsilon^2 - 1 \approx 10^3$, one appreciates the magnitude of this overestimate.

As discussed in Sec. III and indicated in evaluating $j_{2z}^t$, the local approximation is not adequate to describe the variation of $E_z$ in the immediate vicinity of the metal surface, and one must include nonlocal effects. Such a calculation is performed in Appendix B to determine the appropriate expression to replace (2). It is found that only $j_{2z}^t$ is modified by nonlocal effects, while $\vec{j}_{2\parallel}^{\,t}$ remains the same. A general demonstration that $\vec{j}_{2\parallel}^{\,t}$ should be the same is contained in Appendix C.

In summary, we find that the magnitude of SH surface currents parallel to the surface has been correctly estimated by previous investigators but the value of the normal SH surface current has been greatly overestimated. Both nonlocal effects and a correct application of self-consistency between the charge and the fields reduce the value of the normal surface current to a value much smaller than previously calculated.

## V. EFFECT OF BOUNDARY

The discussion in Sec. IV neglected band effects and surface roughness, replacing the surface with a current sheet in an isotropic medium. In this section we discuss in what manner the presence of a boundary changes the results of Sec. IV.

As mentioned in Sec. II, the sources of the SH radiation can be divided into three categories: (a) bulk current, (b) surface current parallel to the boundary, and (c) surface current normal to the boundary. As pointed out previously,[7] all of the bulk current within a penetration depth of the surface contributes to the SH radiation. The presence of a clean and flat real surface may modify the bulk current in a region of the order of a small fraction of the penetration depth. Thus one expects the boundary to cause only a small change in the value of contribution (a). The presence of a real boundary will cause variations in contribution (a) of the same order as variations in the linear fields.

If the surface is flat so that momentum transverse to it is conserved, the boundary has no effect on the value of contribution (b), as is shown explicitly in Appendix C. If the boundary is not flat so that current flowing parallel to it can be scattered, one expects that $\vec{v}_1$ of Eqs. (7) and (8) and thus $\vec{j}_{2\parallel}^{\,t}$ will be decreased. We can express this by writing (20) as

$$\vec{j}_{2\parallel}^{\,t} = (ibn_0 e^3/m^2\omega^3)\, E_z^i \vec{E}_\parallel^i , \tag{20'}$$

where $|b| < 1$.

A change introduced by the presence of a real flat boundary occurs in contribution (c). A completely new mechanism is introduced by the boundary. To estimate the size of the SH surface current introduced by this mechanism, consider Fig. 2. Assume a uniform electric field outside the metal present in the $z$ direction varying in time as $e^{-i\omega t}$. The electric field will not remain uniform throughout but will have a rapid variation at the surface, reaching a new but uniform value of $Ee^{-i\omega t}$ inside the metal. It is clear that in the surface region of dimension $\lambda$, major nonlinearities in the induced current will occur when electrons inside the metal have an average displacement of $\lambda$. The displacement of the electrons in the interior of the metal is given by

$$z = -(eE/m\omega^2)\, e^{-i\omega t} . \tag{24}$$

We define the field $E_0$ as that which produces an amplitude of $z=\lambda$ and large nonlinearities in the surface current:

$$E_0 = m\omega^2\lambda/e . \tag{25}$$

Expanding the current in the surface region in a power series in $E$, we can write

$$j_z = \sigma E_0[E/E_0 - \tfrac{1}{2}a\,(E/E_0)^2 + \cdots] . \tag{26}$$

When $E=E_0$, we expect the $E^2$ term to be of the order of the $E$ term (large nonlinearity), or $a\approx 1$. Our estimate of the SH term is therefore

$$j_{2z} \approx -\sigma a E^2/2E_0 . \tag{27}$$

An estimate for $\sigma$ is the linear conductivity in the interior of the metal, so

$$\sigma \approx i n_0 e^2/m\omega . \tag{28}$$

Inserting (28) and (25) into (27) and multiplying by $\lambda$ to estimate the integral over the region where the nonlinearity is appreciable, we find

$$j_{2z}^t = (ie\omega_p^2 a/8\pi m\omega^3)\,(E_z^i)^2 , \tag{29}$$

where now the fact that $E$ is the interior field in the $z$ direction is explicitly shown and $a$ is a number of the order of 1. It should be emphasized that the derivation of (29) did not depend on the local approximation being valid in the surface region, which of course it is not.

Comparing with (A25) in Appendix A, we see that the magnitude of the coefficient of (29) is the same order as that obtained with the neglect of the breaking of inversion symmetry. Thus the inversion breaking symmetry of the boundary must be included to correctly calculate $j_{2z}^t$.

## VI. RADIATION BY SH CURRENT

Experimentally, the SH effect is detected by the nature of the radiation generated at frequency $2\omega$ for light incident at frequency $\omega$. We must therefore calculate expressions for the radiation emitted by the SH current sources discussed in Sec. V. Such expressions are derived in Appendix A for the nonlocal case using the model of an infinite medium with a current sheet to represent the surface. Expressions for the radiation from SH current sources using the local approximation have already been given covering many differing situations.[7,9,10] In this section we discuss when the local approximation breaks down and we give theoretical estimates of the SH intensity generated by an incident EM wave.

As shown in Ref. 7, the SH radiation is found by solving Maxwell's equations with the SH current as external sources. The local approximation assumes that the response of the medium to EM fields can be treated by a dielectric constant depending only on frequency and not on the wavelength of the EM field. This approximation is valid, as discussed in Sec. III, when $v_F q \ll \omega$, where $v_F$ is the Fermi velocity, $\omega$ is the angular frequency of the EM field, and $q$ is the wave number of the most important variation of the field. As discussed in Sec. III, all the fields except for the normal component of $E$ vary in a distance equal to the skin depth, which is slowly enough to validate the local approximation. The normal component of $E$ has a rapid change at the boundary and cannot be handled within the local approximation.

However, the error introduced by using the local approximation is not serious for the radiation emitted by the parallel surface current and the bulk current. In both cases the error introduced affects only a small fraction of the total radiating currents, a fraction of the order of the surface dimension of a few angstroms divided by a penetration depth of light of about 200 Å. For the case of the normal surface current the local approximation does introduce a serious error. This can be illustrated by comparing in the local approximation the radiation emitted by a normal current sheet which is placed just inside the metal and then just outside.

Consider a model of a metal described by a dielectric constant $\epsilon(\omega)$ filling the half-space $z<0$. The rest of the space, $z>0$, is a vacuum. We calculate the radiation from a current source of the form

$$\vec{j}_2^- = \hat{z}\, j_{2z}^t\, \delta(z-0^-)\, e^{2i(qx-\omega t)} , \tag{30}$$

where $\hat{z}$ is a unit vector in the positive $z$ direction. The minus superscript in the argument of the $\delta$ function signifies that the limit to zero is obtained using only negative values of $z$. Solving Maxwell's equation in this case, we find for the magnitude of the magnetic field in the region $z>0$

$$H^- = \frac{-i8\pi q j^t_{2z}}{\epsilon(2\omega)K(2\omega)+K'(2\omega)} , \tag{31}$$

where

$$K^2(2\omega) = (2q)^2 - (2\omega/c)^2 ,$$

$$[K'(2\omega)]^2 = (2q)^2 - \epsilon(2\omega)(2\omega/c)^2 ,$$

and

$$\mathrm{Re}(K', K) > 0 , \quad \mathrm{Im}(K', K) < 0 .$$

Here Re and Im signify real and imaginary parts, respectively.

Now if we calculate the radiation emitted by a current source of the form

$$\vec{j}^{\,+}_2 = \hat{z}\, j^t_{2z}\, \delta(z - 0^+)\, e^{2i(qx - \omega t)} , \tag{32}$$

where the plus superscript in the argument of the $\delta$ function signifies that the limit to zero uses only positive values of $z$, we obtain for the magnitude of the magnetic field in the region $z > 0$

$$H^+ = \epsilon(2\omega) H^- . \tag{33}$$

We obtain different values for the radiated field depending on how we take the limit to place the current sheet on the metal surface. Bloembergen *et al.*[10] have already noted that the radiation of the normal surface current depends sensitively on how the limit is taken. We now show that this ambiguity arises because we have used the local approximation where it is not valid.

Physically the longitudinal current source (30) or (32) sets up a separation of charge. Inside the metal, assuming the local approximation, this charge is shielded by the metal and reduced in magnitude by a factor $[\epsilon(2\omega)]^{-1}$, while outside the metal no shielding or reduction occurs. Thus the self-consistent charge and driving current of the source inside the metal is $\epsilon(2\omega)^{-1}$ times that outside. We therefore understand that the fields from a source just outside the surface is $\epsilon(2\omega)$ times that from one just inside as given in (33).

Clearly, the local approximation is not valid in this problem since the charge separation is infinitesimal in extent. In the real case, the normal surface current extends over the surface dimension of a few angstroms, again too small a dimension to validate the local approximation. The problem can be handled correctly by including nonlocal effects as is done in Appendix A. The calculation in Appendix A approximates the boundary by a model of an infinite medium with a current sheet which itself introduces some error. The error introduced by Appendix A is in estimating the dielectric constant that shields the current source. However, the extent of the current source is so small in the $z$ direction that the appropriate dielectric constant in any case does not deviate much from 1 and the error introduced will be small. In fact, we can estimate the radiation to more accuracy than we can estimate $j^t_{2z}$ by assuming that the current source is just outside the metal and the radiation is given by (33).

We now summarize results for the SH radiation induced from a metal surface by an incident EM wave. As mentioned previously, the radiation from the parallel SH surface currents and the bulk SH current if the metal surface is clean and flat is given correctly by the standard local approximation, or it can be obtained from the nonlocal theory given in Appendix A. Expressions for that radiation are in the Appendix. Using (29), (31), (33), and (A15), we obtain for the magnitude of the radiation due to the normal SH surface current

$$E_\perp = \frac{4ae\omega_p^2 \epsilon(2\omega) E^2 \cos\phi \sin^3\theta}{mc^3[\epsilon(\omega)K(\omega)+K'(\omega)]^2[\epsilon(2\omega)K(2\omega)+K'(2\omega)]} . \tag{34}$$

$\theta$ is the angle of incidence of the incoming radiation, measured relative to the normal to the surface, $\phi$ is the angle between its polarization and the plane of incidence, and

$$K(\omega) = \tfrac{1}{2} K(2\omega) = -i(\omega/c)\cos\theta ,$$

$$K'(\omega) = -i(\omega/c)[\sin^2\theta - \epsilon(\omega)]^{1/2} ,$$

$$K'(2\omega) = -2i(\omega/c)[\sin^2\theta - \epsilon(2\omega)]^{1/2} .$$

$E_\perp$ is polarized in the plane of incidence of the incident radiation and it, along with all the rest of the induced SH radiation, propagates out in the same direction as the specularly reflected radiation at the fundamental frequency.

If the frequency is sufficiently small that we can set $\epsilon(\omega) = 1 - \omega_p^2/\omega^2 \approx -\omega_p^2/\omega^2$ and $\epsilon(2\omega) \approx -\omega_p^2/4\omega^2$, then we obtain the following approximate relations between $E_\perp$, $E_{\parallel p}$, $E_{\parallel s}$, and $E_B$, where $E_{\parallel p}$ $E_{\parallel s}$ are the magnitudes of the radiating fields due to the parallel surface currents in and perpendicular to the plane of incidence and $E_B$ is the radiation due to the bulk current:

$$\frac{E_\perp}{E_{\pi/2}} \approx \tfrac{1}{2} a \cos^2\phi \tan^2\theta , \tag{35}$$

$$\frac{E_{\parallel p}}{E_{\pi/2}} \approx \frac{2b\cos^2\phi}{\cos^2\theta} , \tag{36}$$

$$\frac{E_B}{E_{\pi/2}} \approx 1 + \cos^2\phi \tan^2\theta , \tag{37}$$

$$\frac{E_{\parallel s}}{E_{\pi/2}} \approx 2b\cos\phi \sin\phi , \tag{38}$$

$$E_{\pi/2} \approx \frac{\omega E^2 \cos\theta}{\pi n_0 e i c} \sin\theta . \tag{39}$$

$b$ in Eq. (36) is the same as $b$ in Eq. (20). It indicates the effect of surface conditions on the parallel surface current and is equal to 1 when the metal surface is clean and flat. $E_{\parallel p}$, $E_{\perp}$, and $E_B$ are polarized in the plane of incidence and $E_{\parallel s}$ is polarized perpendicular to the plane of incidence. When the right-hand side of (35) or (36) is negative, the two fields on the left-hand side are polarized in opposite directions. $E_{\pi/2}$ is the magnitude of the SH radiating field generated when the incoming radiation is polarized perpendicular to the plane of incidence. It is due entirely to a bulk current and is polarized in the plane of incidence.

From the expressions above we obtain an expression for the ratio between the SH fields when the incoming radiation is polarized in the plane of incidence and when it is polarized perpendicular to the plane of incidence:

$$\frac{E_0}{E_{\pi/2}} \approx \frac{2b+1}{\cos^2\theta} + \tfrac{1}{2} a \tan^2\theta \ . \qquad (40)$$

## VII. DISCUSSION

The theory presented here assumed that the electron gas dominates over interband contributions and that at both frequencies $\omega$ and $2\omega$ the dielectric constant of the metal is given by the expression $\epsilon(\omega) = 1 - (\omega_p/\omega)^2 \approx -(\omega_p/\omega)^2$. This requires that at both $\omega$ and $2\omega$ the interband contributions to $\epsilon$ be small.[13] Of the various experiments that have been performed on the SH generation of light at metal surfaces only the ones performed on Ag metal at a frequency $\omega$ corresponding to that of the Nd-glass laser, wavelength equal to 1.06 $\mu$, satisfied this requirement. We therefore must limit our comparison between the theory presented here and experiment to this case.

Recently Brown and Matsuoka[14] have discovered that the SH generation from freshly evaporated Ag surfaces for an incidence $E$ field polarized in the plane of incidence ($\phi = 0°$ and $\theta = 54°$) increases by a factor of $(0.28)^{-1} \approx 4$ from that of Ag surfaces exposed to gases and presumably coated with a gaseous layer. In addition, they measure for these fresh silver surfaces the ratio $M$ of generation efficiencies with the incident $E$ field parallel and perpendicular to the plane of incidence,

$$M = |E_{\pi/2}/E_0|^2 = 0.046 \pm 0.010 \ .$$

It was not possible to measure $M$ for the exposed Ag surface because of the lower intensity. However, it was estimated that $|E_{\pi/2}|^2$ decreased for the exposed Ag surface relative to the fresh surface.

Brown and Matsuoka estimated that the SH radiation from the absorbed gases themselves could not be large enough to explain the measured effect; nor could changes in the linear dielectric constant explain the effect. They concluded by default that the electrons in the metal near the surface are the cause of the effect. They proposed an explanation based on the surface dipole layer induced by adsorbed gases. This dipole layer sets a dc electric field which then permits a SH generation from the third-order polarizability $\chi^{(3)}$ of magnitude $\chi^{(3)} E_{dc} \times (E^i)^2$, where $E_{dc}$ is introduced by the surface dipole layer and $E^i$ is the $E$ field of the EM wave at the surface. They estimate that this produced the correct order of magnitude if one assumes the local approximation. As discussed in Sec. IV, the local approximation is not valid in this case and taking it into account decreases the SH currents by several orders of magnitude. Thus it is unlikely that this explanation is valid.

To further complicate matters, recent preliminary measurements in our laboratory[15] also show intensity variations in the SH generation but opposite from that found by Brown and Matsuoka. The SH radiation is more intense for the exposed surface than the fresh surface. The sample is prepared by evaporation in ultrahigh-vacuum conditions as compared to high-vacuum conditions in the case of Brown and Matsuoka. Clearly, the experimental condition of the surface of the metal surfaces is a very important parameter and its state must be more completely defined before a comparison with the theory presented here is possible. A full test of the theory awaits further experimental measurements.

In place of the comparison with experiment we will estimate the values of the parameters of the theory and use these to obtain an estimate of the various contributors to the SH radiation. Expressions (46′)–(50′) have two unknown parameters, $a$ and $b$. The estimate of $|a| \approx 1$ has already been given in Sec. V. The parameter $b$ is introduced to account for the effects of boundary scattering on the velocity parallel to the surface induced by $\vec{E}_{\parallel}$. If the boundary is perfectly reflecting, then $b = 1$. If the boundary is flat but scatters diffusely, then we expect that $b = \frac{1}{2}$ by the following reasoning. Remembering that the metal occupies the half-space $z < 0$, an electron with a $v_z > 0$ will have a $\vec{v}_{\parallel}$ induced by $\vec{E}_{\parallel}$ which is independent of the presence of the boundary. All electrons with $v_z < 0$ will give essentially no contributions to $\vec{j}_{\parallel}$. These electrons will have collided with the boundary, losing all memory of $\vec{E}_{\parallel}$, and have no net $\vec{v}_{\parallel}$ immediately after the collision. Only when they are within the surface region of a few angstroms can they contribute to $\vec{j}_{\parallel}$ but their acceleration during this distance is negligible compared to the $\vec{v}_{\parallel}$ they attained in moving to the boundary where the $\vec{E}_{\parallel}$ acted over a skin depth. Thus, to a good approximation with an error of the order of the ratio of the surface dimension to the skin depth, only one-half of the electrons—those with $v_z > 0$—contribute to $\vec{j}_{\parallel}$. Since the effective electrons contribute the same as though no boundary were present, we have that

$b=\frac{1}{2}$.

Another possibility is that the boundary is not flat but consists of pits and bumps with dimensions perpendicular to the boundary comparable or larger than the thickness of the surface region of a flat surface. If the dimensions parallel to the boundary of these imperfections are at the same time of the same order as, or smaller than, the distance $v_F/\omega$, then the induced $\vec{j}_{\parallel}$ of the electrons with $v_z>0$ will be decreased by the boundary. Approximating this effect by a relaxation time $\tau$, we estimate $b=\frac{1}{2}\omega/(\omega+i/\tau)$, where $\tau\approx\sigma/v_F$, $\sigma$ is an average imperfection dimension parallel to the surface, and we still assume diffuse scattering as the electron collides with the boundary.

Since we do not know what surface is appropriate to describe the typical experimental situation, we will take the value $b=\frac{1}{2}$ corresponding to a flat diffusely scattering surface in order to have something with which to work. However, it must be emphasized that the typical experimental situation could be quite different.

With $a=1$, $b=\frac{1}{2}$, $\phi=0°$ so that the incident light is $p$ polarized, and a typical value of $\theta=45°$, we have from (40) for the total electric field in the SH radiation

$$E_0/E_{\pi/2}=4.5\ . \tag{41}$$

Tracing back to the contribution of each mechanism, we see that the radiation is $p$ polarized and and is dominated by the bulk SH current and the SH surface current in the plane of incidence, each of which contributes an equal magnitude and in phase. Even if the value of $b$ is much smaller because of unfavorable surface conditions, the radiation remains dominated by the bulk SH current. Thus it appears that the large changes in the SH radiation due to changes in the sample surface condition are produced by the changes in $b$ and not $a$. The SH radiation intensity varies by about a factor of 6 between the extreme limits of $b=0$ to $b=1$.

## VIII. SUMMARY

In this paper only the contribution of the conduction electrons is considered and it is assumed that they can be treated as an electron gas. The SH radiation is generated by three different source terms. One is a bulk current, the second is a surface current parallel to the boundary, and the third is a surface current perpendicular to the boundary. The bulk current is the well-understood Lorentz-force-produced longitudinal current. The local approximation is valid to calculate the radiation from this source. That radiation should not be very sensitive to surface variations, varying in the same way as the linear fields do.

The magnitude of the parallel surface current source for a flat surface is correctly given by a theory which assumes the local approximation. Inconsistencies between the results of different authors were shown to be due to use of different models of the metal surface. A careful accounting of the self-consistency between electric charges and fields shows that the final result is the same if the respective models are consistently employed. A realistic surface will have scattering present, decreasing the parallel surface current. This effect is accounted for here phenomenologically.

The normal surface current is not correctly given by the local approximation. Neglecting the inversion symmetry breaking of the surface, nonlocal effects affect the normal current somewhat. Correctly including the self-consistency between electric charges and fields also makes an important correction to the value of the theoretical normal current. When the inversion symmetry breaking of the surface is included, a new mechanism for producing the normal surface current is introduced. This mechanism is proportional to $E^2$ and requires no gradient as is the case of the interior. The nonlinearity is caused by the fact that electrons flowing away from the boundary are freer to move than when they flow into the boundary. The normal surface current generated by this new mechanism is of the order of that calculated neglecting the inversion symmetry breaking of the surface.

A theoretical estimate of the pertinent parameter indicates that variations in the SH radiation with changes in the condition of Ag surface are caused by variations in the surface scattering which affects the parallel surface current. The normal surface current never seems to be an important contributor to the SH radiation. However, further experiments must be performed before any definite conclusions can be made about the applicability of the theory presented here to real cases.

In the appendices general relationships for a second-order response of an electron gas are given. Explicit functional forms of these response functions are given. In addition, general relationships involving first-order response functions are given for the second-order response in the limit that the wavelength of one of the electric fields becomes very large.

## APPENDIX A

A metal is assumed to fill the half-space $z<0$. In the model used here its conduction electrons are represented as a homogeneous electron gas which occupies the half-space $z<0$. A current sheet in the $z=0$ plane is adjusted to provide matching between the EM fields at $z=0^-$ and the appropriate vacuum fields.

Two situations are considered. In the first, the half-space metal is stimulated by an EM wave incoming from the vacuum. The solutions for the fields inside the metal will be used as the driving fields which, through the second-order response of the metal, produce the SH source currents. In the second situation, there are externally driven source currents inside the metal. The solution of that problem will be used to yield the radiation due to the SH source currents.

We assume that the response of the electron gas can be approximated by that of an isotropic medium, and the fields and currents in the half-space $z>0$ are assumed to be given by reflecting those in the half-space $z<0$ through the $z=0$ plane. Those two assumptions approximate the response of a half-space electron gas with specular reflection at its bounding surface. They neglect the effects of interference between incident and reflected wave functions as well as effects due to the structure of the bounding potential and therefore do not accurately represent electron dynamics in the immediate vicinity of the bounding surface. However, the model does allow the response of the electron gas to be treated as nonlocal.

As a final simplification, the transverse dielectric constant is taken equal to the wavelength- and frequency-dependent longitudinal dielectric constant $\epsilon(Q, \omega)$. Such a simplification is valid in the long-wavelength region ($\lambda \gg v_F/\omega$, $v_F$ being the Fermi velocity), where they approach a common limit. Outside that region, only the longitudinal response will be important, as will be made clear later on.

### A. Fields Due to Stimulation by EM Field Incident from Vacuum

Suppose we have an isotropic electron gas with an externally driven source current in it of the form

$$\vec{j}(\vec{r}, t) = \int \vec{j}_0(\vec{Q}) e^{i(\vec{Q}\cdot\vec{r} - \omega t)}\, d^3Q \ . \tag{A1}$$

Then Maxwell's equations give for the electric field in the electron gas

$$\vec{E}(\vec{r}, t) = \frac{4\pi}{i\omega}\int \frac{1}{\epsilon(Q,\omega)} \times \frac{(\omega/c)^2\epsilon(Q,\omega)\vec{j}_0(\vec{Q}) - \vec{Q}[\vec{Q}\cdot\vec{j}_0(\vec{Q})]}{(\omega/c)^2\epsilon(Q,\omega) - Q^2}\, d^3Q \ , \tag{A2a}$$

with the magnetic field given by

$$\vec{B}(\vec{r}, t) = (c/i\omega)\,\vec{\nabla}\times\vec{E}(\vec{r}, t) \ . \tag{A2b}$$

In the model adopted here for the half-space metal, stimulation of the metal by an incident EM field is accomplished by placing an appropriate current on the current sheet in the $z=0$ plane. It is assumed that all quantities have the following $x$ and $y$ dependence:

$$e^{iqx} \ .$$

Then, the Fourier transform of the necessary source current is of the form

$$\vec{j}_0(Q) = (\hat{x}\, j_x^{(s)})\,\delta(Q_x - q)\,\delta(Q_y) \ . \tag{A3}$$

Using (A2a), the electric fields in the electron gas are given by

$$\vec{E}(\vec{r}, t) = \vec{E}(z)\, e^{i(qx-\omega t)} \ ,$$

where

$$E_x(z) = \frac{4\pi j_x^{(s)}}{i\omega}\int_{-\infty}^{\infty} \frac{[(\omega/c)^2\epsilon(Q,\omega) - q^2]\, e^{ikz}\, dk}{\epsilon(Q,\omega)[(\omega/c)^2\epsilon(Q,\omega) - k^2 - q^2]}$$

$$\approx \frac{-4\pi^2 i K'(\omega)}{\omega\epsilon(\omega)}\, j_x^{(s)}\, e^{-K'(\omega)|z|} \ , \tag{A4}$$

$$E_y(z) = \frac{4\pi}{i}\,\frac{\omega}{c^2}\, j_y^{(s)}\int_{-\infty}^{\infty} \frac{e^{ikz}\, dk}{(\omega/c)^2\epsilon(Q,\omega) - k^2 - q^2}$$

$$\approx \frac{4\pi^2 i\omega}{K'(\omega)c^2}\, j_y^{(s)}\, e^{-K'(\omega)|z|} \ , \tag{A5}$$

$$E_z(z) = \frac{4\pi}{i\omega}\, j_x^{(s)}\int_{-\infty}^{\infty} \frac{-kq e^{ikz}\, dk}{\epsilon(Q,\omega)[\epsilon(Q,\omega)^2(\omega/c)^2 - k^2 - q^2]} \ . \tag{A6}$$

The replacement $k\equiv Q_z$ has been made and $K'(\omega)$ is given by $K'(\omega) = [q^2 - (\omega/c)^2\epsilon(\omega)]^{1/2}$, $\mathrm{Re}(K') > 0$. The approximations in Eqs. (A4) and (A5) consist of replacing the integrals by their dominant contribution, which is from the region in which $k$ is the order of an inverse optical wavelength. $\epsilon(\omega)$ in these approximations is the $Q=0$ limit of $\epsilon(Q,\omega)$. The approximations are in error to order $v_F/c$, such errors being considered negligible for our purposes. An analogous approximation for $E_z(z)$ is not in general correct, though one can be made for $|z|$ sufficiently large. That approximation will be exhibited later in this section.

To find the fields at the surface of the metal, which, in this model, is at $z=0^-$ in the electron gas, we note that by the symmetry of our model

$$E_z(0^-) = (-4\pi^2 k/\omega)\, j_x^{(s)} \ , \tag{A7}$$

$$B_x(0^-) = (-4\pi^2/\omega)\, j_y^{(s)} \ . \tag{A8}$$

The $x$ and $y$ components of the electric field at the metal surface are found by setting $z=0$ in (A4) and (A5).

Outside of the metal, in the half-space $z>0$, the electric field is given by

$$\vec{E}(\vec{r}, t) = \{E_p(c/\omega)[\hat{x} iK(\omega) + \hat{z}q] + E_s\,\hat{y}\}\, e^{i[qx - iK(\omega)z - \omega t]} + \{E_p^{(r)}(c/\omega)[\hat{x} iK(\omega) - \hat{z}k] + E_s^{(r)}\hat{y}\} \times e^{i[qx + iK(\omega)z - \omega t]} \ , \tag{A9}$$

where the superscriptless field is incident and the superscript $(r)$ stands for "reflected." $K(\omega)$ is defined following (31) and (34). Matching the tangential electric and magnetic fields at the surface of the metal yields for the surface current in terms of the incident electric field

$$j_x^{(s)} = \frac{-2\epsilon(\omega)c}{4\pi^2} \frac{K(\omega)}{\epsilon(\omega)K(\omega)+K'(\omega)} E_p , \qquad \text{(A10)}$$

$$j_y^{(s)} = \frac{-2ic}{4\pi^2\omega} \frac{K(\omega)K'(\omega)}{K(\omega)+K'(\omega)} E_s . \qquad \text{(A11)}$$

In the electron gas, then,

$$E_x(z) \approx \frac{2icE_p}{\omega} \frac{K(\omega)K'(\omega)}{\epsilon(\omega)K(\omega)+K'(\omega)} e^{-K'(\omega)|z|} , \qquad \text{(A12)}$$

$$E_y(z) \approx 2E_s \frac{K(\omega)}{K(\omega)+K'(\omega)} e^{-K'(\omega)|z|} , \qquad \text{(A13)}$$

and

$$E_z(z) = \frac{2E_p\epsilon(\omega)c}{i\pi\omega} \frac{K(\omega)}{\epsilon(\omega)K(\omega)+K'(\omega)} \times \int_{-\infty}^{\infty} \frac{-kq\, e^{ikz}\, dk}{\epsilon(Q,\omega)[(\omega/c)^2\epsilon(Q,\omega)-k^2-q^2]} . \qquad \text{(A14)}$$

For $|z|$ large compared to a shielding length, the oscillations of the exponential in (A14) ensure that the major contribution to the integral comes from the region in which $k$ is the order of an inverse optical wavelength and we obtain

$$E_z(z) \approx -2E_p \frac{cq}{\omega} \frac{K(\omega)\operatorname{sgn}(z)}{\epsilon(\omega)K(\omega)+K'(\omega)} e^{-K'(\omega)|z|} , \qquad \text{(A15)}$$

with errors of order $(z/z_{sh})^2$, where $z_{sh}$ is a shielding length.

Equations (A12), (A13), and (A15) for $z<0$ are the solutions for the electric field inside the half-space metal given by the local, or dipole, approximation with the local frequency-dependent dielectric constant $\epsilon(\omega)$. They are correct throughout the metal except for the $z$ component of the electric field in the immediate vicinity of the metal surface. If we compare (A15) for $z$ small with respect to an optical wavelength but still sizable compared to a shielding length with (A7), with $j_x^{(s)}$ replaced by the right-hand side of (A10), we see that over a distance the order of a shielding length the $z$ component of the electric field goes from $[1/\epsilon(\omega)] \times E_z(0^-)$ just inside the shielding region to $E_z(0^-)$ just outside the metal surface. In the shielding region, contributions from $k$ the order of an inverse shielding length are important in the integral in (A14). We note that in that integral the electric field is pointing in the direction of its major variation, so in evaluating the right-hand side of (A14) in the shielding region the longitudinal dielectric constant is to be used.

### B. Fields Due to Source Currents inside Metal

If there are source currents inside the electron gas of the form

$$\vec{j}(\vec{r},t) = e^{2i(qx-\omega t)} \int_{-\infty}^{\infty} \vec{j}^{(0)}(k) e^{ikz}\, dk , \qquad \text{(A16)}$$

then the electric field in the electron gas is given by

$$\vec{E}(\vec{r},t) = \vec{E}(z) e^{2i(qx-\omega t)} ,$$

where, to order $v_F/c$,

$$E_x(z) = \frac{2\pi}{i\omega} \int_{-\infty}^{\infty} \frac{\{4[(\omega/c)^2\epsilon(Q,2\omega)-q^2]j_x^{(0)}(k) - 2kqj^{(0)}(k)\} e^{ikz}\, dk}{\epsilon(Q,2\omega)[4(\omega/c)^2\epsilon(Q,2\omega)-4q^2-k^2]} - \frac{4\pi^2 iK'(2\omega)}{\omega\epsilon(2\omega)} j_x^{(s)} e^{-K'(2\omega)|z|} , \qquad \text{(A17)}$$

$$E_y(z) = \frac{8\pi}{i} \frac{\omega}{c^2} \int_{-\infty}^{\infty} \frac{j_y^{(0)}(k) e^{ikz}\, dk}{4(\omega/c)^2\epsilon(Q,2\omega)-k^2-4q^2} + \frac{4\pi^2 i\omega}{c^2K'(2\omega)} j_y^{(s)} e^{-K'(2\omega)|z|} , \qquad \text{(A18)}$$

$$E_z(z) = \frac{2\pi}{i\omega} \int_{-\infty}^{\infty} \frac{\{[4(\omega/c)^2\epsilon(Q,2\omega)-4q^2]j_z^{(0)}(k) - 2kq[j_x^{(0)}(k)+j_x^{(s)}]\} e^{ikz}\, dk}{\epsilon(Q,2\omega)[4(\omega/c)^2\epsilon(Q,2\omega)-4q^2-k^2]} , \qquad \text{(A19)}$$

$$K(2\omega) = 2[q^2-(\omega/c)^2]^{1/2} , \quad K'(2\omega) = 2[q-(\omega/c)^2\epsilon(2\omega)]^{1/2} .$$

Remembering that in this model the currents and fields in the two half-spaces are related by reflection about the $z=0$ plane yields (A7) and (A8) for $E_z(-0)$ and $B_x(-0)$, respectively. Equations (A17) and (A18) evaluated at $z=0$ give the $x$ and $y$ components of the electric field at the metal surface. In the vacuum, the EM fields due to the source currents are purely outgoing, the electric field being given by

$$\vec{E}(\vec{r},t) = \{E_p(c/2\omega)[\hat{x}iK(2\omega) - 2\hat{z}q] + \hat{y}E_s\} \times e^{i[qx+iK(2\omega)z-\omega t]} . \qquad \text{(A20)}$$

Equating the tangential fields at the metal surface yields

$$E_p = -\frac{4\pi}{c}\,\frac{\epsilon(2\omega)}{\epsilon(2\omega)K(2\omega)+K'(2\omega)}\int_{-\infty}^{\infty}\frac{\{4[(\omega/c)^2\epsilon(Q,2\omega)-q^2]j_x^{(0)}(k)-2kqj_z^{(0)}(k)\}\,dk}{\epsilon(Q,2\omega)[4(\omega/c)^2\epsilon(Q,2\omega)-4q^2-k^2]}\ , \tag{A21}$$

$$E_s = \frac{8\pi\omega}{ic^2}\,\frac{K'(2\omega)}{K'(2\omega)+K(2\omega)}\int_{-\infty}^{\infty}\frac{j_y^{(0)}(k)\,dk}{4(\omega/c)^2\epsilon(Q,2\omega)-4q^2-k^2}\ . \tag{A22}$$

### C. SH Generation Due to Incident EM Field

The results of Secs. A and B of this appendix can be combined with those of Appendix B for the second-order response of an electron gas to yield the SH radiation from a half-space metal due to stimulation by an incoming EM wave. The method by which they are combined has already been outlined at the beginning of this appendix. The metal is replaced by an electron gas filling all of space. The fields in the electron gas at the fundamental frequency are found in Sec. A. Those fields are combined with the second-order response expressions developed in Appendix B to find the SH source currents. The source currents are then inserted into (A21) and (A22) to obtain the SH radiation.

Carrying through the calculations we obtain with errors of order $V_F/C$ the following expressions for $E_{\parallel p}$, $E_{\parallel s}$, $E_B$, and $E_{\pi/2}$, which are defined in the text immediately preceding and following Eqs. (35)–(39):

$$\frac{E_{\pi p}}{E_{\pi/2}} = -2b\left(\frac{c}{\omega}\right)^2 K'(\omega)K'(2\omega)\cos^2\phi\, G^{-2}(\omega)\ , \tag{A21a}$$

$$\frac{E_B}{E_{\pi/2}} = \epsilon(\omega)G^{-2}(\omega)\cos^2\phi + \sin^2\phi\ , \tag{A21b}$$

$$E_{\pi/2} = \frac{(2e\omega_p^2/mc^4)\sin\theta\cos^2\theta}{[\epsilon(2\omega)K(2\omega)+K'(2\omega)][K(\omega)+K'(\omega)]}\ , \tag{A21c}$$

$$\frac{E_{\parallel s}}{E_{\pi/2}} = -4bG(2\omega)G^{-1}(\omega)\cos\phi\sin\phi\ , \tag{A22a}$$

$$G(\omega) = \frac{\epsilon(\omega)K(\omega)+K'(\omega)}{K(\omega)+K'(\omega)}\ .$$

$b$ in (A21a) and (A22a) is a phenomenological parameter described in Sec. V which is equal to 1 when the metal surface is perfectly flat. The expressions (A21a)–(A22a) correspond to Eqs. (34) and (35) in the work of Bloembergen *et al.*[10] The two sets of equations are equivalent if the parameter $\bar{\beta}$ in their equations is set equal to its "plasma" value and the term multiplied by $\bar{\delta}$, which corresponds to their normal surface current contribution, is neglected. Furthermore, to obtain their equations $b$ in (A21a) and (A22a) must be set equal to 1. The parallel surface currents are therefore just those predicted by the long-wavelength response theory. The reason for that result in this model is straightforward. It is, essentially, that all of the integrals for the radiation, except that connected with the contribution of the normal surface current, are dominated by long-wavelength contributions. The second-order response operators in the integrals can therefore be replaced by their long-wavelength limits and the results of long-wavelength theory are obtained, In Appendix C it is shown that the long-wavelength prediction for the contribution of the parallel SH current to the radiation is correct even beyond the model chosen here, as long as the effects of the periodic ionic potential and surface roughness are neglected.

The one contribution to the SH radiation that is not correctly given by long-wavelength theory is the contribution due to the normal surface current. It is contained in the expression giving the SH radiation due is the product of the $z$ component of the electric field at the fundamental frequency [Eq. (A14)] with itself. The part of the expression of interest is

$$E_{2z}^{(0)} = [\hat{x}iK(\omega) - \hat{z}q]\,e^{2i[qx+iK(\omega)z/2-\omega t]}$$
$$\times\frac{64i}{\pi}\,\frac{c^2q^3}{\omega^2}\,\frac{\epsilon(2\omega)}{\epsilon(2\omega)K(2\omega)+K'(2\omega)}$$
$$\times\left(\frac{E_p\epsilon(\omega)K(\omega)}{\epsilon(\omega)K(\omega)+K'(\omega)}\right)^2$$
$$\times\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{kk'(k+k')[L_{zzz}(\vec{Q},\vec{Q}',\omega)/2i\omega]\,dk\,dk'}{R(Q,\omega)R(Q,\omega)R(|\vec{Q}+\vec{Q}'|,2\omega)}\ , \tag{A23}$$

where

$$R(Q,\omega) = \epsilon(Q,\omega)[(\omega/c)^2\epsilon(Q,\omega) - k^2 - q^2]\ .$$

$L_{zzz}(\vec{Q},\vec{Q},\omega)$ is the second-order response operator calculated in Appendix B giving the $z$ component of the second-order current in terms of the product of the $z$ component of the first-order field with itself. When $k$ is the order of an inverse optical skin depth, the integral over $k'$ has its greatest contribution from the region in which $k'$ is the same order of magnitude. The part of the integral in which $k$ and $k'$ are in the optical region gives the part of the contribution to the radiation due to the bulk SH current.

When $k$ is outside of the optical region, the integral over $k'$ has comparable contributions from $k'$ throughout the region in which it is the order of an inverse shielding length. The integral (A23) with $k$ and $k'$ not both in the optical region gives the SH contribution due to the normal surface current. When $k$ and $k'$ are large compared to an inverse optical skin depth, a few simplifications of the integral can be made. First, the $x$ components of the wave numbers in the integral can be neglected. The electrical fields can then be considered longitudinal, and the second-order operator can be replaced by the operator giving the response due to two longitudinal fields varying in the same direction—in our model, that being the operator given by (B11). Additionally, if the frequency $\omega$ is small compared to characteristic frequencies of the electron gas (i.e., $\omega_p E_F/\hbar$), it can be set equal to zero in the integrand. Making those simplifications yields for the integral

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{L(k,k',0)\,dk\,dk'}{\epsilon(k)k^2\epsilon(k')k'^2\epsilon(k+k')(k+k')^2}\;, \qquad \text{(A24)}$$

where $\epsilon(k)$ is the $\omega=0$ value of $\epsilon(k,\omega)$. There are no special contributions to (A24) from either $k$ or $k'$ in the optical region, so the regions of integration have been extended to include all values of $k$ and $k'$. In order for the above to be true, the frequency must be kept equal to zero in the optical regions.

The integral was evaluated numerically using the static Lindhard dielectric constant appropriate to an electron gas with a density corresponding to $r_s=3.07$—the density of the conduction electrons in silver. The result for the integral is

$$1.97\frac{e^3}{\pi^2}\frac{m^2}{h^4k_F^5}\;.$$

Inserting that value in the place of the integral in (A23) gives the SH radiation due to the normal surface current. To compare the result obtained here with that of the text we divide them to obtain a value for the coefficient $a$ in Eq. (40) for the normal surface current. We obtain

$$a=\frac{-11.8}{\pi^2}\,\omega^4[\epsilon(\omega)]^2\frac{m^4}{h^4k_F^8}\;.$$

Replacing $\epsilon(\omega)$ by the Drude dielectric constant and retaining leading orders in $\omega_p/\omega$, we obtain

$$a=\frac{-23.64}{\pi^2}\frac{m^4\omega_p^4}{h^4k_F^8}=\frac{-2.63}{\pi^2}\left(\frac{k_{\mathrm{TF}}}{k_F}\right)^4$$

$$\approx -1.06\;, \qquad \text{(A25)}$$

where we have taken $r_s=3.07$ again, and $k_{\mathrm{TF}}$ is the inverse of the Thomas-Fermi screening length.

An interesting relationship between the SH radiation due to the normal surface current and the static surface response of a metal is suggested by (A24). It is, in fact, possible to prove in this model the following. Consider a half-space metal in the presence of a static electric field. If we expand the potential jump across the shielding layer in terms of the applied field strength as follows:

$$\phi=\phi_1Ez+\phi_2E^2+\phi_3E^3+\cdots\;,$$

then we have

$$|\vec{E}_{sz}|=\frac{2q\epsilon(2\omega)(\omega/c)}{i[\epsilon(2\omega)K(2\omega)+K'(2\omega)]}\left(\frac{2E_p\epsilon(\omega)cq\,K(\omega)}{\epsilon(\omega)K(\omega)+K'(\omega)}\right)^2\phi_2\;, \qquad \text{(A26)}$$

where $E_{sz}$ is the radiating electric field due to the normal surface current. The relationship (A26) can be shown to be valid beyond the model used here as long as the effects of the ionic potential and surface roughness are neglected and the frequency $\omega$ of the radiation is small. It can be used to facilitate calculation of the radiation due to the normal component of the SH surface current in a more realistic model than the one used here.

## APPENDIX B: SECOND-ORDER RESPONSE OF ISOTROPIC NONINTERACTING ELECTRON GAS

If a homogeneous electron gas is perturbed by an electric field of the form

$$\vec{E}(\vec{r},t)=\vec{E}_1e^{i(\vec{q}_1\cdot\vec{r}-\omega t)}+\vec{E}_2e^{i(\vec{q}_2\cdot\vec{r}-\omega t)}\;, \qquad \text{(B1)}$$

then, due to the second-order response of the electron gas, there will be an induced current of the form

$$\vec{j}(\vec{r},t)=\vec{j}_2e^{i[(\vec{q}_1+\vec{q}_2)\cdot\vec{r}-2\omega t]}\;. \qquad \text{(B2)}$$

In a noninteracting electron gas, time-dependent perturbation theory taken to second order gives for $\vec{j}_2$

$$j_2=-\frac{e^3\hbar}{4m^2\omega^2}\frac{2}{(2\pi)^3}(\vec{E}_1\cdot\vec{E}_2)\int\frac{(2\vec{k}+\vec{q}_1+\vec{q}_2)[f(\vec{k})-f(\vec{k}+\vec{q}_1+\vec{q}_2)]\,d^3k}{E(\vec{k})-E(\vec{k}+\vec{q}_1+\vec{q}_2)+2(h\omega+i\delta)}$$

$$\times\frac{-e^3\hbar}{2m^2\omega^2}\frac{2}{(2\pi)^3}\vec{E}_1\int\frac{(2\vec{k}+\vec{q}_2)\cdot\vec{E}_2[f(\vec{k})-f(\vec{k}+\vec{q}_2)]d^3k}{E(\vec{k})-E(\vec{k}+\vec{q}_2)+(\hbar\omega+i\delta)}$$

$$\times\frac{-e^3\hbar^3}{8m^3\omega^2}\frac{2}{(2\pi)^3}\int\frac{[(2\vec{k}-\vec{q}_2)\cdot\vec{E}_2](2\vec{k}+\vec{q}_1-\vec{q}_2)[(2\vec{k}+\vec{q}_1)\cdot\vec{E}_1][f(\vec{k}+\vec{q}_1)-f(\vec{k})]\,d^3k}{[E(\vec{k})-E(\vec{k}+\vec{q}_2)+(\hbar\omega+i\delta)][E(\vec{k}-\vec{q}_2)-E(\vec{k}+\vec{q}_1)+2(\hbar\omega+1\delta)]}$$

$$+\frac{[(2\vec{k}-\vec{q}_2)\cdot\vec{E}_2](2\vec{k}+\vec{q}_1-\vec{q}_2)[(2\vec{k}+\vec{q}_1)\cdot\vec{E}_1][f(\vec{k}-\vec{q}_2)-f(\vec{k})]\,d^3k}{[E(\vec{k}-\vec{q}_2)-E(\vec{k})+(\hbar\omega+i\delta)][E(\vec{k}-\vec{q}_2)-E(\vec{k}+\vec{q}_2)+2(\hbar\omega+i\delta)]}$$

$$+\text{the same function with } \vec{E}_1,\ \vec{q}_1 \longrightarrow \vec{E}_2,\ \vec{q}_2\ . \qquad \text{(B3)}$$

$f(\vec{k})$ is a Fermi factor defined by

$$f(\vec{k})=0 \text{ if } k>k_F$$
$$=1 \text{ if } k<k_F\ ,$$
$$E(\vec{k})=\hbar^2k^2/2m\ ,$$

and $\delta$ is a real positive infinitesimal. Equation (B3) is a special case of the response formula derived for a metal with general band structure by Cheng and Miller.[6]

If $\vec{q}_1$ and $\vec{q}_2$ are small compared to $\omega/v_F$, where $v_F$ is the Fermi velocity, then (B3) can be evaluated to lowest order in the two wave numbers to yield

$$\vec{j}_2=-\frac{n_0e^3}{2m^2\omega^3}(\vec{q}_1+\vec{q}_2)(\vec{E}_1\cdot\vec{E}_2)$$

$$-\frac{n_0e^3}{m^2\omega^3}[\vec{E}_1(\vec{q}_2\cdot\vec{E}_2)+\vec{E}_2(\vec{q}_1\cdot\vec{E}_1)]\ . \qquad \text{(B4)}$$

This result can be Fourier transformed into configuration space to yield Eq. (2), which is valid if the perturbing electric field is spatially slowly varying. The low-$q$ limit (B4) is a general result for a homogeneous electron gas—as is shown in Appendix C—and can also be derived from a simple hydrodynamic picture of electron gas response.

If one of the wave numbers is small and the other has a general value, then the second-order response of the noninteracting electron gas can be expressed in terms of its first-order response operators. Suppose, for instance, that $q_2 \ll \omega/v_F$. Then (B3) yields to zeroth order in $q_2$

$$\vec{j}_2=-\frac{e\vec{q}_1}{m\omega}\left(\frac{\vec{E}_1\cdot\vec{E}_2}{q_1^2}-\frac{4(\vec{q}_1\cdot\vec{E}_1)(\vec{q}_1\cdot\vec{E}_2)}{q_1^4}\right)\alpha(q_1,2\omega)+\frac{e}{m\omega^3}(\vec{q}_1\cdot\vec{E}_2)\left(\vec{E}_1-\frac{\vec{q}_1(\vec{q}_1\cdot\vec{E}_1)}{q_1^2}\right)\beta(q_1,2\omega)$$
$$-\frac{e}{m\omega^3}(\vec{q}_1\cdot\vec{E}_1)\frac{1}{q_1^2}\left(\vec{E}_2+\frac{\vec{q}_1\cdot\vec{E}_2}{q_1^2}\right)\alpha(q_1,\omega)-\frac{e}{m\omega^3}(\vec{q}_1\cdot\vec{E}_2)\left(\vec{E}_1-\frac{\vec{q}_1\cdot\vec{E}_1}{q_1^2}\right)\beta(q_1,\omega)\ . \qquad \text{(B5)}$$

$\alpha(q,\omega)$ and $\beta(q,\omega)$ are defined by the first-order response equation for the homogeneous noninteracting electron gas,

$$\vec{j}(\vec{q},\omega)=-\frac{\omega}{iq^4}(\vec{q}\cdot\vec{E})\vec{q}\,\alpha(q,\omega)+\frac{\vec{E}-(\vec{q}\cdot\vec{E})\vec{q}}{q^2}\ \frac{[-1-\beta(q,\omega)]}{i\omega}\ . \qquad \text{(B6)}$$

They are given by the following expressions:

$$\alpha(q,\omega)=-\frac{1}{4\pi}\frac{k_{\text{TF}}^2}{2}\left\{\frac{1}{2q'}\left[1-\left(\frac{q'}{2}-\frac{\omega'}{2q'}\right)^2\right]\ln\left(\frac{1+q'/2-\omega'/2q'}{-1+q'/2-\omega'/2q'}\right)\right.$$
$$\left.+\frac{1}{2q'}\left[1-\left(\frac{q'}{2}+\frac{\omega'}{2q'}\right)^2\right]\ln\left(\frac{1+q'/2+\omega'/2q'}{-1+q'/2+\omega'/2q'}\right)+1\right\}\ , \qquad \text{(B7)}$$

$$\beta(q,\omega)=-\frac{1}{4\pi}\frac{\hbar^2k_F^2k_{\text{TF}}^2}{3M}\left\{\frac{3}{16q'}\left[1-\left(\frac{q'}{2}-\frac{\omega'}{2q'}\right)^2\right]^2\ln\left(\frac{1+q'/2-\omega'/2q'}{-1+q'/2-\omega'/2q'}\right)\right.$$
$$\left.+\frac{3}{16q'}\left[1-\left(\frac{q'}{2}+\frac{\omega'}{2q'}\right)^2\right]^2\ln\left(\frac{1+q'/2-\omega'/2q'}{-1+q'/2-\omega'/2q'}\right)+\frac{5}{8}-\frac{q'^2}{8}-\frac{3\omega'^2}{8q'^2}\right\}\ , \qquad \text{(B8)}$$

where

$$k_{\text{TF}}=(3\omega_p/v_F)^{1/2}\ ,$$
$$q'\equiv q/k_F\ ,$$
$$\omega'\equiv 2M(\omega+i\delta)/\hbar k_F^2\ .$$

Expression (B5) can also be verified in generality for an interacting isotropic electron gas (see Appendix C). By taking (B5) plus the expression obtained by interchanging $\vec{E}_1$, $\vec{q}_1$ with $\vec{E}_2$, $\vec{q}_2$ in it and evaluating the sum to leading orders in $q_1$ and $q_2$ for small $q_1$ and $q_2$ one obtains (B4), as is to be expected.

The second-order response kernel for the isotropic noninteracting electron gas can be evaluated for general values of $\vec{q}_1$ and $\vec{q}_2$. However, because in the problem of interest only the longitudinal components of the electric fields are significant for large wave numbers, we evaluate (B3) for $\vec{E}_1$, $\vec{E}_2$ longitudinal only. Setting $E_i = i\vec{q}_i\phi_i$, we obtain for arbitrary $\vec{q}_i$'s

$$\vec{j}_2 = \frac{-2\omega(\vec{q}_1+\vec{q}_2)}{|\vec{q}_1+\vec{q}_2|^3}\,\frac{e^3m^2}{\hbar^2}\,\frac{\phi_1\phi_2}{2\pi^2}\left[\frac{1}{q_1'}F_1\left(\frac{q_1'+\omega'}{2},\ \frac{|\vec{q}_1'+\vec{q}_2'|+2\omega'}{2},\ \theta_1\right)\right.$$
$$-\frac{1}{q_1'}F_1\left(\frac{-q_1'+\omega'}{2},\ \frac{q_2'^2-q_1'^2}{2|\vec{q}_1+\vec{q}_2'|}+\omega',\ \theta_1\right)+\frac{1}{q_2'}F_1\left(\frac{-q_2'+\omega'}{2},\ \frac{-|\vec{q}_1'+\vec{q}_2'|+2\omega'}{2},\ \theta_2\right)$$
$$\left.-\frac{1}{q_2'}F_1\left(\frac{q_2'+\omega'}{2},\ \frac{q_2'^2-q_1'^2}{2|\vec{q}_1'+\vec{q}_2'|}+\omega',\ \theta_2\right)+\text{the same function of } -\omega\right]. \tag{B9}$$

$\theta_1$ and $\theta_2$ are defined in Fig. 3, $\vec{q}_1'$ and $\vec{q}_2'$ are defined analogously to the definitions after (B8), and

$$F(x,y,\theta) = -\frac{1}{\sin^2\theta}\,(x^2+y^2-2xy\cos\theta-\sin^2\theta')^{-1/2}\ln\left(\frac{[(x^2+y^2-2xy\cos\theta-\sin^2\theta)^{1/2}+xy-\sin^2\theta]^2}{(1-x^2)(1-y^2)}\right)$$
$$+\frac{1}{\sin^2\theta}\left[(x\cos\theta-y)\ln\left(\frac{x+1}{x-1}\right)+(y\cos\theta-x)\ln\left(\frac{y+1}{y-1}\right)\right]. \tag{B10}$$

If $\vec{q}_1$ and $\vec{q}_2$ are parallel, then the second-order current is given by

$$\vec{j}_2 = \frac{\vec{q}_1+\vec{q}_2}{q_1+q_2}\,2i\omega\,L(q_1,q_2,\omega)\phi_1\phi_2\,, \tag{B11}$$

where

$$L(q_1,q_2,\omega) = -\frac{2em}{\hbar^2k_F^2}\,\frac{q_1'q_2'(q_1'+q_2')}{[q_1'q_2'(q_1'+q_2')]^2-[\omega'(q_1'+q_2')]^2}\,[q_1'\alpha(q_1,\omega)+q_2'\alpha(q_2,\omega)-(q_1'+q_2')\alpha(q_1+q_2,2\omega)]\,. \tag{B12}$$

## APPENDIX C: SOME GENERAL RESULTS FOR INTERACTING ELECTRON GAS

Results (B4) and (B5) are not unique to a noninteracting electron gas. They also hold in general for an isotropic interacting electron gas. That will be established in this appendix, along with a demonstration that the magnitude of the SH surface current is given by (38) and (39), with $b=1$, for an interacting electron gas if we neglect the effects of the periodic ionic background and surface roughness. We start by considering the second-order response of an isotropic electron gas. If we have a perturbing field of the form (B1), the $\vec{j}_2$ as defined by (B2) is given by

$$\vec{j}_2 = \frac{e}{m\omega q_1^2}\,\vec{E}_2(\vec{q}_1\cdot\vec{E}_1)\,\alpha(q_1,\omega)+\frac{e(\vec{E}_1\cdot\vec{E}_2)(\vec{q}_1+\vec{q}_2)}{m\omega|\vec{q}_1+\vec{q}_2|^2}\,\alpha(|\vec{q}_1+\vec{q}_2|,2\omega)$$
$$-\frac{1}{\omega^2}\sum_{m,n}\left(\frac{\langle 0|\vec{j}(\vec{q}_1+\vec{q}_2)|m\rangle\langle m|\vec{j}(-\vec{q}_2)\cdot\vec{E}_2|n\rangle\langle n|\vec{j}(-\vec{q}_1)\cdot\vec{E}_1|0\rangle}{[E_0-E_m+2(\hbar\omega+i\delta)][E_0-E_n+(\hbar\omega+i\delta)]}\right.$$
$$+\frac{\langle 0|\vec{j}(-\vec{q}_1)\cdot\vec{E}_1|m\rangle\langle m|\vec{j})(\vec{q}_1+\vec{q}_2)|n\rangle\langle n|\vec{j}(-\vec{q}_2)\cdot\vec{E}_2|0\rangle}{[E_0-E_m-(\hbar\omega+i\delta)][E_0-E_n-2(\hbar\omega+i\delta)]}$$
$$\left.+\frac{\langle 0|\vec{j}(-\vec{q}_1)\cdot\vec{E}_1|m\rangle\langle m|\vec{j}(-\vec{q}_2)\cdot\vec{E}_2|n\rangle\langle n|\vec{j}(\vec{q}_1+\vec{q}_2)|0\rangle}{[E_0-E_m-(\hbar\omega+i\delta)][E_0-E_n-2(\hbar\omega+i\delta)]}\right)$$
$$+\text{the same function with } \vec{E}_1,\ \vec{q}_1 \longleftrightarrow \vec{E}_2,\ \vec{q}_2\,, \tag{C1}$$

where $\alpha(a,\omega)$ is defined by the first-order response equation (B6), the equation being now for an interacting electron gas.

We now specify that we are considering the irreducible second-order response of the electron gas. What that means physically is that we are interested in the response that gives the unshielded second-order current in terms of the self-consis-

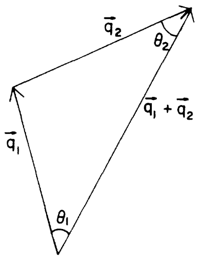


FIG. 3. Defining figure for $\theta_1$ and $\theta_2$, which appear in (B9) and (B10).

tent electric fields. Diagrammatically that excludes all diagrams that can be cut into two by severing a single interaction line. A reducible and an irreducible three-point diagram, corresponding to the term in large parentheses in (C1), are shown in Fig. 4.

The specification just adopted allows us to simplify the response in (C1) if $\vec{q}_1$ or $\vec{q}_2$ is small. Suppose, for instance, that $\vec{q}$ is small. Then, in the term in large parentheses in (C1), $\vec{j}(-\vec{q}_2)$ can be replaced with errors of order $q_2 v_F/\omega$ by the total current operator. That operator when applied to an energy eigenstate with momentum $\hbar\vec{q}$ simply multiplies it by $e\hbar\vec{q}/m$. Using that fact and the low-$q$ properties of the irreducible $\alpha(\vec{q},\omega)$, we obtain to zeroth order in $q_2$

$$\vec{j}_2=-\frac{e}{m\omega q_1^2}\vec{E}_2(\vec{q}_1\cdot\vec{E}_1)\,\alpha(q_1,\omega)-\frac{e(\vec{E}_1\cdot\vec{E}_2)}{m\omega q_1^2}\,\vec{q}_1\,\alpha(q_1,2\omega)$$
$$-\frac{1}{\omega^2}\,\frac{e\hbar(\vec{q}_1\cdot\vec{E}_2)}{m}\sum_m\left(\frac{\langle 0|\vec{j}(\vec{q}_1)|m\rangle\langle m|\vec{j}(-\vec{q}_2)\cdot\vec{E}_1|0\rangle}{[E_0-E_m+2(\hbar\omega+i\delta)][E_0-E_m+(\hbar\omega+i\delta)]}\right.$$
$$\left.-\frac{\langle 0|\vec{j}(-\vec{q}_1)\cdot\vec{E}_1|m\rangle\langle m|\vec{j}(\vec{q}_1)|0\rangle}{[E_0-E_m-2(\hbar\omega+i\delta)][E_0-E_m-(\hbar\omega+i\delta)]}\right)\,. \quad \text{(C2)}$$

Manipulating the term in large parentheses in (C2) so as to obtain single energy denominators gives the response in terms of first-order response operators. Using the symmetry properties of the isotropic electron gas leads to (B5) with the defining response equation (B6) being the irreducible first-order response equation for an interacting electron gas. Taking the sum of (B5) and the equation obtained by interchanging $\vec{E}_1$, $\vec{q}_1$ and $\vec{E}_2$, $\vec{q}_2$ in it and using the small-$q$ properties of the irreducible first-order response operators[16] leads to the response equation (B4) in an interacting electron gas when $\vec{q}_1$ and $\vec{q}_2$ are small.

It is necessary that the response be irreducible in order for the statements about the convergence of the long-wavelength current operator to the total current operator to be true. Allowing plasma-wave collective excited states as intermediate states—those states being excluded from the irreducible response—destroys the smooth convergence.[16] We note that dealing with the irreducible response operator is consistent with the method adopted in this paper for calculating the SH radiation in which the first-order EM fields to be inserted into the second-order response equation are found by solving the self-consistent Maxwell's equations and the second-order current is used as the unshielded driving current to find the SH radiation.

A result similar to (B5) can be obtained in an electron gas with translational symmetry in two dimensions only. Suppose that the electron gas is translationally symmetric in the $x$ and $y$ directions and is perturbed by an electric field of the form

$$\vec{E}(\vec{r},t)=\vec{E}_1(z)e^{i(\vec{q}_1\cdot\vec{R}-\omega t)}+\vec{E}_2(z)e^{i(\vec{q}_2\cdot\vec{R}-\omega t)}\,,$$
$$\vec{R}=\hat{x}x+\hat{y}y\,. \quad \text{(C3)}$$

Then the second-order current is of the form

$$\vec{j}(\vec{r},t)=\vec{j}_2(z)\,e^{i[(\vec{q}_1+\vec{q}_2)\cdot\vec{R}-2\omega t]}\,. \quad \text{(C4)}$$

Suppose now that $\vec{E}_2(z)$ is slowly varying with a characteristic length of variation much greater than $v_F/\omega$, that it has no $z$ component, and that $q_1$, $q_2 \ll \omega/v_F$. Then, using reasoning similar to that used above, we obtain for $\vec{j}_2(z)$ to lowest order in $\vec{q}_1$, $\vec{q}_2$ and the variation in $z$ of $\vec{E}_2(z)$, due to the irreducible response,

$$\vec{j}_2(z)=-\frac{e}{m\omega^2}\vec{E}_2(z)\int\sum_m\left(\frac{\langle 0|\rho(z)|m\rangle\langle m|j_z(z')|0\rangle}{E_0-E_m+(h\omega+i\delta)}+\frac{\langle 0|j_z(z')|m\rangle\langle m|\rho(z)|0\rangle}{E_0-E_m-(h\omega+i\delta)}\right)\vec{E}_{1z}(z')\,dz'$$
$$-\frac{e}{\omega^2}\,\hat{z}\,\vec{E}_2(z)\left(\int\sum_m\frac{\langle 0|j_z(z)|m\rangle\langle m|\rho(z')|0\rangle}{E_0-E_m+(\hbar\omega+i\delta)}+\frac{\langle 0|\rho(z')|m\rangle\langle m|j_z(z)|0\rangle}{E_0-E_m-(h\omega+i\delta)}\;\vec{E}_1(z')\,dz'\right). \quad \text{(C5)}$$

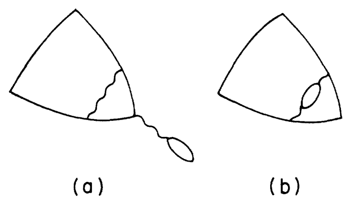


FIG. 4. (a) Reducible and (b) irreducible three-point diagrams.

We are interested in a strongly localized $\vec{j}_2(z)$ which is in the region of a rapid variation in $\vec{E}_1(z)$. In an electron gas considered here a rapidly varying electric field is longitudinal, so the rapidly varying part of $\vec{E}_1(z)$ is in the $z$ direction. The strongly localized $\vec{j}_2(z)$ is then parallel to $\vec{E}_2(z)$ and corresponds to the parallel surface current. To find the radiation due to such a $\vec{j}_2(z)$ it is sufficient to know the total integrated strength. We therefore integrate (C5) over a region large compared to the region of variation of $E_{1z}(z)$ but small compared to the characteristic variation length of $\vec{E}_2(z)$, which in the problem considered in this paper is the order of an optical skin depth. Performing such an integration allows us to take $\vec{E}_2(z)$ out of the integral and to expand the denominator of the response operator in terms of $\hbar\omega/(E_0 - E_m)$. Only the first term in that expansion is retained, the rest being smaller by orders of $\omega l/v_F$, where $l$ is the distance integrated over. We obtain

$$\int_{\bar{z}-l/2}^{\bar{z}+l/2} \vec{j}_2(z) \approx -\frac{e}{\hbar m\omega^3} E_2(\bar{z}) \int_{\bar{z}-l/2}^{\bar{z}+l/2} \int_{-\infty}^{\infty} \langle 0 | [\rho(z) j_z(z') - j_z(z')\rho(z)] | 0 \rangle E_{1z}(z')\, dz'\, dz$$

$$= \frac{-e^3}{im\omega^3} \vec{E}_2(\bar{z}) \int_{\bar{z}-l/2}^{\bar{z}+l/2} \frac{d}{dz} [n(z) E_{1z}(z)]\, dz = \frac{-e^3}{im\omega^3} \vec{E}_2(z) [n(z) E_{1z}(z)] \Big|_{\bar{z}-l/2}^{\bar{z}+l/2} . \qquad \text{(C6)}$$

In going from the first line on the right-hand side of (C6) to the second, the equal-time commutation properties of the current and charge density operators were used. The result (C6) applied to the surface of a half-space metal yields a parallel surface current with magnitude (38) and (39) with $b$ equal to 1. We note that the magnitude of the current is not sensitive to the detailed structure of the longitudinal first-order electric field in the surface region.

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