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Effects of electron band structure on optical second-harmonic generation at metal surfaces[*]

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A quantum-mechanical calculation of optical second-harmonic generation at highly conductive surfaces shows that the process is extremely sensitive to any changes in the optical density of states at the Fermi level and the states one- and two-photon energies above and below. The results indicate that this method can give detailed resolution of the energy-band structure of electrons in the surface layer of atoms.

I. INTRODUCTION

Recent experiments in optical second-harmonic generation at metal surfaces have shown great sensitivity to surface condition. The most dramatic example to date is found in the second harmonic generated when a ruby laser beam is reflected from a freshly evaporated copper film in ultrahigh vacuum. With the addition of a submonolayer film of Na, sufficient to lower the work function 0.02 eV, the second harmonic increases more than 35%. Additional Na to reduce the work function another 0.02 eV reduces the second harmonic by a factor greater than 7.[1] This occurs with a total Na coverage of the order of 0.01 monolayer.

This paper is an investigation of the second-harmonic generation process at metal surfaces. The most likely cause of large changes in generation efficiency with small changes in surface condition is found to be shifts in electron energy levels within the surface layer of atoms.

A calculation of the second-harmonic current is presented in Sec. II. This current is the source of the second-harmonic radiation field, and it is found by second-order time-dependent perturbation theory. No particular model of the surface is needed in the derivation. The current is given in terms of the unperturbed electron energies and wave functions in the surface layer. The calculation does assume that the material is a good conductor and that the bulk crystal structure has inversion symmetry.

The most general quantum-mechanical calculation of optical harmonic generation at a metal surface was published in 1967 by Jha and Warke.[2] This calculation agreed with an earlier result of Jha's based on a classical calculation.[3] This showed that the nonlinear polarization, which is the source of the second-harmonic field, may be given by $\vec{P}^{NL}_{(2\omega)} = \alpha(\vec{E}\times\vec{H}) + \beta\vec{E}(\vec{\nabla}\cdot\vec{E})$. This result is derived using the assumptions that (i) the band gaps are not equal to or near $\hbar\omega$ and (ii) the incident electromagnetic wave $\vec{E} = \vec{E}_0 e^{i(\vec{q}\cdot\vec{x}-\omega T)}$ may be treated in the $\vec{q}\rightarrow 0$ limit.

The first term in the above expression for $\vec{P}^{NL}_{(2\omega)}$ is a magnetic dipole and the second an electric quadrupole in nature. It was soon found in experiment that the quadrupole term is dominant in reflection from metals and semiconductors having inversion symmetry.[4] The magnitude of the quadrupole term is clearly controlled by the magnitude of $\vec{\nabla}\cdot\vec{E}$ which is largest in the surface layer of atoms, where the normal component of the electric field is reduced by a factor $1/\epsilon$ in a distance of the order of 10^{-8} cm. Therefore the quadrupole term is also called the surface term.

By using earlier results on the quantum-mechanical calculation of the dielectric tensor by Adler,[5] it was found that the constant α could be expressed in terms of $\epsilon(2\omega)$, the value of $\vec{\nabla}\cdot\vec{E}$ could be expressed in terms of $\epsilon(\omega)$, and β was a constant, independent of the material involved.[2]

This provides the connection to nonlinear optical theories treating the fields within transparent crystals lacking inversion symmetry. These theories treat ϵ as a tensor, and find $\vec{P}$ by a power series in the electric fields. A large range of frequency mixing and higher-harmonic generation phenomena are currently studied in nonlinear optics.

The difficulty in this earlier theory is that the effects of surface condition are not well explained. They are qualitatively explained as caused by a difference in ϵ of an adsorbed layer,[4] or a contribution from the third-order susceptibility $\chi^{(3)}$ arising from the dc field produced by a permanent dipole layer.[6] These surface-condition effects were not noticed in the first experimental measurements of second harmonics from silver[7] but were soon found to be important.[8]

The first quantum-mechanical calculations of these surface effects were carried out by Rudnick and Stern.[9] They used a free-electron-gas model to calculate the second-harmonic response to an external field and the second-harmonic radiation from the resultant second-harmonic current sources. They found that within the surface layer the current normal to the surface was different from that found earlier because of two factors; the breaking of inversion symmetry at the surface and the rapid variation of the surface normal field. In regard to the second of these, the electromagnetic field cannot be treated in the $\vec{q} \rightarrow 0$ limit because the rapid variation of the field requires large values of $\vec{q}$ normal to the surface in the Fourier expansion. This leads to the use of the nonlocal, or wave-vector dependent, $\epsilon(\vec{q}, \omega)$ in the radiation equations. They further found that the surface currents involved are sensitive to the surface condition, and that changes in radiation with changes in surface condition are caused primarily by variations in the parallel surface currents. These, in turn, are caused by variations in electron scattering at the surface. As Rudnick and Stern point out, of the various experimental studies in this field, their theory applies well only to studies of second harmonics from Ag using the 1.06-μm Nd-glass laser. For other wavelengths and other materials interband transitions are important. The Jha and Warke theory is designed to account for interband transitions but does not include the dispersion of $\vec{q}$ values.

The result presented here is a modification of the Jha and Warke theory. The large values of $\vec{q}$ from the surface normal field are included and lead to the conclusion that the second-harmonic currents are very sensitive to the density of states at the Fermi level and the states one- and two-photon energies above or below. Any variation in the electron structure at these energies will produce variations in the radiated intensity. This variation is in addition to the variation caused by scattering found by Rudnick and Stern. The reason for this lies essentially in the calculation of the parallel surface current from the term $\beta\vec{E}(\vec{\nabla}\cdot\vec{E})$. In deriving their Eq. (20), Rudnick and Stern use the Drude formula $\epsilon = 1 - \omega_p^2/\omega^2$. In the Jha and Warke calculation there are terms which they show are equivalent to Adler's $\epsilon(\vec{q}, \omega)$. It is these terms which are modified by including all $\vec{q}$ values from the normal field, and the interband effects on the nonlocal ϵ lead to the new results. The dielectric constant of the surface layer is, in fact, a tensor which is not well represented by the dielectric constant of the bulk.

An expression for the anisotropic dielectric tensor at metal surfaces has been derived,[10] and could be included in either of these previous theories. However, because of the complicated nature of the expression for the tensor, it seems more reasonable to express the second-harmonic currents which are most sensitive to surface conditions in terms of the electron energies and wave functions directly.

Section III presents a discussion of the range of $\vec{q}$ values which must be included in the calculations. Because the interband contributions to the currents are central to the theory and experiment, we also discuss the band structure at the surface and the changes to be expected under experimental conditions.

II. QUANTUM-MECHANICAL THEORY

This section describes a modified quantum-mechanical theory of second-harmonic generation from the surface layer of atoms on a conductive material. The development follows that of Jha,[11] as extended by Jha and Warke,[2] up to the point where the momentum-space Fourier expansion of the electromagnetic field is inserted. At that point the development changes because large momentum components are important in the surface-charge-region fields, resulting in quite different conclusions.

The generated second-harmonic radiation can be found from the Maxwell wave equations with the nonlinear second-harmonic current in the metal as the source.

The microscopic Maxwell equations are

$$\vec{\nabla}\cdot\vec{E} = 4\pi\rho, \quad \vec{\nabla}\times\vec{E} + \frac{1}{c}\frac{d\vec{B}}{dT} = 0 ,$$

$$\vec{\nabla}\cdot\vec{B} = 0, \quad \vec{\nabla}\times\vec{B} = \frac{4\pi}{c}\vec{J} + \frac{1}{c}\frac{d\vec{E}}{dT} .$$

By choosing a gauge such that $d\phi/dt = 0$, with $\vec{B} = \vec{\nabla}\times\vec{A}$ and $\vec{E} = -(1/c)\,d\vec{A}/dT$, these become

$$\vec{\nabla}\times\vec{\nabla}\times\vec{A} + \frac{1}{c^2}\frac{d^2\vec{A}}{dT^2} = \frac{4\pi}{c}\vec{J}, \quad -\frac{1}{c}\frac{d}{dT}(\vec{\nabla}\cdot\vec{A}) - \nabla^2\phi_0 = 4\pi\rho . \tag{1}$$

The second-harmonic field $\vec{A}$ is found from its source current $\vec{J}$.

We can find the current $\vec{J}$ induced by the incident light in terms of the electron wave functions in the metal. The current is found by second-order time-dependent perturbation theory. Jha and Warke[2] find an expression for $\vec{J}(2\vec{q})$, where $\vec{J}(\vec{r}, T) = \vec{J}(2\vec{q})\,e^{i2(\vec{q}\cdot\vec{r}-\omega T)}$. The factors $2\vec{q}$ and 2ω arise from the square of the incident radiation field, which is taken to be $\vec{A}(\vec{r}, T) = \vec{a}(\vec{q})\,e^{i(\vec{q}\cdot\vec{r}-\omega T)}$. In our derivation we wish to keep all the Fourier components of the field in the surface-charge layer, so we have taken $\vec{A}(\vec{r}, T) = \sum_q \vec{a}(\vec{q})\,e^{i(\vec{q}\cdot\vec{r}-\omega T)}$. The square of this field is

$$\sum_q \sum_{q'} \vec{a}(\vec{q})\vec{a}(\vec{q}\,')\,e^{i[(\vec{q}+\vec{q}\,')\cdot\vec{r}-2\omega T]},$$

so we will accordingly take

$$\vec{J}(\vec{r}, T) = \sum_q \sum_{q'} \vec{J}(\vec{q}, \vec{q}\,')\,e^{i[(\vec{q}+\vec{q}\,')\cdot\vec{r}-2\omega T]} ,$$

where $\vec{J}(\vec{q}, \vec{q}\,')$ is [from Ref. 2, Eqs. (3.10)-(3.12)]

$$\begin{aligned}\vec{J}(\vec{q},\vec{q}\,') = {} & \left(\frac{e^3}{2m^2c^2}\right)\vec{a}(\vec{q})\cdot\vec{a}(\vec{q}\,') \sum_{kbb''} (b\vec{k}\,|\vec{p}+\hbar\vec{k}+\hbar(\vec{q}+\vec{q}\,')/2\,|\,b''\vec{k}+\vec{q}+\vec{q}\,')(b''\vec{k}+\vec{q}+\vec{q}\,'\,|\,b\vec{k})M(b''\vec{k}+\vec{q}+\vec{q}\,',\, b\vec{k},\, 2\omega)\\ & +\left(\frac{e^3}{m^2c^2}\right)\vec{a}(\vec{q}\,')\sum_{kbb'} (b\vec{k}\,|\,b'\vec{k}+\vec{q})(b'\vec{k}+\vec{q}\,|\,\vec{a}(\vec{q})\cdot(\vec{p}+\hbar\vec{k}+\hbar\vec{q}/2)\,|\,bk)M(b'\vec{k}+\vec{q},\, b\vec{k},\, \omega)\\ & -\left(\frac{e^3}{m^3c^2}\right)\sum_{kbb'b''} (b\vec{k}\,|\vec{p}+\hbar\vec{k}+\hbar(\vec{q}+\vec{q}\,')/2\,|\,b''\vec{k}+\vec{q}+\vec{q}\,')\,(b''\vec{k}+\vec{q}+\vec{q}\,'\,|\,\vec{a}(\vec{q}\,')\cdot[\vec{p}+\hbar(\vec{k}+\vec{q})+\hbar\vec{q}\,'/2]\,|\,b'\vec{k}+\vec{q})\\ & \times(b'\vec{k}+\vec{q}\,|\,\vec{a}(\vec{q})\cdot(\vec{p}+\hbar\vec{k}+\hbar\vec{q}/2)\,|\,b\vec{k})N(b''\vec{k}+\vec{q}+\vec{q}\,',\, b'\vec{k}+\vec{q},\, b\vec{k},\, \omega,\, \omega)\ ,\end{aligned} \tag{2}$$

where

$$M(b'\vec{k}\,',\, b\vec{k},\, \omega) = -\frac{f_0(E_{b'\vec{k}'}) - f_0(E_{b\vec{k}})}{E_{b'\vec{k}'} - E_{b\vec{k}} - \hbar\omega - i\epsilon} \tag{3}$$

and

$$N(b''\vec{k}\,'',\, b'\vec{k}\,',\, b\vec{k},\omega,\,\omega) = \frac{M(b'\vec{k}\,',\, b\vec{k},\, \omega) - M(b''\vec{k}\,'',\, b'\vec{k}\,',\, \omega)}{E_{b''\vec{k}''} - E_{b\vec{k}} - 2\hbar\omega - 2i\epsilon}\ . \tag{4}$$

In the original derivation, the first term is the $\alpha(\vec{E}\times\vec{H})$ current, the second is $\beta\vec{E}\vec{\nabla}\cdot\vec{E}$, and the third is unimportant if there are no band gaps equal to $\hbar\omega$. The original unperturbed wave functions are assumed to be Bloch function solutions to the one electron wave equation, located in a band b. Then $|\vec{k}b\rangle = |\vec{k}b)\,e^{i\vec{k}\cdot\vec{r}}$. The summations are over all states $|\vec{k}b\rangle$ in all bands. $f_0(E_{b\vec{k}})$ is the Fermi-Dirac distribution at the energy of state $|b\vec{k}\rangle$. $\vec{p}$ is the momentum operator $-i\hbar\vec{\nabla}$.

We will examine the three terms separately. First, we take the second term which leads to the $\beta\vec{E}(\vec{\nabla}\cdot\vec{E})$ current. We may write

$$\begin{aligned}\vec{J}_\beta(\vec{r}) = {} & \sum_q\sum_{q'} e^{i(\vec{q}+\vec{q}\,')\cdot\vec{r}}\left(\frac{e^3}{m^2c^2}\right)\vec{a}(\vec{q}\,')\sum_{kbb'}(b\vec{k}\,|\,b'\vec{k}+\vec{q})\\ & \times(b'\vec{k}+\vec{q}\,|\,\vec{a}(\vec{q})\cdot(\vec{p}+\hbar\vec{k}+\tfrac{1}{2}\hbar\vec{q})\,|\,b\vec{k})\\ & \times M(b'\vec{k}+\vec{q},\, b\vec{k},\, \omega)\ .\end{aligned} \tag{5}$$

We use the equation $\vec{a}(\vec{r}) = \sum_{q'}\vec{a}(\vec{q}\,')\,e^{i\vec{q}\,'\cdot\vec{r}}$ and the vector $\vec{n}=\vec{k}+\vec{q}$ to write

$$\vec{J}_\beta(\vec{r}) = \frac{e^2}{mc}\vec{a}(\vec{r})\sum_q\sum_{kbb'}(b\vec{k}\,|\,b'\vec{n})I_{\vec{n}\vec{k}}M(b'\vec{n},\, b\vec{k},\, \omega)\,e^{i\vec{q}\cdot\vec{r}}\ , \tag{6}$$

$$I_{\vec{n}\vec{k}} = \frac{e}{mc}(b'\vec{n}\,|\,\vec{a}(\vec{q})\cdot(\vec{p}+\hbar\vec{k}+\tfrac{1}{2}\hbar\vec{q})\,|bk)\,\delta(\vec{n}-\vec{k}-\vec{q})\ . \tag{7}$$

Here $I_{\vec{n}\vec{k}}$ is a first-order electromagnetic interaction matrix element between states $|b'\vec{n})$ and $|b\vec{k})$.

The sum over all $\vec{q}$ is equivalent to a sum over all $\vec{n}$ because of the condition $\vec{n}=\vec{k}+\vec{q}$. We can drop the band indices b and b' if we remember that the sums of $\vec{n}$ and $\vec{k}$ involve all states with those wave vectors in all bands. Then

$$\begin{aligned}\vec{J}_\beta(\vec{r}) = {} & \frac{e^2}{mc}\,\vec{a}(\vec{r})\sum_b\sum_k\sum_n(\vec{k}\,|\,\vec{n})\\ & \times e^{i(\vec{n}-\vec{k})\cdot\vec{r}}\,I_{\vec{n}\vec{k}}M(\vec{n},\,\vec{k},\,\omega)\ .\end{aligned} \tag{8}$$

Equation (2) was derived under the assumption that the wave functions were Bloch functions with well-defined wave vectors. However, at the surface of the metal we may have localized states or covalent bonds which do not have a single well-defined wave vector. In that case we may still write the current as in Eq. (8), with the substitution of $\psi^*_{\vec{k}}\psi_{\vec{n}}$ for $(\vec{k}|\,\vec{n})\,e^{i(\vec{n}-\vec{k})\cdot\vec{r}}$ and

$$I_{\vec{n}\vec{k}} = \frac{e}{mc}\sum_q\langle\vec{n}\,|\,\vec{a}(\vec{q})\,e^{i\vec{q}\cdot\vec{r}}\cdot(\vec{p}+\hbar\vec{q}/2)\,|\,\vec{k}\rangle\ . \tag{9}$$

Equation (9) is the more general form. If we substitute $|\vec{k}\rangle = |\vec{k})\,e^{i\vec{k}\cdot\vec{r}}$ and similarly for $|\vec{n}\rangle$ we get back to Eq. (7).

To carry out the summations in $\vec{n}$ and $\vec{k}$, we convert the summations to integrals over a density of states. This is complicated by the factor $M(\vec{n},\vec{k},\omega)$ [Eq. (3)] with its singularity in the energy denominator. We end up with a double integral over energies E_k and E_n and integrals over vectors $\vec{n}$ and $\vec{k}$ within each energy shell. The singularity may be handled by separation of real and imaginary parts or a contour integral. In either case we reach the same result. The term arising from the singularity, in the $\epsilon\to 0$ limit, is

$$\vec{J}_{\beta s} = \frac{i\pi e^2}{mc}\vec{a}(\vec{r})\int dE_k\sum_b\int d^3k\int d^3n\,\delta(E_k-E(\vec{k}))\delta(E(\vec{n})-E(\vec{k})-\hbar\omega)\rho(\vec{k})\rho(\vec{n})(\vec{k}\,|\,\vec{n})\,e^{i\vec{q}\cdot\vec{r}}I_{\vec{n}\vec{k}}[f_0(E_k)-f_0(E_n)]\ . \tag{10}$$

The principal-value integral past the singularity is

$$\vec{J}_{\beta\text{pv}} = \frac{e^2}{mc}\,\vec{a}(\vec{r})\int dE_n\int dE_k\left(\sum_b\int d^3k\int d^3n\,\delta(E_k-E(\vec{k}))\delta(E_n-E(\vec{n}))\rho(\vec{k})\rho(\vec{n})(\vec{k}\,|\,\vec{n})\,e^{i\vec{q}\cdot\vec{r}}I_{\vec{n}\vec{k}}\right)M(\vec{n},\vec{k},\omega)\ . \tag{11}$$

We would expect that $\vec{J}_{\beta pv}$ is a current term leading to second-harmonic radiation, while the term $\vec{J}_{\beta s}$, which involves states separated by $\hbar\omega$, should represent absorbtion of radiation. An analysis of the terms shows that this is the case. The momentum-space integrals in Eqs. (10) and (11) are complex, but it is possible to rearrange them. Instead of integrating over all space, we can add together the current contributions of states involving vectors $\vec{n}, \vec{k}$, and $\vec{q}$ and those involving $-\vec{n}$, $-\vec{k}$, and $-\vec{q}$. If we do this we find that one is the complex conjugate of the other. The integral of this sum over half of momentum space is pure real. The factor $\vec{a}(\vec{r})$ is imaginary, so $\vec{J}_{\beta pv}$ is imaginary and $\vec{J}_{\beta s}$ is real. From the original perturbation equations[2] it is apparent that the second-harmonic radiation source $\vec{J}_\beta$ must be imaginary. The real current from the singularity term must represent absorbtion.

When the energy integral of Eq. (10) is carried out we find that there will be absorbtion between every pair of states separated by $\hbar\omega$, as long as both are within $\hbar\omega$ of the Fermi level. The strength of absorbtion of each pair is proportional to $(\vec{n}|\vec{k})I_{nk}$, which will vary greatly, but the total absorbtion is unlikely to vary rapidly with small changes of surface condition.

The energy integrals of Eq. (11) make this term extremely sensitive to surface conditions. The integral is of the form

$$\vec{J}_{\beta pv} = \int dE_n \int dE_k \frac{\rho(E_n)\rho(E_k)S[f_0(E_n) - f_0(E_k)]}{E_k + \hbar\omega - E_n},$$

with $\rho(E)$ as an energy density of states and S as an effective interaction strength. The numerator is small. Theoretically, it is the result of a perturbation which is weak compared with the interatomic fields, and, experimentally, the process has very low efficiency. This means the integrand has significant magnitude only when the denominator is near zero. If we hold E_n constant and integrate over E_k, we find that the integrand changes sign at $E_k = E_n - \hbar\omega$. The integral will be zero unless the numerator changes at or near $E_n - \hbar\omega$. To get a large value we must have a band edge or the Fermi level at $E_k = E_n - \hbar\omega$. Similarly, if we hold E_k constant and integrate E_n we will get a large value only if there is a band edge or Fermi level at $E_n = E_k + \hbar\omega$. The double integral is large only if two band edges, or a band edge and the Fermi level, are separated by $\hbar\omega$. This point will be considered further in Sec. III, after a discussion of the surface fields and band structure.

We can make a similar analysis of the other two terms in Eq. (2) to find $\vec{J}_\alpha(\vec{r})$ from the first term and $\vec{J}_\gamma(\vec{r})$ from the third. We sum the $\vec{J}(\vec{q}, \vec{q}')$ terms as in Eq. (5), convert the sums of $\vec{k}, \vec{q}, \vec{q}'$ to sums of $\vec{k}, \vec{n}$ and these to energy integrals with singularities, and separate these into principal value and singularity components. In these cases also, we are interested only in the imaginary parts of the currents.

$$\vec{J}_\alpha(\vec{r}) = \vec{J}_{\alpha pv} + \vec{J}_{\alpha s}, \tag{12}$$

$$\vec{J}_{\alpha pv} = \frac{e^2}{2mc} \int dE_n \int dE_k \Big(\sum_b \int d^3k \int d^3n \, \delta(E_k - E(\vec{k}))\delta(E_n - E(\vec{n}))\rho(\vec{k})\rho(\vec{n})(\vec{n}|\vec{k})\vec{V}_{\vec{k}\vec{n}} \Big) M(\vec{n}, \vec{k}, 2\omega), \tag{13}$$

$$\vec{J}_{\alpha s} = \frac{i\pi e^2}{2mc} \int dE_k \sum_b \int d^3k \int d^3n \, \delta(E(\vec{n}) - E(\vec{k}) - 2\hbar\omega)\delta(E_k - E(\vec{k}))\rho(\vec{k})\rho(\vec{n})(\vec{n}|\vec{k})\vec{V}_{\vec{k}\vec{n}}[f_0(E_k) - f_0(E_n)], \tag{14}$$

$$\vec{V}_{\vec{k}\vec{n}} = \frac{e}{mc} \sum_q \vec{a}(\vec{q}) \cdot \vec{a}(\vec{q}') \, e^{i(\vec{q}+\vec{q}')\cdot\vec{r}} (\vec{k}|\vec{p} + \hbar\vec{k} + \hbar(\vec{q} + \vec{q}')/2|\vec{n})\delta(\vec{n} - \vec{k} - \vec{q} - \vec{q}'). \tag{15}$$

The vector $\vec{V}_{\vec{k}\vec{n}}$ becomes its negative complex conjugate with the change of $\vec{n}, \vec{k}, \vec{q}, \vec{q}'$ to $-\vec{n}$, $-\vec{k}$, $-\vec{q}$, $-\vec{q}'$. Thus $\vec{J}_{\alpha pv}$ is imaginary and part of the radiation source. $\vec{J}_{\alpha s}$ is real and represents the absorbtion of second-harmonic photons. In these terms the factor $\vec{V}_{kn}$ contains the vector giving the current direction. If the wave functions are not Bloch functions, change $(\vec{n}|\vec{k})$ to $\langle\vec{n}|\vec{k}\rangle$ in (13) and (14), change the momentum-space integrals to sums of states at energies E_n and E_k, and rewrite (15) as

$$\vec{V}_{\vec{k}\vec{n}} = \frac{e}{mc} \sum_q \sum_{q'} \vec{a}(\vec{q}) \cdot \vec{a}(\vec{q}') \, e^{i(\vec{q}+\vec{q}')\cdot\vec{r}} \, \tfrac{1}{2}(\psi_{\vec{k}}^* \vec{p}\psi_{\vec{n}} - \psi_{\vec{n}}\vec{p}\,\psi_{\vec{k}}^*).$$

Because of the energy integrals in Eq. (13), with the energy denominator of $M(\vec{n}, \vec{k}, 2\omega)$, $\vec{J}_{\alpha pv}$ will be large only if two band edges or a band edge and the Fermi level are separated by $2\hbar\omega$.

The $\vec{J}_\gamma(\vec{r})$ term is more complicated because the factor N[Eq. (4)] requires a large number of integrations. To make $\vec{J}_\gamma(r)$ a little simpler, we will leave it in the energy integral form before the singularity terms are separated. We use the three vectors $\vec{k}$, $\vec{m}=\vec{k}+\vec{q}$, $\vec{n}=\vec{k}+\vec{q}+\vec{q}\,'=\vec{m}+\vec{q}\,'$,

$$\begin{aligned}\vec{J}_\gamma(\vec{r}) = -\frac{e^3}{m^3c^2}\int dE_n\int dE_m\int dE_k\Big(\sum_b\int d^3n\int d^3m\int d^3k \\ \times\delta(E_n-E(\vec{n}))\delta(E_m-E(\vec{m}))\delta(E_k-E(\vec{k}))\rho(\vec{k})\rho(\vec{m})\rho(\vec{n})\delta(\vec{m}-\vec{k}-\vec{q})\delta(\vec{n}-\vec{m}-\vec{q}\,') \\ \times(\vec{k}|\vec{p}+\hbar\vec{k}+\hbar(\vec{q}+\vec{q}\,')/2\,|\vec{n})\,(\vec{n}|\vec{a}(\vec{q}\,')\cdot(\vec{p}+\hbar\vec{m}+\hbar\vec{q}\,'/2)|\vec{m})\,(\vec{m}|\vec{a}(\vec{q})\cdot(\vec{p}+h\vec{k}+\hbar\vec{q}/2)|\vec{k})N(\vec{n},\vec{m},\vec{k},\omega,\omega)\ .\end{aligned} \tag{16}$$

The singularities occur at $E_m=E_k+\hbar\omega$, $E_n=E_m+\hbar\omega$, and $E_n=E_k+2\hbar\omega$. The current is a sum of terms which are products of principal-value and singularity terms. The products which are three principal values, or two singularities and one principal value, will be imaginary and thus part of the radiation source. The products of three singularities, or one singularity and two principal values, will be real and contribute to the absorption. The conditions on band edge-Fermi level separations which lead to large radiation source currents are the same as those for $\vec{J}_{\alpha pv}$ or $\vec{J}_{\beta pv}$ or both.

This term may also be written in terms of non-Bloch function wave equations. For computation it is probably easiest to use Eqs. (7), (10), (11), (13), (14), (15), and (16) with Fourier components of the energy eigenfunctions $\psi_i(\vec{r})=\sum_k|\vec{k},i)\,e^{i\vec{k}\cdot\vec{r}}$. The total current for Eq. (1) is

$$\vec{J}_{2\omega}(\vec{r},T)=[\vec{J}_\alpha(\vec{r})+\vec{J}_\beta(\vec{r})+\vec{J}_\gamma(\vec{r})]e^{-i2\omega T}\ .$$

III. FIELDS AND ELECTRON STATES AT METAL SURFACES

A. Surface fields

When a light wave is reflected from a surface, the electric field component normal to the surface induces a polarization charge layer. The field-induced charge layer on metal surfaces has been calculated.[12,13] Through the relations

$$\vec{\nabla}\cdot\vec{E}=4\pi\rho(\vec{r})\,e^{-i\omega T},\quad \vec{E}=(i\omega/c)\vec{A},$$

$$\vec{A}=\sum_q\vec{a}(\vec{q})\,e^{i(\vec{q}\cdot\vec{r}-\omega T)}\ .$$

We can find $\vec{a}(\vec{q})$ in terms of the Fourier components of the charge density. Taking the divergence of the expansion of $\vec{A}$ and eliminating the time dependence, we get

$$-\frac{\omega}{c}\sum_q\vec{q}\cdot\vec{a}(\vec{q})\,e^{i\vec{q}\cdot\vec{r}}=4\pi\sum_q\rho(\vec{q})\,e^{i\vec{q}\cdot\vec{r}}$$

with

$$\rho(\vec{q})=\frac{1}{2\pi}\int\rho(\vec{r})\,e^{-i\vec{q}\cdot\vec{r}}\,d\vec{r}\ . \tag{17}$$

Matching terms, we have

$$-(\omega/c)\vec{q}\cdot\vec{a}(\vec{q})=4\pi\rho(\vec{q})\ . \tag{18}$$

The published charge distributions show a narrow nearly symmetric surface charge, with a half-width of about one angstrom. The asymmetry consists of a charge tail extending into the bulk and a sharp drop to zero outside. We carry out the integration of Eq. (17) with the plane $z=0$ at the center of the symmetric part of the distribution. The real part of $\rho(\vec{q})$ corresponds to the cosine expansion and the imaginary part is the sine expansion. The imaginary part will be smaller than the real part because of the near symmetry of the distribution.

If the charge varies only in the z direction, Eqs. (17) and (18) give $\vec{q}$ and $\vec{a}(\vec{q})$ vectors normal to the surface, with $|\vec{q}|$ covering the entire first Brillouin zone. Any variations along the surface will give rise to $\vec{q}$ and $\vec{a}(\vec{q})$ vectors parallel to the surface. The magnitude of $\vec{q}\cdot\vec{a}(\vec{q})$ will vary with $\vec{q}$, but the important point is that because the field-induced charge is narrower than the interatomic spacing all $\vec{q}$ normal to the surface are included in the second-harmonic current terms.

B. Electron states

The problem of the electron states at the surface is quite complex. Many models of surfaces show surface states or bands, and these are sensitive to the exact surface-potential model used. Rather than try to calculate what the electron states at the surface are, we will take them as given and analyze how they change with surface condition. The changes in surface electron structure lead to changes in the currents of Sec. II, which are measured as changes in second-harmonic intensity. The equations suggest (Sec. II) that these changes are at least partly changes in electron energies. If the potential at the surface changes by ΔV, the electron energies will change by $\langle\psi|\Delta V|\psi\rangle$.

When alkali-metal atoms are deposited on a metal surface they transfer an electron, or a fractional electron charge, to the substrate metal. This forms a dipole layer, with the negative charge on the substrate, and leads to a lower work function. We can consider two factors: the increase in dipole strength with its attendant work function change, and the states associated with the adatoms.

In semiconductors, the induced dipole charge is accumulated in the bulk, producing band bending. A similar result may be expected in metals, with two important differences. First, the bending extends only about one atomic diameter into the surface. This is the charge shielding length, and the same region that produces second harmonics. Second, because the shielding length is so small, the bending is quite sharp and should cause distortion of the band structure. Because the shielding depth is so small, band bending may be a poor analogy to the electron energy changes at metal surfaces.

However, the energy shift of states at metal surfaces can be seen in some published photoelectric data. For instance, when a Ce surface is exposed to oxygen, some oxygen states appear 5 eV below the Fermi level. With added oxygen the work function decreases about 1 eV and the oxygen levels move down about 0.2 eV. This indicates that as electrons are added to the surface, the surface bands are pushed down. With even greater oxygen exposure, the work function and oxygen energy levels rise again.[14] Similar behavior is seen for oxygen on a Sr surface.

As an alternative to the band-bending picture we can note that x-ray photoelectric data show a chemical shift of electron energies for elements in various compounds. The chemical shift refers to deep energy levels of the atoms, but higher energy states shift to the extent that they are localized within the same atoms. As the first monolayer of adatoms is deposited on a metal surface, the substrate atoms acquire a chemical shift. If a covalent bond is formed, states may disappear from the previous bands and reappear in new chemically shifted bands. If the adatoms form bonds with surface bands, rather than specific surface atoms, we may expect the surface bands to shift from the clean metal levels to the chemical compound levels as coverage increases. This takes place within the coverage region in which the work function is changing.

This provides a possible explanation of the rapid changes in second-harmonic generation efficiency which are observed with changes in surface condition.[1] If electron band-edge energies are changing with surface potential changes, their relative separations and distances from the Fermi level will change. Whenever one of these energy separations becomes near $\hbar\omega$ or $2\hbar\omega$, the current source changes rapidly with surface condition.

The metal surface-laser wavelength combinations studied to date have no known band gaps near $\hbar\omega$ or $2\hbar\omega$, although the surface bands may have separations somewhat different than bulk band gaps. The most likely interpretation of features in the experimental data is that they represent band edges one or two photon energies above or below the Fermi level.

The process of second-harmonic generation seems to be an exceptionally sensitive technique to study the details of the electronic structure of conductive surfaces. It should prove useful in the study of surface bands, chemical bonds, and other properties of electrons at real surfaces in varying conditions. The results could be greatly extended by using more than one laser frequency. A gigawatt, picosecond pulse, tunable laser would be ideal to fully exploit the possibilities of the technique.

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