Local field at an irradiated adatom on jellium—exact microscopic results

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The first microscopic correction to the image theory of the local field at an irradiated adatom has been calculated in the limit that the adatom is far from a jellium surface. The result of the calculation is the frequency-dependent position of the effective image plane in terms of the properties of semi-infinite jellium. The image plane position is found to be a *complex* number, reflecting the fact that the response of the surface electrons is lossy. Numerical calculations for $r_s = 2$ jellium suggest that the imaginary component of the image plane position is large enough to prevent large image enhancement of the local field at an adatom, casting doubt on the idea that such enhancement is responsible for the recently observed surface-enhanced Raman effect.

I. INTRODUCTION

The recent discovery of very strong surface enhancement of the Raman effect[1] has focused attention on the magnitude of the local field at an irradiated adatom as a possible source of the enhancement.[2,3] However, the Raman effect is only one of several optical-excitation experiments that probe surface structure. Other important examples include photoemission, ellipsometry, and surface reflection spectroscopy. In all these experiments the interpretation of the intensity of the optical excitation requires a knowledge of the electromagnetic field in the surface region.

Until now there has been no *microscopic* calculation of the local field at an adatom. However, it has recently been shown that a microscopic treatment of surface dielectric response,[4] including the effects of nonlocality,[4,5] is essential in explaining the frequency dependence of the photoelectric current from clean Al (001) (which, incidentally shows a dramatic enhancement at about 80% of the plasma frequency).[6] This result strongly indicates the importance of assessing the limitations of classical (Fresnel) models[2,3,7] in the evaluation of local-field effects. I present here the results of a first attempt in this direction, in which an atom adsorbed on jellium is assumed to be sufficiently far from the surface that classical image theory provides an accurate zeroth approximation to the results.[3,7,8] I have determined the lowest order microscopic corrections to the classical results and have come to the following main conclusions, which are amplified and derived in the remainder of this article.

(1) The position of the image plane, $\mathfrak{z}_{\rm im}$, depends on ω, the frequency of the incident radiation, and is in general a *complex* quantity. $\mathrm{Im}(\mathfrak{z}_{\rm im}) \neq 0$ because the breaking of translation invariance implied by the existence of a surface permits a loss process which would otherwise not be allowed, namely, the "surface photoexcitation" of electron-hole pairs. $\mathrm{Im}(\mathfrak{z}_{\rm im})$ is directly proportional to the cross section for this process. The fact that $\mathrm{Im}(\mathfrak{z}_{\rm im}) \neq 0$ weakens the image enhancement of the local field at the adatom and, specifically, suggests that a theory which correlates surface enhancement of Raman yields with a small absorptive part of the *bulk* dielectric constant[2,3] may be misleading.

(2) Since, by assumption, the adatom is far from the jellium surface, the fields induced by its presence are weak and of long wavelength. Consequently the dielectric response of the adatom-jellium system can be separated into the long wavelength, linear response of the adatom and that of the semi-infinite jellium. The latter can be entirely characterized in terms of two response functions, $d_{\parallel}(\omega)$ and $d_{\perp}(\omega)$, which are the surface analogs (respectively, for electric field components parallel and perpendicular to the surface) of the bulk dielectric constant $\epsilon(\omega)$. These response functions have the dimensions of length and can be thought of as effective surface positions for the corresponding electric field directions. The same response functions are found to describe the surface contribution to the reflectivity of semi-infinite jellium[9] and the surface-plasmon dispersion relation at long wavelengths,[10] as well as the first corrections to the static image force[11] and to the van der Waals force on a physisorbed atom.[12] The complex function $d_{\perp}(\omega)$ is the centroid of the induced density fluctuation below the plasma frequency ω_p and is a generalization of this quantity above ω_p, where because of bulk-plasmon photoexcitation the induced density fluctuation is not confined to the surface region.[4] $d_{\parallel}(\omega)$ is the centroid of the derivative with respect to depth z of the parallel-parallel (x-x) component of the jellium conductivity tensor [cf. Eq. (5.1) below]. Calculations of these universal surface positions for Al-density jellium (i.e., for electron radius

$r_s = 2$), based on the random-phase approximation (RPA) to the conductivity tensor, are presented below, together with numerical results for $\eth_{\rm im}(\omega)$.

The remainder of this article is organized as follows. In the next section I set up the problem of the irradiation of an adatom and show how it simplifies the case where the adatom-surface distance is long compared to microscopic distances. In Sec. III I review the solution of the classical adatom irradiation problem, and in Sec. IV I show how to generalize to the microscopic case. Finally, in Sec. V I present numerical calculations of $\eth_{\rm im}(\omega)$ and discuss their implications with respect to experiments which probe surface structure via optical excitation.

II. IRRADIATION OF AN ADATOM FORMULATION OF THE PROBLEM

Assume that an adatom is centered at $(0, 0, -Z_A)$, far outside a two-dimensionally translation-invariant substrate, whose surface is in the neighborhood of $z = 0$. When the system is irradiated with long-wavelength light, the fields induced by the presence of the adatom are characterized by the distance scale Z_A. Thus if $Z_A \gg r_A$, the adatom radius, a multipole expansion of the adatom response, is very rapidly convergent. In leading order, the local field induces an adatom dipole moment $\vec{p}$. Its value is determined self-consistently in that the local field is the sum of the incident field plus the reflected wave from the surface *and in addition*, the field of its image, which is of $O(Z_A^{-3})$ plus corrections of $O(Z_A^{-4})$. In what follows, I determine the form of the $O(Z_A^{-4})$ correction terms and neglect contributions to the local fields of $O(Z_A^{-5})$ and smaller. For this reason the induced quadrupole and higher multipole moments induced on the adatom are strictly negligible,[13] and the actual adatom may be replaced by a "point polarizable adatom." Thus the scattering equation for the electromagnetic vector potential $\vec{A}_\omega(\vec{r})$ can be written in the form[14]

$$\vec{A}_\omega(\vec{r}) = \vec{A}^{(0)} e^{i\vec{q}\cdot\vec{r}} + (q^2\overleftrightarrow{1} + \vec{\nabla}\vec{\nabla})\cdot\left(\vec{p}\frac{e^{iq|\vec{r}-\vec{R}_A|}}{iq|\vec{r}-\vec{R}_A|} + \frac{i}{\omega}\int d^3r' d^3r'' \frac{e^{iq|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}\overleftrightarrow{\sigma}(\vec{r}', \vec{r}''; \omega)\cdot\vec{A}_\omega(\vec{r}'')\right), \tag{2.1}$$

where $q \equiv \omega/c$, $\vec{A}^{(0)}$ is the vector potential of the incident wave of wave vector $\vec{q}$, $\overleftrightarrow{\sigma}(\vec{r}, \vec{r}'; \omega)$ is the nonlocal conductivity tensor of the jellium, and $\vec{p}$ is the induced dipole moment of the "point adatom," which resides at $\vec{R}_A \equiv (0, 0, -Z_A)$. The value of $\vec{p}$ is the product of the adatom polarizability $\chi(\omega)$ and the local electric field at $\vec{R}_A$. Thus one has the self-consistency relation

$$\vec{p} = iq\chi(\omega)\left(\vec{A}^{(0)} e^{i\vec{q}\cdot\vec{R}_A} + (q^2\overleftrightarrow{1} + \vec{\nabla}_{R_A}\vec{\nabla}_{R_A})\cdot\frac{i}{\omega}\int d^3r' d^3r'' \frac{e^{iq|\vec{R}_A-\vec{r}'|}}{|\vec{R}_A-\vec{r}'|}\overleftrightarrow{\sigma}(\vec{r}', \vec{r}''; \omega)\cdot\vec{A}_\omega(\vec{r}'')\right), \tag{2.2}$$

which together with Eq. (2.1) completely specifies the problem to be solved.

The key simplifying feature of the point adatom approximation is that the scattering equation (2.1) implies that $\vec{A}_\omega(\vec{r})$ can be written as

$$\vec{A}_\omega(\vec{r}) = \vec{A}_\omega^{(c)}(\vec{r}) + \vec{A}_\omega^{(A)}(\vec{r}), \tag{2.3}$$

where the clean-surface vector potential $\vec{A}_\omega^{(c)}(\vec{r})$ is the solution of Eq. (2.1) with $\vec{p} = 0$, and the radiating adatom vector potential $\vec{A}_\omega^{(A)}(\vec{r})$ solves (2.1) with $\vec{A}^{(0)} = 0$. In the first of Ref. 4, I have described in detail the reduction of the equation for $\vec{A}_\omega^{(c)}(\vec{r})$ to a tractable form in the long-wavelength equation within the RPA approximation to $\overleftrightarrow{\sigma}(\vec{r}, \vec{r}'; \omega)$. Here, therefore, I focus on the radiating adatom part of the problem, finding that for large Z_A, $\vec{A}_\omega^{(A)}(\vec{r})$ can be expressed directly in terms of $\vec{A}_\omega^{(c)}(\vec{r})$.

The first step in solving for $\vec{A}_\omega^{(A)}(\vec{r})$ is to take advantage of the assumed two-dimensional translation invariance of the jellium solid by Fourier transforming in x and y. Thus one obtains, with $\vec{q}_\parallel \equiv (q_x, q_y)$,

$$\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z) = \overleftrightarrow{D}_{\vec{q}_\parallel,\omega}\cdot\frac{2\pi}{Q_\perp}\left(\frac{\vec{p}}{iq}e^{-Q_\perp|z+z_A|} + \frac{i}{\omega}\int dz' dz'' e^{-Q_\perp|z-z'|}\overleftrightarrow{\sigma}_{\vec{q}_\parallel}(z', z''\omega)\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z'')\right), \tag{2.4}$$

where $\vec{A}^{(A)}_{\vec{q}_\parallel}(z', z''; \omega)$ are, respectively, the $\vec{q}_\parallel$th Fourier components of $\vec{A}_\omega^{(A)}(\vec{r})$ and $\overleftrightarrow{\sigma}(x-x', y-y', z, z'; \omega)$,[15] where

$$Q_\perp \equiv \begin{cases} (q_\parallel^2 - q^2)^{1/2}, & q_\parallel^2 > q^2 \\ -i(q^2 - q_\parallel^2)^{1/2}, & q_\parallel^2 \leq q^2 , \end{cases} \qquad (2.5)$$

and where

$$\overleftrightarrow{D}_{\vec{q}_\parallel,\omega} \equiv q^2 \overleftrightarrow{1} + \left(i\vec{q}_\parallel + \hat{u}\frac{d}{dz}\right)\left(i\vec{q}_\parallel + \hat{u}\frac{d}{dz}\right). \qquad (2.6)$$

In Eq. (2.6) $\hat{u}$ is a unit vector in the plus z direction (into the jellium).

There are two cases in which one can proceed to solve Eq. (2.4) without the immediate necessity of numerical computation, the classical case specified by

$$\frac{4\pi i}{\omega}\overleftrightarrow{\sigma}_{\vec{q}_\parallel}(z, z'; \omega) \sum \overleftrightarrow{1}[\epsilon(\omega) - 1]\delta(z - z')\Theta(z), \qquad (2.7)$$

where $\epsilon(\omega)$ is the bulk infinite-wavelength jellium dielectric function, and the large Z_A limit for a general conductivity tensor. In the next section I review the solution of the classical problem [first published in 1907 (Ref. 16)]. The method I adopt serves as a prototype for the solution of the asymptotic (large Z_A) microscopic case which is given in Sec. IV.

The results of the lengthy derivations in those sections can be neatly summarized here, noting that for $z > -Z_A$ the clean-surface vector potential satisfies Eq. (2.4) with the replacements

$$-Q_\perp \rightarrow iq_\perp \qquad (2.8)$$

and

$$\overleftrightarrow{D}_{\vec{q}_\parallel,\omega} \cdot \frac{\vec{p}}{iq} \rightarrow \vec{A}^{(0)} . \qquad (2.9)$$

Well outside the surface region, $\vec{A}^{(c)}_{\vec{q}_\parallel,\omega}(z)$ is of the form[9]

$$\vec{A}^{(c)}_{\vec{q}_\parallel,\omega}(z) = \vec{A}^{(0)} e^{iq_\perp z} + e^{-iq_\perp z}\left[\vec{A}^{(0)}R^{(s)}_{\vec{q}_\parallel,\omega} - \hat{q}_\parallel(\hat{q}_\parallel \cdot \vec{A}^{(0)}) \; (R^{(s)}_{\vec{q}_\parallel,\omega} + R^{(p)}_{\vec{q}_\parallel,\omega}) + \hat{u}A^{(0)z}R^{(p)}_{\vec{q}_\parallel,\omega}\right], \qquad (2.10)$$

in which the reflected wave is governed by the reflection amplitudes $R^{(s)}_{\vec{q}_\parallel,\omega}$ and $R^{(p)}_{\vec{q}_\parallel,\omega}$, respectively, for s- and p-polarized light. (Their values are given in the Appendix.) The induced field component of $\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z)$ can thus be obtained from the reflection term of Eq. (2.10) by making the inverse substitution of Eq. (2.9) for the $\vec{A}^{(0)}$ components and the inverse of Eq. (2.8) for the normal wave vectors. [For the interior normal wave vector $q'_\perp$, one substitutes $i\alpha$ where α is the interior normal attenuation coefficient obtained from Snell's law, cf. Eq. (3.3).] This relation between the "clean" and "adatom" vector potentials makes it clear why the same $d_\perp(\omega)$ and $d_\parallel(\omega)$ functions enter the local field and surface reflectance problems[9] (cf. also the last of Ref. 10). Of course it must be *proven* that the replacements of Eqs. (2.8) and (2.9) can be inverted in Eq. (2.10) to obtain the enhancement of the adatom local field, and this proof is the subject of Secs. III and IV.

III. ADATOM LOCAL FIELD IN THE CLASSICAL LIMIT–REVIEW

In the classical limit, where $\overleftrightarrow{\sigma}_{\vec{q}_\parallel}(z, z'; \omega)$ is specified by Eq. (2.7), Eq. (2.4) assumes the greatly simplified form

$$\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z) = \overleftrightarrow{D}_{\vec{q}_\parallel,\omega} \cdot \frac{2\pi}{Q_\perp}\left(\frac{\vec{p}}{iq}e^{-Q_\perp|z+Z_A|} + \frac{\epsilon(\omega) - 1}{4\pi}\int_0^\infty dz' \, e^{-Q_\perp|z-z'|}\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z')\right). \qquad (3.1)$$

This equation is solved with the ansatz,

$$\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z > 0) = \vec{\mathfrak{A}}_{\vec{q}_\parallel,\omega} e^{-\alpha z}. \qquad (3.2)$$

Substituting Eq. (3.2) into (3.1) and carrying out the indicated integration and differentiation one easily finds the following results:

$$\alpha = [Q_\perp^2 - q^2(\epsilon - 1)]^{1/2}, \qquad (3.3)$$

which is Snell's law for evanescent waves,

$$\vec{\mathfrak{A}}^{\parallel}_{\vec{q}_\parallel,\omega} = \frac{4\pi}{iq}e^{-Q_\perp Z_A}\left(\frac{q^2\vec{p}_\parallel}{Q_\perp + \alpha} + \frac{i\vec{q}_\parallel(i\vec{q}_\parallel - \hat{u}\alpha)\cdot\vec{p}}{\epsilon Q_\perp + \alpha}\right), \qquad (3.4)$$

and

$$\mathfrak{A}^{z}_{\vec{q}_\parallel,\omega} = \frac{4\pi}{iq}e^{-Q_\perp Z_A}\frac{q_\parallel^2 p_z - iQ_\perp\vec{q}_\parallel\cdot\vec{p}_\parallel}{\epsilon Q_\perp + \alpha}. \qquad (3.5)$$

Here

$$\vec{\mathfrak{a}}_{\vec{q}_{\parallel},\omega} \equiv (\vec{\mathfrak{a}}^{\parallel}_{\vec{q}_{\parallel},\omega}, \mathfrak{a}^{z}_{z_{\parallel},\omega})$$

and $\vec{p} \equiv (\vec{p}_{\parallel}, p_z)$. To obtain $\vec{A}^{(A)}_{\vec{q}_{\parallel},\omega}$ $(z<0)$, one substitutes Eqs. (3.2)–(3.5) back into Eq. (3.1) and carries out the quadrature and differentiations. Then one completes the calculation by solving the self-consistency condition for $\vec{p}$ which, using Eqs. (2.1)–(2.3), (2.6), (3.1), and (3.2) assumes the form

$$\vec{p}_{\vec{q}^{(0)}_{\parallel},\omega} = iq\chi(\omega)\left(\vec{A}^{(c)}_{\vec{q}^{(0)}_{\parallel},\omega}(-Z_A) + \int \frac{d^2q_{\parallel}}{(2\pi)^2}[q^2\vec{1} + (i\vec{q}_{\parallel} + \hat{u}Q_{\perp})(i\vec{q}_{\parallel} + \hat{u}Q_{\perp})]\vec{\mathfrak{a}}_{\vec{q}_{\parallel},\omega}\Big/(Q_{\perp}+\alpha)\right). \tag{3.6}$$

In this equation the parallel wave vector of the incident field has been renamed $\vec{q}^{\,(0)}_{\parallel}$ to avoid confusion with the dummy vector $\vec{q}_{\parallel}$, and the $\vec{q}^{\,(0)}_{\parallel}$ and ω dependence of $\vec{p}$ has been made explicit.

$$\vec{A}^{(c)}_{q^{(0)}_{\parallel}}(-Z_A)$$

is the clean-surface vector potential at the adatom site. Its value is given in the Appendix.

The simplest way to evaluate the right-hand side of Eq. (3.6) is to make use of the transverseness condition

$$(i\vec{q}_{\parallel} - \hat{u}\alpha)\cdot\vec{\mathfrak{a}}_{q_{\parallel},\omega} = 0, \tag{3.7}$$

which Eqs. (3.4) and (3.5) are easily seen to satisfy. Substituting Eq. (3.7) into Eq. (3.6) and making use of the cylindrical symmetry of the problem to evaluate the integral on the azimuth of $\vec{q}_{\parallel}$, one obtains

$$\vec{p}_{\vec{q}^{(0)}_{\parallel},\omega} = \chi(\omega)\,[\,\vec{E}^{(c)}_{\vec{q}^{(0)}_{\parallel},\omega}(-Z_A) + \vec{p}^{\,\parallel}_{\vec{q}^{(0)}_{\parallel},\omega}I_{\parallel}(\omega) + \hat{u}p^{z}_{\vec{q}^{(0)}_{\parallel},\omega}I_{\perp}(\omega)], \tag{3.8}$$

where

$$\vec{E}^{\parallel}_{\vec{q}^{(0)}_{\parallel},\omega}(-Z_A) \equiv iq\vec{A}^{(c)}_{\vec{q}^{(0)}_{\parallel},\omega}(-Z_A) \tag{3.9}$$

is the electric field at the adatom site in the absence of the adatom, and $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ are the integrals[16,7]

$$I_{\parallel}(\omega) \equiv q^3\int_0^{\infty}\lambda\,d\lambda\frac{e^{-2qZ_A(\lambda^2-1)^{1/2}}}{(\lambda^2-1)^{1/2}} \times\left[\frac{(\lambda^2-1)^{1/2}-(\lambda^2-\epsilon)^{1/2}}{(\lambda^2-1)^{1/2}+(\lambda^2-\epsilon)^{1/2}} + \lambda^2\left(\frac{1}{2} - \frac{(\lambda^2-1)^{1/2}}{\epsilon(\lambda^2-1)^{1/2}+(\lambda^2-\epsilon)^{1/2}}\right)\right] \tag{3.10}$$

and

$$I_{\perp}(\omega) = q^3\int_0^{\infty}\lambda^3 d\lambda\frac{e^{-2qZ_A(\lambda^2-1)^{1/2}}}{(\lambda^2-1)^{1/2}}\left(\frac{\epsilon(\lambda^2-1)^{1/2}-(\lambda^2-\epsilon)^{1/2}}{\epsilon(\lambda^2-1)^{1/2}+(\lambda^2-\epsilon)^{1/2}}\right) \tag{3.11}$$

In Eqs. (3.10) and (3.11), $q_{\parallel}, Q_{\perp}$, and α have been replaced by $q\lambda$, $q\sqrt{\lambda^2-1}$, and $q\sqrt{\lambda^2-\epsilon}$, respectively [cf. Eqs. (2.5) and (3.3)], and $\mathrm{Im}(\lambda^2-1)^{1/2}$ and $\mathrm{Im}(\lambda^2-\epsilon)^{1/2}$ are presumed to be less than or equal to zero in accordance with an outgoing-wave boundary condition as $z\to\infty$.

Equation (3.8) can now be solved, yielding

$$\vec{p}^{\,\parallel}_{\vec{q}^{(0)}_{\parallel},\omega} = \frac{\chi(\omega)\vec{E}^{(c)\parallel}_{\vec{q}^{(0)}_{\parallel},\omega}(-Z_A)}{1-\chi(\omega)I_{\parallel}(\omega)} \tag{3.12}$$

and

$$p^{z}_{\vec{q}^{(0)}_{\parallel},\omega} = \frac{\chi(\omega)E^{(c)z}_{\vec{q}^{(0)}_{\parallel},\omega}(-Z_A)}{1-\chi(\omega)I_{\perp}(\omega)}. \tag{3.13}$$

These equations show that the local fields parallel and normal to the surface are the fields which solve the clean-surface reflection problem, enhanced, respectively, by the factors $[1-\chi(\omega)I_{\parallel}(\omega)]^{-1}$ and $[1-\chi(\omega)I_{\perp}(\omega)]^{-1}$. To complete the consideration of the classical local-field problem, therefore, one must ask when these enhancement factors are significant.

Equations (3.10) and (3.11) show that any contributions to the enhancement of the local fields which are larger than $O(q^3)$ (and for $\hbar\omega \lesssim 30$ eV, $q^3 \lesssim 3\times10^{-6}$Å^{-3}) must come either from the range of integration $\Lambda<\lambda<\infty$, where Λ is arbitrarily large, or from singularities of the integrand. Thus one finds the asymptotic $(q\to0)$ formulas

$$I_{\perp}(\omega) = 2I_{\parallel}(\omega) = \frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\frac{1}{4Z_A^3} + O\left(\frac{q^2}{Z_A}\right) + \frac{q^3}{(\epsilon+1)^2}\left(\frac{1}{qZ_A} + \frac{1}{|\epsilon+1|^{1/2}}[e^{-2qZ_A|\epsilon+1|^{-1/2}}\mathrm{Ei}(2qZ_A|\epsilon+1|^{-1/2}+i\delta) - e^{2qZ_A|\epsilon+1|^{-1/2}}\mathrm{Ei}(-2qZ_A|\epsilon+1|^{-1/2}]\right), \tag{3.14}$$

where

$$\mathrm{Ei}(x) \equiv -\int_{-x}^{\infty} \frac{dt}{t} e^{-t} . \tag{3.15}$$

In Eq. (3.14), the first term is identical to the result of classical image theory and comes from the region of integration $\lambda > \Lambda$. The second term comes from the surface-plasmon singularity at $\lambda = [\epsilon/(\epsilon+1)]^{1/2}$ and is an approximate result for frequencies such that $\epsilon(\omega)+1 \approx -q^2 Z_A^2$. It is only in this range of ω's that (cf. Ref. 7) the surface-plasmon term is large, and indeed is of the same order there, $O(q^{-2}Z_A^{-5})$, as the image term. (Note, however, that $\epsilon+1 \approx -q^2 Z_A^2$ cannot be satisfied unless Imϵ is small.) The square-root singularities at $\lambda^2 = 1$, ϵ, being integrable, do not contribute to the asymptotic results of Eq. (3.14). One thus concludes that outside a narrow range of ω's near the surface-plasma frequency, the image approximation provides a completely adequate description of the solution to the classical problem of the local field at an adatom.[17,18]

The local-field enhancements given by the classical dielectric theory have been investigated numerically in Ref. 3 using realistic values of $\epsilon(\omega)$.[19] There is no reason to repeat that work here. Two facts concerning the classical model should be kept in mind in evaluating the significance of the numerical results:

(1) The enhancement factors only become large when $\chi(\omega)I_\perp(\omega)$ and $\chi(\omega)I_\parallel(\omega)$ become comparable to 1. Since $\chi(\omega)$ is typically characterized by an atomic volume,[20] the enhancement of the local fields only occurs if Z_A is comparable to an atomic diameter, which violates the spirit of the point-polarizable adatom model (to say nothing of the infinitely sharp interface approximation), or if $\epsilon(\omega)+1$ is small, i.e., very near the surface-plasma frequency.

(2) Above the *bulk*-plasma frequency, which satisfies $\epsilon^L(\omega)=0$, where $\epsilon^L(\omega)$ is the longitudinal dielectric constant, the classical model is ill-defined without the addition of a supplementary boundary condition that determines the strength of bulk-plasmon photoexcitation.[18]

Both these *caveats* indicate the importance of developing a microscopic picture of the local field at an irradiated adatom, which is addressed in the next section.

IV. LOCAL FIELD FOR AN ADATOM ON A GENERAL JELLIUM SURFACE—CORRECTIONS TO IMAGE THEORY

In this section I solve the general equation (2.4) for the fields produced by a radiating dipole $\vec{p}$ in the asymptotic case that it is at a large distance Z_A from a two-dimensionally translation-invariant surface. Once $\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}$ is known for this case, the value of the electric field at an irradiated adatom at $(0,0,-Z_A)$ can be obtained trivially, as was seen for the classical problem in Sec. III.

It was pointed out in Sec. II that the final formula for $\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}$ can be guessed from the perception that for $z > -Z_A$, Eq. (2.4) is the same as the equation describing the vector potential for reflection at a clean surface with $q_\perp'$ replaced by $i\alpha$. The reader who is not interested in the proof that this replacement is valid is encouraged to skip from here to Eqs. (4.54) and (4.55) which embody this result and are the generalizations of the classical equations (3.10) and (3.11).

The reason that Eq. (2.4) simplifies in the large Z_A regime is that in this case the inhomogeneous term vanishes unless $Q_\perp \lesssim Z_A^{-1}$ (assuming z to be in or near the jellium solid). Thus everywhere but in the $\exp(-Q_\perp Z_A)$ term in Eq. (2.4) (for $z+Z_A>0$), one is in the long-wavelength or small-$Q_\perp$ limit.[21] Unfortunately however, one cannot simply expand Eq. (2.4) in powers of $Q_\perp$, because the z' integral on the right-hand side (RHS) diverges at $Q_\perp = 0$. In order to take advantage of the smallness of $Q_\perp$, it is therefore necessary to reduce the z' integral to an integral over a compact domain by learning and taking advantage of the asymptotic behavior of $A^{(A)}_{\vec{q}_\parallel,\omega}(z)$ as $z \to \infty$. The lower limit of the z' integral is not a problem because $\overleftrightarrow{\sigma}_{\vec{q}}(z',z'';\omega)$ falls exponentially to zero as z' (or z'') $\to -\infty$.

In order to reduce Eq. (2.4) to an equation on what is effectively a compact domain, it is convenient to define a cutoff depth $z = Z$ which is large compared to the jellium surface thickness (a few Å), but small compared to Z_A and thus to $Q_\perp^{-1}$. For example, Z might be ~30 Å, with $Z_A \sim$ a few hundred Å. For $z \le Z$, Eq. (2.4) may be rewritten exactly as

$$\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z \le Z) = \overleftrightarrow{D}_{\vec{q}_\parallel,\omega} \circ \frac{2\pi}{Q_\perp}\left(\frac{\vec{p}}{iq} e^{-Q_\perp |z+Z_A|} + \frac{i}{\omega} e^{Q_\perp z} \vec{C}^{(+)}_{\vec{q}_\parallel,\omega}(Z) + \frac{i}{\omega}\int_{-\infty}^{Z} dz' \int dz'' \, e^{-Q_\perp |z-z'|} \overleftrightarrow{\sigma}_{\vec{q}_\parallel}(z',z'';\omega) \circ \vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z'')\right), \tag{4.1}$$

where

$$\vec{C}^{(+)}_{\vec{q}_{\parallel},\omega}(Z) \equiv \int_Z^{\infty} dz' \int dz''\, e^{-Q_\perp z'} \overleftrightarrow{\sigma}_{\vec{q}_{\parallel}}(z', z''; \omega) \cdot \vec{A}^{(A)}_{\vec{q}_{\parallel},\omega}(z'') . \tag{4.2}$$

Since $\overleftrightarrow{\sigma}_{\vec{q}_{\parallel}}(z', z''; \omega)$ falls rapidly to zero as $|z'-z''| \to \infty$, Eq. (4.1) is formally an integral equation on an effectively compact domain. However, one still needs to learn how to determine the constant $\vec{C}^{(+)}_{\vec{q}_{\parallel},\omega}(Z)$ in the long-wavelength limit.

To this end, consider Eq. (2.4) for $z = Z^+$, i.e., for z infinitesimally greater than Z. In this case, carrying out the differentiations implied by $\overleftrightarrow{D}_{\vec{q}_{\parallel},\omega}$ and defining

$$\overleftrightarrow{\mathfrak{D}}_{\vec{q}_{\parallel},\omega}(\gamma) \equiv [q^2 \overleftrightarrow{1} + (i\vec{q}_{\parallel} + \hat{u}\gamma)(i\vec{q}_{\parallel} + \hat{u}\gamma)] , \tag{4.3}$$

one finds that

$$\vec{A}^{(A)}_{\vec{q}_{\parallel},\omega}(Z^+) = \frac{2\pi}{Q_\perp} e^{-Q_\perp Z} \overleftrightarrow{\mathfrak{D}}_{\vec{q}_{\parallel},\omega}(-Q_\perp) \left(\frac{\vec{p}}{iq} e^{-Q_\perp z_A} + \frac{i}{\omega} \vec{C}^{(-)}_{\vec{q}_{\parallel},\omega}(Z) \right) + \frac{2\pi i}{Q_\perp \omega} e^{Q_\perp Z} \overleftrightarrow{\mathfrak{D}}_{\vec{q}_{\parallel},\omega}(Q_\perp) \cdot \vec{C}^{(+)}_{\vec{q}_{\parallel},\omega}(Z)$$
$$- \frac{4\pi i}{\omega} \hat{u} \int dz'' \sigma^{zj}_{\vec{q}}(Z, z''; \omega) \circ A^{(A)j}_{\vec{q}_{\parallel},\omega}(z'') , \tag{4.4}$$

where

$$\vec{C}^{(-)}_{\vec{q}_{\parallel},\omega}(Z) \equiv \int_{-\infty}^{Z} dz' \int_{-\infty}^{\infty} dz''\, e^{Q_\perp z'} \overleftrightarrow{\sigma}_{\vec{q}_{\parallel}}(z', z''; \omega) \cdot \vec{A}^{(A)}_{\vec{q}_{\parallel},\omega}(z'') , \tag{4.5}$$

and where the vector index j is summed over x, y, and z. There is of course no physical significance to the depth $z = Z$. Consequently the + may be dropped in $\vec{A}^{(A)}_{\vec{q}_{\parallel},\omega}(Z^+)$ in Eq. (4.4), and using this equation to substitute for the $\vec{C}^{(+)}_{\vec{q}_{\parallel},\omega}(Z)$ term in Eq. (4.1), one finds the (still exact) equation,

$$\vec{A}^{(A)}_{\vec{q}_{\parallel},\omega}(z \le Z) = \overleftrightarrow{D}_{\vec{q}_{\parallel},\omega} \cdot \frac{2\pi}{Q_\perp} \left(\frac{\vec{p}}{iq} e^{-Q_\perp |z+z_A|} + \frac{i}{\omega} \int_{-\infty}^{Z} dz' \int_{-\infty}^{\infty} dz''\, e^{-Q_\perp |z-z'|} \overleftrightarrow{\sigma}_{\vec{q}_{\parallel}}(z', z''; \omega) \cdot \vec{A}_{\vec{q}_{\parallel},\omega}(z'') \right)$$
$$+ e^{Q_\perp z} \left[e^{-Q_\perp Z} \left(\vec{A}^{(A)}_{\vec{q}_{\parallel},\omega}(Z) + \hat{u} \frac{4\pi i}{\omega} \int dz'' \sigma^{zj}_{\vec{q}_{\parallel}}(z, z''; \omega) A^{(A)j}_{\vec{q}_{\parallel},\omega}(z'') \right) \right.$$
$$\left. - \frac{2\pi}{Q_\perp} e^{-2Q_\perp Z} \overleftrightarrow{\mathfrak{D}}_{\vec{q}_{\parallel},\omega}(-Q_\perp) \left(\frac{\vec{p}}{iq} e^{-Q_\perp z_A} + \frac{i}{\omega} \vec{C}^{(-)}_{\vec{q}_{\parallel},\omega}(Z) \right) \right] . \tag{4.6}$$

Despite its formidable aura, Eq. (4.6) represents a considerable simplification of Eq. (2.4) in that the only values of z' which appear are less than or equal to Z. It remains to determine the form of $\vec{A}^{(A)}_{\vec{q}_{\parallel},\omega}(z \sim Z)$ so that the z'' integrals in Eq. (4.6) can be performed and the RHS can be expanded in powers of $Q_\perp$.

This program requires that one investigate Eq. (2.4) in the region $z > Z$, where it assumes the form

$$\vec{A}^{(A)}_{\vec{q}_{\parallel},\omega}(z > Z) = \overleftrightarrow{D}_{\vec{q}_{\parallel},\omega} \cdot \frac{2\pi}{Q_\perp} \left[e^{-Q_\perp z} \left(\frac{\vec{p}}{iq} e^{-Q_\perp z_A} + \frac{i}{\omega} \vec{C}^{(-)}_{\vec{q}_{\parallel},\omega}(Z) \right) \right.$$
$$\left. + \frac{i}{\omega} \int_Z^{\infty} dz'\, e^{-Q_\perp |z-z'|} \int dz'' \overleftrightarrow{\sigma}^{(B)}_{\vec{q}_{\parallel}}(|z'-z''|; \omega) \circ \vec{A}^{(A)}_{\vec{q}_{\parallel},\omega}(z'') \right] . \tag{4.7}$$

Here it has been assumed that Z is sufficiently far inside the jellium so that in the last term of (4.7), $\overleftrightarrow{\sigma}_{\vec{q}_{\parallel}}(z', z''; \omega)$ can be replaced by its bulk, translation, and rotation-invariant form,

$$\overleftrightarrow{\sigma}^{(B)}_{\vec{q}_{\parallel}}(|z'-z''|; \omega) = \int d^2\rho\, e^{-i\vec{q}_{\parallel} \cdot \vec{\rho}} \times \overleftrightarrow{\sigma}^{(B)}([\rho^2 + (z'-z'')^2]^{1/2}; \omega) , \tag{4.8}$$

where $\vec{\rho} \equiv (x, y)$ and [22]

$$\overleftrightarrow{\sigma}^{(B)}(|r-r'|; \omega) \equiv \sigma^{(1)}(|\vec{r}-\vec{r}'|; \omega) \overleftrightarrow{1} - \int d^3r'' \sigma^{(2)}(|r-r''|; \omega) \times \frac{1}{4\pi |\vec{r}''-\vec{r}'|} \vec{\nabla}' \vec{\nabla}' . \tag{4.9}$$

If $\overleftrightarrow{\sigma}^{(B)}_{\vec{q}_{\parallel}}(|z'-z''|; \omega)$ is sufficiently short ranged so that

$$\vec{\sigma}^{(B)}_{\vec{q}_\parallel}(\alpha;\omega) \equiv \int dz'\, e^{-\alpha z'}\vec{\sigma}^{(B)}_{\vec{q}_\parallel}(|z'|;\omega) \tag{4.10}$$

is a well-defined quantity, then Eq. (4.7) can be trivially solved with the ansatz

$$\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z \gtrsim Z) = \vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(Z)\, e^{-\alpha(z-Z)}, \tag{4.11}$$

and the remainder of the calculation is straightforward. However, the exact asymptotic behavior of $\vec{\sigma}^{(B)}_{\vec{q}_\parallel}(|z'|\to\infty;\omega)$ is unknown, and in the RPA where it can be determined[4] it is of the Friedel oscillation form

$$z'^{-2}\sum \text{sinusoids}, \tag{4.12}$$

for which the RHS of Eq. (4.10) is divergent if $\alpha\neq 0$. Thus one must make a more careful ansatz than Eq. (4.11), specifically

$$\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z \gtrsim Z) = \vec{T}_{\vec{q}_\parallel,\omega}\, e^{-\alpha(z-Z)} + \vec{R}_{\vec{q}_\parallel,\omega}(z), \tag{4.13}$$

where one hopes to show that the "remainder term" $\vec{R}_{\vec{q}_\parallel,\omega}(z)$ is small in some asymptotic sense.

To this end I define a distance U sufficiently large that $\vec{\sigma}^{(B)}_{\vec{q}_\parallel}(U;\omega)$ has fallen virtually to zero, and assume that Eq. (4.13) holds true for $z \geq Z - U$. This assumption implicitly requires that $z = Z-U$ lie deeper in the solid than the selvedge region and is the first real restriction on the value of Z. Now I substitute Eq. (4.13) into (4.17), and *defining* $\vec{R}_{\vec{q}_\parallel,\omega}(z)$ by

$$\vec{R}_{\vec{q}_\parallel,\omega}(z) = \vec{D}_{\vec{q}_\parallel,\omega}\cdot\frac{2\pi i}{Q_\perp\omega}\int_z^\infty dz'\int dz''\, e^{-Q_\perp|z-z'|}\vec{\sigma}^{(B)}_{\vec{q}_\parallel}(|z'-z''|;\omega) \times\left[\Theta(z''-z'+U)\vec{R}_{\vec{q}_\parallel,\omega}(z'') + \Theta(z'-U-z'')\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z'')\right], \tag{4.14}$$

find that

$$\vec{T}_{\vec{q}_\parallel,\omega}\, e^{-\alpha(z-Z)} = \vec{D}_{\vec{q}_\parallel,\omega}\circ\frac{2\pi}{Q_\perp}\left[e^{-Q_\perp z}\left(\frac{\vec{p}}{iq}e^{-Q_\perp z_A} + \frac{i}{\omega}\vec{C}^{(-)}_{\vec{q}_\parallel,\omega}(Z)\right) + \frac{i}{\omega}\left(\frac{2Q_\perp}{Q_\perp^2-\alpha^2}e^{-\alpha(z-Z)} - \frac{e^{-Q_\perp(z-Z)}}{Q_\perp-\alpha}\right)\vec{\sigma}^{(B)}_{\vec{q}_\parallel}(\alpha;U;\omega)\cdot\vec{T}_{\vec{q}_\parallel,\omega}\right]. \tag{4.15}$$

Here

$$\vec{\sigma}^{(B)}_{\vec{q}_\parallel}(\alpha;U;\omega) \equiv \int_{-U}^{\infty} du\, e^{-\alpha u}\vec{\sigma}^{(B)}_{\vec{q}_\parallel}(u;\omega), \tag{4.16}$$

and the tacit assumption is that for small α,

$$\vec{\sigma}^{(B)}_{\vec{q}_\parallel}(\alpha\to\text{small};U;\omega) \approx \text{constant in } U. \tag{4.17}$$

If this asymptotic relation is not true, one cannot recover the classical limit, because the nonlocality of the conductivity tensor is effectively long ranged.

Note that the definition (4.14) does imply that $\vec{R}_{\vec{q}_\parallel,\omega}(z)$ is small since the inhomogeneous term (the last on the RHS) is of $O(\vec{\sigma}^{(B)}_{\vec{q}_\parallel}(U;\omega))$. Thus one proceeds to solve Eq. (4.15) by equating the coefficients of $\exp(-\alpha z)$ and $\exp(-Q_\perp z)$ separately to zero to determine the dominant terms in $\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z>Z)$. One finds that

$$\vec{T}_{\vec{q}_\parallel,\omega} = \vec{\mathfrak{D}}_{\vec{q}_\parallel,\omega}(-\alpha)\cdot\frac{4\pi i/\omega}{Q_\perp^2-\alpha^2}\vec{\sigma}^{(B)}_{\vec{q}_\parallel}(\alpha;U;\omega)\cdot\vec{T}_{\vec{q}_\parallel,\omega}, \tag{4.18}$$

and

$$\vec{\mathfrak{D}}_{\vec{q}_\parallel,\omega}(-Q_\perp)\cdot\left(\frac{\vec{p}}{iq}e^{-Q_\perp z_A} + \frac{i}{\omega}\vec{C}^{(-)}_{\vec{q}_\parallel,\omega}(Z) - \frac{i}{\omega}\frac{e^{Q_\perp Z}}{Q_\perp-\alpha}\vec{\sigma}^{(B)}_{\vec{q}_\parallel}(\alpha;U;\omega)\circ\vec{T}_{\vec{q}_\parallel,\omega}\right) = 0. \tag{4.19}$$

Equation (4.18) determines the propagation vector α while Eq. (4.19) determines the amplitude $\vec{T}_{\vec{q}_\parallel,\omega}$.

To solve Eq. (4.18) one dots $(i\vec{q}_\parallel - \hat{u}\alpha)$ into both sides. Noting that according to Eq. (4.9),

$$\vec{\sigma}^{(B)}_{\vec{q}_\parallel}(\alpha;U;\omega) = \sigma^{(1)}_{\vec{q}_\parallel}(\alpha;U;\omega)\vec{1} - \sigma^{(2)}_{\vec{q}_\parallel}(\alpha;U;\omega)(q_\parallel^2-\alpha^2)^{-1} \times (i\vec{q}_\parallel - \hat{u}\alpha)(i\vec{q}_\parallel - \hat{u}\alpha), \tag{4.20}$$

one thus finds that either

$$(i\vec{q}_\parallel - \alpha\hat{u})\cdot\vec{T}_{\vec{q}_\parallel,\omega} = 0, \tag{4.21}$$

which says that $\vec{T}_{\vec{q}_\parallel,\omega}$ is the amplitude of a transverse wave, or

$$\epsilon^{(L)}_{\vec{q}_{\parallel}}(\alpha;U;\omega) \equiv 1+\frac{4\pi i}{\omega}[\sigma^{(1)}_{\vec{q}_{\parallel}}(\alpha;U;\omega) + \sigma^{(2)}_{\vec{q}_{\parallel}}(\alpha;U;\omega)]=0\,, \qquad (4.22)$$

and the wave is longitudinal.[23] In the former case, substituting Eq. (4.21) back into Eq. (4.19) one obtains

$$Q_{\perp}^2-\alpha^2=q_{\parallel}^2\,4\pi i\sigma^{(1)}(\alpha;U;\omega)/\omega\,, \qquad (4.23)$$

which, identifying

$$\epsilon^{(T)}(\alpha;U;\omega)\equiv 1+4\pi i\sigma^{(1)}(\alpha;U;\omega)/\omega \qquad (4.24)$$

as the transverse dielectric constant,[24] one recognizes to be Snell's law for evanescent waves [cf. Eq. (3.3)]. In the latter case identifying $\epsilon^{(L)}(\alpha;U;\omega)$ as the longitudinal dielectric constant,[24] one sees that Eq. (4.22) is the equation for the bulk-plasmon dispersion relation. It has solutions above the plasma frequency for real propagation vectors, i.e., for[25]

$$\alpha=-ik^{(L)}(\omega)\,. \qquad (4.25)$$

Collecting these results, one sees that for $z\gtrsim Z$ one has generally not Eq. (4.13) but

$$\vec{A}^{(A)}_{\vec{q}_{\parallel},\omega}(z\gtrsim Z)=\vec{T}_{\vec{q}_{\parallel},\omega}e^{-\alpha(z-Z)} + \vec{L}_{\vec{q}_{\parallel},\omega}e^{ik^{(L)}(z-Z)}+\vec{R}_{\vec{q}_{\parallel},\omega}(z)\,, \qquad (4.26)$$

where α and $k^{(L)}$ are given by Eqs. (4.23) and (4.22), respectively, $\vec{R}_{\vec{q}_{\parallel},\omega}(z)$ is the small function given by Eq. (4.14), and $\vec{T}_{\vec{q}_{\parallel},\omega}$ and $\vec{L}_{\vec{q}_{\parallel},\omega}$ are constant vectors to be determined. $\vec{T}_{\vec{q}_{\parallel},\omega}$ satisfies Eq. (4.21) and $\vec{L}_{\vec{q}_{\parallel},\omega}$, which vanishes below ω_p, the plasma frequency,[26] satisfies the longitudinal condition

$$(\vec{q}_{\parallel}+\hat{u}k^{(L)})\times\vec{L}_{\vec{q}_{\parallel},\omega}=0\,. \qquad (4.27)$$

Because of the longitudinal term, Eq. (4.19) generalizes to

$$\vec{P}_{\vec{q}_{\parallel},\omega}(Z)=\vec{\mathfrak{D}}_{\vec{q}_{\parallel},\omega}(-Q_{\perp})\cdot\frac{e^{Q_{\perp}Z}}{4\pi}\left(\frac{\epsilon-1}{Q_{\perp}-\alpha}\vec{T}_{\vec{q}_{\parallel},\omega} - \frac{1}{Q_{\perp}+ik^{(L)}}\vec{L}_{\vec{q}_{\parallel},\omega}\right), \qquad (4.28)$$

in which

$$\vec{P}_{\vec{q}_{\parallel},\omega}(Z)\equiv\vec{\mathfrak{D}}_{\vec{q}_{\parallel},\omega}(-Q_{\perp})\cdot\left(\frac{\vec{p}}{iq}e^{-Q_{\perp}Z_A}+\frac{i}{\omega}\vec{C}^{(-)}_{\vec{q}_{\parallel},\omega}(Z)\right), \qquad (4.29)$$

and where $\epsilon^{(T)}(\alpha;U;\omega)$ has been abbreviated as ϵ.

I now solve Eq. (4.28) for $\vec{T}_{\vec{q}_{\parallel},\omega}$ in preparation for the simplification of the fundamental integral equation (4.6). Taking the z component of (4.28) and using Eqs. (4.21), (4.23), (4.24), and (4.27), I find

$$P^{z}_{\vec{q}_{\parallel},\omega}(Z)=\frac{e^{Q_{\perp}Z}}{4\pi}[(\epsilon Q_{\perp}+\alpha)T^{z}_{\vec{q}_{\parallel},\omega}+(iq_{\parallel}^2/k^{(L)})L^{z}_{\vec{q}_{\parallel},\omega}]\,. \qquad (4.30)$$

The ratio of $T^{z}_{\vec{q}_{\parallel},\omega}$ and $L^{z}_{\vec{q}_{\parallel},\omega}$ is a surface property[27] and thus cannot be determined by solving the bulk equation (4.28). Therefore I define the ratio

$$r_{\vec{q}_{\parallel},\omega}\equiv L^{z}_{\vec{q}_{\parallel},\omega}e^{-ik^{(L)}Z}/T^{z}_{\vec{q}_{\parallel},\omega} \qquad (4.31)$$

[which *can* be determined by solving Eq. (4.6) for the fields in the surface region]. Using Eq. (4.31), Eq. (4.30) can be solved to obtain

$$T^{z}_{\vec{q}_{\parallel},\omega}=\frac{4\pi e^{-Q_{\perp}Z}P^{z}_{\vec{q}_{\parallel},\omega}(Z)}{\epsilon Q_{\perp}+\alpha+q_{\parallel}^2\Lambda^L}\,, \qquad (4.32)$$

where

$$\Lambda^L\equiv i\,r_{\vec{q}_{\parallel},\omega}e^{ik^{(L)}Z}/k^{(L)}\,. \qquad (4.33)$$

[Notice that Eq. (4.32) is the generalization of the classical result, Eq. (3.5).]

Taking the parallel component of Eq. (4.28), I proceed similarly to determine $\vec{T}^{\parallel}_{\vec{q}_{\parallel},\omega}$. Use of Eqs. (4.21) and (4.27) leads to the result

$$\vec{T}^{\parallel}_{\vec{q}_{\parallel},\omega}+\vec{L}^{\parallel}_{\vec{q}_{\parallel},\omega}=\frac{4\pi e^{-Q_{\perp}Z}}{Q_{\perp}+\alpha}\times\left(\vec{P}^{\parallel}_{\vec{q}_{\parallel},\omega}(Z) + i\vec{q}P^{z}_{\vec{q}_{\parallel},\omega}(Z)\frac{\epsilon-1-\alpha\Lambda^L}{\epsilon Q_{\perp}+\alpha+q_{\parallel}^2\Lambda^L}\right). \qquad (4.34)$$

Equations (4.32) and (4.34) are now substituted into Eq. (4.6), recognizing that according to Eq. (4.26),

$$\vec{A}^{(A)}_{\vec{q}_{\parallel},\omega}(Z)+\hat{u}\frac{4\pi i}{\omega}\int dz'\sigma^{zj}_{\vec{q}_{\parallel}}(Z,z';\omega)A^{(A)j}_{\vec{q}_{\parallel},\omega}(z') =\vec{T}^{\parallel}_{\vec{q}_{\parallel},\omega}+\vec{L}^{\parallel}_{\vec{q}_{\parallel},\omega}+\hat{u}\epsilon T^{z}_{\vec{q}_{\parallel},\omega}+\vec{S}_{q_{\parallel},\omega}(Z)\,, \qquad (4.35)$$

where $\vec{S}_{\vec{q}_{\parallel},\omega}(z)$ is the sum of small terms defined by[28]

$$\vec{S}_{\vec{q}_\parallel,\omega}(z) \equiv \vec{R}_{\vec{q}_\parallel,\omega}(z) + \hat{u}\frac{4\pi i}{\omega}\int dz'\sigma^{zj}_{\vec{q}_\parallel}(z,z';\omega)[\Theta(z'-z+U)R^{j}_{\vec{q}_\parallel,\omega}(z') + \Theta(z-U-z')A^{(A)j}_{\vec{q}_\parallel,\omega}(z')]\Theta(z-Z). \tag{4.36}$$

Thus Eq. (4.6) takes a form in which the long-wavelength limit can be investigated explicitly, viz.,

$$\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z) + \hat{u}\frac{4\pi i}{\omega}\int_{-\infty}^{\infty} dz'\sigma^{zj}_{\vec{q}_\parallel}(z,z';\omega)A^{(A)j}_{\vec{q}_\parallel,\omega}(z')$$
$$= \overleftrightarrow{D}_{\vec{q}_\parallel,\omega}\cdot\frac{2\pi\vec{p}}{iqQ_\perp}e^{-Q_\perp|z+Z_A|} + \frac{2\pi i}{Q_\perp\omega}\int_{-\infty}^{Z} dz'\, e^{-Q_\perp|z-z'|}\overleftrightarrow{\mathfrak{D}}_{\vec{q}_\parallel,\omega}(-Q_\perp\,\mathrm{sgn}(z-z'))\int_{-\infty}^{\infty} dz''\overleftrightarrow{\sigma}_{\vec{q}_\parallel}(z',z'';\omega)\cdot\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z'')$$
$$+ \frac{2\pi}{Q_\perp}e^{Q_\perp(z-2Z)}\;\frac{Q_\perp-\alpha}{Q_\perp+\alpha}\vec{P}^{\parallel}_{\vec{q}_\parallel,\omega}(Z) + \frac{2Q_\perp}{Q_\perp+\alpha}\,\frac{\epsilon-1-\alpha\Lambda^L}{\epsilon Q_\perp+\alpha+q_\parallel^2\Lambda^L}i\vec{q}_\parallel P^{z}_{\vec{q}_\parallel,\omega}(Z) + \hat{u}\frac{\epsilon Q_\perp-\alpha-q_\parallel^2\Lambda^L}{\epsilon Q_\perp+\alpha+q_\parallel^2\Lambda^L}P^{z}_{\vec{q}_\parallel,\omega}(Z)$$
$$+ e^{Q_\perp(z-Z)}\vec{S}_{\vec{q}_\parallel,\omega}(Z). \tag{4.37}$$

To carry out the long-wavelength expansion, one recalls that the smallness of Z_A^{-1} implies that $Q_\perp$, α, and $|\vec{q}_\parallel|$ are all small compared to microscopic distances. Henceforth these will be referred to as "the small wave numbers." It is also useful to assume that ω is far enough from ω_p that $Q_\perp\Lambda^L$, $\alpha\Lambda^L$, and $|\vec{q}_\parallel|\Lambda^L$ are all much less than 1.[29]

Now consider the RHS of Eq. (4.37) for z in the surface region. The first term is zeroth order in the small wave numbers. The second (integral) term is first order *times* the order of $\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z)$. Finally, referring to the definition of $\vec{p}_{\vec{q}_\parallel,\omega}(Z)$, Eq. (4.29), one has that the third term is again zeroth order in the small wave numbers.

Temporarily neglecting the "small" $\vec{S}_{\vec{q}_\parallel,\omega}(Z)$ term, one thus finds that for z in the surface region, $\vec{A}_{\vec{q}_\parallel,\omega}(z)$ is zeroth order in the small wave numbers. Dropping *all*[30] higher order terms and noting that by rotational symmetry about the surface normal $\sigma^{zx}_{\vec{q}_\parallel}(z,z';\omega)$ and $\sigma^{zy}_{\vec{q}_\parallel}(z,z';\omega)$ are first order in q_x and q_y, respectively, Eq. (4.37) reduces to the form (for z in the surface region)

$$\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z) + \hat{u}\frac{4\pi i}{\omega}\int dz'\sigma^{zz}_{\vec{q}_\parallel\to 0}(z,z';\omega)A^{(A)z}_{\vec{q}_\parallel,\omega}(z')$$
$$= \overleftrightarrow{\mathfrak{D}}_{\vec{q}_\parallel,\omega}(-Q_\perp)\cdot\frac{2\pi\vec{p}}{iqQ_\perp}e^{-Q_\perp Z_A} + \vec{S}_{\vec{q}_\parallel\to 0,\omega}(Z)$$
$$+ \frac{2\pi}{Q_\perp}\left[\frac{Q_\perp-\alpha}{Q_\perp+\alpha}\vec{P}^{\parallel}_{\vec{q}_\parallel\to 0,\omega}(Z) + \left(\frac{2Q_\perp}{Q_\perp+\alpha}(\epsilon-1)i\vec{q}_\parallel + (\epsilon Q_\perp-\alpha)\hat{u}\right)\frac{1}{\epsilon Q+\alpha}P^{z}_{q_\parallel\to 0,\omega}(Z)\right]. \tag{4.38}$$

The important feature of Eq. (4.38) is that its RHS is *independent of z.* Thus in this zeroth-order approximation, $\vec{A}^{(A)\parallel}_{\vec{q}_\parallel\to 0,\omega}(z)$ is constant in z, and $A^{(A)z}_{\vec{q}_\parallel\to 0,\omega}(z)$ is trivially related to the z component of the clean-surface vector potential, which, when normalized to a unit magnitude transverse wave inside the jellium, satisfies[4]

$$A_\omega(z) + \frac{4\pi i}{\omega}\int_{-\infty}^{\infty} dz'\sigma^{zz}_{\vec{q}_\parallel\to 0,\omega}(z,z';\omega)A_\omega(z') = \epsilon. \tag{4.39}$$

The numerical results given in the next section are accordingly based on the numerical solutions of Eq. (4.39) given in the first of Ref. 4 for an RPA model conductivity tensor, and require little new computational effort.

Before proceeding, it is important to establish the order of $\vec{S}_{\vec{q}_\parallel\to 0,\omega}(Z)$ in the small wave numbers. According to Eq. (4.14), $\vec{R}_{\vec{q}_\parallel,\omega}(z)$ is zeroth order, i.e., the same as $\vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z)$. For $z>Z$ Eq. (4.14) yields, upon carrying out the differentiations implied by $\overleftrightarrow{D}_{\vec{q}_\parallel,\omega}$,

$$\vec{S}_{\vec{q}_\parallel,\omega}(z) = \frac{2\pi i}{Q_\perp\omega}\int_{Z}^{\infty} dz'\, e^{-Q_\perp|z-z'|}\overleftrightarrow{\mathfrak{D}}_{\vec{q}_\parallel,\omega}(-Q_\perp\,\mathrm{sgn}(z-z'))$$
$$\times\int_{-\infty}^{\infty} dz''\overleftrightarrow{\sigma}_{\vec{q}_\parallel}(z',z'';\omega)[\vec{R}_{\vec{q}_\parallel,\omega}(z'')\Theta(z''-z'+U) + \vec{A}^{(A)}_{\vec{q}_\parallel,\omega}(z'')\Theta(z'-U-z'')]. \tag{4.40}$$

Now one lets $z\to Z^+$. Retaining only the lowest-order terms in the small wave numbers, one has

$$\vec{S}_{\vec{q}_{\parallel},\omega}(Z^+) = \frac{2\pi i}{Q_\perp \omega}\int_Z^\infty dz' \overleftrightarrow{\mathfrak{D}}_{\vec{q}_{\parallel},\omega}(Q_\perp)\cdot\int_{-\infty}^{\infty} dz'' \overleftrightarrow{\sigma}_{q_{\parallel}\to 0}(z',z'';\omega)\cdot[\vec{R}_{\vec{q}_{\parallel}\to 0,\omega}(z'')\Theta(z''-z'+U) + \vec{A}^{(A)}_{\vec{q}_{\parallel}\to 0,\omega}(z'')\Theta(z'-U-z'')]. \tag{4.41}$$

Since $\overleftrightarrow{\mathfrak{D}}_{\vec{q}_{\parallel},\omega}(Q_\perp)$ is second order, the fact that the integrals converge on the RHS of Eq. (4.41) implies that $\vec{S}_{\vec{q}_{\parallel},\omega}(Z)$ (Ref. 28) is first order and thus can be dropped in the zeroth-order equation (4.38), for the vector potential in the surface region.

Thus one obtains the exact zeroth-order results for z in the surface region

$$\vec{A}^{(A)\parallel}_{\vec{q}_{\parallel}\to 0,\omega}(z) = \text{const} = \frac{2\pi}{iqQ_\perp}e^{-Q_\perp Z_A}[q^2\vec{p}_{\parallel} - \vec{q}_{\parallel}(\vec{q}_{\parallel}\cdot\vec{p}_{\parallel}) - iQ_\perp\vec{q}_{\parallel}p_z] + \frac{2\pi}{Q_\perp}\left(\frac{Q_\perp-\alpha}{Q_\perp+\alpha}\vec{P}^{\parallel}_{\vec{q}_{\parallel}\to 0,\omega}(Z) + \frac{2Q_\perp}{Q_\perp+\alpha}\frac{\epsilon-1}{\epsilon Q_\perp+\alpha}i\vec{q}_{\parallel}\vec{P}^{z}_{\vec{q}_{\parallel}\to 0,\omega}(Z)\right), \tag{4.42}$$

and

$$A^{(A)z}_{\vec{q}_{\parallel}\to 0,\omega}(z) = \frac{2\pi}{Q_\perp\epsilon}A_\omega(z)\left([q_{\parallel}^2 p_z - iQ_\perp(\vec{q}_{\parallel}\cdot\vec{p}_{\parallel})]\frac{e^{-Q_\perp Z_A}}{iq} + \frac{\epsilon Q_\perp-\alpha}{\epsilon Q_\perp+\alpha}P^z_{\vec{q}_{\parallel}\to 0,\omega}(Z)\right), \tag{4.43}$$

where $A_\omega(z)$ is the solution to Eq. (4.39). All that remains is to evaluate $\vec{P}_{\vec{q}_{\parallel}\to 0,\omega}(Z)$ via Eqs. (4.29), (4.5), (4.42), and (4.43), and then to use the latter two equations to determine the local field at $\vec{R}_A \equiv (0,0,-Z_A)$.

Consider first the evaluation of $\vec{P}_{q_{\parallel}\to 0,\omega}(Z)$. In the long-wavelength limit the definition, Eq. (4.29) can be rewritten as

$$\vec{P}_{\vec{q}_{\parallel}\to 0,\omega}(Z) = \overleftrightarrow{D}_{q_{\parallel}\to 0,\omega}(-Q_\perp)\cdot\frac{\vec{p}}{iq}e^{-Q_\perp Z_A} + \frac{1}{4\pi}\vec{C}_\omega(Z), \tag{4.44}$$

where, cf. Eq. (4.5),

$$C^j_\omega(Z) \equiv \frac{4\pi i}{\omega}\int_{-\infty}^{Z} dz'\int_{-\infty}^{\infty} dz''\sigma^{jj}_{\vec{q}_{\parallel}\to 0}(z',z'';\omega) \times A^{(A)j}_{\vec{q}_{\parallel}\to 0,\omega}(z''). \tag{4.45}$$

Since in Eq. (4.45) only z'''s in the surface region contribute, $\vec{C}_\omega(Z)$ can be evaluated immediately by means of Eqs. (4.42) and (4.43). The fact that $\vec{A}^{(A)\parallel}_{\vec{q}_{\parallel}\to 0,\omega}(z)$ is independent of z implies that

$$\vec{C}^{\parallel}_\omega(Z) = \vec{A}^{(A)\parallel}_{\vec{q}_{\parallel}\to 0,\omega}(\epsilon-1)[Z-d_{\parallel}(\omega)], \tag{4.46}$$

where[31]

$$d_{\parallel}(\omega) \equiv Z - \frac{4\pi i/\omega}{\epsilon-1}\int_{-\infty}^{Z} dz'\int_{-\infty}^{\infty} dz''\sigma^{xx}_{\vec{q}_{\parallel}\to 0}(z',z'';\omega). \tag{4.47}$$

At the same time, the fact that $A^{(A)z}_{\vec{q}_{\parallel}\to 0,\omega}(z)$ is proportional to $A_\omega(z)$ leads to the conclusion that

$$C^z_\omega(Z) = \frac{4\pi}{iq}[q_{\parallel}^2 p_z - iQ_\perp(\vec{q}_{\parallel}\cdot\vec{p}_{\parallel})] \times e^{-Q_\perp Z_A}\frac{(\epsilon-1)[Z-d_\perp(\omega)]+\Lambda^L}{\epsilon Q_\perp+\alpha} \tag{4.48}$$

to lowest order in the small wave numbers, where

$$d_\perp(\omega) \equiv Z - \frac{1}{\epsilon-1}\left(\int_{-\infty}^{Z} dz[\epsilon - A_\omega(z)] - \Lambda^L\right). \tag{4.49}$$

Now one is ready to evaluate the local field at $(0,0,-Z_A)$. Using the exact equation, (4.37), and retaining the lowest *two* orders in the small wave numbers, one has

$$\vec{A}^{(A),\text{loc}}_{\vec{q}_{\parallel}\to 0,\omega}(-Z_A) = \frac{1}{2Q_\perp}\overleftrightarrow{D}_{\vec{q}_{\parallel},\omega}(Q_\perp)\cdot\vec{C}_\omega(Z) + e^{-Q_\perp Z}\vec{S}_{\vec{q}_{\parallel}\to 0,\omega}(Z) + \frac{2\pi}{Q_\perp}e^{-Q_\perp Z_A}(1-2Q_\perp Z)\left[\frac{Q_\perp-\alpha}{Q_\perp+\alpha}\vec{P}^{\parallel}_{\vec{q}_{\parallel}\to 0,\omega}(Z) + i\vec{q}_{\parallel}P^z_{\vec{q}_{\parallel}\to,\omega}(Z)\left(\frac{2Q_\perp}{Q_\perp+\alpha}\frac{\epsilon-1}{\epsilon Q_\perp+\alpha} - \frac{2\epsilon Q_\perp^2\Lambda^L}{(\epsilon Q_\perp+\alpha)^2}\right) + \hat{u}P^z_{\vec{q}_{\parallel}\to 0,\omega}(Z)\left(\frac{\epsilon Q_\perp-\alpha}{\epsilon Q_\perp+\alpha} - \frac{2\epsilon q_{\parallel}^2 Q_\perp\Lambda^L}{(\epsilon Q_\perp+\alpha)^2}\right)\right]. \tag{4.50}$$

The superscript loc, for "local," means simply that the direct radiation term, the first on the RHS of (4.37) (which diverges at $z=-Z_A$), has been subtracted out. To obtain the local field in real space one now performs the necessary $\vec{q}_{\parallel}$ integral, i.e.,

$$\vec{A}_\omega^{(A),\mathrm{loc}}(\vec{\rho}=0, z=-Z_A) = \int \frac{d^2q_\parallel}{(2\pi)^2} \vec{A}^{(A),\mathrm{loc}}_{\vec{q}_\parallel \to 0,\omega}(-Z_A). \tag{4.51}$$

Substituting Eqs. (4.44), (4.46), (4.42), and (4.48) into Eq. (4.50), dropping the small $\vec{S}_{\vec{q}_\parallel\to 0,\omega}(Z)$ term, and taking advantage of cylindrical symmetry via the identities

$$\int \frac{d\hat{q}_\parallel}{2\pi} \vec{q}_\parallel \equiv 0 \tag{4.52}$$

and

$$\int \frac{d\hat{q}_\parallel}{2\pi} \vec{q}_\parallel (\vec{q}_\parallel \cdot \vec{p}_\parallel) \equiv \frac{1}{2} q_\parallel^2 \vec{p}_\parallel, \tag{4.53}$$

one obtains the results

$$iqA_\omega^{(A),\mathrm{loc}\,z}(\vec{\rho}=0, -Z_A) = q^3 p_z \int_0^\infty \frac{\lambda^3 d\lambda \exp[-2qZ_A(\lambda^2-1)^{1/2}]}{(\lambda^2-1)^{1/2}[\epsilon(\lambda^2-1)^{1/2}+(\lambda^2-\epsilon)^{1/2}]} \times \Bigg([\epsilon(\lambda^2-1)^{1/2}-(\lambda^2-\epsilon)^{1/2}][1-2qd_\perp(\omega)(\lambda^2-1)^{1/2}] + \frac{2q[d_\perp(\omega)-d_\parallel(\omega)](\epsilon-1)(\lambda^2-\epsilon)(\lambda^2-1)^{1/2}}{\epsilon(\lambda^2-1)^{1/2}+(\lambda^2-\epsilon)^{1/2}} \Bigg) \tag{4.54}$$

and

$$iq\vec{A}_\omega^{(A),\mathrm{loc}\,\parallel}(\vec{\rho}=0, z=-Z_A) = q^3 \vec{p}_\parallel \int^\infty \lambda\, d\lambda \exp[-2qZ_A(\lambda^2-1)^{1/2}] \times \Bigg\{ \left[\frac{(\lambda^2-1)^{1/2}-(\lambda^2-\epsilon)^{1/2}}{(\lambda^2-1)^{1/2}+(\lambda^2-\epsilon)^{1/2}} + \frac{\lambda^2}{2}\left(1-\frac{2(\lambda^2-1)^{1/2}}{\epsilon(\lambda^2-1)^{1/2}+(\lambda^2-\epsilon)^{1/2}}\right)\right] \frac{1}{(\lambda^2-1)^{1/2}} - \frac{q(\epsilon-1)(\lambda^2-1)^{1/2}[\epsilon d_\perp(\omega)(\lambda^2-1)^{1/2}+d_\parallel(\omega)(\lambda^2-\epsilon)^{1/2}]\lambda^2}{[\epsilon(\lambda^2-1)^{1/2}+(\lambda^2-\epsilon)^{1/2}]^2} - [(\lambda^2-1)^{1/2}-(\lambda^2-\epsilon)^{1/2}]qd_\parallel(\omega)\left(\frac{2}{(\lambda^2-1)^{1/2}+(\lambda^2-\epsilon)^{1/2}} - \frac{\lambda^2}{\epsilon(\lambda^2-1)^{1/2}+(\lambda^2-\epsilon)^{1/2}}\right)\Bigg\}. \tag{4.55}$$

Not surprisingly, the $O(q^3)$ terms in Eqs. (4.54) and (4.55) are identical to those found in the classical model, cf. Eqs. (3.10) and (3.11). The $O(q^4d)$ terms are new and incorporate the effects of the structure of the surface in the functions $d_\perp(\omega)$ and $d_\parallel(\omega)$. The analytic structure of the integrands for the new terms is essentially the same as that for the classical terms, leading, as before, to singular behavior near the surface-plasma frequency. Away from this frequency range the leading contributions to Eqs. (4.54) and (4.55) come from the region of large λ, and $iq\vec{A}_\omega^{(A),\mathrm{loc}}(\vec{\rho}=0,-Z_A)$ takes the form

$$iq\vec{A}_\omega^{(A),\mathrm{loc}}(\vec{\rho}=0, -Z_A) = \frac{\epsilon-1}{\epsilon+1}\frac{\frac{1}{2}\vec{p}_\parallel + p_z\hat{u}}{4Z_A^3} \times \left(1-\frac{3}{Z_A}\frac{\epsilon d_\perp(\omega)+d_\parallel(\omega)}{\epsilon+1}\right), \tag{4.56}$$

or, more suggestively,

$$iq\vec{A}_\omega^{(A),\mathrm{loc}}(\vec{\rho}=0, -Z_A) = \frac{1}{4}\frac{\epsilon-1}{\epsilon+1}(\tfrac{1}{2}\vec{p}_\parallel + p_z\hat{u}) \times \frac{1}{\left(Z_A + \frac{\epsilon d_\perp(\omega)+d_\parallel(\omega)}{\epsilon+1}\right)^3}. \tag{4.57}$$

This result shows that the adatom-induced local field is given by image theory, provided that the image plane lies at

$$\mathfrak{z}_{\mathrm{im}} = \frac{\epsilon d_\perp(\omega)+d_\parallel(\omega)}{\epsilon+1} \tag{4.58}$$

for frequencies not too close to the surface-plasmon resonance. Equation (4.58) constitutes the main new result of this work. In the next section its significance is explored in the light of numerical calculations based on the RPA model of the jellium conductivity tensor.

Incidentally, note that Eq. (4.58) does not complete the calculation of the local field because $\vec{p}$ must still be determined via the self-consistency relation, Eq. (2.2). However, using Eq. (2.3) and the clean-surface fields appropriate to the jellium problem (Appendix) the evaluation of $\vec{p}$ is as trivial as in the classical case and the results are formally identical to those in Eqs. (3.12) and (3.13), with $I_{\parallel}(\omega)$ and $I_{\perp}(\omega)$ replaced by their generalized versions in Eqs. (4.55) and (4.54).

V. IMAGE PLANE IN ADATOM IRRADIATION—NUMERICAL RESULTS AND DISCUSSION

In the last section I showed that, for $\epsilon+1$ not too close to zero, the parallel and normal components of the local field at an irradiated adatom are enhanced by the image factor

$$\frac{1}{1-\frac{\epsilon-1}{\epsilon+1}\frac{\chi(\omega)}{n}\frac{1}{[Z_A+\mathfrak{z}_{\rm im}(\omega)]^3}},$$

where $n=8(4)$ for the parallel (normal) field component, $\chi(\omega)$ is the adatom polarizability in free space, and $\mathfrak{z}_{\rm im}(\omega)$ is the frequency-dependent image plane position which [cf. Eq. (4.58)] depends on the microscopic structure of the surface via the depth parameters $d_{\parallel}(\omega)$ and $d_{\perp}(\omega)$. Here I discuss the significance of these depth parameters and present numerical results for the position of the image plane as a function of photon energy. I discuss the implications of these results regard- the possibility of large enhancement of the local field and point out the direction for future research in this area.

First consider the meaning of $d_{\parallel}(\omega)$. Integrating Eq. (4.47) by parts and then letting $Z\rightarrow\infty$, one finds that

$$d_{\parallel}(\omega)=\frac{\int_{-\infty}^{\infty}dz\,z\frac{d}{dz}\int_{-\infty}^{\infty}dz'\sigma^{xx}_{q_{\parallel}\rightarrow 0}(z,z';\omega)}{\int_{-\infty}^{\infty}dz\frac{d}{dz}\int_{-\infty}^{\infty}dz'\sigma^{xx}_{q_{\parallel}\rightarrow 0}(z,z';\omega)}. \quad (5.1)$$

Since the conductivity tensor is short ranged and rapidly heals to its bulk form inside the jellium,

$$\frac{d}{dz}\int_{-\infty}^{\infty}dz'\sigma^{xx}_{q_{\parallel}\rightarrow 0}(z,z';\omega)$$

is a function which is sharply peaked in the surface region, and $d_{\parallel}(\omega)$ measures the surface position as its centroid. Within the RPA it is easy to show[4] that

$$\frac{4\pi i}{\omega}\int_{-\infty}^{\infty}dz'\sigma^{xx}_{q_{\parallel}\rightarrow 0}(z,z';\omega)=-\frac{4\pi n(z)e^2}{m\omega^2}, \quad (5.2)$$

where $n(z)$ is the jellium charge-density profile. Thus in this approximation, $d_{\parallel}(\omega)$ is frequency independent and real, and is given by

$$d_{\parallel}=\int_{-\infty}^{\infty}dz\,z\frac{dn}{dz}\Big/\int_{-\infty}^{\infty}dz\frac{dn}{dz}. \quad (5.3)$$

The interpretation of $d_{\perp}(\omega)$ is easiest for $\omega<\omega_p$, where $\Lambda^L=0$. In this regime, again integrating by parts [this time in Eq. (4.49)] and letting $Z\rightarrow\infty$, one finds

$$d_{\perp}(\omega)=\int_{-\infty}^{\infty}dz\,z\frac{dA_{\omega}(z)}{dz}\Big/\int_{-\infty}^{\infty}dz\frac{dA_{\omega}(z)}{dz}, \quad (5.4)$$

using the facts[4] that $A_{\omega}(z\rightarrow\infty)=1$ and $A_{\omega}(z\rightarrow-\infty)=\epsilon$. Next one uses Poisson's equation, which in the long-wavelength limit is[4]

$$\frac{dA_{\omega}(z)}{dz}=-\frac{4\pi}{iq}\delta n_{\omega}(z), \quad (5.5)$$

where $\delta n_{\omega}(z)$ is the fluctuating charge induced at the jellium surface. Substituting (5.5) into Eq. (5.4) thus implies that

$$d_{\perp}(\omega)=\int_{-\infty}^{\infty}dz\,z\,\delta n_{\omega}(z)\Big/\int_{-\infty}^{\infty}dz\,\delta n_{\omega}(z), \quad (5.6)$$

or in words, that $d_{\perp}(\omega)$ is the centroid of the induced charge-density profile. This result immediately explains why $d_{\perp}(\omega)$ is a more complicated quantity above ω_p. There, because of the photoexcitation of bulk plasmons, $A_{\omega}(z)$ has the large z form

$$A_{\omega}(z)=1+r_{\vec{q}_{\parallel}\rightarrow 0,\omega}e^{ik^{(L)}z}, \quad (5.7)$$

cf. Eqs. (4.26) and (4.31). Consequently there are induced density fluctuations at all depths inside the jellium, and the integrals in Eq. (5.6) are undefined. Equation (4.49) remains a perfectly satisfactory definition of $d_{\perp}(\omega)$, which, using Eq. (5.7), can easily be shown to be Z independent for large Z. It should be thought of as a generalization of Eq. (5.6) in which the plasmon contribution is subtracted out.

I turn now to the result that, to lowest order in the microscopic theory, image theory holds with the image plane at

$$\mathfrak{z}_{\rm im}=[\epsilon d_{\perp}(\omega)+d_{\parallel}(\omega)]/(\epsilon+1). \quad (5.8)$$

The first interesting feature of this result is that since $\epsilon(\omega\rightarrow 0)=-\infty$ for jellium,

$$\mathfrak{z}_{\rm im}(\omega\rightarrow 0)=\int_{-\infty}^{\infty}dz\,z\,\delta n_{\omega\rightarrow 0}(z)\Big/\int_{-\infty}^{\infty}dz\,\delta n_{\omega\rightarrow 0}(z). \quad (5.9)$$

This static limit is in accord with the result of Lang and Kohn.[11]

The second important feature of Eq. (5.8) is that for finite frequency, there is no reason why $\mathfrak{z}_{\rm im}$ should be a real quantity. Since $\delta n_{\omega}(z)$ is lossy, $d_{\perp}(\omega)$ is generally complex and so is $d_{\rm im}$. This fact implies that the maximum value of an image enhancement factor such as [cf. Eq. (4.57)]

$$\left(1-\frac{\epsilon-1}{\epsilon+1}\,\frac{\chi(\omega)}{4(Z_A+d_{\rm im})^3}\right)^{-1},$$

even if $\mathrm{Im}\epsilon=\mathrm{Im}\chi(\omega)=0$, is limited to $\sim\frac{1}{3}Z_A/\mathrm{Im}(d_{\rm im})$. Model calculations described below show that this maximum enhancement is small compared to what one would need to explain the factor of $\sim10^6$ enhancement of the Raman effect for pyridine on Ag.[2,3] Thus even if one violates the assumption that Z_A must be asymptotically large [at least a few times the nonlocality range of $\tilde{\sigma}_{q_\parallel}(z,z';\omega)$ according to Sec. IV] for the image model to be valid, this model still does not predict a very large local-field enhancement at an adatom.

The RPA model used to evaluate $d_{\rm im}$ has been described in great detail in the first of Ref. 4 (see also the Appendix). The calculations reported here are based on the use of the Lang-Kohn self-consistent potential barrier for $r_s=2$.[32] Similar results should obtain for other values of r_s.[4] The origin of the z axis was chosen so that $d_\parallel$ equaled zero and values of $d_\perp(\omega)$ were obtained via the general equation (4.49) by a simple numerical integration. Because of the large Friedel oscillations and large dielectric mismatch at the surface at lower frequencies ($\epsilon=1-\omega_p^2/\omega^2$ in the RPA), values of $d_\perp(\omega)$ were difficult to calculate to better than ~15% around $\hbar\omega\sim8$ eV. But for 10 eV and above, the numerical stability of the integral equation for $A_\omega(z)$ is greatly improved ($\hbar\omega_p$ 016.7 eV for $r_s=2$) and the value of $d_\perp(\omega)$ could easily be obtained with two-place accuracy.

Calculated values of $d_{\rm im}(\omega)$ are given in Fig. 1. Using an "optical theorem" which follows from Eq. (4.39) it can easily be shown[33] that if there is no bulk power absorption, i.e., if ϵ is real, as it is in the RPA, then $\epsilon\,\mathrm{Im}d_\perp(\omega)$ is directly proportional to the power loss due to surface photoexcitation of electron-hole pairs. Thus $\epsilon\,\mathrm{Im}d_\perp(\omega)$ is a positive quantity and $\mathrm{Im}d_{\rm im}$ has the sign of $\epsilon+1$, negative below the surface-plasma frequency and positive above. Near and above ω_p (16.7 eV for $r_s=2$), $\mathrm{Im}(d_{\rm im})$ becomes quite small because the surface photoeffect becomes weak as the variation of the electromagnetic field across the surface region becomes small.[6] Near the surface-plasma frequency (11.8 eV for $r_s=2$), as in the classical local-field problem of Sec. III, one may not drop the pole contributions to Eqs. (4.54) and (4.55) and thereby derive the image result of Eq. (4.57). Thus, the anomaly seen in Fig. 1 near $\epsilon+1=0$ is an indication of the breakdown of the concept of an image plane for ω near the surface-plasma resonance. Below 11.8 eV is

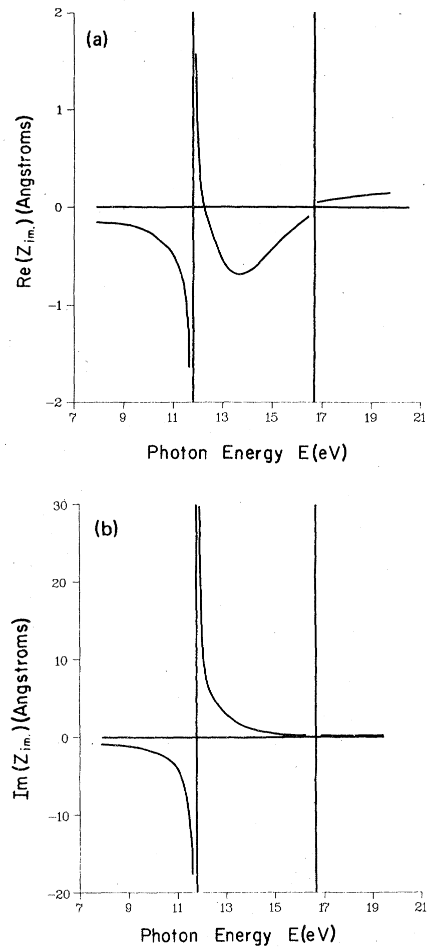

FIG. 1. The position of the image plane relative to the centroid of dn/dz as a function of frequency, for $r_s=2$ jellium (a) $\mathrm{Re}d_{\rm im}(\omega)$ and (b) $\mathrm{Im}d_{\rm im}(\omega)$.

the region of interest for the surface-enhanced Raman effect as well as other optical experiments. $\mathrm{Im}d_{\rm im}(\omega)$ is not small, approximately several tenths of an Å or more. Thus the maximum effect is $\sim Z_A/$(a few Å). Since Z_A is of O(Å) in the Raman experiments where enhancement is seen, this result suggests that image effects are not likely the cause of it. In this regard, however, one must make an important qualification. In the present paper, I have only calculated the local field at $-Z_A$ asymptotically, i.e., for $|Z_A|$ large. It is not at all obvious that the asymptotic results are valid for $Z_A\sim$a few Å. However, if one assumes the validity of the image approximation as in Refs. 2 and 3 then one must grant the validity of a calculation of the first correction to it. And to this extent the negative result obtained here is a significant one.

The direction of future research into local-field effects in irradiation of an adatom is obvious. One must look into the problem when Z_A is not large. Here there will be two complicating effects. First, the atom and surface wave functions will overlap, so the response of the clean surface and of the atom will not be separable. Second, the point dipole approximation will no longer be relevant. On the other hand, the wide use of optical probes of surfaces assures the value of studying this complicated problem.

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APPENDIX: FIELDS FOR A CLEAN JELLIUM SURFACE

For light incident on a clear jellium surface the field in the vacuum region ($z<0$) is given by[9]

$$\vec{A}^{(c)}_{\vec{q}_\parallel,\omega}=\vec{A}^{(0)}e^{iq_\perp z}+e^{-iq_\perp z}\left[\vec{A}^{(0)}R^{(s)}_{\vec{q}_\parallel,\omega}-\hat{q}_\parallel(\hat{q}_\parallel\cdot\vec{A}^{(0)})(R^{(p)}_{\vec{q}_\parallel,\omega}+R^{(s)}_{\vec{q}_\parallel,\omega})+\hat{u}A^{(0)z}R^{(p)}_{\vec{q}_\parallel,\omega}\right], \quad \text{(A1)}$$

where

$$q_\perp \equiv (q^2-q_\parallel^2)^{1/2}. \quad \text{(A2)}$$

In Eq. (A1) the reflection amplitudes for s- and p-polarized light are given, respectively, by

$$R^{(s)}_{\vec{q}_\perp,\omega}=\frac{q_\perp-q'_\perp}{q_\perp+q'_\perp}\left[1+2iq_\perp d_\parallel(\omega)\right] \quad \text{(A3)}$$

and

$$\mathrm{R}^{(p)}_{\vec{q}_\parallel,\omega}=\frac{\epsilon q_\perp-q'_\perp}{\epsilon q_\perp+q'_\perp}\left(1-\frac{2iq_\perp(\epsilon-1)}{q_\perp'^2-\epsilon^2q^2}\times\left[q_\perp'^2 d_\parallel(\omega)-\epsilon q_\parallel^2 d_\perp(\omega)\right]\right), \quad \text{(A4)}$$

with

$$q'_\perp\equiv(q_\perp^2+q^2(\epsilon-1))^{1/2}, \quad \text{(A5)}$$

and where $d_\parallel(\omega)$ and $d_\perp(\omega)$ are given by Eqs. (4.47) and (4.49). The same equations apply in the case of a classical dielectric interface at $z=0$, if $d_\parallel(\omega)$ and $d_\perp(\omega)$ are set equal to zero.

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[1]D. L. Jeanmaire and R. P. Van Duyne, J. Electroanal. Chem. 84, 1 (1977).

[2]F. W. King, R. P. Van Duyne, and G. C. Schatz, J. Chem. Phys. 69, 4472 (1978).

[3]S. Efrima and H. Metiu, J. Chem. Phys. 70, 1602 (1979); 70, 1939 (1979); 70, 2297 (1979).

[4]P. J. Feibelman, Phys. Rev. B 12, 1319 (1975); Phys. Rev. Lett. 34, 1092 (1975).

[5]K. L. Kliewer, Phys. Rev. B 14, 1412 (1976); 15, 3759 (1977).

[6]H. J. Levinson, E. W. Plummer, and P. J. Feibelman, Phys. Rev. Lett. 43, 952 (1979).

[7]M. R. Philpott, J. Chem. Phys. 62, 1812 (1975); H. Morawitz and M. R. Philpott, Phys. Rev. B 10, 4863 (1974).

[8]As pointed out in Ref. 7, the classical results are only equivalent to "image theory" sufficiently far from the surface-plasma frequency. This point is discussed further below.

[9]P. J. Feibelman, Phys. Rev. B 14, 762 (1976).

[10]P. J. Feibelman, Phys. Rev. B 9, 5077 (1974); J. Harris and A. Griffin, Phys. Lett. A34, 51 (1971); B. B. Dasgupta and A. Bagchi, Phys. Rev. B 19, 4935 (1979).

[11]N. D. Lang and W. Kohn, Phys. Rev. B 7, 3541 (1973).

[12]E. Zaremba and W. Kohn, Phys. Rev. B 13, 2270 (1976).

[13]The quadrupole moment induced on the adatom is proportional to the *gradient* of the local field and the field due to its image is of $O(Z_A^{-4})$ or smaller. Thus the leading quadrupole contributions to the local field are of $O(Z_A^{-5})$ and $O(qZ_A^{-4})$, where q is the magnitude of the incident light wave vector.

[14]The gauge used is that for which the scalar potential is identically zero.

[15]This is where the assumption of two-dimensional translation invariance enters the problem. In the general case, $\vec{q}_\parallel$ is not a good quantum number.

[16]Zenneck, Ann. Phys. (Leipzig) 23, 846 (1907); A. Sommerfeld, *Partial Differential Equations* (Academic, New York, 1949), p. 236 ff.

[17]This is something of an overstatement, actually. At and above the bulk-plasma frequency the classical problem is ill-defined without an additional boundary condition that determines the amplitude of bulk-plasmon photoexcitation. See Ref. 18, for example.

[18]F. Forstmann, Z. Phys. 32, 385 (1979); M. F. Bishop and A. A. Maradudin, Phys. Rev. B 14, 3384 (1976).

[19]P. B. Johnson and R. W. Christy, Phys. Rev. B 6, 4370 (1972).

[20]Near a resonance, where $\chi(\omega)\approx a^3\omega_0/(\omega_0-\omega-i\Gamma)$ with $a^3\sim$ an atomic volume, one finds that

$$\chi(\omega)[1 - I(\omega)\chi(\omega)]^{-1} = a^3\omega_0/[\omega_0 - \omega - i\Gamma - \omega_0 a^3 I(\omega)] .$$

Thus, the argument that $I(\omega)$ must be of the order of an inverse atomic volume to have an appreciable effect is *still* true.

[21] Since $q = \omega/c$ is small, the smallness of $Q_\perp$ implies the smallness of $|\vec{q}_\parallel|$ as well, via Eq. (2.5).

[22] P. M. Platzman and P. A. Wolff, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1973), Suppl. 13.

[23] This can be proven by taking the cross product of $(i\vec{q} - \alpha\hat{u})$ with both sides of Eq. (4.18) and thereby showing that Eq. (4.20) implies that $(i\vec{q} - \alpha\hat{u}) \times \vec{T}_{\vec{q}_\parallel,\omega} = 0$. See the first of Ref. 4.

[24] Here is where the assumption that $\vec{\sigma}^{(B)}(\alpha;U;\omega)$ is independent of U is necessary to recover the classical limit.

[25] The minus sign is closen so that the bulk plasmons generated will be outgoing waves.

[26] Very close to but below ω_p one might wish to retain $\vec{L}_{\vec{q}_\parallel,\omega}$ since the "evanescent bulk plasmon" can be of long attenuation length.

[27] P. J. Feibelman, Phys. Rev. B 12, 4282 (1975). See also the first of Ref. 4.

[28] The $\Theta(z - Z)$ on the RHS of (4.36) makes $\vec{S}_{\vec{q}_\parallel,\omega}(z)$ a continuous function of z, as can be seen from Eq. (4.14).

[29] Since the original equation (4.6) is linear, the order of p is irrelevant and is here taken to be zeroth order. q is taken to be a small wave vector in the argument that follows, although of course its smallness depends on the low energy of the incident radiation, not the largeness of Z_A.

[30] Here $Q_\perp Z$ is treated as being small and thus Z must be assumed to be small compared to Z_A.

[31] Note that this definition can also be written, integrating by parts and then letting $Z \to \infty$, as

$$d_\parallel(\omega) = \int_{-\infty}^{\infty} z \frac{d}{dz}\sigma^{-x}(z) \Big/ \sigma^{-x}(\infty)$$

$$\equiv \int_{-\infty}^{\infty} z \frac{d}{dz}\sigma^{-x}(z) \Big/ \int_{-\infty}^{\infty} dz \frac{d}{dz}\sigma^{-x}(z) ,$$

where

$$\sigma^{-x}(z) \equiv \int dz' \sigma^{xx}_{\vec{q}_\parallel \to 0}(z, z';\omega) .$$

[32] N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1070).

[33] P. J. Feibelman (unpublished).