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Electrodynamics at a metal surface with applications to the spectroscopy of adsorbed molecules. I. General theory

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Recently, a large number of surface-spectroscopic phenomena have been discussed in terms of models which provide phenomenological equations for the response of the adsorbed molecule to the external fields and compute these fields by assuming that the macroscopic Maxwell equations are valid. Since the macroscopic equations neglect the spatial dispersion of the dielectric constant of the metal and its variation with the distance to the surface, one expects that the computation of the field near or inside the interface may have substantial errors. In order to study the extent of such errors, we use a jellium–electron-gas model to develop a microscopic theory of the electromagnetic fields at the interface. The electron-gas properties needed in such calculations are obtained by using the random-phase approximation. Numerical results are planned to be presented in future papers.

I. INTRODUCTION

The interpretation of the experimental data obtained by surface spectroscopy has widely used phenomenological models based on Maxwell equations. The properties of the metal are described by the frequency-dependent, zero-wave-vector dielectric constant; the surface is represented by the boundary conditions; the role of the molecule is mimicked by a system of permanent or polarizable charge whose classical equation of motion is specified.

There are many important examples of such calculations. In infrared, electron-energy loss, and electron-tunneling spectroscopy image-field interactions have been invoked to explain frequency shifts caused by chemisorption and change of coverage.[1] In Raman,[2] resonance Raman,[3] and fluorescence spectroscopy,[4] a Drude-Lorentz model and image forces are used to compute surface-induced changes in the molecular polarizability. Similar effects were invoked to argue that the enhanced Raman scattering may be a surface-induced resonance Raman effect.[5] Finally, the van der Waals interactions between two adsorbed atoms is influenced by the presence of the metal and Maxwell's equations have been used[6] to include this effect.

In using macroscopic Maxwell's equations to compute electromagnetic fields very close to a metal interface, one may make substantial errors. Two of them are discussed here: (1) The field exerted by the molecular charges on the metal electrons varies rapidly with distance. The spatial Fourier transform of this field contains high-wave-vector components, and the response of the metal to such a field is described by a wave-vector-dependent dielectric tensor.[7] In using phenomenological Maxwell equations with optically measured dielectric constants, this wave-vector dependence (i.e., spatial dispersion or nonlocality) is ignored. (2) The electromagnetic field near the interface is certainly influenced by the details of the continuous polarization charge in the interface region. The use of boundary conditions in the macroscopic theory replaces the real charge distribution with a sudden jump, thus making an error that becomes more important the closer one gets to the surface.

In this series of papers we use a jellium model and the random-phase approximation (RPA), previously developed by Newns,[8] Beck and Celli,[9] and Feibelman,[10] to inquire numerically into the magnitude of the errors introduced by the two approximations mentioned above.

Since we are particularly interested in the implications of those errors to surface spectroscopy we must be able to compute the electromagnetic fields induced by (a) long-wavelength transverse fields, caused by the laser source, and (b) high-wave-vector longitudinal fields, caused by oscillating charge densities and/or currents located near the surface and representing the molecules. Previous numerical work by Feibelman[10] has been concerned with long-wavelength fields only. In the procedure developed by him, the smallness of the wave vector is used to simplify the numerical work and it would have to be substantially modified if applied to the case of high-wave-vector fields.

In the present work we develop and apply a method that can be used for all wave vectors. The idea is very simple. We expand the RPA equation for the polarization tensor in Fourier series and turn this integral equation into an infinite, discrete matrix equation. By truncation, this becomes a finite matrix equation which can be solved numerically. By taking a larger and larger truncated basis set we can test whether the computation is convergent.

It turns out, however, that this simple procedure is not easy to implement. Difficulties appear because there are always two types of fields in the problem: a sharply varying field, localized in the immediate vicinity of the electron-gas boundary and a smoothly varying field, which is extended over a very large range on a microscopic scale. In most cases these two ranges overlap, thus leading to *nonadditive* mixing of Fourier components of very high and very low wave numbers. To describe simultaneously both the smooth and the sharp parts of the field, an extremely large basis set is therefore required. We find that within the normal financial limitations it is not practically possible to get good convergence in the interface region. For example, even in the favorable case of a dipole oscillating near the surface, where one expects a sharply varying, short-range (screened) field only, one runs into difficulties. If the dipole frequency is below that of the surface plasmon threshold and the dipole is close to the surface, the convergence obtained in a direct application of the method in the interface region is excellent. Once the dipole frequency is increased, however, and the plasmon is excited, the direct application of the method is prohibitively expensive, since one cannot easily describe both the smooth plasmon and the sharply varying interface field in the same calculation.

For this reason the implementation of the above idea must take advantage of specific details of each problem and find ways of treating the smooth and the sharp parts of the field separately. This requires nontrivial analysis, which is the subject of the present work.

This planned series of papers is organized as follows. The present one (paper I) contains a very brief presentation of the basic theory and of those computational aspects common to all planned applications. In paper II we plan to present results for the interface field caused by laser radiation. Paper III will apply the method to thin films and paper IV to the case of a dipole or, more generally, a time-varying charge density located near the interface. The specific methods used to treat separately the smooth and the sharp parts of the field will be discussed in papers II through IV.

The outline of paper I is given below. In Sec. II we give the basic equations in a mixed Fourier representation, which we found very convenient for numerical work. In Sec. III we show how one can define a dielectric matrix which includes surface effects but results in equations that look like those used for the bulk. In Sec. IV we introduce the relaxation-time approximation in a manner which preserves gauge invariance and conserves charge.

II. OUTLINE OF THE MODEL

A. The basic equations

In what follows, A_0 is the scalar potential multiplied by minus one, and A_1, A_2, A_3 are the components A_x, A_y, A_z of the vector potential. An external field, described by $A_\nu^{\text{ext}}(\vec{r}, t)$, $\nu = 0, \ldots, 3$, polarizes the metal and induces a charge density and a current. The electromagnetic fields caused by them is given by

$$A_\nu(\vec{K}, z; \omega) = -\int_0^l \int_0^l D_\nu^0(K, z - z_1; \omega) \sum_{\mu=0}^{3} \Pi_{\nu,\mu}(\vec{K}, z_1, z_2; \omega) A_\mu^{\text{ext}}(\vec{K}, z_2; \omega)\, dz_1 dz_2 \,. \tag{2.1}$$

Here D_ν^0 is the retarded bare-photon Green function in the Lorentz gauge; $\Pi_{\nu,\mu}$ is the retarded-polarization tensor. All quantities are Fourier transformed with respect to time and the coordinates x and y (which are parallel to the surface of the metal). $\vec{K}$ is the parallel momentum and ω is the frequency. We consider a metal slab of thickness l. We use a model in which the electrons are confined inside the metal by infinite barriers located at $z = 0$ and $z = l$. The expressions for D_ν^0 and $\Pi_{\nu,\mu}$ are given below.

The random-phase approximation[11] gives for $\Pi_{\nu,\mu}$ the integral equation

$$\begin{aligned}\Pi_{\nu,\mu}(\vec{K}, z_1, z_2; \omega) = {} & \Pi_{\mu,\nu}^0(\vec{K}, z_1 - z_2; \omega) \\ & - \int_0^l dz_3 \int_0^l dz_4 \sum_{\lambda=0}^{3} \Pi_{\nu,\lambda}^0(\vec{K}, z_1, z_3; \omega) D_\lambda^0(\vec{K}, z_3 - z_4; \omega) \Pi_{\lambda,\mu}(\vec{K}, z_4 z_2; \omega) \,.\end{aligned} \tag{2.2}$$

Here $\Pi_{\nu,\lambda}^0$ is the retarded bare polarization tensor, i.e., the retarded polarization of a free-electron gas.

B. The mixed Fourier representation

The first step in solving Eq. (2.2) is the expansion of $\Pi_{\lambda,\mu}(\vec{K}, z_1, z_2; \omega)$ in Fourier series. Since $\Pi_{\lambda,\mu}$ vanishes when z_1 or z_2 is equal to 0 or l, one would think that a sine expansion will be the most convenient. It turns out, however, that subsequent calculations are greatly simplified when we use what we call the mixed representation. For an arbitrary four-vector $f_\nu(z)$, $\nu = 0, \ldots, 3$, this is defined by

$$f_\nu(z) = \sum_{k \geq 0} f_\nu(k)\phi_\nu(kz), \tag{2.3}$$

with

$$\phi_\nu(kz) = \begin{cases} \cos kz & \text{for } \nu = 0, 1, 2 \\ \sin kz & \text{for } \nu = 3 \end{cases} \tag{2.4}$$

and

$$f_\nu(k) = \frac{2}{l}\int_0^l \phi_\nu(kz) f_\nu(z)\, dz. \tag{2.5}$$

In a similar manner the components $T_{\nu\nu'}(z, z')$ of a four-tensor are expanded in

$$T_{\nu\nu'}(z, z') = \sum_{k \geq 0}\sum_{k' \geq 0} T_{\nu\nu'}(k, k')\phi_\nu(kz)\phi_{\nu'}(k'z'), \tag{2.6}$$

with

$$T_{\nu\nu'}(k, k') = \left(\frac{2}{l}\right)^2 \int_0^l dz \int_0^l dz'\, T_{\nu\nu'}(z, z')\phi_\nu(kz) \times \phi_{\nu'}(k'z'). \tag{2.7}$$

The expressions for $\Pi^0_{\mu,\nu}$ and D^0 in this representation are given below.

C. The bare polarization

To compute $\Pi^0_{\mu,\nu}$ we use a model in which the electrons are confined inside the metal by two infinite barriers located at $z = 0$ and $z = l$. Computationally this amounts to using in the one-particle Green function

$$G^0(\vec{r}, \vec{r}\,'; \omega) = (4L^2)^{-1} \sum_{\vec{K},\kappa} e^{-i\vec{K}\cdot(\vec{R}-\vec{R}')} \psi_\kappa(z)\psi_\kappa(z')\left(\frac{f(\omega_{\vec{K},\kappa})}{\omega - \omega_{\vec{K},\kappa} + i\eta} - \frac{1 - f(\omega_{\vec{K},\kappa})}{\omega - \omega_{\vec{K},\kappa} - i\eta}\right)$$

the basis set

$$\psi_\kappa(z) = (2/l)^{1/2} \sin kz, \; k = n\pi/l, \quad n = 0, 1, 2, \ldots,$$

where l is the thickness of the slab. Furthermore, we use $(\hbar^2 k^2 + \hbar^2 K^2)/2m$ instead of $\hbar\omega_k$. The above specification of G^0 determines completely[11] $\Pi^0_{\nu,\nu'}$.

As is well known the polarization tensor has a diamagnetic $\Pi^{0,d}_{\nu,\nu'}$ and a paramagnetic $\Pi^{0,p}_{\nu,\nu'}$ part:

$$\Pi^0_{\nu,\nu'}(\vec{K}, k, k'; \omega) = \Pi^{0,p}_{\nu,\nu'}(\vec{K}, k, k'; \omega) + \Pi^{0,d}_{\nu,\nu'}(\vec{K}, k, k'; \omega). \tag{2.8}$$

The expressions for these two quantities in the mixed representation are given below.

1. The paramagnetic part

We can write $\Pi^{0,p}_{\nu,\nu'}$ as the sum of a surface part and a bulk part:

$$\Pi^{0,p}_{\nu,\nu'}(\vec{K}, k, k'; \omega) \equiv P^{0,b}_{\nu,\nu'}(\vec{K}, k; \omega)\delta_{kk'} - P^{0,s}_{\nu,\nu'}(\vec{K}, k, k'; \omega). \tag{2.9}$$

The bulk term is given by

$$P^{0,b}_{\nu,\nu'}(\vec{K}, k; \omega) = \frac{1}{2c^2} \sum_{q=-\infty}^{\infty} \sum_{\vec{Q}} J_\nu(\vec{Q} + \tfrac{1}{2}\vec{K}, q + \tfrac{1}{2}k; 1) J^*_{\nu'}(\vec{Q} + \tfrac{1}{2}\vec{K}, q + \tfrac{1}{2}k; 1) R(\vec{Q}, \vec{Q} + \vec{K}, q, q + k; 1) \tag{2.10}$$

and the surface term by

$$P^{0,s}_{\nu,\nu'}(\vec{K}, k, k'; \omega) = \frac{1}{2c^2} \sum_{\alpha=1}^{2} \sum_{\vec{Q}} J_\nu(\vec{Q} + \tfrac{1}{2}\vec{K}, \tfrac{1}{2}k'; \alpha) J^*_{\nu'}(\vec{Q} + \tfrac{1}{2}\vec{K}, \tfrac{1}{2}k; \alpha) R\left(\vec{Q}, \vec{Q} + \vec{K}, \frac{k' - k}{2}, \frac{k' + k}{2}; \alpha\right) \tag{2.11}$$

if the integers n, n' defined by $k = n\pi/l$, $k' = n'\pi/l$ have the same parity. If the parity of n and n' is different, $P^0_{\nu,\nu'}(\vec{k}, k, k'; \omega) = 0$. The functions J_ν and R are

$$J_\nu(\vec{Q}, q; \alpha) \equiv \begin{cases} \dfrac{\hbar e}{m} Q_\nu (-1)^{\alpha+1}, & \nu = 1, 2 \\[2ex] \dfrac{\hbar e}{im} q(-1)^{\alpha+1}, & \nu = 3 \\[1ex] ec, & \nu = 0 \end{cases} \tag{2.12}$$

and

$$R(\vec{Q}_1,\vec{Q}_2,q_1,q_2;\alpha)\equiv\left(\frac{1}{2L^2l}\right)^2\frac{1}{\hbar}\frac{f(\vec{Q}_1,q_1)-f(\vec{Q}_2,q_2)}{\omega(\vec{Q}_2,q_2)-\omega(\vec{Q}_1,q_1)+(-1)^{\alpha}(\omega+i\eta)}\,, \tag{2.13}$$

where $f(\vec{Q},q)\equiv\Theta(k_F^2-Q^2-q^2)$ is the Fermi function.

2. *The diamagnetic part*

The diamagnetic part of the retarded-polarization tensor in the mixed representation is

$$\Pi^{0,d}_{\nu,\nu'}(\vec{K},k,k';\omega)\equiv\Delta^0_{\nu}(k,k')\delta_{\nu,\nu'}(1-\delta_{\nu,0})\,, \tag{2.14}$$

where Δ^0_ν has a bulk plus a surface part:

$$\Delta^0_\nu(k,k')=\Delta^{0,b}_\nu(k)\delta_{kk'}-\Delta^{0,s}_\nu(k,k')\,. \tag{2.15}$$

The bulk term $\Delta^{0,b}_\nu(k)$ is

$$\Delta^{0,b}_\nu(k)=-\frac{n^0e^2}{mc^2}\frac{1}{2L^2l}\,, \tag{2.16}$$

where n^0 is the density of a homogeneous electron gas, $n^0\equiv k_F^3/3\pi^2$. The surface term is

$$\Delta^{0,s}_\nu(k,k')=-\frac{e^2}{mc^2}\frac{1}{2L^2l}\left(n^0_\nu(k,k')(1-\delta_{kk'})+\frac{1}{4\pi l}[2k_F^2+\delta_\nu(k_F^2-k^2)\Theta(k_F^2-k^2)\delta_{kk'}]\right)\,, \tag{2.17}$$

where $\delta_\nu=1$ for $\nu=1,2$ and $\delta_\nu=-1$ for $\nu=3$, and

$$n^0_\nu(k,k')=\frac{1}{4\pi l}\sum_{\alpha=1}^{2}\eta_\nu(\alpha)\left[k_F^2-\left(\frac{k'+(-1)^\alpha k}{2}\right)^2\right]\Theta\left(k_F^2-\left(\frac{k'+(-1)^\alpha k}{2}\right)^2\right) \tag{2.18}$$

if the integers n and n' (defined by $k\equiv n\pi/l$ and $k'\equiv n'\pi/l$) have the same parity; furthermore,

$$n^0_\nu(k,k')=0 \tag{2.19}$$

if the parity of n' and n is different. The function $\eta_\nu(\alpha)$ equals 1 for $\alpha=0,1,2$ and $(-1)^{\alpha+1}$ for $\alpha=3$.

D. Sum rules in the mixed representation

For physical reasons the induced charge and current density have to be zero for $z=0$ and $z=l$, since these are the positions of the infinite barriers. This implies that the diamagnetic and paramagnetic parts of the retarded-polarization tensor $\Pi_{\nu,\nu'}(\vec{K},z,z';\omega)$ must also be zero for $z=0$ or l. Furthermore, physical arguments indicate that $\Pi_{\nu,\nu'}(\vec{K},z,z';\omega)$ is zero when $z'\to 0$ or l.

If a sine Fourier series is used to represent the polarization, the above conditions are automatically satisfied, since $\sin kz=\sin[(n\pi/l)z]=0$ for $z=0$ or l. If a cosine series is used, then the representation

$$f(z)=\sum_{k\geq 0}f(k)\cos kz=\sum_{n\geq 0}\cos(n\pi z/l)f(n\pi/l)$$

and the condition $f(z)=0$ for $z=0$ imply the sum rule $\sum_{k\geq 0}f(k)=0$.

When applied to the bare-polarization tensor this argument yields a useful equation, relating the bulk and the surface parts:

$$\sum_{k'\geq 0}\Pi^{0,s}_{\nu,\nu'}(\vec{K},k,k';\omega)=\Pi^{0,b}_{\nu,\nu'}(\vec{K},k;\omega) \tag{2.20}$$

for $\nu'=0,1,2$. The $\nu'=3$ component does not satisfy such an equation since a sine series is used for this case. Such sum rules are useful in testing the numerical calculations as well as in assessing whether the finite basis set (of cosines and sines) used to obtain numerical results is large enough.

III. THE SOLUTION OF THE BASIC EQUATIONS

We can now solve electromagnetic problems with the present model by developing a procedure to generate numerical values for $\Pi_{\nu,\nu'}$. For this we use the integral equation (2.2), which in the mixed representation becomes

$$\Pi_{\nu,\nu'}(\vec{K},k,k';\omega)=\Pi^0_{\nu,\nu'}(\vec{K},k,k';\omega)-2L^2l\sum_{\mu=0}^{3}\sum_{q,q'\geq 0}\Pi^0_{\nu,\mu}(\vec{K},k,q;\omega)D^0_\mu(\vec{K},q,q';\omega)\Pi_{\mu,\nu'}(\vec{K},q',k';\omega)\,. \tag{3.1}$$

This equation is valid for both time-ordered- and retarded-polarization tensors. Our numerical calculations are aimed at obtaining the retarded quantity.

Note that k, k', q, q' all take values of the form $n\pi/l$ with $n=0, 1, 2, \ldots$. One can show that $\Pi^0_{\nu,\nu'}(\vec{K}, k, k'; \omega)$, $D^0_\mu(\vec{K}, k, k'; \omega)$, and $\Pi_{\nu,\nu'}(\vec{K}, k, k'; \omega)$ are all zero unless the integers n and n' in $k=\pi n/l$ and $k'=\pi n'/l$ have the same parity. Therefore the equation (3.1) splits into two independent equations relating elements of the polarization tensor having n and n' of the same parity.

In what follows we obtain a formal solution of Eq. (3.1), which we found very useful in carrying out numerical calculations. One could in principle go on and perform numerically the matrix inversion needed to obtain $\Pi_{\nu\nu'}$ from (3.1). Unfortunately, this simple idea does not work. The problem at hand is complicated by the fact that the surface electrodynamic properties vary strongly over a range of few angstroms, while the bulk properties vary on much larger length scale. If we intend to treat surface and bulk behavior simultaneously by inverting Eq. (3.1) we have to use a very large basis set. Many large values of the wave vectors k, k', q, q' are required to generate the surface behavior; furthermore, many small-wave-vector components must be used to obtain the smooth variations characteristic to the fields in the bulk metal and the vacuum. The scheme described below facilitates considerably the inversion procedure and offers a prescription for handling the problem mentioned above.

We start by observing that all the quantities in the problem can be separated into a bulk part and a surface part. In particular, the bare-photon propagator $D^0_\nu(\vec{K}, k, k'; \omega)$ can be written as

$$D^0_\nu(\vec{K}, k, k'; \omega) = (1/2L^2 l) \times [D^0(k)\delta_{k,k'} + \Delta g_\nu(k) D^0(k) g_\nu(k') D^0(k')]\eta_\nu \,. \quad (3.2)$$

Here $\eta_\nu = 1$ for $\nu=0$ and -1 for $\nu=1, 2, 3$ and

$$D^0(k) \equiv 4\pi/(k^2 + K^{*2}) \quad (3.3)$$

is the bare-photon propagator in an infinite vacuum. The other quantities appearing in (3.2) are

$$\Delta \equiv -(1 \pm e^{-K^* l}) K^*/2\pi l \quad (3.4)$$

and

$$g_\nu(k) \equiv \begin{cases} 1 & \text{for } \nu = 0, 1, 2 \\ ik/K^* & \text{for } \nu = 3 \,. \end{cases} \quad (3.5)$$

The plus sign in Eq. (3.4) corresponds to the case when n and n' (in $k=n\pi/l$ and $k'=n'\pi/l$) are both odd integers. The negative sign is for both n and n' even.

Note that the bulk part $D^0(k)$ is diagonal in k and the surface part [second term in (3.2)] is separable in k and k'. We shall take advantage of these facts in what follows.

In order to simplify the equations we introduce the notation

$$\Pi_{k\nu,k'\nu'} \equiv \Pi_{\nu,\nu'}(\vec{K}, k, k'; \omega) \quad (3.6)$$

and rewrite (3.1) in the following form:

$$\Pi_{k\nu,k'\nu'} = \Pi^0_{k\nu,k'\nu'} - 2L^2 l \sum_{q'\mu} \Pi^0_{k\nu,q'\mu}\eta_\mu D^0(q')\Pi_{q'\mu,k'\nu'} - 2L^2 l\Delta \sum_{q\mu} \Pi^0_{k\nu,q\mu}\eta_\mu D^0(q) g_\mu(q) \sum_{q'} g_\mu(q') D^0(q')\Pi_{q'\mu,k'\nu'} \,. \quad (3.7)$$

The third term originates in the surface part of D^0. If we neglect for a moment this surface term, Eq. (3.7) becomes

$$\sum_{q\mu} [\delta_{k\nu,q\mu} + 2L^2 l \Pi^0_{k\nu,q\mu}\eta_\mu D^0(q)]\Pi_{q\mu,k'\nu'} = \Pi^0_{k\nu,k'\nu'} \,, \quad (3.8)$$

and by defining a matrix

$$\bar{\epsilon}_{k\nu,q\mu} \equiv \delta_{k\nu,q\mu} + 2L^2 l \Pi^0_{k\nu,q\mu}\eta_\mu D^0(q) \quad (3.9)$$

we can rewrite (3.8) as

$$\Pi_{k\nu,k'\nu'} = \sum_{q\mu} \bar{\epsilon}^{-1}_{k\nu,q\mu} \Pi^0_{q\mu,k'\nu'} \,. \quad (3.10)$$

By using Eq. (3.9) we can eliminate Π^0 from (3.10) and write

$$\Pi_{k\nu,k'\nu'} = \sum_{q\mu} \bar{\epsilon}^{-1}_{k\nu,q\mu} (\bar{\epsilon}_{q\mu,k'\nu'} - \delta_{q\mu,k'\nu'}) \frac{\eta'_\nu}{D^0(k')} \frac{1}{2L^2 l} = \frac{1}{2L^2 l} \frac{1}{D^0(k')} (\delta_{k\nu,k'\nu'} - \bar{\epsilon}^{-1}_{k\nu,k'\nu'})\eta_{\nu'} \,. \quad (3.11)$$

We now return to the full equation (3.7) and show that by introducing a "renormalized" bare polarization we can write the expression for Π in a form which is identical to that of Eqs. (3.8)–(3.11), even though the surface part is now included. To do this we define a 4×4 matrix

$$B_{\nu,\mu}(k) \equiv 2L^2 l \sum_q \Pi^0_{k\nu,q\mu}\eta_\mu D^0(q) g_\mu(q) \quad (3.12)$$

so that Eq. (3.7) may be written as

$$\sum_{q'\mu}[\delta_{k\nu,q'\mu}+B_{\nu,\mu}(k)C_\mu(q')]\Pi_{q'\mu,k'\nu'}=\Pi^0_{k\nu,k'\nu'}-2L^2l\sum_{q'\mu}\Pi^0_{k\nu,q'\mu}\eta_\mu D^0(q')\Pi_{q'\mu,k'\nu'}\,, \tag{3.13}$$

where

$$C_\mu(q')\equiv\Delta g_\mu(q')D^0(q')\,. \tag{3.14}$$

Defining a matrix $E_{k\nu,q\mu}$ by

$$E_{k\nu,q\mu}\equiv\delta_{k\nu,q\mu}+B_{\nu,\mu}(k)C_\mu(q)\,, \tag{3.15}$$

we transform Eq. (3.13) into

$$\Pi_{k\nu,k'\nu'}=\overline{\Pi}^0_{k\nu,k'\nu'}-2L^2l\sum_{q\mu}\overline{\Pi}^0_{k\nu,q\mu}\eta_\mu D^0(q)\Pi_{q\mu,k'\nu'}\,, \tag{3.16}$$

where $\overline{\Pi}^0_{k\nu,k'\nu'}$ is a renormalized version of the bare polarization tensor $\Pi^0_{k\nu,k'\nu'}$ given by

$$\overline{\Pi}^0_{k\nu,k'\nu'}=\sum_{q\mu}E^{-1}_{k\nu,q\mu}\Pi^0_{q\mu,k'\nu'}\,. \tag{3.17}$$

Equation (3.16) is identical to Eq. (3.8) with $\overline{\Pi}^0$ replacing Π^0. That means we can use any of the Eqs. (3.8)–(3.11) provided that the matrix $\overline{\epsilon}_{k\nu,q\mu}$ is replaced by the dielectric matrix

$$\epsilon_{k\nu,q\mu}=\delta_{k\nu,q\mu}+(2L^2l)\overline{\Pi}^0_{k\nu,q\mu}\eta_\mu D^0(q)\,. \tag{3.18}$$

We are now left with the problem of calculating the renormalized bare polarization tensor $\overline{\Pi}^0_{k\nu,k'\nu'}$ which, in turn, requires $E^{-1}_{k\nu,q\mu}$; this can be done (see the Appendix) and the result is

$$E^{-1}_{k\nu,q\mu}=\delta_{k\nu,q\mu}-[\underline{B}(k)(\underline{I}+\underline{F})^{-1}]_{\nu,\mu}C_\mu(q)\,. \tag{3.19}$$

Here $\underline{I}$ is the 4×4 unit matrix and $\underline{F}$ is a 4×4 matrix defined by

$$F_{\mu',\mu}\equiv\sum_{q'}C_{\mu'}(q')B_{\mu',\mu}(q')\,. \tag{3.20}$$

The quantities $\underline{B}$, $\underline{F}$, and $\underline{I}$ are multiplied and inverted as 4×4 matrices. The expression for $\overline{\Pi}^0_{k\nu,k'\nu'}$ is now given by

$$\overline{\Pi}^0_{k\nu,k'\nu'}=\Pi^0_{k\nu,k'\nu'}-\frac{\Delta}{2L^2l}[\underline{B}(k)(\underline{I}+\underline{F})^{-1}\underline{B}^*(k')]_{\nu,\nu'}\,, \tag{3.21}$$

where

$$B^*_{\mu,\nu'}(k')\equiv 2L^2l\sum_q\Pi^0_{q\mu,k'\nu'}g_\mu(q)D^0(q)\,. \tag{3.22}$$

The final result for the dielectric matrix $\epsilon_{k\nu,q\mu}$, is

$$\epsilon_{k\nu,q\mu}=\delta_{k\nu,q\mu}+2L^2l(\Pi^0_{k\nu,q\mu}-T_{k\nu,q\mu})D^0(q)\eta_\mu\,, \tag{3.23}$$

where

$$T_{k\nu,q\mu}\equiv\frac{\Delta}{2L^2l}[\underline{B}(k)\cdot(\underline{I}+\underline{F})^{-1}\cdot\underline{B}^*(q)]_{\nu,\mu}\,. \tag{3.24}$$

The optical properties of the metal slab are now described, in this model, by an infinite dielectric matrix $\epsilon_{k\nu,q\mu}$. The 4×4 tensor character appears because the presence of the surface destroys the isotropy of the medium.

In particular, this allows a nonzero coupling between the current and the charge density. Owing to this a longitudinal (transverse) field can excite transverse (longitudinal) waves in the slab. This has interesting physical consequences to be discussed when we present numerical applications. The presence of the surface also eliminates momentum conservation in the direction perpendicular to the surface. Owing to this, ϵ depends on both k and q; an excitation with perpendicular momentum q can induce a current or a charge density with a different perpendicular momentum k. On the other hand, the parallel momentum is conserved.

The numerical calculations involve the calculation and inversion of the matrix ϵ. To do this we use a finite basis set of sines and cosines (the mixed representation) to turn the integral equation in a finite dimensional matrix equation. A very useful test whether the size of the set is large enough is provided by the following sum rules:

$$\sum_k\Pi_{k\nu,k'\nu'}=0\quad\text{for }\nu=0,1,2, \tag{3.25}$$

which in turn yields

$$\sum_k\epsilon^{-1}_{k\nu,k'\nu'}=\delta_{\nu,\nu'}\,,\quad\nu=0,1,2\,. \tag{3.26}$$

IV. GAUGE INVARIANCE AND RELAXATION PROCESSES IN THE COMPUTATION OF THE BARE POLARIZATION

The calculation of the bare polarization $\vec{\Pi}^0$ is an intrinsic part in the computational scheme that ultimately yields the electromagnetic fields at the surface. This quantity is expressed in terms of the free-electron Green functions G_0 defined in Sec. II. As a result, near singularities appear in the bare polarization $\vec{\Pi}^0$ in the long-wavelength limit, which are difficult to handle on the computer. Their presence is in a sense unphysical, since they appear because we have ignored electron scattering by impurities or phonons. If these are taken into account, a self-energy correction appears in G_0 and the singularity is thus removed. The simplest way of removing the singularity in a gauge-invariant manner is to use the continuity equation relating the induced charge and current densities:

$$\frac{\partial \rho^{\mathrm{ind}}}{\partial t} = -\vec{\nabla}\cdot\vec{j}^{\,\mathrm{ind}} . \tag{4.1}$$

Since ρ^{ind} and j^{ind} are determined by Π, we can derive[12] relationships between various components of the tensor $\vec{\Pi}^0$:

$$\Pi_{0,0}(\vec{r},\vec{r}\,';\omega) = \frac{i}{\omega}\sum_{\mu=1}^{3}\frac{\partial}{\partial x_\mu}\Pi_{\mu,0}(\vec{r},\vec{r}\,';\omega) \tag{4.2}$$

and

$$\Pi_{0,0}(\vec{r},\vec{r}\,';\omega) = \frac{1}{\omega^2}\sum_{\mu,\mu'=1}^{3}\frac{\partial}{\partial x_\mu}\frac{\partial}{\partial x_{\mu'}}\left(\Pi^{p}_{\mu,\mu'}(\vec{r},\vec{r}\,';\omega) + \frac{e^2}{mc^2}\langle\hat{\rho}(\vec{r})\rangle\delta_{\mu,\mu'}(1-\delta_{\mu,0})\delta(\vec{r}-\vec{r}\,')\right), \tag{4.3}$$

where $\Pi^{p}_{\mu,\mu'}(\vec{r},\vec{r}\,';\omega)$ is the full paramagnetic response function and $\langle\hat{\rho}(\vec{r})\rangle$ is the full electron density (i.e., including electron-electron interaction). These relations should hold to any order in the bare electromagnetic propagator. In particular, one gets to zeroth order (that is, for the case of noninteracting electron gas):

$$\Pi^{0}_{0,0}(\vec{r},\vec{r}\,';\omega) = \frac{i}{\omega}\sum_{\mu=1}^{3}\frac{\partial}{\partial x_\mu}\Pi^{0}_{\mu,0}(\vec{r},\vec{r}\,';\omega) , \tag{4.4}$$

$$\Pi^{0}_{0,0}(\vec{r},\vec{r}\,';\omega) = \frac{1}{\omega^2}\sum_{\mu,\mu'=1}^{3}\frac{\partial^2}{\partial x_\mu \partial x_{\mu'}}\Pi^{0}_{\mu,\mu'}(\vec{r},\vec{r}\,';\omega) . \tag{4.5}$$

Let us now use these equations to introduce the effect of electron scattering (by impurities or phonons) into the polarization tensor. Within the relaxation-time approximation the self-energy insertion into the single-electron lines amounts to the replacement of ω by $\omega + i/\tau$. But if we do this, the resulting polarization tensor does not satisfy the continuity equations. To see this let us write schematically the expressions for $\rho^{\mathrm{ind}}(t)$. We have

$$\rho^{\mathrm{ind}}(t) \sim \int G_0(t-t')G_0(t'-t)\psi^{\mathrm{ext}}(t')dt' .$$

Now, in the relaxation-time approximation the time dependence of G_0 is of the form $e^{+i(\omega+i/\tau)t}$ and therefore the derivative of ρ^{ind} with time is $\partial\rho^{\mathrm{ind}}/\partial t \sim i(\omega+i/\tau)\rho^{\mathrm{ind}}$. Because of this, i/ω in Eq. (4.4) must be replaced in the relaxation-time approximation by $i/(\omega+i/\tau)$. The same argument can be made in Eq. (4.5). Therefore, if we use the relaxation-time approximation to replace $G_0(\omega)$ by $G_0(\omega+i/\tau)$ in the expression of $\Pi^{0}_{\mu,\nu}$, various components of $\vec{\Pi}^0$ are related by

$$\Pi^{0}_{0,0}(\vec{r},\vec{r}\,';\omega+i/\tau) = \frac{i}{\omega+i/\tau}\sum_{\mu=1}^{3}\frac{\partial}{\partial x_\mu}\Pi^{0}_{\mu,0}(\vec{r},\vec{r}\,';\omega+i/\tau) \tag{4.6}$$

and

$$\Pi^{0}_{0,0}(\vec{r},\vec{r}\,';\omega+i/\tau) = \frac{1}{(\omega+i/\tau)^2}\sum_{\mu,\mu'=1}^{3}\frac{\partial^2}{\partial x_\mu \partial x_{\mu'}}\Pi^{0}_{\mu,\mu'}(\vec{r},\vec{r}\,';\omega+i/\tau) . \tag{4.7}$$

However, these equations are different from the continuity equation, and therefore the currents and charge densities computed from $\Pi^{0}_{\mu,\nu}(\vec{K},k,k';\omega+i/\tau)$ will violate charge conservation. A detailed analysis of the diagramatic expansion for Π^0 will indicate that the error comes from the neglect of vertex corrections. Using the continuity equation we can obtain these corrections in a simple manner. We define the polarization tensor $\Pi^{0,\tau}_{\mu,\nu}$ in the presence of impurities or phonons and request it to satisfy the continuity equations

$$\Pi^{0,\tau}_{0,0}(\omega) = \frac{i}{\omega}\sum_{\mu=1}^{3}\frac{\partial}{\partial x_\mu}\Pi^{0,\tau}_{\mu,0}(\omega) , \tag{4.8}$$

$$\Pi^{0,\tau}_{0,0}(\omega) = \frac{1}{\omega^2}\sum_{\mu,\mu'=1}^{3}\frac{\partial^2}{\partial x_\mu \partial x_{\mu'}}\Pi^{0,\tau}_{\mu,\mu'}(\omega) . \tag{4.9}$$

We know that the elements of $\vec{\Pi}^{0,\tau}$ must be proportional to those of $\vec{\Pi}^{0}(\omega+i/\tau)$. In order to satisfy continuity equations we define

$$\Pi^{0,\tau}_{0,0}(\omega) = [(\omega+i/\tau)/\omega]\Pi_{0,0}(\omega+i/\tau) , \tag{4.10}$$

$$\Pi^{0,\tau}_{\mu,0}(\omega) = \Pi^{0}_{\mu,0}(\omega+i/\tau) , \tag{4.11}$$

$$\Pi^{0,\tau}_{0,\mu'}(\omega) = \Pi_{0,\mu}(\omega+i/\tau) , \tag{4.12}$$

$$\Pi^{0,\tau}_{\mu,\mu'}(\omega) = [\omega/(\omega+i/\tau)]\Pi^{0}_{\mu,\mu'}(\omega+i/\tau) , \tag{4.13}$$

where $\mu, \mu' = 1, 2, 3$. Now since the elements of $\Pi^0(\omega+i/\tau)$ satisfy Eqs. (4.6) and (4.7) the elements of $\vec{\Pi}^{0,\tau}$ satisfy the continuity equations (4.8) and (4.9).

Once the relaxation time is introduced into the problem, as specified above, the singularities in G^0 are removed with no violation of conservation laws. We find that the presence of τ in $\Pi^{0,\tau}$ simplifies considerably the computations. Furthermore, in some problems, the presence of τ modifies considerably the results of the calculations. This is planned to be discussed in future papers in which numerical applications are reported.

In using these equations one should keep in mind that the relaxation-time approximation has serious limitations.[13] In addition, we have neglected (when using this approximation) the fact that the impurities renormalize the Fermi level,[14] that the relaxation time may be dependent on wave vector,[15] and that the relaxation time near the surface will differ from that in the bulk.

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APPENDIX

We want to invert the matrix $E_{k\nu,q\mu}$ defined by Eq. (4.15). We begin by considering that

$$A_{k\nu,q\mu} \equiv B_{\nu,\mu}(k)C_\mu(q) \tag{A1}$$

is a perturbation. Since (3.15) can be written as

$$E_{k'\nu,q\mu} = \delta_{k\nu,q\mu} + A_{k\nu,q\mu}\ , \tag{A2}$$

standard perturbation expansion yields

$$E^{-1}_{k\nu,k'\nu'} = \delta_{k\nu,k'\nu'} - A_{k\nu,k'\nu'} + \sum_{q\mu} A_{k\nu,q\mu}A_{q\mu,k'\nu'} - \sum_{q\mu}\sum_{q'\mu'}{}' A_{k\nu,q\mu}A_{q\mu,q'\mu'}A_{q'\mu',k'\nu'} + \cdots\ . \tag{A3}$$

Now let us use the separability of A [Eq. (A1) in the expansion (A3)]. We obtain

$$\delta_{k\mu,k'\nu'} - E^{-1}_{k\nu,k'\nu'} = B_{\nu,\nu'}(k)C_{\nu'}(k') - \sum_{\mu} B_{\nu\mu}(k)F_{\mu\nu'}C_{\nu'}(k') + \sum_{\mu\mu'} B_{\nu\mu}(k)F_{\mu,\mu'}F_{\mu',\nu'}C_{\nu'}(k') + \cdots\ , \tag{A4}$$

with

$$F_{\mu,\mu'} \equiv \sum_q C_\mu(q)\, B_{\mu,\mu'}(q)\ . \tag{A5}$$

This yields

$$E^{-1}_{k\nu,k'\nu'} = \delta_{k\nu,k'\nu'} - \sum_\mu B(k)_{\nu\mu}\,(\underline{I}+\underline{F})^{-1}_{\mu\nu'}C_{\nu'}(k')\ , \tag{A6}$$

where $\underline{I}$ is the unit 4×4 matrix. The advantage of this result is that it allows us to invert the matrix $E_{k\nu,k'\nu'}$ of very high dimension, by inverting the 4×4 matrix $\underline{I}+\underline{F}$.

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