PHYSICAL REVIEW B VOLUME 29, NUMBER 8 15 APRIL 1984

Macroscopic dielectric tensor at crystal surfaces

R. Del Sole and E. Fiorino

Dipartimento di Fisica "Giuglielmo Marconi," Università "La Sapienza," I-00185 Roma, Italy
and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, I-00185 Roma, Italy

(Received 14 July 1983)

We formulate the theory of the macroscopic dielectric tensor for crystals of lower-than-cubic symmetry, using the local-orbital approach to the dielectric response. In the case of noncubic infinite crystals we give a definition of the macroscopic dielectric tensor that is simpler than any previous formulation and allows us to perform realistic calculations with roughly the same computational effort needed in cubic crystals. In the case of semi-infinite crystals, we give for the first time a definition of the macroscopic dielectric tensor and outline a way of computing it from the two-particle Green's function, which can be computed according to the method of Hanke and Sham, including local-field and excitonic effects. A remarkable result is that in both cases the long-range part of the Coulomb interaction does not affect the macroscopic dielectric tensor. Previous formulations of the optical properties of surfaces, which neglected local-field effects, are shown to be yet valid, provided that the macroscopic dielectric tensor replaces the microscopic one.

I. INTRODUCTION

The dielectric response of a crystal to external perturbations always produces microscopic fluctuations of the electric field (local fields), even if the external field is of long wavelength. Local-field effects have been the object of extensive theoretical investigation[1–22] in the last years, in connection with both optical and screening properties of crystals. However, most of this work is confined to the case of cubic infinite crystals, while only a few papers consider systems with lower-than-cubic symmetry, as noncubic infinite crystals[12,16,23] or crystals with surfaces.[24,25]

The main concern of this paper is the effect of local fields upon the optical properties of surfaces. The understanding of these is fundamental in order to give a detailed interpretation of surface optical spectroscopy. In spite of the large amount of experimental work done in the last decade,[26–30] only recently theory has improved over the macroscopic model of McIntyre and Aspnes[31] and the perturbative approximation.[32] Following the early work of Feibelman[33] and the later one of Bagchi and Rajagopal[34] on jellium surfaces, more sophisticated theories have been developed, accounting also for surface anisotropy,[35] bulk spatial dispersion,[36,37] and for strong resonances of the dielectric function at the surface.[37–39] A recent review has been given by Feibelman.[40]

However, none of these papers considers local-field effects at the surface. The only exceptions have been classical (Lorentz-Lorenz) calculations of adsorbate optical absorption[24] and a short account of this work,[25] both showing the importance of local-field effects.

In the case of semiconductors, local-field effects could be more important at the surface than in bulk, since the charge density is more inhomogeneous at the surface, due to the bigger spacing of atomic orbitals [consider for instance a low-density periodic array of chemisorbed atoms, or even the dangling bonds at Si(111) and Ge(111) surfaces]. Furthermore, surface exciton binding energy may be drastically affected by local fields through the dipole-dipole interaction.[41] This, originating from the Coulomb (not exchange) interaction between electrons, is unscreened,[5] so that it survives the huge dielectric screening expected at Si(111) and Ge(111) 2×1, because of the small optical gaps.[26,27,42] An excitonic instability may occur in some cases, which would be the driving force of surface reconstruction. Therefore it is not unreasonable to conjecture a link (through unstable excitons) between local fields and surface reconstruction.

We believe that the study of local-field effects at crystal surfaces is an interesting field. Unfortunately, it is also a very difficult task, involving both conceptual and computational problems. In order to outline them, let us consider the simpler case of infinite crystals. Macroscopic (cell-averaged) quantities are usually of interest, and they can be calculated from macroscopic Maxwell's equations, if the macroscopic dielectric tensor $\overleftrightarrow{\epsilon}_M$ (or polarizability $\overleftrightarrow{\alpha}_M$), relating the macroscopic electric displacement $\vec{D}_M$ (or polarization $\vec{P}_M$) to the macroscopic electric field $\vec{E}_M$, is known. The macroscopic quantities $\overleftrightarrow{\alpha}_M$ and $\overleftrightarrow{\epsilon}_M=\overleftrightarrow{1}+4\pi\overleftrightarrow{\alpha}_M$ cannot be computed directly from the linear-response theory,[43] since the polarization is induced by the total electric field (including local fields) and not by the macroscopic field. More precisely, the macroscopic $\overleftrightarrow{\epsilon}_M$ is not given by simply cell-averaging the microscopic dielectric susceptibility $\overleftrightarrow{\epsilon}(\vec{r},\vec{r}\,')$, and the difference is ascribed to local-field effects.

In cubic crystals a simplification results from the isotropy of the response to long-wavelength perturbations:[16,44] The macroscopic dielectric tensor reduces to one independent component only, the macroscopic dielectric constant ϵ_M, that can be computed, even in the case of optical properties, considering the response to longitudinal fields. Nevertheless, the calculation of ϵ_M involves the inversion of a large matrix[6,20] in the plane-wave representation.[3] The size of such a matrix can be reduced using the local representation;[3–5] detailed calculations have been performed for Si and diamond including also excitonic effects,[3,5] i.e., including the electron-electron (*e-e*) exchange interaction. In this paper we outline a formulation of local-field effects in infinite crystals, which is particularly suited for noncubic crystals. We show how the macroscopic dielectric tensor of a noncubic crystal can be computed using equations similar to those of cubic crystals;[5] this method is simpler than any previous formulations.[12,16,23]

When dealing with surfaces, the very definition of macroscopic averages is unclear. The lack of periodicity in the direction perpendicular to the surface (the *z* direction) makes cell-averaging near the surface meaningless. We define macroscopic fields in $\vec{k}$ space as those with k_z components smaller than a cutoff wave vector k_c; the macroscopic dielectric tensor $\overleftrightarrow{\epsilon}_M(z,z')$ is then defined, in a way analogous to our bulk formation. Its shape (z and z' dependence) near the surface, as that of the macroscopic field, depends upon k_c; nevertheless it provides a meaningful description of measurable quantities, such as reflectivity and transmission, provided that k_c^{-1} is chosen to be much smaller than the light wavelength and much larger than unit-cell dimensions. This definition is general and does not request any approximation. In particular, it does not rely on the random-phase approximation (RPA).

A further complication at surfaces (as well as in noncubic crystals) is that the full macroscopic dielectric tensor is needed to describe optical properties and not only its longitudinal component, as in cubic crystals. The computational effort is increased also by the lack of translational symmetry perpendicular to the surface. The main result of this paper is an expression of the macroscopic dielectric tensor in terms of the two-particle Green's function. The local representation, which is the natural way of dealing with surfaces, makes the calculation feasible.

The plan of this paper is as follows. In Sec. II we consider the induced current and charge generated by an electronic system in the presence of an external disturbance. We treat systems of arbitrary symmetry in the local-orbital representation. Though the results of this section are not completely new, we treat the subject in detail for the sake of completeness.

In Sec. III we define the macroscopic dielectric tensor of an infinite crystal of arbitrary symmetry. Two equivalent definitions are possible, the first one from the microscopic dielectric tensor, as done in Refs. 12 and 15, and the second one directly from the theory of the linear response to the external field, similar to the treatment of excitons by Cho and co-workers.[45,46] Adopting the latter, we bypass two difficult steps, namely the definition of the microscopic dielectric tensor when transverse fields are present, and the elimination of microscopic fields from Maxwell's equations.[12]

In Sec. IV we show how the macroscopic dielectric tensor of a noncubic infinite crystal can be computed. Exchange is accounted for within the many-body perturbation technique.[5] Roughly the same computational effort as in cubic crystals is requested.

In Sec. V we extend this formulation to the case of surfaces, namely to semi-infinite crystals. The macroscopic dielectric tensor is defined and its expression in terms of the local-orbital representation of the two-particle Green's functions is given, which allows realistic calculations of surface optical properties. A common feature of infinite and semi-infinite crystals is that the macroscopic dielectric tensor is not affected by the long-range part of the Coulomb *e-e* interaction, in agreement with the results of Ambegaokar and Kohn (AK) (Ref. 44) for cubic crystals. Some properties of this tensor, which are important to compute optical properties, are discussed in Sec. VI. A discussion of the present approach, with special emphasis on the approximations involved, is given in Sec. VII.

In a planned subsequent paper we will show that the optical properties of surfaces (reflectance, absorption, transmission, and ellipsometry) are given by a few quantities[25] that are functionals of the macroscopic dielectric tensor. These quantities (but not the latter) can be computed from the longitudinal dielectric response, leading to a simplification relevant for computational purposes. A simple model will be carried out, showing the feasibility and relevance of these calculations.

II. RESPONSE TO AN EXTERNAL FIELD IN THE LOCAL REPRESENTATION

In this section we recall the linear response of electrons in a crystal to an external field in the local representation. Even though we do not derive completely new results, we prefer to discuss the subject in some detail, since we do not know any extensive treatment of the general case, where both transverse and longitudinal fields are present.

Let us consider a system of electrons in a crystal, interacting via the Coulomb potential, perturbed by an external electromagnetic field. The induced current can be computed, using the linear-response theory,[47] in terms of the current-current response function and of the perturbing field $\vec{E}^p$. This is the external field $\vec{E}^{ex}$ plus the induced transverse field $\vec{E}^i_T$:

$$\vec{E}^p=\vec{E}^{ex}+\vec{E}^i_T=\vec{E}-\vec{E}^i_L\ , \tag{1}$$

where $\vec{E}$ is the total (microscopic) field and $\vec{E}^i_L$ the induced longitudinal field. The induced transverse field that originates from retardation is not accounted for by the zero-order Hamiltonian, where only the unretarded Coulomb interaction between electrons is retained. Therefore, it must be considered as perturbation, in addition to the external field.

On the other hand, in Ref. 47 the perturbing field is taken as coincident with the external one. This means that the full retarded interaction between electrons is included into the zeroth-order Hamiltonian. In this case the excited states of the system already comprehend the interaction with radiation, being just the normal modes discussed in Sec. III (they are called "real excitons" in the language of Ref. 57). If the definition (1) is used instead, the excited states of the electronic system have the usual meaning, i.e., they are generated by the unretarded Coulomb interaction between electrons (they are called "Coulomb excitons" in the language of Ref. 57), and the normal modes must be investigated by means of Maxwell's equations, as in Sec. III. The difference between the two definitions is usually unimportant in cubic crystals, where, because of symmetry, the longitudinal dielectric function (which is calculated assuming that only *longitudinal fields* are present) is sufficient to describe the propagation of long-wavelength transverse waves.[16] However, it goes without saying that, when transverse fields must be explicitly considered, the approach which includes retardation into the zeroth-order Hamiltonian is mainly formal, since practical calculations become exceedingly difficult.

The polarization is defined as

$$\vec{P}(\vec{r},t)=\int_{-\infty}^{t}\vec{J}^{\,i}(\vec{r},t')dt' , \tag{2}$$

where $\vec{J}^{\,i}(\vec{r},t)$ is the induced current. Its time Fourier transform is given by[47]

$$\vec{P}(\vec{r},\omega)=\int d^3r'\overset{\leftrightarrow}{\tilde{\alpha}}(\vec{r},\vec{r}',\omega)\cdot\vec{E}^{P}(\vec{r}',\omega) , \tag{3}$$

where $\overset{\leftrightarrow}{\tilde{\alpha}}(\vec{r},\vec{r}',\omega)$ is the quasipolarizability tensor defined in Ref. 47, related by the linear-response theory to the current-current (tensor) response function $\chi_{j_\alpha j_\beta}(\vec{r},\vec{r}',\omega)$:

$$\tilde{\alpha}_{\alpha\beta}(\vec{r},\vec{r}',\omega)=[\chi_{j_\alpha j_\beta}(\vec{r},\vec{r}',\omega)-\frac{e^2}{m}\delta_{\alpha\beta}\rho(\vec{r})\delta(\vec{r}-\vec{r}')]/\omega^2 , \tag{4}$$

where $\rho(\vec{r})$ is the ground-state electron density.

For $\omega>0$, the current-current response function is the Fourier transform of the time-ordered response function:[48]

$$\begin{aligned}\tilde{\chi}_{j_\alpha j_\beta}(\vec{r},\vec{r}',t)=\;&\Theta(t)\langle 0\,|\,j_\alpha(\vec{r},t)j_\beta(\vec{r}',0)\,|\,0\rangle\\ &+\Theta(-t)\langle 0\,|\,j_\beta(\vec{r}',0)j_\alpha(\vec{r},t)\,|\,0\rangle .\end{aligned} \tag{5}$$

The relation to the two-particle Green's function $S(\vec{r}_1,t_1;\vec{r}_2,t_2;\vec{r}_3,t_3;\vec{r}_4,t_4)$ is given by

$$\tilde{\chi}_{j_\alpha j_\beta}(\vec{r},\vec{r}',t)=-(e^2/4m^2)\lim_{\substack{\vec{r}_4\to\vec{r},\\ \vec{r}_1\to\vec{r}'}}(\partial r_\alpha-\partial r_{4\alpha})(\partial r'_\beta-\partial r_{1\beta})S(\vec{r}_1,0^+;\vec{r}',0;\vec{r},t;\vec{r}_4,t^+) , \tag{6}$$

where $0^+=\eta$, and $t^+=t+\eta$, η being a vanishing positive time.

We use for the Green's function the same notation as Henke and Sham[5] so that we can use their results from now on. We perform the time Fourier transform of Eq. (6) and express the Green's function on the basis of localized orbitals $\varphi_L(\vec{r})$, as in Ref. 5, where L stands for the orbital ν at the site $\vec{R}$.[49]

With the use of Eq. (6) we find

$$\tilde{\chi}_{j_\alpha j_\beta}(\vec{r},\vec{r}',\omega)=\frac{e^2}{m^2}\sum_{L_1,L'_1,L_2,L'_2}J_{\beta L_1L'_1}(\vec{r}')S_{L_1L'_1L_2L'_2}(\omega)J_{\alpha L'_2L_2}(\vec{r}) , \tag{7}$$

where

$$J_{\beta L_1L'_1}(\vec{r}')=\frac{1}{2}\left[\phi^*_{L_1}(\vec{r}')\frac{\partial\phi_{L'_1}(\vec{r}')}{\partial r'_\beta}-\phi_{L'_1}(\vec{r}')\frac{\partial\phi^*_{L_1}(\vec{r}')}{\partial r'_\beta}\right] , \tag{8}$$

and $S_{L_1L'_1L_2L'_2}(\omega)$ is the two-particle Green's function matrix.[5]

The insertion of (7) into (4) leads to an expression for the quasipolarizability in terms of the basis functions and of $S_{L_1L'_1L_2L'_2}(\omega)$. Finally, we perform the space Fourier transform, and get

$$\tilde{\alpha}_{\alpha\beta}(\vec{k},\vec{k}',\omega)=\frac{1}{(2\pi)^3\omega^2}\left[\frac{e^2}{m^2}\sum_{L_1,L'_1,L_2,L'_2}J_{\beta L_1L'_1}(-\vec{k}')S_{L_1L'_1L_2L'_2}(\omega)J_{\alpha L'_2L_2}(\vec{k})-\delta_{\alpha\beta}\frac{e^2}{m}\rho(\vec{k}-\vec{k}')\right] , \tag{9}$$

where $J_{\alpha L'_2L_2}(\vec{k})$ and $\rho(\vec{k})$ are the Fourier transforms of $J_{\alpha L'_2L_2}(\vec{r})$ and $\rho(\vec{r})$, respectively.

Equation (9) is completely general, valid for infinite crystals as well as for systems without any symmetry. In Sec. III we will specialize it to the case of infinite crystals and in Sec. V to the case of semi-infinite crystals.

Before proceeding, however, we must find similar expressions for the longitudinal-longitudinal part of $\overset{\leftrightarrow}{\tilde{\alpha}}(\vec{k},\vec{k}')$,

$$\tilde{\alpha}^{LL}(\vec{k},\vec{k}')=\frac{\vec{k}\cdot\overset{\leftrightarrow}{\tilde{\alpha}}(\vec{k},\vec{k}')\cdot\vec{k}'}{kk'} , \tag{10}$$

its right-hand longitudinal contraction,

$$\tilde{\alpha}^{\leftarrow,L}(\vec{k},\vec{k}')=\overset{\leftrightarrow}{\tilde{\alpha}}(\vec{k},\vec{k}')\cdot\frac{\vec{k}'}{k'} , \tag{11}$$

and its left-hand longitudinal contraction,

$$\tilde{\alpha}^{L,\rightarrow}(\vec{k},\vec{k}\,')=\frac{\vec{k}}{k}\cdot\tilde{\tilde{\alpha}}(\vec{k},\vec{k}\,')\;, \tag{12}$$

which also enter the definition of the macroscopic dielectric tensor of crystals with lower-than-cubic symmetry.

In the following we indicate by $V^L(\vec{k})$ the longitudinal (with respect to $\vec{k}$) component of a vector $\vec{V}(\vec{k})$, and by $\vec{V}^T(\vec{k})$ its transverse projection.

If the longitudinal contractions of $\tilde{\tilde{\alpha}}$ are computed using Eqs. (10)—(12) in (9), the resulting expressions may be simplified using the longitudinal sum rule.[47] Alternatively, as we do in the Appendix, we can assume *ab initio*, in view of the gauge invariance, that only a scalar potential describes the electric field, when we are interested in the response to a longitudinal field ($\tilde{\alpha}^{\leftarrow,L}$ and $\tilde{\alpha}^{LL}$), or we can relate the longitudinal polarization to the induced charge density, when $\tilde{\alpha}^{L,\rightarrow}$ is of interest. This procedure, described in detail in Appendix A, gives the simplified expressions of the longitudinal contractions quoted below:

$$\tilde{\alpha}^{L,\rightarrow}(\vec{k},\vec{k}\,',\omega)=\frac{1}{(2\pi)^3}\frac{e^2 i}{m\omega k}\sum_{L_1,L_1',L_2,L_2'}\vec{J}_{L_1L_1'}(-\vec{k}\,')S_{L_1L_1'L_2L_2'}(\omega)A_{L_2'L_2}(\vec{k})\;, \tag{13}$$

$$\tilde{\alpha}^{\leftarrow,L}(\vec{k},\vec{k}\,',\omega)=\frac{1}{(2\pi)^3}\frac{e^2 i}{m\omega k}\sum_{L_1,L_1',L_2,L_2'}A_{L_1L_1'}(-\vec{k}\,')S_{L_1L_1'L_2L_2'}(\omega)\vec{J}_{L_2'L_2}(\vec{k})\;, \tag{14}$$

$$\tilde{\alpha}^{LL}(\vec{k},\vec{k}\,',\omega)=-\frac{1}{(2\pi)^3}\frac{e^2}{kk'}\sum_{L_1,L_1',L_2,L_2'}A_{L_1L_1'}(-\vec{k}\,')S_{L_1L_1'L_2L_2'}(\omega)A_{L_2'L_2}(\vec{k})\;, \tag{15}$$

where

$$A_{L_2'L_2}(\vec{k})=\int d^3r\,\phi^*_{L_2'}(\vec{r})\exp(-i\vec{k}\cdot\vec{r})\phi_{L_2}(\vec{r})\;. \tag{16}$$

III. MACROSCOPIC DIELECTRIC TENSOR OF AN INFINITE CRYSTAL

The optical properties of a cubic crystal are described by the macroscopic dielectric constant, which embodies local-field effects.[1,2] This is usually computed starting from the longitudinal microscopic polarizability,[2,4] describing the response of the system to a longitudinal field. The applicability of this procedure in the case of optical properties, which involve transverse fields, is founded on the equality of the longitudinal and transverse components of the dielectric tensor[16,44] for vanishing light wave vector, caused by the cubic symmetry.

In noncubic crystals, all the components of the microscopic dielectric tensor must be considered. Johnson[16] extended the theory of local-field effects to such crystals, but his formulation implies repeated inversions of very large matrices, so that it is not suitable for practical use. A somehow simpler definition of the macroscopic dielectric tensor, which is appropriate also to noncubic crystals, has been given by Pick.[12] The same formula has been derived by us in a different way, within the RPA approximation (although this is not really needed) and has been shown to be suitable for practical calculations in the local representation.[23]

In this section we give an even simpler formulation of the macroscopic dielectric tensor, which is suitable for the extension to surfaces. Most of the complexity of the problem comes from the definition of the microscopic dielectric tensor when dealing with general fields,[12] i.e., not completely longitudinal. On the other hand, the quasipolarizability, that is the crystal response to the external field,[47] can be easily defined in terms of response functions. From it we directly derive the macroscopic dielectric tensor, bypassing two difficult steps, namely the definition of the microscopic dielectric tensor and the elimination of microscopic fields.[12] Our method is similar to that used by Cho and co-workers,[44,45] to describe in a simple way mixed longitudinal-transverse polaritons. The microscopic calculation based on the local representation will be outlined in Sec. IV. In Sec. V we apply this same method to the case of surfaces.

In the following we write $\vec{P}(\vec{q})_{\vec{G}}$ for $\vec{P}(\vec{q}+\vec{G})$, $\tilde{\tilde{\alpha}}(\vec{q})_{\vec{G}\vec{G}'}$ for $[(2\pi)^3/V]\tilde{\tilde{\alpha}}(\vec{q}+\vec{G},\ \vec{q}+\vec{G}\,')$, and analogously for the other quantities. The factor $(2\pi)^3/V$, V being the crystal volume, originates from the transformation of the integral over $\vec{k}\,'$ [in the space Fourier transform of Eq. (3)] into the sum over $\vec{G}\,'$, allowed by the translational symmetry. Here $\vec{q}$ is limited to the first Brillouin zone and $\vec{G}$ and $\vec{G}\,'$ are reciprocal-lattice vectors.

Maxwell's equations, in the absence of external transverse currents,[50] read as

$$[\vec{E}^T(\vec{q})]_{\vec{G}}=\frac{\omega^2}{c^2|\vec{q}+\vec{G}|^2}[\vec{D}^T(\vec{q})]_{\vec{G}}\;, \tag{17}$$

$$[D^L(\vec{q})]_{\vec{G}}=[E^{\mathrm{ex},L}(\vec{q})]_{\vec{G}}\;, \tag{18}$$

where $[\vec{D}(\vec{q})]_{\vec{G}}$ is the electric displacement. Equation (17) implies that the microscopic ($\vec{G}\neq\vec{0}$) components of the transverse field $\vec{E}^T$ are negligible, since $\omega^2/c^2 \ll G^2$. Therefore, assuming that the external field is of long wavelength, the perturbing field $\vec{E}^p$ is such, too, and Eq. (3) becomes

$$[\vec{\mathrm{P}}(\vec{\mathrm{q}})]_{\vec{\mathrm{G}}}=[\overleftrightarrow{\alpha}(\vec{\mathrm{q}})]_{\vec{\mathrm{G}},\vec{0}}\cdot[\vec{\mathrm{E}}^{p}(\vec{\mathrm{q}})]_{\vec{0}}\ . \tag{19}$$

From Eq. (18) we get

$$\begin{aligned}[E^{i,L}(\vec{\mathrm{q}})]_{\vec{\mathrm{G}}}&=-4\pi[P^{L}(\vec{\mathrm{q}})]_{\vec{\mathrm{G}}}\\&=-4\pi[\tilde{\alpha}^{L,\rightarrow}(\vec{\mathrm{q}})]_{\vec{\mathrm{G}},\vec{0}}\cdot[\vec{\mathrm{E}}^{p}(\vec{\mathrm{q}})]_{\vec{0}}\ .\end{aligned} \tag{20}$$

By using this equation for $\vec{\mathrm{G}}=\vec{0}$, and the first of definitions (1), we get a relation between the macroscopic components $(\vec{\mathrm{G}}=\vec{0})$ of the total and perturbing fields, that we solve with respect to $[\vec{\mathrm{E}}^{p}(\vec{\mathrm{q}})]_{\vec{0}}$ and substitute into (19) to find the macroscopic polarization:

$$[\vec{\mathrm{P}}(\vec{\mathrm{q}})]_{\vec{0}}=[\overleftrightarrow{\tilde{\alpha}}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}\cdot\left[\overleftrightarrow{\mathbb{1}}-4\pi\frac{\vec{\mathrm{q}}}{q}\cdot[\tilde{\alpha}^{L,\rightarrow}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}\right]^{-1}\cdot[\vec{\mathrm{E}}(\vec{\mathrm{q}})]_{\vec{0}}\ . \tag{21}$$

Therefore, the macroscopic dielectric tensor, relating $[\vec{\mathrm{D}}(\vec{\mathrm{q}})]_{\vec{0}}$ to $[\vec{\mathrm{E}}(\vec{\mathrm{q}})]_{\vec{0}}$, is given by

$$\overleftrightarrow{\epsilon}_{M}(\vec{\mathrm{q}})=\overleftrightarrow{\mathbb{1}}+4\pi[\overleftrightarrow{\tilde{\alpha}}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}\cdot\left[\overleftrightarrow{\mathbb{1}}-4\pi\frac{\vec{\mathrm{q}}}{q}[\tilde{\alpha}^{L,\rightarrow}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}\right]^{-1}\ . \tag{22}$$

Before discussing this equation in more detail, let us briefly recall that the knowledge of $\overleftrightarrow{\epsilon}_{M}(\vec{\mathrm{q}})$ determines the normal modes of the crystal. These are obtained from Eqs. (17) and (18) for $\vec{\mathrm{G}}=\vec{0}$, in the absence of the external field. Their dispersion is given by the zeros of the determinant

$$\left|\frac{\omega^{2}}{c^{2}}\overleftrightarrow{\epsilon}_{M}(\vec{\mathrm{q}})-q^{2}\overleftrightarrow{\mathbb{1}}+\vec{\mathrm{q}}\vec{\mathrm{q}}\right|=0\ , \tag{23}$$

i.e., by Fresnel's equations.[51]

Equation (22) can be put in a more explicit form inverting the 3×3 matrix in the right-hand side. It results in

$$\begin{aligned}\overleftrightarrow{\mathrm{A}}&\equiv\left[\overleftrightarrow{\mathbb{1}}-4\pi\frac{\vec{\mathrm{q}}}{q}[\tilde{\alpha}^{L,\rightarrow}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}\right]^{-1}\\&=\overleftrightarrow{\mathbb{1}}+4\pi\frac{\vec{\mathrm{q}}}{q}\frac{[\tilde{\alpha}^{L,\rightarrow}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}}{1-4\pi[\tilde{\alpha}^{LL}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}}\ ,\end{aligned} \tag{24}$$

which yields

$$\begin{aligned}\overleftrightarrow{\epsilon}_{M}(\vec{\mathrm{q}})=\overleftrightarrow{\mathbb{1}}&+4\pi[\overleftrightarrow{\tilde{\alpha}}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}\\&+(4\pi)^{2}\frac{[\tilde{\alpha}^{\leftarrow,L}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}[\tilde{\alpha}^{L,\rightarrow}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}}{1-4\pi[\tilde{\alpha}^{LL}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}}\ .\end{aligned} \tag{25}$$

The longitudinal-longitudinal component of $\overleftrightarrow{\epsilon}_{M}$ assumes a simple form, depending only upon the longitudinal quasi-polarizability $\tilde{\alpha}^{LL}$:

$$\epsilon_{M}^{LL}(\vec{\mathrm{q}})=\{1-4\pi[\tilde{\alpha}^{LL}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}\}^{-1}\ . \tag{26}$$

This very result is sufficient to describe the dielectric response in cubic crystals,[47] where a longitudinal external field with $\vec{\mathrm{q}}\rightarrow0$ induces only longitudinal fields.[16] In noncubic crystals transverse fields are generally induced, too, but the relation (26) between the external field $E^{\mathrm{ex},L}$ and the longitudinal component of the macroscopic field $[E^{L}(q)]_{\vec{0}}$ is preserved.

The normal-mode equation (23) can be recast in a more transparent form, using (24) and (25). By factorizing $\overleftrightarrow{A}$ in (23), and choosing the z direction parallel to $\vec{\mathrm{q}}$ for the sake of simplicity, we get the dispersion relation

$$\epsilon_{M}^{LL}(\vec{\mathrm{q}})\begin{vmatrix}1-\frac{c^{2}q^{2}}{\omega^{2}}+4\pi[\tilde{\alpha}_{xx}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}} & 4\pi[\tilde{\alpha}_{xy}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}\\ 4\pi[\tilde{\alpha}_{yx}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}} & 1-\frac{c^{2}q^{2}}{\omega^{2}}+4\pi[\tilde{\alpha}_{yy}(\vec{\mathrm{q}})]_{\vec{0},\vec{0}}\end{vmatrix}=0\ , \tag{23'}$$

where $\epsilon_{M}^{LL}(\vec{\mathrm{q}})$ is the determinant of the matrix $\overleftrightarrow{\mathrm{A}}$. If the first factor is zero, we get purely longitudinal modes, as can be easily seen from Eqs. (17) and (18), considering that also $[\epsilon_{M}(q_{z})]_{iz}$ and $[\epsilon_{M}(q_{z})]_{zi}$ vanish if $\epsilon_{M}^{LL}(q_{z})$ vanishes [see Eq. (25)]. If the second factor, namely the 2×2 determinant is zero, we get mixed longitudinal-transverse modes. It is worthwhile to note, however, that the dispersion relation involves only transverse components of $\overleftrightarrow{\tilde{\alpha}}(\vec{\mathrm{q}})_{00}$. These modes could be thought of as "transverse" modes, which "must" carry also a longitudinal electric field due to the nonvanishing off-diagonal components of $\overleftrightarrow{\tilde{\alpha}}(\vec{\mathrm{q}})_{00}$.

The LL component of the dielectric tensor describes also the energy loss of charged particles. If we assume that the potential generated by a classical particle of velocity $\vec{\mathrm{v}}$ and charge e is sufficiently smooth so that it does not have important microscopic components, we can solve Eqs. (17) and (18) in terms of $\vec{\mathrm{E}}^{\mathrm{ex}}$. However, since q is much larger than $\omega/c=\vec{\mathrm{q}}\cdot\vec{\mathrm{v}}/c$, the transverse field can be neglected, and the perturbing field coincides with the external field. We can compute the energy loss using Eq. (101) of Ref. 47, in the case of scalar external field, and the final result is

$$\frac{dW}{dx}=\frac{2c^2}{\pi v}\int d^3q\frac{\vec{q}\cdot\vec{v}}{q^2}\mathrm{Im}\{[\tilde{\alpha}^{LL}(\vec{q})]_{\vec{0},\vec{0}}\}\ . \tag{27}$$

Comparing this result with Eq. (111) of Ref. 47 and using (26), we see that the loss function, given by $\mathrm{Im}[-1/\epsilon_M(\omega)]$ in the cubic case [$\epsilon_M(\omega)$ is the macroscopic dielectric constant], must be replaced by $\mathrm{Im}[-1/\epsilon_M^{LL}(\vec{q},\omega)]$ in noncubic crystals. Let us emphasize that this result is not as obvious as it might seem. In fact, it is not obvious that $1/\epsilon_M(\omega)$ must be replaced by $1/\epsilon_M^{LL}(\vec{q},\omega)$ and not, for instance, by $[\overleftrightarrow{\epsilon}_M^{-1}(\vec{q},\omega)]^{LL}$.

IV. MICROSCOPIC CALCULATION OF THE MACROSCOPIC DIELECTRIC TENSOR OF AN INFINITE CRYSTAL

In the preceding section we have derived an expression, Eq. (25), for the macroscopic dielectric tensor in terms of the quasipolarizability $[\overleftrightarrow{\tilde{\alpha}}(\vec{q})]_{\vec{0},\vec{0}}$. The purpose of this section is to insert an explicit expression of the latter and to derive henceforth an explicit expression for the macroscopic polarizability.

The quasipolarizability $[\overleftrightarrow{\tilde{\alpha}}(\vec{q})]_{\vec{0},\vec{0}}$ is known from the linear-response theory, in terms of the Green's-function matrix $S_{L_1L_1'L_2L_2'}(\omega)$ [see Eq. (9)]. In an infinite crystal, according to Ref. 5, we express such a matrix in terms of the new variables, $\vec{R}_1$, $\vec{R}_1'-\vec{R}_1$, $\vec{R}_2$, and $\vec{R}_2'-\vec{R}_2$, and Fourier transform with respect to $\vec{R}_1$ and $\vec{R}_2$, yielding wave-vector dependences $\vec{q}_1$ and $\vec{q}_2$. By lattice translational invariance $\vec{q}_1=\vec{q}_2$. Therefore we have

$$S_{L_1L_1'L_2L_2'}(\omega)=N_c^{-1}\sum_{\vec{q}}e^{i\vec{q}\cdot(\vec{R}_1-\vec{R}_2)}S_{\lambda_1\lambda_2}(\vec{q},\omega)\ , \tag{28}$$

where λ_1 is short for $\vec{R}_1'-\vec{R}_1$, ν_1, ν_1', and N_c is the number of cells contained in the crystal. The insertion of (28) into (9) gives, for $\vec{q}\rightarrow\vec{0}$,

$$\tilde{\alpha}_{\alpha\beta}(\vec{q})_{00}=-\delta_{\alpha\beta}\frac{e^2n}{m\omega^2}-\frac{e^2}{m^2\Omega\omega^2}\times\sum_{\lambda_1,\lambda_2}S_{\lambda_1\lambda_2}(-\vec{q},\omega)p_{\lambda_1}^{\beta*}p_{\lambda_2}^{\alpha}\ , \tag{29}$$

where n is the average electron density, Ω the cell volume, λ_1 (λ_2) stands for the ordered couple of orbitals $\mu_1'\vec{R}_1'\mu_1\vec{0}$ [$\mu_2'(\vec{R}_2'\mu_2\vec{0}$], and $p_{\lambda_2}^{\alpha}$ is the momentum matrix element between localized orbitals, which is proportional to the $q\rightarrow 0$ limit of $J_{\alpha\mu_2'\vec{R}_2',\mu_2 0}(\vec{q})$. The local orbitals here considered are the Wannier functions of filled and empty bands. Each couple contains one filled and one empty orbital. This choice avoids considering couples of repeated orbitals ($\nu_2'=\nu_2$) which would make more complicated the calculation of the macroscopic dielectric tensor, as will be clear in the following.

Although the $q\rightarrow 0$ limit has been taken in calculating the matrix element $p_{\lambda_2}^{\alpha}$, nevertheless $\tilde{\alpha}_{\alpha\beta}(\vec{q})_{00}$ is still $\vec{q}$ dependent, via the $\vec{q}$ dependence of $S_{\lambda_1\lambda_2}(-\vec{q},\omega)$, whose $\vec{q}\rightarrow\vec{0}$ limit depends on the $\vec{q}$ direction with respect to the relevant dipoles. In fact, as it will be shown later, it contains the nonanalytic long-range part of the Coulomb potential (the nonanalytic electron-hole exchange, in the excitonic language) which leads, for instance, to the longitudinal-transverse exciton splitting.[52]

An analogous treatment of the $\overleftrightarrow{\tilde{\alpha}}$ contractions entering Eq. (25) yields

$$[\tilde{\alpha}^{L,\rightarrow}(\vec{q})]_{\vec{0},\vec{0}}=\frac{i}{\Omega}\frac{e^2}{\hbar\omega m}\sum_{\lambda_1,\lambda_2}\vec{p}_{\lambda_1}^{\,*}S_{\lambda_1\lambda_2}(-\vec{q},\omega)\mu_{\lambda_2}^{L}\ , \tag{30}$$

$$[\tilde{\alpha}^{\leftarrow,L}(\vec{q})]_{\vec{0},\vec{0}}=-\frac{i}{\Omega}\frac{e^2}{\hbar\omega m}\sum_{\lambda_1,\lambda_2}\mu_{\lambda_1}^{L*}S_{\lambda_1\lambda_2}(-\vec{q},\omega)\vec{p}_{\lambda_2}\ , \tag{31}$$

$$[\tilde{\alpha}^{LL}(\vec{q})]_{\vec{0},\vec{0}}=-\frac{e^2}{\Omega}\sum_{\lambda_1,\lambda_2}\mu_{\lambda_1}^{L*}S_{\lambda_1\lambda_2}(-\vec{q},\omega)\mu_{\lambda_2}^{L}\ , \tag{32}$$

where $\vec{\mu}_{\lambda_1}$ is the dipole matrix element between localized orbitals, coming from the $\vec{q}\rightarrow\vec{0}$ limit of the quantity $A_{\mu_1'\vec{R}_1',\mu_1\vec{0}}(\vec{q})$ defined in Eq. (16).

At this point let us consider in more detail the nonanalytic behavior of $S_{\lambda_1\lambda_2}(-\vec{q},\omega)$. It can be found by solving the Bethe-Salpeter equation:[5]

$$S=N^0[1-(V-\tfrac{1}{2}V^S)N^0]^{-1}\ , \tag{33}$$

where matrix indices are understood in all quantities. $N_{\lambda_1\lambda_2}^0(\vec{q},\omega)$ is the RPA polarizability matrix, not including local-field and excitonic effects, while $V(\vec{q})$ and $-\frac{1}{2}V_S(\vec{q})$ are the Coulomb and exchange parts of the e-e interaction, given, in the framework of the many-body perturbation technique,[5] by

$$V_{\lambda_1\lambda_2}(\vec{q})=\sum_{\vec{R}_m}e^{-i\vec{q}\cdot\vec{R}_m}\int d^3r\int d^3r'\phi_{\mu_1'}^{*}(\vec{r}-\vec{R}_1'-\vec{R}_m)\phi_{\mu_1}(\vec{r}-\vec{R}_m)V(\vec{r}-\vec{r}\,')\phi_{\mu_2}^{*}(\vec{r}\,')\phi_{\mu_2'}(\vec{r}\,'-\vec{R}_2')\ , \tag{34}$$

$$V_{\lambda_1\lambda_2}^{s}(\vec{q})=\sum_{\vec{R}_m}e^{-i\vec{q}\cdot\vec{R}_m}\int d^3r\int d^3r'\phi_{\mu_1'}^{*}(\vec{r}-\vec{R}_1'-\vec{R}_m)\phi_{\mu_1}(\vec{r}\,'-\vec{R}_m)V_s(\vec{r},\vec{r}\,')\phi_{\mu_2}^{*}(\vec{r}\,')\phi_{\mu_2'}(\vec{r}-\vec{R}_2')\ . \tag{35}$$

$V(\vec{r}-\vec{r}\,')$ is the Coulomb potential and $V_S(\vec{r},\vec{r}\,')$ is the statically screened *e-e* exchange interaction (the electron-hole Coulomb interaction, in the excitonic language), which has been discussed in the most general form by Sham and Rice.[35]

The sum in (35) is restricted to small $\vec{R}_m$ values because of the vanishing (as R_m increases) overlap between the localized orbitals. Therefore $\vec{q}\cdot\vec{R}_m$ is nearly zero at small q, and the exchange matrix has a well-determined $\vec{q}\rightarrow\vec{0}$ limit. This is not the case of the Coulomb matrix V; here large $\vec{R}_m$ values are involved, where a dipolar expansion of the Coulomb interaction can be applied, transforming the sum in (34) into a sum of dipole-dipole interactions (plus a term arising from small $\vec{R}_m$'s), which yields a result depending on the direction of $\vec{q}$, as it tends to zero.[52] In the excitonic language, this term is called the nonanalytic part of the electron-hole exchange interaction.[54]

In order to isolate such a nonanalytic part, which will be shown not to affect the macroscopic dielectric tensor, it is better to transform Eq. (34), using Fourier transforms and the translational symmetry, to the following form:[55]

$$V_{\lambda_1\lambda_2}(\vec{q})=\sum_{\vec{G}}A^*_{\lambda_1}(\vec{q}+\vec{G})\frac{4\pi e^2}{|\vec{q}+\vec{G}|^2\Omega}A_{\lambda_2}(\vec{q}+\vec{G})\ . \qquad (36)$$

As $\vec{q}$ tends to zero, we can neglect it with respect to $\vec{G}$ in the $\vec{G}\neq\vec{0}$ terms, which therefore result to be $\vec{q}$ independent, and expand the $\vec{G}=\vec{0}$ form factors $A_{\lambda_2}(\vec{q})$ and $A^*_{\lambda_1}(\vec{q})$ to the first order in $\vec{q}$. The $\vec{G}=\vec{0}$ term is the nonanalytic part of V,

$$V^{na}_{\lambda_1\lambda_2}(\vec{q})=\frac{4\pi e^2}{\Omega q^2}(\vec{\mu}^{\,*}_{\lambda_1}\cdot\vec{q})(\vec{\mu}_{\lambda_2}\cdot\vec{q})\ , \qquad (37)$$

which depends on the direction of $\vec{q}$ with respect to the dipoles $\vec{\mu}^{\,*}_{\lambda_1}$ and $\vec{\mu}_{\lambda_2}$. The sum of the other ($\vec{G}\neq\vec{0}$) terms is called the analytic part of the Coulomb matrix, V^a.

We assume now to have already solved the Bethe-Salpeter equation (33), where the nonanalytic part of V is neglected, and call S^a the resulting matrix. Then S satisfies the following equation:

$$S=S^a(1-V^{na}S^a)^{-1}\ . \qquad (38)$$

The factorized form (37) of V^{na} allows an easy solution of (38), yielding

$$S_{\lambda_1\lambda_2}(\vec{q},\omega)=S^a_{\lambda_1\lambda_2}(\vec{q},\omega)+\frac{4\pi e^2}{\Omega}\frac{\sum\limits_{\lambda_3,\lambda_4}S^a_{\lambda_1\lambda_4}(\vec{q},\omega)\mu^{L*}_{\lambda_4}\mu^{L}_{\lambda_3}S^a_{\lambda_3\lambda_2}(\vec{q},\omega)}{1-\frac{4\pi e^2}{\Omega}\sum\limits_{\lambda_3,\lambda_4}\mu^L_{\lambda_3}S^a_{\lambda_3\lambda_4}(\vec{q},\omega)\mu^{*L}_{\lambda_4}}\ . \qquad (39)$$

The use of this result in Eqs. (29) and (30)—(32) and their insertion into (25) yield, after tedious but simple algebra, the following result for the macroscopic dielectric tensor, where the terms nonanalytic in $\vec{q}$ cancel each other:

$$\epsilon_{M\alpha\beta}(\vec{q},\omega)=\delta_{\alpha\beta}\left[1-\frac{4\pi ne^2}{m\omega^2}\right]-\frac{4\pi}{\Omega}\frac{e^2}{\hbar^2\omega^2m^2}\sum_{\lambda_1,\lambda_2}p^{\alpha*}_{\lambda_2}S^a_{\lambda_1\lambda_2}(-\vec{q},\omega)p^{\beta}_{\lambda_1}\ . \qquad (40)$$

This equation is the main result of this section. A few remarks will elucidate its meaning. First, the macroscopic dielectric tensor results to be an analytic function of $\vec{q}$, as already shown by Pick.[12] Equation (40) is a generalization of AK's result[44] to noncubic crystals. These authors found that in cubic crystals the macroscopic dielectric constant can be computed cutting off the long-range part of the Coulomb potential. We find that the same is true in noncubic crystals for the macroscopic dielectric tensor. A similar result has been recently obtained by Ehara and Cho[46] in the case of an excitonic system.

Finally, we emphasize that Eq. (40) is a very simple way of describing many-body effects in noncubic crystals. It is much simpler, not only than Johnson's formulation,[16] but also than Pick's[12] definition of the macroscopic dielectric tensor, which has been shown to be suitable for practical calculations on a localized basis.[23] This tensor can be computed in noncubic crystals via Eq. (40), basically with the same computational effort that is requested in cubic crystals, namely that needed to solve the Bethe-Salpeter equation for S^a.

V. MACROSCOPIC DIELECTRIC TENSOR OF A SEMI-INFINITE CRYSTAL

The definition of the macroscopic dielectric tensor for a semi-infinite crystal has been given in Refs. 25 and 56, starting from the microscopic dielectric tensor. We repeat it here in more detail for the sake of completeness. We consider a crystal occupying the half-space $z>0$ and showing two-dimensional (2D) periodicity in the xy directions. Let $\vec{q}_{\parallel}$ $(\rightarrow\vec{0})$ be a vector in the 2D Brillouin zone and the $\vec{G}_{\parallel}$'s be the reciprocal vectors.

We define the macroscopic field as having Fourier components[58] $\vec{E}(\vec{q}_{||},k_z)_{\vec{G}_{||}}$ limited to $\vec{G}_{||}=\vec{0}$ and $|k_z|$ smaller than a cutoff wave vector k_c, such that

$$\frac{\omega}{c} \ll k_c \ll G \ . \tag{41}$$

The other Fourier components are called microscopic fields and are, to a good approximation, longitudinal, as can be seen from Eq. (17), recalling that ω/ck_c or $\omega/cG_{||}$ are small numbers.

The microscopic fields are eliminated using Eq. (18), that in the surface case, reads

$$\int_{-k_c}^{k_d} dk_z' \epsilon^{L,\rightarrow}(\vec{q}_{||},k_z,k_z')_{\vec{G}_{||},0} \cdot \vec{E}(\vec{q}_{||},k_z')_0 + \sum_{\vec{G}_{||}'} \int_{(m)} dk_z' [\epsilon^{LL}(\vec{q}_{||},k_z,k_z')]_{\vec{G}_{||},\vec{G}_{||}'} [E^L(\vec{q}_{||},k_z')]_{\vec{G}_{||}'} = 0 \tag{42}$$

for $\vec{G}_{||}\neq\vec{0}$, or $\vec{G}_{||}=\vec{0}$ and $|k_z| > k_c$. The microscopic components of the external fields are assumed to be negligible. The subscript (m) below the integral means that k_z' is limited to the microscopic fields, namely that $|k_z'| > k_c$, if $\vec{G}_{||}'=\vec{0}$. Here $[\overleftrightarrow{\epsilon}(\vec{q}_{||},k_z,k_z']_{\vec{G}_{||},\vec{G}_{||}'}$ is the microscopic dielectric tensor, defined in Ref. 12. This approach is particularly useful in the RPA, where the microscopic dielectric tensor can be easily computed from one-electron wave functions.

The microscopic fields are found from Eq. (42) inverting

$$[\tilde{\epsilon}^{LL}(\vec{q}_{||},k_z,k_z']_{\vec{G}_{||},\vec{G}_{||}'} \ ,$$

i.e.,

$$[\epsilon^{LL}(\vec{q}_{||},k_z,k_z')]_{\vec{G}_{||},\vec{G}_{||}'}$$

restricted to microscopic fields. Substituting into Eqs. (17) and (18) for the macroscopic components ($\vec{G}_{||}=\vec{0}$ and $|k_z| < k_c$) yields the propagation equation for the macroscopic field $\vec{E}_M(\vec{q}_{||},k_z)$:

$$-(\vec{q}_{||}+\vec{k}_z)\times(\vec{q}_{||}+\vec{k}_z)\times\vec{E}_M(\vec{q}_{||},k_z) = \frac{\omega^2}{c^2}\int_{-k_c}^{k_c} dk_z' \overleftrightarrow{\epsilon}_M(\vec{q}_{||},k_z,k_z')\cdot\vec{E}_M(\vec{q}_{||},k_z') - \frac{4\pi i\omega}{c^2}[\vec{j}^{\,\mathrm{ex}}(\vec{q}_{||},k_z)]_{\vec{0}} \ , \tag{43}$$

where $\vec{k}_z$ means k_z times the versor of the z axis.

The first term on the right-hand side of Eq. (43) is just $\omega^2/c^2[\vec{D}(\vec{q}_{||},k_z)]_{\vec{0}}$ which is related to the macroscopic field $\vec{E}_M(\vec{q}_{||},k_z')$ via the macroscopic dielectric tensor. This is given by (for $|k_z|$ and $|k_z'| < k_c$)

$$\begin{aligned}\overleftrightarrow{\epsilon}_M(\vec{q}_{||},k_z,k_z') = {} & [\overleftrightarrow{\epsilon}(\vec{q}_{||},k_z,k_z')]_{\vec{0},\vec{0}} - \sum_{\vec{G}_{||}} \int_{(m)} d\tilde{k}_z \sum_{\vec{G}_{||}'} \int_{(m)} d\tilde{k}_z' [\epsilon^{\leftarrow,L}(\vec{q}_{||},k_z,\tilde{k}_z)]_{\vec{0},\vec{G}_{||}} [\tilde{\epsilon}^{LL}(\vec{q}_{||},\tilde{k}_z,\tilde{k}_z')]_{\vec{G}_{||},\vec{G}_{||}'} \\ & \times [\epsilon^{L,\rightarrow}(\vec{q}_{||},\tilde{k}_z',k_z')]_{\vec{G}_{||}'\vec{0}} \ .\end{aligned} \tag{44}$$

The external current appearing in (43) does not have any role in the definition of $\overleftrightarrow{\epsilon}_M$. It has been kept, for the sake of generality, to be able to describe the energy loss of charged particles.

The solution of (43) yields the macroscopic field, that is enough to determine optical properties, which are given by the behavior of the electric field far away from the surface. Even surface absorption can be computed from the energy balance, knowing reflectivity and transmission. However, other properties, such as the photoemission cross section, imply the explicit determination of the microscopic fields, which in principle can be achieved from (42).

The main shortcoming of this approach is that the macroscopic dielectric tensor has a complicated definition, in terms of the microscopic one, which in turn is not simple,[12] except as in the RPA. Although it is possible to carry out explicit calculations of the optical properties using this definition,[25] however, it is difficult to control the spatial behavior of $\overleftrightarrow{\epsilon}_M$ near the surface. A crucial assumption of all the methods of solution of light-propagation equations[32,34–39] is that the surface perturbation on $\overleftrightarrow{\epsilon}_M$ vanishes after a distance much smaller than the light wave vector. This is difficult to check using the expression (44).

In order to get a clearer expression of $\overleftrightarrow{\epsilon}_M$, it is possible to use an approach similar to that of Sec. III, based on the linear response to the external field. Repeating the arguments of Sec. III, with minor changes appropriate to the semi-infinite crystal, we get

$$\overleftrightarrow{\epsilon}_M(\vec{q}_{||},k_z,k_z') = \delta(k_z-k_z')\overleftrightarrow{1} + 4\pi\int_{-k_c}^{k_c} dk_z''[\overleftrightarrow{\tilde{\alpha}}(\vec{q}_{||},k_z,k_z'')]_{\vec{0},\vec{0}}\cdot\overleftrightarrow{A}(\vec{q}_{||},k_z'',k_z'), \quad |k_z|,|k_z'| < k_c \ . \tag{45}$$

The tensor operaor $\overleftrightarrow{A}$ is the solution of the equation

$$\int_{-k_c}^{k_c} dk_z'' \overleftrightarrow{A}(\vec{q}_{\|},k_z,k_z'') \left[\overleftrightarrow{1}\delta(k_z''-k_z') - 4\pi \frac{\vec{q}_{\|}+\vec{k}_z''}{|\vec{q}_{\|}+\vec{k}_z''|} [\tilde{\alpha}^{L,\rightarrow}(\vec{q}_{\|},k_z'',k_z')]_{\vec{0},\vec{0}} \right] = \overleftrightarrow{1}\delta(k_z-k_z') \ , \tag{46}$$

i.e., is the inverse of the tensor integral operator in the large parentheses.

If we multiply by $[\overleftrightarrow{\tilde{\alpha}}(\vec{q}_{\|},k_z''',k_z)]_{\vec{0},\vec{0}}$ and integrate over k_z from $-k_c$ to k_c, we get an integral equation for the macroscopic polarizability $\overleftrightarrow{\alpha}_M(\vec{q}_{\|},k_z,k_z')$. If we take the right-hand longitudinal contraction of this equation, it reduces to a vector equation for $\alpha_M^{\leftarrow,L}(\vec{q}_{\|},k_z''',k_z')$:

$$\int_{-k_c}^{k_c} dk_z \alpha_M^{\leftarrow,L}(\vec{q}_{\|},k_z''',k_z) O_P(\vec{q}_{\|},k_z,k_z') = [\tilde{\alpha}^{\leftarrow,L}(\vec{q}_{\|},k_z''',k_z')]_{\vec{0},\vec{0}} \ , \tag{47}$$

where the integral operator O_p is given by

$$O_p(\vec{q}_{\|},k_z,k_z') = \delta(k_z-k_z') - 4\pi[\tilde{\alpha}^{LL}(\vec{q}_{\|},k_z,k_z')]_{\vec{0},\vec{0}} \ . \tag{48}$$

Let us assume that we are able to invert such operator. Then we can solve (47) and get the macroscopic polarizability

$$\overleftrightarrow{\alpha}_M(\vec{q}_{\|},k_z''',k_z') = [\overleftrightarrow{\tilde{\alpha}}(\vec{q}_{\|},k_z''',k_z')]_{\vec{0},\vec{0}} + 4\pi \int_{-k_c}^{k_c} dk_z \int_{-k_c}^{k_c} dk_z'' [\tilde{\alpha}^{\leftarrow,L}(\vec{q}_{\|},k_z''',k_z)]_{\vec{0},\vec{0}} \times O_p^{-1}(\vec{q}_{\|},k_z,k_z'')[\tilde{\alpha}^{L,\rightarrow}(\vec{q}_{\|},k_z'',k_z')]_{\vec{0},\vec{0}} \ . \tag{49}$$

The inversion of the operator $O_p(\vec{q}_{\|},k_z,k_z')$ is the main step of this section. It can be achieved using the local expansions of the response functions. Henceforth, before solving Eq. (49), we proceed to express the quasipolarizability and its longitudinal contractions in the localized orbital basis, in a way appropriate to a semi-infinite crystal.

In this case we write $[\overleftrightarrow{\tilde{\alpha}}(\vec{q}_{\|},k_z,k_z')]_{\vec{G}_{\|},\vec{G}_{\|}'}$ for $[(2\pi)^2/A_s]\overleftrightarrow{\tilde{\alpha}}(\vec{q}_{\|}+\vec{G}_{\|},k_z;\ \vec{q}_{\|}+\vec{G}_{\|}',\ k_z')$, where A_s is the surface area. Then we exploit the 2D periodicity and express $S_{L_1L_1'L_2L_2'}(\omega)$ in terms of the new variables $\vec{R}_{1\|}$, $\vec{R}_{1\|}'-\vec{R}_{1\|}$, R_{1z}, R_{1z}', $\vec{R}_{2\|}$, $\vec{R}_{2\|}'-\vec{R}_{2\|}$, R_{2z}, and R_{2z}', and Fourier transform with respect to $\vec{R}_{1\|}$ and $\vec{R}_{2\|}$, yielding wave-vector dependences $\vec{q}_{1\|}$ and $\vec{q}_{2\|}$. By surface translational invariance, $\vec{q}_{1\|}=\vec{q}_{2\|}$. Therefore we have

$$S_{L_1L_1'L_2L_2'}(\omega) = N_s^{-1}\sum_{\vec{q}_{\|}} e^{i\vec{q}_{\|}\cdot(\vec{R}_{1\|}-\vec{R}_{2\|})} S_{s_1s_2}(\vec{q}_{\|},\omega) \ , \tag{50}$$

where N_s is the number of unit cells in the surface plane, and s_1 is short for $\vec{R}_{1\|}'-\vec{R}_{1\|}$, ν_1 at R_{1z}, and ν_1' at R_{1z}'.

Insertion of Eq. (50) into (9) gives for small $\vec{q}_{\|}$, k_z, and k_z',

$$[\tilde{\alpha}_{\alpha\beta}(\vec{q}_{\|},k_zk_z')]_{\vec{0},\vec{0}} = (2\pi\omega^2)^{-1} \left[-\frac{e^2}{m}\delta_{\alpha\beta}\rho_0(k_z-k_z') - \frac{e^2}{m^2\hbar^2}\frac{1}{A_0}\sum_{s_1,s_2} \exp[i(k_z'R_{1z}-k_zR_{2z})]S_{s_1s_2}(-\vec{q}_{\|},\omega)p_{s_2}^{\alpha}p_{s_1}^{*\beta} \right] . \tag{51}$$

where A_0 is the unit-cell area and $\rho_0(k_z-k_z')$ is the z Fourier transform of the ground-state electronic density $\rho(r)$, averaged on the surface plane.

Analogously we have, using Eqs. (13)—(15):

$$[\tilde{\alpha}^{L,\rightarrow}(\vec{q}_{\|},k_z,k_z')]_{\vec{0},\vec{0}} = \frac{i}{2\pi A_0}\frac{e^2}{m\hbar\omega}\sum_{s_1,s_2} \mu_{s_2}^{L}(\vec{q}_{\|}+\vec{k}_z')S_{s_1s_2}(-\vec{q}_{\|},\omega)\vec{p}_{s_1}^{\,*}\exp[i(k_z'R_{1z}-k_zR_{2z})] \ , \tag{52}$$

$$[\tilde{\alpha}^{\leftarrow,L}(\vec{q}_{\|},k_z,k_z')]_{\vec{0},\vec{0}} = -\frac{i}{2\pi A_0}\frac{e^2}{m\hbar\omega}\sum_{s_1,s_2} \vec{p}_{s_2}S_{s_1,s_2}(-\vec{q}_{\|},\omega)\mu_{s_1}^{L*}(\vec{q}_{\|}+\vec{k}_z)\exp[i(k_z'R_{1z}-k_zR_{2z})] \ , \tag{53}$$

$$[\tilde{\alpha}^{LL}(\vec{q}_{\|},k_z,k_z')]_{\vec{0},\vec{0}} = -\frac{e^2}{2\pi A_0}\sum_{s_1,s_2} \mu_{s_2}^{L}(\vec{q}_{\|}+\vec{k}_z')S_{s_1s_2}(-\vec{q}_{\|},\omega)\mu_{s_1}^{*L}(\vec{q}_{\|}+\vec{k}_z)\exp[i(k_z'R_{1z}-k_zR_{2z})] \ , \tag{54}$$

where $\mu_{s_2}^{L}(\vec{q}_{\|}+\vec{k}_z')$ is the longitudinal component of $\vec{\mu}_{s_2}$ with respect to $\vec{q}_{\|}+\vec{k}_z'$.

The matrix S satisfies the Bethe-Salpeter equation, in analogy with the infinite-crystal case equation (33). The only difference is that the index s_1 (or s_2) stands for R_{1z}' (or R_{1z}), in addition to other labels, rather than for $R_{1z}'-R_{1z}$, as λ_1 in the bulk case. The matrix to be inverted at the surface has a larger size than in bulk, in strict similarity with band calculations. The Coulomb e-e interaction matrix is given by (34). An alternative form, analogous to (36), in terms of the Fourier transform of the Coulomb potential, can be simply worked out:

$$V_{s_1 s_2}(\vec{q}_{||})=A_0^{-1}\sum_{\vec{G}_{||}}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\frac{4\pi e^2}{(\vec{q}_{||}+\vec{G}_{||})^2+k_z^2}A_{s_2}(\vec{q}_{||}+\vec{G}_{||},k_z)A_{s_1}^{*}(\vec{q}_{||}+\vec{G}_{||},k_z)\ . \tag{55}$$

We want to separate at this point the long-range (small-$\vec{k}$) Coulomb interaction, which gives rise to the nonanalytic behavior of $S(\vec{q}_{||},\omega)$ as $\vec{q}_{||}\to\vec{0}$. We define the nonanalytic Coulomb matrix V^{na} as the $\vec{G}_{||}=0$ term of (55), where the k_z integral is limited to $|k_z|<k_c$. The remaining part of V is called the analytic Coulomb matrix V^{a} which results to be $\vec{q}_{||}$ independent, as $\vec{q}_{||}\to\vec{0}$:

$$\begin{aligned}V_{s_1 s_2}^{a}(\vec{q}_{||})=&A_0^{-1}\int_{|k_z|>k_c}\frac{dk_z}{2\pi}\frac{4\pi e^2}{q_{||}^2+k_z^2}A_{s_2}(\vec{q}_{||},k_z)A_{s_1}^{*}(\vec{q}_{||},k_z)\\&+A_0^{-1}\sum_{\vec{G}_{||}(\neq\vec{0})}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\frac{4\pi e^2}{|\vec{q}_{||}+\vec{G}_{||}|^2+k_z^2}A_{s_2}(\vec{q}_{||}+\vec{G}_{||},k_z)A_{s_1}^{*}(\vec{q}_{||}+\vec{G}_{||},k_z)\ ,\end{aligned} \tag{56}$$

$$V_{s_1 s_2}^{na}(\vec{q}_{||})=4\pi e^2 A_0^{-1}\int_{-k_c}^{k_c}\frac{dk_z}{2\pi}\exp[ik_z(R_{1z}-R_{2z})]\mu_{s_1}^{*L}(\vec{q}_{||}+\vec{k}_z)\mu_{s_2}^{L}(\vec{q}_{||}+\vec{k}_z)\ . \tag{57}$$

In order to derive (57) we have used the dipole approximation in computing $A_{s_1}^{*}(\vec{q}_{||},k_z)$ and $A_{s_2}(\vec{q}_{||},k_z)$, which is justified since $\vec{q}_{||}\to\vec{0}$ and $|k_z|<k_c\ll 1/d$, where d is a typical spacing of layers in the z direction. The orthogonality of the orbitals v_1 and v_1' is here important and is achieved by using conduction- and valence-band Wannier functions.

We define, also in the surface case, the matrix $S_{s_1 s_2}^{a}(\vec{q}_{||},\omega)$, which satisfies the Bethe-Salpeter equation where the nonanalytic Coulomb interaction is omitted. The relation between S and S^{a} is again shown in Eq. (38), which can be formally solved with respect to S^{a}.

Now we go back to Eq. (48) and invert the operator O_p, which can be written, using (54), as

$$O_p(\vec{q}_{||},k_z,k_z')=\delta(k_z-k_z')+2e^2A_0^{-1}\sum_{s_1,s_2}\mu_{s_2}^{L}(\vec{q}_{||}+\vec{k}_z)S_{s_1 s_2}(-\vec{q}_{||},\omega)\mu_{s_1}^{*L}(\vec{q}_{||}+\vec{k}_z')\exp[i(k_z'R_{1z}-k_zR_{2z})]\ . \tag{58}$$

We try a solution of the form

$$O_p^{-1}(\vec{q}_{||},k_z',k_z'')=\delta(k_z'-k_z'')-2e^2A_0^{-1}\sum_{s_1,s_2}\mu_{s_2}^{L}(\vec{q}_{||}+\vec{k}_z')N_{s_1 s_2}\mu_{s_1}^{L*}(\vec{q}_{||}+\vec{k}_z'')\exp[i(k_z''R_{1z}-k_z'R_{2z})]\ , \tag{59}$$

getting a matrix equation for N:

$$S(-\vec{q}_{||},\omega)=N+NV^{na}(-\vec{q}_{||})S(-\vec{q}_{||},\omega)\ . \tag{60}$$

To derive this equation, we have use the property

$$V_{s_2 s_1}^{na}(\vec{q}_{||})=V_{s_1 s_2}^{na}(-\vec{q}_{||}) \tag{61}$$

which can be easily demonstrated from the definition (57), if real orbitals are used.

We solve Eq. (60) with respect to N, and compare with S^{a} obtained by inverting (38), yielding, finally,

$$N=S^{a}(-\vec{q}_{||},\omega)\ . \tag{62}$$

We are now able to find the macroscopic polarizability from (49), using (51)–(53) and the inverse operator O_p^{-1} given by (59) and (62). After long but simple algebra, the final result for the macroscopic dielectric tensor is

$$\epsilon_{M\alpha\beta}(\vec{q}_{||},k_z,k_z')=\delta_{\alpha\beta}\left[\delta(k_z-k_z')-\frac{4\pi e^2}{m\omega^2}\rho_0(k_z-k_z')(2\pi)^{-1}\right]-\frac{2e^2}{A_0}(\hbar\omega m)^{-2}\sum_{s_1,s_2}p_{s_2}^{\alpha}e^{-ik_zR_{2z}}S_{s_1 s_2}^{a}(\vec{0},\omega)e^{ik_z^{1}R_{1z}}p_{s_1}^{\beta*}\ . \tag{63}$$

This is the main result of this paper. Again we find that the nonanalytic part of the Coulomb interaction does not affect the macroscopic dielectric tensor, according to AK's results[44] for cubic crystals and to the formulation of Ehara and Cho[46] for crystals of general symmetry in the excitonic approximation.

Insertion of (63) into the propagation equation of the macroscopic field, Eq. (43), enables one to describe the dielectric properties of the semi-infinite crystal. The approximations needed to derive such results are (i) the long-wavelength character of the radiation involved, namely $\omega/c\ll G$, and (ii) the macroscopic character of the external current and field, i.e., with Fourier components only for $\vec{G}_{||}=0$ and $|k_z|<k_c$. The solution of Eq. (43) yields the macroscopic field, which is enough to determine optical reflectivity and absorption. However, this is not yet the complete solution, which should also involve microscopic field components. For instance, we cannot compute from (43) the photoemission yield from surface states, which depends on the actual (microscopic) profile of the electromagnetic field at the surface. The microscopic fields, which are approximately longitudinal,

can be computed from the surface analog of Eq. (20).

In cases where only longitudinal fields are present, Eq. (43) becomes

$$\int_{-k_c}^{k_c} dk_z' \, \epsilon_M^{LL}(\vec{q}_{||},k_z,k_z') E_M^L(\vec{q}_{||},k_z') = [E^{\text{ex},L}(\vec{q}_{||},k_z)]_{\vec{0}} , \tag{64}$$

where ϵ_M^{LL}, obtained from the longitudinal component of the vector equation (47), is just O_p^{-1} given by (59) and (62). Therefore the inversion of (64) gives

$$E_M^L(\vec{q}_{||},\vec{k}_z) = \int_{-k_c}^{k_c} dk_z' \{ \delta(k_z - k_z') - 4\pi [\tilde{\alpha}^{LL}(\vec{q}_{||},k_z,k_z')]_{\vec{0},\vec{0}} \} \times [E^{\text{ex},L}(\vec{q}_{||} k_z')]_{\vec{0}} , \tag{65}$$

which completely describes the macroscopic field.

Static screening and the energy loss of slow particles can be studied using this result.

VI. SOME PROPERTIES OF THE MACROSCOPIC DIELECTRIC TENSOR OF SEMI-INFINITE CRYSTALS

The optical properties of crystal surfaces are found solving the light-propagation equations, i.e., Eq. (43), for the macroscopic electric field. Such equations are similar to those studied by a number of authors[32–39] in the case of jellium or crystal[35] surfaces, who did not consider local-field effects. The difference is that the macroscopic field and the macroscopic dielectric tensor are here concerned, rather than the microscopic ones. We would like to use the method of solution, first formulated by Bagchi and Rajagopal,[34] which is founded on the short-range character of the surface perturbation. More precisely, it is assumed in Refs. 32–39 that the dielectric tensor is different from its bulk value only in a depth d near the surface, much smaller than the light wavelength in the crystal.

We are going to show that this is indeed the case of the macroscopic dielectric tensor $\overleftrightarrow{\epsilon}_M(\vec{q}_{||},z,z')$ here defined. We will show in Appendix B that, as soon as z is larger than a few times k_c^{-1}, the macroscopic electric displacement has the same relation with the macroscopic electric field as in the infinite crystal:

$$\vec{D}_M(\vec{q}_{||},z) \underset{z \gg k_c^{-1}}{\longrightarrow} \overleftrightarrow{\epsilon}_M(\omega) \cdot \vec{E}_M(\vec{q}_{||},z) , \tag{66}$$

where $\overleftrightarrow{\epsilon}_M(\omega)$ is the macroscopic dielectric tensor defined in Sec. III for an infinite crystal in the $q \to 0$ limit. Since k_c is much bigger than ω/c, the surface perturbation depth $\sim k_c^{-1}$ is much smaller than the light wavelength, and the method of Ref. 35, which takes into account a nondiagonal dielectric tensor at the surface, can be applied to find the reflectivity.

The solution of light-propagation equation (43) in the long-wavelength limit has been given in Ref. 35 by generalizing the method of Bagchi and Rajagopal[34] to the case where the dielectric tensor is nondiagonal, as generally occurs at surfaces of real crystals. An important point of the calculation is the symmetry of the dielectric tensor for the interchange of indices:

$$\epsilon_{\alpha\beta}(z,z') = \epsilon_{\beta\alpha}(z',z) , \tag{67}$$

which is a consequence of time-reversal invariance for the RPA microscopic dielectric tensor involved in Ref. 35.

Is this property valid also for the macroscopic dielectric tensor defined in this paper? In the following we show that the answer is yes.

The property (67) is verified by the quasipolarizability tensor, since this a response function, just as the RPA microscopic dielectric tensor. Therefore, we have, using Fourier transforms,

$$[\tilde{\alpha}_{\alpha\beta}(\vec{q}_{||},k_z,k_z')]_{\vec{0},\vec{0}} = [\tilde{\alpha}_{\beta\alpha}(-\vec{q}_{||},-k_z',-k_z)]_{\vec{0},\vec{0}} . \tag{68}$$

The same is true for the operator $O_p(\vec{q}_{||},k_z,k_z')$, from its definition and (68), and also for $O_p^{-1}(\vec{q}_{||},k_z,k_z')$.

We can now use the definition of the macroscopic polarizability to show quite simply that it verifies the property (68). The final result is

$$\epsilon_{M\alpha\beta}(\vec{q}_{||},z,z') = \epsilon_{M\beta\alpha}(-\vec{q}_{||},z',z) , \tag{69}$$

which is equivalent to (67) in the long-wavelength limit, $\vec{q}_{||} \to \vec{0}$.

Therefore, all the mathematics of Ref. 35 can be applied also in the case of the macroscopic dielectric tensor and the reflection coefficient is given by Eqs. (14) and (17) of Ref. 35. Also ellipsometry can be computed in this way, and it is described by Eqs. (8) and (9) of Ref. 25. A more extended treatment of optical properties will be given in a subsequent paper.

VII. CONCLUDING REMARKS

In Secs. III and IV we have given a definition and a method of calculation of the macroscopic dielectric tensor of noncubic crystals, which embodies local-field as well as excitonic effects. It is a generalization of the formula of Adler and Wiser[1,2] for cubic crystals and it is much simpler than any other formulation.[12,16,23] Realistic calculations are not only possible within this formulation, but they request roughly the same computational effort as in the case of cubic crystals. The only approximation involved is the longitudinal nature of microscopic fields, namely that $\omega/c \ll G$. This condition is very well fulfilled in the optical and ultraviolet range, so that we regard our theory as essentially exact.

In Sec. V we have developed the theory of the macroscopic dielectric tensor at crystal surfaces. A common feature of infinite and semi-infinite crystals is that the long-range part of the Coulomb interaction is not involved in the macroscopic dielectric tensor. This is a generalization of AK's result[4] for cubic crystals, and of Ehara and Cho's work,[46] for an excitonic sytsem in an infinite crystal of arbitrary symmetry.

In the case of surfaces more approximations are involved. Microscopic and macroscopic fields are discriminated along z by the cutoff wave vector k_c, which must be chosen in the range $\omega/c \ll k_c \ll G$. Although this range is sufficiently large so that a safe choice of k_c seems to be possible, it is worthwhile to look in more detail at this step. The lower limit, $k_c \gg \omega/c$, is determined by the request that microscopic transverse fields vanish, according to Eq. (17). However, a stricter request comes from the long-wavelength approximation used to solve light-propagation equations. The surface-perturbed region has a depth of about π/k_c, as shown in Sec. VI. The validity of the long-wavelength approximation requires[31]

$$\frac{\pi}{k_c}\frac{\omega}{c}(\epsilon_M^{(B)})^{1/2} \ll 1 , \tag{70}$$

where $\epsilon_M^{(B)}$ is the bulk dielectric constant (we consider here the case of cubic crystals). Taking $\hbar\omega \simeq 1$ eV and $\epsilon_M^{(B)} \simeq 10$, this leads to $k_c^{-1} \ll 137$ Å.

The upper limit, $k_c \ll G$, comes essentially from the dipole expansion used to calculate the form factor $A_s(\vec{q}_{||},k_z)$ in the nonanalytic long-range part of the Coulomb interaction, Eq. (57). This expansion leads to the cancellation of such an interaction in the macroscopic dielectric tensor. Assuming that 1 Å is a typical radius of the overlap region between the empty and filled localized orbitals involved in the form factors, the dipole approximation results to be valid for $k_c^{-1} \gg 1$ Å. Values of k_c^{-1} in the range 10–15 Å fulfill fairly well both requirements. More freedom is allowed if $\hbar\omega < 1$ eV, so that our formulation can be safely used up to optical frequenices. At shorter wavelengths, the formulation of the macroscopic dielectric tensor is still valid, but a different method of solution of light-propagation equations, not founded on the long-wavelength approximation, should be developed.

The near surface profile of the macroscopic dielectric tensor, and therefore of the resulting macroscopic field is obviously k_c dependent. For instance, the surface perturbation depth on the macroscopic dielectric tensor is π/k_c, bigger than the intrinsic depth of perturbed charge density, which is estimated to be a few angstroms. However, the reflection coefficient does not depend on k_c, if this is chosen in the appropriate range. This will be shown in detail in a planned second paper of this series.

ACKNOWLEDGMENTS

One of the authors (R.D.S.) is deeply indebted to the Xerox Corporation for its kind hospitality at the Palo Alto Research Center, where part of this work has been done. It is a pleasure to thank Dr. Annabella Selloni and Giancarlo Strinati for critical readings of the manuscript. This work was supported in part by the Ministero della Pubblica Istruzione.

APPENDIX A

Here we find the right-hand and left-hand longitudinal contractions, as well as the longitudinal-longitudinal component of the quasipolarizability tensor $\tilde{\tilde{\alpha}}(\vec{k},\vec{k}',\omega)$.

1. Left-hand longitudinal contraction

We understand the ω dependence from now on. We perform the Fourier transform of Eq. (3) and then take the longitudinal component

$$P^L(\vec{k}) = \int d^3k' \tilde{\alpha}^{L,\rightarrow}(\vec{k},\vec{k}') \cdot \vec{E}^P(\vec{k}') . \tag{A1}$$

The longitudinal polarization is related to the longitudinal induced current by Eq. (2) and therefore to the induced charge density via the continuity equation,

$$kJ^{\text{ind},L}(\vec{k}) = \omega\rho^{\text{ind}}(\vec{k}) , \tag{A2}$$

yielding the result

$$P^L(\vec{k}) = i\rho^{\text{ind}}(\vec{k})/k . \tag{A3}$$

The induced charge density is related to the perturbing field, which we describe in the vector potential gauge, through the linear-response theory. In this case (zero scalar potential) the link is the density-current response function $\chi_{\rho j_\beta}(\vec{k},\vec{k}')$:[47]

$$\rho^{\text{ind}}(\vec{k}) = \sum_\beta \int d^3k' \chi_{\rho j_\beta}(\vec{k},\vec{k}') E^p_\beta(\vec{k}')/i\omega . \tag{A4}$$

Combining Eqs. (A4) and (A3) and comparing them with (A1), we obtain

$$\tilde{\alpha}^{L,\rightarrow}(\vec{k},\vec{k}') = (\omega k)^{-1} \chi_{\rho \vec{j}}(\vec{k},\vec{k}') . \tag{A5}$$

The density-current response function is related to the two-particle Green's function in a way analogous to Eq. (6). The final result, analogous to Eq. (7), is

$$\begin{aligned}\tilde{\alpha}^{L,\rightarrow}(\vec{k},\vec{k}') = {} & (2\pi)^{-3} e^2 i (m\omega k)^{-1} \\ & \times \sum_{L_1,L_1',L_2,L_2'} \vec{J}_{L_1L_1'}(-\vec{k}') S_{L_1L_1'L_2L_2'}(\omega) \\ & \times A_{L_2'L_2}(\vec{k}) ,\end{aligned} \tag{A6}$$

where

$$A_{L_2'L_2}(\vec{k}) = \int d^3r\, \phi^*_{L_2'}(\vec{r}) e^{-i\vec{k}\cdot\vec{r}} \phi_{L_2}(\vec{r}) . \tag{A7}$$

2. Right-hand longitudinal contraction

Let us assume now that the perturbing field is purely longitudinal. In this case the polarization is given by

$$\vec{P}(\vec{k}) = \int d^3k' \tilde{\alpha}^{\leftarrow,L}(\vec{k},\vec{k}') E^{p,L}(\vec{k}') , \tag{A8}$$

and we can describe the perturbing field via a scalar potential $\varphi^p(\vec{k})$:

$$E^{p,L}(\vec{k}') = -ik'\varphi^p(\vec{k}') . \tag{A9}$$

The induced current is[47]

$$\vec{J}^{\text{ind}}(\vec{k}) = -\int d^3k' \chi_{\vec{J}\rho}(\vec{k},\vec{k}') \varphi^p(\vec{k}') , \tag{A10}$$

where $\chi_{\vec{J}\rho}(\vec{k},\vec{k}')$ is the current-density response function. Using (2) we obtain

$$p_\alpha(\vec{k}) = -i\omega^{-1}\int d^3k'\chi_{j_\alpha\rho}(\vec{k},\vec{k}')\varphi^p(\vec{k}') . \tag{A11}$$

The comparison with (A8), using (A9), gives

$$\tilde{\alpha}^{\leftarrow,L}(\vec{k},\vec{k}') = (\omega k')^{-1}\chi_{\vec{J}\rho}(\vec{k},\vec{k}') . \tag{A12}$$

By relating the current-density response function to the two-particle Green's function, we obtain

$$\tilde{\alpha}^{\leftarrow,L}(\vec{k},\vec{k}') = (2\pi)^{-3}e^2 i(m\omega k')^{-1} \times \sum_{L_1,L_1',L_2,L_2'} A_{L_1L_1'}(-\vec{k}')S_{L_1L_1'L_2L_2'}(\omega) \times \vec{J}_{L_2'L_2}(\vec{k}) . \tag{A13}$$

3. Longitudinal-longitudinal component

We assume again that the perturbing field is purely longitudinal, related to the scalar potential $\varphi^p(k)$ through Eq. (A9). The longitudinal component of the polarization is given by

$$P^L(\vec{k}) = \int d^3k'\tilde{\alpha}^{LL}(\vec{k},\vec{k}')E^{p,L}(\vec{k}') . \tag{A14}$$

However, this is related to the induced charge density by Eq. (A3), and the latter to $\varphi^p(\vec{k}')$ via linear-response theory:[47]

$$P^{\text{ind}}(\vec{k}) = -\int d^3k'\chi_{\rho\rho}(\vec{k},\vec{k}')\varphi^p(\vec{k}') , \tag{A15}$$

where $\chi_{\rho\rho}(\vec{k},\vec{k}')$ is the time and space Fourier transform of the density-density response function. The comparison of (A14) and (A15), by using (A3) and (A9), gives

$$\tilde{\alpha}^{LL}(\vec{k},\vec{k}') = (kk')^{-1}\chi_{\rho\rho}(\vec{k},\vec{k}') . \tag{A16}$$

The final expression involving the two-particle Green's function is

$$\tilde{\alpha}^{LL}(\vec{k},\vec{k}') = -(2\pi)^{-3}e^2(kk')^{-1} \times \sum_{L_1,L_1',L_2,L_2'} A_{L_1L_1'}(-\vec{k}')S_{L_1L_2L_1'L_2'}(\omega) \times A_{L_2'L_2}(\vec{k}) . \tag{A17}$$

APPENDIX B

Here we show that, as soon as z is larger than a few times k_c^{-1}, the macroscopic dielectric tensor assumes its bulk value. The proof proceeds as follows. We take the z and z' Fourier transform of the macroscopic dielectric tensor, which results to be

$$\epsilon_M(\vec{q}_{||}\to\vec{0},z,z') = \delta_{\alpha\beta}\left[\frac{\sin[k_c(z-z')]}{\pi(z-z')} - \frac{4\pi e^2}{m\omega^2}\int_{-\infty}^{\infty} dz''\rho_0(z'')\frac{\sin[k_c(z-z'')]}{\pi(z-z'')}\,\frac{\sin[k_c(z''-z')}{\pi(z''-z')}\right] - \frac{4\pi e^2}{\hbar^2\omega^2 m^2}A^{-1}\sum_{s_1,s_2} p_{s_2}^{\alpha}p_{s_1}^{\beta *}S_{s_1s_2}^{a}(-\vec{q}_{||},\omega)\frac{\sin[k_c(z-R_{2z})]}{\pi(z-R_{2z})}\,\frac{\sin[k_c(z'-R_{1z})]}{\pi(z'-R_{1z})} , \tag{B1}$$

where $\rho_0(z)$ is the plane average of the unperturbed electron density. We look now at the behavior of the second and third terms of (B1) as z and z' penetrate into the bulk. We consider the second term, first. The relevant range of integration is restricted between $z_m-\pi/k_c$ and $z_M+\pi/k_c$, where z_m is the minimum between z and z', and z_M is the maximum. If $z_m-(\pi/k_c)$ is larger than the typical depth of d of surface perturbation on the electron density, which is of the order of a few angstroms, the electron density assumes its bulk form, given by a Fourier series of the reciprocal-(bulk-) lattice vectors $\vec{G}$, with coefficients $\rho_{\vec{G}}^{(B)}$. Because of the condition $k_c \ll G$, k_z and k_z' are contained inside the first Brillouin zone, so that only the $\vec{G}$'s with $G_z=0$ satisfy the δ-function condition $k_z=k_z'+G_z$. Then the second term of (B1) results to be

$$-\delta_{\alpha\beta}\frac{4\pi ne^2}{m\hbar^2\omega^2}\,\frac{\sin[k_c(z-z')]}{\pi(z-z')} , \tag{B2}$$

where $n=\rho_c^{(B)}$ is the average electron density.

Let us consider now the third term in (B1). As z and z' are bigger than π/k_c, only index values s_1, and s_2 with R_{1z} and R_{2z} in the bulk are relevant to the sum. The localized orbitals involved and their momentum matrix elements are bulklike, that is independent of their distance from the surface. Moreover, the matrix $S_{s_1s_2}^{a}(-\vec{q}_{||},\omega)$ converges to its bulk value, and depends on $R_{1z}'-R_{1z}$, $R_{2z}'-R_{2z}$, and on $R_{1z}-R_{2z}$. We split the index s_1 (s_2) into $\lambda_1=\mu_1\mu_1'$, $\vec{R}_1'-\vec{R}_1$ ($\lambda_2=\mu_2\mu_2'$, $\vec{R}_2'-\vec{R}_2$), and R_{1z} (R_{2z}). We also perform the q_z Fourier transform of the bulk matrix $S^{a(B)}$ as follows:

$$S_{\lambda_1\lambda_2R_{1z}R_{2z}}^{a(B)}(-\vec{q}_{||},\omega) = N_z^{-1}\sum_{q_z}\exp[i(R_{1z}-R_{2z})q_z]S_{\lambda_1\lambda_2}^{a(B)}(-\vec{q}_{||},q_z,\omega) , \tag{B3}$$

where N_z is the number of layers in the z directions. The third term of (B1) becomes

$$-\frac{4\pi e^2}{\hbar^2\omega^2 m^2}(A_0 a_z)^{-1}\sum_{\lambda_1,\lambda_2} p_{\lambda_1}^{\beta *} p_{\lambda_2}^{\alpha}\int_{-k_c}^{k_c}\frac{dq_z}{2\pi} S_{\lambda_1\lambda_2}^{\alpha(B)}(-\vec{q}_{||},-q_z,\omega)e^{iq_z(z-z')} \,. \tag{B4}$$

To derive this equation we have extended to the vacuum region, the R_{1z} and R_{2z}-sum in (B1), since these terms are unrelevant because of the rapidly vanishing factors $\sin k_c(z-R_{iz})/\pi(z-R_{iz})$ $(i=1,2)$. a_z is the z periodicity in the bulk, such that $A_0 a_2=\Omega$, a multiple of the unit-cell volume.

At this point we neglect the $\vec{q}$ dependence of $S_{\lambda_1\lambda_2}^{\alpha(B)}(-\vec{q},\omega)$ (for $|q_z|<k_c$), neglecting in this way the nonlocality of the bulk dielectric function. This is known to be important only in special cases, as near strong excitonic or plasmonic resonances, which we exclude from the beginning. We put together (B1), (B2), and (B4) and, comparing with (40), we obtain

$$\epsilon_{M\alpha\beta}(\vec{q}_{||}\rightarrow\vec{0},z,z') \underset{z\gg k_c^{-1}}{\longrightarrow} \frac{\sin[k_c(z-z')]}{\pi(z-z')}\epsilon_{M\alpha\beta}^{(B)}(\omega) \,, \tag{B5}$$

where $\epsilon_{M\alpha\beta}^{(B)}(\omega)$ is the bulk macroscopic dielectric tensor found in Sec. IV. The nonlocality is fictitious, determined by the cutoff k_c; we easily obtain for the macroscopic electric displacement $\vec{D}_M(\vec{q}_{||},z)$:

$$\vec{D}_M(\vec{q}_{||},z) \underset{z\gg k_c^{-1}}{\longrightarrow} \overleftrightarrow{\epsilon}_M^{(B)}(\omega)\cdot\int_{-\infty}^{\infty}dz'\frac{\sin[k_c(z-z')]}{\pi(z-z')}\vec{E}_M(\vec{q}_{||},z')=\overleftrightarrow{\epsilon}_M^{(B)}(\omega)\cdot\vec{E}_M(\vec{q}_{||},z) \,, \tag{B6}$$

where the last equality comes from the very definition of $\vec{E}_M(\vec{q}_{||},z)$, namely from the fact that its k_z Fourier transform is zero for $|k_z|>k_c$. We have shown in this way the validity of Eq. (66), which means that the surface perturbation on $\overleftrightarrow{\epsilon}_M(\vec{q}_{||},z,z')$ extends for a depth $\sim\pi/k_c$. Further discussion of this point and of the choice of k_c are given in Sec. VII.

---

[1] S. Adler, Phys. Rev. 126, 413 (1962).

[2] N. Wiser, Phys. Rev. 129, 62 (1963).

[3] W. Hanke and L. J. Sham, Phys. Rev. Lett. 33, 582 (1974); 43, 387 (1979).

[4] W. Hanke, Adv. Phys. 27, 287 (1978).

[5] W. Hanke and L. J. Sham, Phys. Rev. B 21, 4656 (1980).

[6] S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. Lett. 34, 155 (1975).

[7] E. G. Maksimov and I. I. Mazin, Solid State Commun. 27, 527 (1978).

[8] M. Ortuno and J. C. Inkson, J. Phys. C 12, 1065 (1979).

[9] J. M. F. Gunn and M. Ortuno, J. Phys. C 13, 1669 (1980).

[10] J. M. F. Gunn, J. Phys. C 13, 3755 (1980).

[11] R. M. Pick, M. H. Cohen, and R. M. Martin, Phys. Rev. B1, 910 (1970).

[12] R. M. Pick, Adv. Phys. 19, 269 (1970).

[13] Y. Onodera, Prog. Theor. Phys. 49, 37 (1973).

[14] S. K. Sinha, R. B. Gupta, and D. L. Price, Phys. Rev. B 9, 2564 (1974).

[15] D. L. Johnson, Phys. Rev. B 9, 4475 (1974).

[16] D. L. Johnson, Phys. Rev. B 12, 3428 (1975).

[17] C. H. Wu and W. Hanke, Solid State Commun. 23, 829 (1977).

[18] A. Baldereschi and E. Tosatti, Solid State Commun. 29, 131 (1979).

[19] R. Car and A. Selloni, Phys. Rev. Lett. 42, 1365 (1979).

[20] A. Baldereschi and E. Tosatti, Phys. Rev. B 17, 4710 (1978); R. Car, E. Tosatti, S. Baroni, and S. Leelaprute, *ibid.* B 24, 985 (1981).

[21] R. Bonneville, Phys. Rev. B 21, 368 (1980); *ibid.* 26, 513 (1982).

[22] J. E. Sipe, Can. J. Phys. 55, 2169 (1977).

[23] R. Del Sole and E. Fiorino, Solid State Commun. 38, 169 (1981).

[24] A. Bagchi, R. G. Barrera, and B. B. Dasgupta, Phys. Rev. Lett. 44, 1475 (1980); A. Bagchi, R. G. Barrera, and R. Fuchs, Phys. Rev. B 25, 7086 (1982).

[25] R. Del Sole and E. Fiorino, in Proceedings of the Fifteenth International Conference on the Semiconductors, Kyoto, 1980 [J. Phys. Soc. Jpn. 49, Suppl. A, 1133 (1980)].

[26] G. Chiarotti, S. Nannarone, R. Pastore, and P. Chiaradia, Phys. Rev. B 4, 3398 (1971).

[27] P. Chiaradia, G. Chirotti, S. Nannarone, and P. Sassaroli, Solid State Commun. 26, 813 (1978); S. Nannarone, P. Chiaradia, F. Ciccacci, R. Memeo, P. Sassaroli, S. Selci, and G. Chiarotti, *ibid.* 33, 593 (1980).

[28] F. Meyer, Phys. Rev. B 9, 3622 (1974); H. Luth, M. Buchel, R. Dorn, M. Liehr, and R. Matz, *ibid.* 15, 865 (1977).

[29] G. W. Rubloff, J. Anderson, M. A. Passler, and P. J. Stiles, Phys. Rev. Lett. 32, 667 (1974).

[30] P. E. Wierenga, A. van Silfhout, and M. J. Sparnaay, Surf. Sci. 87, 43 (1979); 99, 59 (1980).

[31] J. D. E. McIntyre and D. E. Aspnes, Surf. Sci. 24, 417 (1971).

[32] M. Nakayama, J. Phys. Soc. Jpn. 39, 265 (1974).

[33] P. J. Feibelman, Phys. Rev. B 12, 1319 (1975); 12, 4248 (1975); 14, 762 (1976).

[34] A. Bagchi and A. K. Rajagopal, Solid State Commun. 31, 127 (1979); A. Bagchi, R. G. Barrera, and A. K. Rajagopal, Phys. Rev. B 20, 4824 (1979).

[35] R. Del Sole, Solid State Commun. 37, 537 (1981).

[36] A. M. Brodsky and M. I. Urbakh, Surf. Sci. 94, 369 (1980).

[37] B. B. Dasgupta and R. Fuchs, Phys. Rev. B 23, 3710 (1981).

[38] J. E. Sipe, Phys. Rev. B 22, 1589 (1980).

[39] R. G. Barrera and A. Bagchi, Phys. Rev. B 24, 1612 (1981).

[40] P. J. Feibelman, Prog. Surf. Sci. 12, 287 (1982).

[41] M. H. Lee and A. Bagchi, Phys. Rev. B 22, 2645 (1980).

[42] R. Del Sole and D. J. Chadi, Phys. Rev. B 24, 743 (1981); D. J. Chadi and R. Del Sole, J. Vac. Sci. Technol. 21, 319 (1982).

[43] R. Kubo, J. Phys. Soc. Jpn. 12, 570 (1957).

[44] V. Ambegaokar, and W. Kohn, Phys. Rev. 117, 423 (1966).

[45] K. Cho, Solid State Commun. 33, 911 (1980).

[46] K. Ehara and K. Cho, Solid State Commun. 44, 453 (1982).

[47] H. Ehrenreich, *The Optical Properties of Solids* (Academic, New York, 1965), p. 106. Response functions are treated as scalar quantities in this reference. However, it is very easy to extend this treatment to the more general tensor case that is of interest in this paper.

[48] A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971), p. 174.

[49] A factor i is missing in Eq. (2.12) of Ref. 5.

[50] Transverse external currents are not present in the case of normal modes, where no external perturbation is present. In the case of the energy loss of slow charged particles, the external current is proportional to the speed v. Therefore, it produces in Eq. (9) an additional term proportional to $(v/c)(\omega/ck^2)$, which can be neglected since $v/c \ll 1$.

[51] M. Born and E. Wolf, *Principles of Optics* (Pergamon, London 1959).

[52] F. Bassani and G. Pastori-Parravicini, in *Electronic States and Optical Transitions in Solids,* edited by R. A. Ballinger (Pergamon, London, 1975) p. 182.

[53] L. J. Sham and T. M. Rice, Phys. Rev. 144, 807 (1966).

[54] K. Cho, Phys. Rev. B 14, 4463 (1976).

[55] P. V. Giaquinta, M. Parrinello, E. Tosatti, and M. P. Tosi, J. Phys. C 9, 2031 (1976).

[56] R. Del Sole and E. Fiorino, in Proceedings of the IVth International Conference on Solid Surfaces and Third European Conference on Surface Science [Suppl. Le Vide, Les Couches Minces, 201, 903 (1980)].

[57] V. M. Agranovich and V. L. Ginzburg, *Spatial Dispersion in Crystal Optics and the Theory of Excitons,* edited by R. E. Marshak (Interscience, New York, 1966), p. 29.

[58] The Fourier transform is here defined as an integral over all space, according to the general formulation of Sec. II. To enforce convergence, any quantity that does not tend to zero as $z \rightarrow +\infty$ is multiplied by $\exp(-\eta z)$, where η is a positive infinitesimal. However, the surface response of interest here, being localized near the surface, is not affected by such problems. It actually depends on the details of the electronic structure near the surface, which determines the dependence on z and z' (and on k_z and k_z') of the macroscopic dielectric tensor.