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Spatial Dispersion Effects in Resonant Polariton Scattering. I. Additional Boundary Conditions for Polarization Fields*

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The normal-incidence propagation of transverse modes in a medium with spatial dispersion is analyzed. A careful examination of discrepancies existing in the literature concerning the boundary conditions shows that they are due to the use of different susceptibilities. Thus they originate from a discrepancy in the solution of Schrödinger's equation and not of Maxwell's equations.

I. INTRODUCTION

In the present paper we shall propose a resolution of a long-standing controversy concerning the additional boundary conditions (ABC) appropriate for the description of the electrodynamics of a bounded spatially dispersive medium.[1-7] From the analysis we give here it is apparent that the different ABC's are intimately related to different assumptions made concerning the proper nonlocal susceptibility $\chi(\vec{r}, \vec{r}')$ governing the spatially dispersive medium. In turn, the susceptibility directly reflects assumptions made concerning the boundary conditions for excitons (the most relevant elementary excitation here) in the bounded medium. Hence, different boundary conditions for the Schrödinger equation produce different ABC's.

To illustrate the essential point, we may focus on the case of spatial dispersion resulting from the coupling of bare photons with wave vector $k_0 = \omega/c$ to a dispersive discrete bare exciton (with center-of-mass motion). In the absence of coupling, the Fourier-transformed susceptibility $\chi(\vec{k}, \omega)$ due to this single-exciton level has a simple pole [see (3.7)] at the wave number $k_e(\omega)$, for each frequency ω. Owing to the coupling, polariton modes are formed which in an infinite medium satisfy the well-known dispersion equation

$$(k_i/k_0)^2 = 1 + 4\pi\chi(k_i, k_0) \ . \quad (1.1)$$

In this case two linearly independent degenerate polaritons can propagate with wave vectors $k_1(\omega)$

and $k_2(\omega)$ for $\omega > \omega_{1s}$.

When an incident plane wave with $\omega > \omega_{1s}$ impinges normally on such a semi-infinite spatially dispersive medium, it will excite two polariton modes in the medium. Let the vacuum be located at $z < 0$, the medium at $z > 0$. Then in the left half-space there will be incident and reflected waves with amplitudes E_{in} and E_{re}, respectively. In the medium there are the two right-running waves with amplitudes E_1 and E_2. The Maxwell boundary conditions on E and B give two relations among the four quantities E_{in}, E_{re}, E_1, and E_2:

$$E_{in}+E_{re}=E_1+E_2 ,\qquad E_{in}-E_{re}=n_1E_1+n_2E_2 , \tag{1.2}$$

where $n_1\equiv k_1/k_0$ and $n_2\equiv k_2/k_0$ are the refractive indices of the two polariton waves. To determine the reflection coefficient E_{re}/E_{in} (and the other amplitude ratios) requires an ABC.

One ABC, originally given by Pekar,[1] requires that the total polarization due to the polaritons must vanish at the surface:

$$P_1+P_2=0 \tag{1.3}$$

or

$$(n_1^2-1)E_1+(n_2^2-1)E_2=0 . \tag{1.4}$$

Another type of ABC arises when the susceptibility in the semi-infinite medium is taken as

$$\chi(\vec{r},\vec{r}')=\chi(\vec{r}-\vec{r}')\,\theta(z)\,\theta(z'), \tag{1.5}$$

where $\chi(\vec{r}-\vec{r}')$ is the nonlocal susceptibility of the infinite medium. The ansatz (1.5) can be shown[6,7] to lead rigorously to an ABC:

$$E_1/(n_1-n_e)+E_2/(n_2-n_e)=0 , \tag{1.6}$$

where

$$n_e=k_e/k_0 . \tag{1.7}$$

Other forms of ABC have also been given in the literature.[4] A more general formula [Eq. (3.10)] contains the reflection coefficient of the Schrödinger wave function of the exciton. Equations (1.3) and (1.6) are then obtained as special cases.

II. SUSCEPTIBILITY OF A BOUNDED MEDIUM

For sufficiently small values of the electric field $E(\vec{r})$, the polarization field $P(\vec{r})$ of a medium depends linearly on E:

$$P(\vec{r})=\int \chi(\vec{r},\vec{r}')E(\vec{r}')d^3\vec{r}' . \tag{2.1}$$

To avoid tensorial complications, we restrict ourselves to an isotropic medium and to one of the two transverse components of the fields. We shall base our investigations on the general expression for χ (adapted to our special problem) following from linear-response theory[8]:

$$4\pi\chi(\vec{r},\vec{r}')=(4\pi\chi_0-\omega_p^2/\omega^2)\,\delta(\vec{r}-\vec{r}')\,\theta(z)\,\theta(z') + \frac{4\pi e^2}{\omega^2}\sum_\nu\left(\frac{\langle 0|j(\vec{r})|\nu\rangle\langle\nu|j(\vec{r}')|0\rangle}{\omega_{\nu 0}+(\omega+i\eta)} + \frac{\langle 0|j(\vec{r}')|\nu\rangle\langle\nu|j(\vec{r})|0\rangle}{\omega_{\nu 0}-(\omega+i\eta)}\right). \tag{2.2}$$

Here χ_0 is a spatially nondispersive "background" dielectric function and the remaining sum in (2.2) is restricted to the resonant spatially dispersive parts. In the following we shall restrict the sum to one exciton branch. The generalization to more than one branch is straightforward. ω_p^2 is supposed to contain that part of the electron density which is associated with the oscillator strengths of this one branch, i.e.,

$$\omega_p^2=\frac{4\pi e^2}{V}\sum_\nu\int d^3r\,d^3r'\,\frac{2\langle 0|j(\vec{r})|\nu\rangle\langle\nu|j(\vec{r}')|0\rangle}{\omega_{\nu 0}} . \tag{2.3}$$

V is the volume of the medium, first kept finite, to keep all quantities occurring in (2.2) and (2.3) finite. Finally one may let $V\to\infty$.

We now introduce exciton wave numbers $\vec{q}$ and "wave functions" $\phi_{\vec{q}}$ in writing

$$(8\pi e^2/\omega_q)^{1/2}\langle 0|j(\vec{r})|\vec{q}\rangle=\omega_p\,\phi_{\vec{q}}(\vec{r}) . \tag{2.4}$$

Neglecting any explicit wave-number dependence of the dipole strength in the infinite medium, one would have

$$\phi_{\vec{q}}(\vec{r})=e^{i\vec{q}\cdot\vec{r}} . \tag{2.5}$$

In (2.5) as well as in (2.6) below, we have disregarded any additional variations on an atomic scale from, for example, the periodic part of the wave function. This is allowed as long as the wavelength of the polarization waves is sufficiently large compared to the lattice spacing. The susceptibility then only depends on the difference $\vec{r}-\vec{r}'$ as it should. The simplest way of taking a boundary into account would be to "chop off" the wave functions (2.5) at the boundary as $\phi_{\vec{q}}(\vec{r})=\theta(z)e^{i\vec{q}\cdot\vec{r}}$. This ansatz would lead directly to (1.6), but would amount to complete neglect of exciton reflection at the boundary. An ansatz taking reflection into account would be

$$\phi_{\vec{q}}(\vec{r})=[e^{iq_z z}+R(q_z)\,e^{-iq_z z}]\,e^{i(q_x x+q_y y)}\,\theta(z), \tag{2.6}$$

for values of z not too close to the boundary. Since the exciton cannot leave the crystal, one must have $|R|=1$, if loss processes are neglected. For small q_z, $R(q_z)\to -1$ which corresponds to a node of the exciton wave function at the boundary (see Appendix A). Inserting (2.6) into (2.2) one finds for the susceptibility

$$\chi(\vec{r},\vec{r}')=[\chi_0\delta(\vec{r}-\vec{r}')+\chi^+(\vec{r},\vec{r}')+\chi^-(\vec{r},\vec{r}')]\,\theta(z)\,\theta(z') \tag{2.7}$$

with

$$\chi^+=\frac{\omega_p^2}{(2\pi)^3}\int d^3q\,\frac{e^{i\vec{q}\cdot(\vec{r}-\vec{r}')}}{\omega_q^2-(\omega+i\eta)^2} \tag{2.8a}$$

and

$$\chi^- = \frac{\omega_p^2}{(2\pi)^3}\int d^3q\, R(q_z) \times \frac{\exp\{i[q_x(x-x')+q_y(y-y')+q_z(z+z')]\}}{\omega_q^2-(\omega+i\eta)^2} . \quad (2.8b)$$

In writing (2.8) we have continued $R(q_z)$ to negative values of the argument using $R(-q_z)=R^*(q_z)$ and the fact that $\omega_{\vec q}=\omega_{-\vec q}$. We neglect Brillouin-zone effects and extend the $\vec q$ integration over the whole $\vec q$ space. Notice that the first term χ^+ depends only on $z-z'$ as in the infinite system. On the other hand, the second term χ^- depends only on $z+z'$. In Sec. III we show that it is this term which makes the difference in the two results for ABC mentioned in the Introduction.

III. SOLUTION OF MAXWELL'S EQUATIONS

In our case the wave equation for the electric field takes the form

$$-(\nabla^2+k_0^2)E(\vec r)=4\pi k_0^2P(\vec r) . \quad (3.1)$$

If this is combined with (2.1) one has an homogeneous integrodifferential equation for $E(\vec r)$. In order to have a unique solution one has to impose some asymptotic condition: We take only "outgoing" (right-running) waves in the half-space $z>0$, i.e., within the medium. In the left half-space there are ingoing as well as outgoing (reflected) waves. At normal incidence we expand the field in the crystal in a Fourier series

$$E(\vec r)=\sum_i E_i\, e^{ik_iz} \qquad \text{for } z>0 . \quad (3.2)$$

If this ansatz together with (2.7) is inserted into (2.1), one first has to calculate the integrals

$$\int \phi^*_{q_z}(r)\, e^{ik_iz}\, d^3r = \frac{i}{k_i-q_z+i\eta}+\frac{iR^*(q_z)}{k_i+q_z+i\eta} . \quad (3.3)$$

After inserting this into (2.1) one can do the q_z integral in the complex q_z plane. There are two kinds of poles in the integrand contributing to the final result: (i) the poles occurring in (3.3) and (ii) the poles of χ itself. The final result can therefore be written in the form

$$P(r)=\sum_i P_i\, e^{ik_iz}+P_e e^{ik_ez} \quad (3.4)$$

with

$$P_i=\chi_i E_i , \quad (3.5)$$

where $\chi_i=\chi(k_i, k_0)$ is the dielectric polarizability of the infinite medium and

$$P_e=-\sum_i r_e\left(\frac{1}{k_i-k_e}+\frac{R^*(k_e)}{k_i+k_e}\right)E_i . \quad (3.6)$$

In deriving (3.6) we have used a partial fraction decomposition

$$\chi(q, k_0)=\chi_0+r_e\left(\frac{1}{q-k_e}-\frac{1}{q+k_e}\right) \quad (3.7)$$

of the susceptibility near its poles. We have also used the fact that $R(q_z)$ is holomorphic in the upper half-plane[9] assuming that there are no bound-surface-exciton solutions of Schrödinger's equation. Both P_i and P_e diverge if one of the k_i approaches k_e, and we therefore assume that $k_i\neq k_e$. The case $k_i=k_e$ is included in (3.4) as a limiting case, since one only has to combine the P_i and P_e terms to yield a finite result in the limit $k_i\to k_e$.

If (3.2) is inserted into the left-hand side of (3.1), and (3.4) in the right-hand side, and the k_i terms are equated, one obtains

$$(k_i^2-k_0^2)E_i=4\pi k_0^2\chi_i E_i . \quad (3.8)$$

Hence either k_i satisfies the dispersion equation

$$k_i^2/k_0^2=1+4\pi\chi(k_i, k_0) \quad (3.9)$$

or else E_i must vanish. We consider this as a mild version of a "proof" of the Ewald–Oseen extinction theorem: the only waves which can propagate in the semi-infinite medium are those which fulfill the dispersion equation of the infinite medium. In particular, none of the k_i can be equal to k_e in agreement with our assumptions in the derivation of (3.4)–(3.6). Furthermore, after equating the k_e terms in (3.4) one obtains the additional boundary condition

$$P_e=-\sum_i r_e\left(\frac{1}{k_i-k_e}+\frac{R^*(k_e)}{k_i+k_e}\right)E_i=0 . \quad (3.10)$$

This is our version of the ABC. It shows directly the intimate connection between the ABC for Maxwell's equation and the boundary conditions in the solution of Schrödinger's equation.

If in Eq. (3.10), $R(k_e)$ is taken to be zero, one obtains exactly the ABC (1.6). If on the other hand $R(k_e)=-1$, one finds using (3.7)

$$(P_1-\chi_0E_1)+(P_2-\chi_0E_2)=0 , \quad (3.11)$$

which only goes over into Pekar's ABC for $\chi_0=0$. The fact that a nonvanishing background susceptibility χ_0 leads to a finite value of P_1+P_2 is particularly obvious in the limit $\omega_p\to 0$ because in that case the usual results of spatially nondispersive media must hold.

The derivation of (3.10) shows that one cannot derive ABC by just looking at (2.1) and noticing that $\chi(\vec r, \vec r')$ vanishes at the boundary, since *all* wave functions contributing to χ have nodes at $z=0$. In fact all the wave functions contributing to χ_0 may well have this property and the functions occurring in (2.2) may only be discontinuous approximations for an actual continuous drop to zero on an atomic scale. The polarization fields occurring in (3.11), however, are associated with the fields well inside the medium, and those are the only ones of interest in the solution of Maxwell's equation in determining the reflectivity. This is discussed in more detail in Appendix B.

We conclude by noting that the right-hand side of (3. 1) is finite. Thus the value and the first derivative of $E(z)$ with respect to z must be continuous at $z = 0$. These two conditions are nothing but the two Maxwell boundary conditions (1. 2) which have to be taken into account in solving (3. 1).

APPENDIX A

As discussed in Ref. 5, the center of mass of the exciton moves in a half-infinite crystal as in an infinite crystal except for a small region near the surface where the exciton experiences a strong repulsive potential $V(z)$. This region has a thickness of the order of the exciton radius. We therefore assume for the bulk region of the half-infinite crystal

$$V(z) = 0 \text{ for } z \geq 0.$$

The wave function for the center-of-mass motion in this region can be written

$$\phi_k(z) = A \sin(kz - \eta_k), \quad 0 \leq \eta_k < \pi \ . \tag{A1}$$

For $z < 0$, $\phi_k(z)$ is exponentially decaying due to the surface potential $V(z)$, and we have in particula $\lim_{z\to-\infty} \phi_k'(z) = 0$. The continuity of the logarithmic derivation of ϕ_k at $x = 0$ gives

$$\phi_k'(0)/\phi_k(0) = k \cot(kz - \eta_k) \ . \tag{A2}$$

Integration of the Schrödinger equation in the region $-\infty < z \leq 0$ yields

$$\lim_{k\to 0} \phi_k'(0) = \frac{2M}{\hbar^2} \int_{-\infty}^{0} V(z)\, \phi_0(z)\, dz \ . \tag{A3}$$

If $\lim_{k\to 0} \phi_k(0) = 0$, then $\lim_{k\to 0} \eta_k = 0$. In the other case we have from (A3)

$$\lim_{k\to 0} \frac{\phi_k'(0)}{\phi_k(0)} \neq 0$$

and in general with (A2)

$$\lim_{k\to 0} |\cot(\eta_k)| \to \infty \text{ or } \lim_{k\to 0} \eta_k = 0 \ .$$

We find therefore, in any case, that the stationary solution for the center-of-mass motion of the exciton has a node at the crystal surface in the long-wavelength limit.

APPENDIX B

To establish the connection with the theory of spatially nondispersive media, we consider the frequency regions below and above the exciton frequency ω_{1s} separately. For ω smaller than ω_{1s}, k_e and k_2 are complex even in the absence of damping. Well inside the crystal ($z \gg 0$) the wave associated with k_e does not need to be extinguished, and there is no second polariton wave. In this case the usual results of the nondispersive theory hold and the macroscopic polarization is nonzero at the surface. Microscopically, the polarization amplitude due to the exciton is still zero at the surface, but it approaches the macroscopic value very rapidly on an atomic distance. For ω larger than ω_{1s}, k_e and k_2 are real. The plane wave with k_e must then be extinguished on a macroscopic scale. This means that the macroscopic polarization due to the exciton must be zero at the surface and it leads to the ABC (3. 10).

The above argument shows that the introduction of a nondispersive "background" susceptibility χ_0 in (2. 2) is justified if we restrict ourselves to frequencies which are smaller than all the "background" oscillators. Particularly the fact that χ_0 leads to a finite value of the polarization at the surface [see Eq. (3. 11)] is not in contradiction with the fact that all wave functions contributing to χ_0 have nodes at $z = 0$.

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