Theory of polaritons in bounded spatially dispersive media

V. N. Piskovoi and E. F. Venger
Institute for Semiconductor Physics, National Academy of Science Ukraine, Kiev 03028, Ukraine

Ya. M. Strelniker
School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel
(Received 6 February 2002; published 4 September 2002)

In crystal optics with spatial dispersion there are two alternative approaches to the polariton problems starting from either mechanical excitons (ME's) or Coulomb excitons (CE's), respectively. The difference between them arises from the different treatment of that part of the polarized crystal unit interaction which is associated with the long-range curl-free proper crystal field, generated by fictitious charges of macroscopic dielectric polarization. In the case of the CE scheme the unperturbed (by electromagnetic field) energy operator contains that part, while in the case of the ME scheme it does not. This is the peculiarity that makes their dispersion laws and all other characteristics, including the boundary conditions, essentially different. Both primary conceptions are equally used in theoretical research and have their own advantages and shortcomings. The agreement between those for infinite space has been proven by a lot of investigations, but solving the same problem for finite media has not been done. Moreover, the majority of papers in the field use the same boundary conditions for excitonic polarizations in both schemes. This makes them all true only for some particular cases but, certainly, the contradictions appearing should be eliminated. The aim of this paper is the critical analysis of the existing inconsistencies and the fitting of the solutions to the boundary-value problems for polaritons formed from those two different types of exciton states. Partially we fill the arised recess by making both approaches in line with the case of the *N*-exponential Frenkel exciton model, when describing the polarization of some bounded spatially dispersive dielectrics in the excitonic spectrum region. The light reflection coefficient is taken as the main quantity to be fitted in both of the above calculation schemes. This is possible only by including several exciton transport mechanisms at once (that is, for $N \geqslant 2$) and by using the concept of Pekar's ''missing'' electromagnetic wave. With success in this particular case, we hope to induce further investigations in the area for other exitonic models and in a general enough case, such as the case for infinite media.

DOI: 10.1103/PhysRevB.66.115402 PACS number(s): 78.20.Bh, 71.35.Aa, 71.36.+c, 77.22.Ch

I. INTRODUCTION

For the simplest case of an infinite macroscopically homogeneous medium the description of the spatial dispersion reduces to a dependence of the permittivity tensor ε, not only on the frequency ω but on the vave vector $\mathbf{k}$ as well.[1] In addition to other well-known crystal optics phenomena it can raise, in principle, the order of the algebraic dispersion relation for the polariton modes $\varepsilon(\omega,k)=(ck/\omega)^2$, which determines the function $\mathbf{k}(\omega)$. In comparison with the traditional nonspatial dispersive case this gives rise to additional roots corresponding to the additional light waves (ALW's). As a result, several plane monochromatic waves can exist with the same frequency and polarization, but with different refractive indexes. Usually it is too delicate an effect to be checked in the optical spectrum, characterized by $kl \ll 1$ (l is the lattice constant). The reality of the phenomenon was shown by Pekar,[2] who analyzed the situation in the vicinity of excitonic resonance in detail. Its description required developing an extended version of light propagation through the solid.

By introducing the ALW one renounces classical birefringence theory in such a manner that the Maxwell-Fresnel boundary conditions (MFBC's) for fields at an interface between two media become insufficient to uniquely define all electromagnetic waves in bounded solids and should be supplemented by some additional boundary conditions (ABC's). This problem was solved by Pekar[2] by introducing an ABC that predicts the partial excitonic polarization $\mathbf{P}_{\mathrm{ex}}(\mathbf{r},t)$ turning to zero in crystal boundary (see Fig. 1) namely,

$$\mathbf{P}_{\mathrm{ex}}(z=0)=0 \tag{1}$$

[the ''first'' Pekar ABC [Ref. 3].

Although the ABC (1) is acknowledged and widely used by the overwhelming majority of theoreticians and experimentalists, their justification has attracted lively debate that

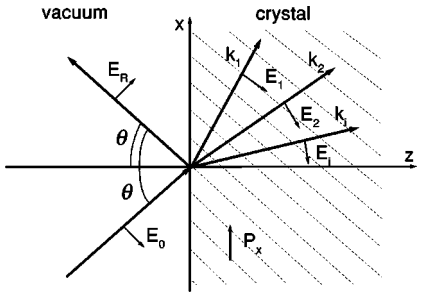

FIG. 1. The coordinate system and the directions of the *p*-polarized incident (E_0), reflected (E_R), and penetrating (E_i) electric field amplitudes. The appearance of the additional rays E_i ($i>1$) is exclusively due to spatial dispersion phenomena.

continues with each new group of investigators in the area (great attention has been paid to the problem of ABC's and their grounding in Ref. 4; the results of the first stages of those investigations are summarized in Refs. 5–8 as well). Solving the ABC problem has become more realistic because of the appearance of real possibilities to confirm their choice experimentally. This is due to the development of nonstandard optical techniques, as well as to studies of different artificial spatially dispersive solid structures (superlattices, and layered and confined systems).[9–12] The interest in the problem can also be explained by the continuous attraction of the Pekar problem as a ''guinea pig'' for critical and (or) self-critical testing and the approval of new or modified calculational methods that are periodically proposed in modern crystal optics with spatial dispersion.[13] And, last but not least, the reason behind the undiminished interest in the problem is that in spite of a vast number of works that have been published in forty five years, still much controversy remains concerning the correct form of the ABC. Just the same might be said about ALW physics and other problems of spatially dispersive media as a whole. One can find some of the most intense arguments on the subject for the last ten years in Refs. 14–19.

Thus it is clear that further studies will be essentially complicated and inconsistent without the elimination of contradictions that have accumulated over recent years. One of the controversies that has also arisen due to the presence of a boundary is connected to the problem of fitting two approaches that are well known in crystal optics with spatial dispersion alternative approaches [based on the concepts of mechanical excitons (ME's) and Coulomb excitons (CE's), respectively] to the theoretical formation of the polaritonic spectrum in finite media. It is always a danger for experimentalists that compare the experimental data to the different theories. This is why the problem is the central focus in such fundamental monographs as Refs. 4, 5, and 20. In addition to the questions relating to the basis, they contain the concrete results of well-known investigations of the problem in infinite media (the necessary summary of those researches, with some generalizations, are discussed briefly in the preamble of Sec. II). At the same time the particular solution of the problem for bounded media is underlined there, as its absence leads to essential disagreement in the computation of identical physical quantities using alternative approaches.[21] The achievement of the necessary agreement is the main objective of this paper.

A number of attempts using different models of excitons have been made in order to remove contradictions that arise when trying to solve the problem,[22] however, they all failed. Their analysis has led us to the conclusion of the impossibility for a solution with a single excitonic transport mechanism only. One needs to take into consideration several such mechanisms simultaneously (at least two—one that is common for CE's and ME's, and another that makes the distinction between them). In this paper we do that by unifying the concept of the universal enough (N)-exponential excitonic model[23] and that of Pekar's ''missing'' wave.[24] Here we confine ourselves to the theoretical aspects of the problem, leaving the prospects of practical calculations to a later publication. Nevertheless, the problem studied is not a specialized aspect of spatial dispersion theory. It concerns practically all excitonlike states irrespective of their specific model and area of application (genuine electron excitons in a variety of models: optical phonons, vibrons, plasmons, quanta of polarized oscillations, etc.). While the models share many properties, parallel exciton transport mechanisms such as resonance (annihilation) and exchange mechanisms in the case of a Wannier-Mott-Rashba exciton,[25–27] or those attached to short-range (A) and long-range (B) interactions in the case of a Frenkel-Heller-Marcus exciton,[28,29] or optical phonon (vibrational exciton),[20] etc. We would remind the reader that ME includes only exchangelike mechanisms (A) while the CE includes both the exchange (A) and resonance (B) mechanisms, which is the peculiarity that makes their dispersion laws and all other characteristics, including the boundary conditions, essentially different.

Since, certainly, the observable quantities must not depend on different starting points of the calculation, some subjective sources of the continually appearing inconsistencies in fitting them must be given. To clear up the situation let us consider the dipole-allowed F_1 exciton states in cubic crystals of O_h symmetry. For $k=0$ they are threefold degenerate in both models. But their behavior at $k\neq 0$, which is important to account for ALW spatial dispersive effects, differs essentially. For ME the degenerate states are split proportionally to $(kl)^2$ and in the general case remain nonpolarized. In the same situation for CE there arise two transverse bands and a longitudinal one split by a finite quantity $\hbar\Delta$. This is the well-known checked experimental effect of the ''longitudinal-transverse'' splitting of the polariton branches. The above-mentioned controversy arose, in fact, when some investigators tried to use the usual ABC (1) formulated initially[2] for ME's in the CE scheme. This might be because of the lack of a correct form of ABC's for the CE that is so popular and generally acknowledged as Eq. (1) is for ME's. It is known that for the particular case when the ''annihilation'' channel of the Coulomb exciton moving prevails over ''the exchange'' one, the contradiction may be removed by reformulation of the ABC (1) to the form

$$\mathbf{P}_{\mathrm{red}}(z=0)=0 \tag{2}$$

(the ''second'' Pekar ABC), where $\mathbf{P}_{\mathrm{red}}(\mathbf{r},t)$ is the reduced excitonic polarization defined in detail in Ref. 4 [see below, Eq. (B7b)]. Another particular case is in Ref. 30. But the essential restriction of those cases induces one to restrict the limits of experimental research or to resort to somewhat verisimilar but not proven postulates.[31]

The questions we hope to solve in the paper presented are as follows.

Does the ABC have the form of Eq. (1) or (2) or some other form in the case when both transport channels bring comparative contributions to its energy?

How, in this case, is the agreement of both approaches in construction of unique polaritonic states in bounded media achieved?

As was mentioned above, for all investigations on ALW physics the ABC's are the source of different difficulties and

ambiguities. So we should briefly explain our position in connection with the methods taken to solve the above problem. We confined ourselves to Pekar's original idea[2] that correct formulations of ABC's should not be a product of some phenomenological guesses but must follow uniquely from the concrete microscopic construction of the material (constitutive) Maxwell equations. This position was upheld in all his further investigations on ALW physics and convincingly grounded by comparison with other possible approaches to the problem.[4] Because of the success the entire procedure had in fitting ME and CE schemes, its fundamentals are presented in this paper in the semiclassical version of polariton theory applied to the nonlocal optics of reflection and transmission of light in the vicinity of definite, namely, Frenkel exciton polarization, described for the bounded spatially dispersive media by a universal enough and exactly soluble generalized exponential model.[23]

Another aspect of the ABC problem is connected to the well-known mathematical fact that if instead of differential equations, the equivalent integral ones are considered, then no boundary conditions (BC's) are required at all. So it is, certainly, with the ideal and material Maxwell equations that are used as often in differential (local) form as in the integral (nonlocal) one. Therefore it is not surprising that the last approach is also under intensive study and developing in crystal optics with spatial dispersion.[32–38] So in the paper we present constitutive equations based on exponential excitonic models.[23,39–41] However, this does not substitute the approach based on Maxwell-Pekar BC's, but serves rather as an addition to it, and all the above described problems remain but can be reformulated in a slightly different form. This is so because for solving the problem of reflection and transmission of waves in a local term one really needs to use some BC, in particular the MFBC added by ABC of ALW theory. Solving the same problem on the basis of a proper nonlocal treatment makes the BC approach unnecessary. However, when constructing nonlocal polarization (or an appropriate Green function) of the bounded media one needs to know the wave functions and the proper boundary conditions for Schrödinger excitons, which is connected with the same problem of choosing the above alternative approaches as starting points. Also, for every concrete realization of a solution to the polariton problem based on a nonlocal term, one usually comes to wave matching conditions that may always be compared, confronted, and even presented in a form analogous to BC's of appropriate locally formulated theory.

In this paper we start *ad hoc* from integral constitutive equations which need no BC's. However, in order to compare the obtained results with the majority of those in other papers on ALW physics (theoretical as well as experimental) performed on a local term, in Appendix B we reformulate our basic equations in an equivalent differential form with microscopically formulated ABC's. The last discussion on the ABC problem[17–19] shows that it is also very useful to ''translate'' each of the integral methods to ABC terms in order to understand which physical situation it corresponds to.

The remainder of this article is organized as follows. In Sec. II the main concepts of CE's and ME's are defined and the appropriate constitutive equations are formulated based on the two-exponential excitonic model. In Sec. III we compare and fit the boundary problem solutions obtained, respectively, in the ME and CE schemes for polariton state formation. We also give the correct form of the light reflection index for exciton resonance region in crystals of C_{6v} symmetry. Section IV provides a summary and discussion of the main results. The generalization of the Ewald's method is presented in Appendix A. In Appendix B the procedure of the local reformulation of the basic integral constitutive equations is given.

II. BASIC EQUATIONS

The general term ''exciton'' refers to any nonconducting state of a crystal that is characterized by one continuous quantum number $\mathbf{k}$ and whose energy is separated from the ground state by an energy gap.[4] This definition contains the main specificity required for understanding most of the results of special dispersion theory, and incorporates the different quasiparticles listed in the Introduction.

When the field part of the energy, transported by an exciton inside the crystal, is of the same order as the energy transported purely by the electromagnetic wave, the mixed exciton-electromagnetic waves become the real states of the system. The corresponding quasiparticles are called polaritons (light or photoexcitons) and are usually treated in the framework of the two alternative approaches, based on the concepts of mechanical and Coulomb[5] (in other terminology[4]—mechanical and Schrödinger) excitons, respectively.

The difference between ME's and CE's ensues from the different treatment of the long-range interaction between the polarized crystal units. This interaction may be described via the macroscopic part of the proper crystal field[4] (the Ewald's ''erregendes feld''[20]), i.e., by the curl-free nonretarded potential Coulomb field $\mathbf{E}'$, generated by fictitious charges of macroscopic dielectric polarization $\mathbf{P}$:

$$\nabla \times \mathbf{E}' = 0, \tag{3}$$

$$\nabla \cdot \mathbf{E}' = -4\pi \nabla \cdot \mathbf{P}. \tag{4}$$

In the case of the CE scheme the unperturbed energy operator contains this part, while in the case of the ME scheme it does not. So the basic equation from which the unique polariton states should be formed depends on the way of splitting the total crystal Hamiltonian $\hat{H}$ into an unperturbed part $\hat{H}^0$ and the part describing the crystal-field interaction $\hat{H}^{\mathrm{int}}$:

$$\hat{H} = \begin{cases} \hat{H}^0_{\mathrm{ME}} + \hat{H}^{\mathrm{int}}_{\mathrm{ME}}(\mathbf{E}) & \text{for ME,} \quad (5a) \\ \hat{H}^0_{\mathrm{CE}} + \hat{H}^{\mathrm{int}}_{\mathrm{CE}}(\mathbf{E}_{\mathrm{pr}}) & \text{for CE,} \quad (5b) \end{cases}$$

where $\mathbf{E}_{\mathrm{pr}}$ is the intensity of the smooth part of the perturbing field, connected with the intensity of the total macroscopic electric field in the media $\mathbf{E}$ by the relation

$$\mathbf{E} = \mathbf{E}_{\mathrm{pr}} + \mathbf{E}'. \tag{6}$$

As a consequence of different splittings of the Hamiltonian (5), for infinite media the dispersion law of CE's differs from that of ME's in the nonanalytic term independent of the absolute value of the wave vector but dependent on its direction **s**, where $\mathbf{s}\equiv\mathbf{k}/|\mathbf{k}|$. Thus for nondegenerate exciton bands in uniaxial crystals (which is the situation we analyze in detail in this paper) with *OX* as the optic axis (see Fig. 1) the energies of ME's and CE's have, respectively, the following form:

$$\mathcal{E}_{\mathrm{ME}}=\hbar\omega_0-\frac{\hbar^2\cos(kl)}{Ml^2}\simeq\hbar\omega_0'+\frac{\hbar^2k^2}{2M}, \tag{7}$$

$$\mathcal{E}_{\mathrm{CE}}=\hbar\omega_0-\frac{\hbar^2\cos(kl)}{Ml^2}+Rs_x^2. \tag{8}$$

Here M is the exciton effective mass, ω_0' is the frequency corresponding to the edge of the exciton absorption band. The last term in (8) represents the nonanalytical part of the CE energy. Note that in other papers the coefficient R in Eq. (8) is expressed in different but equivalent forms:

$$R=\hbar\Delta=\frac{\hbar\omega_p^2 f}{2\omega_0'}=2\pi\hbar\omega_0'\alpha_{\mathrm{st}}=\frac{4\pi d^2}{\varepsilon_0 v}, \tag{9}$$

where ω_p is the plasma frequency, f is the oscillator strength of the excitonic transition, α_{st} is the contribution of the given excitation into the static polarizability of the crystal, d is the unit cell dipole moment, v is the unit cell volume, and ε_0 is the background permittivity. The expression (7) for the excitonic dispersion law is well known from Refs. 20, 25, 26, and 28, and many other publications. The expression (8) was obtained more recently from the analysis of a long-range dipole-to-dipole interaction for each model of the exciton like states listed in the Introduction: optical phonons,[20] Frenkel excitons,[29,42] classical polarization oscillators,[43] Wannier-Mott excitons,[27] plasmons,[44] etc. In the most general form it was obtained on the basis of the polarized macroblocks approach[45] in macroscopic theory of excitons[46] by taking into account the background part of the polarizability in Ref. 47. One can also obtain those results for the exciton model of our paper by passing from inhomogeneous waves to homogeneous ones in Eqs. (38) and (55), respectively. In addition, many papers on this theme may be found among the references in Refs. 4 and 5, as well.

The ALW theory we are interested in here is based mainly on an accounting of the dependence of crystal permittivity on the wave vector via the dependence of exciton energies (7) or (8) on **k**. Thus, as a second consequence of the different splitting of the Hamiltonian (5), it appears that the partial contribution of polaritonic waves of frequency ω into the specific crystal polarization is different in different approaches.[4] For ME it is proportional to the exciton part of the polarizability tensor $\hat{\alpha}(\omega,\mathbf{k})$, which relates the macroscopic polarization vector to the total macroscopic field

$$\mathbf{P}=\hat{\alpha}\cdot\mathbf{E}. \tag{10}$$

(here and below we mark the second rank tensors in Cartesian coordinates with a hat). In this scheme the corresponding material tensor is the ordinary permittivity

$$\hat{\varepsilon}=\hat{I}+4\pi\hat{\alpha}. \tag{11}$$

whose poles are determined by Eq. (7).

For CE's a similar physical quantity is determined by the excitonic part of the tensor $\hat{\beta}(\omega,\mathbf{k})$ that relates **P** to the perturbing field and has poles determined by Eq. (8):

$$\mathbf{P}=\hat{\beta}\cdot\mathbf{E}_{\mathrm{pr}}. \tag{12}$$

Both schemes are used equally often and have their own advantages and disadvantages discussed in detail in Refs. 4 and 5. In particular, the advantage of tensor $\hat{\alpha}$ in comparison with $\hat{\beta}$ is that its poles are the states of Eq. (7) but not of Eq. (8), which correspond to the tensor $\hat{\beta}$. Thus, tensors $\hat{\alpha}$ and (or) the invert tensor $\hat{\alpha}^{-1}$, usually used for ALW calculations in the resonance region, are the analytic functions of the wave vector.[5,48] However, some crucial questions cannot be solved without using tensor $\hat{\beta}$. In particular, as is concluded in Ref. 4, ''with the polarization current being expressed through the perturbation instead of the total electric field, one can introduce the spatial dispersion in the crystal polarizability in a more simple way and involving fewer unknown parameters.'' Reference 5 also notes that ''since the excitonic levels of absorption are located in the vicinity of the Coulomb exciton frequency, the discussion of the form of the exciton absorption line is more convenient to perform using not the mechanical but the Coulomb exciton,'' i.e., Eq. (8) and tensor $\hat{\beta}$, etc. These and other features of those tensors determine the motivation for the choice of either scheme by different investigators on COSD or, even, by the same ones, for solving the concrete problem of polariton physics. This also makes the problem of their fitting especially realistic.

For the infinite crystal and the homogeneous waves, the relation between those two approaches has been clarified for specific exciton models (using, for example, the Ewald-like procedures for the separation of the proper crystal macrofield) and in more general cases (see Refs. 49 and 50–52), with the use of polarization operator constructions. All those procedures are based, in fact, on the existence of a unique causal relation between tensors $\hat{\alpha}(\omega,\mathbf{k})$ and $\hat{\beta}(\omega,\mathbf{k})$, as well as between fields $\mathbf{E}_{\mathrm{pr}}$ and **E**, accordingly, that follows from the set of Eqs. (3)–(6),(10),(12); see Ref. 51. In Sec. III it is shown that one of the points in fitting the two approaches for bounded media consists in a transition from homogeneous waves to inhomogeneous ones. For the latter case some generalization of the method of Ref. 51 leads to the following relation for infinite media:

$$\hat{\alpha}=\hat{\beta}\cdot\left[\hat{I}+\frac{4\pi\mathbf{k}\cdot\mathbf{k}\cdot\hat{\beta}}{k^2-4\pi\mathbf{k}\cdot\hat{\beta}\cdot\mathbf{k}}\right], \tag{13}$$

where $\hat{I}$ is the unit tensor and $\mathbf{k}\cdot\mathbf{k}$ is the dyad. By its derivation the vector $\mathbf{E}_{\mathrm{pr}}$ is assumed to be nonpolarized (i.e., its

curl-free and divergence-free parts are nonzero). This defines Eq. (13) uniquely, and the same is true for the representation of $\mathbf{E}_{\rm pr}$ through $\mathbf{E}$:

$$\mathbf{E}_{\rm pr}=\left(\hat{I}-\frac{4\pi}{k^2}\mathbf{k}\cdot\mathbf{k}\cdot\hat{\alpha}\right)\cdot\mathbf{E}. \tag{14}$$

From a microscopic point of view the discrimination between those types of excitons is arbitrary since it merely corresponds to different splittings of the polariton Hamiltonian and, hence, any observable quantity should not depend on it. While it is clear for polariton dispersion of the bulk, consistency problems arise for bounded media in connection with the problem of ABC's, which are necessary as soon as spatial dispersion is involved and may be, in principle, different in different approaches (see Sec. I).

For the bounded media we are interested in, the primary problem is to formulate the constitutive equations instead of the algebraic ones for the infinite case. So as not to overload the main results by the routine for crystal optics with spatial dispersion calculations we will restrict ourselves to the case of semiinfinite media (see Fig. 1, where the sample is located in the half-space $z\geqslant 0$, and the $y=0, z=0$ planes are those of light incidence and crystal surface, respectively). For further concretization of polarization and field configurations let us consider the uniaxial crystal with an isolated nondegenerate dipole-allowed exciton state in resonance (i.e., for the case $\hbar\omega \simeq \mathcal{E}_{\rm ex}$, where $\mathcal{E}_{\rm ex}$ is defined by Eqs. (7) and (8), correspondingly). Also let the polarization vector $\mathbf{P}_{\rm ex}=\{P_x,0,0\}$ be directed along the OX crystal optical axis and $\mathbf{E}$ lie in the XZ plane. This situation is realized in practice for the longitudinal excitons in crystals with C_{6v} symmetry, illuminated by a p-polarized electromagnetic wave.[4]

To construct the appropriate constitutive equations we take advantage of the generalized (M,N)-exponential excitonic model formulated first in Ref. 23. To make the situation as clear as possible we pick out the simplest yet sufficient version of that model for Frenkel exciton with $M=1$ (ignoring mixing of molecular configurations) and $N=2$ (the two exciton transport mechanisms approximation). Let $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ be the main lattice periods along x, y, and z axes and the integer vector $\mathbf{l}=l_1\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3$ describes the positions of the unit cell centers. Since we consider a semi-infinite crystal, the two indices l_1 and l_2 are changing from $-\infty$ up to ∞, but the third l_3 takes the values $1,2,3,\ldots,\infty$. The ground and perturbed states of the $\mathbf{l}$th unit cell are defined as ψ_l and ϕ_l, respectively. For the chosen crystal symmetry the state $\phi_{\mathbf{l}}$ is nondegenerate and the vector of the dipole moment has only the x component $\mathbf{d}=\{d,0,0\}$, where $d\equiv d_x=\langle\psi|\hat{d}_x|\phi\rangle\neq 0$ and $\hat{\mathbf{d}}$ is the operator of the dipole moment of the unit cell. The wave functions of the entire crystal in the ground Ψ_0 and excited $\Phi_{\mathbf{l}}$ states could be written as the products of cell wave functions

$$\Psi_0=\hat{S}\prod_{\mathbf{l}'}\psi_{\mathbf{l}'}, \tag{15}$$

$$\Phi_{\mathbf{l}}=\hat{S}\phi_{\mathbf{l}}\prod_{\mathbf{l}',\mathbf{l}'\neq\mathbf{l}}\psi_{\mathbf{l}'}, \tag{16}$$

where $\hat{S}$ is the operator of the antisymmetrization procedure and $\mathbf{l}$ is the integer lattice vector and the number of the excited cell at the same time. According to Eq. (5b), the Hamiltonian and the dipole moment of the system ''crystal + perturbing electromagnetic field'' have the form

$$\hat{H}=\hat{H}^0_{\rm CE}+\hat{H}^{\rm int}_{\rm CE}, \tag{17}$$

$$\hat{H}^{\rm int}_{\rm CE}=-\sum\hat{\mathbf{d}}_l\cdot\mathbf{E}_{\rm pr}(\mathbf{l},t), \tag{18}$$

$$\hat{\mathbf{P}}(\mathbf{r})=\sum_{\mathbf{l}}\hat{\mathbf{d}}_{\mathbf{l}}\delta(\mathbf{r}-\mathbf{l}), \tag{19}$$

where $\hat{\mathbf{P}}(\mathbf{r})$ is the operator of the specific electric polarization of the medium.

The crystal state, perturbed by the external electromagnetic field may be found in the form

$$\Psi'=\Psi^0+\sum_{\mathbf{l}}b_{\mathbf{l}}(t)\Phi_{\mathbf{l}}. \tag{20}$$

The averaging of operator (19) on the wave function (20) determines the crystal specific polarization in the form

$$P_x(\mathbf{l})=\frac{db_{\mathbf{l}}(t)}{v}, \tag{21}$$

where v is the volume of the unit cell.

In order to find the coefficients $b_{\mathbf{l}}$, we should substitute Eq. (20) into the time-dependent Schrödinger equation [with Eq. (17) as the Hamiltonian]. Taking into account only the first order terms and using the Heitler-London approximation we obtain

$$-i\hbar\frac{\partial b_{\mathbf{l}}}{\partial t}+H^0_{\mathbf{l},\mathbf{l}}b_{\mathbf{l}}+\sum_{\mathbf{l}'\neq\mathbf{l}}H^0_{\mathbf{l},\mathbf{l}'}b_{\mathbf{l}'}=\mathbf{d}\cdot\mathbf{E}_{\rm pr}(\mathbf{l},t), \tag{22}$$

where $H^0_{\mathbf{l},\mathbf{l}'}\equiv H^0_{\mathbf{l}-\mathbf{l}'}$ are the known Frenkel exciton matrix elements.

We are interested in the long enough polaritonic waves with the wave vectors satisfying the inequality $\mathbf{k}\cdot\mathbf{a}\ll 1$. In this case the interaction of the distant neutral cells can be taken in dipole approximation. Let this interaction term be denoted as $H^{(1)}_{\mathbf{l}-\mathbf{l}'}$:

$$H^{(1)}_{\mathbf{l}-\mathbf{l}'}=d^2\left[\frac{1}{|\mathbf{l}-\mathbf{l}'|^3}-3\frac{l_x^2+l_y^2}{|\mathbf{l}-\mathbf{l}'|^5}\right]. \tag{23}$$

Then ''resonance ($\mathbf{l}\neq\mathbf{l}'$) integrals'' in Eq. (22) can be represented in the form

$$H^0_{\mathbf{l}-\mathbf{l}'}=H^{(1)}_{\mathbf{l}-\mathbf{l}'}+H^{(2)}_{\mathbf{l}-\mathbf{l}'}, \tag{24}$$

where $H^{(2)}_{\mathbf{l}-\mathbf{l}'}$ contains the exchange interaction of cells as well as the corrections which are connected with the difference between the real Coulomb interaction and the dipole-

to-dipole approximation at small distances. When $|\mathbf{l}-\mathbf{l}'|$ is larger than several lattice constants, then $H^{(2)}_{\mathbf{l}-\mathbf{l}'}$ becomes negligible. Therefore this term can be represented in the exponential form

$$H^{(2)}_{\mathbf{l}-\mathbf{l}'}=g\hbar e^{-\Gamma|\mathbf{l}-\mathbf{l}'|}. \tag{25}$$

The translation symmetry along $x-$ and y-axes allows to seek the solution of Eq. (22) in the form $\mathbf{b}_\mathbf{l}=b(l_z,t)\exp(ik_x l_x)$ (as we assumed before, $k_y=0$). In this case the short-range interaction in Eq. (22) may be transformed in a manner of Ref. 14 and the dipole-to-dipole part of the cell interaction takes the form (A1) of Appendix A. Substituting Eqs. (21), (24), (25) and Eq. (A1) into Eq. (22) and eliminating the common for P_x and $E_{\rm pr}$ factor $\exp(-i\omega t+ik_x x)$ one obtains the set of equations for polarization oscillators located in the chain of crystalline slabs, which in continuous approximation takes the form of a (1,2)-exponential excitonic model equation in the classification of Ref. 23:

$$\begin{aligned}(\omega_0-\omega)&P_{\mathrm{CE},x}(z)\\ &-G_A\frac{\omega_0}{c}\int_a^\infty \exp\left[-\Gamma_A\frac{\omega\_0}{c}|z-z'|\right]P_{\mathrm{CE},x}(z')dz'\\ &-G_B\frac{\omega_0}{c}\int_a^\infty \exp\left[-\Gamma_B\frac{\omega_0}{c}|z-z'|\right]P_{\mathrm{CE},x}(z')dz'\\ &=FE_{\mathrm{pr},x}(z),\end{aligned} \tag{26}$$

where $\omega_0\equiv H_{1,1}/\hbar$ is the resonance frequency of the excitonic transition and $F=\varepsilon_0 R/4\pi\hbar$ is the coupling constant of the field-crystal interaction connected, directly, with the parameter R (9) that determines the interaction of the dipoles. The parameter a in Eq. (26) takes two values, $-\infty$ and 0, for nonbounded and semi-infinite crystals, respectively; G_i and Γ_i are the coefficients of the intensity and the spatial damping rate, respectively, corresponding to the ith oscillators interaction mechanism. These model coefficients may be expressed through the real crystal parameters for all kinds of excitons. In the case of the Frenkel exciton they correspond to the above parameters of the short-(A) and long-(B) range cell interactions, while in the case of the Wannier-Mott excitons—to the exchange and annihilation transport mechanisms,[27] etc. In particular, if $\Gamma_A\gg 1$ then it may be connected with the excitonic effective mass

$$M=\frac{\hbar\Gamma_A^3}{4G_A}\left(\frac{\omega_0}{c}\right)^2. \tag{27}$$

In this case the exponential excitonic transport channel transforms into the nearest-neighbor (NN) one with the excitonic energy given by Eq. (7), see Ref. 23. In accordance with Eq. (A1) we take for the B channel the parameters that conform the dipole-to-dipole interaction of the polarization oscillators

$$\Gamma_B=n_x,\quad G_B=-2\pi F n_x. \tag{28}$$

In Eq. (26) both A- and B-types of interactions are present, hence it describes the case of CE's. Therefore, in the field-crystal interaction namely, the field $E_{\rm pr}$ arises.

To pass from the CE scheme to the ME one, we use the results in Appendix A, where the macrofield, $\mathbf{E}'$ for a semi-infinite macropolarized crystal is given. By realizing this and using the relation (6) we come to the following constitutive equation:

$$\begin{aligned}(\omega_0-\omega)&P_{\mathrm{ME},x}(z)-G_A\frac{\omega_0}{c}\int_a^\infty\\ &\times\exp\left(-\Gamma_A\frac{\omega_0}{c}|z-z'|\right)P_{\mathrm{ME},x}(z')dz'=FE_x(z).\end{aligned} \tag{29}$$

This equation corresponds to the usual and well-known spatial dispersion (1,1)-exp model, in the terminology of Ref. 23.

Both constitutive equations—(26) and (29)—are integral ones and do not need any boundary conditions. But to compare the results of this paper with those based on local constitutive equations we reformulate them in Appendix B to differential ones together with ABC.

III. FITTING OF THE BOUNDARY PROBLEMS FOR THE POLARITONS FORMED ON THE BASE OF THE MECHANICAL AND COULOMB EXCITONS

For semi-infinite media the light reflection coefficient r is one of the experimentally verified optical characteristics, the theoretical treatment of which is based on the solution of the set of self-consistent field-polarization equations. In this paper we take it as the main quantity to be fitted in both of the above calculation schemes. If those equations allow one to stay in the framework of the plane-wave approximation, then, as is well known, r may be expressed via the refraction indexes. For the excitonic models chosen above such a possibility is proved below and forms the basement of the appropriate extinction theorem. In such a case, as well as in classical birefringence optics, the ideal Maxwell equations are reduced to

$$\mathbf{E}+4\pi\mathbf{P}=(n^2\hat{I}-\mathbf{n}\cdot\mathbf{n})\cdot\mathbf{E}, \tag{30}$$

plus the usual MFBC. Here it is assumed that

$$\{\mathbf{E},\mathbf{P}\}\sim\exp\left(i\frac{\omega}{c}\mathbf{n}\cdot\mathbf{r}-\omega t\right), \tag{31}$$

where $\mathbf{n}=c\mathbf{k}/\omega$ is the refraction vector (RV) governed by the Fresnel dispersion relation and by the crystal boundary as well.

In accordance with Sec. II we use exponential excitonic models as constitutive ones, according to which the polarization oscillators are placed at the lattice sites, where they interact locally with the electromagnetic field and with each other through the exponentially decaying interactions. If we represent the fields and polarization in the form

$$P_x(\mathbf{r},t)=P_x(z)\exp\left(i\frac{\omega}{c}n_x x-i\omega t\right), \tag{32}$$

$$E_{\mathrm{pr},x}(\mathbf{r},t)=E_{\mathrm{pr},x}(z)\exp\left(i\frac{\omega}{c}n_x x-i\omega t\right), \tag{33}$$

where $n_x=\sin\theta$ is the same for all waves x-RV component, determined by the Snell law, and θ is the light incidence angle, then the equation for the x component of the macroscopic polarization $P_x(z)$ can be written in the form (29) for ME's and (26) for CE's, respectively.

Below we present the corresponding evaluations of the main optical characteristics separately for ME's (Sec. III A) and for CE's (Sec. III B). Then we compare and fit them in Sec. III C.

A. ME scheme

As was just said, the material equation corresponding to the ME scheme has the form of Eq. (29). The basic references on its treatment are contained in Ref. 23, so we do it here in a brief form. It is a nonhomogeneous Fredholm equation with a Hermitian and quasi-degenerate kernel. In general, it does not require any additional conditions (AC's), except the finiteness of the electric field and polarization. The necessity of some AC's arises from the specific methods used for its solution, chosen (according to conventional considerations of the light propagating through the vacuum-crystal interfaces) in the form of the finite superposition of the partial excitonic polarizations $\mathbf{P}_{\mathrm{ex}}^{(j)}(\mathbf{r},t)$ and fields $\mathbf{E}^{(j)}(\mathbf{r},t)$, related to the jth light wave, namely,

$$\mathbf{P}_{\mathrm{ex}}(\mathbf{r},t)=\sum_{j=1}^{J}\mathbf{P}_{\mathrm{ex}}^{(j)}(\mathbf{r},t), \tag{34}$$

$$\mathbf{E}(\mathbf{r},t)=\sum_{j=1}^{J}\mathbf{E}^{(j)}(\mathbf{r},t), \tag{35}$$

where the sums go over an unspecified (for the moment) number of transmitted modes.

There are a lot of mathematical methods for treating the integral equations, but the simplest and more convenient for comparison with the other ways is to do it directly by seeking the solution in the form (31)–(35) and equating expressions corresponding to the same z-dependent phase factors in its left and right sides. So we have

$$P_{\mathrm{ME},x}=\alpha_{e,xx}(\omega,\mathbf{n})E_x, \tag{36}$$

$$\alpha_{e,xx}=\frac{F}{\omega_{\mathrm{ME}}(\mathbf{n})-\omega}, \tag{37}$$

$$\omega_{\mathrm{ME}}(\mathbf{n})=\omega_0'+2\frac{G_A}{\Gamma_A}\frac{n_z^2}{\Gamma_A^2+n_z^2}, \tag{38}$$

$$\omega_0'\equiv\omega_0-2\frac{G_A}{\Gamma_A}, \tag{39}$$

where ω_{ME} can be associated with the energy of the mechanical exciton $\mathcal{E}_{\mathrm{ME}}\equiv\hbar\omega_{\mathrm{ME}}$, and where the AC's on the partial polarization takes the form

$$\sum_{j=1}^{J}\frac{P_{\mathrm{ME},x}^{(j)}}{\Gamma_A+in_{zj}}=0 \tag{40}$$

[compare it with the appropriate ABC (B3), arising in the corresponding approach to the problem based on a differential constitutive equation]. In Eq. (40) the total number J of the waves and the corresponding values of the z-RV component n_{zj} are determined by the dispersion equation

$$\det||n^2\hat{I}-\mathbf{n}\cdot\mathbf{n}-\hat{\varepsilon}||=0, \tag{41}$$

following from the substitution (10),(36) into (30). Tensor $\hat{\varepsilon}$ is determined by Eq. (11), where

$$\hat{\alpha}=\begin{array}{c} \\ x \\ y \\ z \end{array}\begin{array}{c} \begin{array}{ccc} x & y & z \end{array} \\ \begin{pmatrix} \alpha_{0\parallel}+\alpha_{e,xx} & 0 & 0 \\ 0 & \alpha_{0\perp} & 0 \\ 0 & 0 & \alpha_{0\perp} \end{pmatrix} \end{array}. \tag{42}$$

Here $\hat{\alpha}_0$ is the background part of polarizability, so that $\hat{\varepsilon}_0=\hat{I}+4\pi\hat{\alpha}_0$ is the appropriate tensor of the background permittivity.

For the p-polarized waves Eq. (41) gives $J=2$ different RV's (in contrary to usual birefringence theory with $J=1$):

$$n_{z(1,2)}^2=\frac{1}{2(1-\mu/\Gamma_A^2)}\left\{\mu+\bar{\varepsilon}_0\left(1+\frac{b-\mu}{\Gamma_A^2}\right)\pm\sqrt{\left[\mu+\bar{\varepsilon}_0\left(1+\frac{b-\mu}{\Gamma_A^2}\right)\right]^2+4\bar{\varepsilon}_0(b-\mu)\left(1-\frac{\mu}{\Gamma_A^2}\right)}\right\}, \tag{43}$$

where

$$\mu=\frac{\omega-\omega_0'}{\omega_0'}\cdot\frac{2Mc^2}{\hbar\omega_0}, \tag{44}$$

$$b=\Delta\left(\frac{2Mc^2}{\hbar\omega_0^2}\right), \tag{45}$$

$$\bar{\varepsilon}_0=\varepsilon_{0\parallel}\left(1-\frac{\sin^2\theta}{\varepsilon_{0\perp}}\right). \tag{46}$$

We also have one AC similar to Eq. (40) which relates the electrical field of the main (normal) light wave to the additional (anomalous) one. Along with the MFBC it allows one to evaluate the reflection coefficient in the ME scheme in the usual way for ALW-theory:[4]

$$r_{\mathrm{ME}}=\left|\frac{E_R}{E_0}\right|^2=\left|\frac{n_0-n_p}{n_0+n_p}\right|^2, \tag{47}$$

$$n_0=\frac{1}{\cos\theta}\left(1-\frac{\sin^2\theta}{\varepsilon_{0\perp}}\right), \tag{48}$$

$$n_p=\frac{n_{z1}n_{z2}+\overline{\varepsilon_0}+i(\overline{\varepsilon_0}/\Gamma_A)(n_{z1}+n_{z2})}{n_{z1}+n_{z2}+i(1/\Gamma_A)(n_{z1}n_{z2}+\overline{\varepsilon_0})} \tag{49}$$

[these formulas correspond to Eqs. (3.28)–(3.29) of Ref. 23]. Here E_0 and E_R denote the amplitudes of the electric field in the incident and reflected waves, respectively, n_0 is the same as in usual birefringence theory (in a spectral region of an isolated nondegenerate and nonspatially dispersive excitonic resonance), n_p is an effective refraction index[53] for a given configuration. As we mentioned above, in the case when $\Gamma_A\gg 1$, the exponential model transforms into a NN one and the relations (38) and (40) reduce to the usual forms for the excitonic energy (7) [with the effective mass (27)] and of Pekar's ABC (1), namely,

$$P_{\mathrm{ME},x}(z=0)=\sum_{j=1}^{2}P^{(j)}_{\mathrm{ME},x}(z=0)=0. \tag{50}$$

B. CE scheme

As follows from Sec. II in this scheme P_{CE} is governed by Eq. (26) with Γ_B, G_B determined by Eq. (28) and $\hat{\beta}_0=0$ in Eq. (10) (as mixing of the molecular configurations is ignored). In the manner of Sec. III A we search for a common solution of the set of the ideal equations (30) and the material equations (26) in the form (31)–(35) for each possible wave. As the perturbed field in our problem is a purely transverse one we can use a simpler correlation between $\mathbf{E}_{\mathrm{pr}}$ and $\mathbf{E}$ than is given by Eq. (14), namely,

$$\mathbf{E}_{\mathrm{pr}}=\left(\hat{I}-\frac{\mathbf{k}\cdot\mathbf{k}}{k^2}\right)\cdot\mathbf{E}. \tag{51}$$

The substitution of Eq. (51) into Eq. (12) introduces a new material tensor $\hat{\epsilon}$ instead of $\hat{\varepsilon}$ (11) (the so-called ''transverse dielectric constant,'' see Refs. 2 and 5):

$$\hat{\epsilon}=\hat{I}+4\pi\hat{\beta}\left(\hat{I}-\frac{\mathbf{k}\cdot\mathbf{k}}{k^2}\right). \tag{52}$$

(Note that in contrast to $\hat{\varepsilon}$, the latter tensor is neither symmetric nor Hermitian.) As a result we obtain the following set of equations in the CE scheme, that substitutes the set of equations (36)–(42) of the ME scheme:

$$P_{\mathrm{CE},x}=\beta_{e,xx}(\omega,\mathbf{n})E_{\mathrm{pr},x}, \tag{53}$$

$$\beta_{e,xx}=\frac{F}{\omega_{\mathrm{CE}}(\mathbf{n})-\omega}, \tag{54}$$

$$\omega_{\mathrm{CE}}(\mathbf{n})=\omega_{\mathrm{ME}}(\mathbf{n})-\frac{2G_B\Gamma_B}{\Gamma_B^2+n_z^2}, \tag{55}$$

$$\det\|n^2\hat{I}-\mathbf{n}\cdot\mathbf{n}-\hat{\epsilon}\|=0, \tag{56}$$

$$\begin{cases}\displaystyle\sum_{j=1}^{J}\frac{P^{(j)}_{\mathrm{CE},x}}{\Gamma_A+in_{zj}}=0, & \text{(57a)}\\ \displaystyle\sum_{j=1}^{J}\frac{P^{(j)}_{\mathrm{CE},x}}{\Gamma_B+in_{zj}}=0, & \text{(57b)}\end{cases}$$

where

$$\hat{\epsilon}=\begin{array}{c} \\ x\\ y\\ z\end{array}\begin{array}{c}\begin{array}{ccc}x & y & z\end{array}\\ \begin{pmatrix}1+4\pi\beta_{e,xx}\dfrac{n_z^2}{n_x^2+n_z^2} & 0 & -4\pi\beta_{e,xx}\dfrac{n_xn_z}{n_x^2+n_z^2}\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}\end{array}. \tag{58}$$

[It would be recalled that accordingly with Sec. III A the usual Pekar's ABC (B4) should be used instead of Eq. (57a) if $\Gamma_A\gg 1$]. The value (55) may be interpreted as the energy of the Coulomb exciton $\mathcal{E}_{\mathrm{CE}}=\hbar\omega_{\mathrm{CE}}$ [see Eqs. (8) with (55) written for homogeneous waves]. The simultaneous presence of two AC's in the CE scheme agrees with the possibility to reduce the integral (26) to a fourth-order differential equation (B5) and two ABC's (B7) in addition. The total number J of the possible waves and the corresponding values n_{zj} are determined from the solution of the dispersion equation (56) which can be written in the form

$$n^4+n^2(1-\mathrm{Tr}\hat{\epsilon})+\det\hat{\epsilon}=0. \tag{59}$$

Substituting Eq. (58) into Eq. (59) we obtain for the p-polarized waves the following bicubic equation

$$n^2=1+\frac{4\pi n_z^2}{n^2}\beta_{e,xx}, \tag{60}$$

the solution of which gives three different values of n_z^2. Similar to the case of ME's (Sec. III A) we calculate the reflection coefficient r_{CE} for the case of CE's using the usual MFBC and AC (57). Omitting the details of rather clumsy evaluations we give the final result

$$r_{\mathrm{CE}}=\left|\frac{E_R}{E_0}\right|^2=\left|\frac{\cos\theta-n_p'}{\cos\theta+n_p'}\right|^2, \tag{61}$$

where the effective index of refraction n_p' is determined by the combination of three RV's, which correspond to three roots of Eq. (60) with positive projection of their real parts on the z axis of Fig. 1:

$$n_p' = \frac{\prod_{j=1}^{3} n_{zj} + \cos^2\theta \sum_{j=1}^{3} n_{zj}}{\sum_{i>j}^{3} n_{zi} n_{zj} + \cos^2\theta}. \tag{62}$$

[Compare Eqs. (61),(62) with Eqs. (3.28),(3.33)–(3.35) of Ref. 23 for the parameters taken here].

Thus we see that the process of light reflection from the same sample can be described in different ways [see Eqs. (47) and (61)] with different numbers of transmitting waves [see Eqs. (49) and (62)]. In Ref. 22 only the CE scheme for treating the boundary problem for a Frenkel exciton in a semi-infinite crystal was used. For the homogeneous waves used there it was possible to perform only in two extreme cases, which lead to ABC's of *A* type (1) [see Eq. (B4)] and essentially different ABC's of *B* type (2) [see Eq. (B7b)], respectively. The first one corresponds to the case where the second term in Eq. (8) is much larger than the third one ($\hbar^2/Ml^2 \gg R$, i.e., the exciton energy band width is larger than its longitudinal-transverse splitting), and the second one appears in the opposite case.[30] In the general case, as follows from Ref. 22, the conditions (*A*) and (*B*) proved to be mutually excluding. This constitutes the main point of the ALW contradiction referred to in the Introduction.

C. Fitting the results

The detailed analyses of previous papers on this theme showed that fitting of the two solutions, discussed above for the bounded media, has not been performed up to now (except some particular cases marked above) for the following reasons.

(1) In the case of homogeneous waves, considered in the majority of papers on ALW theory (including Ref. 22), the third term in formula (8) was assumed to be independent of **n** (i.e., of **k**). There remains a single **n**-dependent factor common for CE's [see Eq. (8)] and ME's [see Eq. (7)] and determined by the effective excitonic mass *M*. In this case, Eq. (56), as well as Eq. (41), gives a single additional wave, which cannot simultaneously satisfy two AC equations (57a) and (57b) [or ABC's (B7a) and (B7b), respectively].

(2) In the other group of papers the inhomogeneous waves are considered but only a single excitonic transport mechanism is taken into account.

In contrast to this we take into account both the above factors simultaneously in order to solve the problem (for a preliminary discussion see Refs. 4 and 31, 54–56, in addition). In our approach (based from the very beginning on the consideration of inhomogeneous waves with n_x fixed by Snell law) the second term in (55) depends on n_z. For given ω_{CE} it determines the additional branch of CE's (in comparison with ME). This, as was shown in Sec. III B, allows one to satisfy the increased number of ABC's in the CE scheme [specifically two, see Eq. (57)], instead of a single one in the ME scheme [see Eq. (40)].

However, some contradictions still remain, because during the calculations of the corresponding reflection coefficients r_{ME} (47) and r_{CE} (61) a different total number of the waves appears: two waves in the ME scheme but three waves in the CE scheme. This fact was already mentioned in Ref. 54, where Eq. (61) was expected to give the more precise result. In the present paper we show that both expressions (for r_{ME} and r_{CE}) lead to the same results in the case of a semi-infinite crystal. To do this we have to use the solutions (43) in the case of ME's and those following from Eq. (60) in the case of CE's. At the same time we should use the same approximations for the results of Secs. III A and III B, that is, to put $\overline{\varepsilon_0} = \cos^2\theta$ in Eqs. (43)–(49). Then the polarizabilities (54) and (37) satisfy the fundamental relations (13), which is the first check point on the way to agreement of both approaches to the unique polariton crystal states. In such a case the reflection coefficient r_{ME} in the ME scheme [see Eqs. (47)–(49)] can be written as

$$r_{\mathrm{ME}} = r_1 r_2, \tag{63}$$

$$r_i = \left| \frac{\cos\theta - n_{zi}}{\cos\theta + n_{zi}} \right|^2. \tag{64}$$

Similarly, for the case of the CE scheme, the reflection index r_{CE} can be represented as a product of the appropriate partial coefficients. From Eqs. (61),(62) it follows that

$$r_{\mathrm{CE}} = r_1 r_2 r_3, \tag{65}$$

where r_i has the form (64) with $n_{z,i}$ as the roots of Eq. (60). It is easy to see, that in above approximation the RV's marked as ''1'' and ''2'' in Eqs. (63) and (65) coincide and have the form of Eq. (43). At the same time for the extra root of the dispersion equation (60) [in comparison with Eq. (41)] the partial coefficient r_3 in Eq. (65) is equal to unity, so the two reflection indices r_{CE} and r_{ME} coincide on a whole. The wave, corresponding to the above extra root in the CE scheme is called a ''missing'' one in Ref. 24.[57] As has been shown above, in reflection and transmission problems this wave allows us to fit the CE and ME approaches for bounded media playing the buffer (coordinative) role.

IV. SUMMARY

Some aspects of the identity of the boundary problem solutions for the two known and widely used schemes of polariton state formation, namely, for ME and CE ones, are analyzed in the framework of ALW physics. Here we have taken the first steps to (i) based on the investigations known from infinite media postulate that to avoid blunders one should use the ME scheme and ABC's such as Pekar's and (ii) to formulate a system of adequate boundary conditions on partial excitonic polarization for theoretics and experimentalists that stay in the framework of the CE concept. It is done on the basis of the exponential excitonic model generalized for the case of the coexistence of several (say *N*) different exciton transport mechanisms. For CE's there always exists one connected with the dipole-to-dipole interaction of the physically infinitely small areas of the polarized medium. The transition from the CE to ME scheme corresponds formally [(i) position] to the substitution into the crystal-light interaction operator of the transverse component

(i.e., curl part) of the electromagnetic field for the total field with the simultaneous elimination of the mechanism above from the part of the CE unperturbed transport equation. The studies performed in this way result in the following conclusions.

(1) In the case of the unbounded media both approaches give the equal number $N-1$ of the homogeneous additional electromagnetic waves for fixed polarization.[4,5]

(2) For bounded crystals the number of additional waves should precisely coincide with the total number of ABC's and vice versa. However, since the transition from CE's to ME's is accompanied by a decrease of one of the numbers of the possible channels of exciton movement in the crystal, the number of ABC's is equal to $N-1$ for ME's and to N for CE's [compare the single Eq. (40) with the system of Eqs. (57)].

The incompatibility of the results defined in the above statements (1) and (2) is known as the ''first Pekar paradox.''[22] For the distinct case of $N=2$ the concrete description of the paradox is given by point (1) of Sec. III C. It leads to the necessity of additional (in comparison with the unbounded media) proof of the equivalence of those two approaches. It turned out to work well by the transition from homogeneous plane waves to the inhomogeneous ones. For the latter case the number of the ALW for CE's is larger by one than for ME and therefore coincides with the corresponding number of ABC's. We prove that this extra root gives the possibility to fit the CE and ME scheme in polariton theory for bounded media. Such is the objective aspects of the problem.

The subjective appreciation of the solved problem is connected with our hope that this paper will help a lot of investigators, using those different calculation schemes, giving possible ways and means for agreement of their results and-research limits.[30] Here we give (as an example) the self-consistent expression for the reflection light index in the vicinity of exciton resonance, corresponding to nondegenerate states in crystals of C_{6v} symmetry (this is a case popular enough in ALW experimental investigations[53]).

In addition we should note that in this problem the ''second Pekar paradox'' also exists'' attached to the case of $\epsilon_0 \neq 1$, see Refs. 4 and 21. It cannot be solved in the framework of the generalized N-exp model used here, but demands a detailed study in the framework of the (M,N)-exp model, introduced in Ref. 23, that takes into account M excitonic states (with $M \geqslant 2$) in addition to N possible excitonic transport canals (with $N \geqslant 2$), which is the effect of the mixing of molecular configurations. The detailed discussion of this will be published elsewhere.

ACKNOWLEDGMENTS

This research was supported in part by the Israel Science Foundation. V.N.P. would also like to thank Professor V. G. Lyapin for helpful discussions.

APPENDIX A

If one seeks the solution of Eq. (22) in the form $\mathbf{b_l} = b(l_z,t)\exp(ik_x l_x)$, then the dipole-to-dipole part of the cell interaction, given by Eq. (23), takes the form

$$\sum_{\mathbf{l}'\neq\mathbf{l}} H^{(1)}_{\mathbf{l}-\mathbf{l}'} b_{\mathbf{l}'} = d^2 \sum_{l'_z \neq l_z} b(l'_z,t) \sum_{l'_x,l'_y} \left[\frac{1}{|\mathbf{l}-\mathbf{l}'|^3} - 3\frac{l_x^2+l_y^2}{|\mathbf{l}-\mathbf{l}'|^5} \right] e^{ik_x l'_x}$$
$$= 2\pi \frac{d^2}{v} k_x a_z \sum_{l'_z \neq l_z} e^{-k_x|l_z-l'_z|} b(l'_z,t) e^{ik_x l_x}. \quad \text{(A1)}$$

In Eq. (A1) we evaluate the lattice sums (in the x,y plane) in continuous approximation using the following formulas

$$I_{n/2} \equiv \int\int \frac{e^{ik_x x} dx dy}{[x^2+y^2+(z-z')^2]^{n/2}}$$
$$= \int_0^\infty \frac{\rho d\rho}{[\rho^2+(z-z')^2]^{n/2}} \int_{-\pi}^{\pi} e^{ik_x \rho \cos\theta} d\theta$$
$$= 2\pi \int_0^\infty \frac{\rho J_0(k_x\rho) d\rho}{[\rho^2+(z-z')^2]^{n/2}}$$
$$= 2\pi \frac{k_x^{n/2-1}|z-z'|^{1-n/2}}{2^{n/2-1}\Gamma(n/2)} K_{1-n/2}(k_x|z-z'|), \quad \text{(A2)}$$

where J_0 and K_n are the Bessel and McDonald functions, respectively.[58] The exact summation of Eq. (A1) is presented in Ref. 23.

To separate the part corresponding to macroscopic field $\mathbf{E}'$ from Eq. (A1) we should use Eqs. (3),(4) for semi-infinite macropolarized media with density of space charge $\rho(\mathbf{r})$, given by relation $\rho(\mathbf{r}) = -\nabla[\Theta(z)\mathbf{P}(\mathbf{r})]$. Putting $\mathbf{E}' = -\nabla\varphi'$, for the above polarization situation we have

$$\nabla^2\varphi' = -4\pi\rho = 4\pi i k_x \Theta(z) P_x(z) e^{ik_x x}. \quad \text{(A3)}$$

The solution of Eq. (A3) gives the following form for macrofield $\mathbf{E}' = \{\mathbf{E}'_x, \mathbf{0}, \mathbf{E}'_z\}$,where E'_x is the component we are interested in, is

$$E'_x = -2\pi k_x \int_0^\infty e^{-k_x|z'-z|} P_c(z') dz'. \quad \text{(A4)}$$

APPENDIX B

For the reasons outlined in the Introduction we present here the constitutive equations of Sec. II as the appropriate differential equations with the determined set of ABC's.

1. ME scheme

In the case of only one interaction parameter G (one-exponential model) it reduces to a second-order differential equation which can be obtained by the sequenced differentiation of Eq. (29)

$$\left[\frac{\partial^2}{\partial z^2}-\left(\Gamma_A\frac{\omega_0}{c}\right)^2\right][(\omega_0-\omega)P_{\mathrm{ME},x}-FE_x]$$

$$+2G_A\Gamma_A\left(\frac{\omega_0}{c}\right)^2P_{\mathrm{ME},x}=0. \tag{B1}$$

Since the use of the differential operator increases the order of the equation, the solutions obtained by this way could be linearly dependent. Because the differential equation (B1) is valid not only for $a=-\infty$ in Eq. (29) but also for $a=0$, its solution should be fulfilled by some additional conditions. These conditions may be as follows: Eq. (29) has to be satisfied identically for the arbitrary value of the z coordinate (in particular for $z=0$), or the same should be true for its z derivatives (or their partial combinations[41]), etc. But the simplest form of ABC is formulated originally in Ref. 23, which results from setting the complement of the truncated (i.e., with $a=0$) Eq. (29) to the non-truncated one (i.e., with $a=-\infty$) to zero:

$$\int_{-\infty}^{0}\exp\left(\Gamma_A\frac{\omega_0}{c}z\right)P_{\mathrm{ME},x}(z)dz=0. \tag{B2}$$

We should underline that being nominally different in form accounts, partially, for the differences given in the Introduction. All of the above boundary conditions give, of course, the same final results for observable quantities. For the solutions of Sec. III A, Eq. (B2) takes the form of AC (40), namely,

$$\sum_{j=1}^{J}\frac{P^{(j)}_{\mathrm{ME},x}(0)}{\Gamma_A+in_{zj}}=0. \tag{B3}$$

In the case when $\Gamma_A\gg 1$ the exponential model transforms into a *NN* one and ABC (B2) reduces to the usual Pekar's ABC (1) at the boundary:

$$P_{\mathrm{ME},x}(z=0)=0. \tag{B4}$$

2. CE scheme

The constitutive Eq. (26) for CE scheme can also be reduced by sequenced differentiation and elimination of integral forms to a differential equation of fourth order:

$$\left[\frac{\partial^2}{\partial z^2}-\left(\Gamma_A\frac{\omega_0}{c}\right)^2\right]\left[\frac{\partial^2}{\partial z^2}-\left(\Gamma_B\frac{\omega_0}{c}\right)^2\right]\times\{(\omega_0-\omega)P_{\mathrm{CE},x}$$

$$-FE_{\mathrm{pr},x}\}+2G_B\Gamma_B\left(\frac{\omega_0}{c}\right)^2\left[\frac{\partial^2}{\partial z^2}-\left(\Gamma_A\frac{\omega_0}{c}\right)^2\right]P_{\mathrm{CE},x}$$

$$+2G_A\Gamma_A\left(\frac{\omega_0}{c}\right)^2\left[\frac{\partial^2}{\partial z^2}-\left(\Gamma_B\frac{\omega_0}{c}\right)^2\right]P_{\mathrm{CE},x}=0. \tag{B5}$$

Since Eq. (B5) is valid for $a=-\infty$ as well as for $a=0$ in Eq. (26) then in the last case its solution should be fulfilled under some additional conditions. For their formulation we use the results of Ref. 23 for the *N*-exp excitonic model. This leads us to the set of ABC's of Eq. (B2) type:

$$\int_{-\infty}^{0}\exp\left(\Gamma_i\frac{\omega_0}{c}z\right)P_{\mathrm{CE},x}(z)dz=0,\quad \text{for } i=A,B. \tag{B6}$$

It is easily seen that for the solutions of Sec. III B that ABC (B6) take the form of Eq. (57), namely,

$$\begin{cases}\displaystyle\sum_{j=1}^{J}\frac{P^{(j)}_{\mathrm{CE},x}(0)}{\Gamma_A+in_{zj}}=0, & \text{(B7a)}\\ \displaystyle P_{red,x}(0)=\sum_{j=1}^{J}\frac{P^{(j)}_{\mathrm{CE},x}(0)}{\Gamma_B+in_{zj}}=0, & \text{(B7b)}\end{cases}$$

where $\mathbf{P}_{\mathrm{red}}(\mathbf{r},\mathbf{t})$ with $\Gamma_B=n_x$ is the vector of reduced polarization defined in Ref. 4 and figured in Eq. (2).

[1] L. D. Landau and E. M. Lifshits, *Electrodynamics of Continuous Media*, 2nd ed. (Pergamon Press, Oxford, 1984).

[2] S.I. Pekar, Zh. Eksp. Teor. Fiz. **33**, 1022 (1957) [Sov. Phys. JETP **6**, 785 (1958)].

[3] We do not discuss the well-known generalizations of ABC (1) which take into account the surface layers of ideal crystals or surface states. ABC (1) should also be changed for nearly degenerate or accidentally degenerate excitonic states, for dipole-forbidden photo-transitions, for exponential excitonic models [see Eqs. (B3) and (B4)], etc. (Ref. 4).

[4] S. I. Pekar, *Crystal Optics and Additional Light Waves* (The Benjamin/Cummings Publishing Company, Menlo Park, California, 1983).

[5] V. M. Agranovich and V. L. Ginzburg, *Crystal Optics with Spatial Dispersion and Excitons*, 2nd ed.(Nauka, Moscow, 1979).

[6] *Excitons*, edited by E. I. Rashba and M. Sturge (North-Holland, Amsterdam, 1982).

[7] A. Stahl and J. Balslev, *Electrodynamics of Semiconductor Band Edge* (Springer, Berlin, 1987).

[8] P. Halevi, *Spatial Dispersion in Solids and Plasmas* (North-Holland, Amsterdam, 1992).

[9] N.Ba. An and G. Mahler, Phys. Rev. B **50**, 17 256 (1994).

[10] E. L. Ivchenko and C. E. Pikus, *Superlattices and other Heterostructures* (Springer-Verlag, Berlin, 1995).

[11] *Excitons in Confined Systems*, edited by R. Del Sole, A. D'andrea, and A. Lapiccirela (Springer, Berlin, 1989)

[12] *Confined Electrons and Photons: New Physics and Applications*, edited by E. Burstein and G. Weisbuch (Plenum, New York, 1995)

[13] D. N. Nelson (unpublished).

[14] B. Chen and D.F. Nelson, Phys. Rev. B **48**, 15 372 (1993).

[15] B. Chen and D.F. Nelson, Phys. Rev. B **48**, 15 365 (1993).

[16] K. Henneberger, Phys. Rev. Lett. **80**, 2889 (1998).

[17] D.F. Nelson and B. Chen, Phys. Rev. Lett. **83**, 1263 (1999).

[18] R. Zeyher, Phys. Rev. Lett. **83**, 1264 (1999).

[19] K. Henneberger, Phys. Rev. Lett. **83**, 1265 (1999).

[20] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954).

[21] S.I. Pekar, Phys. Status Solidi B **82**, 83 (1977).
[22] S.I. Pekar, Zh. Eksp. Teor. Fiz. **74**, 1458 (1978) [Sov. Phys. JETP **47**, 762 (1978)].
[23] V.N. Piskovoi and Ya.M. Strelniker, Semicond. Phys., Quantum Electron. Optoelectron. **1**, 18 (1998).
[24] S.I. Pekar and V.I. Pipa, Solid State Commun. **46**, 363 (1983).
[25] G.H. Wannier, Phys. Rev. **52**, 191 (1931).
[26] N.F. Mott, Trans. Faraday Soc. **34**, 500 (1938).
[27] E.I. Rashba, Zh. Eksp. Teor. Fiz. **36**, 1703 (1959) [Sov. Phys. JETP **9**, 1213 (1959)].
[28] Ya.I. Frenkel, Phys. Rev. **37**, 17 (1931).
[29] W.R. Heller and A. Marcus, Phys. Rev. **84**, 809 (1951).
[30] In addition to the case when the third term in Eq. (8) essentially exceeds the second one, it can be neglected in the trivial case $s_x \simeq 0$ also. For the polarization shown in Fig. 1 it corresponds to the normal light incidence. Then Eq. (8) coincides with Eq. (7) and the ABC for CE's and ME's have the same form (1). Accidentially or deliberately, most authors of theoretical investigations on ALW physics use this situation to avoid serious troubles in the solution of the problems outlined by the presented paper. Other ones use the possibility to stay in any case in the framework of the ME scheme as a postulate (Ref. 31). By happy chance this is the situation of a lot of papers on the experimental proof of ALW theory, see, however, the critical comments of Ref. 21, connected with the experimental investigations of the oblique light incidence.
[31] E. L. Ivchenko, in *Excitons*, edited by E. I. Rashba and M. Sturge (North-Holland, Amsterdam, 1982), p. 141.
[32] V.S. Mashkevich, Zh. Eksp. Teor. Fiz. **38**, 906 (1960); **40**, 1803 (1961); **42**, 133 (1962).
[33] V.I. Sugakov, Fiz. Tverd. Tela **5**, 2204 (1963) [Sov. Phys. Solid State **5**, 1959 (1964)]; **5**, 2682 (1963) [**6**, 1361 (1964)].
[34] C.W. Deutch and C.A. Mead, Phys. Rev. A **138**, 63 (1965).
[35] R. Zeyher, J.L. Birman, and W. Brening, Phys. Rev. B **6**, 4613 (1972).
[36] R. Zeyher, in *Recent Developments in CondenPhysics*, edited by J. T. Devreese (Plenum Press, New York, 1981), Vol. 1, p. 807.
[37] A.S. Davydov and A.A. Eremko, Ukr. Fiz. Zh. (Russ. Ed.) **18**, 1863 (1973).
[38] A. D'Andrea and R. Del Sole, Phys. Rev. B **32**, 2337 (1985).
[39] J.E. Sipe and J. van Kranendonk, Can. J. Phys. **53**, 2095 (1975).
[40] C.A. Mead, Phys. Rev. B **15**, 519 (1977).
[41] N.N. Akhamidiev, Zh. Eksp. Teor. Fiz. **78**, 1615 (1980) [Sov. Phys. JETP **51**, 811 (1980)].
[42] V.N. Piskovoi, Fiz. Tverd. Tela **4**, 1393 (1962) [Sov. Phys. Solid State **4**, 1025 (1962)].
[43] J.J. Hopfield and D.C. Thomas, J. Phys. Chem. Solids **12**, 276 (1960).
[44] V.L. Bonch-Bruevich, Fiz. Met. Metalloved **34**, 546 (1957) [Phys. Met. Metallogr. **4**, 133 (1957)].
[45] S.I. Pekar, Zh. Eksp. Teor. Fiz. **35**, 522 (1958) [Sov. Phys. JETP **8**, 360 (1959)].
[46] S.I. Pekar, Zh. Eksp. Teor. Fiz **38**, 1786 (1960) [Sov. Phys. JETP **11**, 1286 (1960)].
[47] V.N. Piskovoi, Fiz. Tverd. Tela **5**, 1747 (1960) [Sov. Phys. Solid State **5**, 1270 (1963)].
[48] V.N. Piskovoi, Fiz. Tverd. Tela **5**, 701 (1963) [Sov. Phys. Solid State **5**, 511 (1963)].
[49] A.A. Demidenko, S.I. Pekar, and B.E. Tshekvava, Zh. Éksp. Fiz. **76**, 1445 (1979) [Sov. Phys. JETP **49**, 735 (1979)].
[50] A. A. Abrikosov, I. E. Dzyaloshinsky, and L. P. Gor'kov, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Englewood Cliffs, NJ, 1963).
[51] V.N. Piskovoi, Fiz. Tverd. Tela **5**, 3 (1963) [Sov. Phys. Solid State **5**, 1 (1963)].
[52] V.N. Piskovoi and B.E. Tshekvava, Fiz. Tverd. Tela **7**, 1132 (1965) [Sov. Phys. Solid State **7**, 908 (1965)].
[53] J.J. Hopfield and D.G. Thomas, Phys. Rev. **132**, 563 (1963).
[54] S.I. Pekar and V.I. Pipa, Fiz. Tverd. Tela **24**, 1708 (1982) [Sov. Phys. Solid State **24**, 974 (1982)].
[55] V.N. Piskovoi, Fiz. Tverd. Tela **25**, 1201 (1983) [Sov. Phys. Solid State **25**, 688 (1983)].
[56] V.I. Pipa, Ukr. Fiz. Zh. (Russ. Ed.) **32**, 675 (1987).
[57] In addition to Ref. 24 we also assert that in general case (for the excitation of arbitrary polarization and $\varepsilon_0 \neq 1$) the dispersion equation of the CE scheme has one extra root in contrast with the ME scheme. It may be easily shown by using in Eqs. (59), (52) that the universal relation (13) and the algebraic identity $\det||(\mathbf{a}\cdot\mathbf{b})\hat{I} - \mathbf{a}\cdot\mathbf{b}|| \equiv 0$.
[58] H. Bateman and A. Erdei, *Higher Transcendental Functions* (Mc Graw-Hill, New York, 1953), Vol. 2.