Wave propagation of exciton polaritons by a wave-vector-space method

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The constitutive equation for Frenkel exciton polarization in a bounded medium is derived from both macroscopic Lagrangian theory and microscopic coherent-wave theory. The result corresponds to the Hopfield and Thomas model previously thought to apply to the Wannier exciton. We show that the Frenkel exciton must be regarded as a finite-volume object and so the change of the exciton binding energy near a surface must be included in the optics problem of transmission/reflection near its resonance (the so-called additional boundary condition or ABC problem). The combination of the exciton polarization equation and the wave equation is then solved by a new mathematical method in wave-vector space (**k** space). We show that the truly macroscopic nonlocal susceptibility must contain surface terms that previous macroscopic theories did not include. We obtain a different solution to the problem with this theory that requires no boundary conditions. By transforming to real space, we also derive the ABC needed for a macroscopic real-space approach and point out the important (but often confused) difference between macroscopic and microscopic boundary conditions.

I. INTRODUCTION

The need for an "additional boundary condition" (ABC) was first proposed by Pekar[1] in 1957 when dealing with optical transmission/reflection near an exciton resonance. The problem arises from the fact that the resonant wave-vector dispersion[2] in such a region leads to the existence of two transverse waves (for a given direction, frequency, and polarization) in the medium rather than the usual one. Use of Maxwell's boundary conditions is then insufficient to determine all of the unknown wave amplitudes. While early work was based on the introduction of extra assumptions (in the framework of macroscopic theory),[1,3–5] later work attempted to derive the needed boundary condition from either macroscopic approaches[6–9] or microscopic approaches[10–16] (also see references therein; comprehensive reviews of these works can be found in Refs. 17 and 18). In spite of a vast number of works that have been published in thirty-five years, it seems fair to say that much controversy remains concerning the correct form of the ABC.[19]

The longstanding controversy in this field results from the innate complexity of including a surface in the presence of wave-vector dispersion. The so-called dielectric or Hopfield and Thomas (HT) model[4] that is an extension of the classical resonant oscillator model can describe the linear nonlocal susceptibility originating from the translational motion of the center of mass of an exciton in the bulk medium, but not necessarily near the surface.[20–22] Hopfield and Thomas introduced the concept of an exciton-free layer or "dead layer" to describe the surface region throughout which they take the exciton polarization to be zero.[4] Therefore, there is no wave-vector dispersion included in this region. Most work, microscopic or macroscopic, follows this simple approximation to the surface layer. However, Stahl and Balslev[20–22] suggest that such a treatment may be inadequate to understand all the problem's complexities. They also demonstrate more fully that the "no escape" boundary condition alone suffices to solve for the exciton polarization and electric field from a microscopic calculation. The Stahl-Balslev coherent wave solution can, in principle, provide not only the transmission and reflection coefficients but also the link between microscopic and macroscopic solutions through the surface layer. On the other hand, the "dead layer" model breaks this link, which makes the deduction of the macroscopic boundary condition from the microscopic solution very difficult.

The full complexity of the problem can be understood as follows. For the Wannier exciton that is studied most, the phenomenology of the exciton-polariton problem is altered from a macroscopic one in an infinite medium to a mesoscopic one in a bounded medium.[22] This can be argued clearly from a symmetry analysis. The translational invariance symmetry possessed by an infinite medium allows the separation of the center-of-mass motion of the exciton from its internal motion. Therefore, the center-of-mass motion of the exciton in the bulk, which is the mechanism of the wave-vector dispersion, is independent of the internal structure of the exciton. Since the exciton-polariton wavelength is much larger than the lattice constant of the crystal, the corresponding wave-vector dispersive phenomenon is macroscopic. However, this is no longer true for a Wannier exciton in a bounded medium. The internal structure of the Wannier exciton is distorted when its position is within a few of its radii below the surface of the medium. This distorted internal structure of the Wannier exciton, whose size is comparable to the exciton-polariton wavelength, affects its center-of-mass motion and so must be considered. The nature of this combined quantal and electromagnetic interference near the surface is mesoscopic. This explains why a macro-

scopic model for the optics problem of a Wannier exciton may have limited accuracy.[21]

Like the Wannier exciton case, the internal structure of a Frenkel exciton (tightly bound, small size) enters the optics problem. Unlike the Wannier exciton case, the microscopic approach can hardly be used because the short-range interaction between the electron and hole is so complex that the calculation of the Frenkel exciton wave function is impracticable even in an infinite medium. However, the optics problem is still a macroscopic problem since the size of the Frenkel exciton, though we show that it must be considered, is much smaller than the exciton-polariton wavelength. We prove this point from a first-principles derivation of the constitutive equation of the exciton polarization based on the coherent wave theory.[20,21] Though the essential approximation of this model of the Frenkel exciton is that electron and hole must occupy the same atomic site, we show that, contrary to the general belief, the Frenkel exciton still must be treated as a finite-size object when its wave-vector dispersion is considered.

Since the optics problem of the Frenkel exciton is still macroscopic, we show that the continuum version of the constitutive equation can also be derived from an extended macroscopic Lagrangian theory that can describe inhomogeneous dielectrics (of which a bounded dielectric is a special case).[23,24] This is understandable because it makes no difference, in principle, whether a description of a long-wavelength phenomenon is based on classical lattice dynamics or quantum mechanics. The construction of the Lagrangian of a dielectric is as general as possible with only constraints on symmetry. Therefore, all the conservation laws are automatically satisfied in our theory. However, as general as it is, the classical treatment necessarily involves many unknown numerical constants that describe material properties such as effective mass, charge density, etc. On the other hand, the quantum-mechanical derivation gives more specific form and interpretation to the material parameters.

We develop a new mathematical method operating in **k** space to solve the macroscopic problem effectively and consistently.[24,25] One of the advantages of our method is that it can account for the finite-size effect of the Frenkel exciton near the surface of the medium on the long-wavelength optics problem while ignoring the detail of its internal structure. When the macroscopic **k**-space constitutive relation is derived by this method, we find it must contain surface terms which originate from both motional wave-vector dispersion and the change of exciton binding energy in the surface layer. These surface terms can be interpreted as the average values of the corresponding physical quantities in the macroscopically infinitesimal but microscopically finite surface layer. This is easily understandable because a macroscopic theory, by its nature, cannot describe physical quantities in detail on an atomic scale, especially near a surface. These surface terms are the only possible form that can be used to modify the macroscopic nonlocal constitutive relation so as to reflect the lack of translational symmetry of a bounded medium. The presence of these surface terms in our **k**-space method enables us to obtain a complete solution to the optics problem without resorting to a detailed microscopic solution in the surface layer, which is an important characteristic of this new method.

The solution in our **k**-space method arises in a quite different manner from conventional methods in optics. The dispersion relations for both medium and vacuum result from requiring the Fourier transformed electric field wave equation to be finite at the poles of the electric field in the complex **k** plane. Then the functional form of the electric field transform is determined from the knowledge of its poles. The transmission and reflection coefficients are determined by requiring the coefficients of the various powers of **k** in the transformed wave equation to vanish after the poles are eliminated. Interestingly, no boundary conditions are needed or used in our method of solution, simply because the **k**-space transform has no discontinuities. Also interesting is that the surface exciton polarization (it is an average value of the exciton polarization in the surface layer, not the microscopic surface exciton polarization) is found along with the transmission and reflection coefficients. This allows our theory to account for the surface layer effects on the long-wavelength optics. Because of the newness of the entire procedure of the **k**-space method its fundamentals are presented first in the preceding paper[26] as applied to the local optics problem of Fresnel reflection and transmission. While the method is only an alternative method there, its inherent ability to handle surface effects in a wave-vector dispersive phenomenon make it an essential choice here.

While our new method is unusual in many aspects, its physical concept is straightforward. In the optics problem we detect the optical electric field that is far away from the surface which then has the same wavelength as that in an infinite medium. That part of the electric field corresponds to the part of the Fourier transform of the electric field around the bulk exciton-polariton wave vector (in the long-wavelength region). On the other hand, short-wavelength (evanescent) parts of the electric field at the surface are not detected. Therefore, only the long-wavelength part is our main concern, which can be studied separately from the short-wavelength part in **k** space. Conceptually, our **k**-space method is very close to the method used in quantum scattering theory where only asymptotic solutions are of interest. The method there is mostly done in **k** space so that asymptotic solutions can be obtained without considering the "near field" solutions if the scattering potential is complex but short range. The difference is that our method deals with a "scattering potential" made by the medium on one side of a surface and vacuum on the other while the method there deals with a localized scattering center. Because of this difference the mathematical procedures have little similarity.

Foley and Devaney[27] previously worked in wave-vector space on the exciton-polariton problem. They began with a translationally invariant exciton susceptibility in the constitutive relation used in previous macroscopic work[6–9] and obtained the same result. Because of the translationally invariant kernel they were able to use the Weiner-Hopf technique of solution. Since we derive and use a nontranslationally invariant exciton susceptibility,

we cannot use this technique. In fact, our method has little in common with the Weiner-Hopf technique even though both are carried out in **k** space. Notably, our Fourier transformation is done in the entire space while that used by Foley and Devaney in their application of the Weiner-Hopf technique is done in the half-space occupied by the matter, which causes their formulation to contain values of electric and magnetic fields at the surface. This is the reason why the impedance boundary condition must be used in the Foley-Devaney work[27] while there is no need of any type of boundary condition in our method. There is also a conceptual difference between the Weiner-Hopf technique and ours. The Weiner-Hopf technique, just as other techniques developed in Refs. 6–9, is a mathematically rigorous method for the restricted class of (or more precisely, translationally invariant) kernels. On the other hand, our **k**-space method is developed for, and makes explicit use of, the long-wavelength approximation. The macroscopic solution produced cannot describe field variations within the surface layer but can include the layer's effect on the long-wavelength solution. Another wave-vector-space method using the factorization technique has been applied to the study of surface polaritons.[28–30] Each of these studies[28–30] uses impedance boundary conditions.

Macroscopic approaches[6–9] of the early 1970s solved the original problem posed by Pekar, that is, that Maxwell theory did not seem to provide enough boundary conditions thus requiring an ABC. These works cleverly found an additional condition, equivalent to an ABC, by either an extinction theorem type of development or conversion of the second-order differential equation to a fourth-order equation. These works, however, began by assuming a constitutive relation for the nonlocal exciton polarization that used a translationally invariant (that is, bulk) susceptibility even though the presence of a surface breaks that invariance. This limitation was realized and is called the "dielectric approximation." It was thought to be necessary to make the macroscopic problem tractable even though it was later shown to violate energy conservation.[31]

Our approach differs from these previous macroscopic treatments in several ways. While they work in real space, we work in **k** space. While they use Maxwell boundary conditions and a deduced ABC, we use no boundary conditions. While they assume a constitutive relation, we derive it. While they simply cut off the susceptibility at the body boundary, we apply a cutoff at the more fundamental level of material properties such as mass, charge, and restoring force constants, which leads to the surface terms in the susceptibility. While their susceptibility is translationally invariant, ours is not. From the form of the susceptibility that we derive, we see no way to anticipate its form. Thus we believe that starting with a constitutive assumption cannot succeed in this problem. These differences lead to an altered solution to the problem.

Another important finding from our theory is that the macroscopic HT model corresponds only to Frenkel excitons in a bounded medium. This is supported by the derivation of the constitutive equation of the Wannier exciton polarization from coherent wave theory,[20,21] which cannot be reduced to an equation comparable to the HT model. Unlike other conventional microscopic theories, it involves a complex exciton polarization function which depends on the coordinates of both the electron and hole directly. Though, this theory has not provided a solution to the three-dimensional Wannier exciton case, it clarifies conceptually the complexity of the problem and shows, in Stahl and Balslev's words, that the coupling between quantum waves in electron-hole space (internal coordinates) and electromagnetic waves in center-of-mass space must be considered without loss of coherence. Compared with the numerical solution for the one-dimensional Wannier exciton case by coherent wave theory,[21] our solution is analytical and three dimensional for the Frenkel exciton. Therefore our approach demonstrates this coherent coupling.

Though our **k**-space method uses no boundary conditions to obtain the complete solution for the optics problem, it can derive the macroscopic ABC that is needed in a real-space treatment for a Frenkel exciton case by transformation of the **k**-space equation. This transformation helps to reveal the important difference and connection between macroscopic and microscopic boundary conditions, a distinction which often appears confused in this field. From this analysis, it can be seen why using Pekar's boundary condition microscopically is quite different from using it macroscopically.

II. MACROSCOPIC DERIVATION OF THE DIELECTRIC MODEL IN A HALF-SPACE MEDIUM

A. Preliminary

Since the optics problem of transmission/reflection of a Frenkel exciton is a macroscopic problem, as mentioned earlier, we can base our theory on a general Lagrangian formulation of long-wavelength dynamics of a general dielectric crystal interacting with the electromagnetic field.[23] The Lagrangian formulation has been successful in describing all the long-wavelength modes of mechanical motion, both optic and acoustic, of a homogeneous dielectric from an entirely deductive derivation. Unlike most other macroscopic theories which start from assumptions on the dynamic equation and constitutive relations relevant to the problem, this theory starts from a Lagrangian describing the matter, the electromagnetic field, and the interaction between matter and electromagnetic field. The original Lagrangian is microscopic in nature but a long-wavelength limit is performed on the Lagrangian. The construction of the Lagrangian is as general as possible while obeying the symmetries needed to produce the conservation laws. Expansion of the Lagrangian density to the appropriate order of relevant field variables and their derivatives allows consideration of any order of nonlinearity or wave-vector dispersion. The deduced constitutive relations contain, and only contain, the allowed symmetry properties. An example is given by

a study of optical activity (the lowest-order wave-vector dispersive optical effect).[32]

In this paper we extend the Lagrangian formulation to describe an inhomogeneous dielectric crystal as preparation for handling general wave-vector dispersive phenomena in a bounded dielectric. Besides the kinetic energy the matter Lagrangian contains the stored energy describing the binding forces of the crystal which are short-range (contact) forces. The coefficients in the expansion of the stored energy can be labeled by the index of a unit cell to reflect the inhomogeneity of the dielectric crystal. In the continuum limit, these coefficients (material parameters) can be expressed as functions of position coordinates. Also the interaction between the matter and the electromagnetic field involves only the long-range macroscopic electromagnetic field and so can be expressed in a multipole expansion. The multipole moment densities are local quantities and can be expressed as functions of position coordinates. Therefore, the Lagrangian formulation can be extended to describe a general inhomogeneous medium where the material properties vary spatially. Bounded media are special inhomogeneous media where the material properties have abrupt changes near a surface, but constant elsewhere. This theory provides us a deductive basis to examine and hopefully resolve the controversy in the ABC problem at the macroscopic level.

B. Lagrangian density

The Lagrangian density consists of three parts: the matter Lagrangian, the electromagnetic field Lagrangian, and the field-matter interaction Lagrangian. For an optical phenomenon as studied here, the motion of the continuum center-of-mass coordinate is negligible and may be dropped. Therefore the deformation of the crystals can be neglected. The distinction between material and spatial position coordinates vanishes.[23] The Lagrangian density used is then the Lagrangian per unit volume in ordinary space.

The matter Lagrangian is the difference of the kinetic energy and potential or stored energy. The kinetic energy of the center-of-mass or acoustic-mode motion can be dropped. The remaining kinetic energy can be expressed in terms of internal coordinates.[23] The internal coordinates, which in combinations describe optic modes of the crystal, are denoted by $\mathbf{y}^{T\nu}=\mathbf{Y}^{\nu}+\mathbf{y}^{\nu}$, where $\mathbf{Y}^{\nu}$ are the spontaneous or constant parts that exist in the natural or unperturbed state of the crystal and $\mathbf{y}^{\nu}$ are the parts that vary in response to some external influence. A mass m^{ν} and a charge q^{ν} are associated with each $\mathbf{y}^{T\nu}$.

The stored energy is taken as the most general form consistent with the theory conserving energy, momentum, angular momentum, and parity (the last being true only to a high degree of approximation).[23] In the absence of wave-vector dispersion these arguments lead to the simple conclusion that the stored energy can be expressed as a series expansion in $\mathbf{y}^{T\nu}$. To account for wave-vector dispersion, the spatial derivatives of the internal coordinates such as $\nabla\mathbf{y}^{\nu}$ are also included in the series expansion. The terms in the stored energy series expansion linear in $\mathbf{y}^{T\nu}$ give rise to a spontaneous electric field in the internal motion equation. We assume extrinsic surface charge nullifies the spontaneous electric field (the extrinsic natural state) if the crystal is pyroelectric. For this reason, the linear term in the stored energy may be dropped. For example, in order to account for the linear optical activity,[32] only bilinear terms such as $\mathbf{y}^{T\nu}\nabla\mathbf{y}^{T\nu}$ need be retained.

The internal coordinates can describe either ionic motion or electronic motion in a dielectric. Since the electrons in the medium have much lighter effective masses than ions, the wave-vector dispersive terms are always important to these electronic internal coordinates. We introduce a coordinate $\mathbf{y}^{\mathrm{ex}}$ that describes the exciton polarization. This coordinate describes the relative motion of electron and hole coordinates. It is characterized by an effective mass m^{ex} and a charge density q^{ex}. Since we concentrate on its resonance behavior, the second-order wave-vector dispersive terms are important. Besides the bilinear term $y_k^{\mathrm{ex}}y_{i,j}^{\mathrm{ex}}$ we keep the quadratic term $y_{i,k}^{\mathrm{ex}}y_{j,l}^{\mathrm{ex}}$ and another term $y_i^{\mathrm{ex}}y_{j,kl}^{\mathrm{ex}}$ that gives the same form of bulk wave-vector dispersion in the dynamic equation of the exciton polarization in the bulk. For simplicity, we assume the coordinate for the exciton polarization is isolated, that is, the exciton polarization coordinate does not couple to other optic modes because its resonant frequency is far from their resonant frequencies. Thus the matter Lagrangian density $\mathcal{L}_M$ tailored to the model we study is

$$\mathcal{L}_M=\frac{1}{2}\sum_{\nu}m^{\nu}\dot{y}_i^{\nu}\dot{y}_i^{\nu}-\sum_{\nu\mu}\left(M_{ij}^{\nu\mu}y_i^{\nu}y_j^{\mu}+L_{ijk}^{\nu\mu}y_i^{\nu}y_{j,k}^{\mu}\right)-N_{ikjl}y_{i,k}^{\mathrm{ex}}y_{j,l}^{\mathrm{ex}}-O_{ijkl}y_i^{\mathrm{ex}}y_{j,kl}^{\mathrm{ex}},\tag{1}$$

where the summation variables μ, ν include the exciton mode. All the material parameters (m^{ν}, $M_{ij}^{\nu\mu}$, etc.) are assumed to be functions of the spatial coordinate $\mathbf{x}$ to describe the inhomogeneity of the medium.

The electromagnetic field Lagrangian density $\mathcal{L}_F$ is given by the difference of the electric- and magnetic-field energies,

$$\mathcal{L}_F=\frac{\epsilon_0}{2}\left(\mathbf{E}^2-c^2\mathbf{B}^2\right),\tag{2}$$

where the Lagrangian variables are the vector potential $\mathbf{A}$ and the scalar potential Φ given as usual by

$$\mathbf{E}=-\nabla\Phi-\partial\mathbf{A}/\partial t,\tag{3}$$

$$\mathbf{B}=\nabla\times\mathbf{A}.\tag{4}$$

The interaction Lagrangian density $\mathcal{L}_I$ is expressed in general as

$$\mathcal{L}_I=\mathbf{j}\cdot\mathbf{A}-q\Phi,\tag{5}$$

where $\mathbf{j}$ is the current density and q the charge density. Because of charge neutrality in a dielectric, only the dielectric charge and dielectric current remain. They are[23]

$$q^{D}=-\nabla\cdot\mathbf{P}+\nabla\nabla{:}\mathbf{Q},\tag{6}$$

$$\mathbf{j}=\partial\mathbf{P}/\partial t-\partial\nabla\cdot\mathbf{Q}/\partial t+\nabla\times\mathbf{M},\tag{7}$$

where

$$\mathbf{P} = \sum_{\nu} q^{\nu} \mathbf{y}^{T\nu}, \tag{8}$$

$$\mathbf{Q} = \frac{1}{2} \sum_{\mu\nu} q^{\mu\nu} \mathbf{y}^{T\mu} \mathbf{y}^{T\nu}, \tag{9}$$

$$\mathbf{M} = \frac{1}{2} \sum_{\mu\nu} q^{\mu\nu} \mathbf{y}^{T\mu} \times \mathbf{y}^{T\nu}, \tag{10}$$

are polarization, quadrupolarization, and magnetization respectively, and $\nabla\nabla \cdot \mathbf{Q}$ is an alternative notation for $\nabla \cdot (\nabla \cdot \mathbf{Q})$. By rearranging terms in the Lagrangian density and dropping perfect time derivatives and divergences (which cannot affect the equation of motion) the interaction Lagrangian density becomes

$$\mathcal{L}_I = \mathbf{P} \cdot \mathbf{E} + \mathbf{M} \cdot \mathbf{B} - \mathbf{E} \cdot (\nabla \cdot \mathbf{Q}) . \tag{11}$$

The formulation is completed by defining the total Lagrangian density $\mathcal{L}$ as

$$\mathcal{L} = \mathcal{L}_M + \mathcal{L}_F + \mathcal{L}_I \tag{12}$$

and regarding it as a function of all the internal coordinates $\mathbf{y}^{\nu}$, the vector potential $\mathbf{A}$, and the scalar potential Φ.

C. Dynamical equations

The Maxwell-Lorentz equations are readily obtainable from the Euler-Lagrange equations for Φ and $\mathbf{A}$. The derivations of these equations are presented in detail in Refs. 23 and 32. They are

$$\nabla \cdot \mathbf{D} = 0, \tag{13}$$

$$\nabla \times \mathbf{H} - \partial \mathbf{D}/\partial t = 0, \tag{14}$$

where the electric displacement $\mathbf{D}$ and magnetic intensity $\mathbf{H}$ are defined as

$$\mathbf{D} \equiv \epsilon_0 \mathbf{E} + \mathbf{P} - \nabla \cdot \mathbf{Q}, \tag{15}$$

$$\mathbf{H} \equiv (1/\mu_0) \mathbf{B} - \mathbf{M}. \tag{16}$$

The remaining two equations of the four Maxwell equations are implied by Eqs. (3) and (4). They are

$$\nabla \cdot \mathbf{B} = 0, \tag{17}$$

$$\nabla \times \mathbf{E} + \partial \mathbf{B}/\partial t = 0. \tag{18}$$

The derivation of the dynamical equations for the internal coordinates other than that for the exciton polarization is also given in Refs. 23 and 32. Since we are only interested in the wave-vector dispersion of the exciton polarization, we can drop the wave-vector dispersion terms in the dynamical equations for ordinary ionic internal coordinates, which then become

$$m^{\nu} \ddot{y}_i^{\nu} + 2 \sum_{\mu} M_{ij}^{\mu\nu} y_j^{\nu} - q^{\nu} E_i = 0, \quad \nu \neq \text{ex}. \tag{19}$$

The constitutive equation for the exciton polarization follows from the Euler-Lagrange equation for $\mathbf{y}^{\text{ex}}$,

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{y}_i^{\text{ex}}} = \frac{\partial \mathcal{L}}{\partial y_i^{\text{ex}}} - \frac{d}{dx_j} \frac{\partial \mathcal{L}}{\partial y_{i,j}^{\text{ex}}} + \frac{d^2}{dx_l dx_k} \frac{\partial \mathcal{L}}{\partial y_{i,kl}^{\text{ex}}}. \tag{20}$$

If we neglect the terms from the magnetization and quadrupolarization in Eqs. (13) and (11) for simplicity since they yield only optical activity terms that are not essential to the resonance wave-vector dispersion of excitons, we obtain

$$\begin{aligned} m^{\text{ex}} \ddot{y}_i^{\text{ex}} = {} & q^{\text{ex}} E_i - 2M_{ij}^{\text{ex}} y_j^{\text{ex}} - L_{ijk} y_{j,k}^{\text{ex}} - O_{ijkl} y_{j,kl}^{\text{ex}} \\ & + d\left(L_{jik} y_j^{\text{ex}}\right)/dx_k + d\left(2N_{ikjl} y_{j,l}^{\text{ex}}\right)/dx_k \\ & - d^2\left(O_{ijkl} y_j^{\text{ex}}\right)/dx_k dx_l, \end{aligned} \tag{21}$$

where all the material parameters are functions of spatial coordinates in a general inhomogeneous medium of which a bounded medium is a special case. It is not difficult to see that if we ignore the tensorial notation and regard all material parameters as constants, Eq. (21) has the same form as the equation of the dielectric model in the paper of Hopfield and Thomas[4] (see Sec. II of Ref. 4). Note that the last two terms containing N and O have the same form only if these material parameters are constants, rather than functions of spatial coordinates.

III. QUANTUM-MECHANICAL DERIVATION OF THE CONSTITUTIVE EQUATION FOR THE FRENKEL EXCITON POLARIZATION IN A HALF-SPACE MEDIUM

A. Coherent wave theory for the Frenkel exciton

Stahl and Balslev[21] introduce the coherent wave theory as a general formalism for the electrodynamics of the semiconductor band edge. While the conventional Elliot-like treatment[33] requires a two-stage calculation in which the exciton wave function is calculated and then applied to the linear response formulation to obtain the exciton polarization response, this theory starts from the creation and annihilation operators of the electron and hole from which the complex exciton polarization operator can be constructed. Therefore, the constitutive equation for the complex exciton polarization operator can be derived from the Heisenberg equation directly.

Since the optics of transmission/reflection of a Frenkel exciton system is still a macroscopic problem, we can apply the long-wavelength approximation to the constitutive equation for the complex exciton polarization. Subsequently, we can obtain the macroscopic exciton polarization response or susceptibility by using our $\mathbf{k}$-space method without the need for a microscopic calculation of the Frenkel exciton wave function in a bounded medium. Such a calculation is impractical anyway and its avoidance while including its microscopic effect on the macroscopic problem is a very important advantage of the $\mathbf{k}$-space method.

The coherent wave theory is based on the tight-binding model of a two-level quantum system, which is a suitable model to describe the lowest exciton branch in a

semiconductor or insulator. Since a full development of the theory is given in Ref. 21, we present here only a brief description of the model with emphasis on our application of it to a bounded medium. The quantum system consists of a nondegenerate upper s state (spin degeneracy is neglected) denoted by $|c,j\rangle$ and a threefold degenerate lower p state denoted by $|v,\lambda,j\rangle$ at each atomic site j with λ denoting the sublevel. For spinless p states, λ corresponds to the direction of polarization. The ground state of the system consists of one electron at every atomic site in a p state. If an electron is excited into the $|c,j\rangle$ state from the $|v,\lambda,j\rangle$ state, the system now contains a missing $|v,\lambda,j\rangle$ state. A hole, in the terminology of semiconductor physics, is said to be created. A set of Fermion operators, $c_j^\dagger$ and $d_{\lambda j}^\dagger$, c_j and $d_{\lambda j}$, which are the creators and annihilators of the electron and hole, respectively, at the atomic site j is introduced. The Hamiltonian of the simplest model that only allows the electron and hole to be created or annihilated on the same atomic site can be written as

$$H_M = \frac{\hbar\omega_g}{2}\sum_j\left(c_j c_j^\dagger - \sum_\lambda d_{\lambda j} d_{\lambda j}^\dagger\right), \tag{22}$$

where the energy level spacing (gap) between the two states is $E_g = \hbar\omega_g$. Such an electron-hole pair described by Eq. (22) is the so-called Frenkel exciton. The justification of assuming such a Frenkel exciton is as follows. Since a real Frenkel exciton is tightly bound and small in size, the probability of the electron and hole not being at a same atomic site is very small. Therefore, no significant error is introduced by omitting that part of the wave function corresponding to other sites. Also, if that part needs to be accounted for, we can treat $\hat{s}$ by a Taylor expansion around the center-of-mass coordinate of the exciton as long as the size of the exciton is much smaller than its bulk exciton-polariton wavelength.

It is assumed that there is no electric dipole moment in either the upper s state or lower p states, but in the transition a dipole is produced. The component λ of the dipole moment of atom j is represented by the operator

$$\hat{\pi}_{\lambda j} = p_0\left(d_{\lambda j} c_j + d_{\lambda j}^\dagger c_j^\dagger\right), \tag{23}$$

where p_0 is the transition dipole matrix element. The interaction Hamiltonian with the electric field component λ at site j, $E_{\lambda j}$, is then given by

$$H_I = -\sum_{\lambda j}\hat{\pi}_{\lambda j} E_{\lambda j}. \tag{24}$$

For the sake of simplicity, we assume the electric field is polarized in one of the λ directions so that it excites only that component of the dipole moment. Thus we can drop the λ notation. A convenient set of variables which may be used in studying the dynamics of the quantum system under the influence of the electric field consists of the following four quantities:

$\hat{s}_j^\dagger = c_j^\dagger d_j^\dagger$, creator of a Frenkel exciton at site j;

$\hat{s}_j = c_j d_j$, annihilator of a Frenkel exciton at site j;

$\hat{n}_j = c_j^\dagger c_j$, electron number in state $|c,j\rangle$;

$\hat{p}_j = d_j^\dagger d_j$, hole number in state $|v,j\rangle$.

The actual exciton polarization is then expressed as

$$P_j^{\mathrm{ex}} = p_0\left(\hat{s}_j^\dagger + \hat{s}_j\right)/2. \tag{25}$$

To account for the mobility of a Frenkel exciton, a hopping term that describes the transfer of the Frenkel exciton as an entity from one site to another is also added. The hopping Hamiltonian can be written as

$$H_H = \sum_{jk} T_{jk}\hat{s}_j^\dagger \hat{s}_k, \tag{26}$$

where T_{jk} is the "hopping matrix." It is not difficult to see that the diagonal matrix element T_{jj} does not correspond to hopping but rather to the Coulomb interaction between the electron and hole. Thus it represents the exciton binding energy in the model. The total Hamiltonian is then

$$H = H_M + H_H + H_I. \tag{27}$$

Our Frenkel exciton model is simplified considerably compared to a more sophisticated one in Ref. 34 (however, deeper understanding of the exciton problem should be based on Ref. 34). In particular, the assumption that restricts the electron and hole to the same atomic site allows the Frenkel exciton polarization to be expressed as a function of the atomic site j rather than as a function of electron-hole coordinates.

In a low excitation case where the densities of the electron and hole (the expectation values of $\hat{n}_j$ and $\hat{p}_j$) are very small, the dynamic equation for $\hat{s}_j$ can be approximated as[21]

$$\dot{\hat{s}}_j + i\omega_g\hat{s}_j + \frac{i}{\hbar}\sum_k T_{jk}\hat{s}_k = \frac{ip_0}{\hbar}E. \tag{28}$$

While in Ref. 21 the sum is over the atomic sites k of an infinite medium, we restrict the atomic site indices j and k in Eq. (28) to a half-space medium. We assume the material medium fills the $z > 0$ half-space with a boundary plane at $z = 0$. Our formulation can retain the form of Ref. 21 if instead of a restriction on the range of j and k, each $\hat{s}_j$ is multiplied by a unit step function $\Theta((R_j)_z)$ defined by

$$\Theta(z) = \begin{cases} 1 & \text{if } z > 0 \\ 0 & \text{if } z < 0. \end{cases} \tag{29}$$

B. The macroscopic constitutive equation

In the continuum limit of Eq. (28) $\hat{s}_j$ is replaced by its expectation value $s(\mathbf{x})$, a density function. Then Eq. (28) takes on the form

$$\Theta(z)\left[\dot{s}(\mathbf{x})+i\omega_g s(\mathbf{x})\right]+\Theta(z)\frac{i}{\hbar}\int T(\mathbf{x},\mathbf{x}')\,s(\mathbf{x}')\,\Theta(z')\,d\mathbf{x}'=\Theta(z)\frac{ip_0\mathcal{N}}{\hbar}E, \tag{30}$$

where $\mathcal{N}$ is the density of Frenkel excitons in the medium. Since $T(\mathbf{x},\mathbf{x}')$ is of short range, it is reasonable to express it as

$$\begin{aligned}T(\mathbf{x},\mathbf{x}')=T(\mathbf{x},\mathbf{x}+(\mathbf{x}'-\mathbf{x}))&=\exp(-|\mathbf{x}'-\mathbf{x}|/a)\,T'(\mathbf{x},\mathbf{x}+(\mathbf{x}'-\mathbf{x}))\\&\approx\exp(-|\mathbf{x}'-\mathbf{x}|/a)\left[T'(\mathbf{x},\mathbf{x})+(\mathbf{x}'-\mathbf{x})\cdot\frac{\partial}{\partial\mathbf{x}'}T'(\mathbf{x},\mathbf{x}')\Big|_{\mathbf{x}'=\mathbf{x}}\right.\\&\left.+\frac{1}{2}(\mathbf{x}'-\mathbf{x})(\mathbf{x}'-\mathbf{x}):\frac{\partial^2}{\partial\mathbf{x}'\partial\mathbf{x}'}T'(\mathbf{x},\mathbf{x}')\Big|_{\mathbf{x}'=\mathbf{x}}\right],\end{aligned} \tag{31}$$

where a is the effective "hopping" range of excitons and is about the same order of magnitude as the lattice constant of the dielectric crystal. Under the flat-band approximation to the half-space medium, $T'(\mathbf{x},\mathbf{x}')$ is a constant even near the surface. Therefore we can neglect $\partial T'(\mathbf{x},\mathbf{x}')/\partial\mathbf{x}'$ and other higher-order derivatives in the above expansion. This gives $T(\mathbf{x},\mathbf{x}')\approx T'\exp(-|\mathbf{x}'-\mathbf{x}|/a)$. By changing the dummy variable $\mathbf{x}'$ to $\mathbf{x}''\equiv\mathbf{x}'-\mathbf{x}$ in the integral of Eq. (30), it can be reexpressed as

$$\begin{aligned}\frac{i}{\hbar}\int T(\mathbf{x},\mathbf{x}')\,s(\mathbf{x}')\,\Theta(z')\,d\mathbf{x}'&=\frac{i}{\hbar}T'\int\exp(-|\mathbf{x}''|/a)s(\mathbf{x}+\mathbf{x}'')\,\Theta(z+z'')\,d\mathbf{x}''\\&=\frac{i}{\hbar}T'\int\exp(-|\mathbf{x}''|/a)\left(1+\mathbf{x}''\cdot\frac{\partial}{\partial\mathbf{x}}+\frac{1}{2}\mathbf{x}''\mathbf{x}'':\frac{\partial^2}{\partial\mathbf{x}\partial\mathbf{x}}\right)s(\mathbf{x})\,\Theta(z+z'')\,d\mathbf{x}'',\end{aligned} \tag{32}$$

where the Taylor expansion on $s(\mathbf{x}+\mathbf{x}'')$ with respect to $\mathbf{x}$ is used.

The coefficient of $s(\mathbf{x})$ without the factor $i/\hbar$ in Eq. (32) can be evaluated as

$$\begin{aligned}I&=T'\int d\mathbf{x}'\exp(-|\mathbf{x}'|/a)\,\Theta(z+z')\\&=2\pi\int_0^\infty\rho\,d\rho\int_{-z}^{+\infty}dz'e^{-\sqrt{\rho^2+(z')^2}/a}\\&=8T'\pi a^3-4\pi T'\int_0^{\pi/2}\sin\theta\,d\theta\int_{z/\cos\theta}^\infty e^{-r/a}r^2dr\\&=4T'\pi a^3\left\{2-\left[e^{-z/a}\left(2+\frac{z}{a}\right)-2\frac{z}{a}\int_{z/a}^{+\infty}\frac{e^{-y}}{y}dy\right]\right\}.\end{aligned}$$

For example, the above integral at $z=0$ is half of what it is at $z=+\infty$. Thus the integral must have the form

$$I=4T'\pi a^3\{2-e^{-z/a}[1+\alpha_1(z/a)+\cdots]\}. \tag{33}$$

As seen from the Fourier transform, the first- and higher-order terms of z/a lead to higher-order effects (in terms of a) to long-wavelength optics apart from contributing a normalized factor on the first term. Therefore the zero-order moment in Eq. (32) yields a term $i(I/\hbar)\Theta(z)s(\mathbf{x})$ in Eq. (30). When combined with the term $i\omega_g\Theta(z)s(\mathbf{x})$ we can see that the coefficient I actually represents the exciton binding energy in a bounded medium. Thus the resonant energy of the exciton in the medium is

$$\hbar\Omega(z)=\hbar\left[\omega_g-\omega_b\left(1-\ell e^{-z/a}\right)\right]\Theta(z), \tag{34}$$

where $\hbar\omega_b=-8\pi a^3T'$ is the bulk exciton binding energy, and ℓ is the effective change of the exciton binding energy at the surface under the flat-band approximation. It can also be used to account for effects caused by a surface electric field, an extrinsic atomic layer, etc.

The first-order moment in Eq. (32) yields a term of $\nabla s(\mathbf{x})$ type. This is a linear wave-vector dispersive term and is usually omitted for simplicity in studying the exciton polarization. The second-order moment in Eq. (32) yields a second-order wave-vector dispersive term of $\nabla\nabla s(\mathbf{x})$ type. This term, a second-rank tensor, corresponds to the kinetic energy of the translational motion of the exciton in the medium. Its coefficient, also a second-rank tensor, can be interpreted as the reciprocal of the effective-mass tensor of the Frenkel exciton. Again, for the sake of simplicity, we limit ourselves to studying only the case where the effective mass is isotropic. Therefore the effective mass can be defined through

$$\frac{\hbar^2}{M}=-T'\int\exp(-x/a)x^2d\mathbf{x}\propto-T'a^5\propto\hbar\omega_b a^2. \tag{35}$$

Note that the dependence of the effective mass on z leads to terms proportional $T'a^6$ or higher, which contribute only higher-order effects to the long-wavelength optics problem and so are neglected. From the above analysis, Eq. (30) can be simplified as

$$\Theta(z)\,\dot{s}(\mathbf{x})+i\Omega(z)s(\mathbf{x})-i\frac{\hbar}{2M}\Theta(z)\,\nabla^2s(\mathbf{x})=i\frac{p_0\mathcal{N}}{\hbar}\Theta(z)\,E(\mathbf{x}). \tag{36}$$

Equation (36) can be converted to the dynamical equation for the exciton polarization P^{ex}. It is related to the

real part of the complex exciton amplitude s, as seen in Eq. (25), and in the continuum limit can be expressed as

$$P^{\mathrm{ex}}(\mathbf{x}) = p_0 [s(\mathbf{x}) + s^*(\mathbf{x})]/2 . \quad (37)$$

We follow the procedure as given in Ref. 21 to deduce the dynamical equation for $P^{\mathrm{ex}}(\mathbf{x})$. The complex conjugate of Eq. (36) is

$$\Theta(z)\dot{s}^*(\mathbf{x}) - i\Omega(z)s^*(\mathbf{x}) + i\frac{\hbar}{2M}\Theta(z)\nabla^2 s^*(\mathbf{x}) = -i\frac{p_0\mathcal{N}}{\hbar}\Theta(z)E(\mathbf{x}) . \quad (38)$$

By adding Eqs. (36) and (38) and making a time derivative of the sum we obtain

$$\Theta(z)(\ddot{s}+\ddot{s}^*) + i\left[\Omega(z) - \frac{\hbar}{2M}\Theta(z)\nabla^2\right] \times (\dot{s}-\dot{s}^*) = 0. \quad (39)$$

By subtracting Eq. (38) from Eq. (36) we get

$$\Theta(z)(\dot{s}-\dot{s}^*) + i\left[\Omega(z) - \frac{\hbar}{2M}\Theta(z)\nabla^2\right](s+s^*) = 2i\frac{p_0\mathcal{N}}{\hbar}\Theta(z)E. \quad (40)$$

Finally by eliminating $\dot{s}-\dot{s}^*$ in Eq. (39) with Eq. (40) we obtain the constitutive equation for $P^{\mathrm{ex}}(\mathbf{x})$

$$\Theta(z)\partial^2 P_y^{\mathrm{ex}}(\mathbf{x},t)/\partial t^2 + \Omega(z)^2 P_y^{\mathrm{ex}}(\mathbf{x},t) - (\hbar/2M)\{\nabla^2[\Omega(z)P_y^{\mathrm{ex}}(\mathbf{x},t)] + \Omega(z)\nabla^2 P_y^{\mathrm{ex}}(\mathbf{x},t)\} = p_0^2\mathcal{N}\Omega(z)E_y(\mathbf{x},t)/\hbar, \quad (41)$$

where only the lowest-order correction of each term is retained. This equation is easily recognized as the bulk equation of the HT model (see Sec. II of Ref. 4) if the dependence of the exciton binding energy on the spatial coordinate z is neglected. This shows that the macroscopic HT model applies to Frenkel excitons in a bounded medium.

Hopfield and Thomas used a microscopic quantum-mechanical argument when considering the boundary condition for the macroscopic dynamic equation of the exciton polarization (see Sec. III of Ref. 4). Their microscopic theory is rather phenomenological. When they considered a Frenkel exciton, the surface effect contributed by the internal motion was completely neglected. This is the most important difference between their model and ours. We show later that the internal motion effect cannot be neglected even for our Frenkel exciton model (the smallest exciton there can be).

Hopfield and Thomas also considered a similar model for Wannier excitons by adding an effective potential contributed by the surface. They argued that the repulsive potential becomes very large at the surface and produces the "dead layer" needed to explain their data. However, the coherent wave theory shows that center-of-mass motion and its quantal interference near the surface from the internal motion must be solved together for Wannier excitons. The concept of lumping the internal motion effect on the center-of-mass motion into an effective potential cannot be justified from a first-principles derivation.[21] Even for Frenkel excitons, the effective potential formulation is not sufficient as seen in the constitutive equation (41) that we derive. Furthermore, the potential term in that equation can be regarded as a modification of the exciton binding energy, as used in many other theories.[13–15] The exciton binding energy should approach a finite negative number at the surface as shown in our derivation and in Ref. 35 for Frenkel excitons, not a very large positive number. It is well known that an exciton with positive binding energy corresponds to an unbound exciton continuum. Its polarization cannot be described by a classical resonant oscillator. Therefore to use a large positive effective potential to modify the dynamical equation of the extended resonant oscillator is not very meaningful.

When compared with the dielectric model derived macroscopically in the previous section, we can see that Eq. (41) has the same form as Eq. (21) except that the N-type term is missing. We find that if we include the linear wave-vector dispersive term (previously dropped), an N-type term is present in Eq. (41), the quantum-mechanical version of the dynamical equation of the polarization of the Frenkel exciton. This is not surprising since the macroscopic theory is completely general in the sense that the N-type term includes, but not necessarily only includes, second-order terms of linear wave-vector dispersive terms. On the other hand, the quantum-mechanical derivation gives specific form and interpretation to the material parameters. We can attribute this to the fact that we have a more specifically (microscopically) defined system in the quantum-mechanical treatment.

One important finding of our quantum-mechanical derivation is that the finite hopping range a of a Frenkel exciton that determines the mobility of the exciton also determines the change of the exciton binding energy near the surface. In other words, if the wave-vector dispersion originating from translational motion of the exciton, though small in the Frenkel exciton case, is included in a model for studying the exciton polarization, then the change of the exciton binding energy in the surface layer must also be included. In fact, as shown in a later section, they contribute comparably to surface layer effects in long-wavelength optics. Our finding agrees conceptually with the finding from the coherent wave study of a Wannier exciton case[21] that the interference of the in-

ternal structure of an exciton (reflected by the change of its binding energy in our case) with its center-of-mass motion near the surface must be considered consistently.

IV. WAVE-VECTOR-SPACE METHOD

A. The dynamic equations in k space

Unlike the equation of a local long-wavelength optic mode, the dynamic equation for the Frenkel exciton is a partial differential equation. Therefore, from a real-space solution method point of view there is a need for a boundary condition in order to obtain a unique solution to this equation. The information needed to deduce such a boundary condition is, as generally believed, contained in the partial differential equation of the inhomogeneous medium that the surface represents. For example, the Maxwell equations are also partial differential equations. The Maxwell boundary conditions can be obtained directly from the Maxwell equations by applying either Gauss's theorem to a small volume element (pill box) or Stokes's theorem to a small loop enclosing the boundary.[23] However, if wave-vector dispersion is involved, those conventional methods are no longer useful because an indeterminate surface quantity arises (see the Appendix).

The problem is caused by abrupt changes of material properties in the surface transition layer on an atomic scale. As a result, the field variables such as the electric field and polarization also experience rapid changes there. A detailed microscopic description of field variables in this macroscopically infinitesimal but microscopically finite layer is extremely complicated and difficult to obtain but unnecessary for an optics problem of transmission/reflection. There one detects only the optical electric field that is far away from the surface region, and has the bulk wavelength. Therefore, only the part of the electric field spectrum in $\mathbf{k}$ space around the bulk wave-vector is of interest. In contrast, the rapid change of the electric field near the surface is mostly contributed by the short-wavelength part of the wave-vector spectrum. In this section, we show from our $\mathbf{k}$-space method that the short-wavelength part of a field variable has a very small effect on its long-wavelength part if the surface transition layer is very small compared to the bulk wavelength of the field variable. In fact, we can show that the surface layer effect is completely negligible in a local optics problem, which is why the Maxwell boundary conditions can be derived in real space without need for detailed solutions in the surface transition layer. However, in the nonlocal optics problem of a Frenkel exciton system, the surface transition layer effect is not negligible when the problem is treated consistently.

To account for the surface layer effect in real space, the full microscopic solution must be obtained based on a proper microscopic boundary condition. (A macroscopic real-space method is no longer useful because, by its nature, it cannot describe any detail on an atomic scale, especially in the surface transition layer.) If the microscopic problem is fully solved, then the transmission and reflection coefficients can be obtained from the asymptotic part of the solution. Thus the corresponding macroscopic boundary condition can be derived (inversely) but is not necessary. Also the usefulness of deriving the macroscopic boundary condition from the microscopic solution depends on whether the microscopic solution can be obtained analytically. In $\mathbf{k}$ space, the surface effect on a long-wavelength optics problem is translated into a short-wavelength effect on the long-wavelength dynamics. In the case of a Frenkel exciton, the surface effect is small, and thus can be treated perturbationally. That is the distinct advantage of our $\mathbf{k}$-space method over any real-space method.

We now apply our new $\mathbf{k}$-space method introduced in the preceding paper[26] to the exciton problem. While the familiar problem of Fresnel reflectivity was used to illustrate the strikingly different method of solution that the $\mathbf{k}$-space method uses, that application to a local optics problem does not exhibit one of the special features of the method, that is, its handling of the surface effects that a nonlocal optics problem, such as the exciton problem, inherently has.

The various dynamic equations are transformed to $\mathbf{k},\omega$ space. For example, the four-dimensional Fourier transform to $\mathbf{k},\omega$ space of an internal coordinate is

$$\mathbf{y}^{\nu}(\mathbf{k},\omega)=\frac{1}{(2\pi)^4}\int \mathbf{y}^{\nu}(\mathbf{x},t)\,e^{-i\mathbf{k}\cdot\mathbf{x}+i\omega t}d\mathbf{x}\,dt \tag{42}$$

and its inverse transformation is given by

$$\mathbf{y}^{\nu}(\mathbf{x},t)=\int \mathbf{y}^{\nu}(\mathbf{k},\omega)\,e^{i\mathbf{k}\cdot\mathbf{x}-i\omega t}d\mathbf{k}\,d\omega. \tag{43}$$

Similar transformations can be given for $\mathbf{E}$ and $\mathbf{B}$ fields. Also, similar expressions apply to material quantities such as m^{ν}, q^{ν}, $M_{ij}^{\nu\mu}$ except the time or frequency dependence does not occur.

The dynamic motion equation (19) can be transformed into to $\mathbf{k},\omega$ space as

$$\omega^2\int m^{\nu}(\mathbf{k}-\mathbf{k}')\,y_i^{\nu}(\mathbf{k}',\omega)\,d\mathbf{k}'-2\sum_{\mu}\int M_{ij}^{\nu\mu}(\mathbf{k}-\mathbf{k}')\,y_j^{\mu}(\mathbf{k}',\omega)\,d\mathbf{k}'+\int q^{\nu}(\mathbf{k}-\mathbf{k}')\,E_i(\mathbf{k}',\omega)\,d\mathbf{k}'=0. \tag{44}$$

Similarly, the dynamic equation for the exciton motion (21) can be transformed to $\mathbf{k},\omega$ space as

$$\begin{aligned}\omega^2\int m^{\mathrm{ex}}(\mathbf{k}-\mathbf{k}')\,y_i^{\mathrm{ex}}(\mathbf{k}',\omega)\,d\mathbf{k}'-2\int M_{ij}(\mathbf{k}-\mathbf{k}')\,y_j^{\mathrm{ex}}(\mathbf{k}',\omega)\,d\mathbf{k}'-i\int\left[k_l'L_{ijl}(\mathbf{k}-\mathbf{k}')-k_lL_{jil}(\mathbf{k}-\mathbf{k}')\right]y_j^{\mathrm{ex}}(\mathbf{k}',\omega)\,d\mathbf{k}'\\+\int\left[O_{ijlm}(\mathbf{k}-\mathbf{k}')\,k_l'k_m'+O_{jilm}(\mathbf{k}-\mathbf{k}')\,k_lk_m\right]y_j^{\mathrm{ex}}(\mathbf{k}',\omega)\,d\mathbf{k}'-2k_l\int k_m'N_{iljm}(\mathbf{k}-\mathbf{k}')\,y_j^{\mathrm{ex}}(\mathbf{k}',\omega)\,d\mathbf{k}'\\+\int q^{\nu}(\mathbf{k}-\mathbf{k}')\,E_i(\mathbf{k}',\omega)\,d\mathbf{k}'=0.\end{aligned} \tag{45}$$

We also need to transform the Maxwell equations into $\mathbf{k}$ space. Under our approximation that neglects magnetization and quadrupolarization, Eqs. (15) and (16) are simplified to $\mathbf{H} = \mathbf{B}/\mu_0$ and $\mathbf{D} = \epsilon_0\mathbf{E} + \mathbf{P}$. With these two equations and Eq. (18) we can eliminate $\mathbf{B}$ in Eq. (14) and rewrite it as

$$\nabla \times \nabla \times \mathbf{E} - (1/c^2)\partial^2 \left[\mathbf{E} + (1/\epsilon_0)\mathbf{P}\right]/\partial t^2 = 0, \quad (46)$$

which is the wave equation for the electric field. Its $\mathbf{k},\omega$-space transform is

$$\epsilon_0 \left\{\omega^2 E_i(\mathbf{k},\omega) + c^2 \left[\mathbf{k} \times \mathbf{k} \times \mathbf{E}(\mathbf{k},\omega)\right]_i\right\}$$

$$+\omega^2 \sum_\nu \int q^\nu (\mathbf{k} - \mathbf{k}')\, y_i^\nu (\mathbf{k}',\omega)\, d\mathbf{k}' = 0. \quad (47)$$

Note that in Ref. 24 we prove that all the dynamic equations and the Maxwell equations can be obtained from a total Lagrangian density in $\mathbf{k},\omega$ space by applying the Hamilton variational principle to every field variable in $\mathbf{k},\omega$ space. Thus, that approach is equivalent to the procedure of transforming the real-space dynamical equations as presented here.

B. Perfectly abrupt surface model of a half-space medium

As seen in the last subsection, the dynamic equations in $\mathbf{k}$ space for an inhomogeneous medium are generally integral equations which contain convolutions of a Fourier transform of a material parameter with a Fourier transform of a field variable. Integral equations are usually more difficult to solve than differential equations. However, for an optics problem in a half-space medium, these dynamic equations can be reduced to algebraic equations by the mathematical theorem we introduced in the preceding paper.[26]

We assume the material medium fills the $z > 0$ half-space with a boundary plane at $z = 0$. An arbitrary material property of a perfectly abrupt surface model $\mathcal{M}(\mathbf{x})$ has a mathematical expression of

$$\mathcal{M}(\mathbf{x}) = \mathcal{M}\Theta(z), \quad (48)$$

where $\Theta(z)$ is the unit step function defined in Eq. (29). Its Fourier transform is

$$\Theta(k_z) = \frac{1}{2i\pi}\frac{1}{k_z - i\eta},$$

where η is an infinitesimal positive quantity. Thus the Fourier transform of the material property $\mathcal{M}(\mathbf{x})$ is

$$\mathcal{M}(\mathbf{k}) = \frac{1}{2i\pi}\mathcal{M}\delta(k_x)\,\delta(k_y)\frac{1}{k_z - i\eta}. \quad (49)$$

The two delta functions for k_x and k_y are due to the fact that the translational invariance is still preserved in the $\hat{x}$ and $\hat{y}$ directions. The two delta functions make the convolution of the material parameter with an arbitrary field variable, say $f(\mathbf{k})$, in the $\hat{x}$ and $\hat{y}$ directions straightforward. Therefore we only need to deal with the convolution in the $\hat{z}$ direction.

In the preceding paper[26] we proved a theorem applying to the convolution of the transform of a material property as given in Eq. (49) with the transform of a physical wave field $f(k_z)$. It is

$$\frac{1}{2i\pi}\int_{-\infty}^{+\infty} \frac{1}{k_z - k_z' - i\eta} f(k_z')\, dk_z' = f^{(+)}(k_z), \quad (50)$$

where

$$f(k_z) = f^{(+)}(k_z) + f^{(-)}(k_z), \quad (51)$$

and $f^{(+)}(k_z)$ and $f^{(-)}(k_z)$ are the parts of $f(k_z)$ having poles in the upper and lower half complex k_z plane, respectively. As discussed there, poles in the upper (lower) half-plane occur at the propagation constants of the physical wave field inside (outside) the medium. Also, poles do not occur on the real axis in order to have finite transforms.

By using this theorem, we can calculate the convolution of an arbitrary material parameter with an arbitrary field variable in wave-vector space for the half-space medium. It has the form of

$$\int \mathcal{M}(\mathbf{k} - \mathbf{k}')\, f(\mathbf{k}',\omega)\, d\mathbf{k}'$$

$$= \int \frac{\mathcal{M}}{2\pi i}\frac{\delta(k_x - k_x')\,\delta(k_y - k_y')}{k_z - k_z' - i\eta} f(\mathbf{k}',\omega)\, d\mathbf{k}'$$

$$= \mathcal{M} f^{(+)}(k_x, k_y, k_z, \omega). \quad (52)$$

Since the integrals in the dynamic equations for the internal and exciton motions, Eqs. (44) and (45), and the wave equation (47) have the same form as that of Eq. (52), the use of the theorem allows us to carry out the integrations analytically for the perfectly abrupt surface model of a half-space medium. We then obtain the algebraic forms of these equations. As shown in the preceding paper, the equations themselves provide all the information needed to determine the functional forms of the field variables.

C. Gradual surface model

Consider next a material property that is not perfectly abrupt at the surface, but rather varies gradually from its bulk value to a surface value. In general we can describe such a material property by

$$\mathcal{M}(\mathbf{x}) = \mathcal{M}\Theta(z)\left[1 + g(z)\right], \quad (53)$$

where $g(z)$ is the profile function. Often it can be conveniently expressed by an exponentially decaying function as in Eq. (34),

$$g(z) = -\ell e^{-z/a}, \tag{54}$$

since for a thin surface layer, its detailed form is not important to the long-wavelength dynamics as seen later. Here a is the effective distance that the material property is affected by the surface and the dimensionless parameter ℓ describes the extent over which the material property is affected. The $\mathbf{k}$-space transform of the material parameter $\mathcal{M}$ in Eq. (53) is

$$\mathcal{M}(\mathbf{k}) = \frac{\mathcal{M}}{2i\pi}\delta(k_x)\,\delta(k_y)\left(\frac{1}{k_z - i\eta} - \frac{\ell}{k_z - i/a}\right). \tag{55}$$

Since in long-wavelength dynamics, we are only interested in the Fourier transform in the spectrum $|\mathbf{k}| \ll 1/a$, its convolution with a field variable can be treated perturbationally by expanding it about i/a. We carry out the convolution of the second part in Eq. (55) with $f(k)$ as

$$\frac{1}{2\pi i}\int \frac{1}{k - k' - i/a} f(k')\,dk'$$

$$\approx \frac{a}{2\pi}\int (1 - ika + ik'a)\, f(k')\,dk'$$
$$= (a/2\pi)(1 - ika)\, f^{(0)} + \left(a^2/2\pi\right)\left(\partial f/\partial z\right)^{(0)}, \tag{56}$$

which introduces the surface values of $f^{(0)}$ and $(\partial f/\partial z)^{(0)}$,

$$f^{(0)} \equiv \int f(k')\,dk', \tag{57}$$

$$(\partial f/\partial z)^{(0)} \equiv \int ik' f(k')\,dk'. \tag{58}$$

In evaluating the surface terms, a singularity problem may be encountered. However, the problem originates from the extension of the integration limits from the first Brillouin zone of the medium to infinity. Extending the integration limits does not introduce any significant error to a long-wavelength problem because the dominant part of the $\mathbf{k}$-space transform is concentrated in the zone center. In our case, we do not really care about the detailed functional description of the short-wavelength part of a field variable but only about its effect on the long-wavelength part. Knowing the fact that the integration must converge, we can use a series expansion to express the short-wavelength part and invoke a soft cutoff wave vector $k_c \ll 1/a$ to limit the integration range, if necessary.

Introducing the cutoff also makes interpreting the surface terms physically meaningful. For example, the unit step function $\Theta(z)$ that we introduced to describe a perfectly abrupt surface model is not defined at $z = 0$. It has an infinite slope at $z = 0$, too. However, this function is a mathematical idealization of an abrupt surface. In a macroscopic theory the surface transition layer is taken as macroscopically infinitesimal but microscopically finite and $\Theta^{(0)}$ is the function value there. After introducing the cutoff wave vector, it becomes well defined

$$\Theta^{(0)} = \frac{1}{2\pi i}\int_{-k_c}^{k_c} \frac{1}{k - i\eta}dk$$
$$= \frac{1}{2\pi i}\left(\mathcal{P}\int \frac{1}{k}dk + \int i\pi\delta(k)dk\right)$$
$$= \frac{1}{2\pi i}\mathcal{P}\int \frac{1}{k}dk + \frac{1}{2} = \frac{1}{2}, \tag{59}$$

where $\mathcal{P}$ denotes the Cauchy principal value. The result here of $1/2$ is an average value of the function just outside the medium and just inside the medium.

We further look at the spatial derivative of the $\Theta(z)$ function at $z = 0$. It can be calculated as

$$\left(\frac{\partial\Theta}{\partial z}\right)^{(0)} = \frac{1}{2\pi i}\int_{-k_c}^{k_c} \frac{ik}{k - i\eta}dk = \frac{k_c}{\pi}, \tag{60}$$

which means $\Theta(z)$ rises from 0 to 1 in a span that is about π/k_c. Therefore the reciprocal of k_c can be interpreted as a measure of the thickness of the transition layer below the surface. Speaking in mathematical language, a long-wavelength formulation in wave-vector space cannot describe any detail that is spatially smaller than π/k_c because of the need for invoking the cutoff wave vector. Interpreting this statement physically, it simply means that our macroscopic theory is not intended to describe any feature (especially near the surface) on the scale that is spatially much smaller than the wavelength of the optical wave we are interested in. Nevertheless, our wave-vector-space method can include the effect of the transition layer on the long-wavelength dynamics, which is shown in Eq. (56). It is not difficult to see the effect is small since the terms in Eq. (56) are proportional to ka, which is assumed small. The smallest term kept in Eq. (56) is proportional to $(ka)^2$. In an ordinary local optics problem, a can be allowed to approach zero so that the surface layer effect can be totally neglected. However, in the Frenkel exciton problem a, the effective range of the change of exciton binding energy near the surface, albeit small, cannot be allowed to approach zero because it also stands for the hopping range of the Frenkel exciton. Letting $a = 0$ would imply an infinite exciton mass by Eq. (35). An exciton with no mobility would have no wave-vector dispersion.

We also need to emphasize that the value of a field variable $f(0^+) = f(z \to 0, z > 0)$ can be interpreted as the field variable just outside the transition layer in the medium. As seen later, it can be understood as the bulk component of the microscopic solution of the field variable evaluated at $z = 0$. (Note that the bulk components are characterized by the bulk wavelength which is much larger than the thickness of the surface layer. Thus it makes no difference to evaluate it just outside the surface layer or at $z = 0$.) Generally speaking, $f(0^+)$ is not equal to the surface term $f^{(0)}$ either mathematically or physically as shown later.

By now we have shown why the effect of a jump of a material property or a field variable in the transition

layer of the surface is small in the long-wavelength optics problem and how this effect can be accounted for perturbationally in our wave-vector-space method. Because a physical property both inside and outside a material is accounted for simultaneously by its Fourier transform, one can understand why there is no need for boundary conditions in the framework of our **k**-space method.

V. APPLICATION OF THE k-SPACE METHOD TO A FRENKEL EXCITON

A. Susceptibility of the Frenkel exciton model in a half-space geometry

We now apply the mathematical method introduced in the preceding paper[26] and expanded in the previous section to the constitutive equation in **k** space for the Frenkel exciton polarization in a half-space medium. Instead of using the general expression for every material parameter in Eq. (45), we use the more specific and somewhat simplified Frenkel exciton model obtained from coherent wave theory in Sec. III. By defining $e\mathbf{y}^{\mathrm{ex}} \equiv \mathbf{P}^{\mathrm{ex}}$ as the exciton polarization and comparing Eqs. (41) and (21) we obtain the following relations between the material parameters from the macroscopic Lagrangian theory and the coherent wave theory. They are

$$
\begin{aligned}
2M_{ij}(z)/m^{\mathrm{ex}} &\equiv [\Omega(z)]^2\,\delta_{ij},\\
O_{ijkl}(z)/m^{\mathrm{ex}} &\equiv -\Omega(z)\,(\hbar/2M)\,\delta_{ij}\delta_{kl},\\
eq^{\mathrm{ex}}(z)/m^{\mathrm{ex}} &\equiv \Omega(z)p_0^2\mathcal{N}/\hbar,\\
L_{ijk}(z) &\equiv 0,\\
N_{ijkl}(z) &\equiv 0,
\end{aligned}
$$

where $\Omega(z)$ is given in Eq. (34) and expresses all the spatial dependence of the material parameters of this model. The **k**-space transform of $\Omega(z)$ is

$$
\Omega(\mathbf{k}) = \delta(k_x)\,\delta(k_y)\,\frac{1}{2\pi i}\left[\frac{\Omega_0}{k_z - i\eta} + \frac{\ell\omega_b}{k_z - i/a}\right], \tag{61}
$$

where $\Omega_0 \equiv \omega_g - \omega_b$ is the bulk exciton resonant frequency.

The first part of Eq. (61) corresponds to the Fourier transform of the unit step function (multiplied by Ω_0) and its convolution with $\mathbf{P}^{\mathrm{ex}}(\mathbf{k},\omega)$ or $\mathbf{E}(\mathbf{k},\omega)$ can be done similarly to Eq. (52) . The second part of Eq. (61) corresponds to the gradual surface model of Eq. (55) and its convolution with $\mathbf{P}^{\mathrm{ex}}(\mathbf{k},\omega)$ or $\mathbf{E}(\mathbf{k},\omega)$ can be done analogously to Eq. (56). By using these techniques, Eq. (45) can be reduced to an algebraic equation. Note that the second part of Eq. (61) is responsible for the appearance of some of the surface terms in the reduced equation. The wave-vector dispersion terms in Eq. (45) also lead to surface terms. For example, one of the terms is calculated as

$$
\begin{aligned}
\frac{\hbar\Omega_0}{2M}\frac{1}{2\pi i}\int \frac{(k_z')^2}{k_z - k_z' - i\eta}P_i^{\mathrm{ex}}(k_z')\,dk_z' &= \frac{\hbar\Omega_0}{2M}\frac{1}{2\pi i}\int\left(-k_z - k_z' + \frac{k_z^2}{k_z - k_z' - i\eta}\right)P_i^{\mathrm{ex}}(k_z')\,dk_z'\\
&= \frac{\hbar\Omega_0}{2M}\left[\frac{ik_zP_i^{\mathrm{ex}\,(0)}}{2\pi} + \frac{(\partial P_i^{\mathrm{ex}}/\partial z)^{(0)}}{2\pi} + k_z^2P_i^{\mathrm{ex}\,(+)}(k_z)\right],
\end{aligned}
$$

where the dependence on k_x, k_y, and ω is no longer displayed.

After some algebraic manipulations, we obtain the transformed exciton polarization equation to be

$$
\begin{aligned}
&\left[\Omega_0^2 - \omega^2 + \frac{\hbar\Omega_0k^2}{2M}\right]P_i^{\mathrm{ex}\,(+)}(k_z) - \Omega_0\frac{p_0^2\mathcal{N}}{\hbar}E_i^{(+)}(k_z) + \frac{\Omega_0\ell\omega_b a}{\pi}\left[(1 - ik_za)\,P_i^{\mathrm{ex}\,(0)} + a\,(\partial P_i^{\mathrm{ex}}/\partial z)^{(0)}\right]\\
&\quad + \frac{1}{2\pi}\frac{\hbar\Omega_0}{2M}\left[ik_zP_i^{\mathrm{ex}\,(0)} + (\partial P_i^{\mathrm{ex}}/\partial z)^{(0)}\right] - \frac{p_0^2\mathcal{N}\ell\omega_b a}{2\pi\hbar}\left[(1 - ik_za)\,E_i{}^{(0)} + a\,(\partial E_i/\partial z)^{(0)}\right] = 0. \qquad (62)
\end{aligned}
$$

We keep all the surface terms up to the second order of a. Terms that are of higher orders, such as the convolution of the second part of Eq. (61) with the second-order wave-vector dispersive terms, are neglected. This is because its coefficient $\hbar^2/M \propto \hbar\omega_b a^2$ is already a second-order term [see Eq. (35)].

From Eq. (62) we obtain the constitutive relation of the susceptibility for the Frenkel exciton polarization in a half-space medium as

$$
P_i^{\mathrm{ex}\,(+)}(k_z) = \epsilon_0\chi^{\mathrm{ex}}(k)\,E_i{}^{(+)}(k_z) - \frac{\epsilon_0}{2i\pi}\frac{k_0b_i^{(1)} + k_zb_i^{(2)}}{k^2 - k_{\mathrm{ex}}^2}, \tag{63}
$$

where

$$b_i^{(1)} = (i/\epsilon_0 k_0 a)\left\{\beta\left(2P_i^{\mathrm{ex}(0)} - \epsilon_0\chi_{\mathrm{ex}}E_i{}^{(0)}\right) + a\left[(2\beta+1/2)\left(\partial P_i^{\mathrm{ex}}/\partial z\right)^{(0)} - \beta\epsilon_0\chi_{\mathrm{ex}}\left(\partial E_i/\partial z\right)^{(0)}\right]\right\} \tag{64}$$

$$b_i^{(2)} = (1/\epsilon_0)\left[(2\beta - 1/2)\,P_i^{\mathrm{ex}(0)} - \beta\epsilon_0\chi_{\mathrm{ex}}E_i{}^{(0)}\right]. \tag{65}$$

In the above equations, $\chi^{\mathrm{ex}}(k) \equiv \chi_{\mathrm{ex}}k_\Omega^2/\left(k^2 - k_{\mathrm{ex}}^2\right)$ is the bulk exciton susceptibility, $k_\Omega \equiv (M\Omega_0/\hbar)^{1/2}$, $k_{\mathrm{ex}} \equiv k_\Omega\left[\left(\omega^2 - \Omega_0^2\right)/\Omega_0^2\right]^{1/2}$, $\chi_{\mathrm{ex}} \equiv p_0^2\mathcal{N}/(\epsilon_0\hbar\Omega_0)$, $\beta \equiv \ell\,(\omega_b/\Omega_0)\,(k_\Omega a)^2$, and $k_0 \equiv \omega/c$. Equation (63) shows that the susceptibility of the Frenkel exciton in a bounded medium must have surface terms in addition to the bulk part. In Sec. V D we show that the surface terms persist when the exciton polarization is transformed to the spatial representation. Those surface terms are necessary in the constitutive relation to reflect the lack of translational invariance of a bounded wave-vector dispersive medium.

There are two origins of the surface terms. One is due to the wave-vector dispersion resulting from exciton motion. The other surface terms are due to the change of exciton binding energy in the transition layer near the surface, which enters through $\Omega(z)$ and leads to the terms proportional to β in Eqs. (64) and (65). The two origins play comparable roles in Eq. (65) but the latter one plays a larger role in Eq. (64). We conclude that the surface layer effect is essential in treating the optics of a Frenkel exciton.

B. Wave equation for normal incidence

For the sake of simplicity, we only discuss the normal incidence case here assuming $k_x = k_y = 0$ and $E_x = E_z = 0$. The discussion of the general oblique incidence case can be found in Ref. 24. We also use the perfectly abrupt surface model for charge densities of the local (nonexcitonic) internal coordinates in Eq. (47). Similarly to the procedure to reduce the constitutive equation for the exciton polarization, Eq. (47) can be reduced to

$$\epsilon_0\left(k_z^2 - k_0^2\right)E_y(k_z) + P_y{}^{(+)}(k_z) = 0, \tag{66}$$

where $P_y{}^{(+)}(k_z) \equiv P_y^{b\,(+)}(k_z) + P_y^{\mathrm{ex}\,(+)}(k_z)$ is the total polarization of the medium, $P_y^{b\,(+)} = \sum_{\nu\neq\mathrm{ex}} q^\nu y^{\nu\,(+)}$ is the background polarization and $E_y(k_z)$ is $E_y^{(+)}(k_z) + E_y^{(-)}(k_z)$ [there being no convolution with $\Theta(z)$ here].

By using the normal mode technique in Refs. 23 and 32, we obtain $P_y^{b\,(+)}(k_z) \equiv \epsilon_0\chi_b E_y^{(+)}(k_z)$. By using this equation and Eq. (63), Eq. (66) becomes

$$\left[k_z^2 - \kappa(k_z)\,k_0^2\right]E_y^{(+)}(k_z) + \left(k_z^2 - k_0^2\right)E_y^{(-)}(k_z)$$

$$+\left(k_0^2/2\pi i\right)\left(k_0 b_y^{(1)} + k_z b_y^{(2)}\right)/\left(k_z^2 - k_{\mathrm{ex}}^2\right) = 0, \tag{67}$$

where

$$\kappa(k_z) = 1 + \chi_b + \chi_{\mathrm{ex}}k_\Omega^2/\left(k_z^2 - k_{\mathrm{ex}}^2\right) \tag{68}$$

is the bulk dielectric constant. The poles of the electric field can be obtained directly from Eq. (67). If we let k_z approach one of the poles of $E_y^{(+)}(k_z)$ in the upper half complex k_z plane, $E_y^{(+)}(k_z)$ approaches infinity. However, the other terms in Eq. (67) that do not have poles in the upper half complex plane of k_z remain finite. The equation cannot be satisfied unless the coefficient of $E_y^{(+)}(k_z)$ vanishes at the pole so that the term remains finite. In other words, the zeros of the coefficient of a field variable in **k** space determine the poles of that field variable. Therefore $k_z^2 - \kappa(k_z)\,k_0^2 = 0$, or

$$\left(k_z^2\right)^2 - \left[(1+\chi_b)\,k_0^2 + k_{\mathrm{ex}}^2\right]k_z^2 + (1+\chi_b)\,k_{\mathrm{ex}}^2k_0^2$$

$$-\chi_{\mathrm{ex}}k_\Omega^2k_0^2 = 0, \tag{69}$$

gives the locations of the poles for $E_y^{(+)}(k_z)$ and is the dispersion relation of the medium. The two pairs of solutions $k_z = \pm k_1$ and $\pm k_2$ correspond to two distinct transverse waves of the same frequency and electric field polarization in the bulk. Similarly, as k_z approaches the poles of $E_y^{(-)}(k_z)$ in the lower half complex k_z plane, the necessary vanishing of the coefficient of $E_y^{(-)}(k_z)$ gives its poles at $k_z = \pm k_0$ (vacuum dispersion relation).

C. Transmission and reflection coefficients

Since the locations and types of the poles of the electric field transform are known from the previous discussion, we can write down its functional form. We also need to take into account the required asymptotic forms, that is, the absence of backward waves inside the medium. Thus, for a transmission/reflection problem, the **k**-space transform of the electric field has no pole at $k_z = -k_1$, or $-k_2$. Therefore, the functional form of the electric field in **k** space is

$$E_y^{(+)} = \frac{E_0}{2\pi i}\left[\frac{t_1}{k_z - k_1 - i\eta} + \frac{t_2}{k_z - k_2 - i\eta}\right], \tag{70}$$

$$E_y^{(-)} = -\frac{E_0}{2\pi i}\left[\frac{1}{k_z - k_0 + i\eta} + \frac{r}{k_z + k_0 + i\eta}\right], \tag{71}$$

where r, t_1, and t_2 are the amplitude reflection and transmission coefficients, and E_0 is the source electric field amplitude. Substitution of the functional forms of $E_y^{(+)}$ and $E_y^{(-)}$ into the wave equation (67) yields a third-order polynomial in k_z,

$$(t_1+t_2-1-r)\,k_z^3+(k_1t_1+k_2t_2-k_0+k_0r)\,k_z^2-\left(k_2^2t_1+k_1^2t_2-k_{\rm ex}^2-k_{\rm ex}^2r-k_0^2\bar{b}_y^{(2)}\right)k_z$$

$$-\left(k_1k_2^2t_1+k_1^2k_2t_2-k_{\rm ex}^2k_0+k_{\rm ex}^2k_0r-k_0^3\bar{b}_y^{(1)}\right)=0, \quad (72)$$

where $\bar{b}_y^{(i)}\equiv b_y^{(i)}/E_0$ $(i=1,2)$ is the dimensionless measure of $b_y^{(i)}$. Since k_z is the variable of the **E**-field transform and so is arbitrary, the coefficient of each power of k_z must separately vanish resulting in four conditions

$$t_1+t_2-1-r=0, \quad (73)$$

$$k_1t_1+k_2t_2-k_0+k_0r=0, \quad (74)$$

$$k_2^2t_1+k_1^2t_2-k_{\rm ex}^2-k_{\rm ex}^2r-k_0^2\bar{b}_y^{(2)}=0, \quad (75)$$

$$k_1k_2^2t_1+k_1^2k_2t_2-k_{\rm ex}^2k_0+k_{\rm ex}^2k_0r-k_0^3\bar{b}_y^{(1)}=0. \quad (76)$$

There are five unknowns, namely, r, t_1, t_2, $\bar{b}_y^{(1)}$, and $\bar{b}_y^{(2)}$ in the above equations. However we can evaluate the surface terms in $\bar{b}_y^{(1)}$ and $\bar{b}_y^{(2)}$ to provide us additional equations since we already know the functional forms of the exciton polarization and the electric field. By using the constitutive relation (63) we have

$$P_y^{\rm ex\,(0)}=\int P_y^{\rm ex\,(+)}(k_z)\,dk_z$$

$$=-\frac{\epsilon_0\chi_{\rm ex}k_\Omega^2E_0}{2k_{\rm ex}}\left(\frac{t_1}{k_{\rm ex}+k_1}+\frac{t_2}{k_{\rm ex}+k_2}\right)$$

$$-\frac{\epsilon_0E_0k_0\bar{b}_y^{(1)}}{2k_{\rm ex}},$$

where $\int k_z dk_z/\left(k_z^2-k_{\rm ex}^2\right)=0$ is used since the integrand is an odd function. This equation gives an alternate expression for $\bar{b}_y^{(1)}$ and thus avoids the lengthly evaluation of the derivatives of $P_y^{\rm ex\,(0)}$ and $E_y^{(0)}$ present in Eq. (64). With Eq. (65) we then obtain

$$\bar{b}_y^{(1)}=-\left(\alpha\epsilon_0\chi_{\rm ex}+2k_{\rm ex}aP_y^{\rm ex\,(0)}/E_0\right)/\epsilon_0k_0a, \quad (77)$$

$$\bar{b}_y^{(2)}=\left[(2\beta-1/2)\,P_y^{\rm ex\,(0)}-\beta\epsilon_0\chi_{\rm ex}E_y{}^{(0)}\right]/\epsilon_0E_0, \quad (78)$$

where

$$\alpha=(k_\Omega a)^2\left(\frac{t_1}{(k_{\rm ex}+k_1)\,a}+\frac{t_2}{(k_{\rm ex}+k_2)\,a}\right).$$

Similarly, by using the functional form of the electric field, Eqs. (70) and (71), we find

$$E_y^{(0)}=\int E(k_z)\,dk_z=E_0(t_1+t_2), \quad (79)$$

where Eq. (73) is used in the calculation. Note that the technique of using a soft cutoff wave vector to eliminate a divergent integral, as presented in Eq. (59), is also used here. The surface value of the electric field equals the magnitude of the electric field at either side of the surface in this case. This is no surprise because in the normal incidence case the electric field has only a tangential component which is continuous across the boundary.

Note also that, if $\partial P_y^{\rm ex(0)}/\partial z$ and $\partial E_y^{(0)}/\partial z$ were evaluated by Eqs. (58), it would bring in the soft cutoff wave vector k_c in the manner of Eq. (60). This can lead to evaluating the implied value of k_c. Not surprisingly it is found that k_c is of order of, but larger than, $1/a$.

Since $\bar{b}_y^{(1)}$ and $\bar{b}_y^{(2)}$ can be expressed as functions of t_1, t_2, and $P_y^{\rm ex\,(0)}$ [see Eqs. (77) and (78)], the four equations (73)–(76) suffice to solve for the two transmissivities t_1, t_2, the reflectivity r, and the surface exciton polarization $P_y^{\rm ex\,(0)}$. After some algebraic manipulation and by using

$$\left(k_1^2-k_{\rm ex}^2\right)\left(k_2^2-k_{\rm ex}^2\right)=-\chi_{\rm ex}k_0^2k_\Omega^2, \quad (80)$$

which can be derived form Eq. (69), we obtain

$$\frac{t_1}{k_1^2-k_{\rm ex}^2}+\frac{t_2}{k_2^2-k_{\rm ex}^2}=\frac{2P_y^{\rm ex\,(0)}}{\epsilon_0\chi_{\rm ex}k_\Omega^2E_0}=\frac{\zeta}{k_\Omega^2}(t_1+t_2), \quad (81)$$

where

$$\zeta\equiv 2\beta/(2\beta+3/2). \quad (82)$$

Thus the complete solution to the transmission/reflection problem can be found from Eqs. (73), (74), and (81) as

$$t_1=2\left(n_1^2-n_{\rm ex}^2+\zeta\chi_{\rm ex}\right)/(n_1-n_2)\,D, \quad (83)$$

$$t_2=-2\left(n_2^2-n_{\rm ex}^2+\zeta\chi_{\rm ex}\right)/(n_1-n_2)\,D, \quad (84)$$

$$r=-\left(1+\chi_b+\zeta\chi_{\rm ex}+n_1n_2-n_1-n_2\right)/D, \quad (85)$$

$$P_y^{\mathrm{ex}\,(0)} = \epsilon_0 \chi_{\mathrm{ex}} \zeta E_0 \,(t_1 + t_2)\,/\,2, \tag{86}$$

$$D \equiv 1 + \chi_b + \zeta \chi_{\mathrm{ex}} + n_1 n_2 + n_1 + n_2, \tag{87}$$

where $n_1 \equiv k_1/k_0$, $n_2 \equiv k_2/k_0$ are refractive indices of the two transverse waves, and $n_{\mathrm{ex}} \equiv k_{\mathrm{ex}}/k_0$ is a convenient symbol.

Our solution is significantly different from those obtained by using boundary conditions listed in Ref. 19. In the next subsection, we show that our solution is equivalent to that which would be obtained using an inhomogeneous ABC by the real-space method. It also contains the property of the surface, ζ, which is a function of ℓ and a. ℓ is close to $1/2$.[35] Therefore by fitting to the experimental data one can obtain the parameter a, the surface layer thickness. With the parameter ζ determined by comparison to experiment the value of the exciton polarization at surface, $P_y^{\mathrm{ex}\,(0)}$, is given by Eq. (86). This result has not been obtained by any previous theory. As explained earlier, $P_y^{\mathrm{ex}\,(0)}$ represents an average value of the quantity in the surface layer in a macroscopic theory.

As seen from the above procedure, our **k**-space method obtains the poles (dispersion relations) of the electric field from the wave equation and subsequently the functional form of the electric field. Just as with real-space methods, the complete solution by our **k**-space method also requires the knowledge of the asymptotic behavior of the solution, which, in the case studied here is the lack of a backward wave in the medium. However, in **k** space, both parts of the electric field, $E^{(+)}$ (relating to the medium) and $E^{(-)}$ (relating to the vacuum), appear in the same equation. Therefore, there is no need to use a boundary condition to connect the two at a surface, there being no surface in **k** space. In fact, in the process of obtaining the solution, our **k**-space method leads to conditions that are equivalent to the Maxwell boundary conditions as seen from Eqs. (73) and (74). Further, the terms that include the surface layer properties are also in the equation and they are obtained simultaneously with the transmission and reflection coefficients. This allows our theory to account for the surface layer effects on the long-wavelength dynamics, an important accomplishment of this method.

D. ABC from spatial perspective

In order to interpret and compare the above solution from our **k**-space method with that of previous macroscopic theories, we transfer the exciton polarization expressed in Eq. (63) into real space

$$P_y^{\mathrm{ex}}(z>0) = \epsilon_0 \int \chi^{\mathrm{ex}}(k_z,\omega)\, E_y^{(+)}(k_z,\omega)\, e^{ik_z z} dk_z - \frac{\epsilon_0}{2i\pi} \int \frac{k_0 b_y^{(1)} + k_z b_y^{(2)}}{k_z^2 - k_{\mathrm{ex}}^2} e^{ik_z z} dk_z \tag{88a}$$

$$= \epsilon_0 \chi_{\mathrm{ex}} E_0 k_\Omega^2 \left(\frac{t_1 e^{ik_1 z}}{k_1^2 - k_{\mathrm{ex}}^2} + \frac{t_2 e^{ik_2 z}}{k_2^2 - k_{\mathrm{ex}}^2} \right) - \frac{\epsilon_0 E_0}{2k_{\mathrm{ex}}} \left[\chi_{\mathrm{ex}} k_\Omega^2 \left(\frac{t_1}{k_1 - k_{\mathrm{ex}}} + \frac{t_2}{k_2 - k_{\mathrm{ex}}} \right) + k_0 \bar{b}_y^{(1)} + k_{\mathrm{ex}} \bar{b}_y^{(2)} \right] e^{ik_{\mathrm{ex}} z}. \tag{88b}$$

The surface term in Eq. (88a) was absent from the corresponding equation in the real-space method.[6–9] Since the corresponding equation formed an initial assumption of that method, we see no way of anticipating the form of the additional surface term from that approach. By using Eqs. (75), (76), and (80) we find $k_0 \bar{b}_y^{(1)} + k_{\mathrm{ex}} \bar{b}_y^{(2)} + \chi_{\mathrm{ex}} k_\Omega^2 [t_1/(k_1 - k_{\mathrm{ex}}) + t_2/(k_2 - k_{\mathrm{ex}})] = 0$, thus forcing the off-dispersion-relation exp $(ik_{\mathrm{ex}} z)$ term to vanish identically outside the surface layer. This equation is the analog to the ABC of the real-space method but needs significant reexpression to appear as a boundary condition. An alternate algebraic procedure is to obtain the ABC from the bulk form of the exciton polarization that we now have

$$P_y^{\mathrm{ex}}(z>0) = \epsilon_0 \chi_{\mathrm{ex}} k_\Omega^2 E_0 [t_1 e^{ik_1 z}/(k_1^2 - k_{\mathrm{ex}}^2) + t_2 e^{ik_2 z}/(k_2^2 - k_{\mathrm{ex}}^2)]. \tag{89}$$

It only contains the two bulk waves allowed by the dispersion relation.

This reveals a subtle mistake in previous real-space treatments.[6–9] The corresponding nonlocal kernel in Eq. (88a) of those theories yields an extended, off-dispersion-relation wave [exp$(ik_{\mathrm{ex}} z)$] which did not identically vanish. Of course, those treatments realized that there should be no such wave in the bulk medium. By various techniques (conversion to a four-order wave equation or an extinction-theorem-like calculation) they showed that the term involving exp$(ik_{\mathrm{ex}} z)$ can be made to vanish. The condition of vanishing becomes their ABC. Because the surface terms in Eq. (88) involving $\bar{b}_y^{(1)}$ and $\bar{b}_y^{(2)}$ are not included in their formulation, their ABC is then just the vanishing of the other two terms in the coefficient of exp$(ik_{\mathrm{ex}} z)$ in Eq. (88b) and so is incomplete.

Equation (89) can be used to derive the macroscopic boundary condition needed in the coordinate space approach. By letting z approach zero we have $P_y^{\mathrm{ex}}(0^+) = \epsilon_0 E_0 \chi_{\mathrm{ex}} k_\Omega^2 [t_1/(k_1^2 - k_{\mathrm{ex}}^2) + t_2/(k_2^2 - k_{\mathrm{ex}}^2)]$ which is the sum of the amplitudes of the two bulk waves. Note that $P_y^{\mathrm{ex}}(0^+) \neq P_y^{\mathrm{ex}\,(0)}$, the left side being the limiting value of the bulk solution and the right side being the effective average value in the surface layer. If we transform the electric field to real space, the electric field inside the medium is

$$E(z>0) = E_0 t_1 e^{ik_1 z} + E_0 t_2 e^{ik_2 z}, \tag{90}$$

from which we find $E_y(0^+) = E_0(t_1 + t_2)$. From Eq. (81) we then obtain the macroscopic ABC for a Frenkel exciton near resonance as

$$P_y^{\mathrm{ex}}(0^+) = \epsilon_0 \chi_{\mathrm{ex}} \zeta E_y(0^+) . \quad (91)$$

This differs with Pekar's ABC, $P_y^{\mathrm{ex}}(0^+) = 0$, which was thought to be justified by the microscopic "no escape" boundary condition. On the contrary, using Pekar's ABC macroscopically is quite different from and inconsistent with using it microscopically where it is meaningful. The exact microscopic solution of the exciton polarization must contain evanescent waves besides the two bulk waves.[36] These evanescent waves count significantly within a few atomic layers from the surface, and contribute significantly to the polarization in a microscopic boundary condition. Only far away from the surface where the evanescent waves die (almost) completely does the microscopic solution become the same as the macroscopic solution. It is these evanescent waves that are responsible for the difference between $P_y^{\mathrm{ex}}(0^+)$ and $P_y^{\mathrm{ex}\,(0)}$. However, a macroscopic theory, by its nature, has no way to obtain these evanescent waves which describe the details of the exciton polarization on an atomic scale near the surface. This is why our macroscopic method, like all the other macroscopic methods, can only obtain the exciton polarization outside this macroscopically infinitesimal but microscopically finite surface layer, as seen in Eq. (89). On the other hand, our macroscopic theory can and does contain extra elements (surface terms) such as $P_y^{\mathrm{ex}\,(0)}$, to describe, on average, the surface layer properties as altered by the evanescent waves. This leads to including the surface layer properties in our boundary condition (91) through the ζ factor. This ability to treat the effect of the surface layer on the long-wavelength dynamics, without resorting to a detailed microscopic solution there, is an important characteristic of the **k**-space method.

It should be noted that if $a = 0$ then $\zeta = 0$ and the Pekar boundary condition $P^{\mathrm{ex}}(0^+) = 0$ is recovered. However from the coherent wave theory derivation it is clear that $a = 0$ corresponds to a complete absence of wave-vector dispersion (infinite mass, zero mobility). Thus, we conclude that the Pekar boundary condition cannot apply to a Frenkel exciton whose wave-vector dispersion is significant. We surmise the same conclusion applies approximately to Wannier excitons.

Bishop and Maradudin[31] gave a real-space Lagrangian treatment of the exciton-polariton problem in which they invoke a step function cutoff of basic material properties as we do. A derivative of the step function gives them a Dirac delta-function term in their dynamical equation which they eliminate by requiring its coefficient to vanish. This gives them a boundary condition at the medium surface, but it is one involving fields evaluated at the surface, or in our notation, $f^{(0)}$ quantities. However, to use it as a boundary condition they interpreted the quantities as $f(0^+)$. Our development has shown these quantities are not equal. This discrepancy is at the heart of the difficulty of using a real-space method.

VI. DISCUSSION AND CONCLUSION

In this paper, we present a first-principles derivation of the dynamic equation of the dielectric or HT model in a bounded, wave-vector dispersive medium based on a general macroscopic Lagrangian theory. We also derive the constitutive equation for Frenkel exciton polarization in a bounded medium from coherent wave theory. Under the continuum limit we show that the Lagrangian and coherent wave methods agree on the constitutive equation for the Frenkel exciton polarization and that it has the same form as that of the dielectric or HT model, thus proving the two models to be equivalent and that the HT model is valid for the Frenkel exciton, not the Wannier exciton as long believed. In the process of deriving the equation we find that the effect of the surface on the internal structure of the exciton that causes a change of exciton binding energy is comparable to the mobility effect as a cause of wave-vector dispersion in the surface layer.

A new **k**-space method introduced in the preceding paper is applied here to study the macroscopic resonant wave-vector dispersive phenomena in a bounded medium. It is a mathematical method tailored for a long-wavelength physical problem that involves wave-vector dispersion. We find that the macroscopic nonlocal constitutive relation between the exciton polarization and the electric field in a bounded medium must contain surface terms. We use our **k**-space method to obtain a unique solution for transmission and reflection coefficients without using any boundary conditions, let alone an ABC. We also find that the surface exciton polarization is obtained simultaneously with the transmission and reflection coefficients. Analogous conceptually to the quantum scattering theory, our theory has the ability to treat the effect of the surface layer on the long-wavelength dynamics without resorting to a detailed microscopic (near field) solution there. Once transformed into coordinate space, our **k**-space method obtains the macroscopic ABC that naturally includes the surface properties of the model.

It is generally regarded that Pekar's boundary condition is correct for the Frenkel exciton. However, we show that Pekar's boundary condition corresponds to ignoring the wave-vector dispersion of the Frenkel exciton, the property under study. It is also generally regarded that Pekar's boundary condition can be derived from the "no escape" boundary condition on the exciton wave function. However, we show that there is a difference in using it microscopically and macroscopically. A general microscopic solution must contain evanescent wave components besides the extended (bulk) wave components. Therefore, the microscopic boundary solution is imposed upon all these components at the surface while the macroscopic boundary condition is only imposed upon the extended (bulk) wave components. Thus, we believe, it is incorrect to use Pekar's boundary condition macroscopically.

There are a few quantum-mechanical works done specifically for Frenkel excitons in a half-space medium.[15,37] The model proposed by Mead and Philpott[15] is the discretized version of the effective surface potential model used by Hopfield and Thomas[4] to discuss Wannier excitons. As shown in Sec. III by our coherent wave theory this model needs modification. Hyzhnyakov, Maradudin, and Mills[37] introduced a Frenkel ex-

citon model that is similar to ours but more complicated in the sense that it also includes the contribution of the unbound exciton states to the exciton polarization. Because of this, the exciton polarization of their model is more complex than that of the HT model even in the bulk medium. They carried out the calculation for the exciton susceptibility microscopically, which reveals the extremely complex nature of a Frenkel exciton near the surface. However the transmission and reflection coefficients were not obtained from this microscopic susceptibility. Unlike the microscopic real-space treatment that must deal with such a complex phenomenon near the surface, our theory only accounts for the surface layer effect to the long-wavelength optics. Thus our macroscopic method bypasses the difficulty faced in the microscopic real-space method.

Most ABC's listed in Ref. 19 are for Wannier excitons. They can be considered derived without accounting for the effects from distorted internal structure near the surface.[10,11] D'Andrea and DelSole included such effects[16] in their ABC. They suggested that the ABC for a Frenkel exciton may be obtained from the ABC for a Wannier exciton by letting the thickness of the "dead layer" approach zero. However, they cautioned that the effective-mass approximation for the electron and hole in a Wannier exciton does not apply to those in a Frenkel exciton. Thus such a limit is suspect. Also, since the "dead layer" is proportional to the size of an exciton, and (roughly speaking) the smaller the exciton is, the less mobile the exciton is, it is not clear whether the effective mass would approach infinity as the thickness of the "dead layer" approaches zero. If that is the case, as seen from our derivation for a Frenkel exciton, their conclusion for Frenkel excitons may need altering.

In conclusion our work (i) introduces a new **k**-space method for the long-wavelength exciton-polariton problem of transmission/reflection that uses no boundary conditions; (ii) derives the need for surface terms in the constitutive relation of the exciton polarization; (iii) obtains a complete solution to the transmission/reflection problem near a Frenkel exciton resonance; (iv) reveals that the finite size of a Frenkel exciton and the consequent surface layer effect cannot be neglected (contrary to the generally held belief that the size of a Frenkel exciton can be simply set to zero); (v) deepens the understanding of the distinction between macroscopic and microscopic boundary conditions; and (vi) obtains a new form of the macroscopic ABC needed in real-space treatments of the optics problem of a Frenkel exciton near resonance.

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APPENDIX

The problem of encountering a singularity in constructing the boundary conditions is inevitable in a wave-vector dispersive bounded medium. It can be illustrated by constructing the Maxwell boundary condition from Eq. (13) in the traditional "pillbox" way using a simple origin of linear wave-vector dispersion, the quadrupolarization. Let us regard the material surface not as a mathematically abrupt discontinuity but rather as a rapidly varying and continuous transition layer of thickness Δl in which all the material properties drop continuously to zero. In such a layer, **E**, **P**, and **Q** vary continuously. Now consider a small "pillbox" whose flat and parallel ends are coincident with the boundaries of this transition layer at a given instant of time. We can apply Gauss's theorem to a volume integral of Eq. (13) over the pill box obtaining

$$\int_A \mathbf{D}\cdot\mathbf{n}\,da = 0 \tag{A1}$$

where $\mathbf{n}$ is the unit outward vector normal to an element of surface of the pillbox whose area is da. The lateral extent of the flat end surfaces of the pillbox is small enough that **E**, **P**, and **Q** can be taken as constants over each one. However, the existence of $\nabla\cdot\mathbf{Q}$ in **D**, in Eq. (15), makes things far more complicated. Because **Q** contains a material property, the quadrupole moment, a divergence of a rapidly varying material property appears. It can be taken as a constant at the flat surfaces of the two ends of the pillbox ($\mathbf{n}^o$ and $\mathbf{n}^i$ are two corresponding normals and $\mathbf{n}^o = -\mathbf{n}^i$) so that we can express Eq. (A1) as

$$\mathbf{D}^o\cdot\mathbf{n}^o + \mathbf{D}^i\cdot\mathbf{n}^i + \int_{\text{side wall}} \mathbf{D}\cdot\mathbf{n}\,da = 0. \tag{A2}$$

However, if we shrink the transition layer thickness and the pillbox height to zero simultaneously, the side-wall contribution becomes indeterminate because the $\partial\mathbf{Q}/\partial n$ part of **D** becomes infinite while the side wall area goes to zero. Thus the pillbox procedure fails for a wave-vector dispersive term.

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