PHYSICAL REVIEW B VOLUME 11, NUMBER 8 15 APRIL 1975

# Nonlocal dielectric susceptibility of a semi-infinite insulator

V. V. Hyzhnyakov

*Institute of Physics and Astronomy, Academy of Sciences of the Estonian S. S. R., Tartu, Estonia, Union of Soviet Socialist Republics*

A. A. Maradudin* and D. L. Mills*

*Department of Physics, University of California, Irvine, California 92664*

(Received 12 August 1974)

The excitonic contribution to the dielectric susceptibility of a semi-infinite simple cubic semiconductor bounded by a (001) surface is calculated in the tight-binding approximation. The electron and hole hopping integrals in the Hamiltonian for the system couple only nearest-neighbor sites, and the Coulomb interaction between the electron and hole occurs at a single site. A pair of free surfaces is created in an infinitely extended crystal by setting to zero the electron and hole hopping integrals connecting sites on opposite sides of a fictitious plane normal to the [001] direction, but containing no atoms itself. The integral equation for the two-particle Green's function in terms of which the susceptibility is expressed is solved analytically for frequencies in the excitonic regime. The dispersion relation for surface excitons is obtained, and the spatial variation of the polarization in the crystal induced by a spatially uniform macroscopic field is determined from our results.

## I. INTRODUCTION

When the optical properties of a crystal are analyzed, one presumes frequently that the material may be described by a frequency-dependent complex dielectric tensor $\epsilon_{ij}(\omega)$. However, the dielectric tensor may depend on the wave vector $\vec{k}$ of the electromagnetic field as well as on its frequency. In practice, the wave-vector dependence of the dielectric tensor can assume particular importance for frequencies near an exciton absorption line in a semiconducting or insulating crystal. This is because the effective mass of the exciton is often small, and its excitation energy can depend significantly on wave vector by virtue of the contribution from the center-of-mass motion.

When the dielectric tensor depends on wave vector, then it is a short exercise[1] to show that the displacement field $\vec{D}(\vec{x},t)$ [and the electric-dipole moment per unit volume $\vec{P}(\vec{x},t)$] do not depend on the value of the electric field $\vec{E}(\vec{x},t)$ only at the point $\vec{x}$, but rather on an average of the electric field over a certain small volume centered at $\vec{x}$. When this is the case, one says that spatial dispersion is present.

Over the years, there have been a large number of theoretical studies of the effect of spatial dispersion on the reflectivity of semiconductors near exciton absorption lines.[2] It is well known that the standard boundary conditions (conservation of tangential components of $\vec{E}$ and $\vec{H}$, for example) fail to provide sufficient information from which the reflectivity may be computed. An additional boundary condition is required.[2] While recent work has emphasized that Maxwell's equations implicity contain the additional boundary condition when the full information in the nonlocal form of Maxwell's equations is utilized,[3–5] a realistic calculation of the reflectivity requires knowledge of the nature of the nonlocal response of the crystal to an applied electric field very close to the surface. This problem has yet to be fully discussed, and the present paper is devoted to exploration of one aspect of it, within the framework of a simple model for which many calculations may be performed by analytic methods.

An early attempt to study the effect of a surface on the polarization induced in a semiconductor by an external electric field is the work of Mahan and Hopfield.[6] These authors argued that the exciton is excluded from a thin layer near the surface by repulsive exciton-surface interactions. The reflectivity spectra calculated from this model are in very good accord with the data on CdS.[7] More recently, a rather different scheme has been proposed by Zeyher *et al.*[4] If we let $\chi_0(\vec{x}-\vec{x}';\omega)$ be the nonlocal electric susceptibility of the bulk crystal, then Zeyher *et al.* assume that the role of the surface is to reflect the exciton with reflection amplitude $R$. The nonlocal electric susceptibility $\chi(\vec{x},\vec{x}';\omega)$ of the semi-infinite crystal is presumed to have the form

$$\chi(\vec{x},\vec{x}';\omega)=\chi_0(\vec{x}_\parallel-\vec{x}_\parallel,z-z';\omega)+R\chi_0(\vec{x}_\parallel-\vec{x}'_\parallel,z+z';\omega), \tag{1.1}$$

where in this last statement the $z$ direction is normal to the surface, and $\vec{x}_\parallel$ denotes the projection of $\vec{x}$ onto the plane parallel to the surface.

As one of us has pointed out recently,[8] the description of the interaction of the exciton with the surface appears incomplete in one regard. In each calculation, the exciton is presumed to interact with the surface as a single entity, which moves in some presumed external potential. In their discussion, Mahan and Hopfield argue that this potential is long ranged, and suggest that the repulsive image potential experienced by the exciton is an important contribution to the potential. Zehyer *et al.*[4] evidently regard the effective potential as a short-ranged one.

Actually, the exciton is a composite entity which is composed of both an electron and a hole, both of which interact with the surface separately. The purpose of the present paper is to derive the form of the nonlocal susceptibility for a model crystal within the framework of a model that fully recognizes the composite nature of the exciton.

As discussed earlier,[8] one may appreciate the nature of the problem by inspection of the diagrams which describe the interactions of the exciton with the surface. Rather than consider the exciton itself, the point is readily illustrated by considering a free particle-hole pair. In Fig. 1 we show the propagation of a particle-hole pair from a point $\vec{x}$ to a second point $\vec{x}'$, in the presence of the surface. The diagram (a) describes direct propagation of the excitation from $\vec{x}$ to $\vec{x}'$. If the interaction between the electron and hole and the surface is regarded as short ranged, this diagram contributes the term $\chi_0(\vec{x}_\parallel - \vec{x}'_\parallel, z - z'; \omega)$ to the right-hand side of Eq. (1.1). If we examine the diagram in (d), then to the observer at $\vec{x}'$, the excitation appears to arrive at $\vec{x}'$ after emission from a source point outside the crystal. This diagram contributes a term of the form $R\chi_0(\vec{x}_\parallel - \vec{x}'_\parallel; z + z'; \omega)$, if the electron-surface and hole-surface interaction are taken to be short ranged. The diagrams in Figs. 1(b) and 1(c) also contribute to the nonlocal susceptibility, and their contributions have been omitted from Eq. (1.1) These diagrams (in the case of the interaction of an excition with the surface) describe interference between the electron and hole waves, and they have their physical origin in the composite nature of the exciton.

As remarked earlier, in the present paper we wish to present a microscopic derivation of the form of the nonlocal susceptibility of a semi-infinite model crystal. We set up and work within the framework of a model that is sufficiently simple that analytic methods may be utilized in the major part of the calculation. Our purpose is to examine the form of the nonlocal susceptibility within the framework of a model that includes all four diagrams of Fig. 1, with the aim of exploring the range of validity of simple phenomenological expressions such as Eq. (1.1). While the model we use is a very simple one, and cannot be expected to be applicable to real crystals, within it we may explore rather completely the conditions under which various simple forms for the nonlocal electric susceptibility apply.

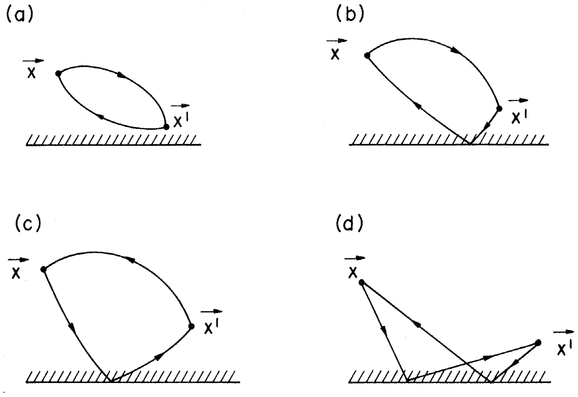

FIG. 1. Schematic illustration of the interaction of a particle-hole pair with a surface.

## DERIVATION OF NONLOCAL SUSCEPTIBILITY

The physical system we consider is a simple cubic crystal of lattice parameter $a_0$, in which the atomic positions are given by the vectors

$$\vec{x}(l) = l_x \vec{a}_1 + l_y \vec{a}_2 + l_z \vec{a}_3, \tag{2.1}$$

where the primitive translation vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ are

$$\vec{a}_1 = (a_0, 0, 0), \quad \vec{a}_2 = (0, a_0, 0), \quad \vec{a}_3 = (0, 0, a_0), \tag{2.2}$$

and $l_x$, $l_y$, $l_z$ are three integers to which we refer collectively as $l$. We assume initially that all lattice point functions in our work obey periodic boundary conditions, with the periodicity volume being a macrocrystal whose edges are defined by $L\vec{a}_1$, $L\vec{a}_2$, $L\vec{a}_3$, so that the total number of atoms in this volume is $L^3 = N$. A pair of adjacent free surfaces will be created in this cyclic crystal, at the planes $l_z = 0$ and $l_z = 1$, by setting equal to zero all interactions between atoms on opposite sides of a fictitious plane midway between these two planes.

Our starting point is the following Hamiltonian for the interacting electron and hole:

$$H = E_g \sum_l b^\dagger(l) b(l) + \sum_{ll'} \gamma_B(ll') b^\dagger(l) b(l') - E_a \sum_l a^\dagger(l) a(l) - \sum_{ll'} \gamma_A(ll') a^\dagger(l) a(l') + u_0 \sum_l a^\dagger(l) a(l) b^\dagger(l) b(l). \tag{2.3}$$

In this expression $b^\dagger(l)$ and $b(l)$ are electron creation and destruction operators at the site $l$, while $a^\dagger(l)$ and $a(l)$ are the corresponding hole operators. $\gamma_B(ll')$ and $\gamma_A(ll')$ are "hopping" integrals associated with the transfer of an electron or a hole from the site $l'$ to the site $l$, respectively. The last term in the Hamiltonian described the interaction between the electron and the hole, which is assumed to be so localized that it is nonvanishing only if both particles are at the same site. The presence of a free surface on the crystal is reflected implicitly in the forms of the coefficients $\{\gamma_A(ll')\}$

and $\{\gamma_B(ll')\}$, for which explicit expressions will be given below.

The electric-dipole-moment operator for the crystal is

$$M_\alpha = -e\int d^3x\, \Psi^\dagger(\vec{x}) x_\alpha \Psi(\vec{x}), \quad \alpha = x, y, z \tag{2.4}$$

where $e$ is the magnitude of the electronic charge and where the field operator $\Psi(\vec{x})$ can be expanded as

$$\Psi(\vec{x}) = \sum_l \varphi_A(\vec{x} - \vec{x}(l)) a(l) + \sum_l \varphi_B(\vec{x} - \vec{x}(l)) b(l), \tag{2.5}$$

with $\varphi_A(\vec{x})$ an $s$-like orbital and $\varphi_B(\vec{x})$ a $p_z$-like orbital. If we keep only the contribution to the dipole-moment operator from interband transitions, and ignore the overlap of orbitals centered on different sites, we obtain for $M_z$

$$M_z = \sum_l M_z(l), \tag{2.6a}$$

where

$$M_z(l) = -em O(l), \tag{2.6b}$$

with

$$O(l) = a^\dagger(l) b(l) + b^\dagger(l) a(l) = O^\dagger(l) \tag{2.6c}$$

and

$$m = \int d^3x\, \varphi_A(\vec{x}) z \varphi_B(\vec{x}). \tag{2.6d}$$

With a spatially varying electric field of the form

$$\vec{E}^-(l;\omega) e^{-i\omega t} + \vec{E}^+(l;\omega) e^{i\omega t}, \tag{2.7}$$

with $\vec{E}^-(l;\omega) = [\vec{E}^+(l;\omega)]^*$ acting on the crystal, the expectation value of the dipole moment induced at the $l$th site can be expressed in the form

$$\langle M_z(l;t)\rangle = a_0^3 \sum_{l'} \chi_{zz}(ll';\omega) E_z^-(l';\omega) e^{-i\omega t + \eta t} + a_0^3 \sum_{l'} \chi_{zz}^*(ll';\omega) E_z^+(l';\omega) e^{i\omega t + \eta t}. \tag{2.8}$$

In this expression $\eta$ is an adiabatic switching parameter. Equation (2.8) gives the dipole moment induced at the site $l$ by the electric field (2.7). The volume per lattice site in the simple cubic crystal we are considering here is $a_0^3$. Consequently, the dipole moment per unit volume, or polarization, induced at the site $l$ is

$$P_z(l;t) = (1/a_0^3)\langle M_z(l;t)\rangle = P_z^-(l;\omega) e^{-i\omega t + \eta t} + P_z^+(l;\omega) e^{i\omega t + \eta t}, \tag{2.9a}$$

where

$$P_z^-(l;\omega) = \sum_{l'} \chi_{zz}(ll';\omega) E_z^-(l';\omega), \tag{2.9b}$$

$$P_z^+(l;\omega) = \sum_{l'} \chi_{zz}^*(ll';\omega) E_z^+(l';\omega). \tag{2.9c}$$

The nonlocal susceptibility $\chi_{zz}(ll';\omega)$ appearing in Eqs. (2.8) and (2.9), with which we will be concerned in what follows, is given by

$$\chi_{zz}(ll';\omega) = -\frac{e^2 m^2}{\hbar a_0^3} [\hat{G}(lll'l';\omega + i\eta) + \hat{G}(l'l'll; -\omega - i\eta)]. \tag{2.10}$$

Here $\hat{G}(l_1 l_2 l_3 l_4; E)$ is the Fourier transform with respect to time of the two-particle (retarded) Green's function $G(l_1 l_2 l_3 l_4; t)$:

$$\hat{G}(l_1 l_2 l_3 l_4; E) = \int_{-\infty}^{\infty} dt\, e^{iEt} G(l_1 l_2 l_3 l_4; t), \tag{2.11a}$$

$$G(l_1 l_2 l_3 l_4; t) = -i\theta(t)\langle [a^\dagger(l_1;t) b(l_2;t), b^\dagger(l_3;0) a(l_4;0)]\rangle, \tag{2.11b}$$

$\Theta(t)$ is the Heaviside unit step function, and the angular brackets $\langle\cdots\rangle$ denote an average with respect to the canonical ensemble defined by the Hamiltonian $H$, Eq. (2.3).

If we obtain the equation of motion obeyed by $G(l_1 l_2 l_3 l_4; t)$, and decouple it at the earliest possible stage, we obtain

$$\begin{aligned} i\hbar \frac{d}{dt} G(l_1 l_2 l_3 l_4; t) = {} & \hbar\delta(t)[\delta_{l_2 l_3}\langle a^\dagger(l_1) a(l_4)\rangle - \delta_{l_1 l_4}\langle b^\dagger(l_3) b(l_2)\rangle] + (E_g + E_a) G(l_1 l_2 l_3 l_4; t) + \sum_l \gamma_A(l_1 l) G(l l_2 l_3 l_4; t) \\ & + \sum_l \gamma_B(l_2 l) G(l_1 l l_3 l_4; t) + u_0[n_A(l_2) - n_B(l_1)] G(l_1 l_2 l_3 l_4; t) + u_0[\langle b^\dagger(l_1) b(l_2)\rangle G(l_1 l_1 l_3 l_4; t) \\ & - \langle a^\dagger(l_1) a(l_2)\rangle G(l_2 l_2 l_3 l_4; t)], \end{aligned} \tag{2.12a}$$

where

$$n_A(l) = \langle a^\dagger(l) a(l)\rangle, \quad n_B(l) = \langle b^\dagger(l) b(l)\rangle. \tag{2.12b}$$

To solve Eq. (2.12a) we introduce the auxiliary Green's function $G_0(l_1 l_2 l_3 l_4; t)$ as the solution of the equation

$$i\hbar\frac{d}{dt}G_0(l_1l_2l_3l_4;t)=\hbar\delta(t)[\delta_{l_2l_3}\langle a^\dagger(l_1)a(l_4)\rangle-\delta_{l_1l_4}\langle b^\dagger(l_3)b(l_2)\rangle]+(E_g+E_a)G_0(l_1l_2l_3l_4;t)$$

$$+\sum_l\gamma_A(l_1l)G_0(ll_2l_3l_4;t)+\sum_l\gamma_B(l_2l)G_0(l_1ll_3l_4;t)+u_0[n_A(l_2)-n_B(l_1)]G_0(l_1l_2l_3l_4;t)\,. \tag{2.13}$$

It follows that the Fourier transforms of these two Green's functions are related by

$$\hat{G}(l_1l_2l_3l_4;E)=\hat{G}_0(l_1l_2l_3l_4;E)-\frac{u_0}{\hbar}\times\sum_{l_1'}\hat{G}_0(l_1l_2l_1'l_1';E)\hat{G}(l_1'l_1'l_3l_4;E)\,. \tag{2.14}$$

This relation is quite general. It holds for an infinitely extended crystal as well as for a semi-infinite crystal. In the latter case the sum on $l_1'$ extends only over the semi-infinite crystal.

The equation of motion of $G_0(l_1l_2l_3l_4;t)$ can be obtained alternatively by starting from the Hamiltonian

$$H_0=\sum_l[E_g+u_0n_A(l)]b^\dagger(l)b(l)+\sum_{ll'}\gamma_B(ll')b^\dagger(l)b(l')-\sum_l[E_a-u_0n_B(l)]a^\dagger(l)a(l)-\sum_{ll'}\gamma_A(ll')a^\dagger(l)a(l')\,, \tag{2.15}$$

and introducing the function

$$G_0(l_1l_2l_3l_4:t)=-i\,\theta(t)\{-\langle b^\dagger(l_3;0)b(l_2;t)\rangle_0\times\langle[a^\dagger(l_1;t)\,,\,a(l_4;0)]_+\rangle_0+\langle a^\dagger(l_1;t)a(l_4;0)\rangle_0\times\langle[b^\dagger(l_3;0)\,,\,b(l_2;t)]_+\rangle_0\}\,, \tag{2.16}$$

where averages with respect to the Hamiltonian $H_0$ are denoted by $\langle\cdots\rangle_0$ and $[A,B]_+$ denotes the anticommutator of the operators $A$ and $B$.

It is readily verified that the function $G_0(l_1l_2l_3l_4;t)$ defined by Eq. (2.16) obeys the equation of motion, Eq. (2.13), when time derivatives are calculated by means of commutators with respect to the Hamiltonian $H_0$, and the equal time averages $\langle a^\dagger(l_1)a(l_4)\rangle$, $\langle b^\dagger(l_3)b(l_2)\rangle$, $n_A(l_2)$, and $n_B(l_1)$ appearing in the latter equation are evaluated with respect to $H_0$ rather than $H$.

If we now introduce the two spectral densities $\rho_A(l_1l_4;\omega)$ and $\rho_B(l_3l_2:\omega)$ by

$$\langle a^\dagger(l_1;t)a(l_4;0)\rangle_0=\int_{-\infty}^{\infty}d\omega e^{i\omega t}\rho_A(l_1l_4;\omega)\,, \tag{2.17a}$$

$$\langle b^\dagger(l_3;0)b(l_2;t)\rangle_0=\int_{-\infty}^{\infty}d\omega e^{-i\omega t}\rho_B(l_3l_2;\omega)\,, \tag{2.17b}$$

we find that the Fourier transform $\hat{G}(l_1l_2l_3l_4;E)$ of the Green's function defined by Eq. (2.16) can be represented in the form

$$\hat{G}(l_1l_2l_3l_4;E)=\int_{-\infty}^{\infty}d\omega_1\int_{-\infty}^{\infty}d\omega_2\frac{e^{\beta\hbar\omega_2}-e^{\beta\hbar\omega_1}}{E-\omega_1-\omega_2}\times\rho_A(l_1l_4;\omega)\rho_B(l_3l_2;\omega_2)\,, \tag{2.18}$$

where $E$ must be understood to be a complex variable.

The spectral densities (2.17) are obtained from the relations

$$\rho_A(l_1l_4;\omega)=\frac{1}{2\pi i}\frac{1}{e^{\beta\hbar\omega}+1}[\hat{g}_A(l_1l_4;-\omega-i0)-\hat{g}_A(l_1l_4;-\omega+i0)]\,, \tag{2.19a}$$

$$\rho_B(l_3l_2;\omega)=\frac{1}{2\pi i}\frac{1}{e^{\beta\hbar\omega}+1}[\hat{g}_B(l_3l_2;\omega-i0)-\hat{g}_B(l_3l_2;\omega+i0)]\,, \tag{2.19b}$$

where $\hat{g}_A(l_1l_4;E)$ and $\hat{g}_B(l_3l_2;E)$ are the Fourier transforms of the single-particle Green's functions

$$g_A(l_1l_4;t)=-i\,\theta(t)\langle[a^\dagger(l_1;t)\,,\,a(l_4;0)]_+\rangle_0\,, \tag{2.20a}$$

$$g_B(l_3l_2;t)=-i\,\theta(t)\langle[b^\dagger(l_3;0)\,,\,b(l_2;t)]_+\rangle_0\,, \tag{2.20b}$$

respectively.

To obtain $\hat{g}_A(l_1l_4;E)$ and $\hat{g}_B(l_3l_2;E)$ we assume that at the absolute zero of temperature

$$\langle a^\dagger(l_1)a(l_4)\rangle_0=\delta_{l_1l_4}\,,\quad\langle b^\dagger(l_3)b(l_2)\rangle_0=0\,,\quad n_A(l)=1\,,\quad n_B(l)=0\,. \tag{2.21}$$

These assumptions are justified by the results based on their adoption. We conjecture that they obtain also when the indicated averages are evaluated with respect to the Hamiltonian $H$, instead of with respect to $H_0$, thus making the identification of the Green's functions $G_0(l_1l_2l_3l_4;t)$ defined by Eqs. (2.13) and (2.16) complete.

With these assumptions the equations of motion obeyed by $\hat{g}_A(l_1l_4;E)$ and $\hat{g}_B(l_3l_2;E)$ are

$$(\hbar E-E_a)\hat{g}_A(l_1l_4;E)-\sum_l\gamma_A(l_1l)\hat{g}_A(ll_4;E)=\hbar\delta_{l_1l_4}\,, \tag{2.22a}$$

$$(\hbar E-E_g-u_0)\hat{g}_B(l_3l_2;E)-\sum_l\gamma_B(l_2l)\hat{g}_B(l_3l;E)=\hbar\delta_{l_2l_3}\,, \tag{2.22b}$$

where in the presence of free surfaces at the atomic planes $l_z=0$ and $l_z=1$ the hopping integrals are given by

$$\gamma_A(ll')=\gamma_A^{(0)}(ll')-\gamma_A\delta_{l_xl_x'}\delta_{l_yl_y'}(\delta_{l_z0}\delta_{l_z'1}+\delta_{l_z1}\delta_{l_z'0})\,, \tag{2.23a}$$

$$\gamma_B(ll')=\gamma_B^{(0)}(ll')-\gamma_B\delta_{l_xl_x'}\delta_{l_yl_y'}(\delta_{l_z0}\delta_{l_z'1}+\delta_{l_z1}\delta_{l_z'0})\,, \tag{2.23b}$$

with

$$\gamma^{(0)}_{A,B}(ll') = \gamma_{A,B} \quad \text{if } l \text{ and } l' \text{ are nearest neighbors}$$
$$= 0 \quad \text{otherwise.} \tag{2.24}$$

The solutions of Eqs. (2.22) for $l_{iz} \geq 1$ ($i = 1, 2, 3, 4$) are found to be

$$\hat{g}_A(l_1 l_4; E) = \frac{\hbar}{N} \sum_{\vec{q}} \frac{\exp\{i\vec{q}_{\parallel} \cdot [\vec{x}_{\parallel}(l_1) - \vec{x}_{\parallel}(l_4)]\}}{\hbar E - E_A(\vec{q})} \times \{\exp[iq_z a_0(l_{1z} - l_{4z})] - \exp[iq_z a_0(l_{1z} + l_{4z})]\} , \tag{2.25a}$$

$$\hat{g}_B(l_3 l_2; E) = \frac{\hbar}{N} \sum_{\vec{k}} \frac{\exp\{i\vec{k}_{\parallel} \cdot [\vec{x}_{\parallel}(l_3) - \vec{x}_{\parallel}(l_2)]\}}{\hbar E - E_g^0 - u_0 - E_B(\vec{k})} \times \{\exp[ik_z a_0(l_{3z} - l_{2z})] - \exp[ik_z a_0(l_{3z} + l_{2z})]\} , \tag{2.25b}$$

where $\vec{q}_{\parallel} = (q_x, q_y, 0)$, $\vec{x}_{\parallel}(l) = l_x \vec{a}_1 + l_y \vec{a}_2$, the sums extend over the first Brillouin zone of the crystal, and we have set

$$E_A(\vec{q}) = 6|\gamma_A| - 2|\gamma_A|(\cos q_x a_0 + \cos q_y a_0 + \cos q_z a_0) , \tag{2.26a}$$

$$E_B(\vec{k}) = 6|\gamma_B| - 2|\gamma_B|(\cos k_x a_0 + \cos k_y a_0 + \cos k_z a_0) , \tag{2.26b}$$

$$E_g = E_g^0 + 6|\gamma_B| . \tag{2.26c}$$

Substituting Eqs. (2.25) into Eqs. (2.19) and then into Eq. (2.18), we obtain finally for $\hat{G}_0(l_1 l_2 l_3 l_4; E)$

$$\hat{G}_0(l_1 l_2 l_3 l_4; E) = \frac{\hbar}{N^2} \sum_{\vec{q}} \sum_{\vec{k}} \frac{\exp\{i\vec{q}_{\parallel} \cdot [\vec{x}_{\parallel}(l_1) - \vec{x}_{\parallel}(l_4)]\} \exp\{-i\vec{k}_{\parallel} \cdot [\vec{x}_{\parallel}(l_2) - \vec{x}_{\parallel}(l_3)]\}}{\hbar E - E_g^0 - u_0 - E_A(\vec{q}) - E_B(\vec{k})} \{\exp[iq_z a_0(l_{1z} - l_{4z})] - \exp[iq_z a_0(l_{1z} + l_{4z})]\}\{\exp[ik_z a_0(l_{3z} - l_{2z})] - \exp[ik_z a_0(l_{3z} + l_{2z})]\} . \tag{2.27}$$

For the calculation of the susceptibility Eq. (2.10), only the Green's function $\hat{G}(lll'l'; E)$ is required. On defining

$$G(ll'; E) \equiv \hat{G}(lll'l'; E) , \tag{2.28a}$$

$$G_0(ll'; E) \equiv \hat{G}_0(lll'l'; E) , \tag{2.28b}$$

we find from Eq. (2.14) that the relation between these two new functions is

$$G(ll'; E) = G_0(ll'; E) - \frac{u_0}{\hbar} \sum_{l''} G_0(ll''; E) G(l''l'; E) . \tag{2.29}$$

We can now express $G_0(ll'; E)$ as

$$G_0(ll'; E) = \frac{1}{L^2} \sum_{\vec{Q}_{\parallel}} G_0(\vec{Q}_{\parallel} E \,|\, l_z l_z') \times \exp\{i\vec{Q}_{\parallel} \cdot [\vec{x}_{\parallel}(l) - \vec{x}_{\parallel}(l')]\} , \tag{2.30}$$

where

$$G_0(\vec{Q}_{\parallel} E \,|\, l_z l_z') = \frac{\hbar}{L^4} \sum_{\vec{q}_{\parallel}} \sum_{q_z k_z} \frac{\exp[iq_z a_0(l_z - l_z')] - \exp[iq_z a_0(l_z + l_z')]}{\hbar E - E_g^0 - u_0 - E_A(\vec{q}) - E_B(\vec{q}_{\parallel} - \vec{Q}_{\parallel}, k_z)} \{\exp[-ik_z a_0(l_z - l_z')] - \exp[-ik_z a_0(l_z + l_z')]\} . \tag{2.31}$$

If we also expand $G(ll'; E)$ in the same form,

$$G(ll'; E) = \frac{1}{L^2} \sum_{\vec{Q}_{\parallel}} G(\vec{Q}_{\parallel} E \,|\, l_z l_z') \times \exp\{i\vec{Q}_{\parallel} \cdot [\vec{x}_{\parallel}(l) - \vec{x}_{\parallel}(l')]\} , \tag{2.32}$$

then Eq. (2.29) reduces to the one-dimensional equation

$$G(\vec{Q}_{\parallel} E \,|\, l_z l_z') = G_0(\vec{Q}_{\parallel} E \,|\, l_z l_z') - \frac{u_0}{\hbar} \sum_{l_z''} G_0(\vec{Q}_{\parallel} E \,|\, l_z l_z'') \times G(\vec{Q}_{\parallel} E \,|\, l_z'' l_z') . \tag{2.33}$$

The expression (2.31) for $G_0(\vec{Q}_{\parallel} E \,|\, l_z l_z')$ can be reduced from a multiple sum to a single integral for $0 < \mathrm{Re}\,\hbar E < E_g^0 + u_0$:

$$G_0(\vec{Q}_{\parallel} E \,|\, l_z l_z') = -\hbar \int_0^{\infty} dt \exp[-t(E_g^0 + u_0 - \hbar E + 6|\gamma_A| + 6|\gamma_B|)] I_0(2\gamma_1 t) I_0(2\gamma_2 t) [I_{l_z - l_z'}(2|\gamma_A|t) I_{l_z - l_z'}(2|\gamma_B|t) - I_{l_z - l_z'}(2|\gamma_A|t) I_{l_z + l_z'}(2|\gamma_B|t) - I_{l_z + l_z'}(2|\gamma_A|t) I_{l_z - l_z'}(2|\gamma_B|t) + I_{l_z + l_z'}(2|\gamma_A|t) I_{l_z + l_z'}(2|\gamma_B|t)] , \tag{2.34}$$

where

$$2\gamma_1 = (4\gamma_A^2 + 8|\gamma_A \gamma_B| \cos Q_x a_0 + 4\gamma_B^2)^{1/2} , \tag{2.35a}$$

$$2\gamma_2 = (4\gamma_A^2 + 8|\gamma_A \gamma_B| \cos Q_y a_0 + 4\gamma_B^2)^{1/2} , \tag{2.35b}$$

and $I_n(x)$ is a modified Bessel function of the first kind. An analogous representation involving the ordinary Bessel function $J_n(x)$ obtains for $\mathrm{Re}\,\hbar E > E_g^0 + u_0$.

We see from Eq. (2.34) that $G_0(\vec{Q}_{\parallel}E\,|\,l_z l_z')$ can be written as the sum of a part that depends on $l_z$ and $l_z'$ only through their difference, and a part which has a more complicated dependence on these indices,

$$G_0(\vec{Q}_{\parallel}E\,|\,l_z l_z') = G_0^{(1)}(\vec{Q}_{\parallel}E\,|\,l_z - l_z') + G_0^{(2)}(\vec{Q}_{\parallel}E\,|\,l_z l_z') \;, \tag{2.36}$$

where

$$G_0^{(1)}(\vec{Q}_{\parallel}E\,|\,l_z - l_z') = -\hbar\int_0^\infty dt\, \exp[-t(E_g^0 + u_0 - \hbar E + 6|\gamma_A| + 6|\gamma_B|)] \times I_0(2\gamma_1 t) I_0(2\gamma_2 t) I_{l_z - l_z'}(2|\gamma_A|t) I_{l_z - l_z'}(2|\gamma_B|t) \;, \tag{2.37}$$

$$G_0^{(2)}(\vec{Q}_{\parallel}E\,|\,l_z l_z') = \hbar\int_0^\infty dt\, \exp[-t(E_g^0 + u_0 - \hbar E + 6|\gamma_A| + 6|\gamma_B|)] I_0(2\gamma_1 t) I_0(2\gamma_2 t) [I_{l_z - l_z'}(2|\gamma_A|t) I_{l_z + l_z'}(2|\gamma_B|t) + I_{l_z + l_z'}(2|\gamma_A|t) I_{l_z - l_z'}(2|\gamma_B|t) - I_{l_z + l_z'}(2|\gamma_A|t) I_{l_z + l_z'}(2|\gamma_B|t)] \;. \tag{2.38}$$

At this point, we pause to comment on the view offered by our model on the validity of the *Ansatz* in Eq. (1.1), which forms the basis of the analysis presented by Zeyher *et al.*[4] The function $G_0(\vec{Q}_{\parallel}E\,|\,l_z l_z')$ may be used to compute the nonlocal susceptibility of the model semi-infinite solid in the absence of the Coulomb interaction between the electron and hole, i.e., in a picture where only the contribution of single-particle interband excitations are included in the dielectric susceptibility, with the effect of Coulomb interactions ignored. This corresponds to the diagrams illustrated in Fig. 1, where the Coulomb interaction is ignored.

The contribution $G_0^{(1)}(\vec{Q}_{\parallel}E\,|\,l_z - l_z')$ on the right-hand side of Eq. (2.36) gives rise to the term $\chi_0(\vec{x}_{\parallel} - \vec{x}_{\parallel}', z - z'; \omega)$ on the right-hand side of Eq. (1.1). The *Ansatz* in Eq. (1.1) is then valid only if the function $G_0^{(1)}(\vec{Q}_{\parallel}E\,|\,l_z l_z')$ is a function only of the sum $l_z + l_z'$, and not of $l_z$ and $l_z'$ separately. Inspection of the terms within the brackets in Eq. (2.38) shows that this is not the case in general. The third term inside the brackets is indeed a function of only $l_z + l_z'$ [this term corresponds to the diagram in Fig. 1(d)], but the first and second terms [which give the contributions from the diagram in Figs. 1(b) and 1(c)] cannot be expressed in simple form. Thus, at this point, even though we have yet to examine the effect of the Coulomb interaction on the nonlocal susceptibility, we can appreciate from our simple model the fact that the *Ansatz* in Eq. (1.1) is not expected to be valid generally.

We now return to the problem of determining the nonlocal susceptibility in the presence of Coulomb interactions for our model.

If $\mathrm{Re}\,\hbar E$ lies in the energy gap sufficiently far from both the valence and conduction band edges that the inequality

$$\frac{E_g^0 + u_0 - \mathrm{Re}\,\hbar E}{2(|\gamma_A| + |\gamma_B|)} \gtrsim 1 \tag{2.39}$$

is satisfied, then $G_0^{(1)}(\vec{Q}_{\parallel}E\,|\,l_z - l_z')$ is a rapidly decreasing function of $|l_z - l_z'|$, and $G_0^{(2)}(\vec{Q}_{\parallel}E\,|\,l_z l_z')$ is a rapidly decreasing function of $l_z$ and $l_z'$ separately. In this limit we can take as the only nonvanishing elements of these matrices $(l_z, l_z' \geq 1)$

$$G_0^{(1)}(\vec{Q}_{\parallel}E\,|\,0) = -A(\vec{Q}_{\parallel}E), \tag{2.40a}$$

$$G_0^{(1)}(\vec{Q}_{\parallel}E\,|\,\pm 1) = -B(\vec{Q}_{\parallel}E), \tag{2.40b}$$

$$G_0^{(2)}(\vec{Q}_{\parallel}E\,|\,11) = C(\vec{Q}_{\parallel}E). \tag{2.40c}$$

The dependence of each of these coefficients on the two-dimensional wave vector $\vec{Q}_{\parallel}$ can be made more explicit by expanding $I_0(2\gamma_j t)$ in powers of $\sin^2\frac{1}{2}Q_j a_0$ $(j = x, y)$ in Eqs. (2.37) and (2.38). In this way we find

$$A(\vec{Q}_{\parallel}E) = \frac{\hbar}{2(|\gamma_A| + |\gamma_B|)} \times \left(a^{(1)}(x) - \frac{2|\gamma_A\gamma_B|}{(|\gamma_A| + |\gamma_B|)^2}\, a^{(2)}(x) g(\vec{Q}_{\parallel}) + \cdots\right) , \tag{2.41a}$$

$$B(\vec{Q}_{\parallel}E) = \frac{\hbar}{2(|\gamma_A| + |\gamma_B|)} \left(b^{(1)}(x) - \frac{2|\gamma_A\gamma_B|}{(|\gamma_A| + |\gamma_B|)^2} \times b^{(2)}(x) g(\vec{Q}_{\parallel}) + \ldots\right) , \tag{2.41b}$$

$$C(\vec{Q}_{\parallel}E) = \frac{\hbar}{2(|\gamma_A| + |\gamma_B|)} \left(c^{(1)}(x) - \frac{2|\gamma_A\gamma_B|}{(|\gamma_A| + |\gamma_B|)^2} \times c^{(2)}(x) g(\vec{Q}_{\parallel}) + \ldots\right) , \tag{2.41c}$$

where we have introduced the functions

$$x = \frac{E_g^0 + u_0 - \hbar E}{2(|\gamma_A| + |\gamma_B|)} \;, \quad g(\vec{Q}_{\parallel}) = \sin^2\tfrac{1}{2}\, Q_x a_0 + \sin^2\tfrac{1}{2}\, Q_y a_0 \;. \tag{2.42}$$

The coefficient integrals are given explicitly by

$$a^{(1)}(x) = \int_0^\infty du\, e^{-u(3+x)} I_0^2(u) I_0(\alpha u) I_0(\beta u) \;, \tag{2.43a}$$

$$a^{(2)}(x)=\int_0^{\infty} du\, e^{-u(3+x)} u\, I_0(u) I_1(u) I_0(\alpha u) I_0(\beta u)\ , \tag{2.43b}$$

$$b^{(1)}(x)=\int_0^{\infty} du\, e^{-u(3+x)} I_0^2(u) I_1(\alpha u) I_1(\beta u)\ , \tag{2.44a}$$

$$b^{(2)}(x)=\int_0^{\infty} du\, e^{-u(3+x)} u\, I_0(u) I_1(u) I_1(\alpha u) I_1(\beta u)\ , \tag{2.44b}$$

$$c^{(1)}(x)=\int_0^{\infty} du\, e^{-u(3+x)} I_0^2(u)[I_0(\alpha u) I_2(\beta u)+I_2(\alpha u) I_0(\beta u) - I_2(\alpha u) I_2(\beta u)]\ , \tag{2.45a}$$

$$c^{(2)}(x)=\int_0^{\infty} du\, e^{-u(3+x)} u\, I_0(u) I_1(u)[I_0(\alpha u) I_2(\beta u) + I_2(\alpha u) I_0(\beta u) - I_2(\alpha u) I_2(\beta u)]\ , \tag{2.45b}$$

where

$$\alpha=\frac{|\gamma_A|}{|\gamma_A|+|\gamma_B|}\ ,\quad \beta=\frac{|\gamma_B|}{|\gamma_A|+|\gamma_B|}\ . \tag{2.46}$$

It is shown in Appendix A that the solution of Eq. (2.33) for the Green's function $G(\vec{Q}_{\parallel}E\,|\,l_z l_z')$ under the assumptions made here can be represented in the form

$$G(\vec{Q}_{\parallel}E\,|\,l_z l_z')=\frac{\hbar}{u_0}\left(\delta_{l_z l_z'}-\frac{\hbar}{u_0 B}\,\frac{e^{-\xi|l_z-l_z'|}-e^{-\xi(l_z+l_z')}}{2\sinh\xi}\right)+\left(\frac{\hbar}{u_0}\right)^2 \frac{C}{B}\,\frac{e^{-\xi(l_z+l_z')}}{B+Ce^{-\xi}}\ , \tag{2.47}$$

where $\xi(\vec{Q}_{\parallel}E)$ is defined as that solution of the equation

$$\cosh\xi(\vec{Q}_{\parallel}E)=-\frac{A(\vec{Q}_{\parallel}E)-(\hbar/u_0)}{2B(\vec{Q}_{\parallel}E)} \tag{2.48}$$

whose real part is positive. The effects of the crystal surface in the result given by Eq. (2.47) are reflected in the presence of the two terms proportional to $e^{-\xi(l_z+l_z')}$.

Combining Eqs. (2.10), (2.28a), and (2.32) we find that the susceptibility $\chi_{zz}(ll';\omega)$ can be Fourier analyzed according to

$$\chi_{zz}(ll';\omega)=\frac{1}{L^2}\sum_{\vec{Q}_{\parallel}} \exp\{i\vec{Q}_{\parallel}\cdot[\vec{x}_{\parallel}(l)-\vec{x}_{\parallel}(l')]\}\times\chi_{zz}(\vec{Q}_{\parallel}\omega\,|\,l_z l_z')\ , \tag{2.49}$$

with

$$\chi_{zz}(\vec{Q}_{\parallel}\omega\,|\,l_z l_z')=-\frac{e^2m^2}{\hbar a_0^3}[G(\vec{Q}_{\parallel}\omega+i\eta\,|\,l_z l_z')+G(-\vec{Q}_{\parallel}-\omega-i\eta\,|\,l_z' l_z)]\ . \tag{2.50}$$

Now, it is readily found from Eq. (2.31) that $G_0(\vec{Q}_{\parallel}E\,|\,l_z l_z')$ is even in $\vec{Q}_{\parallel}$ and is symmetric in $l_z$ and $l_z'$. It follows from Eq. (2.33), therefore, that $G(\vec{Q}_{\parallel}E\,|\,l_z l_z')$ is also even in $\vec{Q}_{\parallel}$ and symmetric in $l_z$ and $l_z'$. Thus we can rewrite Eq. (2.50) as

$$\chi_{zz}(\vec{Q}_{\parallel}\omega\,|\,l_z l_z')=-\frac{e^2m^2}{\hbar a_0^3}[G(\vec{Q}_{\parallel}\omega+i\eta\,|\,l_z l_z')+G(\vec{Q}_{\parallel}-\omega-i\eta\,|\,l_z l_z')]\ . \tag{2.51}$$

If we then substitute Eq. (2.47) into Eq. (2.51), we obtain finally the result that

$$\chi_{zz}(\vec{Q}_{\parallel}\omega\,|\,l_z l_z')=-\frac{2e^2m^2}{u_0 a_0^3}\delta_{l_z l_z'}+\frac{\hbar e^2 m^2}{u_0^2 a_0^3}\left(\frac{e^{-\xi(+)|l_z-l_z'|}}{2B(+)\sinh\xi(+)}+\frac{e^{-\xi(-)|l_z-l_z'|}}{2B(-)\sinh\xi(-)}\right)-\frac{\hbar e^2 m^2}{u_0^2 a_0^3}\left(\frac{e^{-\xi(+)(l_z+l_z')}}{2B(+)\sinh\xi(+)}+\frac{e^{-\xi(-)(l_z+l_z')}}{2B(-)\sinh\xi(-)}+\frac{C(+)}{B(+)}\,\frac{e^{-\xi(+)(l_z+l_z')}}{B(+)+C(+)e^{-\xi(+)}}+\frac{C(-)}{B(-)}\,\frac{e^{-\xi(-)(l_z+l_z')}}{B(-)+C(-)e^{-\xi(-)}}\right)\ , \tag{2.52}$$

where by the arguments (±) we mean $(\vec{Q}_{\parallel}\pm\omega\pm i\eta)$.

The expression for the susceptibility given by Eq. (2.52) has the form obtained by Zeyher *et al.*,[4] viz., it is the sum of a function of $|l_z-l_z'|$ alone and a function of $(l_z+l_z')$ alone. However, although we will base the discussion in the remainder of this paper on the results of this section, it is shown in Appendix B that the form of the susceptibility given by Eq. (2.52) is a consequence of the assumptions represented by Eq. (2.40), in particular, that the only nonzero elements of the matrix $G_0^{(1)}(\vec{Q}_{\parallel}E\,|\,l_z-l_z')$ are those corresponding to $l_z-l_z'=0,\pm 1$. In fact, it is shown in Appendix B that if the nonzero elements of $G_0^{(1)}(\vec{Q}_{\parallel}E\,|\,l_z-l_z')$ are extended to include those for which $l_z-l_z'=\pm 2$, then the susceptibility $\chi_{zz}(\vec{Q}_{\parallel}\omega\,|\,l_z l_z')$ already possesses a more complicated dependence on $l_z$ and $l_z'$ than that found by Zeyher *et al.*, and it is that which is displayed in Eq. (2.52).

The physical interpretation of the inequality in Eq. (2.39) is the following. The quantity $E_g=E_g^{(0)}+u_0$ is the energy gap in the model, after renormalization of the gap by the Coulomb interaction. This quantity is the energy gap one would measure in an optical-absorption measurement. Thus Eq. (2.39) requires, in essence, that $E_g-\hbar E$ be large compared to sum of the width of the valence band and the conduction band. This clearly requires the energy gap to be large compared to the sum of the width of the valence band and the conduction band. It is a condition poorly satisfied in the semiconducting crystals where spatial dispersion effects have been studied in the past (e.g., CdS). In fact, if $\hbar E$ is chosen near a typical exciton energy, then $E_g - \hbar E$ is small compared to the summed bandwidths in general, and the inequality in Eq. (2.39) will be reversed. Thus we obtain a form similar to Eq. (1.1) only under conditions that are unrealistic for real crystals. As one sees explicitly from the results displayed in Appendix B, a form such as that in Eq. (1.1) becomes invalid as soon as the inequality in Eq. (2.39) is violated. While our model is a very special one, physical considerations suggest that a criterion such as that displayed in Eq. (2.39) may be required quite generally for Eq. (1.1) to be valid.

## III. SURFACE EXCITONS

The results of Sec. II enable us to obtain the dispersion relation for a surface exciton, i.e., an electron and hole bound together by their mutual Coulomb attraction, and at the same time localized in the vicinity of the surface of semi-infinite crystal.

This dispersion relation is obtained from the poles of the Green's function $G(\vec{Q}_{\parallel}E\,|\,l_z\,l_z')$ lying in the gap $0 < \mathrm{Re}\hbar E < E_g^0 + u_0$. An examination of Eq. (2.47) reveals that if $G(\vec{Q}_{\parallel}E\,|\,l_z l_z')$ has any poles in this energy range they are given by the solution of the equation

$$e^{-\xi(\vec{Q}_{\parallel}E)} = -\frac{B(\vec{Q}_{\parallel}E)}{C(\vec{Q}_{\parallel}E)} , \tag{3.1}$$

which must be solved together with Eq. (2.48).

In what follows we will assume that $E$ is real, and will denote it by $\omega$. We will find that this assumption leads to a solution of Eqs. (2.48) and (3.1) for $0 < \hbar\omega < E_g^0 + u_0$.

Since for $E$ real both $B(\vec{Q}_{\parallel}E)$ and $C(\vec{Q}_{\parallel}E)$ are positive, for small enough $|\vec{Q}|$, we set

$$\xi(\vec{Q}_{\parallel}\omega) = \xi_0(\vec{Q}_{\parallel}\omega) + i\pi, \quad \mathrm{Re}\,\xi_0(\vec{Q}_{\parallel}\omega) > 0 \tag{3.2}$$

and rewrite Eqs. (3.1) and (2.48) as

$$e^{-\xi_0(\vec{Q}_{\parallel}\omega)} = \frac{B(\vec{Q}_{\parallel}\omega)}{C(\vec{Q}_{\parallel}\omega)} , \tag{3.3a}$$

$$\cosh\xi_0(\vec{Q}_{\parallel}\omega) = \frac{A(\vec{Q}_{\parallel}\omega) - (\hbar/u_0)}{2B(\vec{Q}_{\parallel}\omega)} . \tag{3.3b}$$

If we eliminate $\xi(\vec{Q}_{\parallel}\omega)$ between Eqs. (3.3a) and (3.3b) we obtain the dispersion relation for surface excitons:

$$B^2(\vec{Q}_{\parallel}\omega) + C^2(\vec{Q}_{\parallel}\omega) = C(\vec{Q}_{\parallel}\omega)\,[A(\vec{Q}_{\parallel}\omega) - (\hbar/u_0)] . \tag{3.4}$$

In order that any solution $\omega = \omega(\vec{Q}_{\parallel})$ of this equation be a valid solution, the function $\xi_0(\vec{Q}_{\parallel}\omega(\vec{Q}_{\parallel}))$ obtained from Eq. (3.3a) must have a positive real part. This requires that $B(\vec{Q}_{\parallel}\omega(\vec{Q}_{\parallel})) < C(\vec{Q}_{\parallel}\omega(\vec{Q}_{\parallel}))$.

With the aid of Eqs. (2.41) we can rewrite Eq. (3.5) in a form more convenient for its solution,

$$F(x) + \frac{2\,|\gamma_A\gamma_B|}{(|\gamma_A| + |\gamma_B|)^2}\,G(x)\,g(\vec{Q}_{\parallel}) = 0 , \tag{3.5}$$

to first order in $g(\vec{Q}_{\parallel})$, where

$$F(x) = \left(\frac{2\,(|\gamma_A| + |\gamma_B|)}{u_0} - a^{(1)}(x)\right) c^{(1)}(x) + b^{(1)}(x)^2 + c^{(1)}(x)^2 , \tag{3.6a}$$

$$G(x) = a^{(1)}(x)\,c^{(2)}(x) + a^{(2)}(x)\,c^{(1)}(x) - \frac{2(|\gamma_A| + |\gamma_B|)}{u_0}\,c^{(2)}(x) - 2[b^{(1)}(x)\,b^{(2)}(x) + c^{(1)}(x)\,c^{(2)}(x)] . \tag{3.6b}$$

If we denote by $x_0$ the solution of the equation $F(x) = 0$, then the solution of Eq. (3.5) is given by

$$x(\vec{Q}_{\parallel}) = x_0 - \frac{2\,|\gamma_A\gamma_B|}{(|\gamma_A| + |\gamma_B|)^2}\,\frac{G(x_0)}{F'(x_0)}\,g(\vec{Q}_{\parallel}) , \tag{3.7}$$

to first order in $g(\vec{Q}_{\parallel})$. From Eq. (2.42) we find that the surface-exciton dispersion relation is given by

$$\hbar\omega(\vec{Q}_{\parallel}) = E_g^0 + u_0 - 2(|\gamma_A| + |\gamma_B|)\,x_0 + \frac{4\,|\gamma_A\gamma_B|}{(|\gamma_A| + |\gamma_B|)}\,\frac{G(x_0)}{F'(x_0)}\,g(\vec{Q}_{\parallel}) , \tag{3.8}$$

to first order in $g(\vec{Q}_{\parallel})$.

To obtain numerical results for $\omega(\vec{Q}_{\parallel})$ we assume that

$$u_0 = 8(\gamma_A| + |\gamma_B|) , \quad |\gamma_B| = 5\,|\gamma_A| , \tag{3.9}$$

so that $\alpha = \frac{1}{6}$, $\beta = \frac{5}{6}$. The functions $a^{(1,2)}(x)$, $b^{(1,2)}(x)$, $c^{(1,2)}(x)$ for real $x$ were evaluated from the representations given by Eqs. (2.43)–(2.45), for $0.5 \le x \le 4.0$. The integrals were evaluated by a ten-point Gaussian-Laguerre quadrature formula.

The results of these calculations are summarized by

$$x_0 = 1.2968, \quad F'(x_0) = 0.24367 \times 10^{-3}, \quad G(x_0) = 0.64274 \times 10^{-4} , \tag{3.10}$$

so that the surface-exciton dispersion relation, Eq. (3.8) is, finally

$$\hbar\omega(\vec{Q}_{\parallel}) = E_g^0 + 5.4064\,(|\gamma_A| + |\gamma_B|) + \frac{1.0551\,|\gamma_A\gamma_B|}{(|\gamma_A| + |\gamma_B|)}\,g(\vec{Q}_{\parallel}) . \tag{3.11}$$

The dispersion relation for bulk excitons has been determined in Appendix C. If we set $Q_z = 0$ in the result given there we obtain

$$\hbar\omega(\vec{Q}_{\parallel})_{\mathrm{bulk}} = E_g^0 + 5.2112(|\gamma_A| + |\gamma_B|)$$

$$+\frac{1.1136\,|\gamma_A\gamma_B|}{(|\gamma_A|+|\gamma_B|)}\,g(\vec{Q}_{\parallel})\ . \tag{3.12}$$

From a comparison of the results given by Eqs. (3.11) and (3.12) we see that for the same value of the wave vector $\vec{Q}_{\parallel}$ the dispersion curve for surface excitons lies above that for bulk excitons.

Finally, we note that if the dispersion relation (3.11) is substituted into Eq. (3.3a) the result for $\xi_0(\vec{Q}_{\parallel}\omega)$ so obtained is real and positive, so that Eq. (3.11) is a valid solution of Eq. (3.1).

## IV. SPATIAL VARIATION OF POLARIZATION IN CRYSTAL

To illustrate the result obtained in Secs. I–III we apply them to the determination of the spatial variation of the polarization induced in our model of semi-infinite crystal by a spatially uniform macroscopic electric field.

Our starting point is Eq. (2.9b), and we assume that the amplitude of the electric field in the crystal is spatially uniform,

$$E_z^-(l;\omega)\equiv E_z^-(\omega)\ . \tag{4.1}$$

In this case Eq. (2.9b) becomes

$$P_z^-(l;\omega)=E_z^-(\omega)\sum_{l'}\chi_{zz}(ll';\omega)\ . \tag{4.2}$$

With the aid of the decomposition (2.49) this expression simplifies to

$$P_z^-(l_z;\omega)=E_z^-(\omega)\sum_{l_z'}\chi_{zz}(\vec{0}\omega\,|\,l_zl_z')\ . \tag{4.3}$$

The sum over $l_z'$ is readily evaluated, with the result that

$$P_z^-(l_z;\omega)=\frac{e^2m^2}{u_0a_0^3}E_z^-(\omega)\chi_{zz}(\omega\,|\,l_z)\ , \tag{4.4}$$

where

$$\begin{aligned}\chi_{zz}(\omega\,|\,l_z)=-2&+\frac{2(|\gamma_A|+|\gamma_B|)}{u_0}\left(\frac{1}{4b^{(1)}(x(+))\sinh^2\frac{1}{2}\xi(+)}+\frac{1}{4b^{(1)}(x(-))\sinh^2\frac{1}{2}\xi(-)}\right)-\frac{2(|\gamma_A|+|\gamma_B|)}{u_0}\,e^{-\xi(+)l_z}\\&\times\left(\frac{1}{4b^{(1)}(x(+))\sinh^2\frac{1}{2}\xi(+)}+\frac{c^{(1)}(x(+))}{b^{(1)}(x(+))}\,\frac{1}{b^{(1)}(x(+))+c^{(1)}(x(+))\,e^{-\xi(+)}}\,\frac{e^{-\xi(+)}}{1-e^{-\xi(+)}}\right)\\&-\frac{2(|\gamma_A|+|\gamma_B|)}{u_0}\,e^{-\xi(-)l_z}\left(\frac{1}{4b^{(1)}(x(-))\sinh^2\frac{1}{2}\xi(-)}+\frac{c^{(1)}(x(-))}{b^{(1)}(x(-))}\,\frac{1}{b^{(1)}(x(-))+c^{(1)}(x(-))\,e^{-\xi(-)}}\,\frac{e^{-\xi(-)}}{1-e^{-\xi(-)}}\right)\ .\end{aligned} \tag{4.5}$$

In this expression

$$x(+)=\frac{E_g^0+u_0+\hbar\omega}{2(|\gamma_A|+|\gamma_B|)}+i\,\frac{\hbar\eta}{2(|\gamma_A|+|\gamma_B|)}\ , \tag{4.6a}$$

$$x(-)=\frac{E_g^0+u_0+\hbar\omega}{2(|\gamma_A|+|\gamma_B|)}+i\,\frac{\hbar\eta}{2(|\gamma_A|+|\gamma_B|)}\ , \tag{4.6b}$$

and $\xi(\pm)$ are those solutions of

$$\cosh\xi(\pm)=-\frac{a^{(1)}(x(\pm))-[2(|\gamma_A|+|\gamma_B|)/u_0]}{2b^{(1)}(x(\pm))} \tag{4.7}$$

whose real parts are positive.

We have evaluated the function $\chi_{zz}(\omega\,|\,l_z)$ as a function of $l_z$ for several values of $\hbar\omega$ in the gap between the valence and conduction bands $0<\hbar\omega<E_g^0+u_0$. To present the results conveniently we define a dimensionless photon energy $y$ by

$$y=\frac{\hbar\omega}{E_g^0+u_0}\ ,\quad 0<y<1\ . \tag{4.8}$$

In addition, we choose the values

$$\begin{aligned}&u_0=8(|\gamma_A|+|\gamma_B|),\quad |\gamma_B|=5|\gamma_A|\\&E_g^0+u_0=16(|\gamma_A|+|\gamma_B|),\quad \hbar\eta=(0.005)/2(|\gamma_A|+|\gamma_B|).\end{aligned} \tag{4.9}$$

Consequently, the expressions for $x(\pm)$ take the forms

$$x(+)=8(1-y)-i(0.005)\ , \tag{4.10a}$$

$$x(-)=8(1+y)+i(0.005)\ . \tag{4.10b}$$

The integrals $a^{(1)}(x(\pm))$, $b^{(1)}(x(\pm))$, $c^{(1)}(x(\pm))$ were evaluated by a ten-point Gaussian-Laguerre quadrature formula, and the values of $\xi(\pm)$ were obtained from the results by means of Eq. (4.7).

In Figs. 2 and 3 are plotted $\mathrm{Re}\chi_{zz}(\omega\,|\,l_z)$ and $\mathrm{Im}\chi_{zz}(\omega\,|\,l_z)$, respectively, as functions of $l_z$ for several different values of $y$ in the range $0.5\le y\le 0.95$. In the absence of spatial dispersion, the dielectric susceptibility $\chi_{zz}(ll';\omega)$ would be independent of the site indices $l$ and $l'$, and the polarization $P_z^-(l;\omega)$ induced by a spatially uniform macroscopic electric field (4.1) would be independent of $l$. The departures of the curves in Figs. 2 and 3 from horizontal straight lines therefore give a measure of the importance of spatial dispersion effects in the present model of a semi-infinite insulator.

Several conclusions can be drawn from these results. We see that for values of $y\lesssim 0.5$, i.e., for photon energies $\hbar\omega$ below about half the width of the energy gap, spatial dispersion effects are negligible. However, as $y$ increases and approaches a critical value of $y=0.8379$, which from Eqs. (3.1) and (3.11) is the value corresponding to the energy of a surface exciton at $\vec{Q}_{\parallel}=0$, the effects of spatial dispersion become more pronounced. Even so, for values of $y$ as close to the critical value as $y=0.8$ the polarization has reached its bulk value by the third atomic plane into the crystal from the surface ($l_z=3$). It is only when $y$ gets rather closer to the critical value of 0.8379 that the effects of spatial dispersion are felt deeper into the crystal.

For example, for $y=0.825$ both $\mathrm{Re}\chi_{zz}(\omega\,|\,l_z)$ and $\mathrm{Im}\chi_{zz}(\omega\,|\,l_z)$ are still changing with $l_z$ at $l_z=5$. $\mathrm{Re}\chi_{zz}(\omega\,|\,l_z)$ changes sign at values of $y$ close to the critical, but at a different value for each value of $l_z$. Thus, it goes to zero at $y=0.8379$ for $l_z=1$, $y=0.8265$ for $l_z=2$, $y=0.8261$ for $l_z=3$, $y=0.8258$ for $l_z=4$, and $y=0.8258$ for $l_z\geq 5$. Similarly, $\mathrm{Im}\chi_{zz}(\omega\,|\,l_z)$ has a sharp maximum centered at each of these frequencies. We see also that the magnitude of the real part of the polarization is decreased at the surface with respect to its value in the bulk, for frequencies below the surface exciton frequency, but is increased for frequencies above the surface exciton frequency.

In conclusion, we have presented a calculation in the tight-binding and Hartree approximations of the nonlocal dielectric susceptibility of a semi-infinite simple cubic crystal in the excitonic regime of frequencies. We have shown that if the exciton is sufficiently spatially localized, in the sense that the only nonzero elements of the Green's function $G_0(\vec{Q}_{\parallel}E\,|\,l_z l_z')$ are those for which $l_z$ and $l_z'$ differ at most by $\pm 1$ [see Eqs. (2.40)], then the resulting susceptibility has the form obtained by Zeyher *et al.*, namely, the sum of a function of $|l_z - l_z'|$ alone and a function of $l_z + l_z'$ alone. We have shown explicitly that this result no longer holds for a more extended exciton, and the conditions for the validity of their *Ansatz* are sufficiently severe that they will seldom be met in practice. We have obtained the dispersion relations for both the bulk and surface excitons predicted by our model, and have demonstrated some of the consequences of the nonlocality of the dielectric susceptibility obtained by using it to determine the spatial variation of the polarization induced in the crystal by a spatially uniform macroscopic electric field. A determination of the optical properties of our crystal model based on the dielectric susceptibility obtained in Sec. II will be varried out in a subsequent paper.

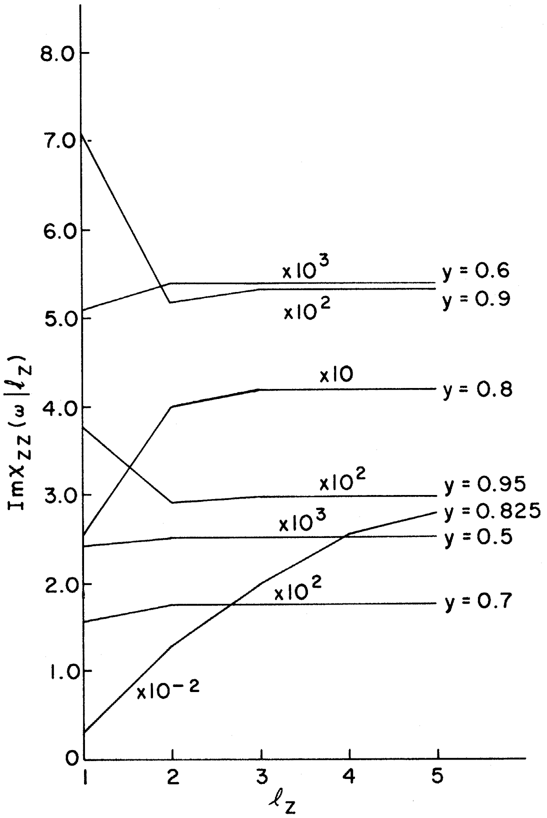

FIG. 2. Plot of $\mathrm{Re}\chi_{zz}(\omega\,|\,l_z)$, defined by Eq. (4.5), as a function of $l_z$ for several values of the dimensionless photon energy. The surface of the insulator corresponds to $l_z=1$.

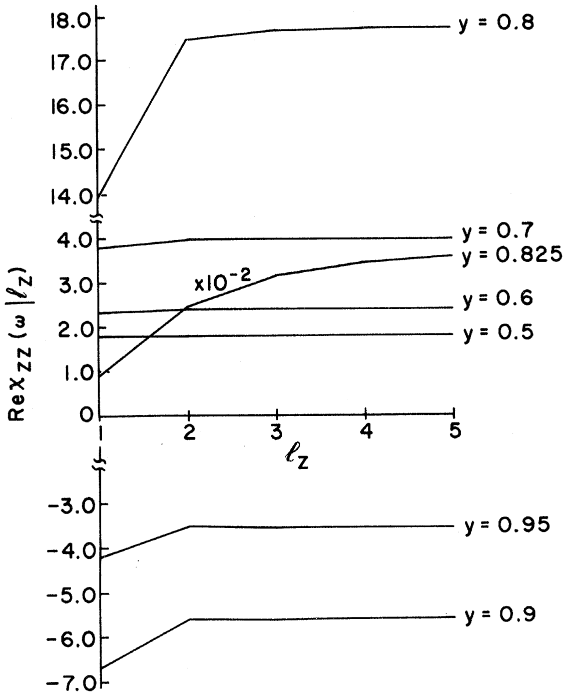

FIG. 3. Plot of $\mathrm{Im}\chi_{zz}(\omega\,|\,l_z)$, defined by Eq. (4.5), as a function of $l_z$ for several values of the dimensionless photon energy. The surface of the insulator corresponds to $l_z=1$.

## ACKNOWLEDGMENTS

The contribution of the first-named author to this work was carried out while he was at the University of California, Irvine, under the auspices of the exchange program of the Academy of Sciences of the USSR and the U. S. National Academy of Sciences. The authors wish to thank M. F. Bishop for carrying out the numerical calculations reported in this work.

## APPENDIX A. SOLUTION OF Eq. (2.33) FOR THE GREEN'S FUNCTION $G(Q_\parallel \omega | l_z l_z')$

In this Appendix we solve the integral equation (2.33) subject to the condition that the only nonzero elements of the Green's function $G_0(\vec{Q}_\parallel E | l_z l_z')$ are given by Eqs. (2.36) and (2.40).

We begin by substituting the decomposition (2.36) into the last term on the right-hand side of Eq. (2.33) and transposing terms in the resulting equation to obtain

$$\sum_{l_z''} \left( \delta_{l_z l_z''} + \frac{u_0}{\hbar} G_0^{(1)}(\vec{Q}_\parallel E | l_z - l_z'') \right) G(\vec{Q}_\parallel E | l_z'' l_z') = G_0(\vec{Q}_\parallel E | l_z l_z') - \frac{u_0}{\hbar} \sum_{l_z''} G_0^{(2)}(\vec{Q}_\parallel E | l_z l_z'') \times G(\vec{Q}_\parallel E | l_z'' l_z') \ . \tag{A1}$$

It should be kept in mind that each of the variables $l_z$, $l_z'$, $l_z''$ assumes only the values 1, 2, 3, ... .

We introduce a Green's function $g(\vec{Q}_\parallel E | l_z l_z')$ as the solution of the equation

$$\sum_{l_z''} \left( \delta_{l_z l_z''} + \frac{u_0}{\hbar} G_0^{(1)}(\vec{Q}_\parallel E | l_z - l_z'') \right) g(\vec{Q}_\parallel E | l_z'' l_z') = \delta_{l_z l_z'} \ . \tag{A2}$$

Because $G_0^{(1)}(\vec{Q}_\parallel E | l_z - l_z')$ is symmetric in $l_z$ and $l_z'$, $g(\vec{Q}_\parallel E | l_z - l_z')$ will also be symmetric in $l_z$ and $l_z'$. In terms of this function the equation for $G(\vec{Q}_\parallel E | l_z l_z')$ can be written

$$G(\vec{Q}_\parallel E | l_z l_z') = \sum_{l_z''} g(Q_\parallel E | l_z l_z'') G_0(\vec{Q}_\parallel E | l_z' l_z'') - \frac{u_0}{\hbar} C(\vec{Q}_\parallel E) g(\vec{Q}_\parallel E | l_z 1) G(\vec{Q}_\parallel E | 1 l_z') \ , \tag{A3}$$

where we have used the assumption that the only nonzero element of $G_0^{(2)}(\vec{Q}_\parallel E | l_z l_z')$ is that given by Eq. (2.40c). If we set $l_z = 1$ in this equation, and solve the resulting equation for $G(\vec{Q}_\parallel E | 1 l_z')$, we obtain for $G(\vec{Q}_\parallel E | l_z l_z')$

$$G(\vec{Q}_\parallel E | l_z l_z') = \sum_{l_z''} g(\vec{Q}_\parallel E | l_z l_z'') G_0(\vec{Q}_\parallel E | l_z'' l_z') - \frac{u_0}{\hbar} C(\vec{Q}_\parallel E) \times \frac{g(\vec{Q}_\parallel E | l_z 1) \sum_{l_z''} g(\vec{Q}_\parallel E | 1 l_z'') G_0(\vec{Q}_\parallel E | l_z'' l_z')}{1 + (u_0/\hbar) C(\vec{Q}_\parallel E) g(\vec{Q}_\parallel E | 11)} \ . \tag{A4}$$

This result can be simplified considerably. If we use the decomposition (2.36) and the symmetry of $g(\vec{Q}_\parallel E | l_z l_z')$ in $l_z$ and $l_z'$, we can rewrite Eq. (A2) as

$$\sum_{l_z''} g(\vec{Q}_\parallel E | l_z l_z'') G_0(\vec{Q}_\parallel E | l_z'' l_z') = \frac{\hbar}{u_0} [\delta_{l_z l_z'} - g(\vec{Q}_\parallel E | l_z l_z')] + \sum_{l_z''} g(\vec{Q}_\parallel E | l_z l_z'') G_0^{(2)}(\vec{Q}_\parallel E | l_z'' l_z') \ . \tag{A5}$$

If we combine this result with Eq. (2.40c), and substitute it into both terms on the right-hand side of Eq. (A4), we obtain the compact result that

$$G(\vec{Q}_\parallel E | l_z l_z') = \frac{\hbar}{u_0} [\delta_{l_z l_z'} - g(\vec{Q}_\parallel E | l_z l_z')] + \frac{g(\vec{Q}_\parallel E | l_z 1) C(\vec{Q}_\parallel E) g(\vec{Q}_\parallel E | 1 l_z')}{1 + (u_0/\hbar) C(\vec{Q}_\parallel E) g(\vec{Q}_\parallel E | 11)} \ , \tag{A6}$$

whose symmetry in $l_z$ and $l_z'$ is manifest.

It remains only to obtain $g(\vec{Q}_\parallel E | l_z l_z')$. With the assumptions represented by Eqs. (2.40a) and (2.40b), Eq. (A2) can be written explicitly as

$$-b g(l_z - 1, l_z') - a g(l_z, l_z') - b g(l_z + 1, l_z') = \delta_{l_z l_z'}, \ l_z, l_z' \geq 1 \tag{A7}$$

where we have introduced the quantities

$$a(\vec{Q}_\parallel E) = \frac{u_0}{\hbar} A(\vec{Q}_\parallel E) - 1 \ , \tag{A8a}$$

$$b(\vec{Q}_\parallel E) = \frac{u_0}{\hbar} B(\vec{Q}_\parallel E) \ . \tag{A8b}$$

To simplify notation we have dropped the arguments $(\vec{Q}_\parallel E)$ in writing Eq. (A7), and will continue to do so in what follows.

Equation (A7) holds for all $l_z, l_z' \geq 1$. However, we notice that when $l_z = 1$ the Green's function $g(0, l_z')$ appears on the left-hand side of this equation. As there is no site with $l_z = 0$ in the semi-infinite crystal, we can write Eq. (A2) in the form (A7) only if we impose the condition

$$g(0, l_z') = 0, \quad l_z' \geq 1 \tag{A9}$$

on the solution.

To solve Eqs. (A7) and (A9) it is convenient to introduce the shift operators $\Delta$ and $\Delta^{-1}$, which are defined in terms of their effect on an arbitrary function of the discrete variable $l_z$:

$$\Delta f(l_z) = f(l_z + 1), \quad \Delta^{-1} f(l_z) = f(l_z - 1) \ . \tag{A10}$$

In terms of these operators we can rewrite Eq. (A7) in the form

$$(\Delta - 2\cosh\xi + \Delta^{-1}) g(l_z l_z') = -(1/b) \delta_{l_z l_z'} \ , \tag{A11}$$

where the parameter $\xi$ is defined as that solution of the equation

$$\cosh\xi = -a/2b \tag{A12}$$

whose real part is positive. We now make use of the results

$$(\Delta - 2\cosh\xi + \Delta^{-1}) e^{-\xi l_z} = 0 \ , \tag{A13a}$$

$$(\Delta - 2\cosh\xi + \Delta^{-1}) \frac{e^{-\xi |l_z - l_z'|}}{-2\sinh\xi} = \delta_{l_z l_z'} \tag{A13b}$$

to write the solution of Eq. (A7) in the form

$$g(l_z l_z') = \frac{e^{-\xi|l_z - l_z'|}}{2b\sinh\xi} + \mu e^{-\xi l_z}\ , \tag{A14}$$

which remains finite as $l_z$ increases without limit. The coefficient $\mu$ is obtained from the boundary condition (A9), with the result that

$$g(l_z l_z') = \frac{e^{-\xi|l_z - l_z'|} - e^{-\xi(l_z + l_z')}}{2b\sinh\xi}, \quad l_z, l_z' \geq 1\ . \tag{A15}$$

When we substitute Eq. (A15) into Eq. (A6), after some simplification we obtain the result

$$G(l_z l_z') = \frac{\hbar}{u_0}\left(\delta_{l_z l_z'} - \frac{e^{-\xi|l_z - l_z'|} - e^{-\xi(l_z + l_z')}}{2b\sinh\xi}\right) + \frac{C}{b^2}\frac{e^{-\xi(l_z + l_z')}}{1 + (u_0/\hbar)(C/b)e^{-\xi}}\ . \tag{A16}$$

When we take account of Eqs. (A8) this result becomes Eq. (2.47) of the text.

## APPENDIX B. GREEN'S FUNCTION $G(\vec{Q}_\parallel E | l_z l_z')$ FOR SPATIALLY EXTENDED EXCITON

In this appendix we extend the result for $G(\vec{Q}_\parallel E | l_z l_z')$ obtained in the preceding appendix by allowing the kernel $G_0(\vec{Q}_\parallel E | l_z l_z')$ in Eq. (2.33) to be nonzero for values of $l_z$ and $l_z'$ differing by more than unity. In doing so we demonstrate explicitly the incorrectness of the conjecture by Zeyher *et al.*[4] concerning the structure of the susceptibility $\chi_{zz}(ll';\omega)$ of a semi-infinite insulator, which we have already discussed in the Introduction to this paper.

We again make the decomposition of $G_0(\vec{Q}_\parallel E | l_z l_z')$ given by Eq. (2.36), and because our demonstration does not depend on the assumptions made about $G_0^{(2)}(\vec{Q}_\parallel | l_z l_z')$, as will be clear from what follows, we will make the simplest possible assumption concerning it, viz., that

$$G_0^{(2)}(Q_\parallel E | l_z l_z') = \delta_{l_z 1}\delta_{l_z' 1} C(\vec{Q}_\parallel E)\ . \tag{B1}$$

This is the same as the assumption made about $G_0^{(2)}(\vec{Q}_\parallel E | l_z l_z')$ in Appendix A, so that the result given by Eq. (A6) for $G(Q_\parallel E | l_z l_z')$ is valid in this appendix as well.

In solving Eq. (A2) for the Green's function $g(\vec{Q}_\parallel E | l_z l_z')$ to substitute into Eq. (A6) we assume that the only nonzero elements of $G_0^{(1)}(\vec{Q}_\parallel E | l_z - l_z')$ are those given by Eqs. (2.40a) and (2.40b), and in addition

$$G_0^{(1)}(\vec{Q}_\parallel E | \pm 2) = -D(\vec{Q}_\parallel E)\ . \tag{B2}$$

With these assumptions Eq. (A2) can be written explicitly as ($l_z, l_z' \geq 1$)

$$-dg(l_z - 2, l_z') - bg(l_z - 1, l_z') - ag(l_z l_z') - bg(l_z + 1, l_z') - dg(l_z + 2, l_z') = \delta_{l_z l_z'}\ , \tag{B3}$$

where $a(\vec{Q}_\parallel E)$ and $b(\vec{Q}_\parallel E)$ have already been defined by Eqs. (A8), and

$$d(\vec{Q}_\parallel E) = (u_0/\hbar)D(\vec{Q}_\parallel E)\ . \tag{B4}$$

Since the atomic planes labeled by $l_z = 0$ and $l_z = -1$ are absent from a semi-infinite crystal, the equations for $g(l_z l_z')$ can be written in the form (B3) only if we require that for $l_z = 1$

$$-dg(-1, l_z') - bg(0, l_z') = 0$$

for all $l_z' \geq 1$, while for $l_z = 2$

$$-dg(0, l_z') = 0$$

for all $l_z' \geq 1$. These conditions are equivalent to the conditions

$$g(0, l_z') = 0, \quad l_z' \geq 1 \tag{B5a}$$

$$g(-1, l_z') = 0, \quad l_z' \geq 1 \tag{B5b}$$

which serve as boundary conditions on the solution of Eq. (B3).

We can rewrite Eq. (B3) in terms of the shift operators defined by Eqs. (A10) as

$$(\Delta - 2\cosh\xi + \Delta^{-1})(\Delta - 2\cosh\eta + \Delta^{-1}) \times g(l_z l_z') = -(1/d)\delta_{l_z l_z'}, \tag{B6}$$

where $\xi$ and $\eta$ are the solutions of the equations

$$\cosh\xi + \cosh\eta = -b/2d\ , \tag{B7a}$$

$$\cosh\xi\cosh\eta = (a/4d) - \tfrac{1}{2}\ , \tag{B7b}$$

with $\mathrm{Re}\,\xi > 0$, $\mathrm{Re}\,\eta > 0$.

In view of the result given by Eq. (A13b), to obtain a particular solution of Eq. (B3) we make the *Ansatz*

$$g_p(l_z l_z') = -\frac{1}{d}\left(\alpha\frac{e^{-\xi|l_z - l_z'|}}{-2\sinh\xi} + \beta\frac{e^{-\eta|l_z - l_z'|}}{-2\sinh\eta}\right)\ . \tag{B8}$$

When we substitute Eq. (B8) into Eq. (B6), we obtain the equation

$$(\alpha + \beta)\delta_{l_z+1, l_z'} - (2\alpha\cosh\eta + 2\beta\cosh\xi)\delta_{l_z l_z'} + (\alpha + \beta)\delta_{l_z-1, l_z'} = \delta_{l_z l_z'}\ . \tag{B9}$$

It follows that

$$\alpha = \frac{1}{2(\cosh\xi - \cosh\eta)} = -\beta\ , \tag{B10}$$

and consequently we find

$$g_p(l_z l_z') = \frac{1}{2d(\cosh\xi - \cosh\eta)}\left(\frac{e^{-\xi|l_z - l_z'|}}{2\sinh\xi} - \frac{e^{-\eta|l_z - l_z'|}}{2\sinh\eta}\right)\ . \tag{B11}$$

If we note Eq. (A13a), the general solution of Eq. (B6) which remains finite as $l_z$ increases without limit is

$$g(l_z l_z') = \mu e^{-\xi l_z} + \nu e^{-\eta l_z} + \frac{1}{2d(\cosh\xi - \cosh\eta)} \times\left(\frac{e^{-\xi|l_z - l_z'|}}{2\sinh\xi} - \frac{e^{-\eta|l_z - l_z'|}}{2\sinh\eta}\right), \tag{B12}$$

where the coefficients $\mu$ and $\nu$ are to be obtained from the boundary conditions (B5). We will not record here the straightforward, if somewhat tedious, determination of their values, and pass directly to the final result:

$$g(l_z l_z') = \frac{1}{2d(\cosh\xi - \cosh\eta)(e^{\xi} - e^{\eta})}\Big(- e^{-\xi l_z - \eta l_z'} - e^{-\eta l_z - \xi l_z'} + \frac{e^{\eta} - e^{-\xi}}{2\sinh\xi} e^{-\xi(l_z + l_z')} + \frac{e^{\xi} - e^{-\eta}}{2\sinh\eta} e^{-\eta(l_z + l_z')}\Big) + \frac{1}{2d(\cosh\xi - \cosh\eta)} \times \left(\frac{e^{-\xi|l_z - l_z'|}}{2\sinh\xi} - \frac{e^{-\eta|l_z - l_z'|}}{2\sinh\eta}\right) . \qquad \text{B13)}$$

The presence of the first two terms on the right-hand side of Eq. (B13) shows that $g(l_z l_z')$ cannot be written as the sum of a function of $l_z - l_z'$ alone and a function of $l_z + l_z'$ alone. Since $G_0^{(2)}(\vec{Q}_{\parallel} E \mid l_z l_z')$ and $g(\vec{Q}_{\parallel} E \mid l_z l_z')$ coincide when $G_0^{(2)}(\vec{Q}_{\parallel} E \mid l_z l_z')$ is identically zero, we have the result that under the assumptions of this appendix $G(\vec{Q}_{\parallel} E \mid l_z l_z')$ cannot be written as the sum of a function of $l_z - l_z'$ alone and a function of $l_z + l_z'$ alone when $G_0^{(2)}(\vec{Q}_{\parallel} E \mid l_z l_z')$ is identically zero. It follows from Eq. (A6) that it cannot be written in this form for arbitrary nonzero values of the elements of $G_0^{(2)}(\vec{Q}_{\parallel} E \mid l_z l_z')$, which is what we set out to show.

## APPENDIX C. BULK-EXCITON DISPERSION RELATION

For comparison with the dispersion relation for surface excitons obtained in Sec. III, we obtain in this appendix the dispersion relation for excitons in an infinitely extended crystal predicted by our model Hamiltonian (2.3).

The starting point for this determination is the integral equation (2.14), which we have noted already holds for an infinitely extended crystal as well as for a semi-infinite crystal. The kernel in this equation is still given by Eqs. (2.18)–(2.22), except that in solving for the single-particle Green's functions $\hat{g}_A(l_1 l_4; E)$ and $\hat{g}_B(l_3 l_2; E)$ only the first term on the right-hand sides of Eqs. (2.23) is retained. The results for these Green's functions now take the form

$$\hat{g}_A^{(0)}(l_1 l_4; E) = \frac{\hbar}{N}\sum_{\vec{q}} \frac{\exp\{i\vec{q}\cdot[\vec{x}(l_1) - \vec{x}(l_4)]\}}{\hbar E - E_A(\vec{q})} , \qquad \text{(C1a)}$$

$$\hat{g}_B^{(0)}(l_3 l_2; E) = \frac{\hbar}{N}\sum_{\vec{k}} \frac{\exp\{i\vec{k}\cdot[\vec{x}(l_3) - \vec{x}(l_2)]\}}{\hbar E - E_g^0 - u_0 - E_B(\vec{k})} . \qquad \text{(C1b)}$$

When these expressions are used in Eqs. (2.18) and (2.19) we find that the function $\hat{G}_0(ll'l';E)$ for an infinitely extended crystal can be expressed in the form

$$\hat{G}_0(ll'l';E) \equiv G_0(ll';E) = \frac{1}{N}\sum_{\vec{Q}} G_0(\vec{Q}E)\exp\{i\vec{Q}\circ[\vec{x}(l) - \vec{x}(l')]\} , \qquad \text{(C2)}$$

where

$$G_0(\vec{Q}E) = \frac{\hbar}{N}\sum_{\vec{q}} \frac{1}{\hbar E - E_g^0 - u_0 - E_A(\vec{q}) - E_B(\vec{q} - \vec{Q})} . \qquad \text{(C3)}$$

If we express $\hat{G}(ll'l';E)$ in a similar fashion,

$$\hat{G}(ll'l';E) \equiv G(ll';E) = \frac{1}{N}\sum_{\vec{Q}} G(\vec{Q}E)\exp\{i\vec{Q}\cdot[\vec{x}(l) - \vec{x}(l')]\} , \qquad \text{(C4)}$$

then the equation for $G_0(ll';E)$ which follows from Eq. (2.14),

$$G(ll';E = G_0(ll';E) - \frac{u_0}{\hbar}\sum_{l''} G_0(ll'';E)G(l''l';E) , \qquad \text{(C5)}$$

can be reduced to the equation for the corresponding Fourier coefficients,

$$G(\vec{Q}E) = G_0(\vec{Q}E) - \frac{u_0}{\hbar} G_0(\vec{Q}E)G(\vec{Q}E) \circ \qquad \text{(C6)}$$

From the solution to Eq. (C6),

$$G(\vec{Q}E) = \frac{G_0(\vec{Q}E)}{1 + (u_0/\hbar)G_0(\vec{Q}E)} , \qquad \text{(C7)}$$

we see that the dispersion relation for bulk excitons is

$$1 + (u_0/\hbar)G_0(\vec{Q}E) = 0 , \qquad \text{(C8)}$$

since the energies of the bound states of our interacting electron-hole system are given by the poles of the corresponding two-particle Green's function.

In what follows we will assume that $E$ is real, and denote it by $\omega$, and will look for solutions of Eq. (C8) for $\hbar\omega$ in the gap between the valence and conduction bands, $0 < \hbar\omega < E_g^0 + u_0$. For $\hbar\omega$ in this range we can rewrite $G_0(\vec{Q}\omega)$ as a single integral

$$G_0(\vec{Q}\omega) = -\hbar\int_0^{\infty} dt \exp[-t(E_g^0 + u_0 - \hbar\omega + 6|\gamma_A| + 6|\gamma_B|)] I_0(2\gamma_1 t) I_0(2\gamma_2 t) I_0(2\gamma_3 t) , \qquad \text{(C9)}$$

where

$$2\gamma_j = (4\gamma_A^2 + 8|\gamma_A\gamma_B|\cos Q_j + 4\gamma_B^2)^{1/2} \qquad \text{(C10)}$$

and $Q_1 = Q_x a_0$, $Q_2 = Q_y a_0$, $Q_3 = Q_z a_0$. If this expression is expanded in powers of $\sin^2\frac{1}{2}Q_j$, the leading terms in this expansion are

$$G_0(\vec{Q}\omega) = -\frac{\hbar}{2(|\gamma_A| + |\gamma_B|)} I(x) + \frac{\hbar|\gamma_A\gamma_B|}{(|\gamma_A + |\gamma_B|)^3} J(x) f(\vec{Q}) + \ldots , \qquad \text{(C11)}$$

the functions $I(x)$ and $J(x)$ have the integral representations

$$I(x)=\int_0^\infty du\, e^{-u(3+x)} I_0^3(u) \ , \tag{C12a}$$

$$J(x)=\int_0^\infty du\, e^{-u(3+x)} u I_0^2(u) I_1(u) \ , \tag{C12b}$$

where $f(\vec{Q})$ is defined by

$$f(\vec{Q})=\sin^2\tfrac{1}{2}Q_x a_0+\sin^2\tfrac{1}{2}Q_y a_0+\sin^2\tfrac{1}{2}Q_z a_0 \ , \tag{C13}$$

and $x$ is defined by Eq. (2.42), with $E$ replaced by $\omega$.

The dispersion relation (C8) can now be rewritten

$$F(x)+\frac{u_0|\gamma_A\gamma_B|}{(|\gamma_A|+|\gamma_B|)^3}J(x)f(\vec{Q})+\ldots=0 \tag{C14}$$

to first order in $f(\vec{Q})$, where

$$F(x)=1-\frac{u_0}{2(|\gamma_A|+|\gamma_B|)}I(x) \ . \tag{C15}$$

If we denote by $x_0$ the solution of $F(x)=0$, then the solution of Eq. (C14) becomes

$$x(\vec{Q})=x_0+\frac{2|\gamma_A\gamma_B|}{(|\gamma_A|+|\gamma_B|)^2}\frac{J(x_0)}{I'(x_0)}f(\vec{Q}) \tag{C16}$$

to first order in $f(\vec{Q})$. From Eq. (2.42) we find that the bulk-exciton dispersion relation is

$$\begin{aligned}\hbar\omega(\vec{Q})&=E_g^0+u_0-2(|\gamma_A|+|\gamma_B|)x(\vec{Q})\\&=E_g^0+u_0-2(|\gamma_A|+|\gamma_B|)x_0\\&\quad-\frac{4|\gamma_A\gamma_B|}{|\gamma_A|+|\gamma_B|}\frac{J(x_0)}{I'(x_0)}f(\vec{Q}) \ ,\end{aligned} \tag{C17}$$

also to first order in $f(\vec{Q})$.

To evaluate this dispersion relation we assume the values for $u_0$ and $|\gamma_B|/|\gamma_A|$ given in Eqs. (3.9). The functions $I(x)$, $I'(x)$, $J(x)$ were evaluated for $0.5<x<4$ by the methods described in Sec. III. The value of $x$ for which $I(x)=\frac{1}{4}$ was found to be $x_0=1.3944$. The value of $J(x_0)/I'(x_0)$ was then determined to be $-0.2784$. Consequently, we obtain finally

$$\begin{aligned}\hbar\omega(\vec{Q})&=E_g^0+5.2112(|\gamma_A|+|\gamma_B|)+\frac{1.1136|\gamma_A\gamma_B|}{(|\gamma_A|+|\gamma_B|)}\\&\quad\times(\sin^2\tfrac{1}{2}Q_x a_0+\sin^2\tfrac{1}{2}Q_y a_0+\sin^2\tfrac{1}{2}Q_z a_0) \ .\end{aligned} \tag{C18}$$

---

[*] Research supported in part by AFOSR Grant No. 71-2018.

[1] See the introductory discussion in Sec. VI of D. L. Mills and E. Burstein, Rept. Prog. Phys. 37, 817 (1974).

[2] See V. M. Agranovich and V. L. Ginzburg, *Spatial Dispersion in Crystal Optics and The Theory of Excitons* (Interscience, London, 1966). Also a brief review of more recent work can be found in Ref. 1.

[3] G. Agarwal, D. Pattanyak, and E. Wolf, Phys. Rev. Lett. 27, 1022 (1971); Optics Commun. 4, 255 (1971); 4, 260 (1971).

[4] R. Zeyher, J. L. Birman, and W. Brenig, Phys. Rev. B 6, 4613 (1972).

[5] A. A. Maradudin and D. L. Mills, Phys. Rev. B 7, 2787 (1973).

[6] G. D. Mahan and J. J. Hopfield, Phys. Rev. 135, A428 (1965). A more detailed discussion of this work may be found in G. D. Mahan, Ph.D. thesis (University of California, 1963) (unpublished).

[7] Evidently there is some question about whether the reflectivity spikes analyzed in Ref. 6 are intrinsic to the CdS surface. For example, in a recent experimental study it was found that such spikes were not present in the data at normal incidence, but could be induced by exposing the sample to band-gap radiation. This is discussed in the paper by S. A. Permogorov, V. V. Travnikov, and A. V. Sel'kin Fiz. Tverd. Tela 14, 3642 (1972) [Sov. Phys.-Solid State 14, 3051 (1973)]}.

[8] D. L. Mills, in *Proceedings of the First Taormina Research Conference on the Structure of Matter, Taormina* 1972, edited by Elais Burstein and Francesco de Martini (Pergamon, New York, 1974), p. 147.