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Intermediate-binding excitons and biexcitons in semiconducting crystals

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Exciton-exciton (biexciton) pairing is considered in an insulating crystal consisting of a simple cubic lattice. With the use of a formalism similar to Gorkov's theory of superconductivity, it is shown that excitons may interact to form charge-transfer bound states. The exciton spectrum is evaluated in the mean-field Hartree-Fock or random-phase approximation by means of a Hamiltonian describing the physical situation which is intermediate between the Wannier and Frenkel models. The gap parameter function $\Delta(ll')$ which binds two excitons at the lattice sites $\vec{R}_l^0$ and $\vec{R}_{l'}^0$ $(l \neq l')$ is produced by the direct Coulomb interaction. The exchange Coulomb interaction (of finite range), on the other hand, is responsible for binding electron-hole pairs to produce excitons. Thus in the absence of the direct Coulomb interaction, the excitons can travel in the crystal independently. A set of coupled equations for the normal (exciton) and anomalous (biexciton) Green's functions is derived. The excitation energies for the exciton and biexciton normal modes are calculated to order $\vec{k}^2$, $\vec{k}$ being the wave vector. The dispersion relations are solved numerically and the results are discussed in detail.

I. INTRODUCTION

Two types of electronic transitions can occur in pure semiconductors and insulators when light is absorbed at the fundamental edge. If the incident photon energies are greater than the energy gap, the absorption of light corresponds to an electron being transferred to the conduction band leaving a hole in the valence band. At energies lower than the band gap, absorption peaks have been observed for which the conduction electron and valence hole are bound to one another in states within the forbidden energy gap. The possibility of an electron and a hole being bound together by the Coulomb interaction to form an excited state, or exciton, was first suggested by Frenkel and Peierls.[1]

Following the two *distinct* points of view of dealing with the band motion of electrons in crystals, the theory of excitons has been developed on the basis of two *extreme* models. One is the *tight-binding* model for Frenkel excitons in which the excited electron and the hole hop from one lattice site to the next simultaneously on account of overlapping wave functions. The other is the *weak-binding* model for Wannier excitons, originally formulated by Wannier and Mott,[2] in which the excitation region for the electron-hole pair is spread out over several lattice spacings. The tight-binding method has been applied and found to be adequate in cases where the atoms or molecules are weakly interacting, such as molecular crystals. The weak-binding approach describes quite well crystals with a high dielectric constant and consequently weak electron-hole interactions such as most inorganic crystals, and particularly small-gap semiconductors. (For literature on excitons and their properties, see Refs. 3–6.)

Neither the tight-binding nor weak-binding model is adequate in several cases such as the lowest exciton states of most insulators. Some theoretical work has been done to find a convenient approach which would be appropriate for the *intermediate-binding* case. Altarelli and Bassani[7] have presented a method which makes use of first quantization to calculate exciton states with intermediate binding. Their integral equation method which takes account of the band structure gives good agreement between the theoretical and experimental values for the whole excitonic series of the solid rare gases.[8,9] In the present paper a simple model for a semiconducting crystal with intermediately bound excitons is presented. The model has some of the qualitative features considered by Altarelli and Bassani.[7] In formulating our problem, second quantization is used since this formalism has proven to be elegant and convenient.

For simplicity we consider a two-band model which is reasonable when the other bands are far away. For concreteness a simple cubic lattice will be used and all considerations due to electron spin will be ignored. On the lattice sites, there are identical one-electron atoms whose thermal vibration will be neglected. The first step in defining the band model is to assume that the electrons and holes are tightly bound on the same lattice site. As we have demonstrated,[10] it is necessary to distinguish between the short-range (on-site) and the long-range term in the exchange interaction. The nearest-neighbor exchange interaction is included in the Hamiltonian because this part of the Coulomb interaction causes the electron and the hole to travel simultaneously from one lattice site to its nearest neighbor. This term is therefore *essential* for collective exciton modes. It is included in the Hamiltonian for Frenkel excitons for which the electron and the hole are bound to one another within an atom or molecule.

Next, the kinetic-energy terms in the model Hamiltonian give rise to *individual* movement of the separate particles and therefore threaten to tear the electron-hole pair apart. In the limiting case of Frenkel excitons, the transfer integrals between lattice sites are assumed to be sufficiently small so as to be neglected. This condition is particularly well satisfied in *molecular crystals*, where the overlap between the molecular orbitals is small and where the size of this overlap determines the magnitude of the transfer integrals between lattice sites. In the present study, as in Ref. 10, the individual transfer is included so that the model allows each particle to hop individually between sites and then recombine to form an exciton. This establishes the difference between the present model and that of Frenkel and Peierls. It also differs from the model of Mott and Wannier for which the exciton has a large radius of several lattice spacings. In our previous study,[10] the direct Coulomb interaction between an electron and a hole on different lattice sites has been ignored. This term does not cause a transfer between sites and, therefore, enhances the attraction between an electron and a hole and should thus be included for completeness. In the present study, this term is included because it leads to bound exciton pairs which form the collective biexciton mode. Another mechanism which leads to an attraction between two excitons is due to the interaction of the excitons with a lattice.[11] This latter effect will, however, be neglected in our model.

The aim of this paper is to extend the formalism of our earlier study[10] so as to analyze the bulk biexciton spectrum in the intermediate-binding model. Such complexes were first predicted by Lampert[12] and Moskalenko[13] and, ever since, has been one of the subjects of experimental and theoretical interest in the spectroscopy of strongly excited solids.[14–16] Bose condensation of biexcitons is another phenomenon which has been observed experimentally using laser light of very high intensity, but this is beyond the scope of the present study.[17,18]

A theory for biexcitons, formed from excitons of the Wannier type, has been developed by Hanamura and co-workers.[19,20] One of the authors[21] has presented a theory for biexcitons of the Frenkel type. Because of the nature of our Hamiltonian, it is anticipated that the biexciton states for the model with intermediate binding should have different characteristics from those found in the two extreme cases. Hanamura's theory is based on the assumption that excitons and biexcitons are Bose particles. We do not make this assumption in our calculation although this is a reasonable one if the number of excited electron-hole pairs is much less than the total number of valence electrons. The idea is that since an exciton consists of two fermions, it should behave like a boson, under some restricted conditions. But, it is well known that an ideal Bose gas undergoes a phase transition—Bose-Einstein condensation—at sufficiently low temperatures. This led to the suggestion that at sufficiently high light intensities incident on an insulator in the exciton band, the crystal may exhibit new properties which may be associated with a Bose-Einstein condensation of the excitons. It is necessary that the net covalent interaction between two single excitons be attractive before an excitonic molecule could be formed. Since excitonic molecules satisfy the necessary conditions of Bose condensation, the repulsive interaction between molecules which arises from the direct Coulomb interaction or Pauli effect must exceed the attractive interaction due to exchange and van der Waals forces.[22] Thus it is believed that molecular formation is a necessary condition for condensation to be achieved.

In the present theory, we assume that biexcitons are formed at concentrations such that changes in the exciton spectrum are small compared with the binding energy of two excitons. If the density is too high, the overlap of the exciton wave functions is considerable and the entire picture breaks down. At very high densities, statistical effects due to the Pauli exclusion principle become important and the solid should be described in terms of an electron-hole plasma.[22]

The problem is formulated in Sec. II where we establish two sets of integro-coupled equations for the exciton and biexciton Green's functions, by using a decoupling procedure similar to Gorkov's theory of superconductivity.[23] By restricting our discussion at zero temperature, the *mathematical* Green's function which we introduce reduces to the Green's function for excitons in the Hartree-Fock (HF) approximation. However, the formalism is general in that it applies at finite temperatures and for crystals with a surface.

The 2×2 matrix Green's functions for excitons and biexcitons is evaluated in Sec. III for crystals in the absence of boundaries, at $T=0$. The poles of the matrix as a function of frequency lie on the real axis. It appears as though there are poles at the energies of free excitons and at the zeros of the denominator which arise in the solution of the set of coupled equations. Analysis of the derived expressions shows that in the absence of the gap function, there are poles corresponding to the energies of free excitons. However, when the gap parameter is finite, the only poles of the Green's function are given by the zeros of the denominator which correspond to bound states of two excitons. The excitation spectrum for biexcitons is examined for a simple case.

II. THE GOVERNING EQUATIONS

In this section we shall formulate our model by defining the Hamiltonian operator in algebraic terms and by deriving the equations which we shall use to determine the normal (exciton) and anomalous (biexciton) Green's functions. The normal modes are obtained from the poles of the matrix of which these Green's functions are elements.

In the ground state of the semiconducting crystal, the valence band is full of electrons, while the conduction band is empty. The Green's functions are used to study the collective modes when some electrons are removed from the valence band, where holes are formed, and transferred to the conduction band. The Hamiltonian for the system of N electrons is given by

$$\begin{aligned} H= &\sum_{\langle ll'\rangle} T_\alpha(ll')\alpha_{l'}^\dagger\alpha_l-\sum_{\langle ll'\rangle} T_\beta(ll')\beta_{l'}^\dagger\beta_l+E_\alpha\sum_l\alpha_l^\dagger\alpha_l-E_\beta\sum_l\beta_l^\dagger\beta_l+u_0\sum_l\beta_l^\dagger\beta_l\alpha_l^\dagger\alpha_l \\ &-\sum_{\langle ll'\rangle} u(ll')\beta_l^\dagger\alpha_l\alpha_{l'}^\dagger\beta_{l'}+\sum_{\langle ll'\rangle} v(ll')\alpha_l^\dagger\alpha_l\beta_{l'}^\dagger\beta_{l'}\,, \end{aligned} \tag{2.1}$$

where $\alpha_l^\dagger$, α_l are the creation and destruction operators for electrons at the lattice site $\vec{\mathbf{R}}_l^0$ in the conduction band, and $\beta_l^\dagger$, β_l are the corresponding operators for electrons in the valence band. E_α, E_β denote the on-site energy of the electron in the conduction and valence bands, respectively, and $\langle ll'\rangle$ denotes that the sum is to be done over nearest-neighbor pairs $\vec{\mathbf{R}}_l^0$ and $\vec{\mathbf{R}}_{l'}^0$. T_α and T_β are the hopping energies for electrons in the respective bands, u_0 is the on-site Coulomb interaction, and $u(ll')$, $v(ll')$ are the exchange and direct Coulomb interactions between electrons on neighboring lattice sites. The last term of Eq. (2.1) was ignored in Ref. 10, for reasons we discussed in the preceding section.

Where the exciton consists of an electron and a hole on the same lattice site, we showed[10] that the surface and bulk excitons are given by the poles of the *normal* Green's function $\langle\langle b_l(t);b_{l'}^\dagger(0)\rangle\rangle$. Here $b_l\equiv\beta_l^\dagger\alpha_l$ is the exciton operator in the Wannier representation and $\langle\langle\,;\,\rangle\rangle$ denotes the retarded Green's functions.[24] In deriving the equation for $\langle\langle b_l(t);b_{l'}^\dagger(0)\rangle\rangle$, we *now* assume that the system differs from the normal state by the presence of bound pairs of excitons. But the equation of motion for $\langle\langle b_l(t);b_{l'}^\dagger(0)\rangle\rangle$ involves a two-particle Green's function $\langle\langle b_l b_{l''};b_{l''}^\dagger b_{l'}^\dagger\rangle\rangle$. Therefore, in describing pairing correlations between excitons on different lattice sites, we follow Gorkov and Nambu[23] in their formalism for the theory of superconductivity and generalize the linearization in Ref. 10 to include terms involving Hartree-type functions $\langle\langle b_l(t);b_{l'}(0)\rangle\rangle$ and $\langle\langle b_l^\dagger(t);b_{l'}^\dagger(0)\rangle\rangle$. These Green's functions which we shall refer to as *anomalons* Green's functions, in analogy to the Gorkov F function used in the theory of superconductivity, are thus coupled to the normal Green's functions. Therefore, it is convenient to consider the equation of motion of the matrix

$$\begin{aligned} \mathbf{G}(ll';t)&\equiv\langle\langle X_l(t);X_{l'}^\dagger(0)\rangle\rangle \\ &=\begin{bmatrix} \langle\langle b_l(t);b_{l'}^\dagger(0)\rangle\rangle & \langle\langle b_l(t);b_{l'}(0)\rangle\rangle \\ \langle\langle b_l^\dagger(t);b_{l'}^\dagger(0)\rangle\rangle & \langle\langle b_l^\dagger(t);b_{l'}(0)\rangle\rangle \end{bmatrix}, \end{aligned} \tag{2.2}$$

where

$$X_l^\dagger(t)\equiv[b_l^\dagger(t)\ b_l(t)]. \tag{2.3}$$

Clearly, $G(ll';t)$ in Eq. (2.2) is obtained as a special case of the function

$$G(l_1 l_2 l_3 l_4;t) \equiv \langle\langle X_{l_1 l_2}(t); X^{\dagger}_{l_3 l_4}(0)\rangle\rangle, \tag{2.4}$$

by setting $l_1 = l_2 = l$ and $l_3 = l_4 = l'$, where $X_{l_1 l_2}(t)$ is defined by

$$X^{\dagger}_{l_1 l_2}(t) \equiv [\beta^{\dagger}_{l_1}(t)\alpha_{l_2}(t)\ \alpha^{\dagger}_{l_2}(t)\beta_{l_1}(t)]^{\dagger}. \tag{2.5}$$

Using the well-known commutation relations for the creation and destruction operators of electrons in the valence and conduction bands, we have

$$(b_l, b_{l'})_- = (b^{\dagger}_l, b^{\dagger}_{l'})_- = 0, \tag{2.6}$$

$$(b_l, b_{l'}{}^{\dagger})_- = (\beta^{\dagger}_l\beta_l - \alpha^{\dagger}_l\alpha_l)\delta_{ll'}. \tag{2.7}$$

Also, commuting b_l with the Hamiltonian in Eq. (2.1), we obtain

$$\begin{aligned}(b_l, H)_- = {} & \sum_{l''} T_{\alpha}(ll'')\beta^{\dagger}_l\alpha_{l''} + \sum_{l''} T_{\beta}(ll'')\beta^{\dagger}_{l''}\alpha_l + (E_{\alpha} + E_{\beta})b_l \\ & - \sum_{l''} u(ll'')(\beta^{\dagger}_l\beta^{\dagger}_{l''}\alpha_{l''}\beta_l - \beta_{l''}\alpha_{l''}\alpha^{\dagger}_l\alpha_l) + \sum_{l''} v(ll'')(\beta^{\dagger}_l\alpha_l\beta^{\dagger}_{l''}\beta_{l''} - \alpha^{\dagger}_{l''}\alpha_{l''}\beta^{\dagger}_l\alpha_l)\end{aligned} \tag{2.8}$$

and the u_0 term does not contribute as has been emphasized in Ref. 10. In Eq. (2.8), we now make the following approximations. In the sum involving the exchange interaction $u(ll')$ we set

$$\beta^{\dagger}_l\beta^{\dagger}_{l''}\alpha_{l''}\beta_l - \beta^{\dagger}_{l''}\alpha_{l''}a^{\dagger}_l\alpha_l \approx b_{l''}\langle\beta^{\dagger}_l\beta_l\rangle - \beta^{\dagger}_l\alpha_{l''}\langle\beta^{\dagger}_{l''}\beta_l\rangle - b_{l''}\langle\alpha^{\dagger}_l\alpha_l\rangle + \beta^{\dagger}_{l''}\alpha_l\langle a^{\dagger}_l\alpha_{l''}\rangle, \tag{2.9}$$

which is the random-phase approximation (RPA) or mean-field approximation. In the term involving the direct interaction $v(ll'')$ we set

$$\begin{aligned}\beta^{\dagger}_l\alpha_l\beta^{\dagger}_{l''}\beta_{l''} - \alpha^{\dagger}_{l''}a_{l''}\beta^{\dagger}_l a_l \approx {} & b_l\langle\beta^{\dagger}_{l''}\beta_{l''}\rangle - \beta^{\dagger}_{l''}\alpha_l\langle\beta^{\dagger}_l\beta_{l''}\rangle - b_l\langle\alpha^{\dagger}_{l''}\alpha_{l''}\rangle \\ & + \beta^{\dagger}_l\alpha_{l''}\langle\alpha^{\dagger}_{l''}\alpha_l\rangle + \langle b_l b_{l''}\rangle b^{\dagger}_{l''}.\end{aligned} \tag{2.10}$$

Therefore, in addition to the Hartree and Fock terms of Eq. (2.9), there is a term which is related to exciton-state pairing and is expressed by the average $\langle b_l b_{l''}\rangle$. The off-diagonal elements of the matrix in Eq. (2.2) thus give rise to a spatially dependent parameter

$$\Delta(ll') = v(ll')\langle b_l b_{l'}\rangle \tag{2.11}$$

and its complex conjugate which have to be self-consistently determined.

Taking the time derivative of Eq. (2.2), and using Eqs. (2.6)–(2.11), we obtain ($\hbar$ will be set equal to 1)

$$\frac{i\partial}{\partial t}G(ll';t) = \delta(t)(\langle\beta^{\dagger}_l\beta_l\rangle - \langle\alpha^{\dagger}_l\alpha_l\rangle)\delta_{ll'}\hat{\sigma}_z + \hat{\sigma}_z S\{G\} + \sum_{l''} M(ll'')G(l''l';t), \tag{2.12}$$

where $M(ll')$ is an off-diagonal matrix which is defined as

$$M(ll') = \begin{bmatrix} 0 & \Delta(ll') \\ \Delta^{*}(ll') & 0 \end{bmatrix} \tag{2.13}$$

and S is a functional of G:

$$\begin{aligned}S\{G\} = {} & (E_{\alpha} + E_{\beta})G(ll';t) + \sum_{l''} T_{\alpha}(ll'')G(ll''l'l';t) + \sum_{l''} T_{\beta}(ll'')G(l''ll'l';t) \\ & - \sum_{l''} u(ll'')(\langle\beta^{\dagger}_l\beta_l\rangle - \langle\alpha^{\dagger}_l\alpha_l\rangle)G(l''l';t) + \sum_{l''} v(ll'')(\langle\beta^{\dagger}_{l''}\beta_{l''}\rangle - \langle\alpha^{\dagger}_{l''}\alpha_{l''}\rangle)G(ll';t) \\ & - \sum_{l''} u(ll'')p(\alpha;ll'')G(l''ll'l';t) + \sum_{l''} u(ll'')p(\beta;l''l)G(ll''l'l';t) \\ & - \sum_{l''} v(ll'')p(\beta;ll'')G(l''ll'l';t) + \sum_{l''} v(ll'')p(\alpha;l''l)G(ll''l'l';t),\end{aligned} \tag{2.14}$$

with

$$p(\alpha;ll') \equiv \begin{bmatrix} \langle \alpha_l^\dagger \alpha_{l'} \rangle & 0 \\ 0 & \langle \alpha_{l'}^\dagger \alpha_l \rangle \end{bmatrix}, \tag{2.15}$$

and a similar definition for $p(\beta;ll')$ with $\alpha,\alpha^\dagger$ replaced by β, $\beta^\dagger$, respectively. $\hat{\sigma}_z$ in Eq. (2.12) is the Dirac matrix with eigenvalues ± 1.

In the Hartree-Fock (HF) approximation, the pairing matrix $M(ll')$ in Eq. (2.13) is ignored. Therefore, denoting the mean-field solution of Eq. (2.12) by G^{HF}, we then find from Eq. (2.12) that G^{HF} satisfies the equation

$$\frac{i\partial}{\partial t} G^{\mathrm{HF}}(ll';t) - \delta(t)(\langle \beta_l^\dagger \beta_l \rangle - \langle \alpha_l^\dagger \alpha_l \rangle)\delta_{ll'}\hat{\sigma}_z - \hat{\sigma}_z S\{G^{\mathrm{HF}}\} \equiv 0. \tag{2.16}$$

Let us now introduce a function $K(ll';t)$, which is defined as the solution of the equation

$$\frac{i\partial}{\partial t} K(ll';t) - \hat{\sigma}_z S\{K\} = \hat{\sigma}_z \delta_{ll'} \delta(t). \tag{2.17}$$

This equation together with Eq. (2.16) permits us to write $G(ll';t)$ of Eq. (2.12) as the solution of a set of coupled equations which are given by

$$G(ll';t) = G^{\mathrm{HF}}(ll';t) + \sum_{l''l'''} \hat{\sigma}_z \int_{-\infty}^{\infty} dt_1 K(ll'';t-t_1) M(l''l''') G(l'''l';t_1). \tag{2.18}$$

We emphasize that the function $K(ll';t)$ is primarily introduced for mathematical convenience. Of course, a solution of Eq. (2.18) would require an explicit expression for this function. However, before we make a further study of this function, let us first consider the HF solution G^{HF}.

Define the noninteracting Green's function G_0 as the solution of the equation

$$\begin{aligned} \frac{i\partial}{\partial t} G_0(ll';t) = {} & \delta(t)(\langle \beta_l^\dagger \beta_l \rangle - \langle \alpha_l^\dagger \alpha_l \rangle)\delta_{ll'}\hat{\sigma}_z \\ & + \hat{\sigma}_z \left[(E_\alpha + E_\beta) G_0(ll';t) + \sum_{l''} T_\alpha(ll'') G_0(ll''l'l';t) + \sum_{l''} T_\beta(ll'') G_0(l''ll'l';t) \right. \\ & \left. - \sum_{l''} u(ll'') p(\alpha;ll'') G_0(l''ll'l';t) + \sum_{l''} u(ll'') p(\beta;l''l) G_0(ll''l'l';t) \right]. \end{aligned} \tag{2.19}$$

This together with Eq. (2.16) gives

$$\begin{aligned} G^{\mathrm{HF}}(ll';t) = {} & G_0(ll';t) - \hat{\sigma}_z \int_{-\infty}^{\infty} dt_1 \sum_{l''l'''} G_0(ll'';t-t_1) u(l''l''') G^{\mathrm{HF}}(l'''l';t_1) \\ & + \hat{\sigma}_z \int_{-\infty}^{\infty} dt_1 \sum_{l''l'''} G_0(l''l''';t-t_1) v(l'''l) G^{\mathrm{HF}}(ll';t_1). \end{aligned} \tag{2.20}$$

The noninteracting Green's-function matrix G_0 is diagonal. With an effective Hamiltonian defined by

$$\begin{aligned} H_{\mathrm{HF}} = {} & \sum_{ll'} [T_\alpha(ll') - u(ll') \langle \beta_{l'}^\dagger \beta_l \rangle] \alpha_{l'}^\dagger \alpha_{l'} - \sum_{ll'} [T_\beta(ll') + u(ll') \langle \alpha_{l'}^\dagger \alpha_l \rangle] \beta_l^\dagger \beta_{l'} \\ & + E_\alpha \sum_l \alpha_l^\dagger \alpha_l - E_\beta \sum_l \beta_l^\dagger \beta_l, \end{aligned} \tag{2.21}$$

it is straightforward to show that Eq. (2.19) is satisfied by a diagonal matrix with

$$\begin{aligned} G_0^{(11)}(l_1 l_2 l_3 l_4;t) = -i\theta(t)\{ & -\langle \alpha_{l_3}^\dagger(0) \alpha_{l_2}(t) \rangle \langle [\beta_{l_1}^\dagger(t), \beta_{l_4}(0)]_+ \rangle \\ & + \langle \beta_{l_1}^\dagger(t) \beta_{l_4}(0) \rangle \langle [\alpha_{l_3}^\dagger(0), \alpha_{l_2}(t)]_+ \rangle \} \end{aligned} \tag{2.22}$$

in the first row and first column, and

$$G_0^{(22)}(l_1 l_2 l_3 l_4;t) = -i\theta(t)\{\, \langle a_{l_2}^{\dagger}(t)\alpha_{l_3}(0)\rangle \langle [\beta_{l_4}^{\dagger}(0),\beta_{l_1}(t)]_+\rangle$$
$$- \langle \beta_{l_4}^{\dagger}(0)\beta_{l_1}(t)\rangle \langle [\alpha_{l_2}^{\dagger}(t),\alpha_{l_3}(0)]_+\rangle\} \tag{2.23}$$

in the second row and second column. The averages in Eqs. (2.21)—(2.23) are to be taken with respect to H_{HF}. Defining the spectral density functions $\rho_\alpha(l'l;\omega)$ and $\rho_\beta(ll';\omega)$ by the equations

$$\langle \alpha_{l'}^{\dagger}(0)\alpha_l(t)\rangle = \int_{-\infty}^{\infty} d\omega\, e^{-i\omega t}\rho_\alpha(l'l;\omega), \tag{2.24}$$

$$\langle \beta_l^{\dagger}(t)\beta_{l'}(0)\rangle = \int_{-\infty}^{\infty} d\omega\, e^{i\omega t}\rho_\beta(ll';\omega), \tag{2.25}$$

we have shown that for $l_1 = l_2 = l$ and $l_3 = l_4 = l'$, the Fourier transform of Eqs. (2.22) and (2.23) is given by

$$G_0(ll';\omega) = \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \frac{e^{\omega_1/T} - e^{\omega_2/T}}{\omega - \omega_1 - \omega_2} \rho_\beta(ll';\omega_2)\rho_\alpha(l'l;\omega_1), \tag{2.26}$$

where T is the temperature and we have set $k_B = 1$. We now express the spectral density functions ρ_α and ρ_β in terms of the Fourier transform of the single-particle Green's functions g_α and g_β defined by

$$g_\alpha(l'l;t) = -i\theta(t)\langle [\alpha_{l'}^{\dagger}(0),\alpha_l(t)]_+\rangle, \tag{2.27}$$

$$g_\beta(ll';t) = -i\theta(t)\langle [\beta_l^{\dagger}(t),\beta_{l'}(0)]_+\rangle. \tag{2.28}$$

The result is

$$\rho_\alpha(l'l;\omega) = \frac{1}{2\pi i}\frac{1}{1+e^{\omega/T}}[g_\alpha(l'l;\omega - i0) - g_\alpha(l'l;\omega + i0)], \tag{2.29}$$

$$\rho_\beta(ll';\omega) = \frac{1}{2\pi i}\frac{1}{1+e^{\omega/T}}[g_\beta(ll';-\omega - i0) - g_\beta(ll';-\omega + i0)]. \tag{2.30}$$

We have therefore established the set of coupled equations which have to be solved in order to study the dynamical motion of biexcitons in an insulating crystal. These are given by Eq. (2.18) where $G^{\mathrm{HF}}(ll';t)$ in that equation is defined as the solution of Eq. (2.20). But the solution of Eq. (2.18) entails the knowledge of the auxiliary Green's function $K(ll';t)$ defined by Eq. (2.17). In this regard, let us recall the assumption that the valence band is full and the conduction band is empty. In addition, we shall ignore *virtual* transitions between the valence and conduction bands. This means that

$$\langle \alpha_l^{\dagger}\alpha_l\rangle = 0, \quad \langle \beta_l^{\dagger}\beta_l\rangle = 1. \tag{2.31}$$

Making use of Eq. (2.31), it is clear that the equation for $G^{\mathrm{HF}}(ll';t)$ [Eq. (2.16)] is the same as that for $K(ll';t)$ [Eq. (2.17)] and therefore these two functions are equal. G^{HF} and K are, however, separate functions in general.

Finally, it is straightforward to show, using the results in Eqs. (2.24) and (2.25) together with Eqs. (2.29) and (2.30), that at $T = 0$

$$\langle \alpha_l^{\dagger}\alpha_{l'}\rangle = 0 \text{ and } \langle \beta_l^{\dagger}\beta_{l'}\rangle = 0, \quad l \neq l'. \tag{2.32}$$

However, at finite temperatures, these averages are nonzero and have to be determined self-consistently.

III. DISPERSION RELATION FOR EXCITONS AND BIEXCITONS

In this section we shall solve Eq. (2.18) for a simple cubic lattice of spacing a_0. The first step is to solve for the single-particle Green's functions g_α and g_β in Eqs. (2.27) and (2.28), respectively. For the bulk crystal, with the usual periodic boundary conditions, these are functions of $l - l'$ only and are given by[10]

$$g_\alpha^B(l-l';\omega) = \frac{1}{N}\sum_{\vec{k}} \frac{e^{i\vec{k}\cdot(\vec{R}_l^0 - \vec{R}_{l'}^0)}}{\omega - E_\alpha(\vec{k})}, \tag{3.1}$$

$$g_\beta^B(l-l';\omega) = \frac{1}{N}\sum_{\vec{k}} \frac{e^{i\vec{k}\cdot(\vec{R}_l^0 - \vec{R}_{l'}^0)}}{\omega - E_\beta^0 - E_\beta(\vec{k})}. \tag{3.2}$$

Here N is the total number of atoms in the crystal, the sums over $\vec{k}$ are to be taken over the first Brillouin zone, and the energy levels $E_\alpha(\vec{k})$ and $E_\beta(\vec{k})$ are given by

$$E_\alpha(\vec{k})=6T_\alpha-2T_\alpha(\cos k_x a_0+\cos k_y a_0+\cos k_z a_0), \tag{3.3}$$

$$E_\beta(\vec{k})=6T_\beta-2T_\beta(\cos k_x a_0+\cos k_y a_0+\cos k_z a_0), \tag{3.4}$$

where $T_{\alpha,\beta}(ll')=-T_{\alpha,\beta}$ for nearest-neighbor atoms. We have chosen $E_\beta=E_\beta^0+6T_\beta$ and $E_\alpha=6T_\alpha$. Making use of the results of Eqs. (3.1) and (3.2) in Eqs. (2.29) and (2.30) and then substituting the results for the spectral density functions into Eq. (2.26), we obtain the noninteracting Green's function for the bulk

$$G_0^B(l-l';\omega)=\frac{1}{N^2}\sum_{\vec{q}\,\vec{q}\,'}\frac{e^{i(\vec{q}-\vec{q}\,')\cdot(\vec{R}_l^0-\vec{R}_{l'}^0)}}{\omega-E_\beta^0-E_\alpha(\vec{q}\,')-E_\beta(\vec{q})}. \tag{3.5}$$

From Eq. (3.5) we deduce that the Fourier transform $G_0^B(\vec{k},\omega)$ defined by

$$G_0^B(l-l';\omega)=\frac{1}{N}\sum_{\vec{k}}e^{i\vec{k}\cdot(\vec{R}_l^0-\vec{R}_{l'}^0)}G_0^B(\vec{k},\omega) \tag{3.6}$$

is given by

$$G_0^B(\vec{k},\omega)=\frac{1}{N}\sum_{\vec{q}}\frac{1}{\omega-E_\beta^0-E_\alpha(\vec{q}-\vec{k})-E_\beta(\vec{q})}. \tag{3.7}$$

Since for the bulk $G^{\mathrm{HF}}(ll';t)$ depends on $l-l'$ only, we may Fourier transform Eq. (2.20) with respect to time and $l-l'$. We obtain

$$G_B^{\mathrm{HF}}(\vec{k},\omega)=G_0^B(\vec{k},\omega)-\hat{\sigma}_z G_0^B(\vec{k},\omega)u(\vec{k})G_B^{\mathrm{HF}}(\vec{k},\omega)+\hat{\sigma}_z G_0^B(\vec{k}=0,\omega)v(\vec{k}=0)G_B^{\mathrm{HF}}(\vec{k},\omega), \tag{3.8}$$

where $u(\vec{k})$ and $v(\vec{k})$ are the Fourier transforms of the nearest-neighbor exchange and direct Coulomb interactions, respectively. We have

$$u(\vec{k})=2u(\cos k_x a_0+\cos k_y a_0+\cos k_z a_0) \tag{3.9}$$

and a similar expression for $v(\vec{k})$ with u on the right-hand side of Eq. (3.9) replaced by v, where u and v are the strengths of the exchange and direct interactions for nearest neighbors. Rearranging the terms of Eq. (3.8) and solving for $G_B^{\mathrm{HF}}(\vec{k},\omega)$ we obtain

$$G_B^{\mathrm{HF}}(\vec{k},\omega)=\begin{bmatrix}\epsilon_+^{-1}(\vec{k},\omega) & 0\\ 0 & \epsilon_-^{-1}(\vec{k},\omega)\end{bmatrix}G_0^B(\vec{k},\omega), \tag{3.10}$$

where

$$\epsilon_\pm(\vec{k},\omega)=1\pm[u(\vec{k})G_0^B(\vec{k},\omega)-v(\vec{k}=0)G_0^B(\vec{k}=0,\omega)]. \tag{3.11}$$

In the absence of boundaries, $G(ll';t)$ also depends on $l-l'$ only. Therefore, Fourier transforming Eq. (2.18) with respect to time and the variable $l-l'$, we find after rearranging the terms that the Fourier transform $G^B(\vec{k},\omega)$ is given by

$$G^B(\vec{k},\omega)=[1-\hat{\sigma}_z G_B^{\mathrm{HF}}(\vec{k},\omega)M(\vec{k})]^{-1}G_B^{\mathrm{HF}}(\vec{k},\omega). \tag{3.12}$$

Substituting the result for $G_B^{\mathrm{HF}}(\vec{k},\omega)$ of Eq. (3.10) into Eq. (3.12), we obtain

$$G^B(\vec{k},\omega)=\frac{1}{D^B(\vec{k},\omega)}\begin{bmatrix}G_0^B(\vec{k},\omega)\epsilon_+^{-1}(\vec{k},\omega) & \epsilon_+^{-1}(\vec{k},\omega)\epsilon_-^{-1}(\vec{k},\omega)\,\Delta(\vec{k})[G_0^B(\vec{k},\omega)]^2\\ -\epsilon_+^{-1}(\vec{k},\omega)\epsilon_-^{-1}(\vec{k},\omega)\Delta^*(\vec{k})[G_0^B(\vec{k},\omega)]^2 & G_0^B(\vec{k},\omega)\epsilon_-^{-1}(\vec{k},\omega)\end{bmatrix}, \tag{3.13}$$

where

$$D^B(\vec{k},\omega)\equiv 1+\epsilon_+^{-1}(\vec{k},\omega)\epsilon_-^{-1}(\vec{k},\omega)\,|\Delta(\vec{k})|^2[G_0^B(\vec{k},\omega)]^2, \tag{3.14}$$

and

$$\Delta(\vec{k})=\frac{1}{N}\sum_{k'}v(\vec{k}-\vec{k}')\langle b_{\vec{k}'}, b_{-\vec{k}'}\rangle . \tag{3.15}$$

$\Delta(\vec{k})$ is the coupling parameter for a biexciton of momentum $\vec{k}$ which is a good quantum number. There is a sum over $\vec{k}'$ in Eq. (3.15) since the two excitons forming the biexciton may be scattered by one another into all possible states. Also since the two excitons are bound by the direct Coulomb interaction, we have $v(\vec{k}-\vec{k}')$ appearing as a coefficient in the sum of Eq. (3.15).

The singularities of $G^B(\vec{k},\omega)$ in Eq. (3.13) are located at the solutions of

$$D^B(\vec{k},\omega)=0 \tag{3.16}$$

and these correspond to bound states (biexcitons) provided the roots of Eq. (3.13) are separated from the solutions of $\epsilon_{\pm}(\vec{k},\omega)=0$, which determine the frequencies of the exciton band. If we set $\Delta(\vec{k})=0$ in Eq. (3.13), the off-diagonal elements vanish and $G^B(\vec{k},\omega)$ has singularities only at the frequencies where the denominators $\epsilon_{\pm}(\vec{k},\omega)$ of the diagonal elements vanish. In Eq. (3.14), we see that the exciton dispersion relations $\epsilon_{\pm}(\vec{k},\omega)$ are coupled by the parameter $\Delta(\vec{k})$, clearly displaying the role this parameter plays in producing a biexciton bound state from two separate exciton states.

To further understand the exciton and biexciton bound states, let us evaluate their normal-mode frequencies in the long-wavelength limit. For frequencies below the elementary excitation spectrum, we may rewrite $G_0^B(\vec{k},\omega)$ of Eq. (3.7) as[10]

$$G_0^B(\vec{k},\omega)=-\int_0^{\infty} ds\, e^{-s[E_\beta^0-\omega+6(T_\alpha+T_\beta)]}P(2\gamma_x s)P(2\gamma_y s)P(2\gamma_z s), \tag{3.17}$$

where ($i=x,y,z$)

$$P(2\gamma_i s)=\frac{1}{2\pi}\int_{-\pi}^{\pi} dq_i \exp[2\gamma_i s\cos(\theta_i-q_i)], \tag{3.18}$$

with

$$\cos\theta_i\equiv(T_\alpha\cos k_i a_0+T_\beta)/\gamma_i, \tag{3.19a}$$

$$\sin\theta_i\equiv(T_\alpha\sin k_i a_0)/\gamma_i, \tag{3.19b}$$

$$\gamma_i\equiv(T_\alpha^2+2T_\alpha T_\beta\cos k_i a_0+T_\beta^2)^{1/2}. \tag{3.19c}$$

In the long-wavelength limit, we have to order k^2

$$G_0^B(\vec{k},\omega)=-\frac{1}{2(T_\alpha+T_\beta)}\int_0^{\infty} ds\, e^{-s(3+\tilde{\omega})}[I_0^3(s)-(ka_0)^2 I_0^2(s)X(s)], \tag{3.20}$$

where the function $X(s)$ is defined to be

$$X(s)\equiv\frac{sT_\alpha}{2(T_\alpha+T_\beta)}\left[I_1(s)-\frac{sT_\alpha}{2(T_\alpha+T_\beta)}[I_0(s)-I_2(s)]\right] \tag{3.21}$$

with $I_n(s)$ the modified Bessel function of the first kind of order n. For convenience, we have introduced the variable $\tilde{\omega}$ in Eq. (3.20). This is defined by the equation

$$\tilde{\omega}\equiv\frac{E_\beta^0-\omega}{2(T_\alpha+T_\beta)} . \tag{3.22}$$

Substituting the power series expansion for $G_0^B(\vec{k},\omega)$ into $\epsilon_+(\vec{k},\omega)$ defined in Eq. (3.11), we obtain the frequency of the bulk exciton mode for long wavelengths,

$$\omega_{\vec{k}}=\omega_0+Dk^2 . \tag{3.23}$$

Here ω_0 is its value at $\vec{k}=0$ and is given by

$$\omega_0=\omega_{\min}(k=0)-2\tilde{\omega}_0(T_\alpha+T_\beta), \tag{3.24}$$

where

$$\omega_{\min}(\vec{k}=0) \equiv E_\beta^0 \tag{3.25}$$

is the value at $\vec{k}=0$ of the wave-vector-dependent lower bound for the particle-hole excitations and $\tilde{\omega}_0$ in Eq. (3.24) is the solution of

$$3(u-v)\int_0^\infty ds\, e^{-s(3+\tilde{\omega}_0)} I_0^3(s) = (T_\alpha + T_\beta). \tag{3.26}$$

The stiffness constant D of Eq. (3.23) depends on *all* the parameters of our Hamiltonian and is given by

$$D \equiv \frac{u}{u-v}\frac{a_0^2}{Y(\tilde{\omega}_0)}\left[(T_\alpha+T_\beta)\int_0^\infty ds\, e^{-s(3+\tilde{\omega}_0)} I_0^3(s) + 3T_\alpha \int_0^\infty dss\, e^{-s(3+\tilde{\omega}_0)} I_0^2(s)\left[I_1(s) - \frac{sT_\alpha}{2(T_\alpha+T_\beta)}[I_0(s)-I_2(s)]\right]\right], \tag{3.27}$$

where $Y(\omega)$ is an integral involving the Bessel function of order zero,

$$Y(\omega) \equiv 3\int_0^\infty dss\, e^{-s(3+\omega)} I_0^3(s). \tag{3.28}$$

Substituting the result of Eq. (3.20) into the dispersion relation of Eq. (3.16), one easily obtains at zero wave vector the frequency Ω_0 of the bulk biexciton mode that lies below the particle-hole excitation spectrum. We have

$$\Omega_0 = \omega_{\min}(\vec{k}=0) - 2\tilde{\Omega}_0(T_\alpha+T_\beta), \tag{3.29}$$

where $\omega_{\min}(\vec{k}=0)$ is defined in Eq. (3.25), $\tilde{\Omega}_0$ is defined as the solution of

$$1 - [9(u-v)^2 - \tfrac{1}{4}|\Delta_0|^2]\alpha^2(\tilde{\Omega}_0) = 0, \tag{3.30}$$

with $\Delta_0 \equiv \Delta(\vec{k}=0)$, and the function $\alpha(\omega)$ is given by

$$\alpha(\omega) \equiv \frac{1}{(T_\alpha+T_\beta)}\int_0^\infty ds\, e^{-s(3+\omega)} I_0^3(s). \tag{3.31}$$

The coupling parameter $\Delta(\vec{k})$ is determined by a nonlinear integral equation. To obtain this equation, the first step is to determine the statistical average $\langle b_{\vec{k}} b_{-\vec{k}} \rangle$ in Eq. (3.15). This average is calculated by taking the difference of the Green's function $\langle\langle b_{-\vec{k}}; b_{\vec{k}} \rangle\rangle$ across the branch cut along the real axis,

$$\langle b_{\vec{k}} b_{-\vec{k}} \rangle = 2\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} f_0(\omega)\,\mathrm{Im}\langle\langle b_{-\vec{k}}; b_{\vec{k}} \rangle\rangle. \tag{3.32}$$

Here, $f_0(\omega) \equiv (e^{\omega/T}-1)^{-1}$, where units with $k_B=1$ are used and $\langle\langle b_{-\vec{k}}; b_{\vec{k}} \rangle\rangle$ is given by one of the off-diagonal elements of Eq. (3.13). For a simple cubic lattice, with nearest-neighbor Coulomb interactions, we have $\Delta(\vec{k}) = \frac{1}{3}(\cos k_x a_0 + \cos k_y a_0 + \cos k_z a_0)\Delta_0$, where the phase is chosen so that $\Delta(\vec{k})$ is real. Substituting Eq. (3.32) into Eq. (3.15) we obtain the equation which determines Δ_0 and, therefore, $\Delta(\vec{k})$. For the present, we choose Δ_0 independent of the other parameters.

It is straightforward to find the correction of Ω_0 for long wavelengths. The lowest-order correction is of order $\vec{k}^2$ and the coefficient of this term can be obtained by means of a calculation similar to that used in calculating the result in Eq. (3.23) for excitons. These results are similar to those derived in connection with the magnon and two-magnon bound state problem for a Heisenberg Hamiltonian.[25] Using the tight-binding Frenkel Hamiltonian for excitons in a molecular crystal, Mavroyannis[21] has also shown that the frequency for a biexciton in the long-wavelength region is quadratic in the wave vector. These similarities are not surprising because of the similarity of our problem with spin systems and also because the Frenkel Hamiltonian is a special case of our Hamiltonian in Eq. (2.1).

Some properties of the collective excitations have been obtained without a detailed numerical calculation. These are now pointed out. The effect of the nearest-neighbor Coulomb interaction is to shift the energy levels of the single-particle electron-hole states forming a continuum, and, in addition to split off discrete states from the continuum for each value of the wave vector. But if the Coulomb interaction is too weak compared to the hopping integrals, no exciton states may be formed. We must therefore choose our parameters so that the condition

$$0 \le \omega_0 < E_\beta^0 \tag{3.33}$$

is satisfied. The role of the direct Coulomb interaction is to reduce the effect which the exchange interaction has in splitting off the exciton state.

This is clear from the appearance of the $(u-v)$ factor in Eq. (3.26). Furthermore, if $u<v$, there is no exciton bound state below the elementary excitation spectrum.

Equations (3.26) and (3.30) which determine ω_0 and Ω_0, the frequency of the exciton and biexciton bound states at zero wave vector, respectively, only differ by the appearance of the coupling parameter in Eq. (3.30). Provided there are exciton states and the coupling parameter satisfies

$$\Delta_0 < 6(u-v)\,, \tag{3.34}$$

Eq. (3.30) has a solution with $\Omega_0 > \omega_0$. We also require that Ω_0 lies outside the continuum of elementary excitations, for, otherwise, it would be too short lived to be a well-defined collective mode.

We have thus established the conditions which have to be satisfied for the formation of excitons and biexcitons in an insulating crystal with intermediate binding. These conditions depend on the band structure unlike those derived in connection with the biexciton mode in a molecular crystal.[12]

For a pure undamped normal excitation, the spectral function is proportional to a δ function. However, if the spectral function has the almost δ function form

$$\bar{a}(\vec{k},\omega)=\frac{Z(\omega_{\vec{k}})\Gamma(\omega_{\vec{k}})}{(\omega-\omega_{\vec{k}})^2+[\frac{1}{2}\Gamma(\omega_{\vec{k}})]^2}\,, \tag{3.35}$$

the mode of frequency $\omega=\omega_{\vec{k}}$ is damped, with damping constant $\Gamma(\omega_{\vec{k}})$. For the individual excitons, Eq. (3.34) is obtained in the neighborhood of a solution of the dispersion relation $\mathrm{Re}\,\epsilon_+(\vec{k},\omega)=0$ provided we define its weight to be

$$Z(\omega_{\vec{k}})=\left[\frac{\partial}{\partial\omega}\mathrm{Re}\,\epsilon_+(\vec{k},\omega)\right]^{-1}_{\omega=\omega_{\vec{k}}}. \tag{3.36a}$$

We also define the weight of a biexciton excitation of frequency $\Omega_{\vec{k}}$ as

$$Z(\Omega_{\vec{k}})=\left[\frac{\partial}{\partial\omega}\mathrm{Re}\,\epsilon_+(\vec{k},\omega)\epsilon_-(\vec{k},\omega)D^B(\vec{k},\omega)\right]^{-1}_{\omega=\Omega_{\vec{k}}}. \tag{3.36b}$$

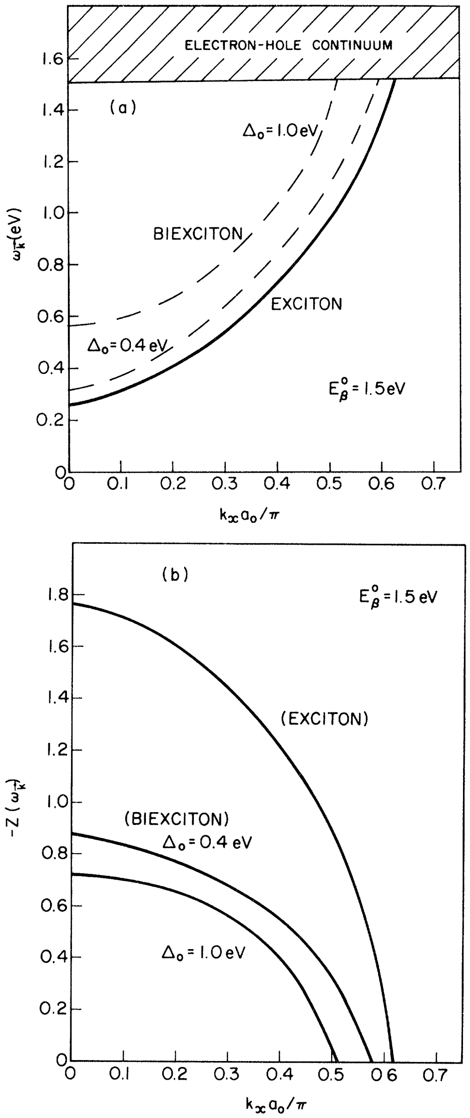

FIG. 1. (a) Excitation spectra in the [100] direction for excitons (solid line) and biexcitons (broken line) on a simple cubic lattice with periodic boundary conditions. The particle-hole excitation region corresponds to the hatched area. The band gap at zero wave vector is $E^0_\beta=1.5$ eV. (b) Plot of the weight function, defined in Eq. (3.36), for the exciton and biexciton modes. The band gap at zero wave vector is $E^0_\beta=1.5$ eV.

We have solved the dispersion relations for the exciton $[\mathrm{Re}\,\epsilon_+(\vec{k},\omega)=0]$ and biexciton $[\mathrm{Re}\,D^B(\vec{k},\omega)=0]$ modes. We have also evaluated the weight function Z, given by Eq. (3.36). The results are plotted in Figs. 1 and 2 for two different values of the energy gap E^0_β between the valence and conduction bands at zero wave vector. The bandwidth of the conduction band $(12T_\alpha)$ and that of the valence band $(12T_\beta)$ are chosen as 0.06 eV. The nearest-neighbor exchange interaction (u) and the nearest-neighbor direct interaction (v) are set equal 0.4 and 0.1 eV, respectively. Two different values of the gap parameter Δ_0 were used in our computer runs. As expected, for a given wave vector Z has a smaller amplitude for the biexciton mode than the exciton mode since its magnitude is

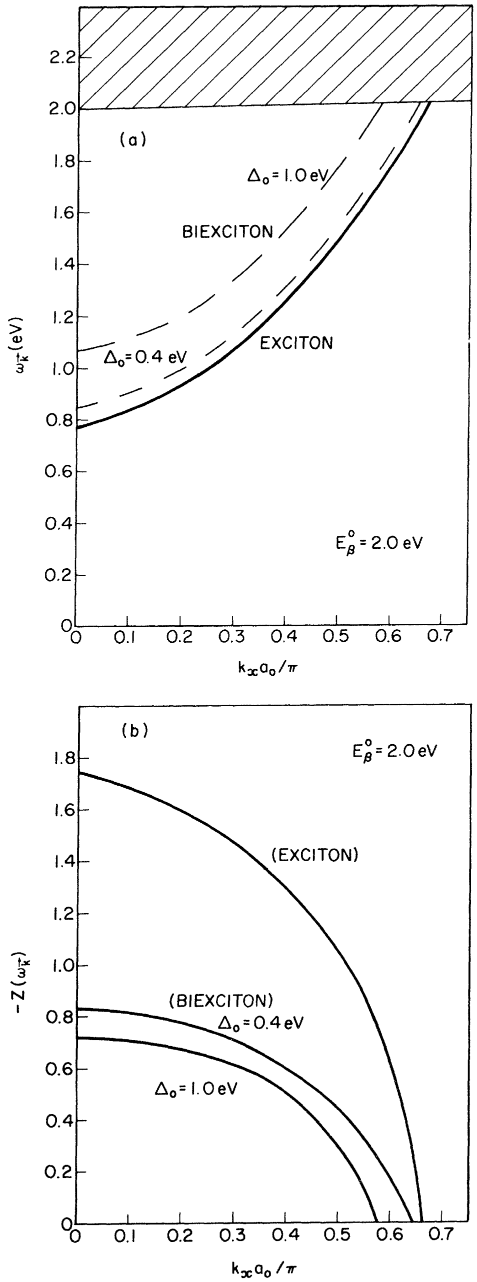

FIG. 2. (a) Same as Fig. 1(a), but with $E_\beta^0=2.0$ eV. (b) Same as Fig. 1(b), but with $E_\beta^0=2.0$ eV.

a measure of the probability for a mode. Comparing Figs. 1(a) and 2(a), it is seen that the exciton energies increase with band gap.

IV. CONCLUDING REMARKS

A model has been presented for excitons and biexcitons in insulating crystals with intermediate binding energies for the electron-hole pairs. A two-band model is used for a simple cubic lattice structure. The exciton and biexciton Green's functions are given as solutions of a set of coupled equations. The problem is simplified at zero temperature and the excitation energies are computed numerically in this case. The electron and the hole are assumed to be tightly bound on the same lattice site but the formulation may be generalized to the case even when they are in different unit cells.

The results obtained in Sec. III are, as we have emphasized, a special case of the more general results derived in Sec. II. However, the formulation leading to the main equations (2.18) and (2.20) is general and may be applied to systems where the translational symmetry has been destroyed by the presence of a surface, for example. The effects of a surface on the excitation spectra of excitons and biexcitons will be presented elsewhere. To our knowledge the method of Altarelli and Bassani[7] to deal with excitons with intermediate binding has not been used to study biexcitons or surface effects on the spectroscopic properties of insulating crystals. The present model is equivalent to the one-site approximation introduced by Andreoni *et al.*[8] which is obtained by assuming in their calculation that the electron and the hole are in the same unit cell.

The numerical results in Figs. 1 and 2 show that the biexciton spectrum lies above that for excitons. This is in contrast to the experimental results reported in the literature for semiconducting crystals such as Ge,[26] CuCl,[27] and CuBr.[28] However, there are so far no results for the biexciton spectrum formed from the lowest exciton states of the rare-gas solids for which our model is relevant. Thus our results present a new challenge to investigate these states experimentally. The way we interpret the results is to say that the exciton states are the lowest electronic excited states of the crystal. When the density of the excitons is increased to the extent that exciton-exciton interaction becomes important but such that changes in the exciton spectrum are small compared with the binding energy of two excitons, new elementary excitations of higher energy per electron-hole pair appear. This new collective state has infinite lifetime outside the electron-hole continuum. However, when the gap parameter becomes too large because of strong exciton-exciton interactions, the biexciton modes would lie in the electron-hole continuum. As a result, the modes become short-lived and the solid is best described in terms of an electron-hole plasma.[22]

Recently, Schwentner *et al.*[29] have reviewed the experimental and theoretical results for bulk and surface excitons. We refer to their article where extensive reference is given for spectroscopic and band-structure results for the condensed rare gases. But we now make a brief comment as a final remark. Electron energy-loss experiments have been used to excite electrons from the valence band to an excited state. Either a free electron-hole pair or an exciton, i.e., a bound electron-hole pair will be created. In the case of large band gaps, energy losses will be of the order of several electron volts. In view of the large band gaps and the pronounced excitonic structure, an insulator whose electronic structure is well described by a two-band model would be ideal to test our results.

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