PHYSICAL REVIEW B VOLUME 16, NUMBER 6 15 SEPTEMBER 1977

Singlet and triplet biexciton spectra of molecular crystals

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(Received 14 April 1977)

The theory of the coherent pairing of Frenkel excitons in the presence of a resonant electromagnetic field is generalized to include the effect of the electron spin. It is shown that at high exciton densities and when the electromagnetic field is at resonance or near resonance, the removal of the spin degeneracy of the exciton pairs results in generating two fields, the singlet and the triplet biexciton fields, respectively. The gap functions Δ_+ and Δ_- due to the singlet and triplet biexciton fields, respectively, are calculated and they are found to be independent of one another only in the limit when the exchange interactions between the charges disappear. In this limit, the energy modes for singlet and triplet biexciton fields have well-defined meaning and propagate through the crystal independently. A dielectric gap is induced by the electromagnetic field, which produces the energy splitting in the singlet biexciton spectrum, and it must be less than that of Δ_+ for the singlet biexciton state. For finite values of the exchange interaction, the gap functions Δ_+ and Δ_- depend strongly on each other and consequently the singlet and triplet biexciton fields are strongly mixed together. Optical transitions to the singlet and triplet biexciton states are considered and the corresponding expressions for the absorption coefficient are derived. The ground-state energy describing the binding energy arising from the singlet and triplet biexciton fields is calculated and discussed. Numerical estimates indicate that at high exciton densities, namely, for exciton concentrations 10^{18}–10^{19} cm^{-3} and when the ratio of the average exciton-exciton interaction over the average kinetic energy is between 0.7 and 2 (strong-coupling limit), the energy gap due to the singlet biexciton state is in the range 40–650 cm^{-1}, the corresponding transition temperature is 33–534°K, while the binding energy is 22–684 cm^{-1}.

I. INTRODUCTION

The ability to produce high exciton densities has led to intensive studies of the collective properties of excitons in insulators and semiconductors. The collective phenomena that have been presently discussed and observed in systems of excitons at high concentrations are: biexcitons, the Bose condensation of excitons or biexcitons, and the electron-hole liquids.[1] The existence of one of these collective states depends on the exciton concentration, the character of the exciton-exciton interaction, the band structure, and other factors.

The elementary collective electronic excitations in molecular crystals are the well-known Frenkel (small radius or molecular) excitons.[2] These consist of tightly bound electron hole pairs that propagate through the crystal with definite energy and wave vector.[3] It has been recently suggested (Ref. 4, referred to as I) that in molecular solids two excitons with opposite wave vectors may interact to form a bound state. The theory of the biexciton spectra arising from the coherent pairing of excitons in the presence of a resonant electromagnetic field for molecular crystals consisting of aromatic organic molecules has been developed in I. It has been shown that the formation of the biexciton state at high exciton densities is possible provided that there exists an attractive interaction between the excitons, that the electromagnetic field is at resonance or near resonance, and that the dielectric gap induced by the electromagnetic field is less than that for the biexciton state. The theory has been generalized to be appropriate to organic crystals which have several molecules in the unit cell[5]; the reader is referred to I and Ref. 5 for further details.

The valence bands for most molecular crystals are filled with electrons having opposite spin alignments. Light absorption by a crystal of organic molecules generates excitons, which may have their spin components either up or down. When the spin degeneracy is removed in the Hartree-Fock approximation, the excitation spectrum consists of two frequency modes, the singlet and triplet exciton modes, which propagate through the crystal independently.[6] At high exciton concentrations, two excitons with parallel or antiparallel spin components may interact to form the corresponding biexciton state. Hence, there is a spin degeneracy in the dense exciton system, the removal of which may lead into the formation of singlet and triplet biexciton states. The purpose of the present study is to generalize the theory of the resonant coherent pairing of excitons to include the effect of the electron spin.

The problem is formulated in Sec. II where use has been made of the same model for a molecular crystal as that considered in I but including the effects of the electron spin. Using the spin-dependent Hamiltonian and that describing the coupling with the transverse resonant electromagnetic field, the equations of motion for the exciton Green's functions are derived. After applying the decoupling approximation defined in I, we get a set of coupled equations for the exciton Green's functions.

The excitation spectrum is discussed in Sec. III. It is shown that the removal of the spin degeneracy results in creating two fields, the singlet and the triplet biexciton fields, respectively. There is an energy splitting in the singlet biexciton spectrum which is caused by the electromagnetic field. When the electromagnetic field is at resonance or near resonance, the gap functions Δ_+ and Δ_- describing the singlet and triplet exciton pairing, respectively, have been calculated at zero temperature and they are shown to be independent of each other only in the limit when the exchange interaction goes to zero. Only in this limit, the energy modes for the singlet and triplet biexciton fields are well defined and propagate through the crystal independently. The gap function Δ_+ for the singlet-biexciton field must be greater than that induced by the electromagnetic field; there is no such restriction for Δ_-. For finite values of the exchange interaction, the gap functions Δ_+ and Δ_- depend on each other and result in the mixing of the singlet and triplet biexciton fields, whose energy modes are no longer well defined.

Expressions for the absorption coefficients describing optical transitions to singlet and triplet biexciton bands are derived in Sec. IV. The binding energies arising from the singlet and triplet biexciton modes are calculated in Sec. V; the results of the numerical computation are listed in Table I and discussed in Sec. VI.

II. FORMULATION OF THE PROBLEM

The Hamiltonian for a two-level system of a molecular crystal describing the coherent exciton-exciton interaction in the presence of a resonant electromagnetic field has been derived in I and is given by Eq. (26) of I. This expression can be easily generalized to include the spin of the electrons and then it takes the form

$$\mathcal{H} = \text{const} + \sum_{\vec{k},\nu,\sigma} \Omega_{\vec{k}\nu\sigma} b^{\dagger}_{\vec{k}\nu\sigma} b_{\vec{k}\nu\sigma} + \sum_{\substack{k,\nu,\sigma,\sigma'\\(\sigma\neq\sigma')}} J_{\sigma\sigma'}(\vec{k})(b^{\dagger}_{\vec{k}\nu\sigma} b_{\vec{k}\nu\sigma'} + b^{\dagger}_{\vec{k}\nu\sigma'} b_{\vec{k}\nu\sigma})$$
$$+ \sum_{\substack{k,\nu,\lambda\\ \sigma}} \frac{i\mu^{\sigma\sigma}_{\vec{k}\lambda\nu}}{2} (b_{-\vec{k}\nu\sigma}\beta^{\dagger}_{\vec{k}\lambda} - b^{\dagger}_{\vec{k}\nu\sigma}\beta_{-\vec{k}\lambda}) - \frac{1}{2N} \sum_{\substack{\vec{k},\vec{q},\nu\\ \sigma,\sigma'}} U_{\sigma\sigma'}(\vec{k}-\vec{q})(b^{\dagger}_{-\vec{q}\nu\sigma} b^{\dagger}_{\vec{q}\nu\sigma'})(b_{\vec{k}\nu\sigma} b_{-\vec{k}\nu\sigma'}) , \tag{1}$$

where the indices σ and σ' indicate the spin components and take the value of spin up (↑) or spin down (↓). $b^{\dagger}_{\vec{k}\nu\sigma}$ and $b_{\vec{k}\nu\sigma}$ are the Frenkel exciton creation and annihilation operators with wave vector $\vec{k}$, band index ν, and spin σ. The effective energy of excitation $\Omega_{\vec{k}\nu\sigma}$ is defined as, Eq. (27) of I,

$$\Omega_{\vec{k}\nu\sigma} = E^{\sigma\sigma}_{\vec{k}\nu} - \omega_{\vec{k}} , \tag{2}$$

where $E^{\sigma\sigma}_{\vec{k}\nu}$ is the energy of the free-exciton field given by Eq. (14a) of I and $\omega_{\vec{k}}$ is the energy of the free transverse photon field. $\beta^{\dagger}_{\vec{k}\lambda}$ and $\beta_{\vec{k}\lambda}$ are photon creation and annihilation operators with wave vector $\vec{k}$ and transverse polarization λ (= 1, 2). The band index ν designates also the kind of the exciton mode, transverse $\nu \equiv \nu_{\perp} = \lambda = 1, 2$ or longitudinal $\nu = \nu_{\parallel} = 3$.

The coupling function $J_{\sigma\sigma'}(\vec{k})$ is defined as[4,6]

$$J_{\sigma\sigma'}(\vec{k}) = \sum_{\vec{R}_{\vec{m}\vec{n}}}{}' J(\vec{n}0\sigma, \vec{m}\nu\sigma' | \vec{n}\nu\sigma, \vec{m}0\sigma') e^{i\vec{k}\cdot\vec{R}_{\vec{m}\vec{n}}} , \tag{3a}$$

$$J(\vec{n}0\sigma, \vec{m}\nu\sigma' | \vec{n}\nu\sigma, \vec{m}0\sigma')$$
$$= \langle \vec{n}0\sigma, \vec{m}\nu\sigma' | V_{\vec{n}\vec{m}} | \vec{n}\nu\sigma, \vec{m}0\sigma' \rangle - \langle \vec{n}0\sigma, \vec{m}\nu\sigma' | V_{\vec{n}\vec{m}} | \vec{m}0\sigma', \vec{n}\nu\sigma \rangle , \tag{3b}$$

while that of $U_{\sigma\sigma'}(\vec{k}-\vec{q})$ is given by Eq. (14c) of I,

$$U_{\sigma\sigma'}(\vec{k}-\vec{q}) = \sum_{\vec{R}_{\vec{m}\vec{n}}}{}' U_{\sigma\sigma'}(\vec{n}, \vec{m}) e^{i(\vec{k}-\vec{q})\cdot\vec{R}_{\vec{m}\vec{n}}} - 2J_{\sigma\sigma'}(\vec{q}) , \tag{4a}$$

where $U_{\sigma\sigma'}(\vec{n}, \vec{m})$ is determined by[4,7]

$$U_{\sigma\sigma'}(\vec{n}, \vec{m}) = U_{0,\sigma\sigma'}(\vec{n}, \vec{m}) + U_{\nu,\sigma\sigma'}(\vec{n}, \vec{m}) , \tag{4b}$$

$$U_{0,\sigma\sigma'}(\vec{n}, \vec{m}) = J(\vec{n}0\sigma, \vec{m}\nu\sigma' | \vec{n}0\sigma, \vec{m}\nu\sigma') - J(\vec{n}0\sigma, \vec{m}0\sigma' | \vec{n}0\sigma, \vec{m}0\sigma') , \tag{4c}$$

$$U_{\nu,\sigma\sigma'}(\vec{n}, \vec{m}) = J(\vec{m}\nu\sigma, \vec{n}0\sigma' | \vec{m}\nu\sigma, \vec{n}0\sigma') - J(\vec{n}\nu\sigma, \vec{m}\nu\sigma' | \vec{n}\nu\sigma, \vec{m}\nu\sigma') , \tag{4d}$$

0 and ν designating the ground and excited electronic states, respectively. The photon-exciton coupling is given by the function $\mu_{\vec{k}\lambda\nu}$,

$$\mu_{\vec{k}\lambda\nu} = \omega_p [f^{\sigma\sigma}_{0\nu}(\vec{k}\lambda) E^{\sigma\sigma}_{\vec{k}\nu} | \omega_{\vec{k}}]^{1/2} , \tag{5}$$

where $f^{\sigma\sigma}_{0\nu}(\vec{k}\lambda)$ is the oscillator strength for the spin-allowed electronic transition $0 \to \nu$ defined by Eq. (17) of I; there are N molecules (atoms) in the crystal volume V. Apart from the spin degeneracy, the expression for the Hamiltonian (1) as well as the notation coincide with that of Eq. (26) of I where the reader is referred to for further details.

To remove the spin degeneracy in the excitation spectrum, we need to calculate the exciton Green's functions $\langle\langle b_{\vec{k}\nu\downarrow}+b_{\vec{k}\nu\uparrow};b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle$ and $\langle\langle b_{\vec{k}\nu\downarrow}-b_{\vec{k}\nu\uparrow};b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle$, respectively, by means of the Hamiltonian (1). We shall make use of the retarded double-time Green's functions of the Zubarev type[8,9] defined by Eq. (19) of I. The exciton Green's functions $\langle\langle b_{\vec{k}\nu\downarrow}\pm b_{\vec{k}\nu\uparrow};b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle$, which consist of linear combinations of exciton operators having a spin up and a spin down, are the appropriate ones for the removal of the spin degeneracy.[6] Using the Hamiltonian (1) and the equation of motion for the Green's function defined by Eq. (20) of I, we derive the following expression

$$\left(\omega-\Omega_{\vec{k}\nu\pm}-\frac{\mu^{2}_{\vec{k}}}{4\omega}(1\pm1)\right)\langle\langle b_{\vec{k}\nu\downarrow}\pm b_{\vec{k}\nu\uparrow};b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle=\frac{1}{2\pi}-\frac{1}{N}\sum_{\vec{q}}U_{\downarrow\downarrow}(\vec{k}-\vec{q})\langle\langle b^{\dagger}_{-\vec{k}\nu\downarrow}(b_{\vec{q}\nu\downarrow}b_{-\vec{q}\nu\downarrow})\pm b^{\dagger}_{-\vec{k}\nu\uparrow}(b_{\vec{q}\nu\uparrow}b_{-\vec{q}\nu\uparrow});b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle$$
$$-\frac{1}{2N}\sum_{\vec{q}}U_{\uparrow\downarrow}(\vec{k}-\vec{q})\langle\langle(b^{\dagger}_{-\vec{k}\nu\uparrow}\pm b^{\dagger}_{-\vec{k}\nu\downarrow})(b_{\vec{q}\nu\uparrow}b_{-\vec{q}\nu\downarrow}+b_{\vec{q}\nu\downarrow}b_{-\vec{q}\nu\uparrow});b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle\,, \qquad (6)$$

where

$$\Omega_{\vec{k}\nu\pm}=\Omega_{\vec{k}\nu\sigma}\pm J_{\uparrow\downarrow}(\vec{k})\,, \qquad (7a)$$

$$\mu^{2}_{\vec{k}}=\omega_{p}^{2}\sum_{\nu,\lambda}f^{\downarrow\downarrow}_{0\nu}(\vec{k}\lambda)(E^{\sigma\sigma}_{\vec{k}\nu}/\omega_{\vec{k}})\,, \qquad (7b)$$

and $f^{\downarrow\downarrow}_{0\nu}(\vec{k}\lambda)=f^{\uparrow\uparrow}_{0\nu}(\vec{k}\lambda)$. In deriving Eq. (6) we have taken

$$U_{\uparrow\uparrow}(\vec{k}-\vec{q})=U_{\downarrow\downarrow}(\vec{k}-\vec{q}),\quad U_{\uparrow\downarrow}(\vec{k}-\vec{q})=U_{\downarrow\uparrow}(\vec{k}-\vec{q})\,, \qquad (8a)$$

$$J_{\uparrow\uparrow}(\vec{k})=J_{\downarrow\downarrow}(\vec{k}),\quad J_{\uparrow\downarrow}(\vec{k})=J_{\downarrow\uparrow}(\vec{k})\,, \qquad (8b)$$

which are valid from symmetry considerations. Then, we make use of the decoupling approximation

$$\langle\langle b^{\dagger}_{-\vec{k}\nu\downarrow}(b_{\vec{q}\nu\downarrow}b_{-\vec{q}\nu\downarrow})\pm b^{\dagger}_{-\vec{k}\nu\uparrow}(b_{\vec{q}\nu\uparrow}b_{-\vec{q}\nu\uparrow});b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle$$
$$\approx\langle\langle b_{\vec{q}\nu\downarrow}b_{-\vec{q}\nu\downarrow}\rangle\rangle\langle\langle b^{\dagger}_{-\vec{k}\nu\downarrow};b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle$$
$$\pm\langle b_{\vec{q}\nu\uparrow}b_{-\vec{q}\nu\uparrow}\rangle\langle\langle b^{\dagger}_{-\vec{k}\nu\uparrow};b_{\vec{k}\nu\downarrow}\rangle\rangle\,, \qquad (9)$$

$$\langle\langle(b^{\dagger}_{-\vec{k}\nu\uparrow}\pm b^{\dagger}_{-\vec{k}\nu\downarrow})(b_{\vec{q}\nu\uparrow}b_{-\vec{q}\nu\downarrow}+b_{\vec{q}\nu\downarrow}b_{-\vec{q}\nu\uparrow});b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle$$
$$\approx(\langle b_{\vec{q}\nu\uparrow}b_{-\vec{q}\nu\downarrow}\rangle+\langle b_{\vec{q}\nu\downarrow}b_{-\vec{q}\nu\uparrow}\rangle)\langle\langle b^{\dagger}_{-\vec{k}\nu\uparrow}\pm b^{\dagger}_{-\vec{k}\nu\downarrow};b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle\,, \qquad (10)$$

as has been done in Eqs. (32) and (33) of I. Substituting Eqs. (9) and (10) into Eq. (6), we get

$$[\omega-\Omega^{\pm}_{\vec{k}\nu}-(\mu^{2}_{\vec{k}}/4\omega)(1\pm1)]\langle\langle b_{\vec{k}\nu\downarrow}\pm b_{\vec{k}\nu\uparrow};b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle$$
$$=1/2\pi-\Delta_{\pm}(\vec{k})\langle\langle b^{\dagger}_{-\vec{k}\nu\downarrow}\pm b^{\dagger}_{-\vec{k}\nu\uparrow};b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle\,, \qquad (11)$$

where

$$\Delta_{\pm}(\vec{k})=\Delta_{\downarrow\downarrow}(\vec{k})\pm\Delta_{\uparrow\downarrow}(\vec{k})\,, \qquad (12a)$$

$$\Delta_{\downarrow\downarrow}(\vec{k})=\Delta_{\uparrow\uparrow}(\vec{k})=\frac{1}{N}\sum_{\vec{q}}U_{\downarrow\downarrow}(\vec{k}-\vec{q})\langle b_{\vec{q}\nu\downarrow}b_{-\vec{q}\nu\downarrow}\rangle\,, \qquad (12b)$$

$$\Delta_{\uparrow\downarrow}(\vec{k})=\Delta_{\downarrow\uparrow}(\vec{k})=\frac{1}{N}\sum_{\vec{q}}U_{\uparrow\downarrow}(\vec{k}-\vec{q})\langle b_{\vec{q}\nu\uparrow}b_{-\vec{q}\nu\downarrow}\rangle\,. \qquad (12c)$$

The expression for the effective energies of excitation of the exciton field given by Eq. (7a) may be rewritten as

$$\Omega^{\pm}_{\vec{k}\nu}=E^{\pm}_{\vec{k}\nu}-\omega_{\vec{k}}\,, \qquad (13a)$$

where

$$E^{\pm}_{\vec{k}\nu}=E^{\downarrow\downarrow}_{\vec{k}\nu}\pm J_{\downarrow\uparrow}(\vec{k})=E_{\nu0}+J_{\downarrow\downarrow}(\vec{k})\pm J_{\uparrow\downarrow}(\vec{k})\,, \qquad (13b)$$

$E_{\nu0}$ being the energy difference between the ground state and the excited state ν and is given by Eq. (10) of I. The energies of excitation $E^{+}_{\vec{k}\nu}$ of the free exciton field arise from Coulomb and exchange interactions while that of $E^{-}_{\vec{k}\nu}$ involves only exchange interactions. Thus, in Eq. (11) the plus (+) and the minus (−) energy modes describe physical processes where the optical transitions involved are spin allowed and spin forbidden, respectively. The expressions for $E^{+}_{\vec{k}\nu}$ and $E^{-}_{\vec{k}\nu}$ given by Eq. (13b) are identical with those describing the singlet and triplet exciton energies of molecular crystals[6,7] and they are correct in the Hartree-Fock approximation. In this approximation, the singlet and triplet exciton modes propagate in the crystal independently.[6]

Equations (12a)–(12c) indicate that the gap functions $\Delta_{+}(\vec{k})$ and $\Delta_{-}(\vec{k})$ for the (+) and (−) energy modes consist of linear combinations of coherent exciton-exciton pairing with parallel and antiparallel spins; they may be interpreted as the energy gaps corresponding to the biexciton states with positive and negative spin projections on the z axis, respectively.

Similarly, the expression for the Green's function $\langle\langle b^{\dagger}_{-\vec{k}\nu\downarrow}\pm b^{\dagger}_{-\vec{k}\nu\uparrow};b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle$, that appears on the right-hand side of Eq. (11) turns out to be

$$[-\omega-\Omega^{\pm}_{\vec{k}\nu}+(\mu^{2}_{\vec{k}}/4\omega)(1\pm1)]\langle\langle b^{\dagger}_{-\vec{k}\nu\downarrow}\pm b^{\dagger}_{-\vec{k}\nu\uparrow};b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle$$
$$=\Delta^{*}_{\pm}(\vec{k})\langle\langle b_{\vec{k}\nu\downarrow}\pm b_{\vec{k}\nu\uparrow};b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle\,. \qquad (14)$$

Equations (13) and (14) form a set of coupled equations, the solution of which will determine the energies of excitation for the system under consideration. If the coupling functions $\Delta_{+}(\vec{k})$ and $\Delta_{-}(\vec{k})$ do not depend on each other then the solutions of the coupled equations (13) and (14) for the (+) and (−) energy modes will be completely separated; as we will see later this is not always possible. The coupling functions $\Delta_+(\vec{k})$ and $\Delta_-(\vec{k})$, which are still unknown parameters, will be calculated self-consistently in connection with the excitation spectrum of the system under consideration.

III. EXCITATION SPECTRUM

To discuss the excitation spectrum we solve the coupled equations (13) and (14) with the result

$$\langle\langle b_{\vec{k}\nu\downarrow}+b_{\vec{k}\nu\uparrow}\,;\,b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle =\frac{1}{2\pi}\,\frac{\omega^2(\omega+\Omega^{+}_{\vec{k}\nu})-\tfrac{1}{2}\omega\mu^{2}_{\vec{k}}}{[\omega^2-\Omega^2_{s+}(\vec{k}\nu)][\omega^2-\Omega^2_{s-}(\vec{k}\nu)]}\,, \qquad (15)$$

$$\langle\langle b^{\dagger}_{-\vec{k}\nu\downarrow}+b^{\dagger}_{-\vec{k}\nu\uparrow};\,b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle =-\frac{1}{2\pi}\,\frac{\omega^2\Delta^{*}_{+}(\vec{k})}{[\omega^2-\Omega^2_{s+}(\vec{k}\nu)][\omega^2-\Omega^2_{s-}(\vec{k}\nu)]}\,, \qquad (16)$$

$$\langle\langle b_{\vec{k}\nu\downarrow}-b_{\vec{k}\nu\uparrow};\,b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle =\frac{1}{2\pi}\left(\frac{\tfrac{1}{2}(1+\Omega^{-}_{\vec{k}\nu}/\epsilon^{-}_{\vec{k}\nu})}{\omega-\epsilon^{-}_{\vec{k}\nu}}+\frac{\tfrac{1}{2}(1-\Omega^{-}_{\vec{k}\nu}/\epsilon^{-}_{\vec{k}\nu})}{\omega+\epsilon^{-}_{\vec{k}\nu}}\right), \qquad (17)$$

$$\langle\langle b^{\dagger}_{-\vec{k}\nu\downarrow}-b^{\dagger}_{-\vec{k}\nu\uparrow}\,;\,b^{\dagger}_{\vec{k}\nu\downarrow}\rangle\rangle =-\frac{1}{2\pi}\,\frac{\Delta^{*}_{-}(\vec{k})}{2\epsilon^{-}_{\vec{k}\nu}}\left(\frac{1}{\omega-\epsilon^{-}_{\vec{k}\nu}}-\frac{1}{\omega+\epsilon^{-}_{\vec{k}\nu}}\right), \qquad (18)$$

where the energies of excitation $\Omega_{s\pm}(\vec{k}\nu)$ and $\epsilon^{-}_{\vec{k}\nu}\equiv\Omega_t(\vec{k}\nu)$ are

$$\Omega_{s\pm}(\vec{k}\nu)=\tfrac{1}{2}[(\epsilon^{+2}_{\vec{k}\nu}+2\mu^{2}_{\vec{k}})^{1/2}\pm\epsilon^{+}_{\vec{k}\nu}]\,, \qquad (19)$$

$$\epsilon^{\pm}_{\vec{k}\nu}=+[\Omega^{\pm 2}_{\vec{k}\nu}+|\Delta_{\pm}(\vec{k})|^2]^{1/2}\,. \qquad (20)$$

The poles of the Green's functions (15) and (16) are determined by the expressions for $\Omega_{s+}(\vec{k}\nu)$ and $\Omega_{s-}(\vec{k}\nu)$ defined by Eq. (19), which indicates that there is an energy splitting that is equal to $\epsilon^{+}_{\vec{k}\nu}$ and is caused by the electromagnetic field. On the other hand, the poles of the Green's functions (17) and (18) are determined by $\Omega_t(\vec{k}\nu)=\epsilon^{-}_{\vec{k}\nu}$ defined by Eq. (20) and there is no energy splitting. Therefore, the excitation spectrum described by the Green's functions (15) and (16) with energies $\Omega_{s\pm}(\vec{k}\nu)$ and that of the Green's functions (17) and (18) with energies $\Omega_t(\vec{k}\nu)\equiv\epsilon^{-}_{\vec{k}\nu}$ may be interpreted as corresponding to the singlet and triplet biexciton states, respectively. The singlet biexciton spectrum is split by the electromagnetic field while that of the triplet biexciton is not.

As has been shown in I, the Green's functions (16) and (18) are used to calculate the gap functions $\Delta_+(\vec{k})$ and $\Delta_-(\vec{k})$ while the imaginary parts of the Green's functions (15) and (17) determine the expression for the absorption coefficient which describes the optical transitions to the singlet and triplet biexciton states, respectively. Using Eq. (42) of I and Eqs. (15)–(18) we derive in the usual way[8,9] the following expressions for the distribution functions at finite temperature:

$$\langle b^{\dagger}_{\vec{k}\nu\downarrow}(b_{\vec{k}\nu\downarrow}+b_{\vec{k}\nu\uparrow})\rangle=\tfrac{1}{2}[1-\Omega^{+}_{\vec{k}\nu}\theta_{\vec{k}}/(\epsilon^{+2}_{\vec{k}\nu}+2\mu^{2}_{\vec{k}})^{1/2}]\,, \qquad (21a)$$

$$\langle b^{\dagger}_{\vec{k}\nu\downarrow}(b^{\dagger}_{-\vec{k}\nu\downarrow}+b^{\dagger}_{-\vec{k}\nu\uparrow})\rangle=\Delta^{*}_{+}(\vec{k})\,\theta_{\vec{k}}/2(\epsilon^{+2}_{\vec{k}\nu}+2\mu^{2}_{\vec{k}})^{1/2}\,, \qquad (21b)$$

$$\langle b^{\dagger}_{\vec{k}\nu\downarrow}(b_{\vec{k}\nu\downarrow}-b_{\vec{k}\nu\uparrow})\rangle=\tfrac{1}{2}[1-(\Omega^{-}_{\vec{k}\nu}/\epsilon^{-}_{\vec{k}\nu})\tanh\tfrac{1}{2}\beta\epsilon^{-}_{\vec{k}\nu}]\,, \qquad (22a)$$

$$\langle b^{\dagger}_{\vec{k}\nu\downarrow}(b^{\dagger}_{-\vec{k}\nu\downarrow}-b^{\dagger}_{-\vec{k}\nu\uparrow})\rangle=(\Delta^{*}_{-}(\vec{k})/2\epsilon^{-}_{\vec{k}\nu})\tanh\tfrac{1}{2}\beta\epsilon^{-}_{\vec{k}\nu}\,, \qquad (22b)$$

where $\theta_{\vec{k}}$ is given by

$$\theta_{\vec{k}}=\tfrac{1}{2}[\tanh\tfrac{1}{2}\beta\Omega_{s+}(\vec{k}\nu)+\tanh\tfrac{1}{2}\beta\Omega_{s-}(\vec{k}\nu)] +(1/2\epsilon^{+}_{\vec{k}\nu})(\epsilon^{+2}_{\vec{k}\nu}+2\mu^{2}_{\vec{k}})^{1/2} \times[\tanh\tfrac{1}{2}\beta\Omega_{s+}(\vec{k}\nu)-\tanh\tfrac{1}{2}\beta\Omega_{s-}(\vec{k}\nu)]\,. \qquad (23)$$

Substituting Eqs. (21) and (22) into Eq. (12a) we get

$$\Delta_+(\vec{k})=\frac{1}{N}\sum_{\vec{q}}\frac{U_+(\vec{k}-\vec{q})\Delta_+(\vec{q})\theta_{\vec{q}}}{2(\epsilon^{+2}_{\vec{q}\nu}+2\mu^{2}_{\vec{q}})^{1/2}} +\frac{1}{N}\sum_{\vec{q}}\frac{U_-(\vec{k}-\vec{q})\Delta_-(\vec{q})\tanh\tfrac{1}{2}\beta\epsilon^{-}_{\vec{q}\nu}}{2\epsilon^{-}_{\vec{q}\nu}}\,, \qquad (24)$$

$$\Delta_-(\vec{k})=\frac{1}{N}\sum_{\vec{q}}\frac{U_+(\vec{k}-\vec{q})\Delta_-(\vec{q})\tanh\tfrac{1}{2}\beta\epsilon^{-}_{\vec{q}\nu}}{2\epsilon^{-}_{\vec{q}}} +\frac{1}{N}\sum_{\vec{q}}\frac{U_-(\vec{k}-\vec{q})\Delta_+(\vec{q})\theta_{\vec{q}}}{2(\epsilon^{+2}_{\vec{q}\nu}+2\mu^{2}_{\vec{q}})^{1/2}}\,, \qquad (25)$$

where

$$U_{\pm}(\vec{k}-\vec{q})=\tfrac{1}{2}[U_{\downarrow\downarrow}(\vec{k}-\vec{q})\pm U_{\uparrow\downarrow}(\vec{k}-\vec{q})]\,. \qquad (26)$$

The solutions of the coupled integral equations (24) and (25) will determine the expressions for $\Delta_+(\vec{k})$ and $\Delta_-(\vec{k})$. In the limit of zero temperature ($\beta\to\infty$), $\tanh\tfrac{1}{2}\beta\epsilon^{-}_{\vec{k}\nu}=1$, $\theta_{\vec{q}}=1$, then following I and in the effective mass approximation Eqs. (24) and (25) become

$$\Delta_+=U_+N_+(0)\int_0^{\bar{\omega}_+}\frac{d(\vec{q}^{\,2}/2m^{+}_{\text{exc}})\Delta_+}{[(E_g+\vec{q}^{\,2}/2m^{+}_{\text{exc}})^2+\Delta^2_++2\mu^2]^{1/2}} +U_-N_-(0)\int_0^{\bar{\omega}_-}\frac{d(\vec{q}^{\,2}/2m^{-}_{\text{exc}})\Delta_-}{[(E_g+\vec{q}^{\,2}/2m^{-}_{\text{exc}})^2+\Delta^2_-]^{1/2}}\,, \qquad (27)$$

$$\Delta_-=U_+N_-(0)\int_0^{\bar{\omega}_-}\frac{d(\vec{q}^{\,2}/2m^{-}_{\text{exc}})\Delta_-}{[(E_g+\vec{q}^{\,2}/2m^{-}_{\text{exc}})^2+\Delta^2_-]^{1/2}} +U_-N_+(0)\int_0^{\bar{\omega}_+}\frac{d(\vec{q}^{\,2}/2m^{+}_{\text{exc}})\Delta_+}{[(E_g+\vec{q}^{\,2}/2m^{+}_{\text{exc}})^2+\Delta^2_++2\mu^2]^{1/2}}\,, \qquad (28)$$

where, $N_{\pm}(0)$ designate the density of states defined as

$$N_{\pm}(0)=(V\xi m^{\pm}_{\text{exc}}/2\pi^2N)=3/2\bar{\omega}_{\pm},\quad \bar{\omega}_{\pm}=\xi^2/2m^{\pm}_{\text{exc}}\,, \qquad (29)$$

$$\begin{aligned} &\xi = (6\pi^2 N/V)^{1/3} = (6\pi^2 n)^{1/3} , \\ &\frac{1}{m^{\pm}_{\text{exc}}} = \left| \frac{\partial^2}{\partial \vec{\text{k}}^2} E^{\pm}_{\vec{\text{k}}\nu} \right|_{\vec{\text{k}}=0} . \end{aligned} \tag{30}$$

$n = N/V$ being the exciton concentration. In Eqs. (27) and (28), E_g is the effective energy gap given by

$$E_g = E_{\nu 0} - \Omega , \tag{31}$$

where, as in I, the dispersion of the electromagnetic field is neglected, namely, $\omega_{\vec{\text{k}}}$ is taken as $\omega_{\vec{\text{k}}} = \Omega$ and $\mu^2_{\vec{\text{k}}} = \mu^2$. The effective masses m^{+}_{exc} and m^{-}_{exc} for the singlet and triplet excitons are defined by Eq. (30) respectively, and depend on the directions of the excitons as well.[3] In Eqs. (27) and (28) use has been made of the notation, $U_{\pm} \equiv U_{\pm}(\vec{\text{k}})$ and $\Delta_{\pm} \equiv \Delta_{\pm}(\vec{\text{k}})$.

After performing the integrations in Eqs. (27) and (28) we obtain

$$\ln \frac{E_g + \bar{\omega}_+ + [(E_g + \bar{\omega}_+)^2 + \Delta_+^2 + 2\mu^2]^{1/2}}{E_g + (E_g^2 + \Delta_+^2 + 2\mu^2)^{1/2}} = \frac{1}{\rho_+} , \tag{32}$$

$$\ln \frac{E_g + \bar{\omega}_- + [(E_g + \bar{\omega}_-)^2 + \Delta_-^2]^{1/2}}{E_g + (E_g^2 + \Delta_-^2)^{1/2}} = \frac{1}{\rho_-} , \tag{33}$$

where the coupling functions $\rho_{\pm}$ are determined by

$$\rho_+ = U_+ N_+ / s_+ , \tag{34a}$$

$$\rho_- = U_+ N_- / s_- , \tag{34b}$$

$$s_+ = [1 - (U_-/U_+)(\Delta_-/\Delta_+)]/[1 - (U_-/U_+)^2] , \tag{34c}$$

$$s_- = [1 - (U_-/U_+)(\Delta_+/\Delta_-)]/[1 - (U_-/U_+)^2] . \tag{34d}$$

A favorable condition for the existence of the scattering amplitudes $\Delta_{\pm}$ is when the electromagnetic field is at resonance,

$$E_g = E_{\nu 0} - \Omega = 0 , \tag{35}$$

or near resonance when $E_g \ll \bar{\omega}_{\pm}$, then Eqs. (32) and (33) become

$$\Delta_+ = [\,|\tilde{\Delta}_+|^2 - 2\mu^2]^{1/2} , \tag{36}$$

$$\tilde{\Delta}_+ = \frac{\bar{\omega}_+}{\sinh(1/\rho_+)} , \tag{37}$$

$$\Delta_- = \frac{\bar{\omega}_-}{\sinh(1/\rho_-)} . \tag{38}$$

Equation (36) implies that $\tilde{\Delta}_+$ must also satisfy the inequality

$$\tilde{\Delta}_+ > 2^{1/2} \mu \tag{39}$$

so that $\Delta_+ \neq 0$. In the limit when $\mu \to 0$, the transition temperature may be obtained from the expression

$$k_B T_c^{\pm} \approx 0.57 \Delta_{\pm} , \tag{40}$$

where k_B is Boltzmann's constant. The expressions for $\tilde{\Delta}_+$ and Δ_- are formally analogous to the corresponding scattering amplitudes for the electron-singlet and electron-triplet exciton bound states given by Eqs. (39) and (40) of Ref. 7, respectively.

Equations (34a)–(34d) for ρ_+ and ρ_- imply that the gap functions Δ_+ and Δ_- depend on each other through the function U_-/U_+, which is the ratio of the exchange interaction over the total Coulomb plus exchange interaction. Whenever the ratio U_-/U_+ has an appreciable value then Δ_+ and Δ_- depend on each other and consequently the singlet and triplet biexciton modes are coupled together. Therefore, the admixture of the singlet and triplet biexciton modes depends on the strength of the exchange interaction and in particular on the value of the ratio U_-/U_+.

In the limiting case when

$$U_-/U_+ \to 0 , \tag{41}$$

then $s_{\pm} \to 1$ and ρ_+ and ρ_- become

$$\rho_+^0 = U_+ N_+(0) , \tag{42a}$$

$$\rho_-^0 = U_+ N_-(0) . \tag{42b}$$

Considering that the effective mass of the triplet exciton is much larger than that of the singlet, $m^{-}_{\text{exc}} > m^{+}_{\text{exc}}$, we have $N_-(0) > N_+(0)$ and hence, $\rho_-^0 > \rho_+^0$. Then substituting $\rho_{\pm}$ by $\rho_{\pm}^0$ in Eqs. (37) and (38), respectively, and taking the ratio $\tilde{\Delta}_+^0/\Delta_-^0$, we get

$$\Delta_+^0 = (|\tilde{\Delta}_+^0|^2 - 2\mu^2)^{1/2} , \tag{43a}$$

$$\tilde{\Delta}_+^0 = \frac{\bar{\omega}_+}{\sinh(1/\rho_+^0)} , \quad \Delta_-^0 = \frac{\bar{\omega}_-}{\sinh(1/\rho_-^0)} , \tag{43b}$$

$$\frac{\tilde{\Delta}_+^0}{\Delta_-^0} = \frac{\bar{\omega}_+}{\bar{\omega}_-} \frac{\sinh(1/\rho_-^0)}{\sinh(1/\rho_+^0)} = \frac{m^{-}_{\text{exc}}}{m^{+}_{\text{exc}}} \frac{\sinh(1/\rho_-^0)}{\sinh(1/\rho_+^0)} > 1 . \tag{43c}$$

We emphasize that the main drawback for the existence of Δ_+^0 is the fulfillment of the inequality (39), i.e., $\tilde{\Delta}_+^0 > 2^{1/2}\mu$. Considering that at resonance $\mu^2 \approx \omega_p^2 f_{0\nu}^{\downarrow\downarrow}$, the satisfaction of the inequality (39) becomes difficult especially for optical transitions carrying large oscillator strengths. On the other hand, there is no such restriction for the existence of the scattering amplitude Δ_-^0. In this case, the only unfavorable condition is the large value of the effective mass of the triplet exciton m^{-}_{exc} which brings about lower values of $\bar{\omega}_-$ in comparison with thos of $\bar{\omega}_+$ given by Eq. (29). However, this disadvantage may be compensated by the fact that $\rho_-^0 > \rho_+^0$, and thus, $\sinh(1/\rho_-^0) < \sinh(1/\rho_+^0)$. Thus under conditions of high exciton density, the formation of triplet biexcitons has more or less equal probability with that of the singlet while in the case of optical transitions having large oscillator strengths, the production of triplet biexciton dominates.

In concluding this section, we point out that when the exchange interaction is strong or the ratio U_-/U_+ is large then the singlet and triplet biexciton modes are coupled together. On the other hand, when the exchange interactions are weak and $U_-/U_+ \to 0$, the singlet and triplet biexciton modes propagate in the crystal independently. Only in this case the singlet and triplet biexciton states have well-defined energies. In general, exchange interactions are known to be extremely weak in molecular organic solids, and hence, Eqs. (42) and (43) are expected to be applicable. In this case and in the presence of high concentrations of excitons, the formation of triplet biexciton modes may dominate those of the singlet ones, especially when the optical transition in question carries a large oscillator strength.

IV. ABSORPTION COEFFICIENT

The expression for the absorption coefficient $\alpha(\vec{k},\omega)$ is given by[9]

$$\alpha(\vec{k},\omega)=-[\pi\omega_p^2/4c\omega\eta(\vec{k},\omega)]$$

$$\times\sum_{\nu,\lambda,\sigma} f_{0\nu}^{\sigma\sigma}(\vec{k}\lambda)E_{\vec{k}\nu}^{\sigma\sigma}\,\mathrm{Im}\langle\langle\tilde{b}_{\vec{k}\nu\sigma};\tilde{b}_{\vec{k}\nu\sigma}^{\dagger}\rangle\rangle\,, \qquad (44)$$

where c is velocity of light in vacuum, $\eta(\vec{k},\omega)$ is the real part of the index of refraction of light waves with wave vector $\vec{k}$ and frequency ω, $\tilde{b}_{\vec{k}\nu\sigma}=b_{\vec{k}\nu\sigma}-b_{-\vec{k}\nu\sigma}^{\dagger}$, and Im refers to the imaginary part of the Green's function in question. In the optical region of frequencies, $\eta(\vec{k},\omega)$ varies slowly with ω and may be taken as a constant $\eta(\vec{k},\omega)=\eta_{\vec{k}}$. Taking the spin components in Eq. (44), we get

$$\alpha(\vec{k},\omega)=-(\pi/4c\omega\eta_{\vec{k}})\mu_{\vec{k}}^2\,\omega_k$$

$$\times\mathrm{Im}(\langle\langle\tilde{b}_{\vec{k}\nu\downarrow}+\tilde{b}_{\vec{k}\nu\uparrow};\tilde{b}_{\vec{k}\nu\downarrow}^{\dagger}\rangle\rangle+\langle\langle\tilde{b}_{\vec{k}\nu\downarrow}-\tilde{b}_{\vec{k}\nu\uparrow};\tilde{b}_{\vec{k}\nu\downarrow}^{\dagger}\rangle\rangle)\,. \qquad (45)$$

From Eqs. (15)–(18), we derive the following expressions for the Green's functions:

$$\langle\langle\tilde{b}_{\vec{k}\nu\downarrow}+\tilde{b}_{\vec{k}\nu\uparrow};\tilde{b}_{\vec{k}\nu\downarrow}^{\dagger}\rangle\rangle$$

$$=\frac{1}{\pi}\,\frac{\omega^2(\omega+\Omega_{\vec{k}\nu}^{+}+\Delta_{+}^{*})}{[\omega^2-\Omega_{s+}^2(\vec{k}\nu)][\omega^2-\Omega_{s-}^2(\vec{k}\nu)]}\,, \qquad (46)$$

$$\langle\langle\tilde{b}_{\vec{k}\nu\downarrow}-\tilde{b}_{\vec{k}\nu\uparrow};\tilde{b}_{\vec{k}\nu\downarrow}^{\dagger}\rangle\rangle$$

$$=\frac{1}{\pi}\left[\frac{1}{2}\left(1+\frac{\Omega_{\vec{k}\nu}^{-}+\Delta_{-}^{*}}{\epsilon_{\vec{k}\nu}^{-}}\right)\Big/(\omega-\epsilon_{\vec{k}\nu}^{-})\right.$$

$$\left.+\frac{1}{2}\left(1-\frac{\Omega_{\vec{k}\nu}^{-}+\Delta_{-}^{*}}{\epsilon_{\vec{k}\nu}^{-}}\right)\Big/(\omega+\epsilon_{\vec{k}\nu}^{-})\right]. \qquad (47)$$

Substituting the imaginary parts of Eqs. (46) and (47) into (45) we obtain

$$\alpha(\vec{k},\omega)=\alpha_s(\vec{k},\omega)+\alpha_t(\vec{k},\omega)\,, \qquad (48)$$

with $\alpha_s(\vec{k},\omega)$ and $\alpha_t(\vec{k},\omega)$ being the absorption coefficients describing the singlet and triplet biexciton bands, respectively, and determined by

$$\alpha_s(\vec{k},\omega)=(\mu_{\vec{k}}^2\omega_{\vec{k}}/4c\omega\eta_{\vec{k}})[u_{s+}^2(\vec{k}\nu)\delta(\omega-\Omega_{s+}(\vec{k}\nu))+v_{s+}^2(\vec{k}\nu)\delta(\omega+\Omega_{s+}(\vec{k}\nu))$$

$$+u_{s-}^2(\vec{k}\nu)\delta(\omega-\Omega_{s-}(\vec{k}\nu))+v_{s-}^2(\vec{k}\nu)\delta(\omega+\Omega_{s-}(\vec{k}\nu))]\,, \qquad (49)$$

$$\alpha_t(\vec{k},\omega)=(\mu_{\vec{k}}^2\omega_{\vec{k}}/4c\omega\eta_{\vec{k}})[u_t^2(\vec{k}\nu)\delta(\omega-\epsilon_{\vec{k}\nu}^{-})$$

$$+v_t^2(\vec{k}\nu)\delta(\omega+\epsilon_{\vec{k}\nu}^{-})]\,, \qquad (50)$$

$$u_{s\pm}^2(\vec{k}\nu)=\frac{\Omega_{s\pm}(\vec{k}\nu)[\Omega_{s\pm}(\vec{k}\nu)+\Omega_{\vec{k}\nu}^{+}+\Delta_{+}]}{2[\Omega_{s\pm}^2(\vec{k}\nu)-\Omega_{s\mp}^2(\vec{k}\nu)]}\,, \qquad (51a)$$

$$u_{s\pm}^2(\vec{k}\nu)=\frac{\Omega_{s\pm}(\vec{k}\nu)[\Omega_{s\pm}(\vec{k}\nu)-\Omega_{\vec{k}\nu}^{+}-\Delta_{+}]}{2[\Omega_{s\pm}^2(\vec{k}\nu)-\Omega_{s\mp}^2(\vec{k}\nu)]}\,, \qquad (51b)$$

$$u_t^2(\vec{k}\nu)=\tfrac{1}{2}[1+(\Omega_{\vec{k}\nu}^{-}+\Delta_{-})/\epsilon_{\vec{k}\nu}^{-}]\,, \qquad (52a)$$

$$v_t^2(\vec{k}\nu)=\tfrac{1}{2}[1+(\Omega_{\vec{k}\nu}^{-}+\Delta_{-})/\epsilon_{\vec{k}\nu}^{-}]\,, \qquad (52b)$$

$$u_{s+}^2(\vec{k}\nu)+v_{s+}^2(\vec{k}\nu)+u_{s-}^2(\vec{k}\nu)+v_{s-}^2(\vec{k}\nu)=1\,,$$

$$u_t^2(\vec{k}\nu)+v_t^2(\vec{k}\nu)=1\,. \qquad (53)$$

The probability amplitudes $u_{s+}^2(\vec{k}\nu)$ and $u_{s-}^2(\vec{k}\nu)$ give a measure of the intensities of the singlet-biexciton absorption peaks with energies $\Omega_{s+}(\vec{k}\nu)$ and $\Omega_{s-}(\vec{k}\nu)$, respectively; $v_{s+}^2(\vec{k}\nu)$ and $v_{s-}^2(\vec{k}\nu)$ are the corresponding ones for the emission bands. The probability amplitudes $u_t^2(\vec{k}\nu)$ and $v_t^2(\vec{k}\nu)$ describe the intensities for the absorption and emission bands of the triplet biexciton mode with energy $\epsilon_{\vec{k}\nu}^{-}$, respectively. As mentioned in the previous section, the singlet and triplet biexciton modes have well-defined meaning only in the limit when $U_-/U_+ \to 0$, therefore the expressions (48)–(50) are applicable when this limit is satisfied ($U_-/U_+ \to 0$), where the singlet and triplet biexciton modes are independent of one another.

In the limit when $\Delta_\pm \to 0$ then Eqs. (49) and (50) for $\alpha_s(\vec{k},\omega)$ and $\alpha_t(\vec{k},\omega)$ with $\Delta_+=\Delta_-=0$, describe optical transitions to the singlet and triplet exciton bands, respectively, in the presence of a resonant electromagnetic field.

V. GROUND-STATE ENERGY

To calculate the ground-state energy of the system we average the Hamiltonian (1) as

$$\langle\mathcal{H}\rangle = \text{const} + \sum_{\vec{k},\nu,\sigma} \Omega_{\vec{k}\nu\sigma}\langle b^{\dagger}_{\vec{k}\nu\sigma} b_{\vec{k}\nu\sigma} + b^{\dagger}_{-\vec{k}\nu\sigma} b_{-\vec{k}\nu\sigma}\rangle + \sum_{\substack{\vec{k},\nu,\sigma,\sigma' \\ (\sigma\neq\sigma')}} J_{\sigma\sigma'}(\vec{k})\langle b^{\dagger}_{\vec{k}\nu\sigma} b_{\vec{k}\nu\sigma'} + b^{\dagger}_{\vec{k}\nu\sigma'} b_{\vec{k}\nu\sigma}\rangle$$

$$+ \sum_{\substack{\vec{k},\nu,\lambda \\ \sigma}} \frac{i\mu^{\sigma\sigma}_{\vec{k}\lambda\nu}}{2}\langle b_{-\vec{k}\nu\sigma}\beta^{\dagger}_{\vec{k}\lambda} - b^{\dagger}_{\vec{k}\nu\sigma}\beta_{-\vec{k}\lambda}\rangle - \frac{1}{2N}\sum_{\substack{\vec{k},\vec{q},\nu \\ \sigma,\sigma'}} U_{\sigma\sigma'}(\vec{k}-\vec{q})\langle b^{\dagger}_{-\vec{q}\nu\sigma} b^{\dagger}_{\vec{q}\nu\sigma'}\rangle\langle b_{\vec{k}\nu\sigma} b_{-\vec{k}\nu\sigma'}\rangle \,. \tag{54}$$

Then, taking in Eq. (54) the spin components explicitly and using Eqs. (21a)–(22b) for the distribution functions in the limit of zero temperature, we derive the expression for the ground-state energy,

$$\langle\mathcal{H}\rangle_0 = \text{const} + \sum_{\vec{k}} \Omega^{+}_{\vec{k}\nu}\left(1 - \frac{\Omega^{+}_{\vec{k}\nu}}{(\epsilon^{+2}_{\vec{k}\nu} + 2\mu^{2}_{\vec{k}})^{1/2}}\right)$$

$$- \sum_{\vec{k}} \frac{|\Delta_{+}(\vec{k})|^2}{2(\epsilon^{+2}_{\vec{k}\nu} + 2\mu^{2}_{\vec{k}})^{1/2}} - \sum_{\vec{k}} \frac{\mu^{2}_{\vec{k}}}{(\epsilon^{+2}_{\vec{k}\nu} + 2\mu^{2}_{\vec{k}})^{1/2}}$$

$$+ \sum_{\vec{k}} \Omega^{-}_{\vec{k}\nu}\left(1 - \frac{\Omega^{-}_{\vec{k}\nu}}{\epsilon^{-}_{\vec{k}\nu}}\right) - \sum_{\vec{k}} \frac{|\Delta_{-}(\vec{k})|^2}{2\epsilon^{-}_{\vec{k}\nu}} \,. \tag{55}$$

The last two terms in Eq. (55) arise from the triplet biexciton field. To proceed further, we consider the case of resonance, namely, when Eq. (35) is satisfied ($E_g = 0$) then we make use of the same approximations as those deriving Eqs. (36)–(38) with the result

$$\langle\mathcal{H}\rangle_0 = \text{const} + W_0^{+} + W_0^{-} - \frac{\mu^2}{U_+} \,, \tag{56}$$

where

$$W_0^{\pm} = -N_{\pm}(0)\bar{\omega}_{\pm}^2\left(-1 + \frac{1}{\tanh(1/\rho_{\pm})}\right) = -\frac{2N_{\pm}(0)\bar{\omega}_{\pm}^2}{e^{2/\rho_{\pm}} - 1} \,. \tag{57}$$

The expressions for W_0^{+} and W_0^{-} describe the binding energies for the singlet and triplet biexcitons, respectively. The expression for $W_0^{+} - \mu^2/U_+$ is similar to the corresponding one for the coherent pairing of the Wannier-Mott type excitons in insulators and semiconductors.[10] Using Eq. (29) for $N_{\pm}(0)$, we may rewrite Eq. (57) as

$$W_0^{\pm} = -3\bar{\omega}_{\pm}/(e^{2/\rho_{\pm}} - 1) \,. \tag{58}$$

Whenever the limit $U_-/U_+ \to 0$ is applicable then $\rho_{\pm}$ in Eqs. (56)–(58) should be replaced by $\rho_{\pm}^0$ given by Eq. (42). The expression for W_0^{+} given by Eq. (57) is formally analogous to that occurring in superconductors.[11,12] Equation (56) indicates that there are singlet and triplet biexciton states which have lower binding energies than that of the corresponding normal exciton states provided that there is a net attractive interaction between the excitons.

To obtain an estimate for the quantities $\bar{\omega}_+$, $\tilde{\Delta}_+^0$, T_c^{+}, and W_0^{+} for the singlet biexciton mode, we rewrite Eqs. (29), (43), (40), and (57) as

$$\bar{\omega}_+/\phi_+ = \xi^2/2m \,, \tag{59}$$

$$\tilde{\Delta}_+^0/\phi_+ = (\xi^2/2m)/\sinh(1/\rho_+^0) \,, \tag{60}$$

$$T_c^{+}/\phi_+ = (0.57\,\xi^2/2mK_B)/\sinh(1/\rho_+^0) \,, \tag{61}$$

$$-W_0^{+}/\phi_+ = (3\xi^2/2m)/e^{2/\rho_+^0} - 1 \,, \tag{62}$$

where

$$\phi_+ = m/m^{+}_{\text{exc}} \,, \tag{63}$$

m being the free electron mass. Excitons produced by light have positive effective masses

TABLE I. Computed values for $\bar{\omega}_+/\phi_+$, the gap function $\tilde{\Delta}_+^0/\phi_+$, transition temperature T_c^{+}/ϕ_+, and binding energy W_0^{+}/ϕ_+, given by Eqs. (59)–(62), respectively.

n (cm^{-3})	ρ_+^0	$U_+/\bar{\omega}_+$	$\bar{\omega}_+/\phi_+$ (cm^{-1})	$\tilde{\Delta}_+^0/\phi_+$ (cm^{-1})	T_c^{+}/ϕ_+ (°K)	$-W_0^{+}/\phi_+$ (cm^{-1})
1×10^{18}	1.0	0.7	47	40	33	22
	1.5	1.0	47	65	53	50
	2.0	1.3	47	90	74	82
	2.5	1.7	47	114	94	115
	3.0	2.0	47	136	111	149
2×10^{18}	1.0	0.7	74	63	52	35
	1.5	1.0	74	104	86	80
	2.0	1.3	74	148	122	129
	2.5	1.7	74	186	152	181
	3.0	2.0	74	222	182	234
4×10^{18}	1.0	0.7	118	100	82	55
	1.5	1.0	118	186	136	127
	2.0	1.3	118	234	192	206
	2.5	1.7	118	292	240	289
	3.0	2.0	118	334	274	374
6×10^{18}	1.0	0.7	154	131	107	72
	1.5	1.0	154	218	178	165
	2.0	1.3	154	308	252	269
	2.5	1.7	154	386	236	377
	3.0	2.0	154	462	378	487
8×10^{18}	1.0	0.7	186	158	130	87
	1.5	1.0	186	264	216	200
	2.0	1.3	186	374	306	325
	2.5	1.7	186	468	384	455
	3.0	2.0	186	562	460	589
1×10^{19}	1.0	0.7	216	184	151	101
	1.5	1.0	216	306	250	232
	2.0	1.3	216	434	376	377
	2.5	1.7	216	542	444	529
	3.0	2.0	216	652	534	684

which may be determined by the width of the corresponding bands.[3] For light excitons, $m_{\text{exc}} \geqslant m$ while for the heavy ones $m_{\text{exc}} > m$. In general, $\phi_+ = m/m^+_{\text{exc}} \leqslant 1$ and in the absence of experimental data, we shall keep ϕ_+ as a free parameter. In Table I, numerical values for $\bar{\omega}_+/\phi_+$, $\tilde{\Delta}^0_+/\phi_+$, T^+_c/ϕ_+, and $-W^+_0/\phi_+$ are listed, which have been determined from Eqs. (59)–(62), respectively, under conditions of high exciton densities $n = 10^{18}$–10^{19} cm^{-3} and in the strong coupling limit where $\rho^0_+ = 1$–3. The exciton concentration of 2×10^{18} cm^{-3} has been recently achieved through optical pumping in anthracence crystals.[13]

VI. DISCUSSION

We have studied the physical process where two excitons with opposite wave vectors interact to form a bound state in the presence of a resonant electromagnetic field. It is found that when the spin degeneracy of the exciton pairs is removed, it results in creating two fields, the singlet and triplet exciton fields, respectively. When the exchange interaction between the charges is weak or in the limit $U_-/U_+ \to 0$, the singlet and triplet biexciton modes (quasiparticles) have well-defined energies and migrate through the crystal independently. In this case, the gap functions Δ^0_+ and Δ^0_- are given by Eq. (43) and may be of comparable magnitude. In view of the inequality (39), the formation of triplet biexcitons may be more preferable than that of the singlet whenever the optical transition under consideration carries a large oscillator strength.

As the strength of the exchange interaction increases or at finite values of the ratio U_-/U_+, the two fields are coupled together. In this case, it is difficult to distinguish between the two fields because of their strong mixing. However, for most organic molecular crystals, exchange interactions are manifested to be extremely weak and therefore, the strong mixing between the two biexciton fields is not expected to occur.

Equations (49) and (50) describe optical transitions to be singlet and triplet biexciton states, respectively. The scattering amplitudes $u^2_{s+}(\vec{k}\nu)$ and $u^2_{s-}(\vec{k}\nu)$ given by Eq. (51) describe the relative intensities of the two singlet biexciton absorption bands with energies $\Omega_{s+}(\vec{k}\nu)$ and $\Omega_{s-}(\vec{k}\nu)$, while $v^2_{s+}(\vec{k}\nu)$ and $v^2_{s-}(\vec{k}\nu)$ are the corresponding ones describing the emission processes, respectively. Equations (52a) and (52b) for $u^2_t(\vec{k}\nu)$ and $v^2_t(\vec{k}\nu)$ represent the relative intensities of the triplet biexciton bands corresponding to the physical process of absorption and emission, respectively. Equation (57) for W^+_0 and W^-_0 describes the binding energies of the singlet and triplet biexciton modes, respectively.

The numerical results in Table I imply that for exciton densities in the range of 10^{18}–10^{19} cm^{-3}, the gap function $\tilde{\Delta}^0_+/\phi_+$ as well as the corresponding binding energy $-W^+_0/\phi_+$ are measurable quantities provided that the strong coupling limit is applicable, i.e., $U_+/\bar{\omega}_+ \gtrsim 1$. The values for $\bar{\omega}_+/\phi_+$ and $U_+/\bar{\omega}_+$ in Table I indicate that in this limit the required strength of the average interaction energy is rather a reasonable one.

At the concentrations considered here, $n = 10^{18}$–10^{19} cm^{-3}, the average distance between the excitons is of the order of 6×10^{-7}–2×10^{-7} cm. Thus at these concentrations, the excitons are at a distance 60–20 Å apart and at such distances the attractive interaction between them may be appreciable. The present experimental situation has been summarized in Ref. 5, to our knowledge, biexcitons have not yet been observed in molecular crystals. We hope that the recent developments in the exciton spectroscopy[1,13] will make possible in the near future the observation of biexciton states in molecular organic crystals.

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