PHYSICAL REVIEW B VOLUME 15, NUMBER 4 15 FEBRUARY 1977

Charge-transfer electron-exciton bound states in molecular crystals

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(Received 31 August 1976)

The theory on the coherent electron-exciton pairing in molecular crystals is generalized to include the effect of the electron spin. It is shown that in the Hartree-Fock approximation, singlet as well as triplet excitons may interact with excited electrons to form charge-transfer bound states provided that certain conditions prevail. The gap functions Δ_+ and Δ_-, due to the electron-singlet and electron-triplet exciton pairing, respectively, are calculated at zero temperature and they are found to be independent of one another only when the exchange interaction between the charges is extremely weak. In this limit, the two frequency modes for the two charge-transfer complexes resulting from the electron-singlet and electron-triplet exciton pairing propagate through the crystal independently. As the strength of the exchange interactions increases the gap functions Δ_+ and Δ_- depend strongly on each other, an effect which brings about the mixing of the two frequency modes corresponding to the two charge-transfer complexes. Expressions for the ground-state energy (binding energy) of the crystal arising from the electron-singlet and electron-triplet exciton bound states are derived and discussed in detail.

I. INTRODUCTION

The valence bands for most molecular crystals are filled with electrons having opposite spin alignments. Thus upon excitation, Frenkel excitons (excitons of small radius) which consist of tightly bound electron-hole pairs and are used to describe the elementary collective electronic excitations of molecular solids[1] may have their spin components either up or down. When the spin degeneracy of the exciton field is removed in the Hartree-Fock approximation, the excitation spectrum[2] consists of two frequency modes which propagate through the crystal independently and correspond to the singlet- and triplet-exciton modes, respectively.[2]

It has been recently suggested that an exciton may interact with an excited electron which is located at an adjacent lattice site of a molecular crystal to form a charge-transfer bound state.[3] The excitation spectrum as well as the electromagnetic properties of the electron-exciton bound states have been discussed in I. Using methods formally analogous to those in the theory of superconductivity,[4] it has been found in I that the process of the coherent electron-exciton pairing is feasible provided that certain conditions prevail and that the created electron-exciton pairs are diamagnetic. Electrons[5] (charge carriers) can be produced in the crystal either by photon absorption[6] as is done for excitons or by photoinjection.[7]

Since both excitons and electrons carry out spin then in forming the electron-exciton complex, the electron and the exciton may have the same or opposite spin alignment. The purpose of the present study is to generalize the theory on the electron-exciton pairing to include the effects 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 a decoupling approximation, a coupled set of equations of motion is derived for the electron and exciton operators. The excitation spectrum is discussed in Sec. III. It is found that the singlet as well as the triplet excitons interact with electrons to form charge-transfer bound states. The gap functions Δ_+ and Δ_- for the electron-singlet and electron-triplet exciton pairing, respectively, are calculated at zero temperature and they are found to be independent of one another only in the limit when the exchange interaction goes to zero. In this case the energy modes describing the electron-singlet and electron-triplet exciton bound states migrate through the crystal independently. For finite values of the exchange interaction the gap functions Δ_+ and Δ_- depend on each other, an effect of which may cause the mixing of the two frequency modes. The binding energies arising from the electron-singlet and electron-triplet exciton pairings are calculated in Sec. IV while a discussion is given in Sec. V.

II. FORMULATION OF THE PROBLEM

The Hamiltonian for a two-level system of a molecular crystal has been derived in I and is given by Eq. (6) of I. This expression can be easily generalized to include the spin of the electrons and then it takes the form

$$\mathfrak{H} = \text{const.} + \sum_{\vec{n},\nu,\sigma} \bar{E}_{\nu 0}\alpha^{\dagger}_{\vec{n}\nu\sigma}\alpha_{\vec{n}\nu\sigma} + \sum_{\sigma,\vec{R}_{\vec{m}\vec{n}}}{}' L(\vec{m}\nu,\vec{n}\nu)\alpha^{\dagger}_{\vec{m}\nu\sigma}\alpha_{\vec{n}\nu\sigma} + \sum_{\substack{\sigma,\vec{R}_{\vec{m}\vec{n}}\\ \sigma'\sigma'}}{}' L(\vec{m}0,\vec{n}0)\alpha^{\dagger}_{\vec{m}0\sigma}\alpha_{\vec{n}0\sigma}$$

$$+ \sum_{\substack{\sigma,\vec{R}_{\vec{m},\vec{n}}\\ \sigma,\sigma'}} J_{\sigma\sigma'}(\vec{n},\vec{m})b^{\dagger}_{\vec{m}\nu\sigma}b_{\vec{n}\nu\sigma'} - \sum_{\substack{\nu,\vec{R}_{\vec{m}\vec{n}}\\ \sigma,\sigma'}} U_{\sigma\sigma'}(\vec{n},\vec{m})b^{\dagger}_{\vec{n}\nu\sigma}b_{\vec{n}\nu\sigma'}\alpha^{\dagger}_{\vec{m}\nu\sigma'}\alpha_{\vec{m}\nu\sigma'}, \tag{1}$$

where the indices σ and σ' indicate the spin component of an electron and take the values of spin up (↑) or spin down (↓). Equation (1) is identical to Eq. (6) of I apart from the inclusion of the electron spin and the neglect of the fifth term of Eq. (6) of I which describes the simultaneous creation and annihilation of two excitations; this term has been also disregarded later on in I. The coupling function $J_{\sigma\sigma'}(\vec{n},\vec{m})$ is defined as[2]

$$J_{\sigma\sigma'}(\vec{n},\vec{m}) = J(\vec{n}0\sigma,\vec{m}\nu\sigma'|\vec{n}\nu\sigma,\vec{m}0\sigma')$$

$$= \langle \vec{n}0\sigma,\vec{m}\nu\sigma'|V|\vec{n}\nu\sigma,\vec{m}0\sigma'\rangle$$

$$-\langle \vec{n}0\sigma,\vec{m}\nu\sigma'|V|\vec{m}0\sigma',\vec{n}\nu\sigma'\rangle, \tag{2a}$$

while that of $U_{\sigma\sigma'}(\vec{n},\vec{m})$ is given by

$$U_{\sigma\sigma'}(\vec{n},\vec{m}) = U_{0,\sigma\sigma'}(\vec{n},\vec{m}) + U_{\nu,\sigma\sigma'}(\vec{n},\vec{m}), \tag{2b}$$

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

$$-J(\vec{n}0\sigma,\vec{m}0\sigma'|\vec{n}0\sigma,\vec{m}0\sigma'), \tag{2c}$$

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

$$-J(\vec{n}\nu\sigma,\vec{m}\nu\sigma'|\vec{n}\nu\sigma,\vec{m}\nu\sigma'), \tag{2d}$$

ν and 0 refer to the excited and ground states of an electron, respectively, and the excitation energy $\bar{E}_{\nu 0}$ is described by Eq. (7a) of I, namely,

$$\bar{E}_{\nu 0} = L(\vec{n}\nu,\vec{m}\nu) - L(\vec{n}0,\vec{m}0) + \sum_{\sigma,\vec{R}_{\vec{m}\vec{n}}} U_{0,\sigma\sigma}(\vec{n},\vec{m}). \tag{2e}$$

The electron creation and annihilation operators $\alpha^{\dagger}_{\vec{n}\nu\sigma}$ and $\alpha_{\vec{n}\nu\sigma}$ describe the electron state ν at the lattice side $\vec{n}$ with the spin projection up ↑($\frac{1}{2}$) or down ↓($-\frac{1}{2}$). Similarly, the Frenkel exciton operators are defined as $b_{\vec{n}\nu\sigma} = \alpha^{\dagger}_{\vec{n}0\sigma}\alpha_{\vec{n}\nu\sigma}$ and $b^{\dagger}_{\vec{n}\nu\sigma} = \alpha^{\dagger}_{\vec{n}\nu\sigma}\alpha_{\vec{n}0\sigma}$. Thus apart from the spin degeneracy, the expression of the Hamiltonian (1) as well as the notation coincide with that of Eq. (6) of I where the reader is referred to for further details.

Using the Hamiltonian (1) we derive the equation of motion for the operator $(\alpha_{\vec{n}\nu\uparrow} \pm \alpha_{\vec{n}\nu\downarrow})$,

$$\left(\frac{id}{dt} - \bar{E}_{\nu 0}\right)(\alpha_{\vec{n}\nu\uparrow} \pm \alpha_{\vec{n}\nu\downarrow}) = \sum_{\vec{R}_{\vec{m}\vec{n}}}{}' L(\vec{m}\nu,\vec{n}\nu)(\alpha_{\vec{m},\nu\uparrow} \pm \alpha_{\vec{m}\nu\downarrow})$$

$$- \sum_{\vec{R}_{\vec{m}\vec{n}}}{}' [U_{\uparrow\uparrow}(\vec{n},\vec{m})\alpha_{\vec{n}\nu\uparrow} \pm U_{\uparrow\downarrow}(\vec{n},\vec{m})\alpha_{\vec{n}\nu\downarrow}]b^{\dagger}_{\vec{m}\nu\uparrow}b_{\vec{m}\nu\uparrow}$$

$$\mp \sum_{\vec{R}_{\vec{m}\vec{n}}}{}' [U_{\uparrow\uparrow}(\vec{n},\vec{m})\alpha_{\vec{n}\nu\downarrow} \pm U_{\uparrow\downarrow}(\vec{n},\vec{m})\alpha_{\vec{n}\nu\uparrow}]b^{\dagger}_{\vec{m}\nu\downarrow}b_{\vec{m}\nu\downarrow}, \tag{3}$$

where from symmetry considerations we have taken

$$U_{\uparrow\uparrow}(\vec{n},\vec{m}) = U_{\downarrow\downarrow}(\vec{n},\vec{m}),\; U_{\uparrow\downarrow}(\vec{n},\vec{m}) = U_{\downarrow\uparrow}(\vec{n},\vec{m}), \tag{4a}$$

$$J_{\uparrow\uparrow}(\vec{n},\vec{m}) = J_{\downarrow\downarrow}(\vec{n},\vec{m}),\; J_{\uparrow\downarrow}(\vec{n},\vec{m}) = J_{\downarrow\uparrow}(\vec{n},\vec{m}). \tag{4b}$$

Equation (3) has been derived in the same approximation as that of Eq. (9) of I.

To decouple Eq. (3) we follow I and apply a similar scheme as that of Eq. (10) of I, namely,

$$\sum U_{\uparrow\uparrow}(\vec{n},\vec{m})\alpha_{\vec{n}\nu\uparrow}b^{\dagger}_{\vec{m}\nu\uparrow}b_{\vec{m}\nu\uparrow} \approx U_{\uparrow\uparrow}(\vec{n},\vec{m})\langle b^{\dagger}_{\vec{m}\nu\uparrow}b_{\vec{m}\nu\uparrow}\rangle \alpha_{\vec{n}\nu\uparrow} + \sum U_{\uparrow\uparrow}(\vec{n},\vec{m})\langle \alpha_{\vec{n}\nu\uparrow}b^{\dagger}_{\vec{m}\nu\uparrow}\rangle b_{\vec{m}\nu\uparrow}, \tag{5a}$$

$$\sum U_{\uparrow\downarrow}(\vec{n},\vec{m})\alpha_{\vec{n}\nu\downarrow}b^{\dagger}_{\vec{m}\nu\uparrow}b_{\vec{m}\nu\uparrow} \approx \sum U_{\uparrow\downarrow}(\vec{n},\vec{m})\langle b^{\dagger}_{\vec{m}\nu\uparrow}b_{\vec{m}\nu\uparrow}\rangle \alpha_{\vec{n}\nu\downarrow} + \sum U_{\uparrow\downarrow}(\vec{n},\vec{m})\langle \alpha_{\vec{n}\nu\downarrow}b^{\dagger}_{\vec{m}\nu\uparrow}\rangle b_{\vec{m}\nu\uparrow}, \tag{5b}$$

$$\sum U_{\uparrow\uparrow}(\vec{n},\vec{m})\alpha_{\vec{n}\nu\downarrow}b^{\dagger}_{\vec{m}\nu\downarrow}b_{\vec{m}\nu\downarrow} \approx \sum U_{\uparrow\uparrow}(\vec{n},\vec{m})\langle b^{\dagger}_{\vec{m}\nu\downarrow}b_{\vec{m}\nu\downarrow}\rangle \alpha_{\vec{n}\nu\downarrow} + \sum U_{\uparrow\uparrow}(\vec{n},\vec{m})\langle \alpha_{\vec{n}\nu\downarrow}b^{\dagger}_{\vec{m}\nu\downarrow}\rangle b_{\vec{m}\nu\downarrow}, \tag{5c}$$

$$\sum U_{\uparrow\downarrow}(\vec{n},\vec{m})\alpha_{\vec{n}\nu\uparrow}b^{\dagger}_{\vec{m}\nu\downarrow}b_{\vec{m}\nu\downarrow} \approx \sum U_{\uparrow\downarrow}(\vec{n},\vec{m})\langle b^{\dagger}_{\vec{m}\nu\downarrow}b_{\vec{m}\nu\downarrow}\rangle \alpha_{\vec{n}\nu\uparrow} + \sum U_{\uparrow\downarrow}(\vec{n},\vec{m})\langle \alpha_{\vec{n}\nu\uparrow}b^{\dagger}_{\vec{m}\nu\downarrow}\rangle b_{\vec{m}\nu\downarrow}. \tag{5d}$$

The first terms on the right-hand side of Eqs. (5a)–(5d) designate corrections to the electron spectrum due to the average exciton density while the last terms describe electron-exciton pairing where the two particles have either parallel or antiparallel spins, respectively; the decoupling approximations described by Eqs. (5a)–(5d) are expected to be valid in the high-density limit.[4] Substitution of Eqs. (5a)–(5d) into Eq. (3) yields

$$\left(\frac{id}{dt}-E_{\nu 0}\right)(\alpha_{\vec{n}\nu\uparrow}\pm\alpha_{\vec{n}\nu\downarrow}) = \sum_{\vec{R}_{\vec{m}\vec{n}}}{}' L(\vec{m}\nu,\vec{n}\nu)(\alpha_{\vec{m}\nu\uparrow}\pm\alpha_{\vec{m}\nu\downarrow}) - \Delta_{\pm}(\vec{n})(b_{\vec{m}\nu\uparrow}\pm b_{\vec{m}\nu\downarrow}), \tag{6}$$

where

$$E_{\nu 0}=\bar{E}_{\nu 0}-2\sum_{\vec{R}_{\vec{m}\vec{n}}} U_{+}(\vec{n},\vec{m})n_{\nu}, \tag{7a}$$

$$U_{\pm}(\vec{n},\vec{m})=\tfrac{1}{2}[U_{\uparrow\uparrow}(\vec{n},\vec{m})\pm U_{\uparrow\downarrow}(\vec{n},\vec{m})], \tag{7b}$$

$$n_{\nu}=\langle b^{\dagger}_{\vec{m}\nu\uparrow}b_{\vec{m}\nu\uparrow}\rangle=\langle b^{\dagger}_{\vec{m}\nu\downarrow}b_{\vec{m}\nu\downarrow}\rangle, \tag{7c}$$

$$\Delta_{\pm}(\vec{n})=\Delta_{\uparrow\uparrow}(\vec{n})\pm\Delta_{\uparrow\downarrow}(\vec{n}), \tag{8a}$$

$$\Delta_{\uparrow\uparrow}(\vec{n})=\Delta_{\downarrow\downarrow}(\vec{n})=\sum_{\vec{R}_{\vec{m}\vec{n}}} U_{\uparrow\uparrow}(\vec{n},\vec{m})\langle\alpha_{\vec{n}\nu\uparrow}b^{\dagger}_{\vec{m}\nu\uparrow}\rangle, \tag{8b}$$

$$\Delta_{\uparrow\downarrow}(\vec{n})=\Delta_{\downarrow\uparrow}(\vec{n})=\sum_{\vec{R}_{\vec{m}\vec{n}}} U_{\uparrow\downarrow}(\vec{n},\vec{m})\langle\alpha_{\vec{n}\nu\uparrow}b^{\dagger}_{\vec{m}\nu\downarrow}\rangle. \tag{8c}$$

Considering the definition of the coupling function $U_{\sigma\sigma'}(\vec{n},\vec{m})$ given by Eqs. (2a)–(2d), we conclude that the function $U_{+}(\vec{n},\vec{m})$ arises from Coulomb and exchange-type interactions but only exchange-type interactions are involved in the expression for $U_{-}(\vec{n},\vec{m})$. The gap functions $\Delta_{\downarrow\downarrow}(\vec{n})$ and $\Delta_{\uparrow\downarrow}(\vec{n})$ describe the electron-exciton pairing where the electron and exciton have parallel and antiparallel spins, respectively.

Using the Hamiltonian we derive the equations of motion for the exciton operators $b_{\vec{m}\nu\uparrow}$ and $b_{\vec{m}\nu\downarrow}$ as

$$\begin{aligned}\left(\frac{id}{dt}-\bar{E}_{\nu 0}\right)b_{\vec{m}\nu\uparrow} ={}& \sum_{\vec{R}_{\vec{n}\vec{m}}}{}' J_{\uparrow\uparrow}(\vec{n},\vec{m})b_{\vec{n}\nu\uparrow}(1-2b^{\dagger}_{\vec{m}\nu\uparrow}b_{\vec{m}\nu\uparrow}) + \sum_{\vec{R}_{\vec{n}\vec{m}}}{}' J_{\uparrow\downarrow}(\vec{n},\vec{m})b_{\vec{n}\nu\downarrow}(1-2b^{\dagger}_{\vec{m}\nu\uparrow}b_{\vec{m}\nu\uparrow}) \\ &- \sum_{\vec{R}_{\vec{n}\vec{m}}} U_{\uparrow\uparrow}(\vec{m},\vec{n})b_{\vec{m}\nu\uparrow}\alpha^{\dagger}_{\vec{n}\nu\uparrow}\alpha_{\vec{n}\nu\uparrow} - \sum_{\vec{R}_{\vec{n}\vec{m}}} U_{\uparrow\downarrow}(\vec{m},\vec{n})b_{\vec{m}\nu\uparrow}\alpha^{\dagger}_{\vec{n}\nu\downarrow}\alpha_{\vec{n}\nu\downarrow},\end{aligned} \tag{9}$$

$$\begin{aligned}\left(\frac{id}{dt}-\bar{E}_{\nu 0}\right)b_{\vec{m}\nu\downarrow} ={}& \sum_{\vec{R}_{\vec{n}\vec{m}}}{}' J_{\downarrow\downarrow}(\vec{n},\vec{m})b_{\vec{n}\nu\downarrow}(1-2b^{\dagger}_{\vec{m}\nu\downarrow}b_{\vec{m}\nu\downarrow}) + \sum_{\vec{R}_{\vec{n}\vec{m}}}{}' J_{\downarrow\uparrow}(\vec{n},\vec{m})b_{\vec{n}\nu\uparrow}(1-2b^{\dagger}_{\vec{m}\nu\downarrow}b_{\vec{m}\nu\downarrow}) \\ &- \sum_{\vec{R}_{\vec{n}\vec{m}}} U_{\downarrow\downarrow}(\vec{n},\vec{m})b_{\vec{m}\nu\downarrow}\alpha^{\dagger}_{\vec{n}\nu\downarrow}\alpha_{\vec{n}\nu\downarrow} - \sum_{\vec{R}_{\vec{n}\vec{m}}} U_{\downarrow\uparrow}(\vec{m},\vec{n})b_{\vec{m}\nu\downarrow}\alpha^{\dagger}_{\vec{n}\nu\uparrow}\alpha_{\vec{n}\nu\uparrow}.\end{aligned} \tag{10}$$

When use is made of the decoupling approximation given by Eqs. (5a)–(5d) and Eqs. (4a)–(4b) then Eqs. (9) and (10) may take the form

$$\left(\frac{id}{dt}-E_{\nu 0}\right)(b_{m\nu\uparrow}\pm b_{\vec{m}\nu\downarrow}) = \sum_{\vec{R}_{\vec{n}\vec{m}}}{}' J_{\pm}(\vec{m},\vec{n})(b_{\vec{n}\nu\uparrow}\pm b_{\vec{n}\nu\downarrow}) - \Delta^{*}_{\pm}(\vec{m})(\alpha_{\vec{n}\nu\uparrow}\pm\alpha_{\vec{n}\nu\downarrow}), \tag{11}$$

where

$$J_{\pm}(\vec{n},\vec{m})=[J_{\uparrow\uparrow}(\vec{n},\vec{m})\pm J_{\uparrow\downarrow}(\vec{n},\vec{m})](1-2n_{\nu}). \tag{12}$$

In the momentum representation the coupled Eq. (6) and (11) become

$$\left(\frac{id}{dt}-\omega_{\vec{k}\nu}\right)(\alpha_{\vec{k}\nu\uparrow}\pm\alpha_{\vec{k}\nu\downarrow})=-\Delta_{\pm}(\vec{k})(b_{\vec{k}\nu\uparrow}\pm b_{\vec{k}\nu\downarrow}), \tag{13}$$

$$\left(\frac{id}{dt}-E^{\pm}_{k\nu}\right)(b_{k\nu\uparrow}\pm b_{\vec{k}\nu\downarrow})=-\Delta^{*}_{\pm}(\vec{k})(\alpha_{\vec{k}\nu\uparrow}\pm\alpha_{\vec{k}\nu\downarrow}), \tag{14}$$

where the excitation energies for the single electron and exciton spectra $\omega_{\vec{k}\nu}$ and $E^{\pm}_{\vec{k}\nu}$ are defined, respectively, as

$$\omega_{\vec{k}\nu}=E_{\nu 0}+\sum_{\vec{R}_{\vec{m}\vec{n}}}{}' L(\vec{m}\nu,\vec{n}\nu)\exp[i(\vec{k}\cdot\vec{R}_{\vec{m}\vec{n}})], \tag{15}$$

$$E^{\pm}_{\vec{k}\nu}=E_{\nu 0}+\sum_{\vec{R}_{\vec{m}\vec{n}}}{}' J_{\pm}(\vec{n},\vec{m})\exp[i(\vec{k}\cdot\vec{R}_{\vec{m}\vec{n}})]. \tag{16}$$

The coupling function $\Delta_{\pm}(\vec{k})$ is given by

$$\Delta_{\pm}(\vec{k})=\Delta_{\uparrow\uparrow}(\vec{k})\pm\Delta_{\uparrow\downarrow}(\vec{k}), \tag{17}$$

where

$$\Delta_{\downarrow\downarrow}(\vec{k})=\Delta_{\uparrow\uparrow}(\vec{k})=\left(\frac{1}{N}\right)\sum_{\vec{q}} U_{\uparrow\uparrow}(\vec{k}-\vec{q})\langle\alpha_{\vec{q}\nu\uparrow}b^{\dagger}_{\vec{q}\nu\uparrow}\rangle, \tag{18a}$$

$$\Delta_{\uparrow\downarrow}(\vec{k})=\Delta_{\uparrow\downarrow}(\vec{k})=\left(\frac{1}{N}\right)\sum_{\vec{q}} U_{\uparrow\downarrow}(\vec{k}-\vec{q})\langle \alpha_{\vec{q}\nu\uparrow} b^{\dagger}_{\vec{q}\nu\downarrow}\rangle, \tag{18b}$$

$$U_{\uparrow\uparrow}(\vec{k}-\vec{q})=\sum_{\vec{R}_{\vec{m}\vec{n}}}{}' \; U_{\uparrow\uparrow}(\vec{n},\vec{m})\exp[i(\vec{k}-\vec{q})\cdot\vec{R}_{\vec{m}\vec{n}}], \tag{18c}$$

$$U_{\uparrow\downarrow}(\vec{k}-\vec{q})=\sum_{\vec{R}_{\vec{m}\vec{n}}}{}' \; U_{\uparrow\downarrow}(\vec{n},\vec{m})\exp[i(\vec{k}-\vec{q})\cdot\vec{R}_{\vec{m}\vec{n}}]. \tag{18d}$$

In the adopted model of I, the molecular crystal consists of neutral molecules in an undisplaced lattice having one molecule (atom) per unit cell; there are N molecules (atoms) in the crystal volume V. The expressions for the energies of excitation for the free electron and exciton fields $\omega_{\vec{k}\nu}$ and $E^{+}_{\vec{k}\nu}$ are described by Coulomb and exchange interactions while that of $E^{-}_{\vec{k}\nu}$ involves only exchange interactions. Therefore, the plus (+) and the minus (−) energy modes for the exciton field describe physical processes where the optical transitions involved are of spin allowed and spin forbidden, respectively. The expressions for $E^{+}_{\vec{k}\nu}$ and $E^{-}_{\vec{k}\nu}$ given by Eq. (16) coincide with those describing the singlet- and triplet-exciton spectra[2] of molecular crystals and they are correct in the Hartree-Fock approximation.[2] In the approximation adopted here and in the absence of external fields, the spin degeneracy of the free-exciton field is removed but not that of the free-electron field.

Inspection of Eqs. (17) and (18) indicate that the parameters $\Delta_{\pm}(\vec{k})$ for the "+" and "−" energy modes involve an admixture of coherent electron-exciton pairing with parallel and antiparallel spins; they have the meaning of the energy gaps for electron-exciton states with positive and negative spin projections on the z axis, respectively. If the functions $\Delta_{+}(\vec{k})$ and $\Delta_{-}(\vec{k})$ do not depend on each other then the coupled Eqs. (13) and (14) describing the "+" and "−" energy modes are completely separated; as we will see later this is not always the case. Up to now the functions $\Delta_{\pm}(\vec{k})$ are still unknown parameters and they will be calculated in a self-consistent way in Sec. III in connection with the excitation spectrum of the system under investigation.

III. EXCITATION SPECTRUM

We shall make use of the retarded double-time Green's functions of the Zubarev type[8,9] defined by Eq. (19) of I. If we introduce the Green's functions $\langle\langle \alpha_{\vec{k}\nu\uparrow} \pm \alpha_{\vec{k}\nu\downarrow}; \alpha^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle$ and $\langle\langle b_{\vec{k}\nu\uparrow} \pm b^{\dagger}_{\vec{k}\nu\downarrow}; \alpha^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle$ then making use of Eq. (20) of I and Eqs. (13) and (14) we derive the following equations of motion:

$$(\omega-\omega_{\vec{k}\nu})\langle\langle \alpha_{\vec{k}\nu\uparrow} \pm \alpha_{\vec{k}\nu\downarrow}; \alpha^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle=(1/2\pi)-\Delta\pm(\vec{k})\langle\langle b_{\vec{k}\nu\uparrow} \pm b_{\vec{k}\nu\downarrow}; \alpha^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle, \tag{19}$$

$$(\omega-E^{\pm}_{\vec{k}\nu})\langle\langle b_{\vec{k}\nu\downarrow} \pm b_{\vec{k}\nu\uparrow}; \alpha^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle=-\Delta^{*}_{\pm}(\vec{k})\langle\langle \alpha_{\vec{k}\nu\uparrow} \pm \alpha_{\vec{k}\nu\downarrow}; \alpha^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle. \tag{20}$$

Similarly,

$$(\omega-E^{\pm}_{\vec{k}\nu})\langle\langle b_{\vec{k}\nu\uparrow} \pm b_{\vec{k}\nu\downarrow}; b^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle=(1/2\pi)-\Delta^{*}_{\pm}(\vec{k})\langle\langle \alpha_{\vec{k}\nu\uparrow} \pm \alpha_{\vec{k}\nu\downarrow}; b^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle, \tag{21}$$

$$(\omega-\omega_{\vec{k}\nu})\langle\langle \alpha_{\vec{k}\nu\uparrow} \pm \alpha_{\vec{k}\nu\downarrow}; b^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle=-\Delta_{\pm}(\vec{k})\langle\langle b_{\vec{k}\nu\uparrow} \pm b_{\vec{k}\nu\downarrow}; b^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle. \tag{22}$$

Solving the coupled Eqs. (19) and (20) or (21) and (22), we have

$$\langle\langle \alpha_{\vec{k}\nu\uparrow} \pm \alpha_{\vec{k}\nu\downarrow}; \alpha^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle=\frac{1}{2\pi}\left(\frac{v^{2}_{\vec{k}\nu\pm}}{\omega-\Omega_{\vec{k}\nu\pm}-\epsilon_{\vec{k}\nu\pm}}+\frac{u^{2}_{\vec{k}\nu\pm}}{\omega-\Omega_{\vec{k}\nu\pm}+\epsilon_{\vec{k}\nu\pm}}\right), \tag{23}$$

$$\langle\langle b_{\vec{k}\nu\uparrow} \pm b_{\vec{k}\nu\downarrow}; \alpha^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle=\langle\langle \alpha_{\vec{k}\nu\uparrow} \pm \alpha_{\vec{k}\nu\downarrow}; b^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle=\left(\frac{1}{2\pi}\right)\frac{\Delta_{\pm}(\vec{k})}{2\epsilon_{\vec{k}\nu\pm}}\left(\frac{1}{\omega-\Omega_{\vec{k}\nu\pm}-\epsilon_{\vec{k}\nu\pm}}-\frac{1}{\omega-\Omega_{\vec{k}\nu\pm}+\epsilon_{\vec{k}\nu\pm}}\right), \tag{24}$$

$$\langle\langle b_{\vec{k}\nu\uparrow} \pm b_{\vec{k}\nu\downarrow}; b^{\dagger}_{\vec{k}\nu\uparrow}\rangle\rangle\frac{1}{2\pi}\left(\frac{u^{2}_{\vec{k}\nu\pm}}{\omega-\Omega_{\vec{k}\nu\pm}-\epsilon_{\vec{k}\nu\pm}}+\frac{v^{2}_{\vec{k}\nu\pm}}{\omega-\Omega_{\vec{k}\nu\pm}+\epsilon_{\vec{k}\nu\pm}}\right), \tag{25}$$

where the energies of excitation $\Omega_{\vec{k}\nu\pm} \pm \epsilon_{\vec{k}\nu\pm}$ are defined as

$$\Omega_{\vec{k}\nu\pm}=\tfrac{1}{2}(\omega_{\vec{k}\nu}+E^{\pm}_{\vec{k}\nu}) \tag{26}$$

$$\epsilon_{\vec{k}\nu\pm}=\left[\left(\frac{\omega_{\vec{k}\nu}-E^{\pm}_{\vec{k}\nu}}{2}\right)^{2}+|\Delta_{\pm}(\vec{k})|^{2}\right]^{1/2}, \tag{27}$$

and the scattering amplitudes $u_{\vec{k}\pm}$ and $v_{\vec{k}\nu\pm}$ are given by

$$u^{2}_{\vec{k}\nu\pm}=\frac{1}{2}\left(1+\frac{E^{\pm}_{\vec{k}\nu}-\omega_{\vec{k}\nu}}{2\epsilon_{\vec{k}\nu\pm}}\right), \tag{28a}$$

$$v^{2}_{\vec{k}\nu\pm}=\frac{1}{2}\left(1-\frac{E^{\pm}_{\vec{k}\nu}-\omega_{\vec{k}\nu}}{2\epsilon_{\vec{k}\nu\pm}}\right), \tag{28b}$$

$$u^{2}_{\vec{k}\nu\pm}+v^{2}_{\vec{k}\nu\pm}=1. \tag{28c}$$

We note that in Eqs. (23)–(28) the occurrence of either $u^2_{\vec{k}\nu\pm}$ or $v^2_{\vec{k}\nu\pm}$ depends on the sign of the quantity $E^{\pm}_{\vec{k}\nu}-\omega_{\vec{k}\nu}$, which for convenience has been taken as positive. It will be more accurate if it is understood to denote the absolute value, i.e.,

$$E^{\pm}_{\vec{k}\nu}-\omega_{\vec{k}\nu}\rightarrow \operatorname{sgn}(E^{\pm}_{\vec{k}\nu}-\omega_{\vec{k}\nu})\rightarrow |E^{\pm}_{\vec{k}\nu}-\omega_{\vec{k}\nu}|.$$

Using the Green's functions (23)–(25), we calculate the following expressions for the corresponding distribution functions[8,9] in the limit of zero temperature

$$\langle \alpha^{\dagger}_{\vec{k}\nu\uparrow}(\alpha_{\vec{k}\nu\uparrow}\pm\alpha_{\vec{k}\nu\uparrow})\rangle = u^2_{\vec{k}\nu\pm}, \tag{29a}$$

$$\langle b^{\dagger}_{\vec{k}\nu\uparrow}(b_{\vec{k}\nu\uparrow}\pm b_{\vec{k}\nu\uparrow})\rangle = v^2_{\vec{k}\nu\pm}, \tag{29b}$$

$$\begin{aligned}\langle \alpha^{\dagger}_{k\nu\uparrow}(b_{\vec{k}\nu\uparrow}\pm b_{\vec{k}\nu\downarrow})\rangle &= \langle b^{\dagger}_{\vec{k}\nu\uparrow}(\alpha_{k\nu\uparrow}\pm\alpha_{\vec{k}\nu\downarrow})\rangle\\ &=\Delta_{\pm}(\vec{k})/2\epsilon_{\vec{k}\nu\pm}.\end{aligned} \tag{29c}$$

Then from Eq. (29c) we obtain

$$\langle \alpha^{\dagger}_{\vec{k}\nu\uparrow}b_{\vec{k}\nu\uparrow}\rangle = \frac{1}{2}\left(\frac{\Delta_+(\vec{k})}{2\epsilon_{\vec{k}\nu+}}+\frac{\Delta_-(\vec{k})}{2\epsilon_{\vec{k}\nu-}}\right), \tag{30a}$$

$$\langle \alpha^{\dagger}_{\vec{k}\nu\uparrow}b_{\vec{k}\nu\downarrow}\rangle = \frac{1}{2}\left(\frac{\Delta_+(\vec{k})}{2\epsilon_{\vec{k}\nu+}}-\frac{\Delta_-(\vec{k})}{2\epsilon_{\vec{k}\nu-}}\right). \tag{30b}$$

Substitution of Eqs. (30a) and (30b) into Eqs. (17) and (18) we derive the following set of coupled integral equations

$$\begin{aligned}\Delta_+(\vec{k}) &= \frac{1}{2N}\sum_{\vec{q}}\frac{U_+(\vec{k}-\vec{q})\Delta_+(\vec{q})}{\epsilon_{\vec{q}\nu+}}\\ &\quad+\frac{1}{2N}\sum_{\vec{q}}\frac{U_-(\vec{k}-\vec{q})\Delta_-(\vec{q})}{\epsilon_{\vec{q}\nu-}}.\end{aligned} \tag{31}$$

$$\begin{aligned}\Delta_-(\vec{k}) &= \frac{1}{2N}\sum_{\vec{q}}\frac{U_-(\vec{k}-\vec{q})\Delta_+(\vec{q})}{\epsilon_{\vec{q}\nu+}}\\ &\quad+\frac{1}{2N}\sum_{\vec{q}}\frac{U_+(\vec{k}-\vec{q})\Delta_-(\vec{q})}{\epsilon_{\vec{q}\nu-}}.\end{aligned} \tag{32}$$

In the effective-mass approximation we make use of Eqs. (37a)–(37c) of I, then Eqs. (31) and (32) become

$$\begin{aligned}\Delta_+(\vec{k}) &= \frac{1}{2N}\sum_{\vec{q}}\frac{U_+(\vec{k}-\vec{q})\Delta_+(\vec{q})}{[(\vec{q}^{\,2}/2\mu_+)^2+|\Delta_+(\vec{q})|^2]^{1/2}}\\ &\quad+\frac{1}{2N}\sum_{\vec{q}}\frac{U_-(\vec{k}-\vec{q})\Delta_-(\vec{q})}{[(\vec{q}^{\,2}/2\mu_-)^2+|\Delta_-(\vec{q})|^2]^{1/2}},\end{aligned} \tag{33}$$

$$\begin{aligned}\Delta_-(\vec{k}) &= \frac{1}{2N}\sum_{\vec{q}}\frac{U_-(\vec{k}-\vec{q})\Delta_+(\vec{q})}{[(\vec{q}^{\,2}/2\mu_+)^2+|\Delta_+(\vec{q})|^2]^{1/2}}\\ &\quad+\frac{1}{2N}\sum_{\vec{q}}\frac{U_+(\vec{k}-\vec{q})\Delta_-(\vec{q})}{[(\vec{q}^{\,2}/2\mu_-)^2+|\Delta_-(\vec{q})|^2]^{1/2}},\end{aligned} \tag{34}$$

where the reduced mass $\mu_{\pm}$ is defined as

$$\frac{2}{\mu_{\pm}}=\left|\frac{1}{m^{\pm}_{\text{exc}}}-\frac{1}{m_e}\right|=\left|\frac{m_e-m^{\pm}_{\text{exc}}}{m_e m^{\pm}_{\text{exc}}}\right|. \tag{35a}$$

In Eq. (35a), m_e is the effective mass of the electron while m^{+}_{exc} and m^{-}_{exc} denote the effective masses for the singlet and triplet excitons, respectively. The effective mass of transverse singlet excitons is negative while that of the longitudinal ones is positive.[1] The exciton effective mass is defined as[1] ($\hbar=1$),

$$\frac{1}{m^{\pm}_{\text{exc}}}=\left|\frac{\partial^2}{\partial^2\vec{k}}E^{\pm}_{\vec{k}\nu}\right|_{\vec{k}=0}, \tag{35b}$$

and depends on the direction of the exciton. Considering that the effective mass for the triplet exciton is very large, $m^{-}_{\text{exc}}\gg m^{+}_{\text{exc}}$, $m^{-}_{\text{exc}}\gg m_e$ then from Eq. (35a) the reduced mass μ_- may be well approximated as

$$\mu_-\approx 2m_e. \tag{35c}$$

Similarly, we may derive from Eqs. (35a) and (35c) the approximate relations

$$\mu^{t}_{+}\lesssim 2m^{t}_{e},\quad \mu^{l}_{+}\gtrsim 2m^{l}_{e}, \tag{35d}$$

where t and l refer to the transverse and longitudinal modes, respectively.

To solve the integral Eqs. (33) and (34) we follow I and replace the summations by integrations over the first Brillouin zone with the result

$$\begin{aligned}\Delta_+ &= U_+N_+(0)\int_0^{\bar{\omega}_+}\frac{d(\vec{q}^{\,2}/2\mu_+)\Delta_+}{[(\vec{q}^{\,2}/2\mu_+)^2+|\Delta_+|^2]^{1/2}}\\ &\quad+U_-N_-(0)\int_0^{\bar{\omega}_-}\frac{d(\vec{q}^{\,2}/2\mu_-)\Delta_-}{[(\vec{q}/2\mu_-)^2+|\Delta_-|^2]^{1/2}},\end{aligned} \tag{36}$$

$$\begin{aligned}\Delta_- &= U_-N_+(0)\int_0^{\bar{\omega}_+}\frac{d(\vec{q}^{\,2}/2\mu_+)\Delta_+}{[(\vec{q}^{\,2}/2\mu_+)^2+|\Delta_+|^2]^{1/2}}\\ &\quad+U_+N_-(0)\int_0^{\bar{\omega}_-}\frac{d(\vec{q}^{\,2}/2\mu_-)\Delta_-}{[(\vec{q}^{\,2}/2\mu_-)^2+|\Delta_-|^2]^{1/2}},\end{aligned} \tag{37}$$

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

$$N_{\pm}(0)=\left(\frac{V\xi\mu_{\pm}}{2\pi^2N}\right)=\frac{3}{2\bar{\omega}_{\pm}}, \tag{38a}$$

$$\bar{\omega}_{\pm}=\xi^2/2\mu_{\pm},\quad \xi=(6\pi^2N/V)^{1/3}=(6\pi^2 n)^{1/3}, \tag{38b}$$

$n=N/V$ being the exciton (electron) concentration. In Eqs. (36) and (37) use has been made of the notation

$$U_{\pm}=U_{\pm}(\vec{k}),\quad \Delta_{\pm}(\vec{k})=\Delta_{\pm}. \tag{38c}$$

After performing the integration in Eqs. (36) and (37) we obtain

$$\Delta_+=\bar{\omega}_+/\sinh(1/\rho_+), \tag{39}$$

$$\Delta_-=\bar{\omega}_-/\sinh(1/\rho_-), \tag{40}$$

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

$$\rho_+=U_+N_+(0)/s_+, \tag{41a}$$

$$\rho_-=U_+N_-(0)/s_-, \tag{41b}$$

$$s_+ = \frac{1-(U_-/U_+)(\Delta_-/\Delta_+)}{1-(U_-/U_+)^2},$$

$$s_- = \frac{1-(U_-/U_+)(\Delta_+/\Delta_-)}{1-(U_-/U_+)^2}. \qquad (41c)$$

The transition temperatures $T_c^{\pm}$ may be then determined by the relations

$$K_B T_c^{\pm} = 0.57\Delta_{\pm}, \qquad (41d)$$

where K_B is Boltzmann's constant. In the weak-coupling limit, i.e., when $\rho_{\pm} \ll 1$, then Eqs. (39) and (40) may be replaced by

$$\Delta_+ \approx 2\overline{\omega}_+ e^{-1/\rho_+}, \qquad (41e)$$

$$\Delta_- \approx 2\overline{\omega}_- e^{-1/\rho_-}. \qquad (41f)$$

In the limiting case when

$$(U_-/U_+) \to 0, \qquad (42a)$$

i.e., $s_{\pm} \to 1$, then ρ_+ and ρ_- given by Eqs. (41a) and (41b) become

$$\rho_+^0 = 1/U_+N_+(0), \quad \rho_-^0 = 1/U_+N_-(0), \qquad (42b)$$

respectively. In view of Eqs. (35c) and (35d) we may also have

$$N_-(0) \gtrsim N_+(0) \text{ and } \rho_+^0 \lesssim \rho_-^0 \qquad (42c)$$

for the transverse modes, while the reverse inequalities hold for the longitudinal ones. Thus in such a case where Eq. (42a) is applicable, Eqs. (39) and (40) assume the form

$$\Delta_+^0 = \frac{\overline{\omega}_+}{\sinh(1/\rho_+^0)} \text{ and } \Delta_-^0 = \frac{\overline{\omega}_-}{\sinh(1/\rho_-^0)}, \qquad (43)$$

which indicates that Δ_+^0 and Δ_-^0 are independent of one another. This will be the case when the exchange coupling is extremely weak in comparison with that arising from the Coulomb interactions. The ratio

$$\left(\frac{\Delta_+^0}{\Delta_-^0}\right) = \left(\frac{\overline{\omega}_+}{\overline{\omega}_-}\right)\frac{\sinh(1/\rho_-^0)}{\sinh(1/\rho_+^0)} \approx \left(\frac{2m_e}{\mu_+}\right)\frac{\sinh(1/\rho_-^0)}{\sinh(1/\rho_+^0)}. \qquad (44)$$

Equations (43) and (44) indicate that the energy gaps Δ_+^0 and Δ_-^0 are more or less of the same order of magnitude.

For finite values of the ratio U_-/U_+, Eqs. (39)–(41) indicate that the gap functions Δ_+ and Δ_- depend strongly on each other. This suggests that a mixing between the frequencies of the plus and minus fields occurs the extent of which will depend on the strength of the exchange interaction. This will be referred to as the strong coupling case and it may occur whenever electrons and excitons come close together so that the interaction between them is of the short range. However, in general exchange interactions are known to be extremely weak in molecular solids and therefore, in most cases Eq. (42a) is expected to be applicable.

IV. GROUND-STATE ENERGY

To calculate the ground-state energy of the system in the same approximation in which the excitation spectrum has been considered, we average the Hamiltonian (1) as

$$\begin{aligned}\langle \mathcal{H} \rangle = \text{const.} &+ \sum_{\vec{k},\nu} \omega_{\vec{k}\nu} \langle a^\dagger_{\vec{k}\nu\downarrow} a_{\vec{k}\nu\downarrow} + a^\dagger_{\vec{k}\nu\uparrow} a_{\vec{k}\nu\uparrow} \rangle + \sum_{\vec{k},\nu} [E_{\nu 0} + J_{\uparrow\uparrow}(\vec{k})] \langle b^\dagger_{\vec{k}\nu\uparrow} b_{\vec{k}\nu\uparrow} + b^\dagger_{\vec{k}\nu\downarrow} b_{\vec{k}\nu\downarrow} \rangle \\ &+ \sum_{\vec{k},\nu} J_{\uparrow\downarrow}(\vec{k}) \langle b^\dagger_{\vec{k}\nu\downarrow} b_{\vec{k}\nu\uparrow} + b^\dagger_{\vec{k}\nu\uparrow} b_{\vec{k}\nu\downarrow} \rangle - \sum_{\vec{k},\nu} \Delta_{\uparrow\uparrow}(\vec{k}) \langle b^\dagger_{\vec{k}\nu\uparrow} a_{\vec{k}\nu\uparrow} + b^\dagger_{\vec{k}\nu\downarrow} a_{\vec{k}\nu\downarrow} \rangle \\ &- \sum_{\vec{k},\nu} \Delta_{\uparrow\downarrow}(\vec{k}) \langle b_{\vec{k}\nu\uparrow} a^\dagger_{\vec{k}\nu\downarrow} + b_{\vec{k}\nu\downarrow} a^\dagger_{\vec{k}\nu\uparrow} \rangle. \end{aligned} \qquad (45)$$

Then using Eqs. (29a)–(30b), we derive from Eq. (45) the following expression for the ground-state energy of the system:

$$\langle \mathcal{H} \rangle_0 = \text{const} + \sum_{\vec{k},\nu} \left((\Omega_{\vec{k}\nu+} + \Omega_{\vec{k}\nu-}) - \frac{\frac{1}{4}(E^+_{\vec{k}\nu} - \omega_{\vec{k}\nu})^2}{\epsilon_{\vec{k}\nu+}} - \frac{\frac{1}{4}(E^-_{\vec{k}\nu} - \omega_{\vec{k}\nu})^2}{\epsilon_{\vec{k}\nu-}} - \frac{|\Delta+(\vec{k})|^2}{2\epsilon_{\vec{k}\nu+}} - \frac{|\Delta+(\vec{k})|^2}{2\epsilon_{\vec{k}\nu-}} \right). \qquad (46)$$

In particular, we are interested in the difference of the total ground-state energy minus that of the normal state, i.e.,

$$W_0 = \langle \mathcal{H} \rangle_0 - \langle \mathcal{H}_n \rangle_0 = -\sum_{\vec{k},\nu} \left(\frac{\frac{1}{4}(E^+_{\vec{k}\nu} - \omega_{\vec{k}\nu})^2}{\epsilon_{\vec{k}\nu+}} + \frac{\frac{1}{4}(E^-_{\vec{k}\nu} - \omega_{\vec{k}\nu})^2}{\epsilon_{\vec{k}\nu-}} + \frac{|\Delta+(\vec{k})|^2}{2\epsilon_{\vec{k}\nu+}} + \frac{|\Delta-(\vec{k})|^2}{2\epsilon_{\vec{k}\nu-}} \right), \qquad (47)$$

where

$$\langle \mathcal{H}_n \rangle_0 = \sum_{\vec{k},\nu} (\Omega_{\vec{k}\nu+} + \Omega_{\vec{k}\nu-}).$$

We next replace the summation over $\vec{k}$ in Eq. (47) by an integration over the first Brillouin zone and using the same approximations as those for the derivation of Eqs. (39) and (40), we obtain

$$
\begin{aligned}
W_0 &= -N_+(0)\bar{\omega}_+^2[1+(\Delta_+/\bar{\omega}_+)^2]^{1/2} \\
&\quad - N_-(0)\bar{\omega}_-^2[1+(\Delta_-/\bar{\omega}_-)^2]^{1/2} \\
&= -\frac{N_+(0)\bar{\omega}_+^2}{\tanh(1/\rho_+)} - \frac{N_-(0)\bar{\omega}_-^2}{\tanh(1/\rho_-)} .
\end{aligned}
\tag{48}
$$

Equation (48) is formally analogous to that in the theory of superconductivity[4] and is a generalization of Eq. (43b) of I. The two terms in Eq. (48) describe the binding energy corresponding to the coherent electron-singlet exciton and electron-triplet exciton pairing respectively. These two terms are independent of one another as long as the relation given by Eq. (42a) is applicable. On the other hand, in the presence of strong exchange interactions where the coupling functions ρ_+ and ρ_- are determined via Eqs. (41a) and (41b), respectively, both terms in Eq. (48) depend strongly on each other.

V. DISCUSSION

We have considered that physical processes where electrons interact with either a singlet or a triplet exciton to form bound charge-transfer states. It is shown that both physical processes are feasible provided that certain conditions are satisfied. When the exchange interactions are negligibly small, namely when Eq. (42a) is satisfied then below some critical temperatures defined by Eq. (41), the two frequency modes corresponding to the electron-singlet and electron-triplet exciton complexes propagate through the crystal independently. In this case the gap functions Δ_+^0 and Δ_-^0 given by Eq. (43) are more or less of the same order of magnitude ($\Delta_+^0 \gtrsim \Delta_-^0$).

When the electron-exciton exchange interactions become dominant, i.e., the interaction is of the short range, then the gap functions Δ_+ and Δ_- depend on each other. In this case the two frequency modes corresponding to the two charge-transfer complexes are mixed and the excitation spectrum is getting extremely complicated. Hopefully, for most molecular crystals electron-exciton interactions are expected to be of the long range and not of the short one which corresponds to the range where chemical reactions occur. Of course, this statement could be only verified experimentally. The two terms in Eq. (48) correspond to the binding energies for the two charge-transfer complexes, respectively.

The conclusion from this study is that triplet excitons interact with electrons as easy as the singlet excitons to form charge-transfer complexes. The advantage of the interaction with the triplets is that because of the long lifetime of the triplet state, the accumulation of high concentration of triplets is easier established than that of the singlets; of course, experimental difficulties may be also encountered for the production of high concentration of triplet excitons. Also, in most molecular solids and in some biological systems the triplet state is much lower in energy than the singlet; and in the case of π electrons which are energetically near then in such systems the formation of electron-triplet complexes will be facilitated.

The experimental situation is at the moment rather gloomy. Haarer and Castro[6] in their experiment on the external photoemission of electrons from the anthracene crystal have concluded that the enhanced photoemission is caused by an exciton-electron collision process. This physical process is similar to the well-known phenomenon of ionization of F centers by excitons in ionic crystals. It seems to us that such kind of experiments[6] where by the use of two light sources operating at different wavelengths, one of which produces excitons and the other excitons plus electrons, seem to be very promising for the study of mechanisms involving electron-exciton interactions; more experiments should be encouraged in this direction. As it has been repeatedly mentioned, electron-exciton complexes are undoubtedly of the charge-transfer type and therefore, their existence in molecular solids consisting of aromatic molecules as well as in biological systems consisting of macromolecules will be of utmost importance. We hope that the present study will stimulate experimental interest to investigate electron-exciton interactions in molecular systems with the understanding of the extremely complicated nature of such experiments.

In the present study as well as in I, use has been made of methods formally analogous to those in the theory of superconductivity and hence the gap functions $\Delta_\pm(\vec{n})$ in Eqs. (6)–(8) or $\Delta_\pm(\vec{k})$ in Eqs. (17) and (18) refer to the coherent electron-exciton pairing where the total momentum of the pair is equal to zero. Since it is known from the theory of superconductivity[10] that only the coherent pairing leads to the lowest possible ground-state energy, we have confined our attention to zero-momentum pairs.

The problem of the incoherent electron-exciton pairing is quite similar to that of the exciton-phonon bound states in molecular crystals[11] and to that of the two-magnon bound states in ferromagnets.[12] In accordance with these methods[11,12] for certain values of the total momentum of the pair, one may expect to have the formation of either the two-particle bound state or the continuum of the two-particle scattering states. Our treatment here is limited to the description of the electron-exciton bound states with zero total momentum. The physical process where an electron and an exciton form the continuum of the two-particle scattering states is excluded here by the decoupling approximation given by Eqs. (5a)–(5d).

To describe physical processes which are due to the incoherent electron-exciton pairing, the decoupling approximation defined by Eq. (5) should not be used. Instead, one has to calculate Green's functions of the form of

$$\langle\langle b^{\dagger}_{\vec{m}\nu} b_{\vec{m}\nu} \alpha_{\vec{n}\nu}; \alpha^{\dagger}_{\vec{n}'\nu} b^{\dagger}_{\vec{m}'\nu} b_{\vec{m}'\nu} \rangle\rangle$$

and

$$\langle\langle \alpha^{\dagger}_{\vec{m}\nu} \alpha_{\vec{m}\nu} b_{\vec{n}\nu}; b^{\dagger}_{\vec{n}'\nu} \alpha^{\dagger}_{\vec{m}'\nu} \alpha_{\vec{m}'\nu} \rangle\rangle,$$

which are coupled to the single-particle Green's functions

$$\langle\langle \alpha_{\vec{n}\nu}; \alpha^{\dagger}_{\vec{n}'\nu} \rangle\rangle \quad \text{and} \quad \langle\langle b_{\vec{m}\nu}; b^{\dagger}_{\vec{m}'\nu} \rangle\rangle,$$

by making use of the Hamiltonian (1). In general this is rather an extremely difficult problem; details of such treatment will be presented in a future publication.

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