

Theory of charge-transfer electron-exciton bound states in molecular crystals

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The theory of the coherent electron-exciton pairing is generalized to describe the electron-exciton bound states of molecular crystals which contain several molecules (atoms) in the unit cell. The excitation spectrum for crystals like anthracene having two molecules per unit cell is discussed in detail. Expressions for the absorption coefficient for the anthracene-like crystals are derived describing the optical transitions to four electron-exciton bands. Two of the electron-exciton bands represent a modification of the two components of the exciton doublet, while the other two bands are due entirely to the electron-exciton pairing. The electron-exciton bands have the same polarization directions but different intensities and energies from those of the corresponding exciton bands. The ground-state energy describing the electron-exciton binding energy is calculated and discussed. Numerical estimates indicate that at high exciton densities, i.e., for exciton concentrations 2×10^{18} – 10^{19} cm^{-3} and when the ratio of the average electron-exciton interaction to the average kinetic energy is between 1 and 2 (strong-coupling limit), the energy gap due to the electron-exciton pairing is in the range 50–320 cm^{-1} , the corresponding transition temperature is 40–260°K, while the binding energy is 90–500 cm^{-1} .

I. INTRODUCTION

The collective electronic excitations of molecular crystals are usually described by Frenkel (molecular or small-radius) excitons.¹ They consist of tightly bound electron-hole pairs that migrate through the crystal with definite energy and wave vector. It has been recently suggested² that at high exciton densities and low temperatures, an exciton may interact with an excited electron³ which is located at an adjacent lattice site of a molecular crystal to form a charge-transfer (CT) bound state. Electrons (charge carriers) can be produced in the crystal either by the use of photoabsorption⁴ or photoinjection techniques.⁵

The excitation spectrum and the electromagnetic properties of the electron-exciton bound states have been discussed in Ref. 2, hereafter referred to as I. The effects of the electron spin have been also included.⁶ It has been shown in Ref. 6, referred to as II that singlet excitons as well as triplet excitons may interact with electrons to form electron-singlet and electron-triplet CT complexes provided that certain conditions prevail. The reader is referred to I and II for details as well as for the literature on the subject.

Most of the molecular crystals contain several molecules (atoms) per unit cell; for example, the monoclinic crystals such as anthracene, naphthalene, etc., which have a center of symmetry, contain two identical molecules per unit cell. For such crystals having two identical molecules in the unit cell, the excitation spectrum consists of two exciton bands, which have not only different energies but also different polarizations; the energy splitting is usually referred to as the Davydov

splitting.¹ The existence of the two components, which have different energies and different polarizations, has made possible the observation of the exciton bands in molecular crystals.¹ The theory in I and II has been restricted to crystals having one molecule per unit cell; the purpose of the present study is to generalize the theory of electron-

TABLE I. Computed values for the gap function Δ_+/ σ_+ , transition temperature T_c^+ / σ_+ , binding energy W_0^+ / σ_+ , and average kinetic energy $\bar{\omega}_+ / \sigma_+$ determined by Eqs. (61)–(64), respectively.

n (cm^{-3})	ρ_+	$U / \bar{\omega}_+$	Δ_+ / σ_+ (cm^{-1})	T_c^+ / σ_+ (°K)	$-W_0^+ / \sigma_+$ (cm^{-1})	$\bar{\omega}_+ / \sigma_+$ (cm^{-1})
2×10^{18}	1.5	1.0	52	43	96	37
	2.0	1.3	74	61	121	37
	2.5	1.6	93	76	146	37
	3.0	2.0	111	91	174	37
4×10^{18}	1.5	1.0	83	68	152	59
	2.0	1.3	117	96	191	59
	2.5	1.6	146	120	232	59
	3.0	2.0	167	137	277	59
6×10^{18}	1.5	1.0	109	89	200	77
	2.0	1.3	154	126	250	77
	2.5	1.6	193	158	304	77
	3.0	2.0	231	189	363	77
8×10^{18}	1.5	1.0	132	108	242	93
	2.0	1.3	187	153	303	93
	2.5	1.6	234	192	369	93
	3.0	2.0	281	230	440	93
1×10^{19}	1.5	1.0	153	125	281	108
	2.0	1.3	217	188	352	108
	2.5	1.6	271	222	428	108
	3.0	2.0	326	267	511	108

exciton bound states to be appropriate for organic crystals that have several molecules in the unit cell. Optical transitions to the electron-exciton bands and computations of the parameters involved in the strong-coupling limit are considered as well.

The problem is formulated in Sec. II, where use is made of the same model for a molecular crystal as in I but the molecular Hamiltonian describes crystals having several molecules per unit cell. Using the same decoupling approximation as in I and II, we derive a set of coupled equations for the electron-exciton Green's functions. The excitation spectrum is discussed in Sec. III, where expressions for the energies of excitations and for the energy-gap functions arising from the electron-exciton pairing are derived for crystals like anthracene. Optical transitions to the electron-exci-

ton states are discussed in Sec. IV and the corresponding expressions for the absorption coefficient are obtained. The binding energy arising from the electron-exciton pairing is calculated in Sec. V, while the results of the numerical computation are listed in Table I and discussed in Sec. VI.

II. FORMULATION OF THE PROBLEM

The Hamiltonian describing the electron and exciton fields as well as electron-exciton interactions for a two-level system of a molecular crystal having one molecule (atom) per unit cell has been derived in I and is given by Eq. (6) of I. This expression can be generalized to describe the general case when there are several molecules in the unit cell of the crystal and it may take the form

$$\begin{aligned} \mathcal{H} = \text{const} + \sum_{\vec{n}, \nu, \beta} \bar{E}_{\nu 0 \beta} \alpha_{\vec{n} \nu \beta}^{\dagger} \alpha_{\vec{n} \nu \beta} + \sum'_{\substack{\nu, \vec{R}_{\vec{m}\vec{n}} \\ \beta, \gamma}} L_{\beta \gamma}(\vec{m} \nu, \vec{n} \nu) \alpha_{\vec{m} \nu \beta}^{\dagger} \alpha_{\vec{n} \nu \gamma} + \sum'_{\substack{\vec{R}_{\vec{m}\vec{n}} \\ \beta, \gamma}} L_{\beta \gamma}(\vec{m} 0, \vec{n} 0) \alpha_{\vec{m} 0 \beta}^{\dagger} \alpha_{\vec{n} 0 \gamma} \\ + \frac{1}{2} \sum_{\substack{\nu, \vec{R}_{\vec{m}\vec{n}} \\ \beta, \gamma}} J(\vec{n} 0 \beta, \vec{m} \nu \gamma | \vec{n} \nu \beta, \vec{m} 0 \gamma) (b_{\vec{n} \nu \beta}^{\dagger} b_{\vec{m} \nu \gamma} + b_{\vec{m} \nu \gamma}^{\dagger} b_{\vec{n} \nu \beta}) + \frac{1}{2} \sum_{\substack{\nu, \vec{R}_{\vec{m}\vec{n}} \\ \beta, \gamma}} J(\vec{n} 0 \beta, \vec{m} 0 \gamma | \vec{n} \nu \beta, \vec{m} \nu \gamma) (b_{\vec{n} \nu \beta} b_{\vec{m} \nu \gamma}^{\dagger} + b_{\vec{m} \nu \gamma}^{\dagger} b_{\vec{n} \nu \beta}^{\dagger}) \\ - \sum_{\substack{\nu, \vec{R}_{\vec{m}\vec{n}} \\ \beta, \gamma}} U_{\beta \gamma}(\vec{n}, \vec{m}) b_{\vec{n} \nu \beta}^{\dagger} b_{\vec{n} \nu \beta} \alpha_{\vec{m} \nu \gamma}^{\dagger} \alpha_{\vec{m} \nu \gamma}. \end{aligned} \quad (1)$$

The operators $b_{\vec{n} \nu \beta}$, $b_{\vec{n} \nu \beta}^{\dagger}$ and $\alpha_{\vec{n} \nu \beta}$, $\alpha_{\vec{n} \nu \beta}^{\dagger}$ describe the exciton and electron fields, respectively. β and γ ($\beta, \gamma = 1, 2, \dots, s$) enumerate the number of molecules per unit cell, $\vec{R}_{\vec{m}\vec{n}} = \vec{r}_{\vec{m}} - \vec{r}_{\vec{n}}$, where $\vec{r}_{\vec{m}}$ and $\vec{r}_{\vec{n}}$ are the position vectors for the electrons at the lattice sites \vec{m} and \vec{n} respectively, and the prime in the sum indicates that the term with $\vec{R}_{\vec{m}\vec{n}} = 0$ should be omitted. The notation as well as the coupling functions in Eq. (1) are described in detail by Eqs. (7a)–(7e) and (8) of I, where the reader is referred

to for details.

The coupling functions $J(\vec{n} 0 \beta, \vec{m} \nu \gamma | \vec{n} \nu \beta, \vec{m} 0 \gamma)$ and $J(\vec{n} 0 \beta, \vec{m} 0 \gamma | \vec{n} \nu \beta, \vec{m} \nu \gamma)$ differ only by exchange terms¹ and if such exchange contributions are neglected for the exciton field then we may take

$$\begin{aligned} J(\vec{n} 0 \beta, \vec{m} \nu \gamma | \vec{n} \nu \beta, \vec{m} 0 \gamma) &\simeq J(\vec{n} 0 \beta, \vec{m} 0 \gamma | \vec{n} \nu \beta, \vec{m} \nu \gamma) \\ &\equiv \bar{J}_{\beta \gamma}(\vec{n}, \vec{m}). \end{aligned} \quad (2)$$

Substituting Eq. (2) into Eq. (1) we have

$$\begin{aligned} \mathcal{H} = \text{const} + \sum_{\vec{n}, \nu, \beta} \bar{E}_{\nu 0 \beta} \alpha_{\vec{n} \nu \beta}^{\dagger} \alpha_{\vec{n} \nu \beta} + \sum'_{\substack{\nu, \vec{R}_{\vec{m}\vec{n}} \\ \beta, \gamma}} L_{\beta \gamma}(\vec{m} \nu, \vec{n} \nu) \alpha_{\vec{m} \nu \beta}^{\dagger} \alpha_{\vec{n} \nu \gamma} + \sum'_{\substack{\nu, \vec{R}_{\vec{m}\vec{n}} \\ \beta, \gamma}} L_{\beta \gamma}(\vec{m} 0, \vec{n} 0) \alpha_{\vec{m} 0 \beta}^{\dagger} \alpha_{\vec{n} 0 \gamma} \\ + \frac{1}{2} \sum_{\substack{\nu, \vec{R}_{\vec{m}\vec{n}} \\ \beta, \gamma}} \bar{J}_{\beta \gamma}(\vec{n}, \vec{m}) (b_{\vec{n} \nu \beta}^{\dagger} b_{\vec{m} \nu \gamma} + b_{\vec{m} \nu \gamma}^{\dagger} b_{\vec{n} \nu \beta} + b_{\vec{n} \nu \beta} b_{\vec{m} \nu \gamma}^{\dagger} + b_{\vec{m} \nu \gamma}^{\dagger} b_{\vec{n} \nu \beta}^{\dagger}) - \sum'_{\substack{\nu, \vec{R}_{\vec{m}\vec{n}} \\ \beta, \gamma}} U_{\beta \gamma}(\vec{n}, \vec{m}) b_{\vec{n} \nu \beta}^{\dagger} b_{\vec{n} \nu \beta} \alpha_{\vec{m} \nu \gamma}^{\dagger} \alpha_{\vec{m} \nu \gamma}. \end{aligned} \quad (3)$$

The term in Eq. (4) involving the operators $(b_{\vec{n} \nu \beta} b_{\vec{m} \nu \gamma}^{\dagger} + b_{\vec{m} \nu \gamma}^{\dagger} b_{\vec{n} \nu \beta}^{\dagger})$, which describe the simultaneous annihilation and creation of two particle excitations, has been discarded in I and II. This approx-

imation is valid provided that the inequality

$$\bar{J}(\vec{n}, \vec{m}) \ll \bar{E}_{\nu 0} \quad (4)$$

is satisfied. For most molecular crystals when ν

is the first excited state,¹ $\bar{E}_{\nu 0} \sim 3 \times 10^4 \text{ cm}^{-1}$ while $\bar{J}(\bar{n}, \bar{m}) \sim 10^3 \text{ cm}^{-1}$ in which case the inequality (4) is well satisfied. For molecular crystals for which $\bar{J}(\bar{n}, \bar{m}) \sim 10^4 \text{ cm}^{-1}$, the term describing the two particle excitations should be included in the calculation. For the sake of convenience, we shall consider the general case where the inequality (4) is satisfied and, therefore the term proportional to the operators $(b_{\bar{\nu}\beta} b_{\bar{m}\nu\gamma} + b_{\bar{\nu}\beta}^\dagger b_{\bar{m}\nu\gamma}^\dagger)$ will be omitted in the calculation. In Sec. VI, a discussion is given on how this effect may be incorporated in the final results whenever the inequality (4) is violated.

Using the Hamiltonian (3) we derive the equations of motion for the operators $\alpha_{\bar{\nu}\beta}$ and $b_{\bar{m}\nu\beta}$ as

$$\left(\frac{id}{dt} - \bar{E}_{\nu 0\beta}\right) \alpha_{\bar{\nu}\beta} = \sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} L_{\beta\gamma}(\bar{m}\nu, \bar{n}\nu) \alpha_{\bar{m}\nu\gamma} - \sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} U_{\beta\gamma}(\bar{n}, \bar{m}) \alpha_{\bar{\nu}\beta} b_{\bar{m}\nu\gamma}^\dagger b_{\bar{m}\nu\gamma}, \quad (5)$$

$$\left(\frac{id}{dt} - \bar{E}_{\nu 0\beta}\right) b_{\bar{m}\nu\beta} = \sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} \bar{J}_{\beta\gamma}(\bar{n}, \bar{m}) b_{\bar{m}\nu\gamma} (1 - 2b_{\bar{m}\nu\gamma}^\dagger b_{\bar{m}\nu\gamma}) - \sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} U_{\beta\gamma}(\bar{m}, \bar{n}) b_{\bar{m}\nu\beta} \alpha_{\bar{\nu}\gamma}^\dagger \alpha_{\bar{m}\nu\gamma}. \quad (6)$$

In deriving Eqs. (5) and (6) we have followed I and II and exciton-hole scattering effects have been discarded. This approximation is applicable as long as these kinds of processes produce very little effect or not at all on the formation of electron-exciton bound states.

Making use of the same decoupling approximation as in I, i.e.,

$$\sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} U_{\beta\gamma}(\bar{n}, \bar{m}) (\alpha_{\bar{\nu}\beta} b_{\bar{m}\nu\gamma}^\dagger b_{\bar{m}\nu\gamma}) \approx \sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} U_{\beta\gamma}(\bar{n}, \bar{m}) N_{\nu\gamma} \alpha_{\bar{\nu}\beta} + \sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} U_{\beta\gamma}(\bar{n}, \bar{m}) \langle \alpha_{\bar{\nu}\beta} b_{\bar{m}\nu\gamma}^\dagger \rangle b_{\bar{m}\nu\gamma}, \quad (7)$$

$$\sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} \bar{J}_{\beta\gamma}(\bar{m}, \bar{n}) b_{\bar{m}\nu\gamma} (1 - 2b_{\bar{m}\nu\gamma}^\dagger b_{\bar{m}\nu\gamma}) \approx \sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} \bar{J}_{\beta\gamma}(\bar{m}, \bar{n}) (1 - 2N_{\nu\gamma}) b_{\bar{m}\nu\gamma}, \quad (8a)$$

$$\sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} U_{\beta\gamma}(\bar{m}, \bar{n}) (b_{\bar{m}\nu\beta} \alpha_{\bar{\nu}\gamma}^\dagger \alpha_{\bar{m}\nu\gamma}) \approx \sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} U_{\beta\gamma}(\bar{m}, \bar{n}) N_{\nu\gamma} b_{\bar{m}\nu\beta} + \sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} U_{\beta\gamma}(\bar{n}, \bar{m}) \langle b_{\bar{m}\nu\beta} \alpha_{\bar{\nu}\gamma}^\dagger \rangle \alpha_{\bar{m}\nu\gamma}, \quad (8b)$$

where $N_{\nu\gamma} = \langle \alpha_{\bar{\nu}\gamma}^\dagger \alpha_{\bar{m}\nu\gamma} \rangle = \langle b_{\bar{m}\nu\gamma}^\dagger b_{\bar{m}\nu\gamma} \rangle$. The first terms on the right-hand side of Eqs. (7)–(8b) describe corrections to the electron (exciton) spectrum arising from the electron (exciton) density while the last terms describe the pairing between an electron and an exciton located at different lattice sites of the crystal. Substitution of Eqs. (7)–(8b) into Eqs. (5) and (6) results

$$\left(\frac{id}{dt} - E_{\nu 0\beta}\right) \alpha_{\bar{\nu}\beta} = \sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} L_{\beta\gamma}(\bar{m}\nu, \bar{n}\nu) \alpha_{\bar{m}\nu\gamma} - \sum'_{\gamma} \Delta_{\beta\gamma}(\bar{n}, \bar{m}) b_{\bar{m}\nu\gamma}, \quad (9)$$

$$\left(\frac{id}{dt} - E_{\nu 0\beta}\right) b_{\bar{m}\nu\beta} = \sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} J_{\beta\gamma}(\bar{n}, \bar{m}) b_{\bar{m}\nu\gamma} - \sum'_{\gamma} \Delta_{\gamma\beta}^*(\bar{n}, \bar{m}) \alpha_{\bar{m}\nu\gamma}, \quad (10)$$

$$E_{\nu 0\beta} = \bar{E}_{\nu 0} - \sum'_{\gamma, \bar{R}_{\bar{m}\bar{n}}} U(\bar{n}, \bar{m}) N_{\nu\gamma}, \quad (11a)$$

$$J_{\beta\gamma}(\bar{n}, \bar{m}) = \bar{J}_{\beta\gamma}(\bar{n}, \bar{m}) (1 - 2N_{\nu\gamma}), \quad (11b)$$

$$\Delta_{\beta\gamma}(\bar{n}, \bar{m}) = \sum'_{\bar{R}_{\bar{m}\bar{n}}} U_{\beta\gamma}(\bar{n}, \bar{m}) \langle \alpha_{\bar{\nu}\beta} b_{\bar{m}\nu\gamma}^\dagger \rangle. \quad (11c)$$

In the momentum representation Eqs. (9) and (10) become

$$\left(\frac{id}{dt} - \omega_{\bar{k}\nu\beta}\right) \alpha_{\bar{k}\nu\beta} = \sum'_{\gamma \neq \beta} L_{\beta\gamma}(\bar{k}) \alpha_{\bar{k}\nu\gamma} - \sum_{\gamma} \Delta_{\beta\gamma}(\bar{k}) b_{\bar{k}\nu\gamma}, \quad (12)$$

$$\left(\frac{id}{dt} - E_{\bar{k}\nu\beta}\right) b_{\bar{k}\nu\beta} = \sum'_{\gamma \neq \beta} J_{\beta\gamma}(\bar{k}) b_{\bar{k}\nu\gamma} - \sum_{\gamma} \Delta_{\gamma\beta}^*(\bar{k}) \alpha_{\bar{k}\nu\gamma}, \quad (13)$$

where

$$\omega_{\bar{k}\nu\beta} = E_{\nu 0\beta} + L_{\beta\beta}(\bar{k}), \quad (14a)$$

$$L_{\beta\gamma}(\bar{k}) = \sum'_{\bar{R}_{\bar{m}\bar{n}}} L_{\beta\gamma}(\bar{m}\nu, \bar{n}\nu) \exp[i(\bar{k} \cdot \bar{R}_{\bar{m}\bar{n}})], \quad (14b)$$

$$J_{\beta\gamma}(\bar{k}) = \sum'_{\bar{R}_{\bar{m}\bar{n}}} J_{\beta\gamma}(\bar{n}, \bar{m}) \exp[i(\bar{k} \cdot \bar{R}_{\bar{m}\bar{n}})], \quad (14c)$$

$$E_{\bar{k}\nu\beta} = E_{\nu 0\beta} + J_{\beta\beta}(\bar{k}), \quad (14d)$$

$$\Delta_{\beta\gamma}(\vec{k}) = \frac{1}{N} \sum_{\vec{q}} U_{\beta\gamma}(\vec{k} - \vec{q}) \langle \alpha_{\vec{q}\nu\gamma} b_{\vec{q}\nu\beta}^\dagger \rangle, \quad (15a)$$

$$U_{\beta\gamma}(\vec{k} - \vec{q}) = \sum_{\vec{R}, \vec{m}, \vec{n}} U_{\beta\gamma}(\vec{n}, \vec{m}) \exp[i(\vec{k} - \vec{q}) \cdot \vec{R}_{\vec{m}\vec{n}}], \quad (15b)$$

where N is the number of unit cells in the crystal volume V , and \vec{k} and \vec{q} are wave vectors in the first Brillouin zone.

In Eqs. (12)–(15), $\omega_{\vec{k}\nu\beta}$ and $E_{\vec{k}\nu\beta}$ are the energies of excitation for the free electron and exciton, respectively, while the coupling functions $L_{\beta\gamma}(\vec{k})$ and $J_{\beta\gamma}(\vec{k})$ describe the transfer of electronic charge and excitation energy, respectively, from the molecule β into the molecule γ within the unit cell of the crystal. Eqs. (12), (13), and (15) will be used in Sec. III to discuss the excitation spectrum for the electron-exciton interacting system.

III. EXCITATION SPECTRUM

To discuss the excitation spectrum we shall make use of the retarded double-time Green's functions defined by Eq. (19) of I, as well as the equation of motion for the Green's functions given by Eq. (20) of I. Then using Eqs. (12) and (13) we derive the following expressions for the electron $\langle\langle \alpha_{\vec{k}\nu\beta}; \alpha_{\vec{k}\nu\beta}^\dagger \rangle\rangle$ and exciton-electron $\langle\langle b_{\vec{k}\nu\beta}; \alpha_{\vec{k}\nu\beta}^\dagger \rangle\rangle$ Green's functions

$$\begin{aligned} (\omega - \omega_{\vec{k}\nu\beta}^-) \langle\langle \alpha_{\vec{k}\nu\beta}; \alpha_{\vec{k}\nu\beta}^\dagger \rangle\rangle &= \frac{1}{2\pi} + \sum_{\gamma \neq \beta} L_{\beta\gamma}(\vec{k}) \langle\langle \alpha_{\vec{k}\nu\gamma}; \alpha_{\vec{k}\nu\beta}^\dagger \rangle\rangle \\ &\quad - \sum_{\gamma} \Delta_{\beta\gamma}(\vec{k}) \langle\langle b_{\vec{k}\nu\gamma}; \alpha_{\vec{k}\nu\beta}^\dagger \rangle\rangle, \quad (16) \end{aligned}$$

$$\begin{aligned} (\omega - E_{\vec{k}\nu\beta}^-) \langle\langle b_{\vec{k}\nu\beta}; \alpha_{\vec{k}\nu\beta}^\dagger \rangle\rangle &= \sum_{\gamma \neq \beta} J_{\beta\gamma}(\vec{k}) \langle\langle b_{\vec{k}\nu\gamma}; \alpha_{\vec{k}\nu\beta}^\dagger \rangle\rangle \\ &\quad - \sum_{\gamma} \Delta_{\gamma\beta}^*(\vec{k}) \langle\langle \alpha_{\vec{k}\nu\gamma}; \alpha_{\vec{k}\nu\beta}^\dagger \rangle\rangle. \quad (17) \end{aligned}$$

Similar expressions hold for the exciton $\langle\langle b_{\vec{k}\nu\beta}; b_{\vec{k}\nu\beta}^\dagger \rangle\rangle$ and electron-exciton $\langle\langle \alpha_{\vec{k}\nu\beta}; b_{\vec{k}\nu\beta}^\dagger \rangle\rangle$ Green's functions. Equations (16) and (17) form a set of coupled algebraic equations the solution of which will determine the energies of excitation. If s is the number of molecules simultaneously present in the unit cell of the crystal then there will be $4s$ coupled equations whose solutions will determine the energy bands of the system under consideration.

For the sake of simplicity and as an illustration let us consider monoclinic crystals such as anthracene, naphthalene, etc., which have center of symmetry and contain two identical molecules in the unit cell.¹ For the senses of the wave vector \vec{k} that are perpendicular or parallel to the plane of symmetry of the crystal, we have¹

$$J_{11}(\vec{k}) = J_{22}(\vec{k}) \equiv J(\vec{k}), \quad J_{12}(\vec{k}) = J_{21}(\vec{k}) \equiv \hat{J}(\vec{k}), \quad (18a)$$

$$L_{11}(\vec{k}) = L_{22}(\vec{k}) \equiv L(\vec{k}), \quad L_{12}(\vec{k}) = L_{21}(\vec{k}) \equiv \hat{L}(\vec{k}), \quad (18b)$$

hence,

$$E_{\vec{k}\nu 1} = E_{\vec{k}\nu 2} \equiv E_{\vec{k}\nu}, \quad \omega_{\vec{k}\nu 1} = \omega_{\vec{k}\nu 2} \equiv \omega_{\vec{k}\nu}. \quad (18c)$$

If we also take

$$\Delta_{11}(\vec{k}) = \Delta_{22}(\vec{k}) \equiv \Delta(\vec{k}), \quad \Delta_{12}(\vec{k}) = \Delta_{21}(\vec{k}) \equiv \hat{\Delta}(\vec{k}) \quad (19)$$

and make use of the following notation:

$$\omega_{\vec{k}\nu\pm} = \omega_{\vec{k}\nu} \pm \hat{L}(\vec{k}), \quad (20a)$$

$$E_{\vec{k}\nu\pm} = E_{\vec{k}\nu} \pm \hat{J}(\vec{k}) \equiv E_{\nu 0} + J_{\pm}(\vec{k}), \quad (20b)$$

$$J_{\pm}(\vec{k}) = J(\vec{k}) \pm \hat{J}(\vec{k}), \quad (20c)$$

$$\Delta_{\pm}(\vec{k}) = \Delta(\vec{k}) \pm \hat{\Delta}(\vec{k}), \quad (20d)$$

then for $\beta, \gamma = 1, 2$ from Eqs. (16) and (17), we have

$$\begin{aligned} (\omega - \omega_{\vec{k}\nu\pm}) \langle\langle \alpha_{\vec{k}\nu 1} \pm \alpha_{\vec{k}\nu 2}; \alpha_{\vec{k}\nu 1}^\dagger \rangle\rangle \\ = (1/2\pi) - \Delta_{\pm}(\vec{k}) \langle\langle b_{\vec{k}\nu 1} \pm b_{\vec{k}\nu 2}; \alpha_{\vec{k}\nu 1}^\dagger \rangle\rangle, \quad (21) \end{aligned}$$

$$\begin{aligned} (\omega - E_{\vec{k}\nu\pm}) \langle\langle b_{\vec{k}\nu 1} \pm b_{\vec{k}\nu 2}; \alpha_{\vec{k}\nu 1}^\dagger \rangle\rangle \\ = -\Delta_{\pm}(\vec{k}) \langle\langle \alpha_{\vec{k}\nu 1} \pm \alpha_{\vec{k}\nu 2}; \alpha_{\vec{k}\nu 1}^\dagger \rangle\rangle. \quad (22) \end{aligned}$$

Similarly,

$$\begin{aligned} (\omega - E_{\vec{k}\nu\pm}) \langle\langle b_{\vec{k}\nu 1} \pm b_{\vec{k}\nu 2}; b_{\vec{k}\nu 1}^\dagger \rangle\rangle \\ = 1/2\pi - \Delta_{\pm}(\vec{k}) \langle\langle \alpha_{\vec{k}\nu 1} \pm \alpha_{\vec{k}\nu 2}; b_{\vec{k}\nu 1}^\dagger \rangle\rangle, \quad (23) \end{aligned}$$

$$\begin{aligned} (\omega - \omega_{\vec{k}\nu\pm}) \langle\langle \alpha_{\vec{k}\nu 1} \pm \alpha_{\vec{k}\nu 2}; b_{\vec{k}\nu 1}^\dagger \rangle\rangle \\ = -\Delta_{\pm}(\vec{k}) \langle\langle b_{\vec{k}\nu 1} \pm b_{\vec{k}\nu 2}; b_{\vec{k}\nu 1}^\dagger \rangle\rangle. \quad (24) \end{aligned}$$

Solving the coupled Eqs. (21) and (22) or (23) and (24), we obtain

$$\begin{aligned} \langle\langle \alpha_{\vec{k}\nu 1} \pm \alpha_{\vec{k}\nu 2}; \alpha_{\vec{k}\nu 1}^\dagger \rangle\rangle &= \frac{1}{2\pi} \left(\frac{v_{\vec{k}\nu\pm}^2}{\omega - \Omega_{\vec{k}\nu\pm}^- - \epsilon_{\vec{k}\nu\pm}} \right. \\ &\quad \left. + \frac{u_{\vec{k}\nu\pm}^2}{\omega - \Omega_{\vec{k}\nu\pm}^+ + \epsilon_{\vec{k}\nu\pm}} \right), \quad (25) \end{aligned}$$

$$\begin{aligned} \langle\langle b_{\vec{k}\nu 1} \pm b_{\vec{k}\nu 2}; \alpha_{\vec{k}\nu 1}^\dagger \rangle\rangle &= \langle\langle \alpha_{\vec{k}\nu 1} \pm \alpha_{\vec{k}\nu 2}; b_{\vec{k}\nu 1}^\dagger \rangle\rangle \\ &= -\frac{1}{2\pi} \frac{\Delta_{\pm}(\vec{k})}{2\epsilon_{\vec{k}\nu\pm}} \left(\frac{1}{\omega - \Omega_{\vec{k}\nu\pm}^- - \epsilon_{\vec{k}\nu\pm}} \right. \\ &\quad \left. - \frac{1}{\omega - \Omega_{\vec{k}\nu\pm}^+ + \epsilon_{\vec{k}\nu\pm}} \right), \quad (26) \end{aligned}$$

$$\begin{aligned} \langle\langle b_{\vec{k}\nu 1} \pm b_{\vec{k}\nu 2}; b_{\vec{k}\nu 1}^\dagger \rangle\rangle &= \frac{1}{2\pi} \left(\frac{u_{\vec{k}\nu\pm}^2}{\omega - \Omega_{\vec{k}\nu\pm}^- - \epsilon_{\vec{k}\nu\pm}} \right. \\ &\quad \left. + \frac{v_{\vec{k}\nu\pm}^2}{\omega - \Omega_{\vec{k}\nu\pm}^+ + \epsilon_{\vec{k}\nu\pm}} \right), \quad (27) \end{aligned}$$

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

$$\Omega_{\vec{k}\nu\pm} = \frac{1}{2}(E_{\vec{k}\nu\pm} + \omega_{\vec{k}\nu\pm}), \quad (28)$$

$$\epsilon_{\vec{k}\nu\pm} = \left[\frac{1}{2}(E_{\vec{k}\nu\pm} - \omega_{\vec{k}\nu\pm})^2 + |\Delta_{\pm}(\vec{k})|^2 \right]^{1/2}, \quad (29)$$

and the amplitudes $u_{\vec{k}\nu\pm}^{\pm}$ and $v_{\vec{k}\nu\pm}^{\pm}$ are defined by

$$u_{\vec{k}\nu\pm}^2 = \frac{1}{2} [1 + (E_{\vec{k}\nu\pm} - \omega_{\vec{k}\nu\pm}) / 2\epsilon_{\vec{k}\nu\pm}], \quad (30a)$$

$$v_{\vec{k}\nu\pm}^2 = \frac{1}{2} [1 - (E_{\vec{k}\nu\pm} - \omega_{\vec{k}\nu\pm}) / 2\epsilon_{\vec{k}\nu\pm}], \quad (30b)$$

and $u_{\vec{k}\nu\pm}^2 + v_{\vec{k}\nu\pm}^2 = 1$. Using the Green's functions (25)–(27) we derive the corresponding expressions for the distributions functions^{7,8} in the limit of zero temperature as

$$\langle \alpha_{\vec{k}\nu 1}^{\dagger} (\alpha_{\vec{k}\nu 1} \pm \alpha_{\vec{k}\nu 2}) \rangle = u_{\vec{k}\nu\pm}^2, \quad (31a)$$

$$\langle b_{\vec{k}\nu 1}^{\dagger} (b_{\vec{k}\nu 1} \pm b_{\vec{k}\nu 2}) \rangle = v_{\vec{k}\nu\pm}^2, \quad (31b)$$

$$\begin{aligned} \langle b_{\vec{k}\nu 1}^{\dagger} (\alpha_{\vec{k}\nu 1} \pm \alpha_{\vec{k}\nu 2}) \rangle &= \langle \alpha_{\vec{k}\nu 1}^{\dagger} (b_{\vec{k}\nu 1} \pm b_{\vec{k}\nu 2}) \rangle \\ &= \Delta_{\pm}(\vec{k}) / 2\epsilon_{\vec{k}\nu\pm}. \end{aligned} \quad (31c)$$

From Eq. (31c) we have the relations

$$\langle b_{\vec{k}\nu 1}^{\dagger} \alpha_{\vec{k}\nu 1} \rangle = \frac{1}{2} \left(\frac{\Delta_+(\vec{k})}{2\epsilon_{\vec{k}\nu+}} + \frac{\Delta_-(\vec{k})}{2\epsilon_{\vec{k}\nu-}} \right), \quad (32a)$$

$$\langle b_{\vec{k}\nu 1}^{\dagger} \alpha_{\vec{k}\nu 2} \rangle = \frac{1}{2} \left(\frac{\Delta_+(\vec{k})}{2\epsilon_{\vec{k}\nu+}} - \frac{\Delta_-(\vec{k})}{2\epsilon_{\vec{k}\nu-}} \right). \quad (32b)$$

Using Eqs. (15), (19), (20), (32a), and (32b) we get

$$\Delta_+(\vec{k}) = \frac{1}{2N} \sum_{\vec{q}} \frac{U(\vec{k}-\vec{q})\Delta_+(\vec{q})}{\epsilon_{\vec{q}\nu+}}, \quad (33)$$

$$\Delta_-(\vec{k}) = (1/2N) \frac{U(\vec{k}-\vec{q})\Delta_-(\vec{q})}{\epsilon_{\vec{q}\nu-}}. \quad (34)$$

In deriving Eqs. (33) and (34), the coupling functions have been taken to be

$$U_{11}(\vec{k}-\vec{q}) = U_{22}(\vec{k}-\vec{q}) = U_{12}(\vec{k}-\vec{q}) = U(\vec{k}-\vec{q}). \quad (35)$$

Though the approximation $U_{11}(\vec{k}-\vec{q}) = U_{12}(\vec{k}-\vec{q})$ is not always applicable, it facilitates the solution of the problem because now the gap functions $\Delta_+(\vec{k})$ and $\Delta_-(\vec{k})$ given by Eqs. (33) and (34) are independent of each other. If we define the exciton and electron effective masses m_{exc}^{\pm} and m_e^{\pm} , respectively,¹ as

$$\frac{1}{m_{\text{exc}}^{\pm}} = \left| \frac{\partial^2}{\partial \vec{k}^2} E_{\vec{k}\nu\pm} \right|_{\vec{k}=0}, \quad \frac{1}{m_e^{\pm}} = \left| \frac{\partial^2}{\partial \vec{k}^2} \omega_{\vec{k}\nu\pm} \right|_{\vec{k}=0}, \quad (36)$$

then in the effective-mass approximation and using Eqs. (37a)–(37c) of I, Eqs. (33) and (34) may take the form

$$\Delta_+(\vec{k}) = \frac{1}{2N} \sum_{\vec{q}} \frac{U(\vec{k}-\vec{q})\Delta_+(\vec{q})}{[(\vec{q}^2/2\mu_+)^2 + |\Delta_+(\vec{q})|^2]^{1/2}}, \quad (37)$$

$$\Delta_-(\vec{k}) = \frac{1}{2N} \sum_{\vec{q}} \frac{U(\vec{k}-\vec{q})\Delta_-(\vec{q})}{[(\vec{q}^2/2\mu_-)^2 + |\Delta_-(\vec{q})|^2]^{1/2}}. \quad (38)$$

The reduced mass μ_{\pm} is defined as

$$\frac{2}{\mu_{\pm}} = \left| \frac{1}{m_{\text{exc}}^{\pm}} - \frac{1}{m_e^{\pm}} \right| = \left| \frac{m_e^{\pm} - m_{\text{exc}}^{\pm}}{m_{\text{exc}}^{\pm} m_e^{\pm}} \right|, \quad (39)$$

where the effective mass of the exciton m_{exc}^{\pm} depends on the direction of the exciton and takes negative and positive values for transverse and longitudinal exciton modes, respectively.¹ The integral equations (37) and (38) are similar to Eq. (38) of I and Eqs. (31) and (32) of II. Therefore, we quote here the final results for the gap functions $\Delta_{\pm}(\vec{k})$.

$$\Delta_+(\vec{k}) = \bar{\omega}_+ / \sinh(1/\rho_+), \quad (40)$$

$$\Delta_-(\vec{k}) = \bar{\omega}_- / \sinh(1/\rho_-), \quad (41)$$

where

$$\bar{\omega}_{\pm} = \xi^2 / 2\mu_{\pm}, \quad \xi = (6\pi^2 N/V)^{1/3} = (6\pi^2 n)^{1/3}, \quad (42a)$$

$$N_{\pm}(0) = \frac{V\xi\mu_{\pm}}{2\pi N} = \frac{3}{2\omega_{\pm}}, \quad \rho_{\pm} = U(\vec{k})N_{\pm}(0) = \frac{3U(\vec{k})}{2\bar{\omega}_{\pm}}, \quad (42b)$$

$n = N/V$ being the exciton (electron) concentration. Considering that for the effective masses we have $m_{\text{exc}}^- \gg m_{\text{exc}}^+, m_e^- \gg m_e^+$, then $\mu_+ > \mu_-$, and hence, $\rho_+ > \rho_-$. Then the ratio

$$\frac{\Delta_+(\vec{k})}{\Delta_-(\vec{k})} = \left(\frac{\mu_-}{\mu_+} \right) \left(\frac{\sinh(1/\rho_-)}{\sinh(1/\rho_+)} \right) < 1. \quad (43)$$

In the weak coupling limit when $\rho_{\pm} < 1$, then Eqs. (40) and (41) are reduced to

$$\Delta_+(\vec{k}) \approx 2\bar{\omega}_+ e^{-1/\rho_+}, \quad (44a)$$

$$\Delta_-(\vec{k}) \approx 2\bar{\omega}_- e^{-1/\rho_-}, \quad (44b)$$

and the transition temperatures T_c^{\pm} may be determined by the relation

$$K_B T_c^{\pm} = 0.57 \Delta_{\pm}, \quad (45)$$

where K_B is Boltzmann's constant.

IV. ABSORPTION COEFFICIENT

The expression for the absorption coefficient $\alpha(\vec{k}, \omega)$ is given by⁸

$$\begin{aligned} \alpha(\vec{k}, \omega) &= - \left(\frac{\pi \omega_p^2}{4c \omega \eta(\vec{k}, \omega)} \right) \sum_{\substack{\nu, \lambda \\ \beta, \gamma}} f_{0\nu}^{\beta\gamma}(\vec{k}\lambda) (E_{\vec{k}\nu\beta} E_{\vec{k}\nu\gamma})^{1/2} \\ &\quad \times \text{Im} \langle \bar{b}_{\vec{k}\nu\beta}^{\dagger}; \bar{b}_{\vec{k}\nu\gamma}^{\dagger} \rangle, \end{aligned} \quad (46)$$

where c is the velocity of light in vacuum, $\eta(\vec{k}, \omega)$ is the real part of the index of refraction of the transverse light waves with wave vector \vec{k} and frequency ω , $\bar{b}_{\vec{k}\nu\beta}^{\dagger} = b_{\vec{k}\nu\beta}^{\dagger} - b_{\vec{k}\nu\beta}^{\dagger}$, β and γ enumerate the number of molecules per unit cell of the crystal, ω_p is the plasma frequency and Im refers to the

imaginary part of the Green's function in question. $f_{0\nu}^{\beta}(\vec{k}\lambda)$ is the oscillator strength for the allowed electronic transition $0 \rightarrow \nu$ of the molecule β and $\lambda (=1, 2)$ represents the two possible values of polarization perpendicular to the direction of propagation \vec{k} . In the optical region of frequencies $\eta(\vec{k}, \omega)$ varies slowly with ω and may be taken as a constant $\eta(\vec{k}, \omega) \equiv \eta_{\vec{k}}$.

When there are two identical molecules per unit cell, $\beta, \gamma (=1, 2)$, then Eq. (46) takes the form

$$\alpha(\vec{k}, \omega) = -\pi \omega_p^2 / 4c\eta_{\vec{k}} \omega \times \sum_{\lambda, \nu} E_{\vec{k}\nu} [f_{0\nu}^{(+)}(\vec{k}\lambda) \text{Im} \langle \langle \vec{b}_{\vec{k}\nu 1} + \vec{b}_{\vec{k}\nu 2}; \vec{b}_{\vec{k}\nu 1}^{\dagger} \rangle \rangle + f_{0\nu}^{(-)}(\vec{k}\lambda) \text{Im} \langle \langle \vec{b}_{\vec{k}\nu 1} - \vec{b}_{\vec{k}\nu 2}; \vec{b}_{\vec{k}\nu 1}^{\dagger} \rangle \rangle], \quad (47)$$

where

$$f_{0\nu}^{(\pm)}(\vec{k}\lambda) = f_{0\nu}(\vec{k}\lambda) \pm \hat{f}_{0\nu}(\vec{k}\lambda). \quad (48)$$

In deriving Eq. (47) we have taken $f_{0\nu}^{11}(\vec{k}\lambda) = f_{0\nu}^{22}(\vec{k}\lambda)$

$$\alpha_{\pm}(\vec{k}, \omega) = \frac{\omega_p^2}{8c\eta_{\vec{k}}\omega} \sum_{\lambda, \nu} f_{0\nu}^{(\pm)}(\vec{k}\lambda) E_{\vec{k}\nu} \{ u_{\vec{k}\nu\pm}^2 [\delta(\omega - \Omega_{\vec{k}\nu\pm} - \epsilon_{\vec{k}\nu\pm}) + \delta(\omega + \Omega_{\vec{k}\nu\pm} + \epsilon_{\vec{k}\nu\pm})] + v_{\vec{k}\nu\pm}^2 [\delta(\omega - \Omega_{\vec{k}\nu\pm} + \epsilon_{\vec{k}\nu\pm}) + \delta(\omega + \Omega_{\vec{k}\nu\pm} - \epsilon_{\vec{k}\nu\pm})] \}. \quad (52)$$

The expressions for the absorption coefficients $\alpha_{+}(\vec{k}, \omega)$ and $\alpha_{-}(\vec{k}, \omega)$ describe optical transitions for which ω satisfies the equations

$$\omega = \pm(\Omega_{\vec{k}\nu\pm} \pm \epsilon_{\vec{k}\nu\pm}) \quad (53a)$$

and

$$\omega = \pm(\Omega_{\vec{k}\nu\pm} \pm \epsilon_{\vec{k}\nu\pm}), \quad (53b)$$

respectively; positive and negative values of ω refer to the physical processes of absorption and emission, respectively. Thus the excitation spectrum consists of four energy bands which have δ -function distributions.

In the limit when $\Delta_{\pm}(\vec{k}) = 0$, i.e., in the absence of electron-exciton coupling, then $v_{\vec{k}\nu\pm} = 0$, $u_{\vec{k}\nu\pm} = 1$ and $\alpha^{\text{exc}}(\vec{k}, \omega) = \alpha_{+}^{\text{exc}}(\vec{k}, \omega) + \alpha_{-}^{\text{exc}}(\vec{k}, \omega)$, where

$$\alpha_{\pm}^{\text{exc}}(\vec{k}, \omega) = \frac{\omega_p^2}{8c\eta_{\vec{k}}\omega} \sum_{\lambda, \nu} f_{0\nu}^{\pm}(\vec{k}\lambda) E_{\vec{k}\nu} \times [\delta(\omega - E_{\vec{k}\nu\pm}) + \delta(\omega + E_{\vec{k}\nu\pm})], \quad (54)$$

with the energies of excitation $E_{\vec{k}\nu\pm}$ defined by Eq. (20) describing the Davydov components of the exciton states.¹ Thus the excitation bands described

$= f_{0\nu}(\vec{k}\lambda)$ and $f_{0\nu}^{12}(\vec{k}\lambda) = f_{0\nu}^{21}(\vec{k}\lambda) = \hat{f}_{0\nu}(\vec{k}\lambda)$. For the anthracene crystal, which belongs to the monoclinic system having two identical molecules in the unit cell, we have¹

$$f_{0\nu}^{(\pm)}(\vec{k}\lambda) = f_{0\nu} [1 \pm 2 \sin[\vec{k}_z^1 (\vec{a} + \vec{b})]], \quad (49)$$

where $\vec{a}, \vec{b}, \vec{c}$ are the three basis vectors of the base crystal of which \vec{b} coincides with the monoclinic axis, $\vec{a} \cdot \vec{b} = \vec{b} \cdot \vec{c} = 0$ and $\vec{a} \cdot \vec{c} = ac \cos 125^\circ$.

Taking the imaginary part of Eq. (27) and its complex conjugate, we obtain

$$-2\pi \text{Im} \langle \langle \vec{b}_{\vec{k}\nu 1}^{\dagger} \pm \vec{b}_{\vec{k}\nu 2}^{\dagger}; \vec{b}_{\vec{k}\nu 1}^{\dagger} \rangle \rangle = u_{\vec{k}\nu\pm}^2 [\delta(\omega - \Omega_{\vec{k}\nu\pm} - \epsilon_{\vec{k}\nu\pm}) + \delta(\omega + \Omega_{\vec{k}\nu\pm} + \epsilon_{\vec{k}\nu\pm})] + v_{\vec{k}\nu\pm}^2 [\delta(\omega - \Omega_{\vec{k}\nu\pm} + \epsilon_{\vec{k}\nu\pm}) + \delta(\omega + \Omega_{\vec{k}\nu\pm} - \epsilon_{\vec{k}\nu\pm})]. \quad (50)$$

Substitution of Eq. (50) into (47) yields

$$\alpha(\vec{k}, \omega) = \alpha_{+}(\vec{k}, \omega) + \alpha_{-}(\vec{k}, \omega), \quad (51)$$

where

by the expressions $\alpha_{+}(\vec{k}, \omega)$ and $\alpha_{-}(\vec{k}, \omega)$ will have the same polarization directions as those of the Davydov's components but different intensities and energies of excitation. The amplitude $u_{\vec{k}\nu\pm}^2$ gives a measure of the polarization ratio between the electron-exciton bands with energies $\Omega_{\vec{k}\nu\pm} + \epsilon_{\vec{k}\nu\pm}$ and the corresponding Davydov's components of the exciton bands with energies $E_{\vec{k}\nu\pm}$, respectively. The other two electron-exciton bands with energies $\Omega_{\vec{k}\nu\pm} - \epsilon_{\vec{k}\nu\pm}$ and scattering amplitudes $v_{\vec{k}\nu\pm}^2$ are due entirely to the electron-exciton coupled system. Considering that $u_{\vec{k}\nu\pm}^2 > v_{\vec{k}\nu\pm}^2$, the former two bands are expected to dominate the latter ones. The quantity $u_{\vec{k}\nu\pm}^2 / v_{\vec{k}\nu\pm}^2$ is a measure of the ratio of the intensities of the corresponding electron-exciton bands. The corresponding energy splittings are determined by $2\epsilon_{\vec{k}\nu\pm}$ given by Eq. (29).

V. GROUND-STATE ENERGY

The excitation spectrum given by the Green's functions (25)–(27) may be represented by an effective Hamiltonian describing independent quasi-particles in the form

$$\begin{aligned} \mathcal{H}_{\text{eff}} = \langle \mathcal{H} \rangle + \sum_{\vec{k}, \nu} [& (\Omega_{\vec{k}\nu+} + \epsilon_{\vec{k}\nu+}) \xi_{\vec{k}\nu+}^\dagger \xi_{\vec{k}\nu+} + (\Omega_{\vec{k}\nu-} + \epsilon_{\vec{k}\nu-}) \xi_{\vec{k}\nu-}^\dagger \xi_{\vec{k}\nu-} \\ & - (\Omega_{\vec{k}\nu+} - \epsilon_{\vec{k}\nu+}) \hat{\xi}_{\vec{k}\nu+}^\dagger \hat{\xi}_{\vec{k}\nu+} \\ & - (\Omega_{\vec{k}\nu-} - \epsilon_{\vec{k}\nu-}) \hat{\xi}_{\vec{k}\nu-}^\dagger \hat{\xi}_{\vec{k}\nu-}], \end{aligned} \quad (55)$$

where the energies of excitation $\Omega_{\vec{k}\nu\pm} \pm \epsilon_{\vec{k}\nu\pm}$ are determined by Eqs. (28), (29), (40), and (41). The operators $\xi_{\vec{k}\nu\pm}$ and $\hat{\xi}_{\vec{k}\nu\pm}$ describe the fields of the quasiparticle with energies $(\Omega_{\vec{k}\nu\pm} + \epsilon_{\vec{k}\nu\pm})$ and $(\Omega_{\vec{k}\nu\pm} - \epsilon_{\vec{k}\nu\pm})$, respectively, and satisfy Fermi-Dirac statistics. The exciton $b_{\vec{k}\nu 1}$, $b_{\vec{k}\nu 2}$ and electron $\alpha_{\vec{k}\nu 1}$, $\alpha_{\vec{k}\nu 2}$ operators are related with the new operators $\xi_{\vec{k}\nu\pm}$ and $\hat{\xi}_{\vec{k}\nu\pm}$ by the relations

$$b_{\vec{k}\nu 1} \pm b_{\vec{k}\nu 2} = \sqrt{2}(u_{\vec{k}\nu\pm} \xi_{\vec{k}\nu\pm} + v_{\vec{k}\nu\pm} \hat{\xi}_{\vec{k}\nu\pm}^\dagger), \quad (56a)$$

$$\alpha_{\vec{k}\nu 1} \pm \alpha_{\vec{k}\nu 2} = \sqrt{2}(-v_{\vec{k}\nu\pm} \xi_{\vec{k}\nu\pm} + u_{\vec{k}\nu\pm} \hat{\xi}_{\vec{k}\nu\pm}^\dagger), \quad (56b)$$

along with their complex conjugates. The inverse transformation to Eqs. (56a) and (56b) are given by

$$\xi_{\vec{k}\nu\pm} = \frac{1}{\sqrt{2}} [u_{\vec{k}\nu\pm} (b_{\vec{k}\nu 1} \pm b_{\vec{k}\nu 2}) - v_{\vec{k}\nu\pm} (\alpha_{\vec{k}\nu 1} \pm \alpha_{\vec{k}\nu 2})], \quad (57a)$$

$$\hat{\xi}_{\vec{k}\nu\pm} = \frac{1}{\sqrt{2}} [v_{\vec{k}\nu\pm} (b_{\vec{k}\nu 1} \pm b_{\vec{k}\nu 2}) + u_{\vec{k}\nu\pm} (\alpha_{\vec{k}\nu 1} \pm \alpha_{\vec{k}\nu 2})], \quad (57b)$$

where the scattering amplitudes $u_{\vec{k}\nu\pm}$ and $v_{\vec{k}\nu\pm}$ are defined by Eqs. (30a) and (30b).

In Eq. (55), $\langle \mathcal{H} \rangle$ represents the average energy of system. To calculate $\langle \mathcal{H} \rangle$, we average the Hamiltonian (1) for the case of a crystal having two identical molecules in the unit cell and then in the limit of zero temperature and after making use of the distribution functions given by Eqs. (30a)-(32b) we obtain the following expression for the ground-state energy:

$$\begin{aligned} \langle \mathcal{H} \rangle_0 = \sum_{\vec{k}} \left(\Omega_{\vec{k}\nu+} + \Omega_{\vec{k}\nu-} - \frac{\frac{1}{4}(E_{\vec{k}\nu+} - \omega_{\vec{k}\nu+})^2}{\epsilon_{\vec{k}\nu+}} \right. \\ \left. - \frac{\frac{1}{4}(E_{\vec{k}\nu-} - \omega_{\vec{k}\nu-})^2}{\epsilon_{\vec{k}\nu-}} \right) - \frac{|\Delta_+|^2}{U} - \frac{|\Delta_-|^2}{U}. \end{aligned} \quad (58)$$

We are interested in the binding energy due to the electron-exciton pairing, namely, in the expression W_0 .

$$\begin{aligned} W_0 = \langle \mathcal{H} \rangle_0 - \sum_{\vec{k}} (\Omega_{\vec{k}\nu+} + \Omega_{\vec{k}\nu-}) \\ = - \sum_{\vec{k}} \left(\frac{\frac{1}{4}(E_{\vec{k}\nu+} - \omega_{\vec{k}\nu+})^2}{\epsilon_{\vec{k}\nu+}} + \frac{\frac{1}{4}(E_{\vec{k}\nu-} - \omega_{\vec{k}\nu-})^2}{\epsilon_{\vec{k}\nu-}} \right) \\ - \frac{|\Delta_+|^2}{U} - \frac{|\Delta_-|^2}{U}. \end{aligned} \quad (59)$$

To calculate Eq. (59), we make use of the same approximations as those deriving Eqs. (40) and (41), with the result

$$W_0 = W_0^+ + W_0^-, \quad (60a)$$

where

$$W_0^\pm = - \frac{N_\pm(0)\bar{\omega}_\pm^2}{\tanh(1/\rho_\pm)} = - \frac{3}{2} \frac{\bar{\omega}_\pm}{\tanh(1/\rho_\pm)}. \quad (60b)$$

Equation (60) is a generalization of Eq. (43) of I for a crystal having two identical molecules per unit cell. Eq. (60) indicates that there is a coherent electron-exciton state which has lower energy than the normal exciton state provided that there is an attractive electron-exciton interaction.

To get an estimate for the gap function $\Delta_+(\vec{k})$, the transition temperature T_c^* and the binding energy W_0^+ corresponding to the plus energy mode, we rewrite Eqs. (40), (45), and (60) in the form

$$\Delta_+/\sigma_+ = \frac{\xi^2}{4m} / \sinh(1/\rho_+), \quad (61)$$

$$T_c^*/\sigma_+ = \frac{0.57\xi^2}{4mK_B} / \sinh(1/\rho_+), \quad (62)$$

$$W_0^*/\sigma_+ = - \frac{3}{2} \frac{\xi^2}{4m} / \tanh(1/\rho_+), \quad (63)$$

$$\bar{\omega}_+/\sigma_+ = \xi^2/4m, \quad (64)$$

$$\sigma_+ = \left| \frac{m}{m_e^*} - \frac{m}{m_{\text{exc}}^*} \right|, \quad (65)$$

m being the free-electron mass and ρ_+ is determined by Eq. (42b). It is easily seen from Eq. (64) that $\sigma_+ \geq 1$ and in the absence of any experimental data, σ_+ will be taken as a parameter. Since we are concerned with the region of high exciton concentrations we make use of the value of $n = 2 \times 10^{18} \text{ cm}^{-3}$ and upwards. The exciton concentration of $2 \times 10^{18} \text{ cm}^{-3}$ has been recently attained through optical pumping in anthracene crystals.⁹ The computed values of Δ_+/σ_+ , T_c^*/σ_+ , W_0^*/σ_+ , and $\bar{\omega}_+/\sigma_+$ for different values of n and ρ_+ are listed in Table I.

VI. DISCUSSION

We have extended the theory for the CT electron-exciton bound states to be applicable to molecular crystals having several molecules per unit cell. Detailed expressions for the energies of excitation are calculated for crystals like anthracene having two identical molecules in the unit cell. The excitation spectrum consists of four excitation bands, two of which are modifications of the Davydov's doublet while the other two are caused entirely by the electron-exciton pairing. Optical transitions to the electron-exciton bands indicate that the electron-exciton states have the same polarization directions but different intensities and energies from those of the corresponding exciton bands. The scattering amplitude $u_{\vec{k}\nu\pm}^2$ describes the polarization ratio, i.e., the ratio of the intensities of

the two electron-exciton bands with energies $\Omega_{\vec{k}\nu_{\pm}} + \epsilon_{\vec{k}\nu_{\pm}}$ and the corresponding components of the exciton doublet with energies $E_{\vec{k}\nu_{\pm}}$ respectively. The polarization ratio of the electron-exciton bands with energies $\Omega_{\vec{k}\nu_{\pm}} + \epsilon_{\vec{k}\nu_{\pm}}$ and those of $\Omega_{\vec{k}\nu_{\pm}} - \epsilon_{\vec{k}\nu_{\pm}}$ is given by $u_{\vec{k}\nu_{\pm}}^2/v_{\vec{k}\nu_{\pm}}^2$, respectively.

In our calculation we have made the assumption that the inequality (4) is satisfied and thus we have omitted terms from the Hamiltonian (3) which describe the simultaneous creation and annihilation of two excitations. In the case that the inequality (4) is violated then our expressions remain again valid provided that in all derived formulas the expression for $E_{\vec{k}\nu_{\pm}}$ given by Eq. (20b) must be replaced by the expression $E_{\nu_0}[1 \pm 2J_{\pm}(\vec{k})/E_{\nu_0}]^{1/2}$, which takes into account the fact the ratio $J_{\pm}(\vec{k})/E_{\nu_0}$ is no longer a small quantity.

The numerical results in Table I indicate that

for exciton concentrations $n \geq 2 \times 10^{18} \text{ cm}^{-3}$, the energy-gap function is a measurable quantity provided that we are dealing with the strong-coupling limit, i.e., when the average interaction energy is equal or greater than the average kinetic energy ($U \geq \bar{\omega}_*$). The last column in Table I gives the values of $\bar{\omega}_*/\sigma_*$ for different exciton densities. The values of $\bar{\omega}_*/\sigma_*$ indicate that the condition for the strong coupling limit $U \geq \bar{\omega}_*$ can be fulfilled with a reasonable strength of the required interaction U . The present experimental situation has been outlined in II. With the improvement of the experimental techniques there is the possibility of creating higher and higher exciton concentrations. The results of the present study indicate that at exciton densities $n \geq 2 \times 10^{18} \text{ cm}^{-3}$, the observation of the charge carrying electron-exciton states is feasible in molecular organic solids.

¹A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971). Subsequently, Frenkel excitons will be referred to as excitons.

²C. Mavroyannis, *Physica (Utr.)* **77**, 343 (1974). Henceforth, this paper will be referred to as I. Also, equations from I will be referred to as, for example, Eq. (5) of I.

³Hereafter, excited electrons will be referred to as electrons.

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⁵For a review on the subject, see D. M. Hanson, CRC

Crit. Rev. Solid State Sci. **3**, 243 (1973).

⁶C. Mavroyannis, *Phys. Rev. B* **15**, 1906 (1977). Henceforth, this paper will be referred to as II. Also equations from II will be referred to, say, Eq. (8) of II.

⁷D. N. Zubarev, *Usp. Fiz. Nauk.* **71**, 71 (1960) [*Sov. Phys.-Usp.* **3**, 320 (1960)].

⁸C. Mavroyannis, in *Physical Chemistry, Vol. XIA: Mathematical Methods* (Academic, New York, 1975).

⁹V. A. Benderskii, V. Kh. Brikenshtein, V. L. Broude, and I. I. Tartakovski, *Zh. Eksp. Teor. Fiz. Pis'ma Red.* **22**, 332 (1975) [*Sov. Phys.-JETP Lett.* **22**, 156 (1975)].