Resonant coherent pairing of excitons in molecular crystals

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(Received 19 February 1974)

A self-consistent approach is used to study the coherent pairing of Frenkel excitons produced by a resonant electromagnetic field in molecular crystals. In the presence of the resonant electromagnetic field the effective energy gap is equal to the difference between the transition frequency and the frequency of the field and vanishes at resonance. A dielectric energy gap is induced by the electromagnetic field that depends on the oscillator strength of the electronic transition in question. It is shown that under resonance or near resonance conditions and at temperatures below some value T_c, the existence of a bound biexciton state with zero total wave vector is possible, provided that the dielectric gap is less than that for the biexciton state. The excitation spectrum is formally analogous to that of a superconductor but the new state is not expected to carry current because of the neutrality of the electron-hole pairs. A splitting of the excitation spectrum occurred arising from the existence of the dielectric gap. The contribution to the ground-state energy of the crystal arising from the coherent pairing of excitons is calculated and the possibility of observing the biexciton spectrum is discussed.

I. INTRODUCTION

Light absorption by a crystal of organic molecules leads to the formation of molecular (or Frenkel-type) excitons.[1] In a tight-binding model of a molecular crystal, a Frenkel exciton may be viewed as a tightly bound electron-hole pair migrating through the crystal. Considerable interest has arisen in the behavior of exciton systems at high densities where interaction effects between excitons become substantial. This interaction has a pronounced effect on the emission spectrum of semiconductors at low temperatures. Such emission lines have been observed in Si, Ge, CdS, ZnO, and CuCl.[2-7] Haynes[2] proposed that the emission lines in Si and Ge were due to the biexciton decay, while it is now generally believed that they arise from droplets of a metallic electron-hole plasma.[8,9] Electron-hole pairs in such systems as Si and Ge undergo a gas-liquid-type transition at low temperatures and as a function of density.[8,9]

Thus the formation of electron-hole metallic liquids[10] as well as the appearance of biexcitons[11] in semiconductors has been confirmed as arising at low temperatures from the interaction between large-radius (or Mott-type) excitons. In the case of organic crystals, where the excitons are of the molecular (Frenkel or small radius) type, the formation of a biexciton state at low temperatures may be possible if the attractive interaction between the excitons predominates.

The aim of the present study is to examine the possibility of the formation of a biexciton state arising from coherent pairing of excitons in the presence of a resonant electromagnetic field in molecular crystals consisting of aromatic organic molecules. The Hamiltonian for a two-level system of a molecular crystal is developed in Sec. II in the Frenkel-exciton representation including exciton-exciton interactions. Then the coupling with a transverse resonant electromagnetic field is considered and the equations of motions for the exciton Green's functions are derived. To consider coherent pairing between the excitons a decoupling approximation is used which is valid in the high-density limit and a set of coupled equations for the exciton Green's functions is obtained.

The excitation spectrum is discussed in Sec. III, which is formally analogous to that of a superconductor[12,13] as well as to that of the excitonic insulator of semimetals and semiconductors.[14-16] The dielectric energy gap, which is induced by the electromagnetic field and depends on the oscillator strength of the electronic transition in question, causes a splitting of the energies of excitation. The integral equation for the gap function $\Delta(\vec{k})$ arising from the coherent pairing of excitons is solved at zero temperature. Under resonance conditions, the gap function $\Delta(\vec{k})$ is finite provided that the induced dielectric gap μ is much less than that of $\Delta(\vec{k})$. The parameters that appear in the expression for $\Delta(\vec{k})$ are the exciton density, the effective mass of the exciton, and the strength of the attractive exciton-exciton interaction. Since $\Delta(\vec{k})$ arises from the coherent pairing of neutral excitons, the biexciton state, if it exists, is bound to be electrically neutral.

The contribution to the ground-state energy of the crystal arising from the coherent pairing of excitons is calculated in Sec. IV. The derived expression for the ground-state energy is similar in form to that of a super-conductor but with different parameters. The possibility of observing the biexciton state in molecular crystals is discussed in Sec. V.

II. FORMULATION OF THE PROBLEM

The Hamiltonian of a crystal with an undisplaced lattice is taken as[17,18]

$$\mathcal{H}_e = \sum_{f,f'} L(f,f')\alpha_f^\dagger \alpha_{f'} + \frac{1}{2}\sum_{f,f_1,f',f_1'} \langle f,f_1 | V | f',f_1' \rangle \alpha_f^\dagger \alpha_{f_1}^\dagger \alpha_{f_1'} \alpha_{f'} , \tag{1}$$

where $f = (\vec{n}, i, s)$, $\vec{n}$ being the lattice site and i and s designate the electron state and the spin component of an electron ($\pm \frac{1}{2}$). The creation and annihilation operators $\alpha_f^\dagger$ and α_f satisfy Fermi anticommutation relations

$$[\alpha_f, \alpha_{f'}^\dagger]_+ = \delta_{ff'}, \quad [\alpha_f, \alpha_{f'}]_+ = [\alpha_f^\dagger, \alpha_{f'}^\dagger]_+ = 0 .$$

The matrix elements of $L(f,f')$ are

$$L(f,f') = \langle f | L | f' \rangle = \int \psi_f^*(\vec{r}_{\vec{n}}) \left(\frac{-1}{2m}\nabla^2 + \sum_{f''} V(\vec{r}_{\vec{n}} - \vec{r}_{\vec{n}''}) \right) \times \psi_{f'}(\vec{r}_{\vec{n}''})\, d\tau , \tag{2}$$

where $V(\vec{r}_{\vec{n}} - \vec{r}_{\vec{n}'})$ is the periodic potential of an electron at the lattice site $\vec{n}$. The matrix elements

$$\langle f,f_1 | V | f',f_1' \rangle = \int \psi_f^*(\vec{r}_{\vec{n}}) \psi_{f_1}^*(\vec{r}_{\vec{m}}) V(\vec{r}_{\vec{n}} - \vec{r}_{\vec{m}}) \psi_{f'}(\vec{r}_{\vec{n}}) \psi_{f_1'}(\vec{r}_{\vec{m}})\, d\tau_1\, d\tau_2 ,$$

$$V(\vec{r}_{\vec{n}} - \vec{r}_{\vec{m}}) = e^2 / |\vec{r}_{\vec{n}} - \vec{r}_{\vec{m}}| , \tag{3}$$

correspond to the potential energy of the electron-electron interaction[19] and e^2 is the square of the electronic charge divided by the dielectric constant of the substance. The ψ's are the Wannier functions describing the electronic states and $\vec{r}_{\vec{n}}$ and $\vec{r}_{\vec{m}}$ are the position vectors of an electron at the lattice sites $\vec{n}$ and $\vec{m}$, respectively. The matrix elements satisfy the following symmetry relations:

$$\langle f,f_1 | V | f',f_1' \rangle = \langle f_1,f | V | f_1',f' \rangle , \tag{4}$$

$$\langle f,f_1 | V | f',f_1' \rangle^* = \langle f_1',f | V | f_1,f \rangle . \tag{5}$$

The system of units with $\hbar = 1$ is used throughout and the overlap between the wave functions is neglected.

We adopt a simple tight-binding model for a molecular crystal consisting 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 effects of the electron spin are discarded and only spin-allowed transitions will be considered. We shall also assume that the molecules (atoms) in the crystal possess only two electronic states 0 and ν, the ground and excited state, respectively. For a two-level system, the relation

$$\alpha_{\vec{n}0}^\dagger \alpha_{\vec{n}0} + \alpha_{\vec{n}\nu}^\dagger \alpha_{\vec{n}\nu} = 1 \tag{6}$$

is satisfied; then

$$\alpha_{\vec{n}0}^\dagger \alpha_{\vec{n}0} = b_{\vec{n}\nu} b_{\vec{n}\nu}^\dagger, \quad \alpha_{\vec{n}\nu}^\dagger \alpha_{\vec{n}\nu} = b_{\vec{n}\nu}^\dagger b_{\vec{n}\nu} , \tag{7}$$

and hence

$$b_{\vec{n}\nu} b_{\vec{n}\nu}^\dagger + b_{\vec{n}\nu}^\dagger b_{\vec{n}\nu} = 1 , \tag{8}$$

where $b_{\vec{n}\nu}^\dagger = \alpha_{\vec{n}\nu}^\dagger \alpha_{\vec{n}0}$ and $b_{\vec{n}\nu} = \alpha_{\vec{n}0}^\dagger \alpha_{\vec{n}\nu}$ are the Frenkel-exciton creation and annihilation operators, respectively. Thus for the two-level system under consideration,[20] the exciton operators anticommute when they are located at the same lattice site while they commute at different lattice sites.

Using Eqs. (6)–(8), we write the Hamiltonian (1) in the tight-binding approximation and for a two-level system of a molecular solid in the form

$$\mathcal{H}_e = \text{const} + \sum_{\vec{n},\nu} E_{\nu 0} b_{\vec{n}\nu}^\dagger b_{\vec{n}\nu} + {\sum_{\vec{R}_{\vec{m}\vec{n}}}}' J(\vec{n}0, \vec{m}\nu \,|\, \vec{n}\nu, \vec{m}0) b_{\vec{n}\nu}^\dagger b_{\vec{m}\nu} + \frac{1}{2}{\sum_{\vec{R}_{\vec{m}\vec{n}}}}' J(\vec{n}0, \vec{m}0 \,|\, \vec{n}\nu, \vec{m}\nu)(b_{\vec{n}\nu} b_{\vec{m}\nu} + b_{\vec{m}\nu}^\dagger b_{\vec{n}\nu}^\dagger) - \frac{1}{2}{\sum_{\vec{R}_{\vec{m}\vec{n}}}}' U(\vec{n},\vec{m}) b_{\vec{n}\nu}^\dagger b_{\vec{n}\nu} b_{\vec{m}\nu}^\dagger b_{\vec{m}\nu} , \tag{9}$$

where

$$E_{\nu 0} = L(\vec{n}\nu, \vec{n}\nu) - L(\vec{n}0, \vec{n}0) + \sum_{\vec{R}_{\vec{m}\vec{n}}} U_0(\vec{n},\vec{m}) , \tag{10}$$

$$U(\vec{n},\vec{m}) = U_0(\vec{n},\vec{m}) + U_\nu(\vec{n},\vec{m}) , \tag{11a}$$

$$U_0(\vec{n},\vec{m}) = J(\vec{n}0, \vec{m}\nu \,|\, \vec{n}0, \vec{m}\nu) - J(\vec{n}0, \vec{m}0 \,|\, \vec{n}0, \vec{m}0) , \tag{11b}$$

$$U_\nu(\vec{n},\vec{m}) = J(\vec{m}\nu, \vec{n}0 \,|\, \vec{m}\nu, \vec{n}0) - J(\vec{n}\nu, \vec{m}\nu \,|\, \vec{n}\nu, \vec{m}\nu) , \tag{11c}$$

$$J(f_1,f_2 \,|\, f_3,f_4) \equiv \langle f_1,f_2 | V | f_3,f_4 \rangle - \langle f_1,f_2 | V | f_4,f_3 \rangle , \tag{11d}$$

$\vec{R}_{\vec{m}\vec{n}} = \vec{r}_{\vec{m}} - \vec{r}_{\vec{n}}$ and the prime in the sum indicates that the term with $\vec{R}_{\vec{m}\vec{n}} = 0$ should be omitted. The coupling functions in the second and third term of Eq. (9) are responsible for the formation of the Frenkel excitons while the functions $U_0(\vec{n},\vec{m})$ and $U_\nu(\vec{n},\vec{m})$ involve interband as well as intraband interactions and may be attributed as arising from the valence and excitation band, respectively. The coupling function $U(\vec{n},\vec{m})$ is responsible for the formation of Mott-type excitons (loosely bound electron-hole pairs) in semiconductors. This is due to the fact that in view of Eqs. (6)–(8), the relation

$$(b_{\vec{n}\nu}^\dagger b_{\vec{n}\nu})(b_{\vec{m}\nu}^\dagger b_{\vec{m}\nu}) = (\alpha_{\vec{m}\nu}^\dagger \alpha_{\vec{n}0})(\alpha_{\vec{n}0}^\dagger \alpha_{\vec{m}\nu}) \tag{11e}$$

holds as well.

Going into the momentum representation by means of the transformation

$$b_{\vec{n}\nu} = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}_{\vec{n}}} b_{\vec{k}\nu} ,$$

where $\vec{k}$ is a wave vector in the first Brillouin zone, then the Hamiltonian (9) may be written as

$$\mathcal{H}_e = \text{const} + \sum_{\vec{k},\nu} E_{\vec{k}\nu} b^{\dagger}_{\vec{k}\nu} b_{\vec{k}\nu} - \left(\frac{1}{2N}\right) \sum_{\vec{k},\vec{q},\nu}{}' U(\vec{k}-\vec{q}) \times b^{\dagger}_{-\vec{q}\nu} b^{\dagger}_{\vec{q}\nu} b_{\vec{k}\nu} b_{-\vec{k}\nu} , \tag{13}$$

where $E_{k\nu}$ is the energy of an exciton with wave vector k defined as

$$E_{\vec{k}\nu} = E_{\nu 0} + J(\vec{k}), \tag{14a}$$

$$J(\vec{k}) = \sum_{\vec{R}_{\vec{m}\vec{n}}}{}' J(\vec{n}0, \vec{m}\nu \,|\, \vec{n}\nu, \vec{m}0)\, e^{i\vec{k}\cdot\vec{R}_{\vec{m}\vec{n}}} , \tag{14b}$$

$$U(\vec{k}-\vec{q}) = \sum_{\vec{R}_{\vec{m}\vec{n}}}{}' U(\vec{n},\vec{m})\, e^{i(\vec{k}-\vec{q})\cdot\vec{R}_{\vec{m}\vec{n}}} - 2J(\vec{q}) . \tag{14c}$$

In deriving Eq. (13) we have neglected the third term on the right-hand side of Eq. (9) for the sake of convenience. This implies that the exciton energy given by Eq. (14a) is correct in the Heitler-London approximation.[1] The last term in Eq. (13) describes exciton-exciton interactions and the summations are over the first Brillouin zone. The last term in Eq. (14c) arises from the well known fact that excitons are not, strictly speaking, Bose particles but they are bound states of two Fermions. Since we consider only one excitation band, the index μ indicates the kind of the exciton mode, transverse $\nu = 1$, 2 or longitudinal $\nu = 3$.

The Hamiltonian for the transverse radiation field has the form

$$\mathcal{H}_r = \sum_{\vec{k},\lambda} \omega_{\vec{k}} \beta^{\dagger}_{\vec{k}\lambda} \beta_{\vec{k}\lambda} , \tag{15}$$

where $\beta^{\dagger}_{\vec{k}\lambda}$ and $\beta_{\vec{k}\lambda}$ are the creation and annihilation operators of a photon with wave vector $\vec{k}$ and polarization $\lambda (= 1, 2)$, representing the two possible values of polarization perpendicular to the direction of propagation $\vec{k}$, and $\omega_{\vec{k}}$ is the energy for the photon field. The photon operators $\beta^{\dagger}_{\vec{k}\lambda}$ and $\beta_{\vec{k}\lambda}$ satisfy Bose statistics. The interaction between the transverse excitons and the electromagnetic field is taken as[17,21]

$$\mathcal{H}_{\text{int}} = \left(\frac{i\omega_p}{2}\right) \sum_{\vec{k},\lambda,\nu} \left[f_{0\nu}(\vec{k}\lambda) \left(\frac{E_{\vec{k}\nu}}{\omega_{\vec{k}}}\right) \right]^{1/2} (b_{-\vec{k}\nu} \beta^{\dagger}_{\vec{k}\lambda} - b^{\dagger}_{\vec{k}\nu} \beta_{-\vec{k}\lambda}) , \tag{16}$$

where ω_p is the plasma frequency and $f_{0\nu}(\vec{k}\lambda)$ is the oscillator strength for the spin-allowed electronic transition $0 \rightarrow \nu$ defined as[17]

$$f_{0\nu}(\vec{k}\lambda) = \left(\frac{2m}{e^2}\right) \left| \sum_i (e_{\vec{k}\lambda} \cdot P^i_{0\nu}) \right|^2 E_{\vec{k}\nu} e^{i\vec{k}\cdot\vec{R}_{\vec{m}\vec{n}}} , \tag{17}$$

and $P^i_{0\nu}$ is the dipole moment operator of the ith electron. In the expression for the interaction Hamiltonian (16) we have considered only the resonance interaction between transverse excitons and photons. Exciton-photon scattering effects will not be taken into consideration in the present study.[22] Thus our total Hamiltonian is given by

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_r + \mathcal{H}_{\text{int}} . \tag{18}$$

We shall make use of the retarded double-time Green's functions defined as[23]

$$\langle\langle A(t);\ B(t')\rangle\rangle = -i\Theta(t-t') \langle [A(t), B(t')]_{-\eta} \rangle , \tag{19}$$

where

$$\langle U \rangle = \text{tr} U e^{-\beta\mathcal{H}} / \text{tr} e^{-\beta\mathcal{H}}, \quad \beta = (k_B T)^{-1} ,$$

K_B is Boltzmann's constant, T is the absolute temperature, and $\mathcal{H}$ is the total Hamiltonian of the system. $\Theta(t)$ is the usual step function and the operators are in the Heisenberg representation and η is taken to be either + 1 or − 1 depending upon considerations of convenience. The equation of motion for the Fourier transform of the Green's function $\langle\langle A(t);\ B(t')\rangle\rangle_{(\omega)}$ is given by

$$\omega \langle\langle A(t);\ B(t')\rangle\rangle_{(\omega)} = (1/2\pi) \langle [A(t), B(t)]_{-\eta} \rangle + \langle\langle [A(t), \mathcal{H}]_{-};\ B(t')\rangle\rangle_{(\omega)} . \tag{20}$$

The subscript (ω) as well as the time arguments of the operators will be suppressed for convenience.

Using the total Hamiltonian (18) we consider the equations of motion for the number operators for the exciton and photon field, respectively, as

$$i\frac{d}{dt} b^{\dagger}_{\vec{k}\nu} b_{\vec{k}\nu} = [b^{\dagger}_{\vec{k}\nu} b_{\vec{k}\nu}, \mathcal{H}]_{-} = -\sum_{\lambda} \left(\frac{i\mu_{\vec{k}\lambda\nu}}{2}\right) (b_{\vec{k}\nu} \beta^{\dagger}_{-\vec{k}\lambda} + b^{\dagger}_{\vec{k}\nu} \beta_{-\vec{k}\lambda}), \tag{21}$$

$$i\frac{d}{dt} \beta^{\dagger}_{\vec{k}\lambda} \beta_{\vec{k}\lambda} = [\beta^{\dagger}_{\vec{k}\lambda} \beta_{\vec{k}\lambda}, \mathcal{H}]_{-} = \sum \left(\frac{i\mu_{\vec{k}\lambda\nu}}{2}\right) (b_{-\vec{k}\nu} \beta^{\dagger}_{\vec{k}\lambda} + b^{\dagger}_{-\vec{k}\nu} \beta_{\vec{k}\lambda}) , \tag{22}$$

where

$$\mu_{\vec{k}\lambda\nu} \equiv \omega_p [f_{0\nu}(\vec{k}\lambda)(E_{\vec{k}\nu}/\omega_{\vec{k}})]^{1/2} . \tag{23}$$

Since we are concerned only with one excitation band we must have $\lambda = \nu$ for nonvanishing coupling between the transverse excitons and photons. Equations (21) and (22) imply that

$$i\frac{d}{dt} (b^{\dagger}_{\vec{k}\nu} b_{\vec{k}\nu} + \beta^{\dagger}_{\vec{k}\lambda} \beta_{\vec{k}\lambda}) = 0, \tag{24}$$

and hence

$$\beta_{\vec{k}\lambda}\beta_{\vec{k}\lambda} = -b^{\dagger}_{\vec{k}\nu}b_{\vec{k}\nu} + C \ , \tag{25}$$

where C is a constant. Using Eq. (25) we may rewrite our Hamiltonian (18) as

$$\mathcal{H} = \text{const} + \sum_{\vec{k}\nu}\Omega_{\vec{k}\nu}b^{\dagger}_{\vec{k}\nu}b_{\vec{k}\nu} + \sum_{\vec{k},\lambda,\nu}\left(\frac{i\mu_{\vec{k}\lambda\nu}}{2}\right)(b_{-\vec{k}\nu}\beta^{\dagger}_{\vec{k}\lambda} - b^{\dagger}_{\vec{k}\nu}\beta_{-\vec{k}\lambda})$$
$$- \left(\frac{1}{2N}\right)\sum_{\vec{k},\vec{q},\nu}{}' U(\vec{k}-\vec{q})(b^{\dagger}_{-\vec{q}\nu}b^{\dagger}_{\vec{q}\nu})(b_{\vec{k}\nu}b_{-\vec{k}\nu}) \ , \tag{26}$$

where

$$\Omega_{\vec{k}\nu} = E_{\vec{k}\nu} - \omega_{\vec{k}} \ . \tag{27}$$

Using Eqs. (20) and (26) we derive the equations of motion for the Green's functions $\langle\langle b_{\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle$ and $\langle\langle b^{\dagger}_{-\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle$ as

$$(\omega - \Omega_{\vec{k}\nu})\langle\langle b_{\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle = \left(\frac{1-2n_{\vec{k}\nu}}{2\pi}\right) - \sum_{\lambda}\left(\frac{i\mu_{\vec{k}\lambda\nu}}{2}\right)$$
$$\times\langle\langle \beta_{-\vec{k}\lambda};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle - \left(\frac{1}{N}\right)\sum_{\vec{q}}{}' U(\vec{k}-\vec{q})$$
$$\times\langle\langle b^{\dagger}_{-\vec{k}\nu}b_{-\vec{q}\nu}b_{\vec{q}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle \ , \tag{28}$$

$$(-\omega - \Omega_{\vec{k}\nu})\langle\langle b^{\dagger}_{\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle = \sum_{\lambda}\left(\frac{i\mu_{\vec{k}\lambda\nu}}{2}\right)\langle\langle \beta^{\dagger}_{\vec{k}\lambda};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle$$
$$+ \left(\frac{1}{N}\right)\sum_{\vec{q}}{}' U(\vec{q}-\vec{k})\langle\langle b^{\dagger}_{\vec{q}\nu}b^{\dagger}_{\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle \ , \tag{29}$$

where $n_{\vec{k}\nu} = \langle b^{\dagger}_{\vec{k}\nu}b_{\vec{k}\nu}\rangle$. Similarly,

$$\omega\langle\langle \beta_{-\vec{k}\lambda};b^{\dagger}_{\vec{k}\nu}\rangle\rangle = \sum_{\nu}\left(\frac{i\mu_{\vec{k}\lambda\nu}}{2}\right)\langle\langle b^{\dagger}_{\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle \ , \tag{30}$$

$$\omega\,\langle\langle \beta^{\dagger}_{\vec{k}\lambda};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle = \sum_{\nu}\left(\frac{i\mu_{\vec{k}\lambda\nu}}{2}\right)\langle\langle b_{-\vec{k}\nu};b^{\dagger}_{\vec{k}\nu}\rangle\rangle \ . \tag{31}$$

To proceed further we introduce the following decoupling approximation:

$$\langle\langle b^{\dagger}_{-\vec{k}\nu}\,b_{-\vec{q}\nu}b_{\vec{q}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle \approx \langle\, b_{-\vec{q}\nu}b_{\vec{q}\nu}\rangle\langle\langle b_{-\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle \ , \tag{32}$$

$$\langle\langle b^{\dagger}_{-\vec{q}\nu}b^{\dagger}_{\vec{q}\nu}b_{\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle \approx \langle\, b^{\dagger}_{\vec{q}\nu}b^{\dagger}_{-\vec{q}\nu}\rangle\langle\langle\, b_{\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle \ , \tag{33}$$

which implies the possibility of the coherent pairing of excitons with opposite wave vectors. Since coherent pairing of electrons is responsible for most of the macroscopic phenomena observed in superconductors,[12,13] the approximations (32) and (33) will be sufficient for describing exciton condensation.[24] The decoupling scheme described by Eqs. (32) and (33) is valid in the high-density limit. Using Eqs. (28)–(33), we derive the following set of coupled equations:

$$\left(\omega - \Omega_{\vec{k}\nu} - \frac{\mu^2_{\vec{k}}}{4\omega}\right)\langle\langle b_{\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle = \left(\frac{1-2n_{\vec{k}\nu}}{2\pi}\right) - \Delta(\vec{k})\,\langle\langle b^{\dagger}_{-\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle, \tag{34}$$

$$\left(-\omega - \Omega_{\vec{k}\nu} + \frac{\mu^2_{\vec{k}}}{4\omega}\right)\langle\langle b^{\dagger}_{-\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle = \Delta^{*}(\vec{k})\langle\langle b_{\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle \ , \tag{35}$$

where

$$\mu^2_{\vec{k}} = \omega_p^2\sum_{\nu,\lambda} f_{0\nu}(\mathrm{k}\lambda)\left(\frac{E_{\vec{k}\nu}}{\omega_{\vec{k}}}\right) , \tag{36}$$

$$\Delta(\vec{k}) = \left(\frac{1}{N}\right)\sum_{\vec{q}}{}' U(\vec{k}-\vec{q})\langle b_{-\vec{q}\nu}b_{\vec{q}\nu}\rangle \ . \tag{37}$$

The coupling function $\Delta(\vec{k})$ describes the coherent pairing of two excitons with opposite wave vectors and will be calculated self-consistently. Similar equations to those of (34) and (35) hold for the Green's functions $\langle\langle b^{\dagger}_{-\vec{k}\nu};\ b_{-\vec{k}\nu}\rangle\rangle$ and $\langle\langle b_{\vec{k}\nu};\ b_{-\vec{k}\nu}\rangle\rangle$. Equations (34) and (35) will be used in Sec. III to discuss the excitation spectrum. Considering the approximations that have been made so far, the excitation spectrum will be correct in the Hartree-Fock approximation.

III. EXCITATION SPECTRUM

Solving the coupled equations (34) and (35), we have

$$\langle\langle b_{\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle = \left(\frac{1-2n_{\vec{k}\nu}}{2\pi}\right)\frac{\omega^2(\omega+\Omega_{\vec{k}\nu}) - \omega\,\mu^2_{\vec{k}}/4}{[\omega^2-\Omega^2_{+}(\vec{k}\nu)]\,[\omega^2-\Omega^2_{-}(\vec{k}\nu)]} \ , \tag{38}$$

$$\langle\langle b^{\dagger}_{-\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle = -\left(\frac{1-2n_{\vec{k}\nu}}{2\pi}\right)\frac{\omega^2\Delta^{*}(\vec{k})}{[\omega^2-\Omega^2_{+}(\vec{k}\nu)]\,[\omega^2-\Omega^2_{-}(\vec{k}\nu)]} , \tag{39}$$

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

$$\Omega_{\pm}(\vec{k}\nu) = \tfrac{1}{2}\left[(\epsilon^2_{\vec{k}\nu} + \mu^2_{\vec{k}})^{1/2} \pm \epsilon_{\vec{k}\nu}\right] , \tag{40}$$

$$\epsilon_{\vec{k}\nu} = +\left[\Omega^2_{\vec{k}\nu} + |\Delta(\vec{k})|^2\right]^{1/2} , \tag{41}$$

with $\Omega_{\vec{k}\nu}$ defined by Eq. (27). The splitting of the energies of excitation is caused by the gap function $\mu_{\vec{k}}$ given by Eq. (36), which is induced by the electromagnetic field. The distribution functions $\langle b^{\dagger}_{\vec{k}\nu}\,b_{\vec{k}\nu}\rangle$ and $\langle b^{\dagger}_{\vec{k}\nu}b^{\dagger}_{-\vec{k}\nu}\rangle$ can be calculated by means of the relations[23]

$$\langle b^{\dagger}_{\vec{k}\nu}b_{\vec{k}\nu}\rangle = -2\int_{-\infty}^{+\infty} d\omega\ \mathrm{Im}\,\langle\langle b_{\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle(e^{\beta\omega}+1)^{-1}, \tag{42a}$$

$$\langle b^{\dagger}_{\vec{k}\nu}b^{\dagger}_{-\vec{k}\nu}\rangle = -2\int_{-\infty}^{+\infty} d\omega\ \mathrm{Im}\,\langle\langle b^{\dagger}_{-\vec{k}\nu};\ b^{\dagger}_{\vec{k}\nu}\rangle\rangle(e^{\beta\omega}+1)^{-1} \ . \tag{42b}$$

Substituting the imaginary parts of Eqs. (38) and (39) into Eqs. (42a) and (42b) and after integrating over ω we find

$$\langle b^{\dagger}_{\vec{k}\nu} b_{\vec{k}\nu}\rangle = (1-2n_{\vec{k}\nu})\left[\tfrac{1}{2} - \frac{\Omega_{\vec{k}\nu}}{2(\epsilon^2_{\vec{k}\nu}+\mu^2_{\vec{k}})^{1/2}}\theta_{\vec{k}}\right], \quad (43)$$

$$\langle b_{\vec{k}\nu} b^{\dagger}_{\vec{k}\nu}\rangle = (1-2n_{\vec{k}\nu})\left[\tfrac{1}{2} + \frac{\Omega_{\vec{k}\nu}}{2(\epsilon^2_{\vec{k}\nu}+\mu^2_{\vec{k}})^{1/2}}\theta_{\vec{k}}\right], \quad (44)$$

$$\langle b^{\dagger}_{\vec{k}\nu} b^{\dagger}_{-\vec{k}\nu}\rangle = (1-2n_{\vec{k}\nu})\frac{\Delta^*(\vec{k})}{2(\epsilon^2_{\vec{k}\nu}+\mu^2_{\vec{k}})^{1/2}}\theta_{\vec{k}}, \quad (45)$$

$$\langle b_{-\vec{k}\nu} b_{\vec{k}\nu}\rangle = (1-2n_{\vec{k}\nu})\frac{\Delta(\vec{k})}{2(\epsilon^2_{\vec{k}\nu}+\mu^2_{\vec{k}})^{1/2}}\theta_{\vec{k}}, \quad (46)$$

where θ_k is the temperature-dependent factor given by

$$\theta_{\vec{k}} = \tfrac{1}{2}[\tanh\tfrac{1}{2}\beta\Omega_+(\vec{k}\nu) + \tanh\tfrac{1}{2}\beta\Omega_-(\vec{k}\nu)] + (1/2\epsilon_{\vec{k}\nu}) \times(\epsilon^2_{\vec{k}\nu}+\mu^2_{\vec{k}})^{1/2}[\tanh\tfrac{1}{2}\beta\Omega_+(\vec{k}\mu) - \tanh\tfrac{1}{2}\beta\Omega_-(\vec{k}\mu)]. \quad (47)$$

Then Eq. (37) takes the form

$$\Delta(\vec{k}) = \left(\frac{1}{N}\right)\sum_{\vec{q}}{}' U(\vec{k}-\vec{q})\frac{\Delta(\vec{q})}{2(\epsilon^2_{\vec{q}\nu}+\mu^2_{\vec{q}})^{1/2}}(1-2n_{\vec{q}\nu})\theta_{\vec{q}}. \quad (48)$$

The scattering amplitude $\Delta(k)$ is determined by the solutions of the integral equation (48) at finite temperatures. In the limit of zero temperature, $\beta\to\infty$, the function $\theta_{\vec{k}}$ goes to unity and $n_{\vec{q}\nu}=0$ and Eq. (48) becomes

$$\Delta(\vec{k}) = \left(\frac{1}{N}\right)\sum_{\vec{q}}{}' U(\vec{k}-\vec{q})\frac{\Delta(\vec{q})}{2(\epsilon^2_{\vec{q}\nu}+\mu^2_{\vec{q}})^{1/2}}, \quad (49)$$

which is formally analogous to that for superconductors.[12,13]

We proceed now to solve the integral equation (49) for $\Delta(\vec{k})$. To do so we shall make a number of simplifications similar to those made in the theory of superconductivity.[12,13] We consider the exciton energy in the effective-mass approximation[1]

$$E_{\vec{k}\nu} = E_{\nu 0} + \vec{q}^2/2m_{\rm exc}, \quad (50)$$

where $m_{\rm exc}$ is the effective mass of the exciton. We then assume that in the range of frequencies within the exciton band, the interaction $U(\vec{k}-\vec{q})$ is constant, $U(\vec{k})$, and positive (attractive interaction) for $\Delta(\vec{q})=\Delta(\vec{k})\neq 0$, and zero otherwise. We also take the quantities characterizing the electromagnetic field as independent of the wave vector, that is, $\mu_{\vec{k}}=\mu=$ const and the energy of the electromagnetic field $\omega_{\vec{k}}=\Omega$. Then the summation in Eq. (49) is replaced by an integration over the first Brillouin zone and neglecting the $\vec{q}$ variation of the density of states we have

$$\left(\frac{1}{\rho}\right) = \int_0^{\xi}\frac{d(\vec{q}^2/2m_{\rm exc})}{[(E_g+\vec{q}^2/2m_{\rm exc})^2+|\Delta(\vec{k})|^2+\mu^2]^{1/2}}, \quad (51)$$

$$E_g = E_{\nu 0}-\Omega, \quad \xi = (6\pi^2N/V)^{1/3}, \quad (52a)$$

$$\rho = N(0)U(\vec{k}) = \tfrac{3}{2}U(\vec{k})/\bar{\omega}, \quad (52b)$$

$$\bar{\omega} = \xi^2/2m_{\rm exc} = L_{\rm exc},\ N(0) = V\xi m_{\rm exc}/2\pi^2N = 3/2\bar{\omega}, \quad (52c)$$

where $L_{\rm exc}$ is the width of the exciton band.[1] Carrying the integration in Eq. (51) and after some algebra we obtain

$$\Delta(\vec{k}) = \left[\frac{\bar{\omega}}{\sinh(1/\rho)}\right]\left\{1 - 2\left(\frac{E_g}{\bar{\omega}}\right)\left(1+\frac{E_g}{\bar{\omega}}\right)\left[\cosh\left(\frac{1}{\rho}\right)-1\right] - \frac{\mu^2}{[\bar{\omega}/\sinh(1/\rho)]^2}\right\}^{1/2}, \quad (53)$$

which describes the scattering amplitude due to coherent pairing of excitons in the presence of a resonant electromagnetic field.

We shall consider the favorable conditions under which $\Delta(\vec{k})\neq 0$. It is clear that $\Delta(\vec{k})$ becomes appreciable when both the second and third terms in the curly brackets of Eq. (53) become negligibly small. In fact, the second term vanishes when the resonance conditions are satisfied, i.e., when

$$E_g = E_{\nu 0}-\Omega \approx 0. \quad (54)$$

Thus at resonance or near resonance when $(E_g/\bar{\omega}) \ll 1$, Eq. (53) may be written as

$$\Delta(\vec{k}) \approx \left\{\left[\frac{\bar{\omega}}{\sinh(1/\rho)}\right]^2 - \mu^2\right\}^{1/2}, \quad (55)$$

which implies that μ must be

$$\mu < \Delta_0(\vec{k}), \quad (56a)$$

where

$$\Delta_0(\vec{k}) = \frac{\bar{\omega}}{\sinh(1/\rho)}, \quad (56b)$$

so that $\Delta(\vec{k})\neq 0$. If we define the static dielectric constant ϵ_0 for the exciton band in question as

$$\epsilon_0 = 1 + \omega_p^2 f_{0\nu}/E^2_{\nu 0}, \quad (57)$$

then μ, under resonance conditions, may take the form

$$\mu \sim \omega_p f_{\nu 0}^{1/2} \sim E_{\nu 0}(\epsilon_0-1)^{1/2} \sim \Omega(\epsilon_0-1)^{1/2}. \quad (58a)$$

Equation (58a) indicates that a small value of the oscillator strength or that a small ϵ_0 is required in order to give a sufficiently small value for the dielectric gap μ. Thus a finite value of $\Delta(\vec{k})$ is feasible when the electromagnetic field is at resonance or near resonance with the exciton band in question, whose oscillator strength should be as

small as possible. It is concluded that although the resonant radiation field helps in minimizing or reducing to zero the effects of the insulating gap $E_{\nu 0}$, it sets up the dielectric gap μ, which is in competition with that of $\Delta_0(\vec{k})$. The dielectric gap function μ is also responsible for the splitting of the excitation spectrum given by Eq. (40).

When $U(\vec{k}) > \bar{\omega}$, where $\bar{\omega}$ is of the order of the width of the exciton band, then $\rho > 1$ and $\sinh(1/\rho) < 1$. This case corresponds to the strong coupling limit and an enhancement for $\Delta_0(\vec{k})$ is expected to occur. The expression (55) is formally analogous to that derived by Elesin and Kopaev[25] for the superconducting gap in semiconductors under similar conditions. The transition temperature T_c may be determined in the same way as it has been done in Ref. 25 for the case when $\mu \ll \Delta_0(\vec{k})$ and under resonance conditions by the approximate expression

$$K_B T_c \approx 0.57 \Delta(\vec{k}) \left[\frac{1 - 0.3(\mu/\Delta_0)^2}{1 - (\mu/\Delta_0)^2}\right], \tag{58b}$$

and in the limit $\mu \to 0$,

$$K_B T_c \approx 0.57 \Delta_0(\vec{k}). \tag{58c}$$

Thus when $\mu \ll \Delta_0$ there is a small increase in the value of T_c in comparison with that when $\mu \to 0$.

IV. GROUND-STATE ENERGY

In order to find the contribution to the ground-state energy of the crystal arising from the coherent pairing of excitons we average the Hamiltonian (26) as

$$\langle \mathcal{H} \rangle = \text{const} + \sum_{\vec{k}\nu} \Omega_{\vec{k}\nu} \langle b^\dagger_{\vec{k}\nu} b_{\vec{k}\nu} \rangle + \sum_{\vec{k},\lambda,\nu} \left(\frac{i\mu_{\vec{k}\lambda\nu}}{2}\right) \times \langle b_{-\vec{k}\nu} \beta^\dagger_{\vec{k}\lambda} - b^\dagger_{\vec{k}\nu} \beta_{-\vec{k}\lambda} \rangle - \left(\frac{1}{2N}\right) \sum_{\vec{k},\vec{q},\nu}{}' U(\vec{k} - \vec{q}) \langle b^\dagger_{-\vec{q}\nu} b^\dagger_{\vec{q}\nu} \rangle \langle b_{\vec{k}\nu} b_{-\vec{k}\nu} \rangle . \tag{59}$$

Using Eqs. (30), (31), and (44)–(46) then Eq. (59) assumes the form

$$\langle \mathcal{H} \rangle = \text{const} + \frac{1}{2} \sum_{\vec{k}} \Omega_{\vec{k}\nu}(1 - 2n_{\vec{k}\nu}) - \frac{1}{2} \sum_{\vec{k}} \frac{\Omega^2_{\vec{k}\nu} \theta_{\vec{k}} (1 - 2n_{\vec{k}\nu})}{(\epsilon^2_{\vec{k}\nu} + \mu^2_{\vec{k}})^{1/2}} - \frac{1}{4} \sum_{\vec{k}} \frac{|\Delta(\vec{k})|^2 \theta_{\vec{k}} (1 - 2n_{\vec{k}\nu})}{(\epsilon^2_{\vec{k}\nu} + \mu^2_{\vec{k}})^{1/2}} - \frac{1}{4} \sum_{\vec{k}} \frac{\mu^2_{\vec{k}} (1 - 2n_{\vec{k}\nu})}{(\epsilon^2_{\vec{k}\nu} + \mu^2_{\vec{k}})^{1/2}} \times [\tanh \tfrac{1}{2}\beta \Omega_+(\vec{k}\nu) + \tanh \tfrac{1}{2}\beta(-\Omega_-(\vec{k}\nu)]. \tag{60}$$

Taking the limit of zero temperature, $\beta \to \infty$, $\theta_{\vec{k}} \to 1$, $n_{\vec{k}\nu} \to 0$, then the difference between the total ground-state energy and that of the normal state, i.e.,

$$W_0 = \langle \mathcal{H} \rangle_0 - \left(\text{const} + \frac{1}{2} \sum_{\vec{k}} \Omega_{\vec{k}\nu}\right) = -\frac{1}{2} \sum_{\vec{k}} \frac{\Omega^2_{\vec{k}\nu}}{(\epsilon^2_{\vec{k}\nu} + \mu^2_{\vec{k}})^{1/2}} - \frac{1}{4} \sum_{\vec{k}} \frac{|\Delta(\vec{k})|^2}{(\epsilon^2_{\vec{k}\nu} + \mu^2_{\vec{k}})^{1/2}} - \frac{1}{2} \sum_{\vec{k}} \frac{\mu^2_{\vec{k}}}{(\epsilon^2_{\vec{k}\nu} + \mu^2_{\vec{k}})^{1/2}}, \tag{61}$$

which is responsible for the coherent pairing of excitons. Employing the same approximations as those used for the derivation of Eq. (53) from Eq. (49), we find

$$W_0 = \tfrac{1}{2}(|\Delta|^2 + \mu^2)/U - \tfrac{1}{2}|\Delta|^2/U - \tfrac{1}{2}N(0)\{(E_g + \bar{\omega})[(E_g + \bar{\omega})^2 + |\Delta|^2 + \mu^2]^{1/2} - E_g[E_g^2 + |\Delta|^2 + \mu^2]^{1/2}\}$$

$$-\frac{\mu^2}{U} = -\frac{1}{2} \frac{N(0)\bar{\omega}^2}{\tanh(1/\rho)} \left[\left(1 + \frac{E_g}{\bar{\omega}}\right)^2 + \left(\frac{E_g}{\bar{\omega}}\right)^2 - 2\left(\frac{E_g}{\bar{\omega}}\right)\left(1 + \frac{E_g}{\bar{\omega}}\right) \frac{1}{\cosh(1/\rho)}\right] - \frac{\mu^2}{2U}, \tag{62}$$

where $\Delta \equiv \Delta(0)$ and $U \equiv U(0)$. At resonance or near resonance where $(E_g/\bar{\omega}) \ll 1$, Eq. (62) is reduced to

$$W_0 \approx -\frac{1}{2} \frac{N(0)\bar{\omega}^2}{\tanh(1/\rho)} - \frac{\mu^2}{2U}. \tag{63}$$

The first term in Eq. (63) is similar to that for superconductors.[12]

Finally, we define the biexciton operators

$$\gamma_{\vec{q}\nu} = b_{\vec{q}\nu} b_{-\vec{q}\nu}, \quad \gamma^\dagger_{\vec{q}\nu} = b^\dagger_{-\vec{q}\nu} b^\dagger_{\vec{q}\nu}.$$

These operators satisfy the commutation relations

$$[\gamma_{\vec{q}\nu}, \gamma^\dagger_{\vec{q}'\nu'}]_- = (1 - b^\dagger_{\vec{q}\nu} b_{\vec{q}\nu} - b^\dagger_{-\vec{q}\nu}) \delta_{\vec{q}\vec{q}'} \delta_{\nu\nu'},$$

$$[\gamma_{\vec{q}\nu}, \gamma_{\vec{q}'\nu'}]_- = 0,$$

$$[\gamma_{\vec{q}\nu}, \gamma_{\vec{q}'\nu'}]_+ = 2\gamma_{q\nu}\gamma_{q'\nu'}(1 - \delta_{\vec{q}\vec{q}'}\delta_{\nu\nu'}),$$

which are analogous to those for the Cooper pairs.[12]

V. DISCUSSION

We have considered that physical process where two excitons with opposite wave vectors interact to form a bound state in a molecular solid.[26] It is found that such a process is feasible provided that the electromagnetic field is at resonance or near resonance, i.e., when the effective energy gap E_g is less than the width of the exciton band (or equivalently the binding energy of the exciton) and that the induced by the field dielectric gap must be less than that for the biexciton state. When the favorable conditions are satisfied then below the critical temperature T_c given by Eq. (58b), a phase transition exists similar to that occurring in superconductors. However, superconductivity is not expected to arise because of the neutrality of the electron-hole pairs. The new phase can be described as a condensate of bound exciton pairs due to the effective attractive interaction between them. According to Kohn and Sherrington,[27] when bound complexes consisting of equal numbers of electrons and their holes condense, the resultant state is not a superfluid. Such systems exhibit long-range order in the coordinate space[16,27] (diagonal long-range order) but they lack the off-diagonal one[16,28]; for further details we refer to Ref. 27.

Thus under favorable conditions, i.e., when $E_g < \bar{\omega}$ and $\mu < \Delta_0$, the excitation spectrum consists of two intense narrow lines peaked at frequencies $\Omega_+(\vec{k}\nu)$ and $\Omega_-(\vec{k}\nu)$, respectively, the splitting of which is equal to $\epsilon_{\vec{k}\nu}$ given by Eq. (41). The observation of such an excitation spectrum will imply the existence of bound exciton pairs and will shed new light on the dynamical properties of excitons. Since scattering effects arising from the participation of phonons or impurities have not been considered, our results are applicable at rather low temperatures and for pure crystals. We hope that the present study will stimulate experimental interest for the investigation of the excitation spectrum of molecular crystals under the influence of a resonant electromagnetic field.

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*Issued as NRCC No. 13970

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