EFFECTIVE ELECTRON-HOLE INTERACTION IN MOLECULAR CRYSTALS. III. TWO EXCITON DISSOCIATION TERMS*

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An effective electron-hole interaction is investigated which arises due to the two--exciton dissociation terms of the Hamiltonian. The Fröhlich-type unitary transformation is adopted and the transformed Hamiltonian is discussed. Effective exciton-exciton and electron-hole interactions are demonstrated to appear. The sign and strength of the effective electron-hole interaction is found to depend on the energy difference between the exciton pair and electron-hole pair states. The results are compared with those obtained in the previous papers for single-exciton dissociation terms. Possibilities of experimental verification are discussed.

1. Introduction

The interactions between electrons and holes in crystals are of considerable interest and are extensively studied [1–7]. These interactions are essential in determining the energy levels of the Wannier-Mott excitons. They are also expected to influence the equilibrium charge carrier concentration, recombination kinetics and energies of localized charge--transfer states in molecular crystals.

The studies were, so far, concerned mainly with interaction via the polarizable phonon field [1–5], and were usually confined to polar semiconductors [1–4].

The interactions via the exciton field [6, 7] were apparently less thoroughly studied, though the important role of excitons in electrical properties of molecular solids is at present indisputable [8–10]. In particular, charge carrier creation in molecular crystals is known to occur due to the one- and two-particle dissociation of the Frenkel excitons [8–12].

The same matrix elements which are relevant to exciton dissociation also give rise to the specific electron-hole interaction.

In the previous papers of this series [13, 14] we considered the interaction via the single-exciton dissociation terms of the Hamiltonian. The present paper is devoted to the interaction via the terms corresponding to the annihilation of two excitons from the same or from different exciton bands. Such dissociation processes were proposed to account for the photoconductivity of an anthracene crystal upon irradiation with light of energy below 3.9 eV [15–18]. The semiempirical calculations of the corresponding rate constants were confirmed by experimental results [19, 20].

2. The Hamiltonian and its transformation

Let us assume the system of electrons, holes and excitons to interact according to the model Hamiltonian [11, 12]

$$H = H_0 + H_1, \tag{1}$$

$$H_0 = \sum_k \left[E^\alpha(k) B^+_{\alpha k} B_{\alpha k} + (1 - \delta_{\alpha\beta}) E^\beta(k) B^+_{\beta k} B_{\beta k} + E^e(k) A^+_k A_k + E^h(k) C^+_k C_k \right], \tag{2}$$

$$H_1 = \sum_k \left[T(k, p, q) B_{\alpha k} B_{\beta p} A^+_{k-q} C^+_{p+q} + T^*(k, p, q) C_{p+q} A_{k-q} B^+_{\beta p} B^+_{\alpha k} \right], \tag{3}$$

where $B^+_{\alpha k}, B^+_{\beta k}, A^+_k, C^+_k$ are the creation operators for an exciton species α, β, for an electron and a hole in the Bloch states of quasimomentum k, with corresponding band energies $E^\alpha(k), E^\beta(k), E^e(k), E^h(k)$, respectively. $B_{\alpha k}, B_{\beta k}, A_k, C_k$ are the corresponding annihilation operators.

$$T(k, p, q) = \langle \psi_{ex,\alpha}(k) \psi_{ex,\beta}(p) | \hat{V} | \psi_e(k-p) \psi_h(p+q) \rangle,$$

with $\psi_{ex,\alpha,\beta}(k)$, $\psi_e(k)$, $\psi_h(k)$ standing for the wavefunctions of an exciton from the band α, β, an electron and a hole, respectively.

The interaction Hamiltonian H_1 (3) describes the dissociation of the exciton pair into an electron-hole pair. If $\alpha = \beta$, both excitons are from the same band (singlet-singlet or triplet-triplet annihilation), if $\alpha \neq \beta$ the excitons are derived from different bands as e.g. in the case of singlet-triplet exciton annihilation. The Hamiltonian (3) permits one to treat both cases on an equal footing.

The matrix elements $T(k, p, q)$ have been calculated by Choi and Rice [15, 16] for singlet-singlet annihilation, and by Kearns for triplet-triplet and singlet-triplet annihilation processes [17].

To simplify the calculations we are neglecting the other interactions, e.g. the Coulomb electron-hole, electron-electron and hole-hole, and kinematical exciton-exciton interaction, since they are not essential for our treatment. We will confine ourselves to low excitation densities. Hence, we will approximate the Pauli commutation relations for exciton operators by the boson relations. For electrons and holes we assume the usual fermion anticommutation relations.

We also assume the rigid lattice model and disregard the coupling to intramolecular vibrations [11, 12].

Now, we remove the interaction (3) up to the terms linear in $T(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q})$ by means of the unitary transformation

$$U = \exp(iS), \tag{4}$$

$$S = \sum_{k,p,q} [\varphi(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q}) B_{\alpha k} B_{\beta p} A^+_{k-q} C^+_{p+q} + \varphi^*(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q}) C_{p+q} A_{k-q} B^+_{\beta p} B^+_{\alpha k}], \tag{5}$$

where

$$\varphi(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q}) = \frac{-iT(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q})}{E^{\alpha}(\boldsymbol{k}) + E^{\beta}(\boldsymbol{p}) - E^{e}(\boldsymbol{k} - \boldsymbol{q}) - E^{h}(\boldsymbol{p} + \boldsymbol{q})}. \tag{6}$$

The transformed Hamiltonian reads

$$H = e^{-iS} H e^{iS} = H_0 + H^{\text{ex}-\text{ex}} + H^{\text{e}-\text{h}} + H^{\text{ex}-\text{e}} + H^{\text{ex}-\text{h}} + \text{higher order terms} \tag{7}$$

$$H_0 = \sum_{k} [E^{\alpha}(\boldsymbol{k}) B^+_{\alpha k} B_{\alpha k} + (1 - \delta_{\alpha\beta}) E^{\beta}(\boldsymbol{k}) B^+_{\beta k} B_{\beta k} + E^{e}(\boldsymbol{k}) A^+_k A_k + E^{h}(\boldsymbol{k}) C^+_k C_k] \tag{8}$$

$$H^{\text{ex}-\text{ex}} = \sum_{k,p,q,k'} X(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q}, \boldsymbol{k}', \boldsymbol{p}+\boldsymbol{k}-\boldsymbol{k}', \boldsymbol{k}'+\boldsymbol{q}-\boldsymbol{k}) B^+_{\beta, p+k-k'} B^+_{\alpha k'} B_{\alpha k} B_{\beta p}, \tag{9}$$

$$H^{\text{e}-\text{h}} = -\sum_{\substack{k,p,q,\\k',p',q'}} [\delta_{kk'} \delta_{pp'} X(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q}, \boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q}')$$

$$+ \delta_{\alpha\beta} \delta_{kp'} \delta_{pk'} X(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q}, \boldsymbol{p}, \boldsymbol{k}, \boldsymbol{q}') + X(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q}, \boldsymbol{k}', \boldsymbol{p}', \boldsymbol{q}')(\delta_{pp'} B^+_{\alpha k} B_{\alpha k} + \delta_{kk'} B^+_{\beta p'} B_{\beta p}$$

$$+ \delta_{\alpha\beta} \delta_{pk'} B^+_{\alpha p'} B_{\alpha k} + \delta_{\alpha\beta} \delta_{kp'} B^+_{\alpha k'} B_{\alpha p}] A^+_{k-q} A_{k'-q'} C^+_{p+q} C_{p'+q'}, \tag{10}$$

$$H^{\text{ex}-\text{e}} = -\sum_{\substack{k,p,q\\k',p'}} X(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q}, \boldsymbol{k}', \boldsymbol{p}', \boldsymbol{p}+\boldsymbol{q}-\boldsymbol{q}') B^+_{\beta p'} B^+_{\alpha k'} B_{\alpha k} B_{\beta p} A^+_{k-q} A_{k'+q'-p-q} \tag{11}$$

$$H^{\text{ex}-\text{h}} = -\sum_{\substack{k,p,q,\\k',p'}} X(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q}, \boldsymbol{k}', \boldsymbol{p}', \boldsymbol{k}'+\boldsymbol{q}-\boldsymbol{k}) B^+_{\beta p'} B^+_{\alpha k'} B_{\alpha k} B_{\beta p} C^+_{p+q} C_{p'+k'+q-k}, \tag{12}$$

where

$$X(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q}, \boldsymbol{k}', \boldsymbol{p}', \boldsymbol{q}') = \frac{1}{2} \left[\frac{T(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q}) T^*(\boldsymbol{k}', \boldsymbol{p}', \boldsymbol{q}')}{E^{\alpha}(\boldsymbol{k}') + E^{\beta}(\boldsymbol{p}') - E^{e}(\boldsymbol{k}' - \boldsymbol{q}') - E^{h}(\boldsymbol{p}' + \boldsymbol{q}')} \right.$$

$$+ \left. \frac{T^*(\boldsymbol{k}, \boldsymbol{p}, \boldsymbol{q}) T(\boldsymbol{k}', \boldsymbol{p}', \boldsymbol{q}')}{E^{\alpha}(\boldsymbol{k}) + E^{\beta}(\boldsymbol{p}) - E^{e}(\boldsymbol{k} - \boldsymbol{q}) - E^{h}(\boldsymbol{p} + \boldsymbol{q})} \right]. \tag{13}$$

3. Consequences

From the formulae of Section 2 the following conclusions can be drawn:

1. Some interaction arises between the excitons owing to the coupling with charge carriers via the two-particle dissociation terms of the Hamiltonian (3). In contrast to the situation encountered for the one-particle dissociation terms [13], renormalization of free exciton energies does not occur.

2. In the Hamiltonian terms corresponding to the direct interaction between electrons and holes appear. This interaction is due to "dressing" of charge carriers in exciton clouds, and is operative via the mutual deformation of the clouds. If the ionic pair state is close on the energy scale to the exciton pair state, the interaction can be quite strong[1]. The sign of the interaction depends on the energy difference between the exciton pair and electron hole pair: the interaction is attractive if the ionic pair state lies below the exciton pair state, and is repulsive otherwise.

It is interesting to note that some additional terms arise if $\alpha = \beta$. They are due to the noncommutativity of the corresponding exciton operators.

The electron-hole interaction Hamiltonian contains some terms proportional to the number of excitons. They can be interpreted as the interaction via real instead of virtual excitons. It is however of minor importance for low exciton densities.

3. Effective exciton-electron and exciton-hole interactions also appear. They depend on the third power of the density of excitations in the crystal, and are therefore of secondary importance for low excitation densities.

The effects of vibronic coupling can be studied starting from the effective Hamiltonians derived by Zgierski [11, 12]. It results that an additional effective electron-hole interaction is operative due to the combined coupling of charge carriers to exciton and phonon subsystems. Consequently, the matrix elements are renormalized and some terms appear which correspond to the electron-hole scattering assisted by absorption or emission of a phonon. In addition to the terms proportional to $(E+E-E^e-E^h)^{-1}$, vibronic coupling yields the terms of the type $[(E+E-E^e-E^h)^2-\omega^2]^{-1}$, ω being the phonon frequency. These terms may become important if the energy separation between the two-exciton state and electron-hole pair is of the order of a vibrational quantum. The calculations are hardly worth presenting: they are elementary but tedious, and completely parallel to those performed in [13].

4. A special case

To get the explicit form of the interaction one is obliged to specify the form of energy bands and matrix elements.

We will consider in more detail the model of a linear crystal. We assume narrow band approximation for electrons and holes

$$E^e(k) = E^e; \quad E^h(k) = E^h,$$

and nearest-neighbour approximations for excitons

$$E^{\alpha,\beta}(k) = E^{\alpha,\beta}+R^{\alpha,\beta}\cos ka,$$

where a is the lattice period, R is exciton transfer integral.

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[1] Obviously, the present formulation is justified only as long as the non-degenerate perturbation theory is valid.

We also assume the nearest-neighbour interaction model for the matrix elements T, i.e. in the coordinate representation

$$T(e, b, c, d) = \langle \psi_{\text{ex},\alpha}(e)\psi_{\text{ex},\beta}(b) \,|\, \hat{V} \,|\, \psi_{\text{e}}(c)\psi_{\text{h}}(d) \rangle$$

$$= T(\delta_{ec}\delta_{bd} + \delta_{ed}\delta_{bc})(\delta_{e,b+1} + \delta_{e,b-1}), \tag{14}$$

with e, b, c, d running over positions of the molecules.

According to the notation of Section 2, we get in the momentum representation

$$T(k, p, q) = \frac{2T}{N}[\cos qa + \cos[(p+q-k)a]\}, \tag{15}$$

where N is the number of molecules in the crystal.

Neglecting the exciton-dependent contributions in (10), we get e.g. for the case $\alpha \neq \beta$

$$H^{\text{e-h}} = -\sum_{k,p,q,q'} X(k, p, q, k, p, q')A^{+}_{k-q}A_{k-q'}C^{+}_{p+q}C_{p+q'}, \tag{16}$$

with

$$X(k, p, q, k, p, q') = \frac{2T^2}{N^2}\{\cos qa + \cos[(p+q-k)a]\}$$

$$\times \{\cos q'a + \cos[(p+q'-k)a]\}(\Delta E + R^{\alpha}\cos ka + R^{\beta}\cos pa)^{-1}, \tag{17}$$

$$\Delta E = E + E - E^{\text{e}} - E^{\text{h}}.$$

The interaction does not resemble the usual Coulomb interaction term of the type $|q-q'|^{-2}$. In the limit of narrow exciton bands $(R \to 0)$, the interaction consists in coordinate representation of a few strongly localized terms. The range of the interaction becomes longer if $R \simeq \Delta E$.

In molecular crystals however, $R \ll E$ is in many cases a reasonable approximation, especially when triplet excitons are considered. The effective interaction is therefore essentially short-range, and quickly decreases with increasing distance. It has no relation to the direct Coulomb electron-hole attraction.

5. Discussion

We demonstrated for a simple model that the two-exciton dissociation terms of the Hamiltonian give rise to an effective interaction of electrons and holes, which adds to the Coulomb term. The corresponding matrix elements are certainly nonzero, since they give rise to the experimentally observed photoconductivity of molecular crystals. They were also calculated by means of semiempirical methods [15–17].

The strength and sign of the interaction depend on the energy difference between the two-exciton and electron-hole pair states.

As follows from this paper and from the previous ones [13, 14], in molecular crystals a variety of non-Coulomb interactions between electrons and holes can be operative due to small energy gaps between the exciton states and electron-hole pair states.

The interactions mentioned above are usually short-range ones. They should affect the energies of charge transfer states. This effect may be especially important for the possible creation of CT states in the electric field of charged defects [21, 22] owing to the enormous sensitivity of this process to changes in energy separation between the CT and exciton states.

Perhaps the existence of the interaction under consideration can be verified by observing the structure of CT states in the crystal. The states lying close to the Frenkel exciton states (or to the energy of an exciton pair) should acquire an additional stabilization (below exciton energy) or destabilization (above exciton energy). The electroreflectance studies [23] seem to be a promising tool. The anomalies should in the future be possible to observe experimentally when the methods of studying e.g. Wannier-Mott excitons in molecular crystals become feasible.

The additional interaction should also affect the recombination rates. In this aspect the theory can be checked by experimental studies of the dependence of recombination kinetics on energy of charge carriers produced e.g. by high energy radiation. We would expect considerable changes in recombination rates for electron+hole energies close to a Frenkel state, or to the biexciton state.

The one-exciton dissociation terms were demonstrated to give some contributions to the effective electron-hole interaction which depended on the concentration of excitons [13]. This situation was encountered only if fermion anticommutation relations for excitons (linear crystal) were assumed, or if vibronic coupling was taken into account. On the contrary, the two-particle dissociation terms yield the exciton-dependent contributions even in the absence of vibronic coupling, and if excitons are treated as bosons (low exciton concentration limit).

The occurrence of the above-described interaction can therefore be revealed by studying the dependence of electron-hole recombination rates on exciton concentration.

Karl and Sommer [24] in their study of recombination kinetics have obtained strange results when strongly absorbed light was used to generate the charge carriers. The results have been interpreted in terms of trapping which prevented a rapid separation of charge carriers in the electric field. The same effect should however result from the additional electron-hole attraction. Furthermore, the exciton-dependent terms of (10) should increase the dependence of recombination kinetics on whether the light is weakly or strongly absorbed (low or high exciton concentrations in the excitation layer). An alternative interpretation of the results [24], based on exciton-dependent electron-hole interaction seems therefore possible.

The additional interactions should affect the concentration of equilibrium charge carriers. This effect is however expected to be less well pronounced since the interaction energies are small compared to the energy gap between the valence and conduction bands.

We hope future experimental research will prove or disprove the expectations presented above.

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