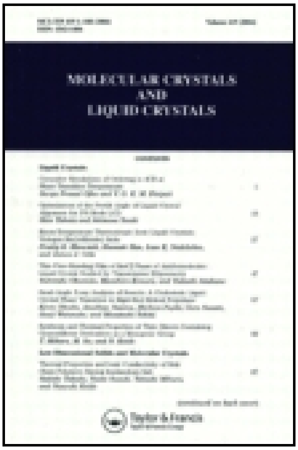

Molecular Crystals and Liquid Crystals

Stability of coupled exciton-electronic complexes in one-dimensional molecular chain

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STABILITY OF COUPLED EXCITON-ELECTRONIC COMPLEXES IN ONE-DIMENSIONAL MOLECULAR CHAIN

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The generalized Green functions method is applied to calculate the coupling energy of three-particle electron-hole complexes in an one-dimensional molecular chain depending on the ratio of electron and hole masses. The problem of stability of such complexes is discussed.

Keywords: exciton-electronic complexes; molecular chain; Green function

INTRODUCTION

Exciton-electronic complexes (EEC) have gained much interest over the last few decades due to the their important role in the both energy and charge transport in organic nature [1]. Superradiance of Frenkel exciton in linear systems [2] and photoinduced absorption in conjugated polymers [3] are only some of aspects of this deep and interesting problem. Recently, the exhibition of EEC has been intensively studied for quantum- and low-dimensional structures (see, e.g., [4,5]), where they becomes more stable, in part because the reduced dimensionality leads to relatively larger binding energies. It results, in particular, from the studies of the charged photoexcitations in thiophene-based molecular semiconductors [6].

It is well known that the complex of Frenkel exciton and electron can form the coupled states in a molecular crystal [7,8]. The stability of such states essentially depends on the mass ratio of an electron and hole in the concrete material. So far, the investigations have been focused mainly on the semiconductors [9], and less well conducted for organic materials. In this communication, some results of theoretical study for simple case of an one-dimensional molecular chain are given.

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MODEL AND METHOD

Let's consider an one-dimensional periodic molecular chain with one molecule in elementary cell, and simple nondegenerate bands whose extrema are located at the center of the Brillouin zone. The excitons are supposed to be able to perform a Bloch-wave-like coherent motion. Let in such chain there is also created arbitrarily the charge carrier, which the energy and wave function can be described within the framework of the tight binding model. The presence of an extra charge at any site polarizes the lattice around of itself, and upon excitation, the exciton can trap to its polarization field and to form the state coupled with it. Consequently, the interaction of two particles has polarization character and decreases with distance faster than r^{-4}.

We shall carry out the theoretical study of the problem in the adiabatic approximation, which implies that the transition frequencies to the states of exciton-charge complex considerably exceed the phonon frequencies. In zero approximation, one may consider molecules are fixed in the certain equilibrium sites, creating the one-dimensional lattice. Let's neglect the interaction of both the electron and Frenkel exciton with the lattice vibrations [10]. Then using the Heitler-London approach, the Hamiltonian of the system in the notation of second quantization can be written down as follows:

$$\begin{aligned}\hat{H} = E_0 + \sum_{\mathbf{n}} \Delta_{\mathbf{n}} \hat{B}_{\mathbf{n}} + \hat{B}_{\mathbf{n}} + \sum_{\mathbf{n} \neq \mathbf{m}} M_{\mathbf{nm}} \hat{B}^{+}_{\mathbf{n}} \hat{B}_{\mathbf{m}} \\ + \sum_{\mathbf{m}} \varepsilon_{\mathbf{m}} \hat{F}^{+}_{\mathbf{m}} \hat{F}_{\mathbf{m}} + \sum_{\mathbf{n} \neq \mathbf{m}} N_{\mathbf{nm}} \hat{F}^{+}_{\mathbf{n}} \hat{F}_{\mathbf{m}} + \sum_{\mathbf{n} \neq \mathbf{m}} V_{\mathbf{nm}} \hat{B}^{+}_{\mathbf{n}}\ \hat{B}_{\mathbf{n}} \hat{F}^{+}_{\mathbf{m}} \hat{F}'_{\mathbf{m}}\end{aligned} \tag{1}$$

where E_0 is the energy of the nonexited crystal, $\Delta_N(\varepsilon_{\mathrm{m}})$ is the formation energy of exciton (electron) in site **n(m)** with zero quasi-momentum, $M_{\mathbf{nm}}(N_{\mathbf{nm}})$ is the matrix element of resonant interaction, describing migration of an exciton (electron) between molecules with coordinates **n** and **m**, $\hat{B}^{+}_{\mathbf{n}}(\hat{B}_{\mathbf{n}})$ are the Bose operators for exciton creation (annihilation), $\hat{F}^{+}_{\mathbf{n}}(\hat{F}_{\mathbf{n}})$ are the Fermi operators for electron creation (annihilation), and $V_{\mathbf{nm}}$ is the matrix element of the interaction potential between exciton and electron.

To find the energy spectrum of coupled states of two particles it is necessary to solve the appropriate Schrödinger equation. It is best to do using the generalized Green functions method for a two-particle problem. Then we obtain the set of equations for the probability amplitude of two particles localization on different lattice sites, which has a nontrivial solution under the condition that

$$\det|\tilde{G}_{\mathbf{r},\mathbf{r}'}\ (\mathbf{k}) \mathbf{V}_{\mathbf{r}',\mathbf{0}}\ - \delta_{\mathbf{r},\mathbf{r}'}| = 0. \tag{2}$$

Here $\mathbf{r} = \mathbf{n} - \mathbf{m}$, $\delta_{\mathbf{r},\mathbf{r}'}$ is the Kronecker symbol, the function $\tilde{G}_{\mathbf{r},\mathbf{r}'} = G_{\mathbf{r},\mathbf{r}'} - G_{\mathbf{r},\mathbf{0}} G^{-1}_{\mathbf{0},\mathbf{0}} G_{\mathbf{0},\mathbf{r}'}$ is expressed through the usual lattice Green function $G_{\mathbf{r},\mathbf{r}'}$ of an unperturbed problem, but excludes the exciton localization on the charged molecule. It is realized for the case, when the concentration of excitons and electrons is not so high, that it was necessary to take into consideration the kinematic interaction, responsible for a strong repulsion of two particles on the same lattice site

Using the method of the residue theory, the Green function for an one-dimensional molecular chain can be calculated exactly for any distances between interacting molecules [11]. However, because the probability amplitude of exciton and electron localization becomes greatest for the adjacent sites, such calculation is performed in a most simply way in the nearest neighbor approximation.

RESULTS AND DISCUSSION

Taking into account only two neighboring molecules, equation (2) reduces to: $\tilde{G}_{\pm 1;0} V_{\pm 1;0} = 1$. Let's introduce now the following notation:

$$\begin{aligned} E &= E_{ex-el} - \Delta - \varepsilon, \\ \Omega_{\pm 1;0} &= 2\sqrt{M^2_{\pm 1;0} + N^2_{\pm 1;0} + 2M_{\pm 1;0} N_{\pm 1;0}\ \cos ka}, \end{aligned} \tag{3}$$

where E_{ex-el} is the coupling energy of the exciton with the electron to be defined, k is the component of quasiparticle momentum along the molecular chain, and the lattice constant. Then for the case, when $\mathrm{E}^2 > \mathbf{\Omega}^2$, the simplest Green function can be obtained in the form

$$\tilde{G}_{\pm 1:0} = \frac{1}{\sqrt{E^2 - \Omega^2_{\pm 1;0}}} \left[1 - \frac{\left(E - \sqrt{E^2 - \Omega^2_{\pm 1;0}} \right)^2}{\Omega^2_{\pm 1;0}} \right]. \tag{4}$$

The matrix element of resonant interaction for structures with one molecule in an elementary cell can be presented for an exciton and electron, accordingly, as

$$M_{\pm 1;0} = d^2_{ex} a^{-3}(1 - \cos^2 \psi_{ex}), \quad N_{\pm 1;0} = d^2_{el} a^{-3}(1 - \cos^2 \psi_{el}), \tag{5}$$

where d_1 is the dipole moment for the exciton (or electron) transition to the l-th state, ψ_l is the angle between directions of the molecular chain and of the dipole moment. Let's consider for simplicity, that d_l are orientated transversely to the direction of a chain, and the oscillator strengths $(F_{ex} \approx F_{el} \equiv F_l)$ and transition frequencies $(\omega_{ex} \approx \omega_{el} \equiv \omega_l)$ to the l-th

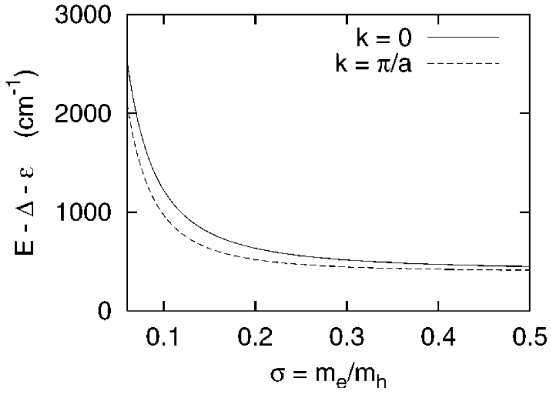

FIGURE 1 The dependence of coupling energy of the exciton-electronic complex vs the ratio of effective electron and hole masses in 1D molecular chain.

state are approximately equal. Then for the points of band extrema ($k = 0$, π/a), we arrive finally at the expression for the coupling energy of the EEC:

$$E_{ex-el} - \Delta - \varepsilon = V_{\pm 1;0} + \frac{1}{V_{\pm 1;0}}\left(\frac{e^2 hF_l}{2a^3 m_h \omega_l}\right)^2 \left(\frac{1}{\sigma} \pm \frac{1}{1+\sigma}\right)^2 \tag{6}$$

where $V_{\pm 1;0}$ is the interaction energy between exciton and electron placed on the lattice sites with numbers 0 and $\pm 1; \sigma = m_e/m_h, m_e, m_h$ are the electron and hole masses, respectively. The plus sign in the above equation is taken for the top of exciton-electronic band, while the minus sign applies to the bottom of it. The formula (6) is obtained provided that the polarization interaction between an exciton and electron considerably exceeds their total resonance interaction.

As it is seen from the equation (6) the coupling energy of the EEC is positive for the wide range of the mass ratio $\sigma \in [0, \infty]$. Thus, for one-dimensional molecular chain, under the condition mentioned above, one can consider the coupled EEC as stable one.

The dependence of the coupling energy of the EEC on the mass ratio σ is given in Figure 1. The calculations were performed with the next parameters: $V = 400\,\mathrm{cm}^{-1}$, $\omega_l = 10^{15}\,\mathrm{sec}^{-1}$, F = 0.1, $m_h = 10m_0$, a = $4A$.

As it is visible from the figure, the decrease of coupling energy with σ is more smoothly varying for $k \to 0$. The coupling energy is minimal for small quasi-momentums, when the hole mass verges towards to the electron one (that is for the limiting case of positronium atom), and further monotonously grows with increasing the mass difference. In the other limiting case (hydrogen atom), when the holes mass exceeds considerably the electron mass, the coupling energy of an electron and exciton becomes maximal.

REFERENCES

[1] Spectroscopy and Excitation Dynamics of Condensed Molecular Systems, ed. (1983) by Agranovich, V. M., & Hochstrasser, R. M., (North-Holland: Amsterdam).

[2] Tokihiro, T., Manabe, Y., & Hanamura, E. (1993). Superradiance of Frenkel exciton in linear systems. *Phys. Rev. B.*, *47*, 2019–2030.

[3] Shimoi, Y., & Abe, S. (1994). Theory of triplet exciton polaron and photoinduced absorption in conjugated polymers. *Phys. Rev. B.*, *49*, 14113–14121.

[4] Xie, W., & Chen, C., (2000). Excitonic trion X- in GaAs quantum dots. *Physica E.*, *8*, 77–80.

[5] Tomioka, A., & Miyano, K. (1996). Numerical study of excitons in a two-dimensional dye aggregate. *Phys. Rev. B.*, *54*, 2963–2967.

[6] Rossi, L., Lanzani, G., & Garnier, F., (1998). Charged photoexcitations in Thiophene-based molecular semiconductors. *Phys. Rev. B.*, *58*, 6684–6687.

[7] Bader, G., Caron, L., & Sanche, L. (1981). Electron-exciton complex formation in organic solids. *Solid State Commun.*, *38*, 849–851.

[8] Singh, J. (1981). Formation of complex charge carrier due to the interaction between a free Frenkel exciton and excess electron in molecular crystals. *Phys. stat. sol. (b).*, *103*, 423–428.

[9] Insepov, Z. A., & Norman, G. E. (1975). Three-particle charged electron-hole complexes in semiconductors. *ZETP.*, *69*, 1321–1324.

[10] Bronold, F. X., & Bishop, A. R. (1996). Nonlinear Optics of conjugated polymers: a coupled exciton-phonon gas approach. *Phys. Rev. B.*, *53*, 13456–13476.

[11] Grigorchuk, N. (1966). Light absorption coefficient for the transition into bound electron-exciton states of the one-dimensional molecular structures. *Solid State Commun.*, *98*, 1099–1100.