

Haldane Model and Molecular Excitons' Spectra

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Abstract. Haldane model is devoted to explore the electron spectra of honeycomb hexagonal 2D lattice. In this paper we treat its connections with the excitonic spectra of two types of molecular excitations, Frenkel excitons (FEs) and Charge Transfer Excitons (CTEs) and study the generalized Haldane model in 2D lattices. Excitations with transition dipole moments perpendicular to the lattice or with in-plane moments are considered in the following cases: a) FEs in simple quadratic 2D lattices and FEs in honeycomb model with two identical nonequivalently positioned molecules in unit cell; b) FEs and CTEs coupling in Donor-Acceptor (DA) solids with two different molecules in unit cell; c) indirect coupling of FEs in DA solids via their coupling with CTEs. The equations for the excitonic spectra, especially in case c, could be used in more precious interpretation of spectroscopic data or in other applications of Haldane model.

KEY WORDS: Frenkel and Charge Transfer Excitons, Donor-Acceptor Solids, Haldane model

1 Introduction

The topic of Haldane model [1] is the impact of topology of 2D honeycomb lattice on the electronic spectra and corresponding explanation of the quantum Hall effect. This model includes the topology trivial coupling between the nearest neighbors and topologically non-trivial coupling with the second neighbors of one sublattice. Haldane model has been used in theoretical explorations of graphene [2] as well as in the studies of topological photonic systems [3].

In the present paper we try to connect this model and our previous investigations on excitonic spectra of 2D hexagonal and square lattices [4–7]. In the study we obtain new point of view on the excitonic model and we treat new more complicated problems. On the other hand, our generalization of Haldane model in-

roduces vector character of coupling (hopping) parameters for excitations with perpendicular to 2D-plane transition moments or in-plane transition moments. A little surprise is the opportunity for indirect coupling of excitons between the nearest Donor-Acceptor (DA) neighbors

Two types of molecular excitons are treated in our study: (i) Frenkel excitons (FEs) which are transferable electronic excitations of neutral molecules (see Ref. [8–10]); (ii) Charge Transfer excitons (CTEs) which represent a pair of positive and negative molecular ions situated on neighbor lattice sites. We consider CTEs in Donor-Acceptor (DA) solids with two different ionized molecules (see Ref. [10–12]).

Our models possess hexagonal symmetry (as it is in Ref. [1]) with two molecules in unit cell or square symmetry. The two molecules can be identical nonequivalently positioned or different molecules in the case of DA solids.

The outline of the paper is the following: in Section 2 we consider the case of simple quadratic lattice and of two identical nonequivalently positioned molecules in unit cell of hexagonal symmetry and obtain the spectra of FEs for excitations with transition dipole moments perpendicular or parallel to the layers. Section 3 is devoted to DA solids with two different molecules in unit cell. The interaction between Donor and Acceptor molecules can produce CTEs which connect nearest neighbors. As a result the equation for FEs-CTEs spectra is cubic or more complicated. In Section 4 the indirect coupling of FEs via CTEs is analyzed. Section 5 contains some concluding remarks.

2 Haldane Model of FEs with Identical Molecules

2.1 Square symmetry

The scheme of a simple quadratic 2D lattice is represented in Figure 1. Dipole active FEs will be treated in this paper (x -, y -, z -FEs correspond to the direction of their transition dipole moment). We consider the case of intermolecular transfer of the molecular excitation as a result of transition dipole coupling and we use well known formula for potential energy of two electric dipoles ($\vec{p}_1, \vec{p}_2$) spaced at radius-vector $\vec{r}$

$$V = \frac{\vec{p}_1 \cdot \vec{p}_2 r^2 - 3(\vec{p}_1 \vec{r}) \cdot (\vec{p}_2 \vec{r})}{4\pi\epsilon_0 r^5} \quad (\epsilon_0 = 8.85 \times 10^{-12} \text{ F/m}). \quad (1)$$

Two types of dipole-active FEs are manifested:

(a) z -excitons with transition dipole moment p_z normal to the layer. Their parameter of “trivial coupling” between the nearest neighbors is V_1 , equal for four neighbors of each molecule and topologically trivial coupling is the following:

$$W_{\text{tr}}^{(z)}(k_1, k_2) = 2V_1 [\cos(k_1 a) + \cos(k_2 a)], \quad (2)$$

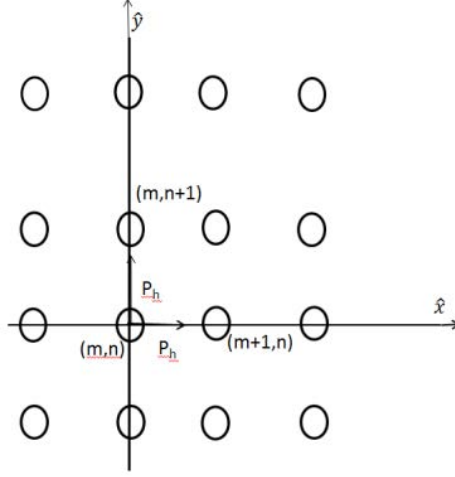


Figure 1. Scheme of a simple quadratic 2D lattice with lattice constant a . Axis $\hat{x}$ and $\hat{y}$ are orthogonal, axis $\hat{z}$ is perpendicular to $(\hat{x}, \hat{y})$, P_h is a transition dipole moment parallel to the layer of x - and y -excitons.

where $V_1 = p_z^2/(4\pi\epsilon_0 a^3)$ (a being lattice constant). Topologically nontrivial coupling with the next “second” neighbors located at diagonal nodes of the molecule (m, n) is the following:

$$\begin{aligned} W_{\text{non}}^{(z)}(k_1, k_2) &= 2V_2 [\cos[(k_1 - k_2)a] + \cos[(k_1 + k_2)a]] \\ &= 4V_2 \cos(k_1 a) \cos(k_2 a), \end{aligned} \quad (3)$$

where $V_2 = p_z^2/(4\pi\epsilon_0 a^3 \sqrt{2}^3)$.

The corresponding part of Hamiltonian is:

$$\hat{H}^{(z)}(k_1, k_2) = \left[E_F + W_{\text{tz}}^{(z)}(k_1, k_2) + W_{\text{non}}^{(z)}(k_1, k_2) \right] B_{z,k_1,k_2}^+ B_{z,k_1,k_2}, \quad (4)$$

where E_F is the excitation energy of the molecule.

(b) xy -excitons with transition dipole moment $p_x = p_y = p_h$ parallel to the layer. Due to the isotropy of the quadratic lattice those excitations are degenerate with equal transition dipole moment along orthogonal axis $\hat{x}$ and $\hat{y}$. Using formula (1) one obtains the trivial coupling parameters ($V_x = V_y = V_3 = p_h^2/(4\pi\epsilon_0 a^3)$) and the corresponding terms are as follows:

$$\begin{aligned} W_{\text{tz}}^{(x)}(k_1, k_2) &= 2V_3 [\cos(k_2 a) - 2 \cos(k_1 a)], \\ W_{\text{tz}}^{(y)}(k_1, k_2) &= 2V_3 [\cos(k_1 a) - 2 \cos(k_2 a)]. \end{aligned} \quad (5)$$

Due to the degeneracy of excitations the nontrivial coupling is really nontrivial. Whereas trivial coupling terms (5) do not mix x - and y -excitons, nontrivial cou-

pling connect them. As a result of transition dipole coupling of molecules of diagonal nodes one obtains two types of terms:

- (p_x, p_x) and (p_y, p_y) terms

$$\begin{aligned} V_{xx, \text{non}}^{(1)} &= V_{yy, \text{non}}^{(1)} = 2V_1 \{ \cos[(k_1 + k_2)a] + \cos[(k_1 - k_2)a] \} \\ &= 4V_4 \cos(k_1 a) \cos(k_2 a) \end{aligned} \quad (6)$$

with $V_4 = -V_3\sqrt{2}/8$;

- (p_x, p_y) terms

$$\begin{aligned} V_{xy, \text{non}}^{(2)}(k_1, k_2) &= 2M \{ \cos[(k_1 - k_2)a] - \cos[(k_1 + k_2)a] \} \\ &= 4M \sin(k_1 a) \sin(k_2 a), \end{aligned} \quad (7)$$

with $M = 3V_3\sqrt{2}/8$.

The corresponding part of Hamiltonian is:

$$\begin{aligned} \hat{H}(k_1, k_2) &= \left[E_{F,1} + W_{tr}^{(x)}(k_1, k_2) + V_{xx, \text{non}}^{(1)} \right] B_{x, k_1 k_2}^+ B_{x, k_1 k_2} \\ &\quad + \left[E_{F,1} + W_{tr}^{(y)}(k_1, k_2) + V_{yy, \text{non}}^{(1)} \right] B_{y, k_1 k_2}^+ B_{y, k_1 k_2} \\ &\quad + V_{x, y, \text{non}}^{(2)}(k_1, k_2) \left[B_{x, k_1 k_2}^+ B_{y, k_1 k_2} + h.c. \right], \end{aligned} \quad (8)$$

where $E_{F,1}$ is excitation energy for (x, y) molecular excitations. By using standard procedure for diagonalization one obtains the following excitonic levels E :

$$E(k_1, k_2) = \left(\frac{1}{2} \right) \left[2(E_{F1} + V_{xx, \text{non}}^{(1)}) + W_{tr}^{(x)} + W_{tr}^{(y)} \pm \sqrt{R} \right], \quad (9)$$

where

$$R = \left[W_{tr}^{(x)}(k_1, k_2) - W_{tr}^{(y)}(k_1, k_2) \right]^2 + 64M^2 \sin^2(k_1 a) \sin^2(k_2 a).$$

We insert expressions (5)-(8) in formula (9) and obtain

$$\begin{aligned} E_{1,2}(k_1, k_2) &= E_{F1} - V_3 \left[\cos(k_1 a) + \cos(k_2 a) + \frac{\sqrt{2}}{2} \cos(k_1 a) \cos(k_2 a) \right] \\ &\quad \pm 3V_3 \left\{ [\cos(k_1 a) + \cos(k_2 a)]^2 + \frac{1}{2} \sin^2(k_1 a) \sin^2(k_2 a) \right\}^{1/2}. \end{aligned} \quad (10)$$

Calculations in this subsection represent an example of Haldane model with degeneracy of the excitations. They exhibit also the impact of anisotropy of coupling parameters (V_1, V_2) and (V_3, V_4, M) .

2.2 Honeycomb model

The case of lattice with two identical molecules in unit cell like graphene is closer to the original Haldane model and has been treated in paper [7].

(a) z -excitons: Two identical and nonequivalently positioned molecules 1 and 2 (Figure 2) create FEs spectra with Davydov splitting [8–10]. We denote with $B_{z1}(k)$ and $B_{z2}(k)$ the operators of annihilation of FEs on molecule 1 (1).

Hamiltonian of 2D-crystal for z -excitations can be represented as follows:

$$\hat{H}_z = \sum_{k, \sigma=1,2} [E_F + V_1 f(k)] B_{z\sigma}^+(k) B_{z\sigma}(k) + \sum_k [M_k B_{z1}^+(k) B_{z2}(k) + h.c.] , \quad (11)$$

in which

$$f(k) = 2 [\cos(k_1 \gamma) + \cos(k_2 \gamma) + \cos(k_1 - k_2)] , \quad (12)$$

where $\gamma = a\sqrt{3}/2$, and a being the length of hexagonal lattice vectors $\vec{a}_1$ and $\vec{a}_2$. In this way the terms with $M(\vec{k})$ express “trivial coupling” and those with V_1 – nontrivial coupling. It is easy to find the following relations:

$$V_1 = \frac{p_z^2}{4\pi\epsilon_0 a^3} ; \quad M(k) = \frac{p_z^2 [1 + e^{-ik_1 \gamma} + e^{-ik_2 \gamma}]}{4\pi\epsilon_0 c^3} \quad (13)$$

with $c = a/\sqrt{3}$, see Figure 2.

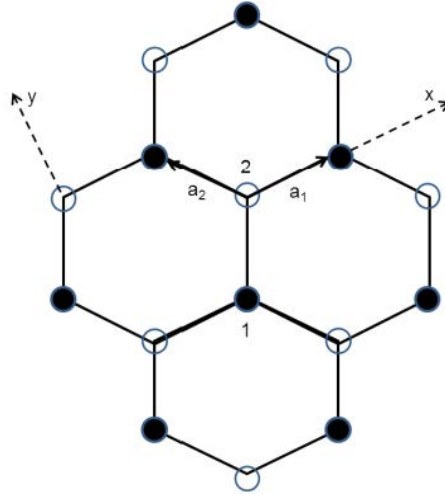


Figure 2. Scheme of Haldane model of graphene-like hexagonal lattice with two identical nonequivalently positioned molecules 1 and 2. Vectors ($\vec{a}_1$, $\vec{a}_2$) are the transition vectors of 2D lattice, axis $\hat{z}$ is normal to the layer.

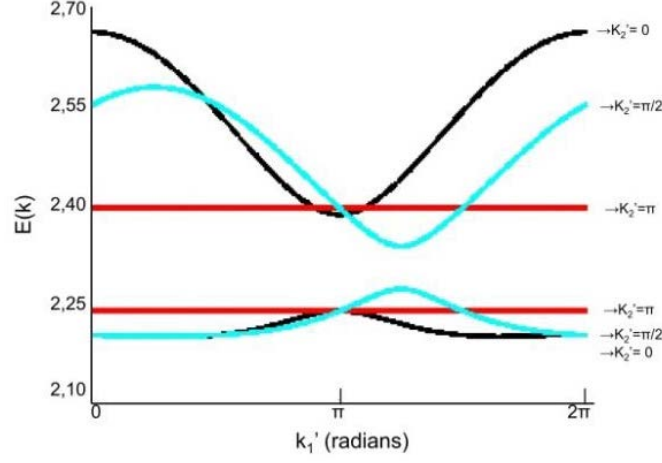


Figure 3. Davydov splitting of z -FEs (formula 14) $E_F = 2.35$ eV, $V_1 = 0.015$ eV, $\varepsilon = 0.04$ eV $k'_i = k_i a \sqrt{3}/2$, $i = 1, 2$.

Here we suppose the case of molecules without mirror symmetry (the case of the plane of layers as mirror plane has been treated also in Ref. [7]). Diagonalization of Hamiltonian (11) gives the following formula for excitonic spectra (and their Davydov splitting):

$$E_z(k) = E_F + V_1 f(k) \pm |M(k)|, \quad |M(k)|^2 = \left[\frac{p_z^2}{4\pi\varepsilon_0 c^3} \right]^2 [f(k) + 3]. \quad (14)$$

Figure 3 illustrates dispersion curves of FEs at different values of $k'_2 = k_2 a \sqrt{3}/2$ for medium value of transition dipole moment p_z ($V_1 = 0.015$ eV). The most interesting effect is relatively big Davidov splitting at $(k_1 = k_2 = 0)$ which will appear in optical phenomena. In our model dispersion curves at $k'_2 = \pi$ are two parallel straight lines.

(b) xy -excitons are degenerate and the equation for their spectra in honeycomb model is quartic. Let introduce two circularly polarized (left and right) electronic excitations in each molecule $\vec{n}$, $\sigma = 1, 2$ using formulas

$$B_{l;r;\sigma}^{(\vec{n})} = \frac{1}{\sqrt{2}} \left[B_{x;\sigma}^{(\vec{n})} \mp i B_{y;\sigma}^{(\vec{n})} \right], \quad (15)$$

in which $B_{x;\sigma}^{(\vec{n})}$ and $B_{y;\sigma}^{(\vec{n})}$ are operators of annihilation of electronic excitations with transition dipole moment p_h along x and y axis, respectively. The transition dipole moment expressed with those new operators is

$$\hat{P}_n = \frac{\hbar}{\sqrt{2}} \left[(e_x - i e_y)(B_{l,\sigma}^{(n)+} + B_{r,\sigma}^{(n)}) + (e_x + i e_y)(B_{r,\sigma}^{(n)+} + B_{l,\sigma}^{(n)}) \right], \quad (16)$$

in which e_x, e_y are unit vectors. We suppose again that the excitonic transfer is a result of dipole-dipole coupling of the transition dipoles (16) of the nearest-neighbor molecules. One obtains the following Hamiltonian in Heitler-London approximation [8, 10]:

$$\begin{aligned} \hat{H}_{l,r} = & \sum_{k,\sigma=1,2} \left\{ [E_{F1} + V_2 f(k)] [B_{l,\sigma}^+(k) B_{l,\sigma}(k) + B_{r,\sigma}^+(k) B_{r,\sigma}(k)] \right. \\ & \left. - 3V_2 [t_1 B_{l,\sigma}^+(k) B_{r,\sigma}(k) + h.c.] \right\} \\ & - \frac{A_3}{2} \sum_k \left\{ [B_{l,2}^+(k) B_{l,1}(k) + B_{r,2}^+(k) B_{r,1}(k)] t_2 + h.c. \right\} \\ & - \frac{3A_3}{2} \sum_k \left\{ B_{l,2}^+(k) B_{r,1}(k) t_3 + B_{l,1}^+(k) B_{r,2}(k) t_4 + h.c. \right\}, \quad (17) \end{aligned}$$

in which

$$\begin{aligned} V_2 &= -\frac{\hbar^2}{8\pi\epsilon_0 a^3}, \quad A_3 = \frac{\hbar^2}{4\pi\epsilon_0 c^3}, \\ t_1 &= \cos(k_1\gamma) + \cos(k_2\gamma) - 2\cos(k_1 - k_2)\gamma + i\sqrt{3}(\cos(k_1\gamma) - \cos(k_2\gamma)), \\ t_2 &= 1 + e^{ik_1\gamma} + e^{ik_2\gamma}, \quad t_3 = e^{-i\frac{\pi}{3}} \left[1 + e^{i(\pm k_1\gamma + \frac{2\pi}{3})} + e^{i(\pm k_2\gamma + \frac{4\pi}{3})} \right], \\ t_4 &= e^{-i\frac{\pi}{3}} \left[1 + e^{i(\pm k_1\gamma + \frac{2\pi}{3})} + e^{i(\pm k_2\gamma + \frac{4\pi}{3})} \right]. \end{aligned}$$

Terms with V_2 express nontrivial coupling and these terms can be neglected compared with terms with A_3 which express trivial coupling. Moreover the impact of terms with t_1 is zero in the center of Brillouin zone ($k = 0$) and for some other values of k . In those cases one obtains the following equation for the excitonic spectra E :

$$\begin{aligned} \varepsilon^4 - \varepsilon^2 \frac{A_3^2}{4} [9|t_4|^2 + 9|t_3|^2 + 2|t_2|^2] \\ + \frac{A_3^4}{16} [|t_2|^4 - 9(t_2^2 t_3 t_4^* + t_2^{*2} t_3^* t_4) + 81|t_3|^2 |t_4|^2] = 0, \quad (18) \end{aligned}$$

in which $\varepsilon = E_{F1} + V_2 f(k) - E$. In the center of Brillouin zone ($k = 0$) we obtain a degenerate pair of excitonic levels:

$$k = 0: \quad \varepsilon_{1,2} = \varepsilon_{3,4} = \pm 3A_3/2.$$

At $k_1\gamma = 2\pi/3, k_2 = -k_1$ one obtains $\varepsilon_{1,2} = \pm 9A_3/2, \varepsilon_{3,4} = 0$.

The lattices considered in Section 2 can be realized if identical molecules possess at least square symmetry (in Section 2.1) and trigonal symmetry (in Section 2.2).

3 Haldane Model in Donor-Acceptor 2D Lattices

In Section 2 the interaction (coupling) between identical molecules causes the intermolecular transfer of one type of excitation (FE). In this section we treat the two-component DA lattices in which the coupling of the nearest neighbor molecules can transform FE to another type of excitation – CTE – which is formation of neighboring positive and negative molecular ions. CTEs exist in one-component materials treated in Section 2. Now we consider DA-model only.

3.1 Hexagonal symmetry

The scheme of the hexagonal DA graphene-like lattice is shown in Figure 4. Two different systems of FEs appear, one – of electronic excitations of donors, another – of acceptors – and both can be described as FEs in a simple hexagonal lattice. Three identical Charge Transfer Excitons (CTEs) of neighboring ionized pair of DA molecules can be excited directly or via transformation of FEs of donors or acceptors. The transformation is more effective if the excitation energy of FEs (E_F) and of CTEs (E_C) are close.

In DA solids the nearest neighbors of D-molecules are A-molecules and direct transfer of FEs is impossible due to different electronic excitations. But so called “trivial coupling” between nearest neighbors can be realized via the transfer of electron from neutral excited D-molecule (with FE on it) to A-molecule transforming FE into CTE (or from neutral nonexcited D-molecule to excited A-molecule with another type of FE on it).

The electron and the hole of CTEs can be transferred to neighbor acceptor (donor) molecule and the different branches of CTEs are interchanged. Fol-

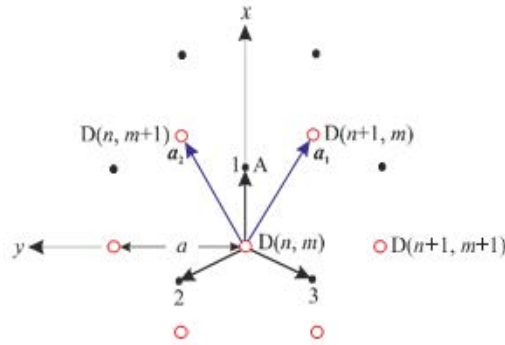


Figure 4. Two hexagonal sublattices of donors (white circles) and acceptors (black). $\vec{a}_1$ and $\vec{a}_2$ are the lattice vectors, a is the lattice constant. Numerals 1-3 denote three identical CTEs.

lowing the results of Ref. [6], Hamiltonian of CTEs can be written as:

$$\begin{aligned} \hat{H}_{\text{CTEs}} = \sum_{k,i=1-3} \left\{ E_c C_{ik}^+ C_{ik} + J_e (C_{1k}^+ C_{2k} + C_{2k}^+ C_{3k} + C_{3k}^+ C_{1k} + h.c.) \right. \\ \left. + J_h \left[C_{2k}^+ C_{1k} \exp(-ik_1\gamma) + C_{3k}^+ C_{2k} \exp(i(k_1 - k_2)\gamma) \right. \right. \\ \left. \left. + C_{1k}^+ C_{3k} \exp(ik_2\gamma) + h.c. \right] \right\}. \quad (19) \end{aligned}$$

in which C_{ik} is operator of annihilation of CTE $i = 1 - 3$, (J_e , J_h) are transfer integrals of electron or hole and represent nontrivial coupling of CTEs. The coupling of FEs and CTEs depend on the symmetry of excitations, notably:

(a) Hamiltonian for z -excitations with transition dipole moment perpendicular to the layer is [6]:

$$\hat{H}^{(z)} = \sum_k [E_F + V_1 f(k)] B_{zk}^+ B_{zk} + \hat{H}_{\text{CTEs}} + \left(\frac{\varepsilon}{\sqrt{3}} \right) \sum_{k,i=1-3} [B_{zk}^+ C_{ik} + h.c.]. \quad (20)$$

The CTEs combination $\frac{1}{\sqrt{3}} \sum_{i=1,3} C_{ik}^+$ has symmetry of z -excitons and ε is coupling parameter between the nearest neighbors (trivial coupling in Haldane model). After some algebra one obtains the following equation for FEs-CTEs spectra [6]:

$$\left[E_F + V_1 f(k) - E \right] D_0(k) + \varepsilon^2 \left[E - E_c + J_e + J_h \left(\frac{f(k)}{3} - 1 \right) \right] = 0, \quad (21)$$

$$D_0(k) = (E_c - E)^2 + (E_c - E)(J_e + J_h) - 2 \left[J_e^2 + J_h^2 + \left(\frac{f(k)}{2} - 1 \right) \right]. \quad (22)$$

The quantities E_F , $V_1 = p_z^2 / (4\pi\varepsilon_0 a^3)$ as well as the coupling parameter ε would be different for FEs which stem from donors and from acceptors. In the case in which the nontrivial coupling in the system of CTEs can be neglected ($J_e = J_h = 0$) one obtains two excitonic levels:

$$E_{1,2}(k) = (E_F + V_1 f(k) + E_c) / 2 \pm \sqrt{\frac{[E_F + V_1 f(k) - E_c]^2}{4} + \varepsilon^2}. \quad (23)$$

Dispersion curves of coupled z -FEs-CTEs are exposed in Figure 5. We note again, as it is in the case of Figure 3, relatively big splitting, at $k_1 = k_2 = 0$ and two parallel straight lines at $k'_2 = \pi$. Dispersion of the levels which stem from $E_c = 2.27$ eV level of CTEs is relatively weaker compared with dispersion of upper curves related with FEs.

(b) situation with (x, y) excitons is more complicated (due to the degeneracy). Analysis in Ref. [6] for the symmetry of linear combinations of the three CTEs leads to the following expressions for trivial coupling with parameter ε_a between

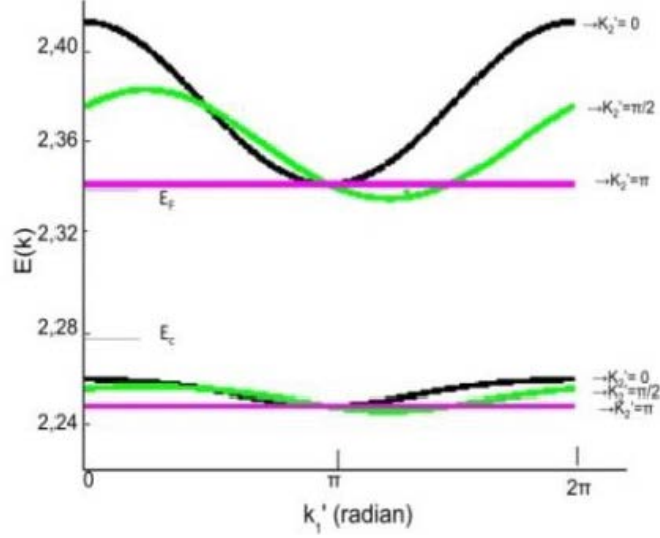


Figure 5. Dispersion curves of coupled z -FEs and CTEs (formula (23), $E_F = 2.34$ eV, $E_c = 2.27$ eV, $V_1 = 0.01$ eV, $\varepsilon = 0.04$ eV. For the other see caption of Figure 3.

the nearest neighbors:

$$\hat{H}_{F,CTEs}^{(x,y)} = \frac{\varepsilon_a}{\sqrt{3/2}} \sum_k \left\{ [C_{1k}^+ - \frac{1}{2}(C_{2k}^+ + C_{3k}^+)] B_{x,k} + \frac{\sqrt{3}}{2} (C_{2k}^+ - C_{3k}^+) B_{y,k} + h.c. \right\}. \quad (24)$$

The transfer terms for x - and y -FEs are the following (instead of $V_1 f(k)$ in formula (20)):

$$\begin{aligned} W_x &= 2V_3 \left\{ -\frac{5}{4} [\cos(k_1\gamma) + \cos(k_2\gamma)] + \cos(k_1 - k_2)\gamma \right\}, \\ W_y &= 2V_3 \left\{ \frac{1}{4} [\cos(k_1\gamma) + \cos(k_2\gamma)] - 2\cos(k_1 - k_2)\gamma \right\}, \end{aligned} \quad (25)$$

in which $V_3 = p_{hx}^2 / (4\pi\varepsilon_0 a^3)$

We treat for simplicity the case $J_e = J_h = 0$ (the same in Section 3.2). Then one obtain the following equations for excitons' levels: E_x and E_y :

$$E_{F1} + W_{x,y} - E_{x,y} - \frac{\varepsilon_a^2}{E_c - E_{x,y}} = 0. \quad (26)$$

Their roots are similar, *mutatis mutandis*, of the levels (23) of z -excitons. Those relatively simple expressions become possible if we neglect the nontrivial coupling (19) in the system of CTEs (but we preserve nontrivial coupling in the system of FEs).

3.2 Square symmetry

Figure 6 contains four identical CTEs of quadratic DA lattice (as it is in Figure 4, white points denote donors, black points – acceptors). The nontrivial coupling of CTEs can be expressed with transfer integrals J_e and J_h like formula (19) in hexagonal lattice [6].

The formulas for FEs-CTEs coupling are as follows:

- for z -excitons:

$$\hat{H}_{\text{FCT}}^{(z)} = \frac{\varepsilon}{2} \sum_{k,i=1-4} \left(B_{z,k}^+ C_{i,k} + h.c \right); \quad (27)$$

- for xy -excitons:

$$\hat{H}_{\text{FCT}}^{(xy)} = \frac{\varepsilon_1}{\sqrt{2}} \sum_k \left[(C_{1k}^+ - C_{3k}^+) B_{xk} + (C_{2k}^+ - C_{4k}^+) B_{yk} + h.c \right]. \quad (28)$$

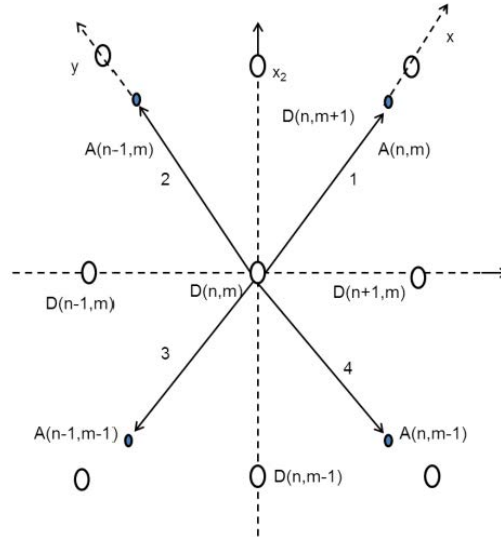


Figure 6. 2D DA quadratic lattice. The donor molecules are positioned at the nodes of the lattice whereas, acceptor molecules (black) occupy the centers of the unit cells. Numerals 1-4 denote the number of CTEs.

Direct transfer of FEs of D origin on four nearest D molecules can be expressed using formulas (2) and (5) (the similar formulas describe the direct transfer of FEs of A origin). Corresponding equations for the excitonic eigenvalues $E_{x,y,z}$ (at $J_e = J_h = 0$ and E_c -excitation energy of CTE) are:

- for z -excitons (see formula (2)):

$$\{E_F + 2V_1 [\cos(k_1 a) + \cos(k_2 a)] - E_z\} (E_c - E_z) - \varepsilon^2 = 0; \quad (29)$$

- for (xy) -excitons (see formulas (5) for $W_{tz}^{(y)}(k_1, k_2)$)

$$\{E_F + W_{tz}^{(x,y)}(k_1, k_2) - E_{xy}^2\} (E_c - E_{x,y}) - \varepsilon_1^2 = 0. \quad (30)$$

4 Indirect Coupling in Haldane Model

Frenkel excitons in Section 3 represent collectivized electronic excitations either of donors or of acceptors. No direct dipole-dipole transfers of excitations between these two different molecules. Nevertheless the coupling of both types of FEs with CTEs creates the opportunity of indirect connection between FEs of the two types.

Let consider the case of hexagonal DA-lattice, and suppose that Hamiltonian (20) concerns z -excitations which stem from donors. The similar Hamiltonian can be written for z -excitons of acceptors' electronic excitations:

$$\hat{H}_{AC}^{(z)} = \sum_k [E_{FA} + V_A f(k)] A_{zk}^+ A_{zk} + \left(\frac{\varepsilon_3}{\sqrt{3}}\right) \sum_{k,i=1-3} [A_{zk}^+ C_{ik} + h.c]. \quad (31)$$

It is easy to find the equation for the excitonic spectrum E at Hamiltonian (20) and (31), notably:

$$1 - d(k) \left[\frac{\varepsilon^2}{E_F + V_1 f(k) - E} + \frac{\varepsilon_3^2}{E_{FA} + V_A f(k) - E} \right] = 0, \quad (32)$$

in which function $d(k)$ depends on the parameters of CTEs only which ensures this indirect coupling. In the case under consideration one obtains:

$$d(k) = \left[E_c - E - J_e - J_h \left(\frac{f(k)}{3} - 1 \right) \right] / D_0(k) \quad (33)$$

(see formula (22)).

Equation (32) is basic in the case of indirect coupling. For z -excitations of hexagonal DA lattice this equation is quartic. Its roots depend on mutual location of the levels E_F , E_{FA} and E_C . For the roots E with $|E_c - E| \gg |J_e|, |J_h|$ function $d(k)$ is $d' \approx 1/(E_c - E)$.

If one of trivial coupling parameters ε or ε_3 is vanishing the excitonic spectra coincide with those discussed in Section 3. The strength of indirect coupling depends on the ratios (εd) and $(\varepsilon_3 d)$.

In calculations of its impact on the excitonic levels $E_F(k)$ in the case of relatively big values of $(1/d') \approx |E_F(k) - E_C|$ or $|E_{FA}(k) - E_C|$ the following formula allows to make some corrections:

$$E_{1,2} = \frac{1}{2} \left\{ E_F(k) + E_{FA}(k) - d'(\varepsilon^2 + \varepsilon_3^2) \pm \sqrt{[E_F(k) - E_{FA}(k) + d'(\varepsilon^2 + \varepsilon_3^2)] + 4d'^2 \varepsilon^2 \varepsilon_3^2} \right\}. \quad (34)$$

For z -excitons in quadratic DA lattice one obtains again formula (28) with $[E_{F1} + W_{\text{non}, A}^{(z)}(k_1, k_2)]$ instead of $E_{F1} + V_1 f(k)$ and $[E_{F1, A} + W_{\text{non}, A}^{(z)}(k_1, k_2)]$ instead of $E_{FA} + V_a f(k)$, see formulas (3) and (4). Function $d(k)$ in the case $J_e, J_h \neq 0$ is relatively complicated:

$$d(k) = \left\{ (E_c - E)^3 - (E_c - E)^2 [2J_e + J_h(\cos(k_1 a) + \cos(k_2 a))] - 2(E_c - E)J_h^2[1 - \cos(k_1 a)\cos(k_2 a)] + 2J_e J_h^2[\cos(k_2 a) - \cos(k_1 a)]^2 \right\} / d_4(k), \quad (35)$$

$$d_4(k) = (E_c - E)^4 - 4(E_c - E)^2 [J_e^2 + J_h^2 + J_e J_h(\cos(k_1 a) + \cos(k_2 a))] + 4J_e^2 J_h^2[\cos(k_1 a) - \cos(k_2 a)]^2. \quad (36)$$

The indirect coupling of FEs via coupling with CTEs represents a specific case of mixing of molecular configurations treated in [8, 10].

5 Conclusions

The main results of this paper can be summarized in two points:

1. Based on the Haldane model several cases of molecular excitons' spectra have been analyzed. We stress on calculations of (xy) -excitons in Section 2.1, on interesting coupling of FEs and CTEs in Section 3, as well as on indirect coupling of two different types of FEs (which stem from donors and from acceptors) in Section 4. Some of these contributions have been published in previous papers of one author and coauthors but some ideas especially that of indirect coupling could be interesting.
2. The second point is generalization of Haldane model including its anisotropy (see the spectra of z - and (xy) -excitations), the "trivial" coupling between nearest neighbors with transformation of the excitations (FEs-CTEs coupling) and again the possibility of indirect coupling. We hope that generalized Haldane model can be applied treating the problems very far from molecular excitons' spectra (like electron bands or topological photonic systems).

A possible enlargement of the studies can be inclusion of exciton-phonon coupling and calculations of vibronic spectra, as they were treated for several cases in [4–7]. The simulations of the excitonic spectra could be useful also in our understanding of Haldane systems.

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