

## Haldane Model and Molecular Excitons' Spectra

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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 of hexagonal symmetry. Excitations with transition dipole moment perpendicular to the lattice or in-plane moments are considered in the following cases: a) 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 precise interpretation of spectroscopic data or in other applications of Haldane model.

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## 1.Introduction

The topic of Haldane model [1] is the impact of topology of 2D honeycomb lattice on the electronic spectra. This model includes “the topology trivial” coupling between the nearest neighbors and “topologically non-trivial” coupling with the second neighbors of one sublattice. The conceptual features of Haldane model have been used in explorations of graphene [2] and of topological photonic systems.

In the present communication we connect this model and our previous investigations on excitonic spectra of 2D hexagonal lattices [3-5]. Using Haldane model we treat more complicated excitonic problems. On the other hand, our generalization of the model introduces vector characters of coupling parameters for excitations with transition dipole moment perpendicular to 2D-layer or in-plane transition moment.

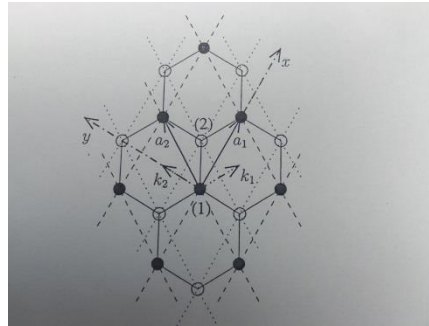
Two types of molecular excitons are treated in our study: a) Frenkel excitons (FEs) which are transferable electronic excitations of neutral molecules [6,7]; b) Charge Transfer excitons (CTEs) which represent a pair of positive and negative ion situated on neighbor lattice sites. We consider CTEs in Donor-Acceptor (DA) solids with two different ionized molecules (see Ref. [7,8,9]).

The outline of the paper is the following: in Section 2 we consider the case of two identical nonequivalently positioned molecules in unit cell of hexagonal symmetry and obtain the spectra of dipole active FEs. In Section 3 the spectra of FEs-CTEs in DA crystal of honeycomb 2D structure are studied. In Section 4 the indirect coupling of FEs via CTEs is analyzed. Section 5 contains some concluding remarks.

## 2.Honeycomb model with two identical molecules

This model is known now using the schemes of graphene studies (Fig. 1). Practically we treat the problem of FEs spectra with two molecules in unit cell [6,7]. Two types of dipole active FEs exist, notably [5],

- a) z-excitons with transition dipole perpendicular to the plane;
- b) xy-excitons with in-plane transition dipole moment.



**FIGURE 1.** Honeycomb model 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.  $\vec{k}_1$  and  $\vec{k}_2$  create the basis in the reciprocal lattice.

Let  $B_{Z1}(\mathbf{n})$  and  $B_{Z2}(\mathbf{n})$  denote the operators of annihilations of FEs on molecule 1(2) of site  $\vec{n}$ . Hamiltonian of z-excitons in momentum space can be represented as follows [5]:

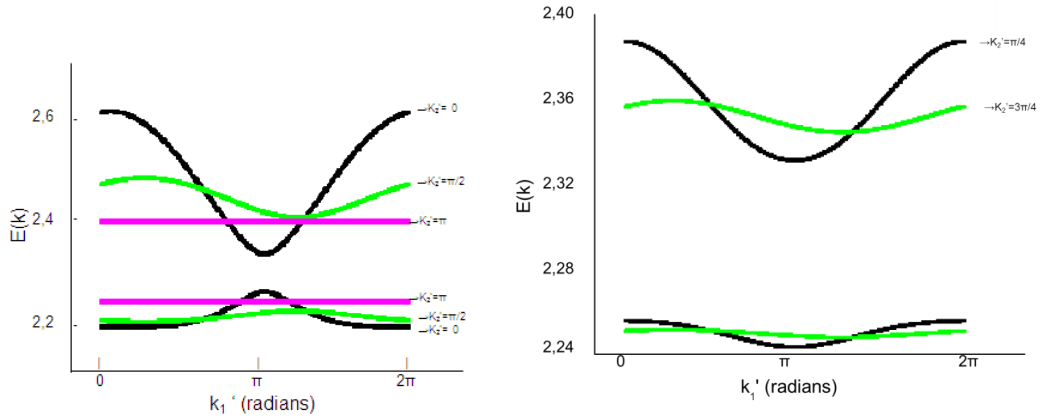
$$\hat{H}_z = \sum_{k,\sigma=1,2} [E_F + V_1 f(k)] B_{z\sigma}^+(k) B_{z\sigma}(k) + \sum_k [M(k) B_{z1}^+(k) B_{z2}(k) + hc], \quad (1)$$

in which terms with  $M(k)$  express “trivial coupling” and with  $V_1 = \frac{p_z^2}{4\pi\epsilon_0 a^3}$  - “nontrivial coupling” (following Haldane).  $p_z$  is z-component of molecular transition dipole moment,  $E_F$  is molecular excitation energy,

$$f(k) = 2[\cos(k_1\gamma) + \cos(k_2\gamma) + \cos((k_1 - k_2)\gamma)]; \quad (\gamma = \frac{a\sqrt{3}}{2}), \quad (2)$$

$a$  being the length of hexagonal lattice vectors  $(\vec{a}_1, \vec{a}_2)$ , and

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



**FIGURE 2.** Davydov splitting of z-FEs (formula (4)).  $E_F=2.35\text{eV}$ ,  $V_1=0.015\text{eV}$ ,  $k_i' = \frac{k_i a\sqrt{3}}{2}$ ,  $i=1,2$   
 1.  $k_2'=0$ (black),  $\pi/2$  (green),  $\pi$  (red) lines b)  $k_2'=\pi/4$ (black)  $3\pi/4$  (green) lines

In the paper we suppose dipole-dipole transfers of FEs on the nearest neighbors only. Diagonalization of Hamiltonian (1) gives the following formula for the excitonic spectra and their Davydov splitting:

$$E_z(k) = E_F + V_1 f(k) \pm |M(k)|; \quad [|M(k)|^2 = [p_z^2 / (4\pi\epsilon_0 c^3)]^2 [f(k) + 3]] \quad (4)$$

Fig.2 illustrates dispersion curves of FEs at different values of  $k_2' = \frac{k_2 a\sqrt{3}}{2}$  for medium transition dipole moment  $p_z$  ( $V_1=0.015$  eV). The most interesting effect is relatively big Davydov 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.

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

$$B_{l,r;\sigma}^{(\vec{n})} = \left(\frac{1}{\sqrt{2}}\right) [B_{x;\sigma}^{(\vec{n})} \mp iB_{y;\sigma}^{(\vec{n})}], \quad (5)$$

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

$$\hat{P}_n = \left(\frac{p_h}{\sqrt{2}}\right) [(e_x - ie_y) (B_{l,\sigma}^{(n)+} + B_{r,\sigma}^{(n)}) + (e_x + ie_y) (B_{r,\sigma}^{(n)+} + B_{l,\sigma}^{(n)})], \quad (6)$$

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 (6) of the nearest- neighbor molecules. One obtains the

following Hamiltonian in Heitler-London approximation [6,7] taking the intensive “trivial” coupling only:

$$\hat{H}_{l,r} = \sum_{k,\sigma} [E_{F1} + V_2 f(k)] [B_{l,\sigma}^+(k) B_{l,\sigma}(k) + B_{r,\sigma}^+(k) B_{r,\sigma}(k)] - \frac{A_3}{2} \sum_k \{ [B_{l,2}^+(k) B_{l,1}(k) + B_{r,2}^+(k) B_{r,1}(k)] t_2 + hc \} - \frac{3A_3}{2} \sum_k [B_{l,2}^+(k) B_{r,1}(k) t_3 + B_{l,1}^+(k) B_{r,2}(k) t_4 + hc], \quad (7)$$

in which

$$V_2 = -\frac{p_h^2}{4\pi\epsilon_0 a^3}, \quad A_3 = \frac{p_h^2}{4\pi\epsilon_0 c^3}$$

$$t_2 = 1 + e^{ik_1\gamma} + e^{ik_2\gamma} \quad t_{3,4} = e^{-i\pi/3} \left[ 1 + e^{i(\pm k_1\gamma + \frac{2\pi}{3})} + e^{i(\pm k_2\gamma + \frac{4\pi}{3})} \right]$$

Strictly speaking the precise calculations of Hamiltonian (7) give additional terms (nontrivial coupling) proportional to  $1/a^3$ , not to  $1/c^3 = 3\sqrt{3}/a^3$  like  $A_3$ . Their impact on the excitonic spectra in the center of Brillouin zone ( $k=0$ ) and for other values of  $(k_1, k_2)$  is zero. In those cases one obtains the following equation for the excitonic spectra E:

$$\varepsilon^4 - \varepsilon^2 \left( \frac{A_3^2}{4} \right) [9|t_4|^2 + 9|t_3|^2 + 2|t_2|^2] + \left[ \frac{A_3^4}{16} \right] [|t_2|^4 - 9(t_2^2 t_3^* t_4^* + t_2^{*2} t_3^* t_4) + 81|t_3|^2 |t_4|^2] = 0 \quad (8)$$

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:

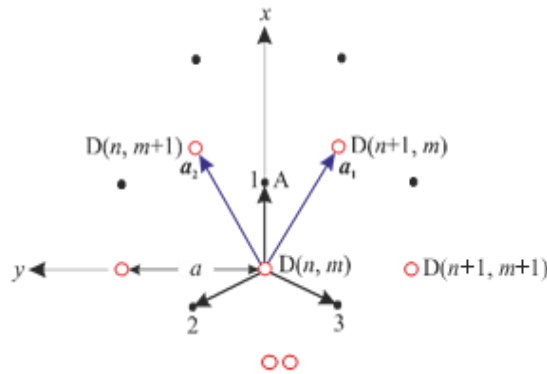
$$k = 0 \quad \varepsilon_{1,2} = \pm 3A_3/2$$

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

Calculations of xy-excitonic spectra represent an example of Haldane model with degeneracy of excitations.

### 3.Honeycomb model in DA lattices

In this section we treat the two-component DA lattices in which the coupling of the nearest neighbor molecules can transform FE into another type of excitation – CTE (see Introduction and Ref. 4). The scheme of the hexagonal DA graphene-like lattice is shown on Fig.3. Two different systems of FEs appear, one – of electronic excitations of donors, another – of acceptors and direct transfer of FEs between the two systems is impossible due to the different molecular excitations.



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

Three identical CTEs of neighboring ionized pair of DA molecules can be excited directly or via transformation of FEs of donors or acceptors. So called “trivial coupling” between DA neighbors can be realized via the transfers of electron from neutral excited D- molecule (with FE on it) to A molecule transforming FE into CTE (or via the transfers of electrons from neutral nonexcited D-molecule to excited A-molecule with another type of FE on it). The transformation is more effective if the excitation energy of FEs ( $E_F$ ) and of CTEs ( $E_C$ ) are close. Hamiltonian of coupled z-FEs and CTEs can be represented as follows:

$$\hat{H}^{(z)} = \sum_k [E_F + V_1 f(k)] B_{zk}^+ B_{zk} + \hat{H}_{CTEs} + \left(\frac{u}{\sqrt{3}}\right) \sum_{k,i=1-3} [B_{zk}^+ C_{ik} + h.c] , \quad (9)$$

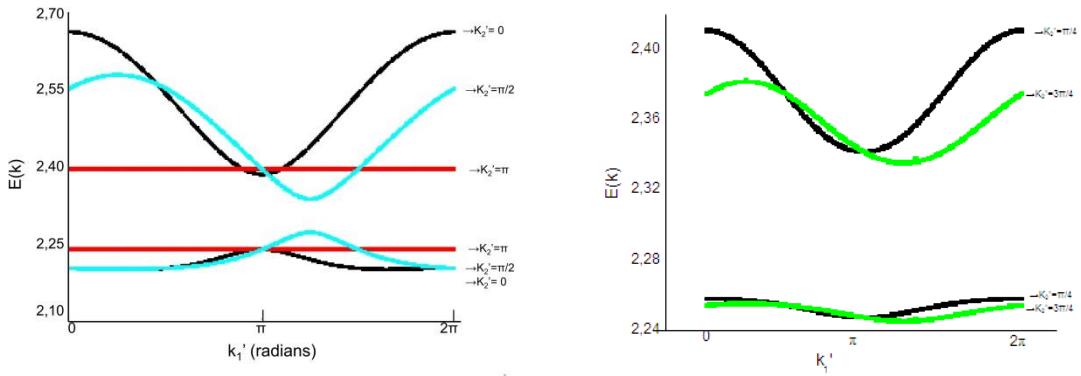
in which

$$\hat{H}_{CTEs} = \sum_{k,i=1-3} \{ E_c C_{ik}^+ C_{ik} + J_e (C_{1k}^+ C_{2k} + C_{2k}^+ C_{3k} + C_{3k}^+ C_{1k} + h.c) + J_h [C_{2k}^+ C_{1k} \exp(-ik_1 \gamma) + C_{3k}^+ C_{2k} \exp(-i(k_1 - k_2) \gamma) + C_{1k}^+ C_{3k} \exp(ik_2 \gamma) + h.c] \} . \quad (10)$$

$C_{ik}$  is operator of annihilation of CTEs,  $i=1-3$ , ( $J_e, J_h$ ) are transfer integrals of electron (hole) and represent nontrivial coupling of CTEs. The CTEs combination  $\left(\frac{1}{\sqrt{3}}\right)(C_{1k} + C_{2k} + C_{3k})$  has symmetry of z-excitons and  $u$  is coupling parameter (“trivial coupling”). Diagonalization of Hamiltonian (9) leads to the following equation for FEs-CTEs spectra [4]:

$$[E_F + V_1 f(k) - E] D_0(k) + u^2 \left[ E - E_c + J_e + J_h \left( \frac{f(k)}{3} - 1 \right) \right] = 0 , \quad (11)$$

$$D_0(k) = (E_c - E)^2 + (E_c - E)(J_e + J_h) - 2 \left[ J_e^2 + J_h^2 + \left( \frac{f(k)}{2} - 1 \right) J_e J_h \right] . \quad (12)$$



**FIGURE 4.** Dispersion curves of coupled z-FEs and CTEs (formula (13),  $E_F=2.34\text{eV}$ ,  $E_c=2.27\text{eV}$ ,  $V_1=0.01\text{eV}$ ,  $u=0.04\text{eV}$ . For the other see Fig.2

The quantities  $E_F$ ,  $V_1$  (see Section 2) as well as the coupling parameter  $u$  would be different for FEs which stem from donors and from acceptors. In the case of negligible transfer integrals  $J_e=J_h=0$  one obtains two excitonic levels:

$$E_{1,2}(k) = (E_F + V_1 f(k) + E_c)/2 \pm \sqrt{\frac{[E_F + V_1 f(k) - E_c]^2}{4} + u^2} . \quad (13)$$

Dispersion curves of coupled z-FEs-CTEs are exposed on Fig.4. We note again as it is in the case of Fig.2 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  $E_c=2.27\text{ eV}$  level of CTEs is relatively smaller compared with dispersion of upper curve related with FEs.

#### 4. Indirect coupling in Haldane model

We repeat that direct coupling of the two types of FEs – originated from donors and from acceptors is impossible. But the coupling of both types of FEs with CTEs creates the opportunity of indirect connection between them.

Let Hamiltonian (9) concerns z-excitons which stem from donors. The similar Hamiltonian can be written for z-excitons of acceptors' electronic excitations:

$$\hat{H}_{AC}^{(z)} = \sum_k [E_{FA} + V_A f(k)] A_{zk}^+ A_{zk} + \left(\frac{u_3}{\sqrt{3}}\right) \sum_{k,i=1-3} [A_{zk}^+ C_{ik} + h.c]. \quad (14)$$

The equation for excitonic spectra E at Hamiltonian (9)+(14) is the following:

$$1 - d(k) \left[ \frac{u^2}{E_F + V_A f(k) - E} + \frac{u_3^2}{E_{FA} + V_A f(k) - E} \right] = 0 \quad (15)$$

in which function d(k) depends on the parameters of CTEs only which ensures this indirect coupling. Hamiltonian (10) for CTEs gives the following function:

$$d(k) = \left[ E_c - E - J_e - J_h \left( \frac{f(k)}{3} - 1 \right) \right] / D_0(k) \quad (16)$$

(see formula (12)).

The basis equation (15) is quartic and its roots depend on mutual location of the levels  $E_F$ ,  $E_{FA}$  and  $E_c$ . In the case of negligible transfer integrals  $J_e = J_h = 0$  function d(k) is

$$d(k) \approx 1 / (E_c - E)$$

If one of the “trivial coupling” parameters  $u$  or  $u_3$  is vanishing we obtain the excitonic spectra described in Section 3.

The three- type excitations coupling contributes to more precise calculations of the spectra of FEs and CTEs. The indirect coupling of FEs via CTEs represents a specific case of mixing of molecular configurations [6,7].

#### 5. Conclusion

The result of this study can be summarized in the following points:

1. Based on the Haldane model we considered several cases of excitonic spectra in honeycomb lattice of identical molecules or of DA-2D lattice. The paper continues the previous contributions of the authors and their co-authors on the excitonic spectra and introduces some new ideas as description of xy-excitons in hexagonal lattice, indirect coupling of FEs via CTEs etc. In some cases we simulate the excitonic spectra in Brillouin zone.

2. The excitonic spectra of honeycomb model give the example of generalization of Haldane model itself, including the anisotropy of coupling parameters, degeneracy of excitations, “trivial coupling” with transformation of excitations (FEs-CTEs coupling) and even indirect coupling. This generalization could be used treating the problems very far from molecular excitons' spectra.

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