Charge Transfer Excitons in a Simple Hexagonal 2D Lattice

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Abstract. The paper treats a model of Charge Transfer Excitons (CTEs) in a simple hexagonal two-dimensional lattice. The symmetry governed combinations of CTEs and the excitonic spectra of pure CTEs have been analyzed. The coupling of CTEs and Frenkel excitons and corresponding equations for the spectra of the coupled excitons with nonvanishing transition dipole moments have been studied.

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1 Introduction

This paper enlarges the studies of the excitonic spectra of a simple 2D quadratic lattice [1, 2] by considering the case of a hexagonal 2D lattice. The main goal is to create a model of Charge Transfer Excitons (CTEs) formed by positive and negative ions of one substance located on the neighbour positions in the lattice and their coupling with Frenkel Excitons (FEs).

Our interest to hexagonal 2D structures has been inspired by graphene studies, studies of the excitonic spectra of bacteriorhodopsin [3, 4], as well as by the possibilities to realize such 2D or quasi-2D structures using modern technologies [5, 6].

Our theoretical model treats the case of a two-dimensional lattice with one molecule in the unit cell. The hexagonal symmetry complicates the studies of excitonic spectra compared with the linear stacks models in perylene derivatives [7, 8] and, on the other hand, with the case of quadratic lattice [1, 2]. Surprisingly, the one-component models of CTEs create additional complications than the models of donor-acceptor lattices which have been treated in [9, 10].

The description and manifestation of CTEs in optical spectra of charge transfer solids have been reviewed in several books [11–13] and in many papers (see for instance Ref. [14] for anthracene–PMDA ; Ref. [7, 8] for perylene derivatives; Ref. [15] for polyacene and others). We follow the same approach for treating CTEs in a hexagonal 2D structure and their coupling with FEs.
The organization of the paper is as follows: Section 2 contains description of CTEs in a simple hexagonal lattice and, especially, we analyze the symmetry governed combinations of CTEs with nonvanishing transition dipole moments. Their coupling with dipole active combinations of FEs is the subject of Section 3. Section 4 contains some conclusions.

2 CTEs in a Hexagonal Simple 2D Lattice

The scheme of a simple hexagonal 2D lattice is represented in Figure 1. We consider the case of point group of symmetry 6 governed by the symmetry of the positions of molecules as well as by the symmetry of each molecule. We suppose the lack of the inversion center. In the case of molecules with inversion center, the point group is \( \bar{6} \) and the treating is analogous, mutatis mutandis.

CTEs sketched in Figure 1 consist of the hole at the node \((n, m)\) and the electrons of the six neighbour molecules. Let \( E_c \) denotes the excitation energy of CTEs which, due to the symmetry, are equivalent quasiparticles. We introduce two transfer integrals: a) \( J_e \) describes the transfer of the electron on the closest neighbour molecules which ensure the mutual transformations of CTEs; b) \( J_h \) describes the corresponding transfers of the hole on the neighbours. The Hamiltonian can be represented in the following way:
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\[ \hat{H}_{\text{CTEs}} = \sum_{nm;i=1,6} E_{c} C_{i,nm}^{+} C_{i,nm} + J_{e} \sum_{nm} \left[ C_{2,nm}^{+} C_{1,nm} + C_{3,nm}^{+} C_{2,nm} + \cdots + C_{1,nm}^{+} C_{6,nm} + \text{h.c.} \right] \\
+ J_{h} \sum_{nm} \left[ C_{2,n+1m-1}^{+} C_{1,nm} + C_{3,n+1m}^{+} C_{2,nm} + \cdots + C_{1,nm-1}^{+} C_{6,nm} + \text{h.c.} \right], \]  

(1)

where \( C_{i,nm}^{+} (i = 1, 2, \ldots, 6) \) is the operator of annihilation of CTE with hole at the node \((nm)\).

The Hamiltonian (1) in the momentum space \((k_{a}, k_{b})\) reads

\[ \hat{H}_{\text{CTEs}} = \sum_{k,i=1,6} E_{c} C_{ik}^{+} C_{ik} + \sum_{k} \left[ (J_{e} + J_{h} e^{i(k_{b}-k_{a})\gamma}) C_{2k}^{+} C_{1k}^{+} \right] \\
+ (J_{e} + J_{h} e^{-i(k_{a})\gamma}) C_{3k}^{+} C_{2k}^{+} + (J_{e} + J_{h} e^{-i(k_{b})\gamma}) C_{4k}^{+} C_{3k}^{+} \\
+ (J_{e} + J_{h} e^{i(k_{a}-k_{b})\gamma}) C_{5k}^{+} C_{4k}^{+} + (J_{e} + J_{h} e^{i(k_{b})\gamma}) C_{6k}^{+} C_{5k}^{+} \\
+ (J_{e} + J_{h} e^{i(k_{a})\gamma}) C_{1k}^{+} C_{63k}^{+} + \text{h.c.}, \]  

(2)

where \( \gamma = a \sqrt{3}/2; a \) is the lattice constant.

Now we analyze the symmetry allowed combinations of CTEs with nonzero transition dipole moment. We follow the approach applied in the Appendix of Ref. [2] for the study of the same combinations in 2D quadratic lattice. CTEs in an hexagonal lattice are six-fold degenerate and their wave functions

\[ \psi_{s}|0\rangle = (a_{1} C_{1}^{+} + a_{2} C_{2}^{+} + \cdots + a_{6} C_{6}^{+})|0\rangle \]  

(3)

are multiplied by the phase factor \( e^{i\alpha} \) at successive symmetry rotations of the hexagonal lattice around the axis of symmetry of sixth order. One obtains

\[ e^{i\alpha} \psi_{s}|0\rangle = (a_{1} C_{6}^{+} + a_{2} C_{1}^{+} + \cdots + a_{6} C_{5}^{+})|0\rangle \]  

(4)

and similar expressions with phase factors of \( \exp(i2\alpha) \).

We insert \( \psi_{s}|0\rangle \) from equation (3) into (4) and find the necessary condition

\[ e^{6i\alpha} - 1 = (e^{3i\alpha} - 1) (e^{3i\alpha} + 1) = 0 \]  

(5)

and the following formula for the coefficients \( a_{p} \):

\[ a_{p} = e^{i\alpha_{s}a_{p-1}}, \quad p = 2, \ldots, 6, \]  

(6)

where \( \alpha_{s} \) are the roots of eq. (5). Then the wave function (3) can be represented as follows:

\[ \psi_{s}|0\rangle = \frac{1}{\sqrt{6}} \left[ C_{1}^{+} \pm C_{4}^{+} + e^{i\alpha_{s}} (C_{2}^{+} \pm C_{5}^{+}) + e^{2i\alpha_{s}} (C_{3}^{+} \pm C_{6}^{+}) \right]|0\rangle, \]  

(7)
where the sign “+” is valid for $\alpha_s$ from the first multiple in (5), and the sign “–” from the second multiple.

In the following we direct the axis $\hat{z}$ to be perpendicular to the lattice plane, the axis $\hat{x}$ to be parallel to the vector $\vec{p}_1$ of the transition dipole moment of CTE 1, and the axis $\hat{y}$ is perpendicular to them. Due to the identity of all CTEs, the $z$-components of their transition dipole moments are equal and parallel to the symmetry axis $\hat{z}$. The corresponding CTEs combination can be obtained from (7) at $\alpha_s = 2\pi$ and sign “+”, notably

$$\alpha_s = 2\pi; \quad \psi_2|0\rangle = \frac{1}{\sqrt{6}} \sum_{i=1,6} C_i^+|0\rangle.$$  \hfill (8)

In the plane of the hexagonal lattice, the transition dipole moments of the pairs, correspondingly $(C_1, C_4)$, $(C_2, C_5)$, $(C_3, C_6)$, are directed in opposite directions and, hence, the combinations with sign “–” in (7) govern the linear optical susceptibility components $\chi_{xx} = \chi_{yy}$ which depend on the $(x, y)$ components of the transition dipole moment. The combinations

$$\alpha_s = \frac{\pi}{3}; \quad \psi_3|0\rangle = \frac{1}{\sqrt{6}} \left[ C_1^+ - C_4^+ + \frac{1}{2} (C_2^+ - C_5^+ - C_3^+ + C_6^+) \right]|0\rangle + \frac{i\sqrt{3}}{2} (C_2^+ - C_5^+ + C_3^+ - C_6^+)|0\rangle$$ \hfill (9)

$$\alpha_s = \frac{5\pi}{3}; \quad \psi_4|0\rangle = \frac{1}{\sqrt{6}} \left[ C_1^+ - C_4^+ + \frac{1}{2} (C_2^+ - C_5^+ - C_3^+ + C_6^+) \right]|0\rangle - \frac{i\sqrt{3}}{2} (C_2^+ - C_5^+ + C_3^+ - C_6^+)|0\rangle$$ \hfill (10)

describe right (r) and left (l) circular polarization of the CTEs. Taking into account the mutual positions of the transition dipole moments $\vec{p}_1$, $\vec{p}_2$, $\vec{p}_3$, we can identify the real parts of combinations (9) and (10) as $x$-CTEs and $y$-CTEs combinations.

Consequently, the operator of the transition dipole moment can be represented as follows:

$$\hat{P} = q[C_1 - C_4 + \frac{1}{2} (C_2 - C_5 - C_3 + C_6)]\hat{x} + q\frac{\sqrt{3}}{2} (C_2 - C_5 + C_3 - C_6)\hat{y} + p_z (C_1 + C_2 + C_3 + C_4 + C_5 + C_6) + h.c. ,$$ \hfill (11)

where $q$ is the parallel of the layer component of the transition dipole moment of one CTE, ($\hat{x}$, $\hat{y}$) are unit vectors and $p_z$ is perpendicular to the lattice component of the same transition moment. Usually $p_z$ component is negligible compared with $q$ (see [11, 15]).

The excitonic spectra of CTEs with Hamiltonian (2) and wave functions of type (3) can be found using necessary conditions for nonzero coefficients $a_i$ at $k \neq 0$. 

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After tedious calculations, one obtains two cubic equations for the excitonic levels $E_k$

$$(E_k - E_c) \left[ (E_k - E_c)^2 - 3(J_e^2 + J_h^2) - 2J_e J_h \mu \right] \pm 2\sqrt{\beta_1 \beta_2 \beta_3} = 0, \quad (12)$$

where

$$\mu = \cos(k_a \gamma) + \cos(k_b \gamma) + \cos((k_a - k_b) \gamma),$$

$$\beta_1 = J_e^2 + J_h^2 + 2J_e J_h \cos((k_a - k_b) \gamma),$$

$$\beta_2 = J_e^2 + J_h^2 + 2J_e J_h \cos(k_a \gamma),$$

$$\beta_3 = J_e^2 + J_h^2 + 2J_e J_h \cos(k_b \gamma).$$

In the center of Brillouin zone $k = 0$, the excitonic levels correspond to six representations of the point groups 6 or $\bar{6}$ and they can be expressed as follows:

sign “+” in (12):

$$E_{k1} = E_{k2} = E_c + J_e + J_h, \quad E_{k3} = E_c - 2(J_e + J_h); \quad (14a)$$

sign “-” in (12):

$$E_{k4} = E_c + 2(J_e + J_h), \quad E_{k5} = E_{k6} = E_c - (J_e + J_h). \quad (14b)$$

Calculations of the linear absorption, see Ref. [1, 10], showed that the level $E_{k4}$ is connected with the $z$-component of the transition moment and $E_{k1} = E_{k2}$ are connected with the $(x, y)$ components. Hence, the sign “+” in eq. (12) corresponds to the second multiple in (5), and sign “-” governs solutions connected with the first multiple.

### 3 Coupling of CTEs and Frenkel Excitons in a Simple Hexagonal 2D Lattice

The excitonic spectra of charge transfer solids contain both spectra of CTEs and of FEs. Due to the close frequencies of these exciton branches and their vibronics, the coupling between the two types of excitons govern both linear and nonlinear spectra [2, 4, 5, 8, 9, 11–13].

Two types of FEs manifest themselves in linear absorption spectra of high symmetry 2D lattice – quadratic [10] and hexagonal [16]:

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\[ H_{F, z} = \sum_k [E_F + 2W\mu]B_{zk}^+ B_{zk}. \] (16)

The coupling of FEs and CTEs is a result of dissociation of FE via transfer of the electron to the neighbour molecule (or inverse process from CTE to FE). Let introduce two dissociation integrals with transfer of the electron \( D_e \) and the hole \( D_h \) from a neutral excited molecule to the neighbours. All CTEs are equally coupled with FE \( z \), and we find the following coupling terms which express dissociation of FE with a transfer of the electron

\[ \hat{H}^{(z)}_{\text{FC}, e} = D_e \sum_{k,i=1,6} \left[ C_{ik}^e B_{zk} + \text{h.c.} \right]. \] (17)

Using this expression, one can construct the following terms with transfer of hole:

\[ \hat{H}^{(z)}_{\text{FC}, h} = D_h \sum_k \left\{ \left[ C_1^+ e^{ik_\alpha\gamma} + C_2^+ e^{ik_\beta\gamma} + C_3^+ e^{i(k_\beta - k_\alpha)\gamma} + C_4^+ e^{-ik_\alpha\gamma} + C_5^+ e^{-ik_\beta\gamma} + C_6^+ e^{i(k_\alpha - k_\beta)\gamma} \right] B_{zk} + \text{h.c.} \right\}. \] (18)

In this Section we are interested in the spectra of coupled FEs–CTEs at \( J_e = J_h = 0 \) in Hamiltonian (2). Then the excitonic levels \( E_k \) can be expressed as follows:

\[ E_{k,1,2}^{(\pm z)} = \frac{E_F + 2W\mu + E_C}{2} \pm \sqrt{\left( \frac{E_F + 2W\mu - E_C}{2} \right)^2 + 6(D_e^2 + D_h^2) + 4D_e D_h \mu}. \] (19)

**b) degenerate FEs** with transition dipole moments parallel to the layer. Let \( B_{zk} \) and \( B_{yk} \) denote the annihilation operators of FEs with transition moment \( h \) on \( x \) and \( y \) axes correspondingly

\[ \hat{P}_{\text{FC},xy} = h[\hat{x}B_{x,0} + \hat{y}B_{y,0} + \text{h.c.}]. \] (20)

Their excitation energies \( E_{F1} \) are equal (due to the symmetry). We introduce two circularly polarized FEs (see Ref. [16])

\[ \psi_{F, i}|0\rangle = \frac{1}{\sqrt{2}}(B_{x}^+ + iB_{y}^+)|0\rangle = B_{i}^+|0\rangle, \]
\[ \psi_{F, i}|0\rangle = \frac{1}{\sqrt{2}}(B_{x}^+ - iB_{y}^+)|0\rangle = B_{i}^+|0\rangle. \] (21)
The nonvanishing FEs–CTEs coupling terms in the Hamiltonian are

\[
\hat{H}_{\text{FC},(xy)}^{(e)} = \mathcal{E}_e \sum_k \left[ B_{\text{FC},k}^+ R_{\text{CT},k}^{(e)} + B_{\text{CT},k}^+ R_{\text{FC},k}^{(l)} + \text{h.c.} \right],
\]

(22)

where, see formulas (9) and (10),

\[
R_{\text{CT}}^{(e,l)} = C_1 - C_4 + \frac{1}{2} (C_2 - C_5 - C_3 + C_6) \mp \frac{i \sqrt{3}}{2} (C_2 - C_5 + C_4 - C_6).
\]

(23)

The coupling part (22) can be represented in the following way:

\[
\hat{H}_{\text{FC},(xy)}^{(e)} = \mathcal{E}_e \left\{ B_{x,k}^+ \left[ C_{1k} - C_{4k} + \frac{1}{2} (C_{2k} - C_{5k} - C_{3k} + C_{6k}) \right]
\]

\[
+ \frac{\sqrt{3}}{2} B_{y,k}^+ (C_{3k} - C_{6k} + C_{2k} - C_{5k}) + \text{h.c.} \right\},
\]

(24)

where \( \mathcal{E}_e = \mathcal{E}_e^{(l)} \sqrt{2} \). By using the same methodics as it is for nongenerate excitons we find the following coupling terms in the case of dissociation of FE via transfer of the hole:

\[
\hat{H}_{\text{FC},(xy)}^{(h)} = \mathcal{E}_h \left\{ B_{x,k}^+ \left[ C_{1k} e^{-i k_a \gamma} - C_{4k} e^{i k_a \gamma}
\right]
\]

\[
+ \frac{1}{2} \left( C_{2k} e^{-i k_b \gamma} - C_{5k} e^{i k_b \gamma} - C_{3k} e^{i (k_a - k_b) \gamma} + C_{6k} e^{i (k_b - k_a) \gamma} \right)
\]

\[
+ \frac{\sqrt{3}}{2} B_{y,k}^+ \left[ C_{2k} e^{-i k_b \gamma} - C_{5k} e^{i k_b \gamma}
\right]
\]

\[
+ C_{3k} e^{i (k_a - k_b) \gamma} - C_{6k} e^{i (k_b - k_a) \gamma} + \text{h.c.} \right\}.
\]

(25)

In this case CTEs are coupled with both \( B_{x,k} \) and \( B_{y,k} \) excitons and the equation for the excitonic levels \( E \) is more complicated (despite of standard procedure), notably

\[
\left\{ \begin{align*}
(E - E_C)(E - E_{F,x}) - 3(\mathcal{E}_e^2 + \mathcal{E}_h^2) - \mathcal{E}_e \mathcal{E}_h \left[ 4 \cos(k_a \gamma) + \cos(k_b \gamma) 
\right. \\
\cos((k_a - k_b) \gamma) \right] \end{align*} \right\}

\[
\left\{ \begin{align*}
(E - E_C)(E - E_{F,y}) \\
- 3 \left[ \mathcal{E}_e^2 + \mathcal{E}_h^2 + \mathcal{E}_e \mathcal{E}_h \left[ \cos(k_b \gamma) + \cos((k_a - k_b) \gamma) \right] \right] \end{align*} \right\}

\[
- 3 \mathcal{E}_e^2 \mathcal{E}_h^2 [\cos(k_b \gamma) - \cos((k_a - k_b) \gamma)]^2 = 0,
\]

(26)

where (see Ref. [10])

\[
E_{F,x}(k) = E_{F1} + 2 V_1 \left[ - \frac{5}{4} \left( \cos(k_a \gamma) + \cos(k_b \gamma) \right) + \cos((k_a - k_b) \gamma) \right],
\]

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\[ E_{F,y}(k) = E_{F1} + 2V_{1}\left[\frac{1}{4}\left(\cos(k_{a}\gamma) + \cos(k_{b}\gamma)\right) - 2\cos((k_{a} + k_{b})\gamma)\right], \quad (28) \]

and \( V_{1} = h^{2}/(4\pi\varepsilon_{0}a^{3}) \), \( \varepsilon_{0} = 8.85 \times 10^{-12} \text{ F/m} \).

In the center of the Brillouin zone, \( k = 0 \), one obtains a pair of double degenerate excitonic levels (see (26))

\[ E_{k=0,1,2} = \frac{E_{F1} - 3V_{1} + E_{C}}{2} \pm \sqrt{\left(\frac{E_{F1} - 3V_{1} - E_{C}}{2}\right)^{2} + 3(E_{e} + E_{h})^{2}}. \quad (29) \]

4 Conclusion

Our theoretical model treats the spectra of charge transfer excitons in a simple hexagonal 2D lattice as well as the case of their coupling with Frenkel excitons. Six equivalent quasiparticles of two ionized molecules influence linear and nonlinear spectra of the system despite of relatively small transition dipole moment of CTEs.

The main results of our study are:

1. classification of CTEs combinations governed by 6-axis symmetry, especially, the combinations with nonzero transition dipole moments;
2. description of the coupling of FEs and dipole-active CTEs via dissociation of FEs with transfer of the electron or of the hole on neighbor molecules.

The most prominent structures in which our model can be available appear to be:
(a) 2D structures of proteins like bacteriorhodopsine in which charge transfer processes govern some functions; (b) artificial hexagonal 2D structures in which CTEs change their optical spectra.

The perspective of further development of the model concerns, beside of its experimental realization, the study of vibronic spectra which can cover the frequency region of CTEs.

References

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