Excitonic spectra of hexagonal 2D compounds

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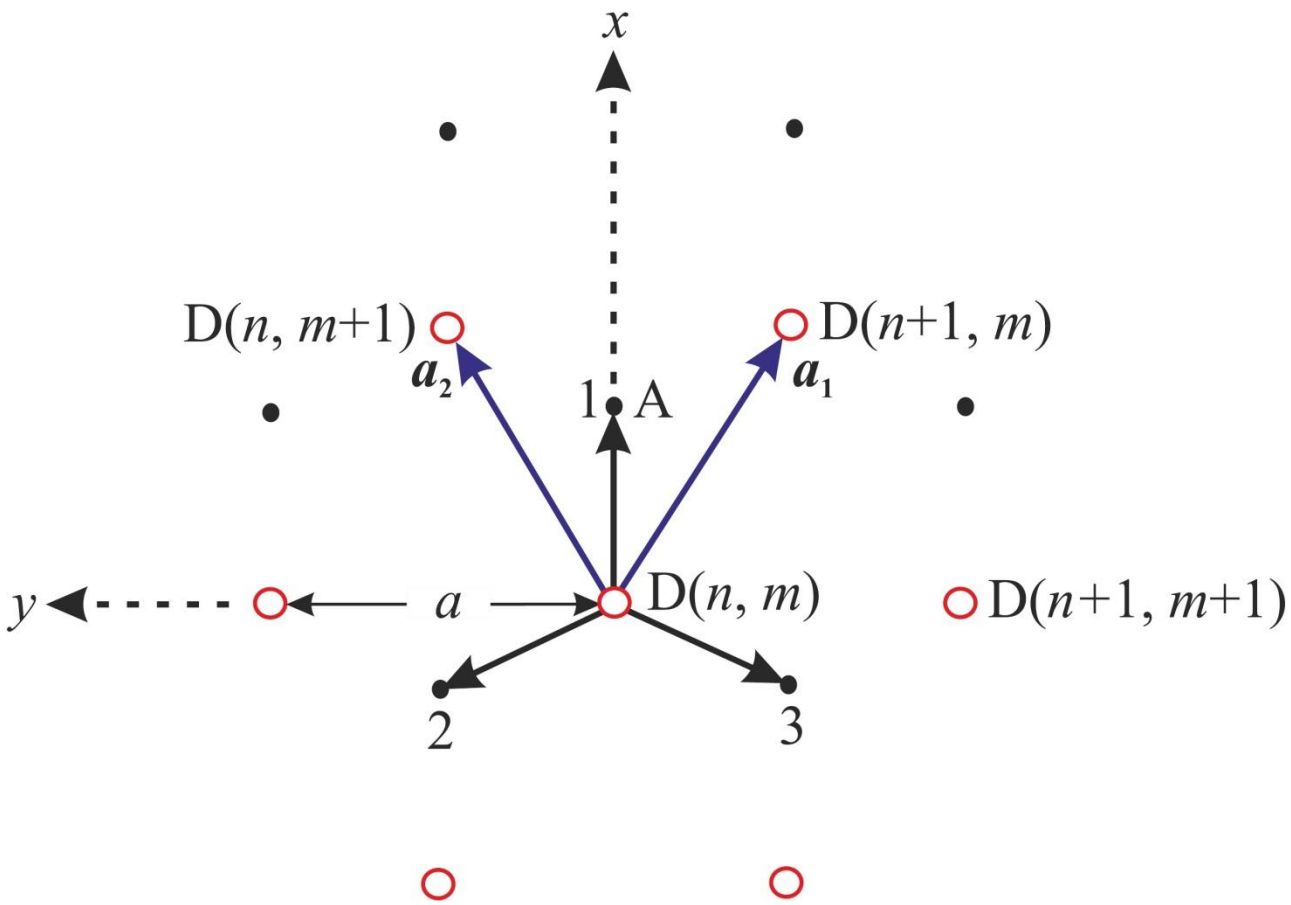
OUTLOOK

- **Two 2D models of donor–acceptor compounds**
- **Frenkel excitons and charge-transfer excitons**
- **Linear absorption spectra in excitonic and vibronic regimes**
- **Simulations of linear absorption spectra**

Two hexagonal sub-lattices of donors and acceptors (DA)

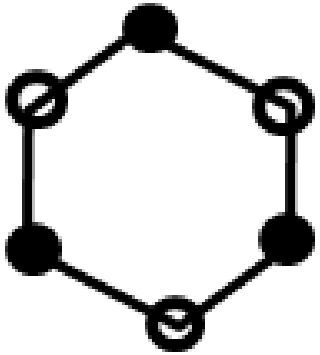


❖**Frenkel excitons** are electronically excited molecules. The excitation is transferred between neighbor molecules. Frenkel excitons are small-radius excitations which possess big oscillator strength.

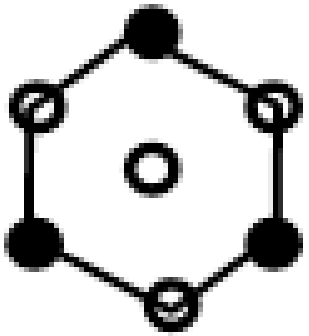
❖**Charge-transfer excitons** consist of one electron and one hole excited on neighbor molecules. CTEs possess relatively small oscillator strength.

FE and CTEs occur in molecular crystals (organic solids)

Realized 2D hexagonal non-molecular structures



hexagonal boron nitride



mxenes

Frenkel and CT excitons and their Coupling in DA (Lalov,Zhelyazkov, BJP,vol.42,p. 172)

Frenkel excitons [z]

$$\hat{H}_{FE} = \sum_{k} [E_F + 2V\mu] B^{+}_{ZK} B_{ZK}$$

$$\mu = \cos k_1 + \cos k_2 + \cos(k_1 - k_2)$$

Collectivization of CTEs

$$\Psi_c|0\rangle = \left[a_1 C_1^{+} + a_2 C_2^{+} + a_3 C_3^{+}\right]|0\rangle,$$

$$a_1 = 1/\sqrt{3},\ a_2 = a_1 \exp(\mathrm{i}\beta),\ a_3 = a_1 \exp(2\mathrm{i}\beta)$$

$$\exp(3\mathrm{i}\beta) = 1.$$

Coupling of FE and CTEs

$$\hat{H}^{(z)}_{\mathrm{FCTE}} = \varepsilon \sum_{k,\, i=1,2,3} \left(C^{+}_{i,k} B_{z,k} + \mathrm{h.c.} \right)$$

$$\hat{H}^{(x,y)}_{\mathrm{FCTE}} = \varepsilon_{\mathrm{a}} \sum_{k} \left\{ \left[C^{+}_{1,k} - \frac{1}{2} \left(C^{+}_{2,k} + C^{+}_{3,k} \right) \right] B_{x,k} + \frac{\sqrt{3}}{2} \left(C^{+}_{2,k} - C^{+}_{3,k} \right) B_{y,k} + \mathrm{h.c.} \right\}$$

Vibronic spectra

- In absorption spectra of isolated molecules the sum of frequencies of molecule's electronic excitations + one or several quanta of intramolecular vibrations forms a vibronic progression.
- In molecular crystals vibronic spectra consist of exciton + one/several intramolecular phonons.

The exciton and phonons are propagating excitations.

We study the linear absorption in excitonic and in one-phonon vibronic spectra.

Exciton–phonon coupling

$$\hat{H}_{\text{ph–d}} = \hbar\omega_0 \sum_{nm,\, i=1\text{–}3} \left[a^{+}_{nm} a_{nm} \right.$$

$$+\xi C^{+}_{i,nm} C_{i,nm} \left(a^{+}_{nm} + a_{nm} \right)$$

$$\left. + \xi_{\text{F}} B^{+}_{nm} B_{nm} \left(a^{+}_{nm} + a_{nm} \right) \right]$$

Linear absorption spectra

Standard procedure for calculating the linear optical susceptibility

Vibronic approach

I.J. Lalov & I. Zhelyazkov
***Phys. Rev.* B 75 (2007) 245435**

Linear absorption spectra in DA

$$\chi_{zz}, \chi_{xx} = \chi_{yy}$$

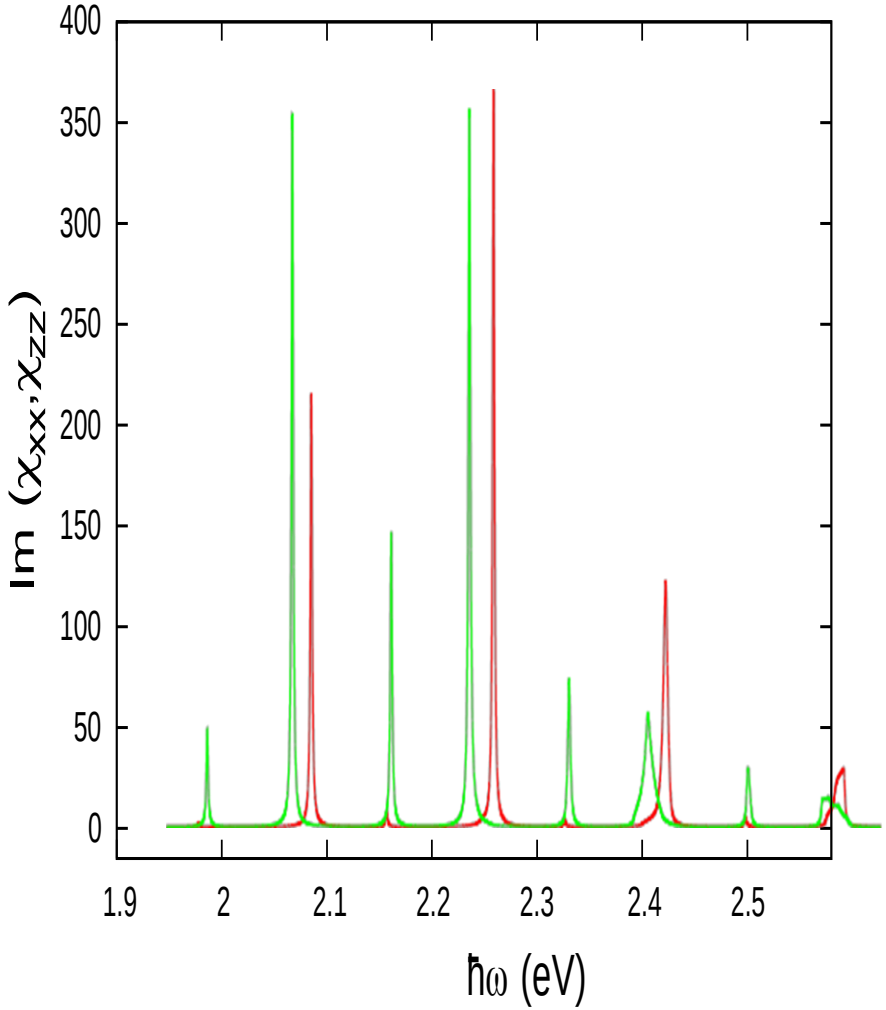
$$\overset{\Lambda}{P}_{x,y} = h[B_{x,0}e_x + B_{y,0}e_y + h.c] + q\left\{\left[C_{1,0} - \frac{1}{2}(C_{2,0} + C_{3,0})\right]e_x + \frac{\sqrt{3}}{2}\left[(C_{2,0} - C_{3,0})e_y + h.c\right]\right.$$

$$\chi_{xx} = \chi_{yy} = -\frac{h^2\alpha_{22} + 3qh\alpha_{12} + \frac{3}{2}q^2\alpha_{11}}{v(\alpha_{11}\alpha_{22} - 3\alpha^2{}_{12}/2)}$$

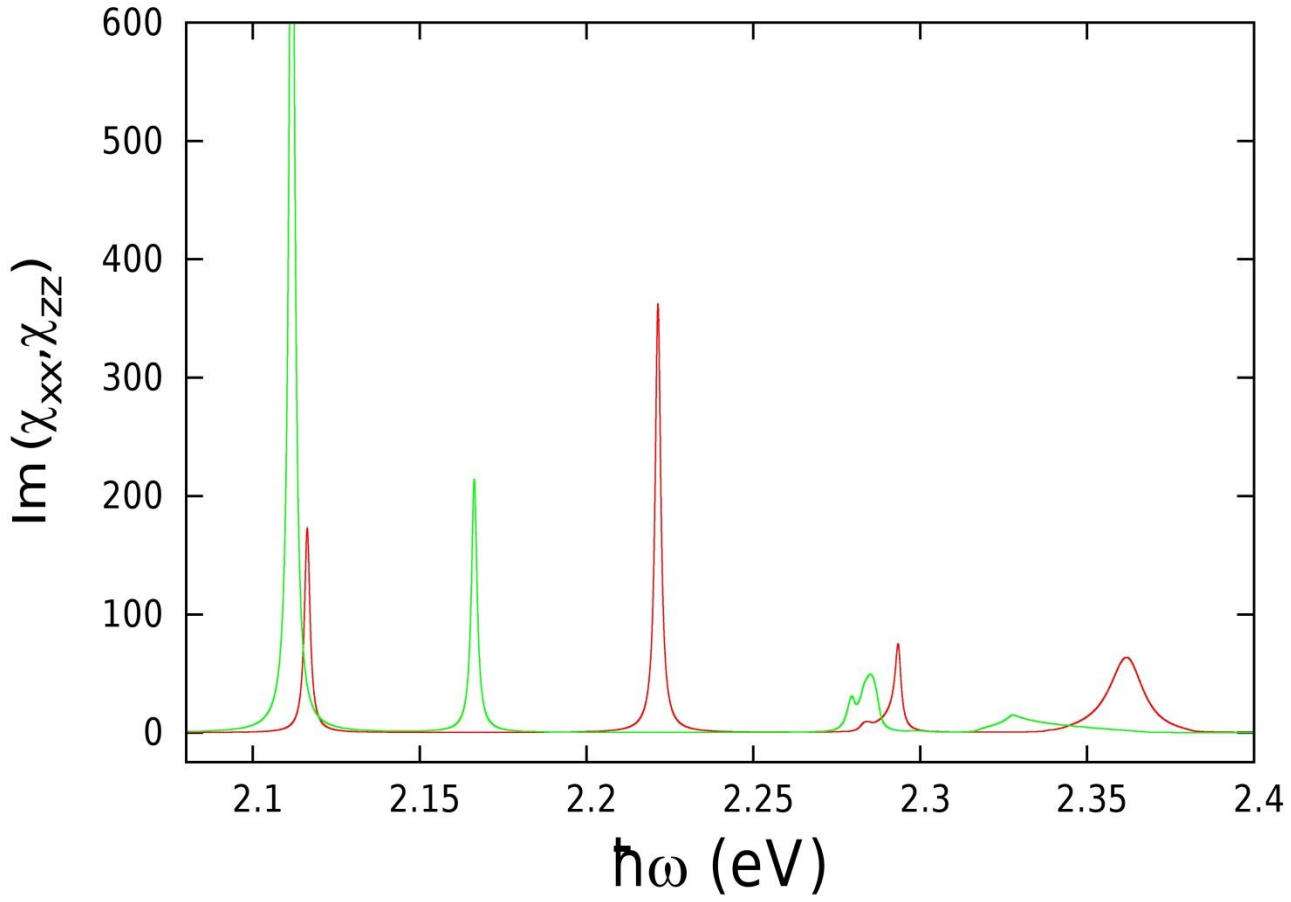
$$\alpha_{11} = \hbar(\omega - \omega_{0F}) - E_F + 3V_1; \alpha_{12} = \varepsilon$$

$$\alpha_{22} = \hbar(\omega - \omega_{0C}) - E_C - J_E + J_h$$

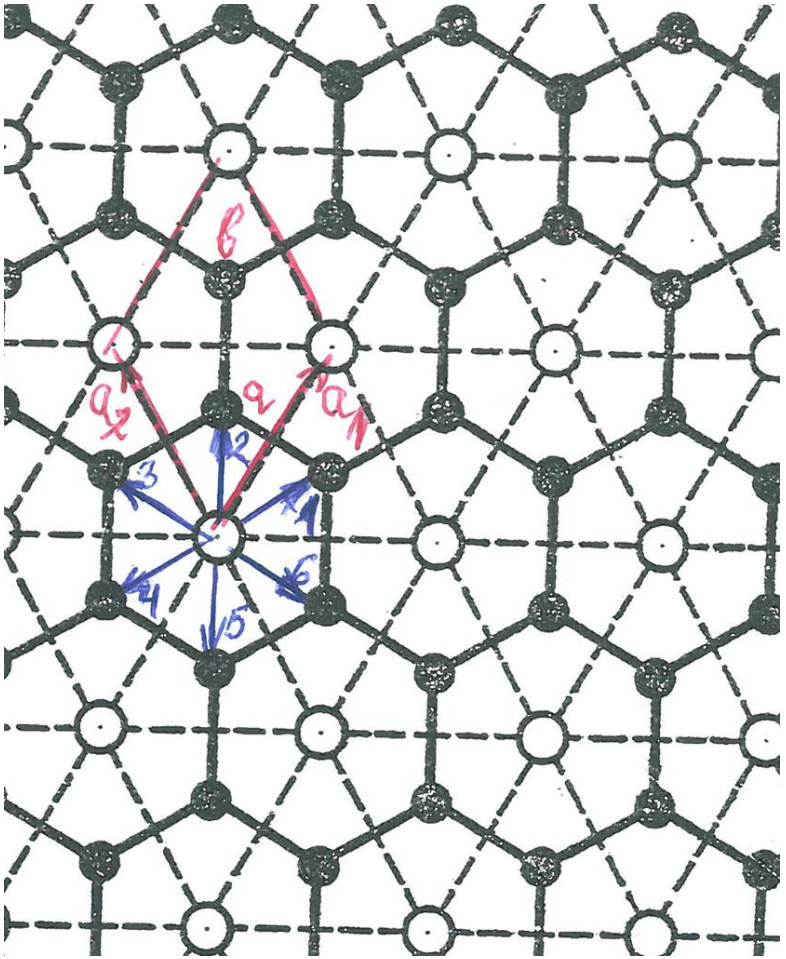
Linear absorption spectra



Linear absorption spectra in the case of weak exciton–phonon coupling



Model of dual hexagonal - trigonal 2D lattices (Lalov, Kojouharova, to be published)



Frenkel excitons in DA_2

- FEs on Donors : $\hat{H}_{FE}^{(D)} = \sum_k [E_F + 2V\mu] B_{ZK}^{+} B_{ZK}$
- FEs on Acceptors :

$$\Delta \hat{H}_{(xy)} = \varepsilon_a \sum_k \left\{ B_x^{+}[C_1 - C_4 + \frac{1}{2}(C_2 - C_5 - C_3 + C_6)] + \frac{\sqrt{3}}{2} B_y^{+}[C_2 - C_5 + C_3 - C_6] + h.c \right\}$$

FEs – CTEs coupling in DA_2

FEs on Donors :

$$\hat{H}_{FE}^{(As)} = \sum_k (E_{Fa} + 2V_1\mu)(B_{F1}^{+}B_{F1} + B_{F2}^{+}B_{F2}) + W\sum [B_{F2}^{+}B_{F1}(1 + e^{ika} + e^{ikb}) + h.c]$$

FEs on Acceptors : $E_e - J_e - E_{(k)} = 12\varepsilon_1^2 \left[\frac{E_{Fa} + 2V_2\mu - E_{(k)} - W_r(1 + \cos k_1 + \cos k_2)}{[E_{Fa} + 2V_2\mu - E_{(k)}]^2 - W_r^2(3 + 2\mu)} \right]$

Linear absorption spectra in DA_2

a) Frenkel excitons on Donors

$$\chi_{xx} = \chi_{yy} = -\frac{h^2\alpha_{22} + 6qh\alpha_{12} + 3q^2\alpha_{11}}{v(\alpha_{11}\alpha_{22} - 3\alpha^2_{12})}$$

b) FEs on Acceptors

$$\chi_{xx} = \chi_{yy} = -\frac{2h^2\alpha_{22} + 12qh\alpha_{12} + 3q^2\alpha_{11}}{v(\alpha_{11}\alpha_{22} - 6\alpha^2_{12})}$$

$$\alpha_{11} = \hbar(\omega - \omega_{0F}) - E_F + 3V_1 + W;\ \alpha_{12} = \varepsilon$$
$$\alpha_{22} = \hbar(\omega - \omega_{0C}) - E_C - J_e + J_h$$

Conclusions

1. **We explored the symmetry and properties of collectivized electronic excitations in two theoretical models of hexagonal 2D structures.**
2. **The excitonic spectra which include Frenkel and CT excitons as well as their coupling strongly depend on anisotropy of the structures (in 2D layer and perpendicular to it)**
3. **The analytical study and simulations of the linear absorption spectra of two models exhibit the excitonic and vibronic spectra influenced by the exciton–phonon coupling.**

4. **The width of the excitonic lines can cover details of the excitonic spectra. But the interpretation of the spectra needs the knowledge of their splitting**
5. **The symmetry considerations and the studies of the spectra of electronic excitation can be applied for the semiconductors and for other 2D non molecular structures**

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