Generalized Haldane Model and Molecular Excitons' Spectra

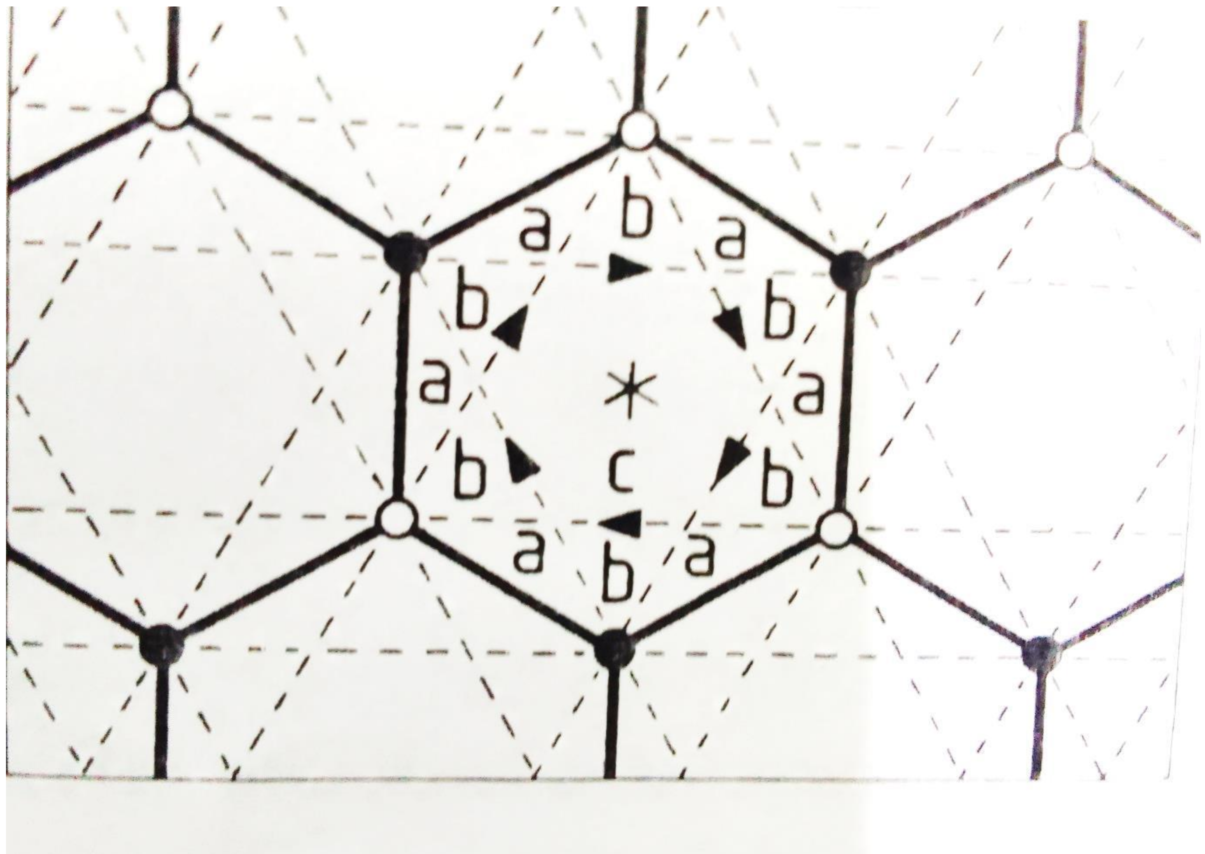
I.J. Lalov,

Faculty of Physics, Sofia University, Sofia, Bulgaria

N. A.Kojouharova

Technical University of Sofia, Department of Applied Physics, Sofia, Bulgaria

Haldane, F.D.M., Phys. Rev. Let., 61 (1988), 2015



Papers with hexagonal 2D models

- **Lalov, I.J.; Zhelyazkov, I., Chem. Phys. (2013), 410, 71-80**
- **Lalov, I.J.; Zhelyazkov, I., Bulg. J. Phys. 42 (2015) 172-199**
- **Lalov, I.J.; Warns Ch., Reineker P., J. Phys. Chem. 124 (2020)4668-4673**

Content

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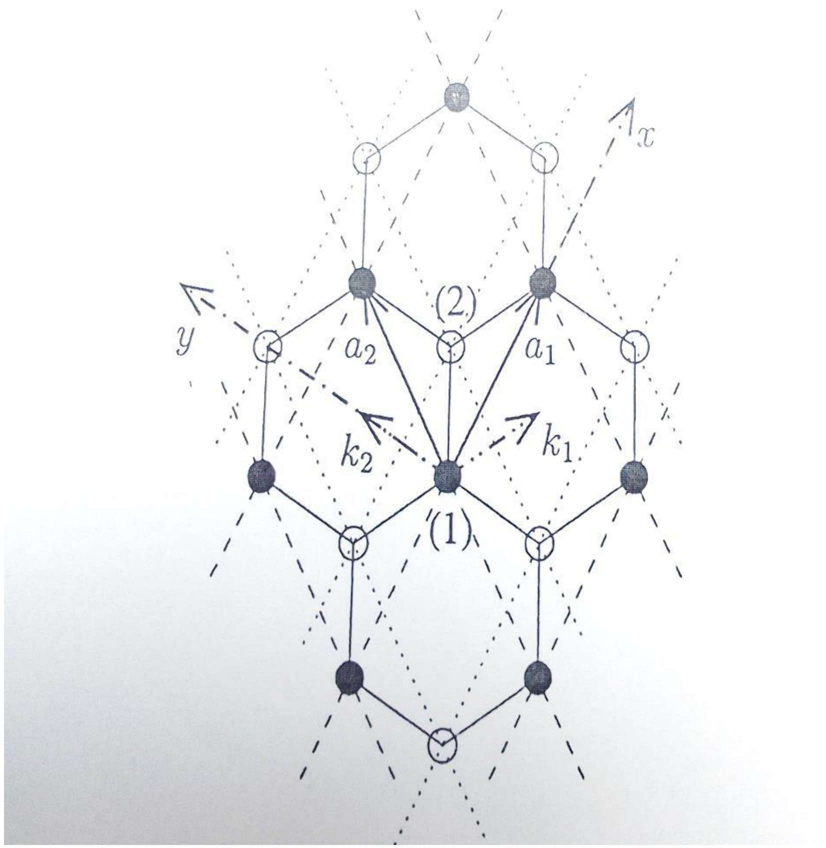
Two types of molecular excitons

1. **Frenkel excitons – transferable electronic excitation of neutral molecule**
2. **Charge Transfer Excitons (CTEs) – pair of positive and negative ions on neighbor lattice sites**

Donor – Acceptor Solids

Honeycomb model of FEs with two identical molecules



z- excitons

xy-excitons

(degenerate)

z-excitons

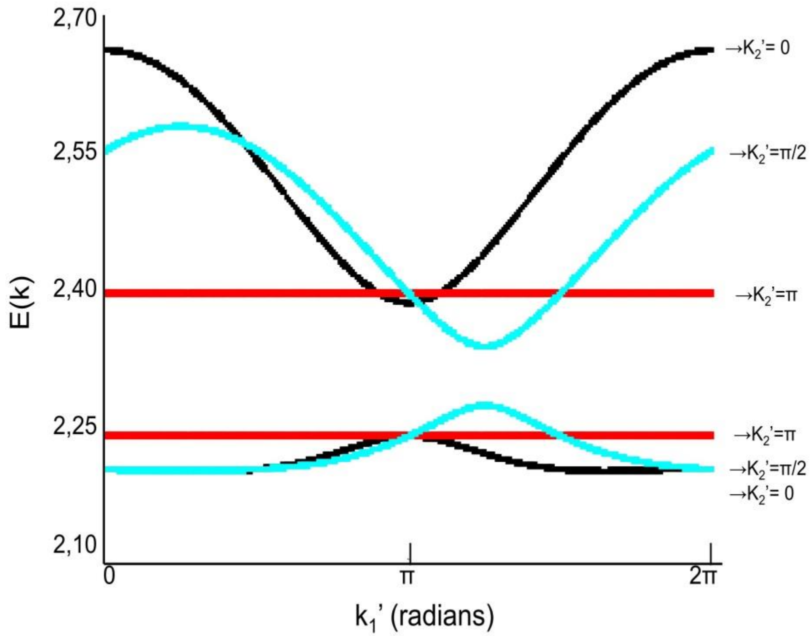
$$\hat{H}_z = \sum_{k,\sigma=1,2} [E_F + V_1 f(k)]\, B^+_{z\sigma}(k) B_{z\sigma}(k) + \sum_k [M(k) B^+_{z1}(k) B_{z2}(k) + hc]$$

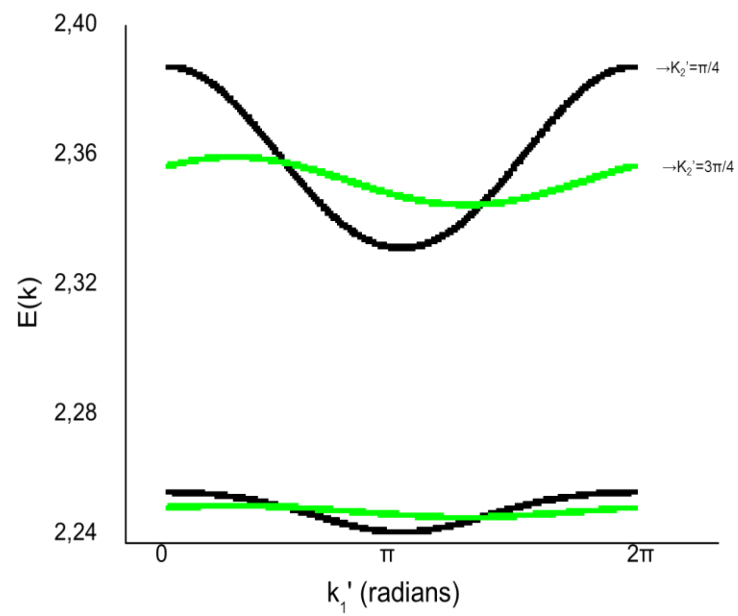
$$M(k) = \frac{p_z^2}{4\pi\varepsilon_0 c^3 [1 + e^{-ik_1\gamma} + e^{-ik_2\gamma}]};\, c = a/\sqrt{3}$$

$$V_1 = \frac{\rho_z^2}{4\pi\varepsilon_0 a^3}$$

$$c = a/\sqrt{3}$$

$$E_z(k) = E_F \pm V_1 f(k) \pm |M(k)|;$$
$$\left[|M(k)|^2 = [p_z^2/(4\pi\varepsilon_0 c^3]^2[f(k)+3]\right]$$
$$f(k) = 2[\cos(k_1\gamma) + \cos(k_2\gamma) + \cos\big((k_1 - k_2)\gamma\big)$$





xy-excitons

$B_{l,\sigma}^{(\vec{n})}$; $B_{r,\sigma}^{(\vec{n})}$ - circularly polarized excitations of the molecule $(\vec{n}\,\sigma)$, σ=1,2

two (l,r) excitons in two nonequivalently positioned molecules for the excitonic spectra E

Equation with trivial coupling only

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

$$A = h^2/(4\pi\varepsilon_0 c^3)$$

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

$$k = 0$$

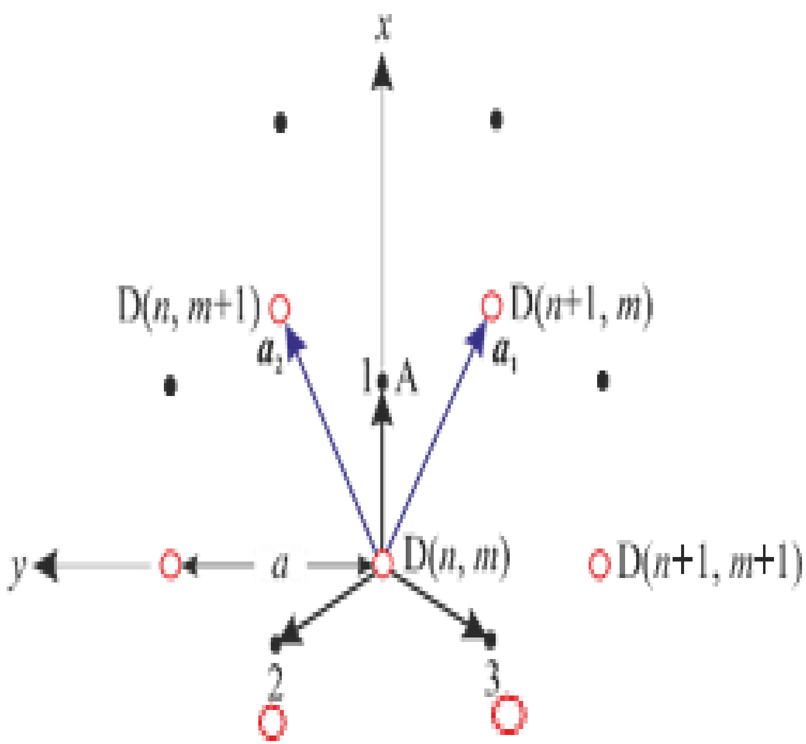
$$\varepsilon_{1,2} = \pm 3A_3/2 \qquad \varepsilon_{3,4} = \varepsilon_{1,2}$$

$$k_1 = -k_2 = \frac{2\pi}{3}$$

$$\varepsilon_{1,2} = 0\,, \varepsilon_{3,4} = \pm 9A_3/2$$

Honeycomb model in DA-lattice

p.



Two systems of
different FEs
(of D or of A)
Three identical CTEs

Hamiltonian of z-FEs of Donors

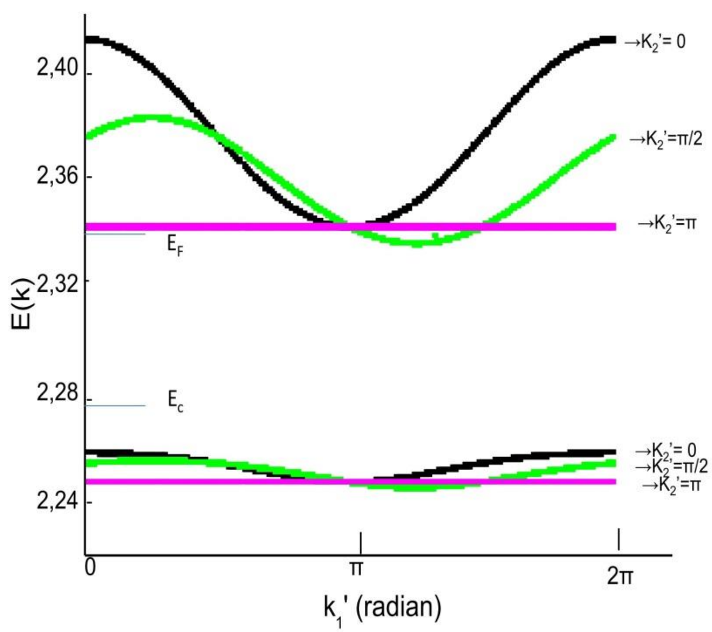
$$\widehat{H}^{(z)} = \sum_k [E_F + V_1 f(k)] B_{zk}^{+} B_{zk0} + \widehat{H}_{CTEs} + (\frac{u}{\sqrt{3}}) \sum_{k,i=1-3} [B_{zk}^{+} C_{ik} + h.c]$$

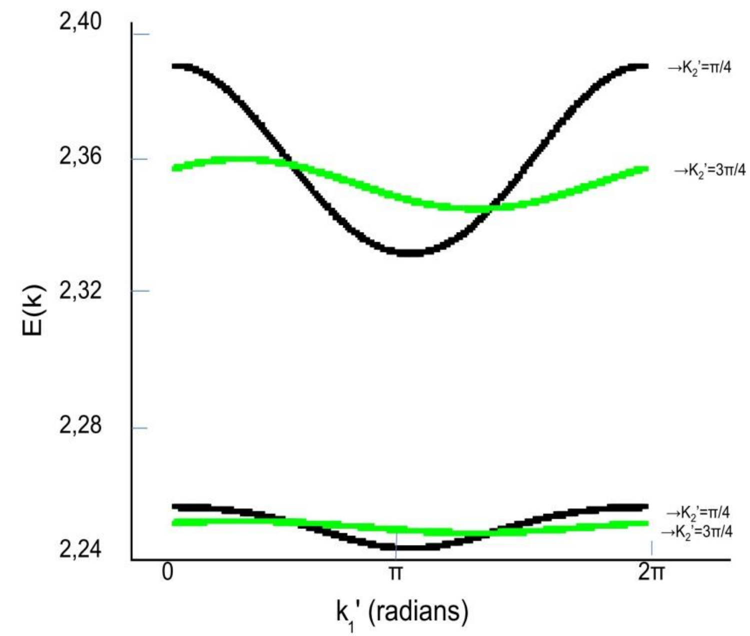
$$\widehat{H}_{CTEs} = \sum_{k,i=1-3} E_c C_{ik}^{+} C_{ik} + \sum_k F(J_e, J_h, k)$$

J_e, J_h- nontrivial coupling of CTEs

Excitonic levels E at $J_e = J_h = 0$

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





Indirect coupling of FEs in DA-lattice

Hamiltonian of z-FEs of Acceptors

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

$$1 - d(k)\left[\frac{u^2}{E_F + V_1 f(k) - E} + \frac{u_3^2}{E_{FA} + V_A f(k) - E}\right] = 0$$

d(k) depends on CTEs parameters only

At $J_e = J_h = 0$ d(k)=1/(E_c-E)

Conclusions

I) Using the symmetry of Haldane model we treat complicate excitonic spectra of honeycomb lattice with two identical nonequivalently positioned molecules and the excitations in DA-2D lattice

II) Our study is an example of generalization of Haldane model, including the anisotropy of coupling parameters, degeracy of excitations, trivial coupling with transformation of excitations and indirect coupling. Similar generalization could concern the problems far from molecular excitons spectra.

Thank you for your attention!