

# Holstein model for exciton and charge transport in organic semiconductors

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1	Introduction . . . . .	1
2	Adiabatic limit . . . . .	1
3	Donor-acceptor system . . . . .	2
4	Independent boson model . . . . .	4
	Appendix . . . . .	7
A	Vibrations . . . . .	7
B	Spectral overlap from experiment . . . . .	8
C	Classical spectral overlap . . . . .	8
D	Evaluation of transition spectral density by saddle point method . . . . .	8
E	Nonorthogonal basis . . . . .	9
F	Estimation of exciton transfer integrals from dimer calculations . . . . .	10
	References . . . . .	10

## §1. Introduction

Our starting point is *Holstein–Peierls* Hamiltonian:

$$\sum_{ij} H_{ij}^{\text{le}} c_i^\dagger c_j + \sum_{\alpha} \hbar \omega_{\alpha} \left( b_{\alpha}^\dagger b_{\alpha} + \frac{1}{2} \right) + \sum_{ij\alpha} \hbar \omega_{\alpha} g_{ij\alpha} \left( b_{\alpha}^\dagger + b_{\alpha} \right) c_i^\dagger c_j, \quad (1.1)$$

where  $c_i^\dagger$  is the quasiparticle (Frenkel excitons, holes etc.) creation operator and  $b_{\alpha}^\dagger$  is the localized phonon (normal mode) creation operator. The notations for the one-electron Hamiltonian are as follows:

$$H_{ij}^{\text{le}} = \delta_{ij} \varepsilon_i + (1 - \delta_{ij}) t_{ij}, \quad (1.2)$$

here  $\varepsilon_i$  is *on-site energy* and  $t_{ij}$  is *transfer integral*. Electron-phonon coupling described by the constants  $g_{ij\alpha} \equiv g_{ji\alpha}$  is called *local* for  $i = j$  (Holstein model [1]) and *nonlocal* otherwise (Peierls model [2]). In (1.1) the localized basis is chosen for phonons, for plane waves  $\alpha$  is the wave vector and the last term must be modified as follows

$$\left( b_{\alpha}^\dagger + b_{\alpha} \right) \rightarrow \left( b_{\alpha}^\dagger + b_{-\alpha} \right). \quad (1.3)$$

The classical limit of the Hamiltonian (1.1) can be obtained by reversing the formulas of Section A yielding

$$\sum_{ij} H_{ij}^{\text{le}} c_i^\dagger c_j + \frac{1}{2} \sum_{\alpha} M_{\alpha} \dot{x}_{\alpha}^2 + \frac{1}{2} \sum_{\alpha\beta} U_{\alpha\beta}'' x_{\alpha} x_{\beta} + \sum_{ij\alpha} \tilde{g}_{ij\alpha} x_{\alpha} c_i^\dagger c_j, \quad (1.4)$$

where

$$\tilde{g}_{ij\alpha} = M_{\alpha} \sum_{\beta} T_{\alpha\beta} \sqrt{2\hbar\omega_{\beta}} \omega_{\beta} g_{ij\beta}, \quad (1.5)$$

## §2. Adiabatic limit

Here the adiabatic limit means that the electronic dynamics is much faster than the vibrational dynamics. In this limit the Holstein model is exactly solvable: at fixed positions of atoms in (1.4) we solve the one-electron Hamiltonian whose matrix elements are

$$H_{ij}^{\text{le}} + \sum_{\alpha} \tilde{g}_{ij\alpha} x_{\alpha}. \quad (2.1)$$