

Holstein model for exciton and charge transport in organic semiconductors

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1	Introduction	1
2	Adiabatic polaron	2
3	Donor-acceptor system and transition spectral density	2
4	Independent boson model	5
4.1	Franck–Condon factors	6
4.2	Wave-function and correlators	6
4.3	Transition spectral density	7
5	Spectral lineshape	8
6	Spectral overlap in semiclassical approximation	11
7	Two-site Holstein model with one boson per site	11
8	Inertia effects	13
	Appendix	14
A	Vibrations	14
B	Perturbation theory for normal modes of weakly interacting systems	15
C	Anharmonism	16
D	Sum rules for Franck–Condon factors of Independent boson model	16
E	Surface hopping	16
F	Spectral overlap from experiment	17
G	Phonon correlator in complex plane	17
H	Nonorthogonal basis	19
I	Estimation of exciton transfer integrals from dimer calculations	20
J	Hopping amplitudes	20
	References	21

§1. Introduction

Our starting point is *Holstein–Peierls* Hamiltonian:

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

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

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

here ε_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 α 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 Appendix A yielding

$$\sum_{ij} H_{ij}^{1e} c_i^{\dagger} c_j + \frac{1}{2} \sum_{\alpha} \hbar\omega_{\alpha} \left(\omega_{\alpha}^{-2} \xi_{\alpha}^2 + \xi_{\alpha}^2 \right) + \sqrt{2} \sum_{ij\alpha} \hbar\omega_{\alpha} g_{ij\alpha} \xi_{\alpha} c_i^{\dagger} c_j \quad (1.4)$$

or

$$\sum_{ij} H_{ij}^{1e} c_i^{\dagger} c_j + \frac{1}{2} \sum_{\alpha} M_{\alpha} \dot{x}_{\alpha}^2 + \frac{1}{2} \sum_{\alpha\beta} U_{\alpha\beta}'' x_{\alpha} x_{\beta} + \sum_{ij\alpha} \tilde{g}_{ij\alpha} x_{\alpha} c_i^{\dagger} c_j, \quad (1.5)$$

where

$$\tilde{g}_{ij\alpha} = M_{\alpha} \sum_{\beta} T_{\alpha\beta} \sqrt{2\hbar\omega_{\beta}} \omega_{\beta} g_{ij\beta}. \quad (1.6)$$

§2. Adiabatic polaron

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 (1.5) we solve the one-electron Hamiltonian whose matrix elements are

$$H_{ij}^{1e} + \sum_{\alpha} \tilde{g}_{ij\alpha} x_{\alpha}. \quad (2.1)$$

Now having the electronic wave-function Ψ we apply $\langle \Psi | \cdot | \Psi \rangle$ averaging to (1.5) and obtain Newton equation for atoms:

$$M_{\alpha} \ddot{x}_{\alpha} + \sum_{\beta} U''_{\alpha\beta} x_{\beta} + \sum_{ij} \tilde{g}_{ij\alpha} \rho_{ij}^{\text{el}} = 0 \quad \text{or} \quad \ddot{\xi}_{\alpha} + \omega_{\alpha}^2 \left(\xi_{\alpha} + \sqrt{2} \sum_{ij} g_{ij\alpha} \rho_{ij}^{\text{el}} \right), \quad (2.2)$$

where ρ^{el} is the electronic density matrix. The solution of this equation is harmonic vibrations with frequencies ω_{α} around the stationary solution which in notations of Appendix A can be written as

$$x_{\alpha}^{(0)} = - \sum_{\beta} T_{\alpha\beta} \sqrt{\frac{2\hbar}{\omega_{\beta}}} \sum_{ij} g_{ij\beta} \rho_{ij}^{\text{el}} \quad \text{or} \quad \xi_{\alpha}^{(0)} = -\sqrt{2} \sum_{ij} g_{ij\alpha} \rho_{ij}^{\text{el}} \quad (2.3)$$

(note that this formula is implicit because the electronic density depends on atomic coordinates). This stationary solution can be called *adiabatic polaron*, which can be hole polaron, electron polaron, Frenkel exciton etc. The polaron total energy is given by $E^{\text{el}} - \lambda$, where

$$\lambda = \sum_{\alpha} S_{\alpha} \hbar \omega_{\alpha} \quad (2.4)$$

is the *polaron relaxation energy* and

$$S_{\alpha} = \left(\sum_{ij} g_{ij\alpha} \rho_{ij}^{\text{el}} \right)^2 \quad (2.5)$$

are *Huang–Rhys factors*. Quantum fluctuations can destroy the classic solution so that the adiabatic polaron is well defined only in the strong coupling limit. In this case it is called *small polaron*.

It is convenient to choose adiabatic polaron wave-functions for the one-electron basis, because in this case (2.3) and (2.5) will read

$$\xi_{\alpha}^{(0)} = -\sqrt{2} g_{ii\alpha} \quad \text{and} \quad S_{\alpha} = g_{ii\alpha}^2, \quad (2.6)$$

where i enumerates the adiabatic polaron solutions. In this basis transfer integrals and the corresponding nonlocal couplings are not independent but must satisfy the condition that for each polaron site i

$$H_{ij}^{1e} + \sum_{\alpha} \tilde{g}_{ij\alpha} x_{\alpha}^{(0)}(i) = 0 \quad \text{if } j \neq i, \quad (2.7)$$

yielding

$$t_{ij} = \sum_{\alpha} 2\hbar \omega_{\alpha} g_{ii\alpha} g_{ij\alpha}. \quad (2.8)$$

§3. Donor-acceptor system and transition spectral density

Let consider two weakly interacting systems such that there are two adiabatic polaron solutions each localized on one system only. The rate of polaron transfer between the systems can be calculated using Fermi's golden rule:¹

$$w = \frac{2\pi}{\hbar} \int \rho_i(E) |\langle f | \mathbf{H}^{\text{int}} | i \rangle(E)|^2 g_f(E) dE, \quad (3.1a)$$

¹Here and throughout the text a sum/integral without limits means the summation/integration over the whole domain.