Holstein model for exciton and charge transport in organic semiconductors

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§1. Introduction

Our starting point is *Holstein–Peierls* Hamiltonian:

$$\sum_{ij} H^{1e}_{ij}\mathsf{c}^\dagger_i\mathsf{c}_j + \sum_\alpha \hbar\omega_\alpha\left(\mathsf{b}^\dagger_\alpha\mathsf{b}_\alpha + \frac{1}{2}\right) + \sum_{ij\alpha}\hbar\omega_\alpha g_{ij\alpha}\left(\mathsf{b}^\dagger_\alpha + \mathsf{b}_\alpha\right)\mathsf{c}^\dagger_i\mathsf{c}_j, \tag{1.1}$$

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

$$H^{1e}_{ij} = \delta_{ij}\varepsilon_i + (1-\delta_{ij})t_{ij}, \tag{1.2}$$

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

$$\left(\mathsf{b}^\dagger_\alpha + \mathsf{b}_\alpha\right) \to \left(\mathsf{b}^\dagger_\alpha + \mathsf{b}_{-\alpha}\right). \tag{1.3}$$

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

$$\sum_{ij} H^{1e}_{ij}\mathsf{c}^\dagger_i\mathsf{c}_j + \frac{1}{2}\sum_\alpha M_\alpha\dot{x}^2_\alpha + \frac{1}{2}\sum_{\alpha\beta}U''_{\alpha\beta}x_\alpha x_\beta + \sum_{ij\alpha}\tilde{g}_{ij\alpha}x_\alpha\mathsf{c}^\dagger_i\mathsf{c}_j, \tag{1.4}$$

where

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

§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

$$H^{1e}_{ij} + \sum_\alpha \tilde{g}_{ij\alpha}x_\alpha. \tag{2.1}$$