

Holstein model for organic semiconductors

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§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

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

For small or vanishing ω_{α} it might be reasonable to use $G_{ij\alpha} = \hbar\omega_{\alpha} g_{ij\alpha}$ as independent constants.

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

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

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

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