A note on temperature-dependent band narrowing in oligo-acene crystals

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K Hannewald, V M Stojanović and P A Bobbert

Group Polymer Physics, Eindhoven Polymer Laboratories, Technische Universiteit Eindhoven,
PO Box 513, 5600 MB Eindhoven, The Netherlands

Abstract
We present a theoretical description of polaron band narrowing in oligo-acene
crystals due to electron–lattice interaction. The analysis is based on a model
which takes both local and nonlocal contributions to the electron–phonon
coupling into account. Different approximation schemes are discussed and
compared. The theory is supplemented by quantitative *ab initio* calculations
of the temperature dependence of polaron bandwidths in oligo-acene crystals
which show the important role of in-plane nonlocal electron–phonon coupling.

1. Introduction

An important class of organic semiconductors are molecular crystals of high purity. Besides
the overall technological potential [1–9], these crystals are interesting model systems for
fundamental studies of optical and transport properties in organic semiconductors. In contrast
to polymers, crystals of high purity do not suffer from structural disorder which makes it
possible to study directly the underlying intrinsic excitations and charge-carrier transport
mechanisms. Several fundamental experimental and theoretical studies have been performed
in recent years, e.g. on oligo-acene crystals such as pentacene [10–15]. Here, we present a
theoretical study of the temperature-dependent polaron band narrowing in oligo-acene crystals
due to electron–phonon interaction.

A milestone towards the understanding of the intrinsic charge-carrier transport
mechanisms in organic semiconductors has been an early paper by Holstein [16] who
studied the influence of electron–phonon interaction on bandwidths and mobilities for a one-
dimensional model crystal. In comparison to covalently bonded inorganic semiconductors,
organic molecular crystals exhibit weak intermolecular van der Waals bonds and, hence,
narrower electron bands and stronger electron–lattice interaction. As a consequence, polaron
effects become important and lead to a temperature-dependent band narrowing. For elevated
temperatures this may even result in a localization of the charge carriers and change the transport
mechanism from band-like conduction into a phonon-assisted hopping motion. Twenty years

later, the interplay between band and hopping transport in organic solids was, indeed, observed in naphthalene crystals [17, 18].

From the computational point of view, Holstein's molecular crystal model has the drawback that it can give only *qualitative* insight since it incorporates only the local electron–phonon coupling which acts purely on-site, i.e. at the site of the electronic excitation. However, it is well known, for example, from the work of Su *et al* [19] that in organic semiconductors the nonlocal electron–phonon coupling, where vibrations influence the transfer of an excitation between lattice sites, may also be very important. Consequently, a number of theoretical studies on nonlocal coupling have been performed in the past [20–24], but only recently a solution in analogy to Holstein's result for local coupling has been found which—in combination with *ab initio* calculations of the material parameters—has been utilized to make *quantitative* predictions for the polaron band narrowing in real systems [25].

In this paper, we extend our considerations from [25] and describe an alternative derivation of its main findings. From this, we obtain additional insight into the approximations involved which may be valuable information with respect to future calculations of related quantities such as the polaron mobilities. This paper is organized as follows. After this introduction, we present in section 2 a theory of polaron band narrowing due to electron–phonon interaction. In section 3, we apply this theory to oligo-acene crystals and compare the results to previous approaches. Finally, a summary is given in section 4.

2. Theory of band narrowing due to electron–phonon interaction

Our theoretical description of polaron bandwidth narrowing is based on a mixed Holstein–Peierls model for the interaction between electrons and phonons. Introducing operators $a_m^{(\dagger)}$ and $b_{\mathbf{Q}}^{(\dagger)} := b_{\mathbf{q}\lambda}^{(\dagger)}$ for annihilation (creation) of electrons at site $\mathbf{R}_m$ and phonons with wavevector $\mathbf{q}$ in the mode λ, respectively, our model Hamiltonian is

$$H = \sum_{mn} E_{mn} a_m^\dagger a_n + \sum_{\mathbf{Q}} \hbar\omega_{\mathbf{Q}}(b_{\mathbf{Q}}^\dagger b_{\mathbf{Q}} + \tfrac{1}{2}), \tag{1}$$

$$E_{mn} = \varepsilon_{mn} + \sum_{\mathbf{Q}} \hbar\omega_{\mathbf{Q}} g_{\mathbf{Q}mn}(b_{\mathbf{Q}}^\dagger + b_{-\mathbf{Q}}). \tag{2}$$

Here, electron–electron interaction has been neglected, which is justified in the limit of low electron densities. The latter assumption is motivated by the typical situation in mobility experiments where the charge carriers are injected into the sample at low concentrations. Due to hermiticity and symmetry requirements, the parameters of the above Hamiltonian fulfil the relations

$$\hbar\omega_{\mathbf{Q}} = \hbar\omega_{-\mathbf{Q}}, \qquad g_{\mathbf{Q}mn} = g_{\mathbf{Q}nm} = g_{-\mathbf{Q}nm}^*, \qquad \varepsilon_{mn} = \varepsilon_{nm}, \tag{3}$$

where $\omega_{\mathbf{Q}}$, $g_{\mathbf{Q}mn}$ and ε_{mn} are the phonon frequencies, electron–phonon coupling values and transfer integrals, respectively. Furthermore, we will henceforth assume all on-site energies ε_{mm} to be equal, i.e. all molecules of the crystal are equivalent.

If the electron–lattice interaction is not taken into account ($E_{mn} = \varepsilon_{mn}$) the electronic bandwidths are determined solely by the transfer integrals. Here, we are interested in the modifications of these quantities due to the electron–phonon interaction which, in general, contains coupling terms of both local ($m = n$, Holstein model) and nonlocal nature ($m{\neq}n$, Peierls model). In order to calculate these modifications, the above Hamiltonian has to be diagonalized which requires a disentangling of the electron and phonon operators in equation (2). In comparison to the original Holstein model, this diagonalization procedure is much more complicated in the presence of nonlocal coupling, even in the coherent limit as explained below.

For an approximate diagonalization of the Holstein–Peierls Hamiltonian, we apply the following nonlocal canonical transformation:

$$H \rightarrow \tilde{H} = e^S H e^{S^\dagger}, \qquad S = \sum_{mn} C_{mn} a_m^\dagger a_n, \qquad C_{mn} = \sum_{\mathbf{Q}} g_{\mathbf{Q}mn}(b_{\mathbf{Q}}^\dagger - b_{-\mathbf{Q}}). \tag{4}$$

This transformation can be looked upon as a generalization of the local transformation $S = \sum_m C_{mm} a_m^\dagger a_m$ used for the solution of the Holstein model but it is more complicated since it involves exponential matrix operators [23–25]. Nevertheless, it allows us to calculate the renormalization of the transfer integrals due to both local *and* nonlocal coupling, in analogy to Holstein's original approach.

Prior to the explicit evaluation of $\tilde{H}$ according to equation (4), it is instructive to introduce analogously the transformed operators $\tilde{a}_m^{(\dagger)} = e^S a_m^{(\dagger)} e^{S^\dagger}$ and $\tilde{b}_{\mathbf{Q}}^{(\dagger)} = e^S b_{\mathbf{Q}}^{(\dagger)} e^{S^\dagger}$ which may be interpreted as annihilation (creation) operators of a polaron and a phonon of the distorted lattice, respectively. Then, the transformed Hamiltonian $\tilde{H}$ can be immediately written down by means of the relation

$$\tilde{H}(\tilde{a}_m^{(\dagger)}, \tilde{b}_{\mathbf{Q}}^{(\dagger)}) = H(a_m^{(\dagger)}, b_{\mathbf{Q}}^{(\dagger)}) \tag{5}$$

which follows from the identity $S^\dagger = -S$. In order to express $\tilde{H}$ in terms of the original operators $a_m^{(\dagger)}$ and $b_{\mathbf{Q}}^{(\dagger)}$, we employ the Baker–Campbell–Hausdorff theorem:

$$\tilde{A} = e^S A e^{-S} = A + [S, A] + \tfrac{1}{2!}[S, [S, A]] + \tfrac{1}{3!}[S, [S, [S, A]]] + \cdots . \tag{6}$$

By virtue of the commutators

$$[S, a_m] = -\sum_n C_{mn} a_n,$$

$$[S, [S, a_m]] = +\sum_n (C^2)_{mn} a_n, \tag{7}$$

$$\vdots$$

and

$$[S, b_{\mathbf{Q}}] = \sum_{mn} [C, b_{\mathbf{Q}}]_{mn} a_m^\dagger a_n,$$

$$[S, [S, b_{\mathbf{Q}}]] = \sum_{mn} [C, [C, b_{\mathbf{Q}}]]_{mn} a_m^\dagger a_n, \tag{8}$$

$$\vdots$$

we obtain from equation (6) the transformation rules

$$\tilde{a}_m = \sum_n (e^{-C})_{mn} a_n, \tag{9}$$

$$\tilde{b}_{\mathbf{Q}} = b_{\mathbf{Q}} + \sum_{mn} (\tilde{b}_{\mathbf{Q}} - b_{\mathbf{Q}})_{mn} a_m^\dagger a_n, \tag{10}$$

where we introduced a compact matrix notation and defined $\tilde{b}_{\mathbf{Q}mn} = (e^C b_{\mathbf{Q}} e^{-C})_{mn}$ and $b_{\mathbf{Q}mn} = b_{\mathbf{Q}} \delta_{mn}$. Inserting equations (9) and (10) into (5), we obtain (again in the limit of low electron densities) the transformed Hamiltonian

$$\tilde{H} = \sum_{mn} \tilde{E}_{mn} a_m^\dagger a_n + \sum_{\mathbf{Q}} \hbar\omega_{\mathbf{Q}}(b_{\mathbf{Q}}^\dagger b_{\mathbf{Q}} + \tfrac{1}{2}) \tag{11}$$

$$\tilde{E}_{mn} = \tilde{\varepsilon}_{mn} + \sum_{\mathbf{Q}} \hbar\omega_{\mathbf{Q}} \left(b_{\mathbf{Q}}^\dagger \delta_{\mathbf{Q}} + \delta_{\mathbf{Q}} b_{-\mathbf{Q}} + \delta_{\mathbf{Q}} \delta_{-\mathbf{Q}} - \tilde{g}_{\mathbf{Q}} \tilde{g}_{-\mathbf{Q}} \right)_{mn}, \tag{12}$$

where $\tilde{\varepsilon}_{mn} = (e^C \varepsilon e^{-C})_{mn}$ and $\tilde{g}_{\mathbf{Q}mn} = (e^C g_{\mathbf{Q}} e^{-C})_{mn}$.

In a previous work [25], equation (12) was simplified to $\tilde{E}_{mn} = \tilde{\varepsilon}_{mn} - \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} (\tilde{g}_{\mathbf{Q}} \tilde{g}_{-\mathbf{Q}})_{mn}$ by arguing that terms containing $\delta_{\mathbf{Q}mn} := (\tilde{g}_{\mathbf{Q}} + \tilde{b}_{\mathbf{Q}} - b_{\mathbf{Q}})_{mn} \equiv (\tilde{g}_{\mathbf{Q}} + \tilde{b}_{-\mathbf{Q}}^{\dagger} - b_{-\mathbf{Q}}^{\dagger})_{mn}$ are of minor importance[1]. Here, we go beyond this approximation and take these terms partially into account. In a first step, we insert the definition of $\delta_{\mathbf{Q}mn}$ into expression (12) and obtain as an exact result for the on-site energies and transfer integrals of the interacting electron–phonon system

$$\tilde{E}_{mn} = \tilde{\varepsilon}_{mn} - \tilde{\Delta}_{mn}, \qquad \tilde{\Delta}_{mn} = \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} \left(b_{\mathbf{Q}}^{\dagger} b_{\mathbf{Q}} - \tilde{b}_{\mathbf{Q}}^{\dagger} \tilde{g}_{\mathbf{Q}} - \tilde{g}_{\mathbf{Q}} \tilde{b}_{-\mathbf{Q}} - \tilde{b}_{\mathbf{Q}}^{\dagger} \tilde{b}_{\mathbf{Q}} \right)_{mn}. \tag{13}$$

By means of the Baker–Campbell–Hausdorff theorem (6) and the identity $\left[C, b_{\mathbf{Q}}^{\dagger} b_{\mathbf{Q}}\right]_{mn} = -\left(g_{\mathbf{Q}} b_{\mathbf{Q}}^{\dagger} + g_{-\mathbf{Q}} b_{\mathbf{Q}}\right)_{mn}$, we can rewrite $\tilde{\varepsilon}_{mn} := \sum_{l=0}^{\infty} \frac{1}{l!} \tilde{\varepsilon}_{mn}^{(l)}$ and $\tilde{\Delta}_{mn} := \sum_{l=0}^{\infty} \left(\frac{1}{l!} - \frac{1}{(l+1)!}\right) \tilde{\Delta}_{mn}^{(l)}$ in terms of power series in C_{mn} where

$$\tilde{\varepsilon}_{mn}^{(l)} = \underbrace{[C, [C, \ldots, [C, \varepsilon] \cdots]]_{mn}}_{l \text{ commutators}}, \tag{14}$$

$$\tilde{\Delta}_{mn}^{(l)} = \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} \underbrace{[C, [C, \ldots, [C, -g_{\mathbf{Q}}(b_{\mathbf{Q}}^{\dagger} + b_{-\mathbf{Q}})] \cdots]]_{mn}}_{l \text{ commutators}}. \tag{15}$$

Apart from assuming the limit of low electron (polaron) densities, no approximations have been made so far in the above calculations. However, the phonon operators still appear in equations (13)–(15). Now, in close analogy to the original work of Holstein [16], we assume that coherent band-like conduction prevails over inelastic phonon-assisted hopping transport, which is a reasonable approximation if one is interested only in the polaron band structure. Additionally, this assumption is motivated by the available experimental mobility data of Warta and Karl [18] that indicate band-like transport for not too high temperatures. Therefore, we replace $\tilde{E}_{mn}$ by the thermal averages $\langle \tilde{E}_{mn} \rangle$ and, as a result, we obtain the desired approximate diagonalization of the Hamiltonian $\tilde{H}$ where the electron and phonon operators are completely disentangled.

For the explicit evaluation of the thermal averages, we start with the calculation of $\langle \tilde{\varepsilon}_{mn} \rangle$ where only even orders $\langle \tilde{\varepsilon}_{mn}^{(2k)} \rangle$ give non-zero contributions. For $k = 1$, we find exactly

$$\left\langle \tilde{\varepsilon}_{mn}^{(2)} \right\rangle = \langle [C, [C, \varepsilon]]_{mn} \rangle = - \sum_{\mathbf{Q}} (1 + 2N_{\mathbf{Q}}) [g_{\mathbf{Q}}, [g_{-\mathbf{Q}}, \varepsilon]]_{mn}. \tag{16}$$

As in [25], we proceed by taking into account only the dominant contributions in equation (16), i.e. terms proportional to ε_{mn}, ε_{nm} and ε_{jj}. As a consequence, we obtain

$$\left\langle \tilde{\varepsilon}_{mm}^{(2)} \right\rangle = 0, \qquad \left\langle \tilde{\varepsilon}_{mn}^{(2)} \right\rangle = \varepsilon_{mn}(-2X_{mn}), \tag{17}$$

where we introduced the abbreviation

$$X_{mn} = \sum_{\mathbf{Q}} (\tfrac{1}{2} + N_{\mathbf{Q}}) G_{\mathbf{Q}mn}, \qquad G_{\mathbf{Q}mn} = |g_{\mathbf{Q}mm} - g_{\mathbf{Q}nn}|^2 + \sum_{k \neq m,n} \left(|g_{\mathbf{Q}mk}|^2 + |g_{\mathbf{Q}nk}|^2 \right), \tag{18}$$

and $N_{\mathbf{Q}} = \langle b_{\mathbf{Q}}^{\dagger} b_{\mathbf{Q}} \rangle$ denotes the phonon occupation number. Similarly, higher orders are evaluated using a cumulant (or linked-cluster) expansion method [27] which approximately leads to

$$\left\langle \tilde{\varepsilon}_{mm}^{(2k)} \right\rangle = 0, \qquad \left\langle \tilde{\varepsilon}_{mn}^{(2k)} \right\rangle = \varepsilon_{mn}(-2X_{mn})^k (2k-1)(2k-3) \cdots 3 \cdot 1, \tag{19}$$

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[1] As becomes clear from a power series expansion, setting $\delta_{\mathbf{Q}mn} = 0$ is actually equivalent to assuming $[C, g_{\mathbf{Q}}]_{mn} = 0$. Hence, one might be tempted to replace immediately also $\tilde{g}_{\mathbf{Q}mn}$ by $g_{\mathbf{Q}mn}$ as we did in a preliminary conference paper [26]. However, the present analysis reveals that this replacement is not favourable since it may lead to overestimated bandwidths at high temperatures, cf figure 1.

so that, by virtue of the identity $(2k-1)(2k-3)\cdots 3 \cdot 1 = \frac{(2k)!}{2^k k!}$, the whole power series can be summed up to give the compact result

$$\langle \tilde{\varepsilon}_{mm} \rangle = \varepsilon_{mm}, \qquad \langle \tilde{\varepsilon}_{mn} \rangle = \varepsilon_{mn} e^{-X_{mn}}. \tag{20}$$

Now, we proceed with the calculation of $\langle \tilde{\Delta}_{mn} \rangle$ where only odd orders $\langle \tilde{\Delta}_{mn}^{(2k+1)} \rangle$ contribute. For $k=0$, we find exactly

$$\left\langle \tilde{\Delta}_{mn}^{(1)} \right\rangle = \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} \left\langle [C, -g_{\mathbf{Q}}(b_{\mathbf{Q}}^{\dagger} + b_{-\mathbf{Q}})]_{mn} \right\rangle = 2\Delta_{mn} \tag{21}$$

with the definition

$$\Delta_{mn} = \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} (g_{\mathbf{Q}} g_{-\mathbf{Q}})_{mn}. \tag{22}$$

Higher orders are calculated in the same approximate way as for $\langle \tilde{\varepsilon}_{mn} \rangle$. This leads to

$$\left\langle \tilde{\Delta}_{mm}^{(2k+1)} \right\rangle = 0, \qquad \left\langle \tilde{\Delta}_{mn}^{(2k+1)} \right\rangle = 2\Delta_{mn}(-2X_{mn})^k (2k-1)(2k-3)\cdots 3 \cdot 1, \tag{23}$$

and, again, after summation of all terms of the power series, the final result can be brought into a compact form:

$$\left\langle \tilde{\Delta}_{mm} \right\rangle = \Delta_{mm}, \qquad \left\langle \tilde{\Delta}_{mn} \right\rangle = \Delta_{mn} \frac{1 - e^{-X_{mn}}}{X_{mn}}. \tag{24}$$

In conclusion, from equations (20) and (24), the on-site energies and transfer integrals in the presence of both local and nonlocal electron–phonon coupling are obtained approximately as

$$\left\langle \tilde{E}_{mm} \right\rangle = \varepsilon_{mm} - \Delta_{mm}, \tag{25}$$

$$\left\langle \tilde{E}_{mn} \right\rangle = \varepsilon_{mn} e^{-X_{mn}} - \Delta_{mn} \frac{1 - e^{-X_{mn}}}{X_{mn}}, \tag{26}$$

where the quantities X_{mn} and Δ_{mn} are defined in equations (18) and (22), respectively. Compared to Holstein's solution for purely local coupling, the polaron shift $-\Delta_{mm}$ of the on-site energies and the exponential renormalization $e^{-X_{mn}}$ of the transfer integrals are now determined by both types of coupling. Furthermore, nonlocal coupling introduces an additional shift of the transfer integrals which reflects the delocalizing effect inherent to nonlocal coupling. As discussed below in more detail, this shift is relatively small and the values of the transfer integrals (i.e. the bandwidths) are mainly determined by the temperature-dependent renormalization factor $e^{-X_{mn}}$. For the numerical calculations in section 3, it is important to note that the shift found in equation (26) is somewhat different from our earlier findings of [25] and [26]:

$$\left\langle \tilde{E}_{mn} \right\rangle = \varepsilon_{mn} e^{-X_{mn}} - \Delta_{mn} e^{-X_{mn}}, \tag{27}$$

$$\left\langle \tilde{E}_{mn} \right\rangle = \varepsilon_{mn} e^{-X_{mn}} - \Delta_{mn}, \tag{28}$$

respectively, where the terms $\delta_{\mathbf{Q}mn}$ discussed above were not taken into account (see footnote 1). However, apart from this small difference, all three descriptions are equivalent.

For dispersionless phonons, we can replace $N_{\mathbf{Q}} \rightarrow N_{\lambda} = [\exp(\hbar\omega_{\lambda}/k_{\mathrm{B}}T) - 1]^{-1}$ and $g_{\mathbf{Q}mn} \rightarrow g_{\lambda mn} \frac{1}{2\sqrt{N}}(e^{-i\mathbf{q}\cdot\mathbf{R}_m} + e^{-i\mathbf{q}\cdot\mathbf{R}_n})$, where N is the number of sites (molecules) and the quantities X_{mn} can be explicitly evaluated from equation (18):

$$X_{mn} = \sum_{\lambda} (\tfrac{1}{2} + N_{\lambda})(G_{\lambda mm} + G_{\lambda nn} - g_{\lambda mn}^2), \tag{29}$$

$$G_{\lambda jj} = g_{\lambda jj}^2 + \tfrac{1}{2} \sum_{k \neq j} g_{\lambda jk}^2. \tag{30}$$

In practice, the terms $-g^2_{\lambda mn}$ in equation (29) will be of minor importance due to the comparably large values of $G_{\lambda jj}$. Therefore, the quantity

$$\sum_\lambda G_{\lambda jj} =: (g_{\text{eff}})^2, \tag{31}$$

may be looked upon roughly as an effective coupling constant. As a side effect, this explains why even the much simpler Holstein model combined with a phenomenological (fitted) coupling parameter works reasonably well in practice and predicts the correct qualitative behaviour [28, 29]. However, for a quantitative *ab initio* modelling of polaron band narrowing, the solution of the full Holstein–Peierls model has to be used, as demonstrated in [25].

3. Application to oligo-acene crystals

In this section, we apply our theory of band narrowing from section 2 to oligo-acene crystals, in particular, naphthalene. Naphthalene crystallizes in a monoclinic structure with two equivalent molecules per unit cell (herringbone stacking). The crystal is described by three lattice vectors a, b and c, with $a \perp b$, $b \perp c$ and a monoclinic angle β between a and c.

In order to obtain the parameters ω_λ, ε_{mn} and $g_{\lambda mn}$ which determine the temperature-dependent bandwidths, we use the same strategy as described in [25]. First, we obtain the equilibrium structure of the crystal by means of DFT–LDA calculations using the *ab initio* total-energy and molecular dynamics program VASP [30]. For the resulting geometry ($a = 7.68$ Å, $b = 5.76$ Å, $c = 8.35$ Å, $\beta = 125.7°$), the intermolecular Γ-point phonon energies $\hbar\omega_\lambda$ and polarizations $\mathbf{e}_\lambda$ are obtained within a rigid-molecule approximation. Using a doubled Brillouin zone corresponding to the lattice $\{\mathbf{R}_m\}$ of the equivalent molecules, we treat the six rotational modes as three dispersionless optical phonon branches ($\hbar\omega_1 = 10.7$ meV, $\hbar\omega_2 = 14.2$ meV and $\hbar\omega_3 = 17.4$ meV). Analogously, the six translational modes are transformed into three acoustical phonon branches which, in consistency with our model, are omitted. Second, the values ε_{mn} are determined from a fit of the ground-state *ab initio* HOMO and LUMO energy bands to a tight-binding model, including the on-site energy and the six most important transfer integrals between nearest neighbours, i.e. $\{mn\} = \{0, a, b, c, ab, ac, abc\}$ belonging to $\mathbf{R}_m - \mathbf{R}_n = \mathbf{0}$, $\pm a$, $\pm b$, $\pm c$, $\pm(\frac{a}{2} \pm \frac{b}{2})$, $\pm(a + c)$ and $\pm(\frac{a}{2} \pm \frac{b}{2} + c)$, respectively. Third, the electron–phonon coupling constants $g_{\lambda mn}$ are determined by rotating the molecules according to the polarizations $\mathbf{e}_\lambda$ of phonon mode λ and fitting the corresponding *ab initio* band structure to the full Holstein–Peierls tight-binding Hamiltonian.

In figure 1, we present the temperature dependence of the effective HOMO and LUMO bandwidths in naphthalene crystals. We compare results obtained from equation (26) with those of equations (27) and (28), with the latter two being results previously reported in [25] and [26], as discussed in section 2. It can be seen immediately that all three approaches yield very similar results, which is especially evident for the HOMO bands. This proves that the main contribution to the polaron bandwidth narrowing arises from the exponential renormalization factor $e^{-X_{mn}}$ of the transfer integrals whereas the small shifts related to the quantities Δ_{mn} are less important. The only significant difference is visible for the LUMO. If equation (28) is used, the bandwidth at high temperatures is overestimated compared to the present work, whereas equation (27) gives a very similar result. This shows that, for materials with significant nonlocal electron–phonon coupling, the choice of equation (28) is not favourable whereas equation (27) still yields accurate results. In contrast, if the nonlocal coupling is weaker as, for example, for higher oligo-acenes such as (monoclinic) tetracene shown in the inset, the results for both the HOMO and LUMO are virtually identical for all three approaches[2]. In conclusion, while the

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[2] For the structural relaxation of the higher oligo-acene crystals anthracene and tetracene, we used a computationally less demanding semi-empirical approach, as described in [25].
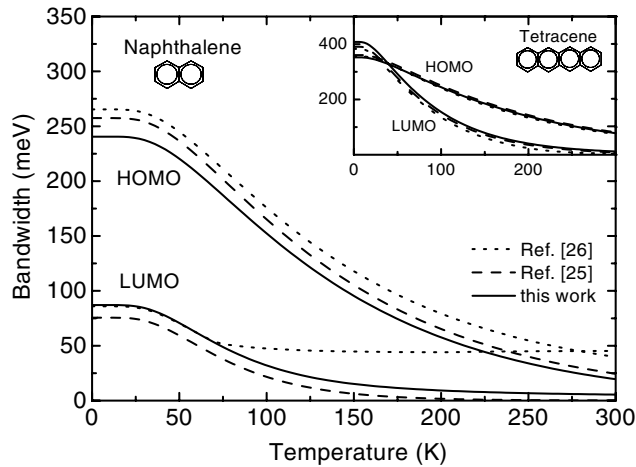
Figure 1. Effective HOMO and LUMO polaron bandwidths versus temperature T for a naphthalene crystal, calculated by means of three different approaches. Full curves: present theory. Broken curves: [25]. Dotted curves: [26]. Inset: same but for a tetracene crystal.

present work, i.e. equation (26), provides the most sophisticated description of temperature-dependent polaron bandwidths, the expression (27), which can be obtained in a conceptually simpler and more straightforward manner [25], already yields very satisfactory results.

In order to demonstrate the importance of nonlocal electron–phonon coupling in naphthalene crystals, we present in tables 1 and 2 the values of all electron–phonon coupling constants for HOMO and LUMO, respectively. The five largest absolute values are printed in boldface. There are two important findings. First, the most dominant contributions stem from the two lowest lying modes whereas the third-lowest mode is already much less important. This finding is also true for the higher oligo-acenes anthracene and tetracene (not shown). Second, the nonlocal electron–phonon coupling (especially within the ab plane) is very important, both for HOMO and LUMO. This can be nicely seen from the calculation of the effective coupling constants (31) which, for the tight-binding model used here, are composed according to

$$(g_{\text{eff}})^2 = \sum_{\lambda=1}^{3} \left(g_{\lambda 0}^2 + 2g_{\lambda ab}^2 + g_{\lambda b}^2 + g_{\lambda a}^2 + 2g_{\lambda abc}^2 + g_{\lambda ac}^2 + g_{\lambda c}^2 \right). \tag{32}$$

In fact, the effective values that would be obtained if only local coupling was considered (HOMO: 0.47, LUMO: 0.14) are significantly smaller than the total values of $g_{\text{eff}} = 0.92$ and 1.52. On the other hand, if the out-of-plane nonlocal coupling is neglected, the resulting effective coupling values (HOMO: 0.88, LUMO: 1.33) are close to the total values, which demonstrates the vital importance of in-plane nonlocal coupling. Finally, we mention that this is also true for the higher oligo-acenes but there the dominance of the nonlocal coupling compared to the local coupling is not so pronounced.

4. Summary

In summary, we have presented a theoretical description of temperature-dependent polaron band narrowing in oligo-acene crystals. The analysis is based on an explicit solution of a Holstein–Peierls model, taking into account both local and nonlocal electron–phonon coupling. Extending our considerations from [25], we have provided an alternative derivation of the main

Table 1. Electron–phonon coupling values for the HOMO band of a naphthalene crystal. The five largest absolute values are printed in boldface. For further explanation see the text.

		$\lambda = 1$	$\lambda = 2$	$\lambda = 3$	$\sum_\lambda (g_{\lambda 0}^2 + 2g_{\lambda ab}^2 + g_{\lambda b}^2 + g_{\lambda a}^2 + 2g_{\lambda abc}^2 + g_{\lambda ac}^2 + g_{\lambda c}^2)$	$= \sum_\lambda G_{\lambda jj}$	$= (g_{\text{eff}})^2$
Local	$g_{\lambda 0}$	-0.04	**0.33**	**0.33**	0.22	$= 0.22$	$= (0.47)^2$
+	$g_{\lambda ab}$	**-0.25**	**-0.25**	0.05	$+ 2 \times 0.13$	$= 0.48$	
nonlocal	$g_{\lambda b}$	**0.43**	0.05	0.20	$+ 0.23$	$= 0.71$	
(in-plane)	$g_{\lambda a}$	-0.03	-0.24	0.01	$+ 0.06$	$= 0.77$	$= (0.88)^2$
+	$g_{\lambda abc}$	0.15	0.08	-0.06	$+ 2 \times 0.03$	$= 0.83$	
nonlocal	$g_{\lambda ac}$	-0.02	0.00	-0.05	$+ 0.00$	$= 0.83$	
(out-of-plane)	$g_{\lambda c}$	0.01	0.09	0.02	$+ 0.01$	$= 0.84$	$= (0.92)^2$
= total	$G_{\lambda jj}$	0.36	0.32	0.16		$= 0.84$	$= (0.92)^2$

Table 2. Same as table 1, but for the LUMO band of a naphthalene crystal.

		$\lambda = 1$	$\lambda = 2$	$\lambda = 3$	$\sum_\lambda (g_{\lambda 0}^2 + 2g_{\lambda ab}^2 + g_{\lambda b}^2 + g_{\lambda a}^2 + 2g_{\lambda abc}^2 + g_{\lambda ac}^2 + g_{\lambda c}^2)$	$= \sum_\lambda G_{\lambda jj}$	$= (g_{\text{eff}})^2$
Local	$g_{\lambda 0}$	-0.08	0.09	0.05	0.02	$= 0.02$	$= (0.14)^2$
+	$g_{\lambda ab}$	0.11	$\mathbf{-0.69}$	-0.11	$+ 2 \times 0.50$	$= 1.02$	
nonlocal	$g_{\lambda b}$	$\mathbf{-0.87}$	0.09	0.00	$+ 0.76$	$= 1.78$	
(in-plane)	$g_{\lambda a}$	0.03	-0.05	0.01	$+ 0.00$	$= 1.78$	$= (1.33)^2$
+	$g_{\lambda abc}$	-0.08	$\mathbf{0.28}$	-0.08	$+ 2 \times 0.09$	$= 1.96$	
nonlocal	$g_{\lambda ac}$	0.07	$\mathbf{-0.18}$	-0.01	$+ 0.04$	$= 2.00$	
(out-of-plane)	$g_{\lambda c}$	-0.15	$\mathbf{0.53}$	-0.05	$+ 0.31$	$= 2.31$	$= (1.52)^2$
= total	$G_{\lambda jj}$	0.83	1.44	0.04		$= 2.31$	$= (1.52)^2$

findings presented there. In particular, we focused on the effect of contributions previously not taken into account and found from our *ab initio* calculations that they are, indeed, of minor importance. This gives additional justification for the conceptually simpler method used in [25]. Furthermore, we discussed the importance of nonlocal electron–phonon coupling in order to quantitatively describe the temperature dependence of polaron bandwidths. Also, the in-plane nonlocal coupling was found to play a pronounced role in naphthalene crystals.

Acknowledgment

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