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## Theory of polaron bandwidth narrowing in organic molecular crystals

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We present a theoretical description of polaron bandwidth narrowing in organic molecular crystals. Based on a solution of a Holstein-Peierls model for tightly bound electrons interacting with phonons, an explicit expression for the temperature dependence of the electronic bandwidths is found. This formula generalizes the result of Holstein polaron theory by treating local and nonlocal electron-phonon coupling on equal footing. The usefulness of the method is demonstrated by model studies for oligo-acene crystals from which microscopic insight into the relevance of the different coupling mechanisms is obtained.

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### I. INTRODUCTION

Organic semiconductors with  $\pi$  conjugation are highly promising candidates for future electronic and optoelectronic applications, such as light-emitting devices,<sup>1-3</sup> lasers,<sup>4</sup> solar cells,<sup>5,6</sup> photodiodes,<sup>7</sup> field-effect transistors (FET's),<sup>8-10</sup> and integrated circuits.<sup>11</sup> An important class of such materials are organic molecular crystals of high purity. Apart from their high technological potential as thin-film transistor materials,<sup>12-14</sup> the strong reduction of structural disorder (if compared to semiconducting polymers) makes organic molecular crystals also ideal candidates to study the underlying intrinsic charge-carrier transport mechanisms. Consequently, several fundamental experimental and theoretical studies have been performed during the last few years, in particular, on oligo-acene crystals such as pentacene.<sup>15-20</sup>

In comparison to covalently bonded inorganic semiconductors, organic crystals are characterized by weak intermolecular van der Waals bonds and, hence, narrower electronic bandwidths, stronger electron-lattice interaction, and more pronounced polaron formation. Consequently, coherent bandlike conduction is expected only for relatively low temperatures. With increasing temperature, the electron-phonon coupling leads to a strong enhancement of the polaron mass accompanied by further bandwidth narrowing which may ultimately result in localization of the charge carriers and change the transport mechanism into phonon-assisted hopping.

The interplay between band and hopping transport in organic solids was first observed in naphthalene crystals,<sup>21,22</sup> and the experimental findings in the low-temperature region have been ascribed to bandwidth narrowing in terms of Holstein's molecular crystal model.<sup>23</sup> This widely used model<sup>24-27</sup> is based on local electron-phonon coupling which acts purely on-site, i.e., at the site of the electronic excitation. On the other hand, vibrations may also influence the transfer of an excitation between lattice sites. The resulting nonlocal coupling leads to Peierls-type models such as the Su-Schrieffer-Heeger model<sup>28</sup> and has been investigated by several authors in the past<sup>29-31</sup>, most notably by Munn *et al.*<sup>32</sup>

and Zhao *et al.*<sup>33</sup> However, all known solutions are too complex to allow a direct *first-principles* evaluation which has prohibited so far a detailed microscopic analysis of the different interaction mechanisms between electrons and lattice vibrations in these materials.

In this paper, we present a theoretical description of electronic bandwidth narrowing in organic molecular crystals which allows quantitative predictions from *ab initio* calculations. The paper is organized as follows. In Sec. II, we derive an explicit expression for the temperature dependence of the polaron bandwidths. This formula generalizes the result of Holstein's theory by treating local and nonlocal electron-phonon coupling on equal footing. In Sec. III, we illustrate the usefulness of our method by applying it to the oligo-acene crystals naphthalene (C<sub>10</sub>H<sub>8</sub>), anthracene (C<sub>14</sub>H<sub>10</sub>), and tetracene (C<sub>18</sub>H<sub>12</sub>). From the numerical results we obtain microscopic insight into the importance of the different types of electron-phonon interaction in organic molecular crystals. A summary is given in Sec. IV.

### II. THEORETICAL DESCRIPTION

Our approach is based on a mixed Holstein-Peierls model for tightly bound electrons interacting with phonons. We consider a Hamiltonian of the form

$$H = \sum_{mn} \varepsilon_{mn} a_m^\dagger a_n + \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} (b_{\mathbf{Q}}^\dagger b_{\mathbf{Q}} + \frac{1}{2}) + \sum_{m\mathbf{Q}} \hbar \omega_{\mathbf{Q}} g_{\mathbf{Q}mn} (b_{\mathbf{Q}}^\dagger + b_{-\mathbf{Q}}) a_m^\dagger a_n, \quad (1)$$

where  $a_m^{(\dagger)}$  and  $b_{\mathbf{Q}}^{(\dagger)} = b_{\mathbf{q}\lambda}^{(\dagger)}$  annihilate (create) an electron at site  $\mathbf{R}_m$  with energy  $\varepsilon_{mm}$  and a phonon with wave vector  $\mathbf{q}$  in the mode  $\lambda$ , respectively. In the noninteracting system, i.e.,  $g_{\mathbf{Q}mn} = 0$ , the electronic bandwidths are determined solely by the transfer integrals  $\varepsilon_{mn}$ . In the following, we will calculate how these quantities are modified by 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 comparison to the pure Holstein model, the diagonalization of the above Hamiltonian is more complicated and necessitates additional simplifications as outlined below. For an approximate solution, we apply here the following nonlocal canonical transformation

$$H \rightarrow \tilde{H} = e^S H e^{S^\dagger}, \quad S = \sum_{mn} C_{mn} a_m^\dagger a_n,$$

$$C_{mn} = \sum_{\mathbf{Q}} g_{\mathbf{Q}mn} (b_{\mathbf{Q}}^\dagger - b_{-\mathbf{Q}}), \quad (2)$$

which will allow us to derive a particularly simple and intuitive result. Due to the identity  $S^\dagger = -S$ , it holds that

$$\tilde{H}(\tilde{a}_m^{(\dagger)}, \tilde{b}_{\mathbf{Q}}^{(\dagger)}) = H(a_m^{(\dagger)}, b_{\mathbf{Q}}^{(\dagger)}), \quad (3)$$

where we introduced 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. By means of the Baker-Campbell-Hausdorff theorem,  $e^S A e^{-S} = A + \frac{1}{1!} [S, A] + \frac{1}{2!} [S, [S, A]] + \dots$ , we find explicitly

$$\tilde{a}_m = \sum_n (e^{-C})_{mn} a_n, \quad (4)$$

$$\tilde{b}_{\mathbf{Q}} = b_{\mathbf{Q}} + \sum_{mn} (e^C b_{\mathbf{Q}} e^{-C} - b_{\mathbf{Q}})_{mn} a_m^\dagger a_n, \quad (5)$$

where we introduced a compact matrix notation for the exponential operators involved and defined  $b_{\mathbf{Q}mn} := b_{\mathbf{Q}} \delta_{mn}$ .

As an exact result of the transformation, we find from Eqs. (1)–(5) that the new Hamiltonian (expressed in terms of the original operators) reads

$$\begin{aligned} \tilde{H} = & \sum_{mn} \tilde{\varepsilon}_{mn} a_m^\dagger a_n + \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} (b_{\mathbf{Q}}^\dagger b_{\mathbf{Q}} + \frac{1}{2}) \\ & + \sum_{mn\mathbf{Q}} \hbar \omega_{\mathbf{Q}} (b_{\mathbf{Q}}^\dagger \delta_{\mathbf{Q}mn} + \delta_{\mathbf{Q}mn} b_{-\mathbf{Q}}) a_m^\dagger a_n \\ & - \sum_{mmm'n'\mathbf{Q}} \hbar \omega_{\mathbf{Q}} (\tilde{g}_{\mathbf{Q}mn} \tilde{g}_{-\mathbf{Q}m'n'} - \delta_{\mathbf{Q}mn} \delta_{-\mathbf{Q}m'n'}) \\ & \times a_m^\dagger a_n a_{m'}^\dagger a_{n'}, \end{aligned} \quad (6)$$

where  $\tilde{\varepsilon}_{mn} = (e^C \varepsilon e^{-C})_{mn}$  and  $\tilde{g}_{\mathbf{Q}mn} = (e^C g_{\mathbf{Q}} e^{-C})_{mn}$ . The ‘‘residual interaction’’ terms originating from the quantities  $\delta_{\mathbf{Q}mn} = \tilde{g}_{\mathbf{Q}mn} + (e^C b_{\mathbf{Q}} e^{-C} - b_{\mathbf{Q}})_{mn}$  can be shown to be of minor importance if the nonlocal coupling is not very strong.<sup>34</sup> Therefore, we neglect them henceforth which amounts to assuming  $[g_{\mathbf{Q}}, g_{\mathbf{Q}'}]_{mn} = 0$  for all pairs  $\mathbf{Q}$  and  $\mathbf{Q}'$ , as becomes clear from a power-series expansion of  $\delta_{\mathbf{Q}mn}$ . Finally, in accordance with the fact that electron-electron interaction has been neglected from the very beginning, we assume the

limit of low electron (polaron) densities which allows the replacement of  $a_m^\dagger a_n a_m^\dagger a_n \rightarrow a_m^\dagger a_n \delta_{nm}$ . Then, the transformed Hamiltonian can be condensed into the compact form

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

$$\tilde{E}_{mn} = (e^C E e^{-C})_{mn}, \quad E_{mn} = \varepsilon_{mn} - \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} (g_{\mathbf{Q}} g_{-\mathbf{Q}})_{mn}. \quad (7)$$

Compared to the original Hamiltonian (1), the new notation has the advantage that it allows a direct evaluation of the on-site energies  $\tilde{E}_{mm}$  and transfer integrals  $\tilde{E}_{mn}$  of the *interacting* electron-phonon system. This evaluation will be done in close analogy to the original work of Holstein.<sup>23</sup>

In the transformed Hamiltonian (7), the phonon operators still appear in the electronic part via  $\tilde{E}_{mn} = (e^C E e^{-C})_{mn}$ . Assuming not too high temperatures, coherent bandlike conduction will prevail over inelastic phonon-assisted hopping transport, and we can replace  $\tilde{E}_{mn}$  by their thermal averages  $\langle \tilde{E}_{mn} \rangle$ . As a result, we obtain the desired approximate diagonalization of the Hamiltonian  $\tilde{H}$  where the electron and phonon operators are completely disentangled. The explicit evaluation of the thermal averages is performed by means of the Baker-Campbell-Hausdorff theorem. Starting from the identities  $\langle [C, E]_{mn} \rangle = 0$  and  $\langle [C, [C, E]]_{mn} \rangle = -\sum_{\mathbf{Q}} (1 + 2N_{\mathbf{Q}}) [g_{\mathbf{Q}}, [g_{-\mathbf{Q}}, E]]_{mn}$ , subsequent application of Wick’s theorem yields

$$\begin{aligned} \langle \tilde{E}_{mn} \rangle = & \sum_{k=0}^{\infty} \frac{1}{k!} \left( -\frac{1}{2} \right)^k \sum_{\mathbf{Q}_1 \dots \mathbf{Q}_k} (1 + 2N_{\mathbf{Q}_1}) \dots (1 + 2N_{\mathbf{Q}_k}) \\ & \times [g_{\mathbf{Q}_1}, [g_{-\mathbf{Q}_1}, \dots [g_{\mathbf{Q}_k}, [g_{-\mathbf{Q}_k}, E]] \dots]]_{mn}, \end{aligned} \quad (8)$$

where  $N_{\mathbf{Q}} = \langle b_{\mathbf{Q}}^\dagger b_{\mathbf{Q}} \rangle$  are the phonon occupation numbers.

While the right-hand side of Eq. (8) may be evaluated numerically for arbitrary matrix elements  $g_{\mathbf{Q}mn}$ , valuable insight can already be obtained if only the most important contributions, i.e., terms proportional to  $E_{mn}$ ,  $E_{nm}$ , and  $E_{jj}$ , are taken into account.<sup>35</sup> As a consequence, the evaluation of the commutators in Eq. (8) becomes analytically tractable, and the solution for the mixed Holstein-Peierls model can be brought into a particularly simple form which, however, retains the essential physics,

$$\tilde{E}_{mm} = E_{mm} \equiv \varepsilon_{mm} - \Delta_{mm}, \quad (9)$$

$$\begin{aligned} \tilde{E}_{mn} = & E_{mn} e^{-\sum_{\mathbf{Q}} (1/2 + N_{\mathbf{Q}}) G_{\mathbf{Q}mn}} \\ \equiv & (\varepsilon_{mn} - \Delta_{mn}) e^{-\sum_{\mathbf{Q}} (1/2 + N_{\mathbf{Q}}) G_{\mathbf{Q}mn}}. \end{aligned} \quad (10)$$

Here, we have introduced the abbreviations

$$G_{\mathbf{Q}mn} = |g_{\mathbf{Q}mn} - g_{\mathbf{Q}nn}|^2 + \sum_{k \neq m, n} (|g_{\mathbf{Q}mk}|^2 + |g_{\mathbf{Q}nk}|^2), \quad (11)$$

$$\Delta_{mn} = \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} \sum_k g_{\mathbf{Q}mk} g_{-\mathbf{Q}kn}. \quad (12)$$

Treating local and nonlocal electron-phonon coupling on equal footing, these formulas generalize the exact result of Holstein's theory ( $g_{\mathbf{Q}mn} = g_{\mathbf{Q}mn} \delta_{mn}$ ) which is given by

$$G_{\mathbf{Q}mn} = |g_{\mathbf{Q}mn} - g_{\mathbf{Q}nn}|^2, \quad (13)$$

$$\Delta_{mn} = \delta_{mn} \sum_{\mathbf{Q}} \hbar \omega_{\mathbf{Q}} |g_{\mathbf{Q}mn}|^2. \quad (14)$$

In fact, the lowering of the on-site energies (9) and the exponential renormalization of the transfer integrals (9) are now determined by both types of coupling. Furthermore, nonlocal coupling introduces an additional shift  $\Delta_{mn}$  of the transfer integrals which reflects the delocalizing effect inherent to nonlocal coupling.

Prior to the explicit calculations, we proceed with a specification of the above theory to crystals in which all molecules are equivalent. Assuming no dispersion in energy and polarization of optical phonon modes, we can replace  $N_{\mathbf{Q}} \rightarrow N_{\lambda} = [\exp(\hbar \omega_{\lambda}/k_B T) - 1]^{-1}$  and  $g_{\mathbf{Q}mn} \rightarrow g_{\lambda mn} (4N)^{-1/2} (e^{-i\mathbf{q} \cdot \mathbf{R}_m} + e^{-i\mathbf{q} \cdot \mathbf{R}_n})$  where the  $\mathbf{q}$  dependence originates from the expressions of the molecule displacements and rotations in terms of phonon operators and  $N$  denotes the number of molecules. As a result, the modified transfer integrals (9) can be written as

$$\tilde{E}_{mn} = (\varepsilon_{mn} - \Delta_{mn}) e^{-\sum_{\lambda} (1/2 + N_{\lambda}) [G_{\lambda mn} + G_{\lambda nn} - g_{\lambda mn}^2]}, \quad (15)$$

where  $G_{\lambda jj} = g_{\lambda jj}^2 + \frac{1}{2} \sum_{k \neq j} g_{\lambda jk}^2$  and

$$\Delta_{mn} = \frac{1}{2} \sum_{\lambda} \hbar \omega_{\lambda} [g_{\lambda mn} (g_{\lambda mm} + g_{\lambda nn}) + \frac{1}{2} \sum_{k \neq m, n} g_{\lambda mk} g_{\lambda kn}].$$

Again, for purely local coupling,  $g_{\lambda mn} = g_{\lambda mn} \delta_{mn}$ , we recover Holstein's result<sup>23</sup>

$$\tilde{E}_{mn} = \varepsilon_{mn} e^{-\sum_{\lambda} (1/2 + N_{\lambda}) (g_{\lambda mm}^2 + g_{\lambda nn}^2)}. \quad (16)$$

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$$\varepsilon(\mathbf{k}) = \varepsilon_0 + 2\varepsilon_a \cos \mathbf{k} \cdot \mathbf{a} + 2\varepsilon_b \cos \mathbf{k} \cdot \mathbf{b} + 2\varepsilon_c \cos \mathbf{k} \cdot \mathbf{c} + 2\varepsilon_{ac} \cos \mathbf{k} \cdot (\mathbf{a} + \mathbf{c})$$

$$\pm 2 \left[ \varepsilon_{ab} \left( \cos \mathbf{k} \cdot \frac{\mathbf{a} + \mathbf{b}}{2} + \cos \mathbf{k} \cdot \frac{\mathbf{a} - \mathbf{b}}{2} \right) + \varepsilon_{abc} \left( \cos \mathbf{k} \cdot \frac{\mathbf{a} + \mathbf{b} + 2\mathbf{c}}{2} + \cos \mathbf{k} \cdot \frac{\mathbf{a} - \mathbf{b} + 2\mathbf{c}}{2} \right) \right], \quad (17)$$


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and the fit is obtained by a least-squares minimization on a regular  $4 \times 4 \times 4$  grid in the corresponding Brillouin zone.

Finally, in the third step, we rotate the molecules by amplitudes  $\Delta u_{\lambda}$  according to the polarizations  $\mathbf{e}_{\lambda}$  of phonon mode  $\lambda$ , repeat the *ab initio* bandstructure calculation, and fit the HOMO and LUMO bands to the full Holstein-Peierls tight-binding Hamiltonian of Eq. (1), employing again relation (17). Then, the electron-phonon coupling constants  $g_{\lambda mn}$

are obtained from the resulting changes in the transfer integrals by numerical differentiation  $g_{\lambda mn} = (1/\hbar \omega_{\lambda}) (\Delta \varepsilon_{mn} / \Delta u_{\lambda})$ , in the limit  $\Delta u_{\lambda} \rightarrow 0$ .<sup>41</sup> The fidelity of this procedure is guaranteed by testing that different amplitudes  $\Delta u_{\lambda}$  yield the same coupling constants  $g_{\lambda mn}$ .

### III. NUMERICAL MODELING AND RESULTS

As a first application of the theory from the preceding section, we perform model studies for the oligo-acene crystal naphthalene. Naphthalene crystallizes in a monoclinic structure ( $P2_1/a$ ) and exhibits a herringbone stacking with two equivalent molecules per unit cell. The crystal is described by three lattice vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$ , with  $\mathbf{a} \perp \mathbf{b}$ ,  $\mathbf{b} \perp \mathbf{c}$ , and a monoclinic angle  $\beta$  between  $\mathbf{a}$  and  $\mathbf{c}$ .

In order to obtain the tight-binding parameters  $\varepsilon_{mn}$  and  $g_{\lambda mn}$ , we use the following three-step strategy. First, we determine the equilibrium structure of the crystal by means of state-of-the-art DFT-LDA calculations using the *ab initio* total energy and molecular dynamics program VASP.<sup>36</sup> For the resulting geometry ( $a = 7.68 \text{ \AA}$ ,  $b = 5.76 \text{ \AA}$ ,  $c = 8.35 \text{ \AA}$ ,  $\beta = 125.7^\circ$ ), the intermolecular  $\Gamma$ -point phonon energies  $\hbar \omega_{\lambda}$  and polarizations  $\mathbf{e}_{\lambda}$  are obtained within the rigid-molecule approximation<sup>37</sup> via the direct method.<sup>40</sup> The six rotational modes are found to have pairwise approximately the same polarizations and phonon energies. This allows us to treat them alternatively as three dispersionless optical phonon branches ( $\hbar \omega_{\lambda} = 10.7, 14.2, \text{ and } 17.4 \text{ meV}$ ) within a doubled Brillouin zone corresponding to the lattice  $\{\mathbf{R}_m\}$  of the equivalent molecules which, in turn, justifies the application of Eqs. (15) and (16). Analogously, the six translational modes are transformed into three acoustical phonon branches which, in consistency with our model, are henceforth omitted.

In the second step, we obtain the values  $\varepsilon_{mn}$  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 neighbors, i.e.,  $\{mn\} = \{0, a, b, c, ab, ac, abc\}$  belonging to  $\mathbf{R}_m - \mathbf{R}_n = \mathbf{0}, \pm \mathbf{a}, \pm \mathbf{b}, \pm \mathbf{c}, \pm (\mathbf{a}/2 \pm \mathbf{b}/2), \pm (\mathbf{a} + \mathbf{c})$ , and  $\pm (\mathbf{a}/2 \pm \mathbf{b}/2 + \mathbf{c})$ , respectively. The solution of this model is

are obtained from the resulting changes in the transfer integrals by numerical differentiation  $g_{\lambda mn} = (1/\hbar \omega_{\lambda}) (\Delta \varepsilon_{mn} / \Delta u_{\lambda})$ , in the limit  $\Delta u_{\lambda} \rightarrow 0$ .<sup>41</sup> The fidelity of this procedure is guaranteed by testing that different amplitudes  $\Delta u_{\lambda}$  yield the same coupling constants  $g_{\lambda mn}$ .

In Fig. 1, we present the temperature dependence of the effective HOMO and LUMO bandwidths in naphthalene crystals. We observe significant differences between the calculations using the Holstein-Peierls model (15) and the Hol-

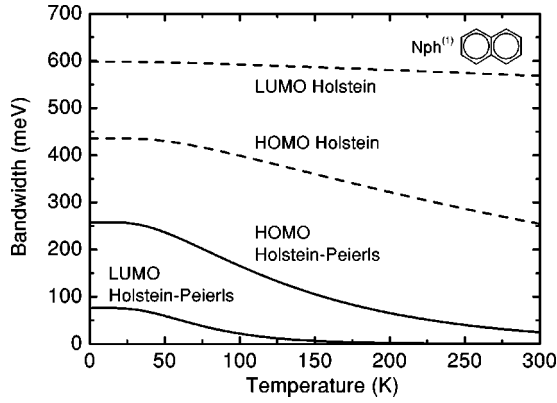


FIG. 1. Effective HOMO and LUMO polaron bandwidths vs temperature  $T$  for a naphthalene crystal, using the parameters from Tables I–III, column Nph<sup>(1)</sup>. Dashed lines: Holstein model, solid lines: Holstein-Peierls model.

stein model (16). As a key result, we find that the full Holstein-Peierls model gives rise to a much stronger temperature dependence of the polaron bandwidths than the Holstein model of purely local coupling. This is especially evident for the LUMO band and can be ascribed to the fact that the exponent in Eq. (15) contains important additional contributions from nonlocal coupling which are absent in Eq. (16). Furthermore, within the Holstein model the LUMO band is found to be broader than the HOMO band at all  $T$ , and the zero-temperature values of 0.60 eV and 0.44 eV are comparable to the bare electronic DFT bandwidths of 0.61 eV and 0.54 eV for LUMO and HOMO, respectively. Hence, the results of both the bare bandwidths and the Holstein-model bandwidths would indicate a low- $T$  electron mobility exceeding that of the holes, which is, however, in contrast to the experiment.<sup>22</sup> On the other hand, the result of the Holstein-Peierls model where local and nonlocal coupling are taken into account complies much better with the experimental data: here, indeed, the HOMO band is significantly broader than the LUMO band and, in particular, for  $T = 0$  K we find values of 0.26 eV (HOMO) and 0.08 eV (LUMO).

We have also performed semiempirical calculations for the structural relaxation, employing an atom-atom potential approach with the Buckingham (6-exp) potential in the parametrization of Williams.<sup>42</sup> This approach allows one to overcome some shortcomings of DFT-LDA in the description of van der Waals crystals (5% underestimation of lattice constants, 20% overestimation of phonon energies), but the overall results for the polaron bandwidth narrowing described in the preceding paragraph remain qualitatively unchanged.<sup>43</sup> While this is a nice consistency check for naphthalene, the real advantage of the semiempirical approach is that it offers a possibility to treat also crystals containing larger molecules such as anthracene and tetracene<sup>44</sup> where full *ab initio* calculations are computationally much more demanding and time consuming. The resulting polaron bandwidths are plotted as a function of temperature in Fig. 2, and the calculated tight-binding and structural parameters are compiled in Tables I, II, and III.

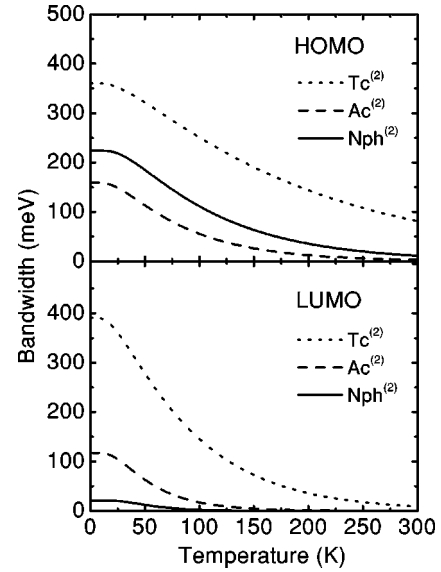


FIG. 2. Effective polaron bandwidths vs temperature  $T$  for naphthalene (solid lines), anthracene (dashed lines), and tetracene crystals (dotted lines), using the parameters from Tables I–III, columns Nph<sup>(2)</sup>, Ac<sup>(2)</sup>, and Tc<sup>(2)</sup>, respectively. Top: HOMO bands, bottom: LUMO bands.

Using the semiempirical approach, we see from Fig. 2 that the temperature dependence of the polaron bandwidths in higher oligo-acenes is similar to that of naphthalene. However, the absolute values of the bandwidths are quite different, especially for the LUMO bands. Here, we observe a large increase of the LUMO bandwidths with increasing conjugation length. This effect can be traced back to the fact that for larger molecules the absolute values of the most important transfer integrals increase (cf.,  $\epsilon_b$  and  $\epsilon_{ab}$  in Table II) and the dominating electron-phonon coupling constants decrease (cf.,  $g_{1b}$ ,  $g_{2ab}$ , and  $g_{2c}$  in Table III). The latter effect can be nicely demonstrated by introduction of the quantities

$$(g_{\text{eff}})^2 =: \sum_{\lambda=1}^3 G_{\lambda jj} = \sum_{\lambda=1}^3 (g_{\lambda 0}^2 + g_{\lambda a}^2 + g_{\lambda b}^2 + g_{\lambda c}^2 + g_{\lambda ac}^2 + 2g_{\lambda ab}^2 + 2g_{\lambda abc}^2), \quad (18)$$

TABLE I. Lattice parameters and intermolecular rotational phonon energies for naphthalene (Nph), anthracene (Ac), and tetracene (Tc), calculated using either (1) DFT-LDA or (2) a semiempirical atom-atom potential approach.

	Nph <sup>(1)</sup>	Nph <sup>(2)</sup>	Ac <sup>(2)</sup>	Tc <sup>(2)</sup>
$a$ (Å)	7.68	7.93	8.18	8.58
$b$ (Å)	5.76	5.88	5.90	5.78
$c$ (Å)	8.35	8.73	11.11	13.80
$\beta$ (°)	125.7	122.2	122.5	125.0
$\hbar \omega_1$ (meV)	10.7	7.8	5.8	4.7
$\hbar \omega_2$ (meV)	14.2	12.0	11.4	10.6
$\hbar \omega_3$ (meV)	17.4	18.7	21.1	21.1



TABLE II. Bare on-site energies and transfer integrals for naphthalene, anthracene, and tetracene, calculated for the equilibrium structures given in Table I. Left panel: HOMO bands, right panel: LUMO bands.

	HOMO bands				LUMO bands			
	Nph <sup>(1)</sup>	Nph <sup>(2)</sup>	Ac <sup>(2)</sup>	Tc <sup>(2)</sup>	Nph <sup>(1)</sup>	Nph <sup>(2)</sup>	Ac <sup>(2)</sup>	Tc <sup>(2)</sup>
$\varepsilon_0$ (eV)	-0.36	-1.06	-0.38	0.12	2.93	2.23	1.89	1.74
$\varepsilon_a$ (meV)	-29	-12	-12	-7	1	1	0	4
$\varepsilon_b$ (meV)	-59	-46	-48	-71	30	24	39	63
$\varepsilon_c$ (meV)	4	0	0	0	1	2	-1	2
$\varepsilon_{ac}$ (meV)	6	3	-3	6	-3	2	0	-3
$\varepsilon_{ab}$ (meV)	17	14	2	1	-72	-29	-57	-80
$\varepsilon_{abc}$ (meV)	-24	-25	-12	-30	-4	-7	4	-2

which may be looked upon as effective coupling constants since they are the dominant contributions to the exponent in Eq. (15). Anisotropy effects may arise, in principle, due to the remaining term in that exponent but, here, they are found to be of minor importance due to the comparably large values of  $g_{\text{eff}}$  which, as a side effect, explains why the simple concept of an effective coupling constant often works quite well in practice, despite the actual complexity of the problem. In fact, a previous theoretical work,<sup>26</sup> where experimen-

tal electron-mobility data for naphthalene were *fitted* to the Holstein model, yielded electron-phonon coupling values between 1.6 and 1.9 (depending on crystallographic direction) which are in good agreement with our *calculated* value of  $g_{\text{eff}}=1.67$  for the LUMO band of naphthalene. It is also worthwhile to mention that our findings of decreasing  $g_{\text{eff}}$  values for the LUMO bands (naphthalene: 1.67, anthracene: 1.27, and tetracene: 0.78) indicate a roughly inverse proportionality between the  $\pi$  conjugation length and the strength

TABLE III. Electron-phonon coupling constants and effective coupling values  $g_{\text{eff}}$  according to Eq. (18) for naphthalene, anthracene, and tetracene, calculated for the phonon modes given in Table I. Left panel: HOMO bands, right panel: LUMO bands.

	HOMO bands				LUMO bands			
	Nph <sup>(1)</sup>	Nph <sup>(2)</sup>	Ac <sup>(2)</sup>	Tc <sup>(2)</sup>	Nph <sup>(1)</sup>	Nph <sup>(2)</sup>	Ac <sup>(2)</sup>	Tc <sup>(2)</sup>
$g_{10}$	-0.04	-0.02	0.23	0.12	-0.08	-0.09	-0.01	-0.40
$g_{1a}$	-0.03	-0.10	-0.02	-0.01	0.03	-0.02	-0.03	-0.05
$g_{1b}$	0.43	0.52	0.62	0.21	-0.87	-1.05	-0.92	-0.33
$g_{1c}$	0.01	0.04	-0.05	0.01	-0.15	-0.12	0.09	-0.13
$g_{1ac}$	-0.02	-0.02	0.07	-0.06	0.07	0.06	0.00	0.04
$g_{1ab}$	-0.25	-0.15	0.24	0.00	0.11	0.12	-0.17	0.11
$g_{1abc}$	0.15	0.30	0.09	0.14	-0.08	-0.06	0.04	-0.04
$G_{1jj}$	0.36	0.51	0.58	0.10	0.83	1.16	0.92	0.32
$g_{20}$	0.33	0.26	0.06	0.03	0.09	0.14	0.17	0.20
$g_{2a}$	-0.24	-0.16	-0.08	-0.02	-0.05	-0.01	0.02	0.05
$g_{2b}$	0.05	-0.05	-0.01	0.05	0.09	0.28	0.09	-0.02
$g_{2c}$	0.09	0.07	-0.06	0.05	0.53	0.47	-0.28	0.12
$g_{2ac}$	0.00	-0.02	-0.02	0.01	-0.18	-0.16	0.06	-0.02
$g_{2ab}$	-0.25	-0.06	0.29	0.11	-0.69	-0.79	-0.50	-0.28
$g_{2abc}$	0.08	0.13	0.00	-0.25	0.28	0.11	-0.06	0.02
$G_{2jj}$	0.32	0.14	0.18	0.16	1.44	1.62	0.63	0.22
$g_{30}$	0.33	0.12	-0.12	-0.18	0.05	0.04	-0.14	-0.18
$g_{3a}$	0.01	0.00	0.02	0.01	0.01	0.01	0.00	-0.01
$g_{3b}$	0.20	0.18	-0.06	-0.05	0.00	-0.02	-0.02	-0.02
$g_{3c}$	0.02	0.00	0.01	0.00	-0.05	-0.03	0.01	0.01
$g_{3ac}$	-0.05	-0.02	-0.01	0.00	-0.01	-0.02	-0.02	0.01
$g_{3ab}$	0.05	0.00	0.05	0.00	-0.11	-0.07	0.14	0.14
$g_{3abc}$	-0.06	-0.06	-0.01	-0.01	-0.08	-0.03	-0.01	0.01
$G_{3jj}$	0.16	0.05	0.02	0.03	0.04	0.02	0.06	0.07
$g_{\text{eff}}$	0.92	0.84	0.88	0.54	1.52	1.67	1.27	0.78

of the *intermolecular* electron-phonon coupling, similar to previous results for the *intramolecular* coupling.<sup>38</sup> However, looking at our calculations for the HOMO bands, we also find that this rule of thumb for the chemical trend can sometimes be violated. Here, we observe, e.g., that anthracene has a slightly larger value of  $g_{\text{eff}}=0.88$  than naphthalene ( $g_{\text{eff}}=0.84$ ) resulting in comparable HOMO bandwidths. In fact, the HOMO bandwidth of anthracene is even a bit smaller than that of naphthalene, whereas tetracene ( $g_{\text{eff}}=0.54$ ) again follows the “expected” trend.

Another important finding for all three oligo-acenes is that the electrons couple apparently stronger to the phonons than the holes as can be seen from a comparison of the  $g_{\text{eff}}$  values for LUMO and HOMO bands. A possible physical explanation for the much stronger phonon-induced renormalization of the LUMO could be that the intermolecular motions tend to keep the overlap between the HOMO orbitals as large as possible in order to retain the binding between the molecules whereas there are no such restrictions on the overlap between the LUMO orbitals. As a consequence, we observe broader HOMO than LUMO bands (except for tetracene at very low  $T$ ) from which we conclude that, in general, the hole mobility in oligo-acene crystals should be higher than the mobility of electrons. Strictly speaking, this statement is true only for the bandlike contribution to the mobility which we have considered here exclusively. In agreement with early measurements,<sup>21</sup> one may expect from the narrow LUMO bands of naphthalene and anthracene at elevated temperatures (cf. Fig. 2) that additional contributions from phonon-assisted hopping play a role for the electrons in these materials but we believe they are not sufficiently large enough to reverse the general trend. Nevertheless, an exten-

sion of the theory described in this article towards the calculation of mobilities including both bandlike and hopping terms remains an interesting and important subject for future research.

#### IV. SUMMARY

In summary, we have presented a theoretical approach to the description of bandwidth narrowing in organic molecular semiconductors. Based on a solution of a mixed Holstein-Peierls model, we have derived an explicit expression for the polaron bandwidths as a function of temperature. This formula generalizes the result of Holstein polaron theory by treating local and nonlocal electron-lattice interaction on equal footing. The predictive nature of the theory has been demonstrated by numerical studies for oligo-acene crystals which have provided microscopic insight into the relevance of the different coupling mechanisms. As a key result, we find that nonlocal coupling plays an important role for the quantitative description of the polaron bandwidths: in comparison to the Holstein model of purely local coupling, the bandwidths exhibit a much more pronounced temperature-dependent narrowing. Furthermore, the LUMO is found to couple stronger to the phonons than the HOMO and, hence, we predict the hole mobilities in oligo-acene crystals to be higher than the electron mobilities.

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- <sup>42</sup>For a review, see E. A. Silinsh, *Organic Molecular Crystals*, (Springer, Berlin, 1980).
- <sup>43</sup>The transfer integrals  $\epsilon_{mn}$  and electron-phonon coupling constants  $g_{\lambda mn}$  are obtained as above, i.e., by fitting the *ab initio* DFT-LDA energy bands to our tight-binding Hamiltonian.
- <sup>44</sup>We consider here exclusively monoclinic tetracene. However, tetracene (like pentacene) may also crystallize in a triclinic structure with two inequivalent molecules per unit cell.<sup>42</sup> In order to describe such low-symmetry crystals, a generalization of the theory (or, more strictly, an appropriately adapted tight-binding model) is necessary but presently not in hand.